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Gold(III)-Catalyzed Glycosidations for 1,2-*trans* and 1,2-*cis* Furanosides

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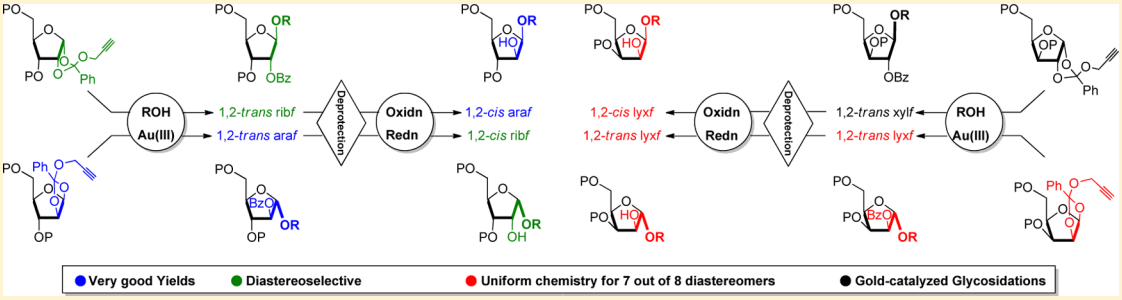
Supporting Information



ABSTRACT: Stereoselective synthesis of furanosides is still a daunting task, unlike the pyranosides, for which several methods exist. Herein, a unified stereoselective strategy for the synthesis of 1,2-*trans* and 1,2-*cis* furanosides is revealed for seven out of eight possible isomers of pentoses. The identified protocol gives access to diastereoselective synthesis of α- and β-ara*f*, rib*f*, lyx*f*, and α-xyl*f* furanosides. 1,2-*trans* glycosides were synthesized by the use of propargyl 1,2-orthoesters under gold-catalyzed glycosidation conditions, and subsequently, they are converted into 1,2-*cis* glycosides through oxidation−reduction as the key functional group transformation. All the reactions are found to be fully diastereoselective, mild, and high yielding.

INTRODUCTION

Glycoconjugates are known to play pivotal roles in a plethora of intracellular and extracellular biological events.[1] Most often, saccharide constituents are in hexopyranosyl form, but sometimes, hexofuranosyl and pentofuranosyl residues are also noticed.[2] Furanose residues were less prevalent in mammalians and humans, though they are found frequently in many parasitical, fungal, bacterial and plant glycans.[2b] Therefore, biomolecules with furanosyl residues have attracted special attention in order to elucidate their function, metabolism, viability, and virulence.[3] However, glycans are difficult to isolate from nature as they are available in minute quantities as micro and heterogeneous forms.[4] 1,2-*trans* and 1,2-*cis* are the two linkages that are possible in glycosides, and as a result the stereocontrolled synthesis of them is of a great significance. More methods are identified for the stereoselective synthesis of pyranosides than for the furanosides either due to the less frequent occurrence or complexity in their synthesis.[5a] Furthermore, pyranosides can be advantageously synthesized by exploiting the anomeric effect and the neighboring group participation for the 1,2-*cis* and 1,2-*trans* pyranosides, respectively.[5b] The anomeric effect is almost negligible and the steric interactions play a major role in defining the outcome of the stereoselectivity in furanosides. In addition, the furanose form is thermodynamically disfavored, whereas the pyranosyl form is more stable due to lesser steric crowding.[6] As a consequence, locking of aldose as a furanoside is the first challenge, which is often achieved through a kinetically controlled Fischer glycosidation in the presence of acid and alcohol.[7] But Fischer glycosidation for stereoselective synthesis is not really suitable for the synthesis of higher oligosaccharides.

The glycosidation is a reaction wherein a glycosyl donor and hydroxyl-bearing glycosyl acceptor are involved.[8] Glycosyl donors often possess an appendage at the anomeric position that in the presence of an activator departs resulting in an intermediate oxocarbenium ion that will be attacked by a suitable hydroxyl-bearing glycosyl acceptor.[8] Hence, the chemistry of glycosyl donors is of paramount importance in the development of any glycosidation reaction. Many furanosyl donors with a range of appendages at the anomeric position viz. halides,[9a,b] silyl glycosides,[9c] alkyl glycosides,[9d] anomeric esters,[9e] thioglycosides,[9f,g] trichloroacetamidates,[9h] *n*-pentenyl glycosides,[9f] orthoesters,[9i,j] 1,2-anhydro sugars,[9k] and *o*-carboxybenzyl glycosides[9l] are developed over the past few decades for the synthesis of furanosides. Development of these methods greatly benefited the synthetic carbohydrate chemists in synthesizing furanosyl oligosaccharides.[9f,10] Yet, there is no uniform method that enables synthesis of both 1,2-*cis* and 1,2-*trans* isomers of all four pentosyl sugars in a stereoselective manner. In this premise, we hypothesized to utilize gold-catalyzed glycosylation for the synthesis of both the isomers of all the four pentosyl sugars stereoselectively. Our hypothesis stems from a recent observation that *Mycobacterium tuberculosis*, the etiological agent for tuberculosis, synthesizes 1,2-*cis* arabinofuranoside indirectly through an oxidation−reduction

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Scheme 1. Synthesis of Propargyl 1,2-Orthoesters

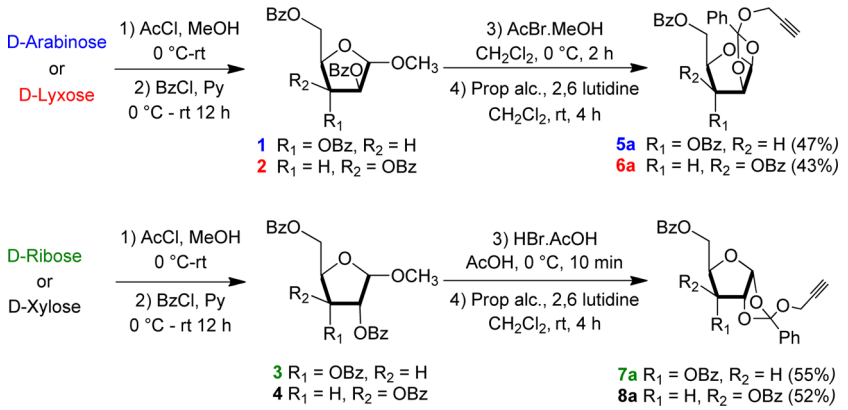
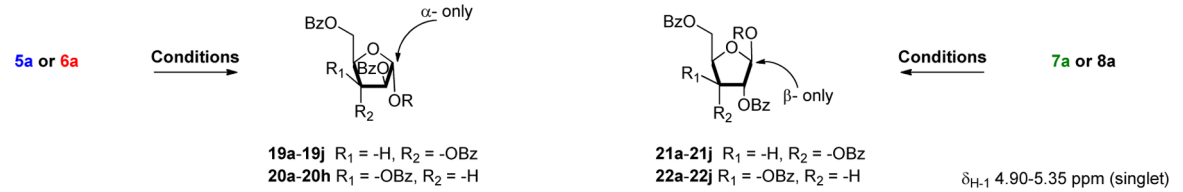


Table 1. Gold-Catalyzed Glycosidation for the Synthesis of 1,2-*trans* Furanosides



ROH / Donor	9	10	11	12	13	14	15	16	17	18
5a	19a 78%	19b 92%	19c 83%	19d 82%	19e 90%	19f 82%	19g 80%	19h 77%	19i 81%	19j 72%
6a	20a 75%	20b 94%	ND[a]	20c 81%	20d 78%	20e 72%	20f 72%	20g 73%	20h 75%	ND[a]
7a	21a 79%	21b 90%	21c 85%	21d 82%	21e 88%	21f 89%	21g 75%	21h 75%	21i 86%	21j 66%
8a	22a 80%	22b 94%	22c 85%	22d 78%	22e 88%	22f 88%	22g 77%	22h 78%	22i 86%	22j 67%

[a]ND denotes not determined.

at the C-2 position of a decaprenyl 1,2-*trans* ribofuranoside.[11] Initial attempts of utilizing propargyl furanosides for the stereoselective synthesis were not very encouraging.[9d] Non-regioselective mixture of 1,2-*cis* and 1,2-*trans* furanosides were observed in ara*f* and xyl*f* donors while performing the gold catalyzed glycosidation, though the propargyl rib*f* and lyx*f* donors gave full 1,2-*trans* diastereoselectivity. As a result, in a preliminary investigation, propargyl 1,2-orthoesters were considered for showing the diastereoselective synthesis of both isomers of arabinofuranosides by gold-catalyzed glycosidation.[12] In continuation, propargyl 1,2-orthoesters were considered next to develop a uniform strategy that would be applicable for the synthesis of all 1,2-*trans* and 1,2-*cis* furanosides stereoselectively. Accordingly, synthesis of propargyl 1,2-orthoesters of all the four pentose sugars is investigated.

RESULTS AND DISCUSSION

Locking of pentosyl aldose in furanosyl conformation was carried out under modified Fischer glycosidation[7c] conditions using AcCl, MeOH at 0−25 °C followed by the per-*O*-benzoylation to obtain methyl per-*O*-benzoyl furanosides **1**−**4**. D-Arabinose required 7 h, D-lyxose and D-xylose required 3 h whereas D-ribose was more reactive and took 30 min for the complete conversion to afford methyl furanosides.[13] Methyl per-*O*-benzoyl furanosides **1** and **2** were conveniently transformed into furanosyl bromides with AcBr−MeOH and then treated with propargyl alcohol, 2,6-lutidine in CH_2Cl_2 to afford required 1,2-orthoester of arabinose (**5a**) and lyxose (**6a**) in 47 and 43% yield over four steps (Scheme 1). The methyl per-*O*-benzoyl furanosides of ribose (**3**) and xylose (**4**) were converted to anomeric bromides using 33% HBr·AcOH in AcOH for 10 min followed by the addition of propargyl alcohol

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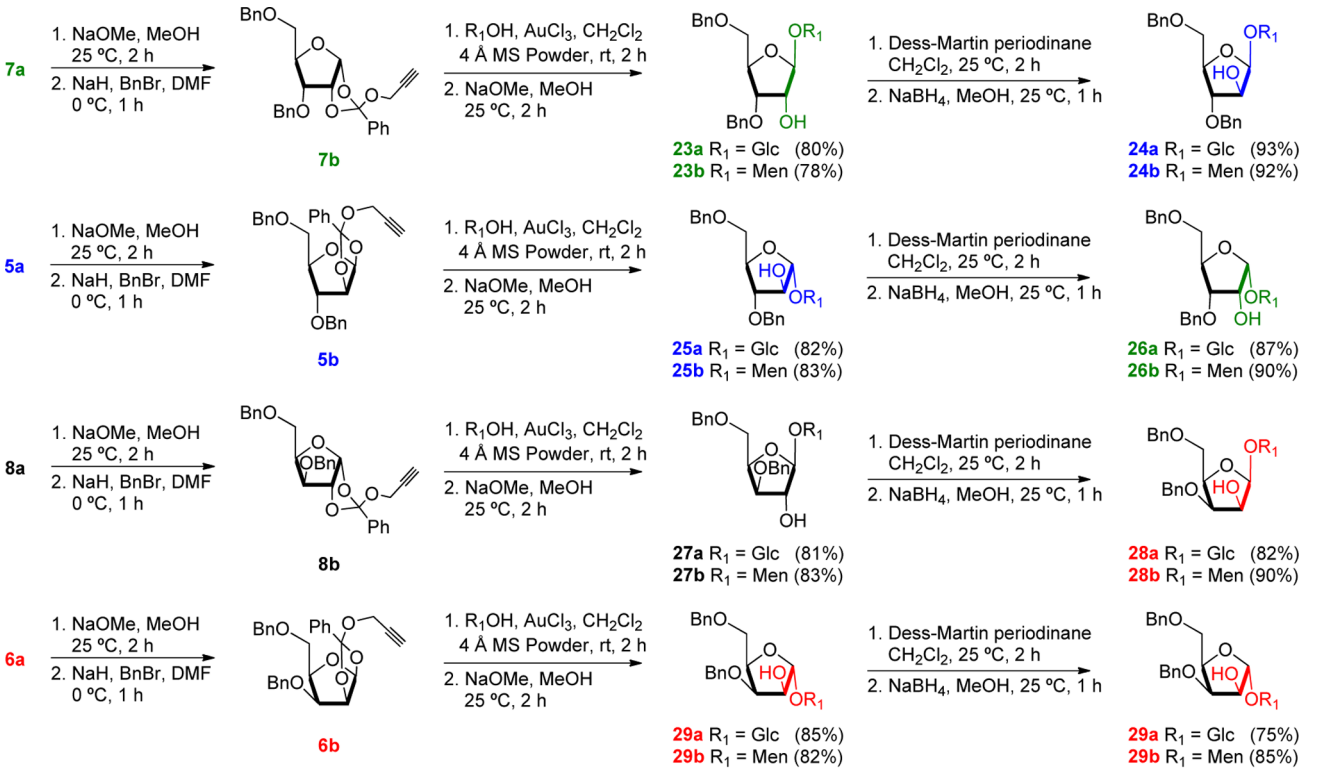
Scheme 2. Conversion of 1,2-*trans* Furanosides into 1,2-*cis* Furanosides



R_1OH = Methyl 2,3,4-tri-O-benzyl α-D-glucopyranoside = GlcOH, Menthol = MenOH

and 2,6-lutidine in CH_2Cl_2 to afford orthoesters **7a** and **8a** in 55 and 52%, respectively (Scheme 1).[13]

Propargyl 1,2-orthoesters are known to undergo gold-catalyzed glycosidation reaction to afford 1,2-*trans* pyranosides.[14] Synthesis of propargyl orthobenzoates in furanosyl form (**5a**, **6a**, **7a** and **8a**) opened the possibility for the 1,2-*trans* stereoselective synthesis of furanosides as well.[12] Hence, orthoesters (**5a**−**8a**) were subjected to standard gold-catalyzed glycosidation conditions [ROH, $AuCl_3$, 4 Å MS powder, CH_2Cl_2, 25 °C] with a selected panel of hydroxyl-bearing glycosyl acceptors **9**−**18**. In all the cases, the 1,2-*trans* stereoselectivity was observed (Table 1).[13] Propargyl 1,2-orthoester **5a** underwent gold-catalyzed furanosylation reaction with hydroxyl-bearing glycosyl acceptors **9**−**18** giving α-arabinofuranosides **19a**−**19j** in very good yields (Table 1).[12] Similarly, propargyl 1,2-orthoester of lyxofuranose **6a** afforded α-lyxofuranosides **20a**−**20h** in very good yields. In continuation, propargyl 1,2-orthoester of ribofuranose (**7a**) and xylofuranose (**8a**) resulted in the formation of β-ribofuranosides (**21a**−**21j**) and β-xylofuranosides (**22a**−**22j**) respectively (Table 1).[13] Singlets between δ_H 4.90−5.35 ppm for the anomeric protons in the ^1H NMR spectrum were observed and anomeric carbons were identified between δ_C 104.5−108.0 ppm in the ^{13}C NMR spectrum.[13]

Stereoselective synthesis of 1,2-*trans* furanosides of all the four pentoses encouraged delving into the development of a facile procedure for the 1,2-*cis* furanosides as well. Two recent independent reports confirmed that the *Mycobacterium tuberculosis* indirectly synthesizes 1,2-*cis* arabinofuranosides present in the cell surface glycan exploiting decaprenylphosphatidyl ribofuranosyl enzymes DprE1 and DprE2.[11] Further, 1,2-*cis* arabinofuranosides are synthesized in two steps from 1,2-*trans* ribofuranosides. DprE1 converts the decaprenylphosphatidyl ribofuranoside into decaprenylphosphatidyl 2-ribulose which upon the stereoselective reduction assisted by DprE2 affords the 1,2-*cis* arabinofuranosides.[11]

1,2-*trans* ribofuranosides can be easily obtained in a fully diastereoselective fashion by the gold-catalyzed glycosidation of propargyl 1,2-orthoesters. Now the challenge is to transform thus obtained 1,2-*trans* ribofuranoside into 1,2-*cis* arabinofuranoside. Synthesis of β-mannopyranosides from β-glucopyranosides through oxidation−reduction process at C-2 position is well-known in the literature.[15a,b] However, similar approaches for furanosides has a rare parallel−except the oxidation−reduction strategy on a highly substituted L-arabinofuranose was one of the key steps in a total synthesis effort.[15c] Oxidation−reduction process was found to be beneficial for the synthesis of hexarabinofuranosyl motif of *Mycobacterial tuberculosis* cell wall.[12]

To test, we require orthoester that would enable us to free the C2-OH group in an orthogonal fashion after the gold-catalyzed furanosylation reaction. Hence, rib*f*-orthoester **7a** was converted into the per-*O*-benzyl rib*f*-orthoester **7b** in two steps.[12] Saponification under Zemplén debenzoylation conditions (NaOMe/MeOH) followed by per-*O*-benzylation with NaH/BnBr/DMF/TBAI/0−25 °C afforded the required orthoester **7b** in good yield. Menthol and glucose-derived alcohol were selected as the model substrates in order to probe the diastereoselective reduction. Accordingly, gold-catalyzed furanosylation reaction under aforementioned conditions was performed using hydroxyl-bearing glycosyl acceptors **14** and menthol to obtain 1,2-*trans* ribofuranosides which were subjected to Zemplén debenzoylation to afford C2-OH free ribofuranosides **23a**,**b** in very high yields. Oxidation of the C-2-OH group was conveniently carried out using Dess−Martin periodinane in CH_2Cl_2 at 25 °C and the resulting C-2 ulose

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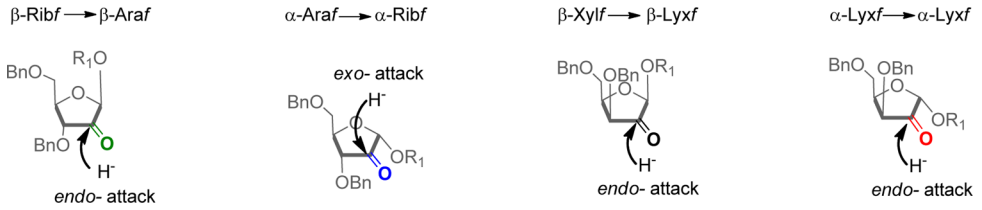

Figure 1. Explanation for the diastereoselectivity.

derivative without further purification was reduced with $NaBH_4$ to observe fully diastereoselective conversion of 1,2-*trans* ribofuranosides **23a,b** into 1,2-*cis* arabinofuranosides **24a,b** in a excellent yields (Scheme 2).

The diastereoselective conversion was confirmed by means of NMR spectral analysis. Anomeric carbons of ribofuranoside **23a** were noticed at δ 97.9, 107.8 ppm, whereas those of arabinofuranoside **24a** were found at δ 98.0 and 102.4 ppm. In addition, $^1J_{C-H}$ values of rib*f* **23a** were found to be 171 and 176 Hz, whereas $^1J_{C-H}$ values of ara*f* **24a** were noticed to be 174 and 183 Hz.[12]

Subsequently, 1,2-*cis* rib*f*, which was also equally challenging, was envisioned from 1,2-*trans* ara*f*. Accordingly, orthoester **5a** was converted into orthoester **5b** under aforementioned conditions in two steps. Gold-catalyzed furanosylation with menthol and **14** afforded easily 1,2-*trans* arabinofuranosides **25a,b**. Oxidation by Dess−Martin periodinane and subsequent reduction with $NaBH_4$ gave 1,2-*cis* ribofuranosides **26a,b** in a fully diastereoselective manner (Scheme 2). A doublet at δ 4.64 (J = 3.7 Hz) ppm and a singlet at δ 5.10 and δ 98.2, 109.5 ppm were noticed for anomeric protons and for carbons in the ^{1}H and ^{13}C NMR spectrum of **25a** respectively, whereas in compound **26a**, two doublets at 4.59 (J = 3.6 Hz) and 5.06 (J = 4.7 Hz) ppm and δ 98.0 and 101.8 were noticed for anomeric protons and carbons, respectively, in the ^{1}H NMR and ^{13}C NMR.[13]

In continuation, 1,2-*cis* lyxofuranosides **28a,b** were obtained by a similar set of reactions from 1,2-*trans* xylofuranosides **27a,b**. Similarly, 1,2-*cis* xylofuranosides are envisaged from 1,2-*trans* lyxofuranosides **29a,b**, which can be conveniently synthesized from orthoester **6a**. However, the oxidation with Dess−Martin periodinane followed by the reduction using $NaBH_4$ resulted into the isolation of starting 1,2-*trans* lyxofuranosides **29a,b** but not the required 1,2-*cis* xylofuranosides (Scheme 2).[13]

The stereochemical outcome can be explained based on the differential steric crowding around the carbonyl group of the C2-ulose derivative. The 5-*O*-benzyl and C-1 glycoside prevent the hydride to attack from the *exo*-face in the case of β-rib*f* → β-ara*f* conversion, and hence, hydride prefers the *endo*-attack on the ketone to give β-ara*f* only (Figure 1). Similarly, *endo*-attack in the α-ara*f* → α-rib*f* conversion is sterically not favorable, and hence, the product resulting from the *exo*-attack was observed. Also, in case of β-xyl*f* → β-lyx*f* conversion, the *exo*-attack is sterically demanding which forces the hydride to attack in the *endo*- fashion. However, in case of α-lyx*f* → α-xyl*f*, and the 3,5-di-*O*-benzyl groups make the *exo*-attack completely unavailable for the hydride attack on the ketone giving back the starting material (Figure 1).

In conclusion, a facile procedure for the fully diastereoselective synthesis of seven out of eight possible pentosyl furanosides is identified. Gold-catalyzed glycosidation afforded the 1,2-*trans* furanosides, which were subsequently converted into 1,2-*cis* furanosides through oxidation−reduction as key steps. All the key reactions were found to be fully diastereoselective. The strategy identified in this endeavor is observed to be not suitable for the synthesis of 1,2-*cis*-xylofuranoside.

EXPERIMENTAL SECTION

General Methods. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Unless otherwise reported all reactions were performed under argon atmosphere. Removal of solvent in vacuo refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Products obtained as solids or syrups were dried under a high vacuum. All gold and transition metal salts were purchased from multinational commercial vendors. Analytical thin-layer chromatography was performed on precoated silica plates (F_{254}, 0.25 mm thickness); compounds were visualized by UV light or by staining with anisaldehyde spray. Optical rotations were measured on a digital polarimeter. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded either on a 400 or a 500 MHz with $CDCl_3$ as the solvent and TMS as the internal standard. High resolution mass spectroscopy (HRMS) was performed using a ESI-ESI-TOF mass analyzer. Low resolution mass spectroscopy (LRMS) was performed on UPLC-MS.

(a). Experimental Procedure[12] for the Synthesis Of 3,5-Di-O-benzoyl-β-D-arabinofuranoside prop-2-ynyl-1,2-orthobenzoate (5a). Acetyl chloride (12 mL, 0.17 mol) was treated with methanol (10 mL) at 0 °C for 30 min, and to this solution was added a CH_3OH (125 mL) solution of arabinose (20.0 g, 0.13 mol) at 0 °C and warmed to room temperature. Progress of the reaction was monitored by the TLC until disappearance of the aldose (∼7 h). The reaction mixture was quenched with pyridine (40 mL) and concentrated in vacuo, and the crude residue of α,β methyl furanoside was redissolved in anhydrous pyridine (200 mL), cooled to 0 °C, and slowly treated with benzoyl chloride (60 mL, 0.53 mol). Further, the reaction mixture was stirred for 12 h at room temperature, and few pieces of ice were added to the reaction mixture, which was stirred for another 30 min at room temperature and then extracted with dichloromethane (2 × 500 mL). The extract was washed with 3 N H_2SO_4, aq. sat. sodium bicarbonate solution, and the organic layer was collected, dried over anhydrous sodium sulfate, and concentrated in vacuo to yield crude residue of α,β methyl 2,3,5-tri-*O*-benzoyl arabinofuranoside **1**.

In continuation, arabinofuranosides **1** (31.0 g, 0.065 mol) prepared vide supra were redissolved in anhydrous CH_2Cl_2 (150 mL) and cooled to 0 °C. Acetyl bromide (26.7 mL, 0.36 mol) was added to the reaction mixture followed by the dropwise addition of methanol (11.85 mL, 0.29 mol) with constant stirring at 0 °C. Additionally, the reaction mixture was stirred for 2 h at 0 °C before diluting with CH_2Cl_2 (500 mL). The reaction mixture was poured into the ice−water mixture, and aqueous layer was extracted with CH_2Cl_2 (2 × 250 mL), and organic layer was washed with cold saturated sodium bicarbonate solution, dried over sodium sulfate, and concentrated under reduced pressure to give arabinofuranosyl bromide as white solid, which was immediately used in the next step without additional purification. The crude arabinofuranosyl bromide was redissolved in 200 mL of anhydrous CH_2Cl_2, propargyl alcohol (5.6 mL, 0.10 mol) and 2,6-lutidine (15.1 mL, 0.13 mol). Tetra-*n*-butyl ammonium iodide (1.44 g, 3.9 mmol) was added to the solution and stirred for 4 h at room temperature. The reaction mixture was diluted with CH_2Cl_2

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(250 mL) and water (500 mL), and the aqueous layer was extracted with CH_2Cl_2 (2×), and the organic extract was washed with saturated oxalic acid solution, saturated sodium bicarbonate solution. The organic phase was collected, dried over sodium sulfate, and concentrated in vacuo. The crude residue of orthoester was purified by silica gel column chromatography (EtOAc:petroleum ether 20:80) to obtain **5a** (25.0 g, 47% over four steps) as white solid.

The same procedure was added for the synthesis of orthoester **6a**.

(b). 3,5-Di-O-benzoyl-α-D-ribofuranoside prop-2-ynyl-1,2-ortho-benzoate (7a). Compound **3** was synthesized by adopting the procedure delineated for compound **1**. Subsequently, compound **3** (25.0 g, 52.5 mmol) was treated with 33% of HBr:AcOH (100.0 mL) in acetic acid (100.0 mL) at 0 °C, gently warmed to room temperature, and stirred for 10 min to obtain the ribofuranosyl bromide. Rest of the procedure was followed as delineated above to get 2,5-di-*O*-benzoyl-α-D-ribofuranoside-prop-2-ynyl-1,2-orthobenzoate **7a** (18.3 g, 55% over four steps) as thick syrup.

The same procedure was added for the synthesis of orthoester **8a**.

(c). General Procedure[12] for the Synthesis of 3,5-Di-O-benzyl-β or α-D-furanosyl propargyl 1,2-O-orthoester. 3,5-Di-*O*-benzoyl-β- or α-D-furanosyl propargyl 1,2-*O*-orthoester (5.00 g, 10 mmol) and sodium methoxide (0.15 g, 2.5 mmol) were stirred in anhydrous CH_2Cl_2:methanol for 2 h at room temperature. After completion of the reaction, the reaction mixture was concentrated in vacuo, redissolved in water and EtOAc, and extracted with EtOAc (2 × 50 mL). The collected extract was dried over sodium sulfate and concentrated in vacuo. The resultant crude residue was stirred in the presence of petroleum ether (for removal of methyl benzoate) for 10 min, and the petroleum ether was decanted to afford pure diol orthoester (2.8 g) in quantitative yield and directly used without any further purification and analytical characterizations. Diol orthoester (2.5 g, 8.6 mmol) was dissolved in anhydrous dimethylformamide (DMF) (20 mL) and cooled to 0 °C in ice bath. Sodium hydride (60% dispersion in mineral oil) (1.5 equiv per −OH) was added portion-wise and the reaction mixture became cake like solid. Benzyl bromide (1.1 equiv per −OH) was added slowly, and after 2 h at 0 °C, MeOH (1 mL) and water (100 mL) were added to reaction mixture, and the compound was extracted with EtOAc (2 × 100 mL). The organic layer was washed with brine solution, dried over sodium sulfate, and concentrated. The concentrated crude residue was purified by silica gel column chromatography (EtOAc:petroleum ether, 15:85) to give 3,5-di-*O*-benzyl-β or α-D-furanosyl propargyl 1,2-*O*-orthoester in good yield.

(d). General Procedure for 1,2-trans Glycosylation. To a CH_2Cl_2 solution (5 mL) containing glycosyl donor (0.20 mmol) and glycosyl acceptor (0.20 mmol)) with 4 Å MS powder (100 mg) was added a catalytic amount of $AuCl_3$ (14 μmol), and the mixture was stirred at room temperature. After 2 h, the reaction mixture was neutralized by the addition of Et_3N (1 mL), filtered through Celite, and concentrated in vacuo. The resulting residue was purified by silica gel column chromatography using ethyl acetate:petroleum ether to obtain 1,2-*trans* furanosides in very good yield.

(e). General Procedure for 1,2-cis Furanosylation. To a CH_2Cl_2 solution (5 mL) containing orthoester donor (0.42 mmol) and hydroxyl-bearing glycosyl acceptor (0.42 mmol)) with 4 Å molecular sieves powder (100 mg) was added a catalytic amount of $AuCl_3$ (29 μmol), and the mixture was stirred at room temperature. After 2 h, the reaction mixture was neutralized by the addition of Et_3N, filtered through Celite, and concentrated in vacuo to obtain a reddish brown residue, which was redissolved in CH_3OH (5 mL). $NaOCH_3$ (20 μmol) was added, and the mixture was stirred at 25 °C for 2 h and concentrated in vacuo. The crude residue was purified by silica gel column chromatography using ethyl acetate-petroleum ether to obtain 1,2-*trans* furanosides with C-2-OH in very good yield.

Obtained C-2-OH (0.13 mmol for Glc and 0.21 mmol for Men) was redissolved in CH_2Cl_2, Dess−Martin periodinane (0.26 mmol for Glc and 0.42 mmol for Men) was added, and the mixture was stirred at 25 °C for 2 h. The reaction mixture was diluted with CH_2Cl_2 and washed with sodium thiosulfate and sodium bicarbonate solutions. Combined organic layers were washed with brine solution, dried over anhydrous Na_2SO_4, and concentrated in vacuo to 2-ribuloside, which was subsequently redissolved in CH_3OH (5 mL) and treated with $NaBH_4$ (0.26 mmol for Glc and 0.42 mmol for Men) in three portions at 0 °C. After 30 min, the reaction mixture was poured over ice and extracted with ethyl acetate, washed with brine, and dried over anhydrous Na_2SO_4. The solution was decanted and concentrated in vacuo to get a pale yellow residue, which upon purification by silica gel column chromatography gave 1,2-*cis* furanosides in very good yield.

3,5-Di-*O*-benzoyl-β-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (5a).[12] $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.5) −15.3; IR (cm^{-1}, $CHCl_3$) 3293, 3071, 2974, 1723, 1594, 1450, 1268, 1107, 717; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.41 (t, *J* = 2.3 Hz, 1H), 3.98 (d, *J* = 2.3 Hz, 2H), 4.30 (d, *J* = 7.2 Hz, 2H), 4.67 (t, *J* = 7.2 Hz, 1H), 5.20 (d, *J* = 4.2 Hz, 1H), 5.55 (s, 1H), 6.41 (d, *J* = 4.2 Hz, 1H), 7.33−7.46 (m, 7H), 7.54 (dt, *J* = 21.2, 7.3 Hz, 2H), 7.70 (dd, *J* = 6.5, 2.9 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.9, 63.6, 73.8, 77.5, 79.2, 84.3, 84.7, 106.5, 122.7, 126.3, 126.3, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.8, 129.5, 129.6, 129.6, 129.7, 129.7, 130.0, 132.9, 133.5, 134.0, 165.1, 165.7; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{29}H_{24}O_8+Na]^+$ 523.1369, found 523.1379.

3,5-Di-*O*-benzoyl-β-D-lyxofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (6a). This compound is prepared using the above-mentioned general procedure using D-lyxose (7.5 g, 50.0 mmol) as the starting material. Yield: (10.8 g, 43% over four steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) −44.7; IR (cm^{-1}, $CHCl_3$) 3290, 3065, 2918, 1723, 1591, 1445, 1269, 1099, 713; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.38 (t, *J* = 2.5 Hz, 1H), 3.97 (d, *J* = 2.5 Hz, 2H), 4.33 (dd, *J* = 11.9, 7.7 Hz, 1H), 4.56 (dd, *J* = 11.9, 5.3 Hz, 1H), 4.77 (td, *J* = 7.5, 5.3 Hz, 1H), 5.31 (dd, *J* = 5.7, 4.3 Hz, 1H), 5.51 (dd, *J* = 7.4, 5.8 Hz, 1H), 6.26 (d, *J* = 4.2 Hz, 1H), 7.29−7.73 (m, 11H), 7.84−8.04 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.9, 63.6, 71.8, 73.8, 78.0, 78.4, 79.2, 105.4, 123.6, 126.4, 126.4, 128.2, 128.2, 128.4, 128.4, 128.5, 128.5, 128.7, 129.6, 129.6, 129.6, 129.9, 129.9, 129.9, 133.0, 133.5, 134.5, 165.4, 165.9; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{29}H_{24}O_8+Na]^+$ 523.1369, found 523.1377.

3,5-Di-*O*-benzoyl-α-D-ribofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (7a). This compound is prepared using the above-mentioned general procedure using D-ribose (10 g, 66.6 mmol) as the starting material. Yield: (18.3 g, 55% over four steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 2.6) +123.1; IR (cm^{-1}, $CHCl_3$) 3291, 3066, 2930, 1725, 1602, 1451, 1271, 1099, 710; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.40 (t, *J* = 2.4 Hz, 1H), 4.07 (dABq, *J* = 15.2, 2.4 Hz, 2H), 4.17−4.29 (m, 1H), 4.39 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.62 (dd, *J* = 12.3, 3.3 Hz, 1H), 5.07 (dd, *J* = 9.3, 5.3 Hz, 1H), 5.33 (dd, *J* = 5.1, 4.3 Hz, 1H), 6.25 (d, *J* = 4.2 Hz, 1H), 7.24−7.81 (m, 11H), 7.89−8.10 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.5, 62.4, 72.8, 73.8, 76.2, 77.7, 79.1, 104.7, 123.5, 126.3, 126.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.8, 129.4, 129.6, 129.7, 129.7, 129.9, 129.9, 133.2, 133.6, 135.8, 165.5, 166.0; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{29}H_{24}O_8+Na]^+$ 523.1369, found 523.1364.

3,5-Di-*O*-benzoyl-α-D-xylofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (8a). This compound is prepared using the above-mentioned general procedure using D-xylose (10.0 g, 66.6 mmol) as the starting material. Yield: (17.34 g, 52% over four steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) −4.2; IR (cm^{-1}, $CHCl_3$) 3290, 3068, 2930, 1725, 1591, 1447, 1268, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.40 (t, *J* = 2.4 Hz, 1H), 4.12−3.93 (m, 2H), 4.64−4.43 (m, 1H), 4.56 (dd, *J* = 7.1, 5.9 Hz, 2H), 5.04 (d, *J* = 4.1 Hz, 1H), 5.66 (d, *J* = 3.1 Hz, 1H), 6.37 (d, *J* = 4.1 Hz, 1H), 7.79−7.32 (m, 11H), 8.16−7.88 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.8, 61.5, 73.8, 76.0, 77.8, 79.2, 84.0, 105.2, 122.8, 126.2, 126.2, 128.3, 128.3, 128.4, 128.4, 128.6, 128.6, 128.7, 129.3, 129.6, 129.6, 129.7, 129.8, 129.9, 133.1, 133.7, 134.9, 165.0, 165.9; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{29}H_{24}O_8+Na]^+$ 523.1369, found 523.1395.

3,5-Di-*O*-benzyl-β-D-arabinofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (5b).[12] This compound is prepared using the above-mentioned general procedure using **5a** (5.0 g, 10.0 mmol) as the starting material. Yield: (3.78 g, 80% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) −16.0; IR (cm^{-1}, $CHCl_3$) 3291, 3033, 2928, 2867, 1721, 1592, 1453, 1275, 1111, 701; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.38 (t, *J* =

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2.3 Hz, 1H), 3.20 (dd, J = 9.8, 7.9 Hz, 1H), 3.33 (dd, J = 9.8, 6.4 Hz, 1H), 3.97 (dd, J = 9.9, 2.4 Hz, 1H), 4.02 (s, 1H), 4.23 (d, J = 12.0 Hz, 1H), 4.35 (d, J = 12.3 Hz, 1H), 4.40 (t, J = 7.3 Hz, 1H), 4.55−4.66 (m, 1H), 4.58 (d, J = 2.6 Hz, 2H), 5.02 (d, J = 4.5 Hz, 1H), 6.25 (d, J = 4.4 Hz, 1H), 7.11−7.17 (m, 2H), 7.31 (m, 11H), 7.54−7.59 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.7, 69.8, 71.5, 73.2, 73.6, 79.4, 82.6, 85.1, 85.1, 106.5, 122.4, 122.4, 126.4, 122.4, 127.6, 127.6, 127.8, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 129.7, 135.2, 137.0, 137.8; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{28}O_6+Na]^+$ 495.1784, found 495.1787.

3,5-Di-*O*-benzyl-β-D-lyxofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (6b). This compound is prepared using the above-mentioned general procedure using **6a** (5.0 g, 10.0 mmol) as the starting material. Yield: (3.54 g, 75% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) −31.0; IR (cm^{-1}, $CHCl_3$) 3290, 3070, 2927, 1592, 1453, 1275, 1115, 715; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ, 2.42 (t, J = 2.1 Hz, 1H), 3.54 (dd, J = 11.3, 2.2 Hz, 1H), 3.71 (d, J = 11.3 Hz, 1H), 4.00−3.88 (m, 2H), 4.07 (d, J = 1.7 Hz, 2H), 4.47 (d, J = 12.2 Hz, 1H), 4.57 (d, J = 13.4 Hz, 2H), 4.81−4.72 (m, 1H), 4.93 (dd, J = 5.6, 2.6 Hz, 1H), 6.11 (d, J = 4.1 Hz, 1H), 7.48−7.14 (m, 13H), 7.85−7.56 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.7, 67.3, 72.1, 73.3, 73.5, 76.9, 77.4, 78.3, 79.6, 104.7, 123.2, 126.4, 126.4, 127.6, 127.6, 127.6, 127.8, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.5, 135.3, 137.3, 137.8; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{28}O_6+Na]^+$ 495.1784, found 495.1780.

3,5-Di-*O*-benzyl-α-D-ribofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (7b).[12] This compound is prepared using the above-mentioned general procedure using **7a** (5.0 g, 10.0 mmol) as the starting material. Yield: (3.87 g, 82% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.7) +21.3; IR (cm^{-1}, $CHCl_3$) 3290, 3060, 2928, 1722, 1590, 1450, 1262, 1110, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 2.40 (t, J = 2.1 Hz, 1H), 3.46−3.58 (m, 1H), 3.69 (d, J = 11.3 Hz, 1H), 3.84−3.98 (m, 2H), 4.01−4.08 (m, 2H), 4.45 (d, J = 12.2 Hz, 1H), 4.54 (d, J = 13.4 Hz, 2H), 4.76 (d, J = 11.5 Hz, 1H), 4.90 (t, J = 4.1 Hz, 1H), 6.09 (dd, J = 4.1, 1.4 Hz, 1H), 7.11−7.46 (m, 13H), 7.62−7.84 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.6, 67.3, 72.1, 73.3, 73.5, 76.9, 77.4, 78.3, 79.6, 104.7, 123.2, 126.4, 126.4, 127.6, 127.6, 127.6, 128.0, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 129.5, 135.3, 137.3, 137.8; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{28}O_6+Na]^+$ 495.1784, found 495.1789.

3,5-Di-*O*-benzyl-α-D-xylofuranoside (prop-2-yn-1-yl)-1,2-orthobenzoate (8b). This compound is prepared using the above-mentioned general procedure using **8a** (5.0 g, 10.0 mmol) as the starting material. Yield: (3.78 g, 80% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) −9.4; IR (cm^{-1}, $CHCl_3$) 3293, 3070, 2925, 1594, 1450, 1270, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 2.39 (t, J = 2.5 Hz, 1H), 3.72 (d, J = 6.1 Hz, 2H), 4.00 (d, J = 3.3 Hz, 1H), 4.02 (dABq, J = 15.5, 2.5 Hz, 2H), 4.13−4.23 (m, 1H), 4.46 (d, J = 11.9 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 4.68 (d, J = 12.0 Hz, 1H), 4.95 (d, J = 4.1 Hz, 1H), 6.23 (d, J = 4.1 Hz, 1H), 7.15−7.50 (m, 13H), 7.54−7.75 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 51.8, 67.2, 72.0, 73.4, 73.6, 79.5, 79.9, 81.1, 82.9, 105.4, 122.4, 126.2, 126.2, 127.6, 127.6, 127.6, 127.7, 127.7, 128.0, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 129.7, 135.1, 137.2, 137.8; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{28}O_6+Na]^+$ 495.1784, found 495.1780.

Methyl-2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (19a).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.148 g, 78%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +28.5; IR (cm^{-1}, $CHCl_3$) 3062, 2928, 1727, 1596, 1453, 1269, 1104, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.44 (s, 3H), 3.79 (d, J = 11.0 Hz, 1H), 4.05 (dd, J = 11.0, 4.1 Hz, 1H), 4.29 (d, J = 8.6 Hz, 1H), 4.61 (dd, J = 11.6, 4.9 Hz, 1H), 4.66−4.70 (m, 1H), 4.74 (dd, J = 11.5, 2.8 Hz, 1H), 5.25 (d, J = 3.5 Hz, 1H), 5.30 (dd, J = 10.1, 3.6 Hz, 1H), 5.35 (s, 1H), 5.54 (d, J = 4.3 Hz, 1H), 5.61 (s, 1H), 5.73 (t, J = 9.9 Hz, 1H), 6.14 (t, J = 9.8 Hz, 1H), 7.14−7.67 (m, 18H), 7.74 (d, J = 8.1 Hz, 2H), 7.93 (dd, J = 17.2, 8.0 Hz, 4H), 7.97−8.01 (m, 4H), 8.22 (d, J = 7.8 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.5, 63.7, 65.0, 68.4, 68.9, 70.6, 72.0, 77.7, 81.3, 81.9, 97.0, 105.4, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.1, 129.1, 129.3, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 132.9, 133.0, 133.3, 133.3, 133.5, 133.5, 165.0, 165.3, 165.8, 165.8, 165.9, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$ 973.2684, found 973.2706.

(Pent-4-enyl) 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (19b).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.098 g, 92%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.1) −4.6; IR (cm^{-1}, $CHCl_3$) 3068, 2929, 1725, 1593, 1266, 1109, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.76 (quintet, J = 6.7 Hz, 2H), 2.19 (q, J = 4.4 Hz, 2H), 3.56 (dt, J = 9.5, 6.2 Hz, 1H), 3.82 (dt, J = 9.5, 6.6 Hz, 1H), 4.58 (q, J = 4.8 Hz, 1H), 4.68 (dd, J = 11.9, 5.0 Hz, 1H), 4.83 (dd, J = 11.9, 3.5 Hz, 1H), 4.96 (dq, J = 10.0, 1.4 Hz, 1H), 5.02 (dq, J = 17.1, 1.6 Hz, 1H), 5.28 (s, 1H), 5.52 (d, J = 1.0 Hz, 1H), 5.58 (d, J = 4.7 Hz, 1H), 5.83 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.49−7.54 (m, 1H), 7.55−7.64 (m, 2H), 8.00 (dd, J = 8.1, 1.1 Hz, 2H), 8.05 (dd, J = 8.0, 1.0 Hz, 2H), 8.09 (dd, J = 8.3, 1.0 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.7, 30.3, 63.8, 66.8, 77.0, 77.9, 81.0, 82.0, 105.7, 115.0, 128.3, 128.3, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.5, 133.5, 138.0, 165.5, 165.8, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{31}H_{30}O_8+Na]^+$ 553.1838, found 553.1844.

Benzyl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (19c).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.092 g, 83%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.5) +5.8; IR (cm^{-1}, $CHCl_3$) 3066, 2928, 1724, 1596, 1452, 1266, 1108, 708; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 4.61 (q, J = 4.6 Hz, 1H), 4.66 (d, J = 12.1 Hz, 1H), 4.69 (dd,, J = 12.7, 5.0 Hz, 1H), 4.84 (dd, J = 11.9, 3.5 Hz, 1H), 4.88 (d, J = 12.0 Hz, 1H), 5.40 (s, 1H), 5.60(d, J = 5.2 Hz, 1H), 5.61 (s, 1H), 7.26−7.70 (m, 14H), 7.98−8.08 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 63.8, 68.8, 77.8, 81.3, 81.9, 104.9, 127.7, 127.7, 127.8, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.8, 129.8, 129.9, 129.9, 130.0, 130.0, 133.1, 133.5, 133.5, 137.3, 165.4, 165.8, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{33}H_{28}O_8+Na]^+$ 575.1682, found 575.1681.

Cholesteryl 2,3,5-tri-*O*-benzoyl-α-D-arabinofuranoside (19d).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.136 g, 82%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1) +3.7; IR (cm^{-1}, $CHCl_3$) 3034, 2940, 1726, 1596, 1455, 1267, 1108, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.68 (s, 3H), 0.86 (d, J = 1.7 Hz, 3H), 0.87 (d, J = 1.7 Hz, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.93−1.71 (m, 24H), 1.78−1.85 (m, 1H), 1.88 (dt, J = 12.8, 3.0 Hz, 1H), 1.99 (td, J = 11.8, 11.2, 4.8 Hz, 3H), 2.41 (d, J = 7.3 Hz, 2H), 3.63 (dtd, J = 11.2, 7.2, 6.5, 4.3 Hz, 1H), 4.62 (q, J = 4.8 Hz, 1H), 4.68 (dd, J = 11.8, 5.0 Hz, 1H), 4.82 (dd, J = 11.8, 3.4 Hz, 1H), 5.35 (d, J = 4.6 Hz, 1H), 5.45 (s, 1H), 5.49 (s, 1H), 5.57 (d, J = 5.0 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 7.8 Hz, 2H), 7.47 (t, J = 7.8 Hz, 2H), 7.49−7.68 (m, 3H), 8.01 (d, J = 7.4 Hz, 2H), 8.05 (d, J = 7.2 Hz, 2H), 8.09 (d, J = 7.5 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 11.8, 18.7, 19.4, 21.0, 22.6, 22.8, 23.8, 24.3, 27.7, 28.0, 28.2, 31.8, 31.9, 35.8, 36.1, 36.7, 37.0, 39.5, 39.7, 40.0, 42.3, 50.0, 56.1, 56.7, 63.8, 76.6, 77.9, 80.7, 82.5, 103.8, 121.9, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 129.1, 129.2, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 133.0, 133.4 133.5, 140.6, 165.5, 165.8, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{53}H_{66}O_8+Na]^+$ 853.4655, found 853.4664

Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-L-serinate (19e).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.139 g, 90%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) −5.3; IR (cm^{-1}, $CHCl_3$) 3064, 2926, 1723, 1594, 1450, 1261, 1120, 703; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 4.09 (qd, J = 10.2, 2.8 Hz, 2H), 4.50 (q, J = 4.4 Hz, 1H), 4.61 (dd, J = 12.0, 5.3 Hz, 1H), 4.65 (dt, J = 2.6, 8.9 Hz, 1H), 4.76 (dd, J = 11.9, 3.5 Hz, 1H), 5.04 (ABq, J = 12.3 Hz, 2H), 5.20 (ABq, J = 12.3 Hz, 2H), 5.22 (s, 1H), 5.42 (s, 1H), 5.53 (d, J = 4.3 Hz, 1H), 5.80 (d, J = 8.7 Hz, 1H), 7.20−7.43 (m, 16H), 7.50 (q, J = 7.5 Hz, 2H), 7.57 (tt, J = 15.0, 7.3, 1.3 Hz,1H), 7.98

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(d, J = 7.3 Hz, 2H), 8.03 (d, J = 7.6 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.3, 63.6, 66.9, 67.4, 67.4, 68.0, 81.4, 81.8, 105.8, 128.0, 128.0, 128.1, 128.2, 128.2, 128.2, 128.2, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.7, 128.8, 129.5, 129.7, 129.7, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 135.1, 136.0, 155.8, 165.2, 165.5, 166.1, 169.7. ; HRMS (ESI-TOF) m/z calcd for $[C_{44}H_{39}O_{12}+Na]^+$ 796.2370, found 796.2372.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (19f).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.149 g, 82%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +17.7; IR (cm^{-1}, $CHCl_3$) 3038, 2924, 1724, 1591, 1450, 1266, 1104, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.58 (dd, J = 9.6, 3.5 Hz, 1H), 3.67 (t, J = 9.3 Hz, 1H), 3.73–3.85 (m, 2H), 3.99 (t, J = 9.2 Hz, 1H), 4.10 (dd, J = 11.0, 3.5 Hz, 1H), 4.47 (q, J = 4.5 Hz, 1H), 4.57 (dd, J = 12.0, 5.0 Hz, 1H), 4.60 (s, 1H), 4.62 (d, J = 6.6 Hz, 1H), 4.67 (d, J = 12.1 Hz, 1H), 4.73 (dd, J = 12.0, 3.3 Hz, 1H), 4.77 (d, J = 1.8 Hz, 1H), 4.80 (s, 1H), 4.82 (d, J = 11.0 Hz, 1H), 4.98 (d, J = 10.9 Hz, 1H), 5.41 (s, 1H), 5.52 (d, J = 4.4 Hz, 1H), 5.59 (s, 1H), 7.14–7.44 (m, 21H), 7.45–7.51 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.97 (d, J = 5.3 Hz, 2H), 7.99 (d, J = 5.1 Hz, 2H), 8.04 (d, J = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.1, 63.7, 66.0, 69.8, 73.4, 75.0, 75.6, 77.8, 77.8, 80.0, 81.7, 81.8, 81.9, 98.0, 106.1, 127.4, 127.4, 127.5, 127.7, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 138.1, 138.2, 138.8, 165.2, 165.6, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3332.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (19g).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.145 g, 80%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.5) +2.4; IR (cm^{-1}, $CHCl_3$) 3020, 2925, 1725, 1596, 1453, 1268, 1105, 758; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.43 (s, 3H), 3.56 (dd, J = 9.6, 3.4 Hz, 1H), 3.66 (dd, J = 9.1, 3.0 Hz, 1H), 3.70 (t, J = 8.3 Hz, 1H), 3.84 (s, 1H), 3.85 (d, J = 4.9 Hz, 1H), 4.06 (t, J = 9.1 Hz, 1H), 4.27 (q, J = 4.4 Hz, 1H), 4.40 (d, J = 12.1 Hz, 1H), 4.48 (dd, J = 18.7, 6.9 Hz, 1H), 4.49 (s, 1H), 4.57 (dd, J = 11.8, 3.8 Hz, 1H), 4.63 (dd, J = 7.8, 4.3 Hz, 2H), 4.76 (d, J = 7.3 Hz, 1H), 4.79 (d, J = 6.1 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 5.47 (d, J = 4.4 Hz, 1H), 5.55 (s, 1H), 5.82 (s, 1H), 6.93–7.71 (m, 24H), 7.85 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.4 Hz, 2H), 8.05–8.10 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.3, 63.7, 69.0, 69.5, 73.3, 73.4, 73.9, 75.4, 77.9, 79.9, 81.7, 81.7, 81.9, 97.9, 106.7, 127.2, 127.5, 127.5, 127.5, 127.5, 127.5, 127.9, 128.1, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.1, 129.6, 129.6, 129.6, 129.8, 129.8, 129.8, 129.8, 132.9, 133.4, 133.5, 137.8, 137.9, 138.2, 165.0, 165.5, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3328.

(Pent-4-enyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-mannopyranoside (19h).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.148 g, 77%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) +3.0; IR (cm^{-1}, $CHCl_3$) 3070, 2926, 1725, 1595, 1440, 1267, 1107, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.58 (quintet, J = 6.9 Hz, 2H), 2.02 (q, J = 13.4, 5.7 Hz, 2H), 3.32 (dt, J = 9.6, 6.3 Hz, 1H), 3.66 (dt, J = 9.6, 6.5 Hz, 1H), 3.75–3.85 (m, 3H), 3.93 (dd, J = 9.4, 3.0 Hz, 1H), 4.11 (t, J = 9.7 Hz, 1H), 4.17 (dd, J = 11.3, 4.5 Hz, 1H), 4.48 (q, J = 7.9, 4.4 Hz, 1H), 4.59 (dd, J = 11.4, 4.6 Hz, 2H), 4.63 (s, 2H), 4.73 (s, 2H), 4.76 (dd, J = 12.1, 3.3 Hz, 1H), 4.83–4.87 (m, 2H), 4.91–5.01 (m, 2H), 5.48 (s, 1H), 5.51 (d, J = 4.4 Hz, 1H), 5.69 (s, 1H), 5.70–5.81 (m, 1H), 7.07–7.71 (m, 24H), 7.93–8.12 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.5, 30.2, 63.8, 66.5, 66.8, 71.1, 72.0, 72.5, 74.6, 74.8, 75.1, 77.9, 80.2, 81.8, 81.9, 97.9, 106.0, 114.9, 127.5, 127.5, 127.5, 127.5, 127.5, 127.5, 127.6, 127.6, 127.6, 127.7, 127.7, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 129.0, 129.1, 129.7, 129.7, 129.7, 129.8, 129.8, 130.0, 130.0, 132.9, 133.3, 138.0, 138.3, 138.3, 138.4, 138.5, 165.1, 165.8, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$ 985.3775, found 985.3784.

Propargyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (19i).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.151 g, 81%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.1) +24.9; IR (cm^{-1}, $CHCl_3$) 3293, 3031, 2925, 1724, 1595, 1446, 1266, 1104, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 2.42 (t, J = 2.4 Hz, 1H), 3.64 (dd, J = 9.7, 3.7 Hz, 1H), 3.70 (t, J = 9.0 Hz, 1H), 3.79 (dd, J = 11.3, 1.6 Hz, 1H), 3.86 (qd, J = 10.0, 3.4, 1.9 Hz, 1H), 4.01 (t, J = 9.3 Hz, 1H), 4.10 (dd, J = 11.3, 3.7 Hz, 1H), 4.27 (ddd, J = 18.3, 15.9, 2.3 Hz, 2H), 4.48 (q, J = 4.7 Hz, 1H), 4.61 (d, J = 4.8 Hz, 1H), 4.62 (d, J = 10.9 Hz, 1H), 4.53–4.71 (m, 1H), 4.74 (d, J = 5.3 Hz, 1H), 4.72–4.77 (m, 1H), 4.79 (d, J = 10.9 Hz, 1H), 4.84 (d, J = 10.9 Hz, 1H), 5.00 (d, J = 10.8 Hz, 1H), 5.08 (d, J = 3.6 Hz, 1H), 5.41 (s, 1H), 5.54 (d, J = 4.5 Hz, 1H), 5.60 (d, J = 0.9 Hz, 1H), 7.10–7.69 (m, 24H), 7.91–8.13 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.4, 63.7, 65.8, 70.4, 73.0, 74.8, 74.9, 75.0, 75.6, 77.5, 77.8, 78.8, 79.5, 81.7, 81.8, 95.0, 106.1, 127.4, 127.4, 127.5, 127.7, 127.8, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.9, 128.9, 129.6, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 133.0, 133.5, 133.5, 137.9, 138.1, 138.7, 165.2, 165.6, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$ 955.3306, found 955.3319.

Propargyl 3,5-di-*O*-benzyl-2-*O*-(2,3,5-tri-*O*-benzoyl-α-D-arabinofuranosyl)-α-D-ara-binofuranoside (19j).[12] This compound is prepared using the above-mentioned general procedure using **5a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.117 g, 72%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +22.3; IR (cm^{-1}, $CHCl_3$) 3297, 3067, 2927, 1724, 1593, 1453, 1267, 1108, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 2.32 (t, J = 2.4 Hz, 1H), 3.66 (dABq, J = 14.0, 10.7 Hz, 2H), 3.97 (dd, J = 6.4, 2.7 Hz, 1H), 4.20–4.26 (m, 1H), 4.28 (d, J = 2.4 Hz, 2H), 4.28–4.30 (m, 1H), 4.56 (ABq, J = 15.7 Hz, 2H), 4.58–4.65 (m, 1H), 4.62 (d, J = 13.3 Hz, 1H), 4.69 (dd, J = 11.7, 4.7 Hz, 2H), 4.78 (dd, J = 11.9, 3.8 Hz, 1H), 5.22 (s, 1H), 5.37 (s, 1H), 5.46 (d, J = 1.3 Hz, 1H), 5.59 (d, J = 4.0 Hz, 1H), 7.09–7.35 (m, 10H), 7.38–7.67 (m, 9H), 7.94–8.16 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.0, 63.6, 69.5, 72.4, 73.4, 74.5, 77.5, 79.0, 81.00, 81.4, 82.2, 83.2, 86.5, 104.7, 105.5, 127.6, 127.7, 127.7, 127.7, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.9, 129.0, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.1, 133.5, 133.6, 137.6, 137.9, 165.3, 165.6, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{48}H_{44}O_{12}+Na]^+$ 835.2730, found 835.2722.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (20a). This compound is prepared using the above-mentioned general procedure using **6a** (0.10 g, 0.2 mmol) as the starting material. Yield: (0.143 g, 75%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.2) +57.5; IR (cm^{-1}, $CHCl_3$) 3073, 2927, 1729, 1594, 1453, 1271, 1104, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.49 (s, 3H), 3.76 (dd, J = 11.1, 2.5 Hz, 1H), 4.03 (dd, J = 11.1, 4.3 Hz, 1H), 4.27 (ddd, J = 10.2, 4.1, 2.5 Hz, 1H), 4.54 (d, J = 6.1 Hz, 2H), 4.79 (q, J = 6.1 Hz, 1H), 5.27 (d, J = 3.7 Hz, 1H), 5.31 (dd, J = 9.9, 3.7 Hz, 1H), 5.37 (d, J = 0.3 Hz, 1H), 5.71 (dd, J = 5.4, 1.0 Hz, 1H), 5.74 (t, J = 10.0 Hz, 1H), 6.11 (t, J = 5.7 Hz, 1H), 6.16 (t, J = 9.8 Hz, 1H), 7.14–7.63 (m, 18H), 7.81–8.03 (m, 12H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.7, 63.2, 65.8, 68.3, 69.0, 70.6, 71.8, 72.1, 75.8, 76.1, 97.1, 104.5, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.9, 129.0, 129.0, 129.1, 129.2, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.9, 129.9, 133.0, 133.0, 133.3, 133.3, 133.3, 133.3, 165.0, 165.2, 165.2, 165.7, 165.8, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$ 973.2684, found 973.2680.

Pent-4-enyl 2,3,5-tri-*O*-benzoyl α-D-lyxofuranoside (20b). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.100 g, 94%); $[\alpha]_D^{25}$ ($CHCl_3$, c 2.4) +11.9; IR (cm^{-1}, $CHCl_3$) 3076, 2929, 1729, 1592, 1449, 1269, 1112, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.72 (quintet, J = 6.7 Hz, 2H), 2.15 (q, J = 6.9 Hz, 2H), 3.53 (dt, J = 9.5, 6.4 Hz, 1H), 3.80 (dt, J = 9.5, 6.5 Hz, 1H), 4.58–4.69 (m, 2H), 4.82 (q, J = 6.2 Hz, 1H), 4.97 (dq, J = 10.1, 1.4 Hz, 1H), 5.04

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(dq, J = 17.1, 1.6 Hz, 1H), 5.31 (d, J = 1.0 Hz, 1H), 5.62 (dd, J = 5.2, 1.2 Hz, 1H), 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 6.05 (t, J = 5.8 Hz, 1H), 7.29 (t, J = 7.8 Hz, 2H), 7.36 (t, J = 7.8 Hz, 4H), 7.44−7.57 (m, 3H), 7.86 (dd, J = 8.3, 1.2 Hz, 2H), 7.92−7.97 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.6, 30.2, 63.4, 67.6, 71.9, 75.5, 76.1, 104.7, 115.0, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.0, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.4, 133.4, 137.9, 165.2, 165.3, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{31}H_{30}O_8+Na]^+$ 553.1838, found 553.1854.

Cholesteryl 2,3,5-tri-*O*-benzoyl-α-D-lyxofuranoside (20c). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.134 g, 81%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.4) +10.3; IR (cm^{-1}, $CHCl_3$) 3072, 2938, 1730, 1599, 1460, 1263, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.67 (s, 3H), 0.84 (d, J = 1.8 Hz, 3H), 0.86 (d, J = 1.8 Hz, 3H), 0.90 (d, J = 6.5 Hz, 3H), 1.01 (s, 3H), 0.97−2.10 (m, 26H), 2.30−2.44 (m, 2H), 3.57 (dt, J = 11.1, 6.2 Hz, 1H), 4.61 (dd, J = 11.3, 5.5 Hz, 1H), 4.65 (dd, J = 11.2, 6.2 Hz, 1H), 4.85 (q, J = 6.2 Hz, 1H), 5.34 (d, J = 5.2 Hz, 1H), 5.46 (d, J = 0.7 Hz, 1H), 5.59 (dd, J = 5.2, 1.1 Hz, 1H), 6.06 (t, J = 6.0 Hz, 1H), 7.25−7.39 (m, 6H), 7.42−7.58 (m, 3H), 7.86 (dd, J = 8.3, 1.1 Hz, 2H), 7.95 (ddd, J = 8.0, 6.4, 1.3 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 11.8, 18.7, 19.4, 21.0, 22.6, 22.8, 23.8, 24.3, 27.9, 28.0, 28.2, 31.8, 31.9, 35.8, 36.1, 36.7, 37.0, 39.5, 39.7, 40.1, 42.3, 50.1, 56.1, 56.7, 63.4, 71.9, 75.3, 76.4, 77.7, 103.0, 121.9, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.8, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 140.5, 165.3, 165.3, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{53}H_{66}O_8+Na]^+$ 853.4655, found 853.4664.

Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-L-serinate (20d). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.121 g, 78%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.4) +1.9; IR (cm^{-1}, $CHCl_3$) 3434, 3368, 3067, 2924, 1727, 1594, 1454, 1267, 1111, 707; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.99 (d, J = 8.9 Hz, 1H), 4.15 (dd, J = 10.5, 2.8 Hz, 1H), 4.52−4.65 (m, 3H), 4.70 (q, J = 5.7 Hz, 1H), 5.03 (d, J = 12.3 Hz, 1H), 5.10 (d, J = 12.1 Hz, 1H), 5.20 (s, 2H), 5.25 (q, J = 12.1 Hz, 1H), 5.49 (d, J = 5.2 Hz, 1H), 5.87 (t, J = 5.5 Hz, 1H), 5.97 (d, J = 8.7 Hz, 1H), 7.21−7.39 (m, 16H), 7.51 (dt, J = 13.6, 7.4 Hz, 3H), 7.86 (d, J = 8.0 Hz, 2H), 7.90 (d, J = 8.2 Hz, 2H), 7.98 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.5, 63.1, 67.0, 67.5, 69.6, 71.5, 75.9, 76.1, 105.5, 128.0, 128.0, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.7, 128.8, 129.5, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.5, 133.5, 135.2, 136.2, 156.0, 165.0, 165.1, 166.1, 169.7; HRMS (ESI-TOF) m/z calcd for $[C_{44}H_{39}O_{12}+Na]^+$ 796.2370, found 796.2372.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (20e). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.131 g, 72%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.2) +33.3; IR (cm^{-1}, $CHCl_3$) 3072, 2924, 1729, 1595, 1456, 1268, 1100, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.37 (s, 3H), 3.57 (dd, J = 9.7, 3.5 Hz, 1H), 3.61 (d, J = 9.5 Hz, 1H), 3.72−3.85 (m, 2H), 4.01 (t, J = 9.3 Hz, 1H), 4.06 (dd, J = 11.3, 3.9 Hz, 1H), 4.53−4.70 (m, 5H), 4.78 (d, J = 12.0 Hz, 1H), 4.79 (q, J = 6.0 Hz, 1H), 4.83 (d, J = 10.9 Hz, 1H), 4.94 (d, J = 10.8 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 5.43 (s, 1H), 5.69 (dd, J = 5.2, 1.3 Hz, 1H), 6.03 (t, J = 5.8 Hz, 1H), 7.19−7.43 (m, 21H), 7.44−7.61 (m, 3H), 7.82−7.88 (m, 2H), 7.89−7.92 (m, 2H), 7.93−7.98 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.2, 63.4, 66.5, 69.8, 71.7, 73.4, 75.1, 75.7, 75.9, 77.5, 75.7, 80.0, 82.0, 98.0, 105.0, 127.5, 127.7, 127.8. 127.8, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.7, 129.0, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 138.1, 138.1, 138.7, 165.0, 165.2, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3314.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (20f). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.127 g, 70%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.2) +24.0; IR (cm^{-1}, $CHCl_3$) 3065, 2923, 1729, 1595, 1454, 1269, 1104, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.41 (s, 3H), 3.52 (dd, J = 9.6, 3.5 Hz, 1H), 3.58−3.68 (m, 1H), 3.73 (d, J = 10.8 Hz, 1H), 3.78 (d, J = 5.4 Hz, 2H), 3.79 (s, 1H), 3.94−4.00 (m, 1H), 4.44−4.51 (m, 4H), 4.61 (d, J = 3.5 Hz, 1H), 4.62 (t, J = 12.5 Hz, 1H), 4.70 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 12.1 Hz, 1H), 4.94 (d, J = 10.9 Hz, 1H), 5.60 (dd, J = 5.1, 1.5 Hz, 1H), 5.79 (d, J = 1.4 Hz, 1H), 5.87 (t, J = 5.2 Hz, 1H), 7.03 (dd, J = 5.1, 1.9 Hz, 3H), 7.14−7.39 (m, 18H), 7.41−7.59 (m, 3H), 7.73−7.84 (m, 4H), 7.87−7.95 (m, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.3, 63.3, 68.9, 69.4, 71.7, 73.2, 73.3, 75.1, 75.5, 75.7, 76.1, 79.8, 81.5, 97.8, 105.6, 127.3, 127.5, 127.6, 127.7, 127.7, 127.9, 128.1, 128.1, 128.1, 128.1, 128.1, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.7, 128.8, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 137.9, 138.0, 138.3, 165.0, 165.1, 166.0; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3315.

Pent-4-enyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-mannopyranoside (20g). This compound is prepared using the above-mentioned general (d) procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.140 g, 73%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.2) +23.6; IR (cm^{-1}, $CHCl_3$) 3079, 2925, 1728, 1592, 1456, 1263, 1103, 714; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.61 (quintet, J = 7.9 Hz, 2H), 2.05 (q, J = 7.6 Hz, 2H), 3.35 (dt, J = 9.7, 6.4 Hz, 1H), 3.66 (dt, J = 9.7, 6.6 Hz, 1H), 3.72−3.79 (m, 2H), 3.85 (dd, J = 11.1, 1.7 Hz, 1H), 3.91 (dd, J = 9.3, 2.9 Hz, 1H), 3.98 (t, J = 9.4 Hz, 1H), 4.09 (dd, J = 11.1, 5.0 Hz, 1H), 4.55 (dd, J = 11.6, 5.4 Hz, 1H), 4.60 (d, J = 6.7 Hz, 1H), 4.63 (s, 2H), 4.67 (d, J = 10.8 Hz, 1H), 4.71 (d, J = 3.8 Hz, 2H), 4.77−4.85 (m, 2H), 4.91−5.01 (m, 3H), 5.48 (s, 1H), 5.69−5.82 (m, 2H), 6.04 (t, J = 6.1 Hz, 1H), 7.20−7.41 (m, 20H), 7.42−7.59 (m, 4H), 7.80−7.87 (m, 2H), 7.93 (dd, J = 8.2, 1.2 Hz, 2H), 7.96 (dd, J = 8.2, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.5, 30.2, 63.5, 67.0, 67.0, 71.3, 71.8, 72.0, 72.5, 74.5, 74.8, 75.2, 75.6, 76.0, 80.2, 97.8, 104.7, 114.9, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.8, 129.1, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.3, 138.0, 138.3, 138.4, 138.5, 165.1, 165.2, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$ 985.3775, found 985.3776.

Prop-2-ynyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-α-D-lyxofuranosyl)-α-D-glucopyranoside (20h). This compound is prepared using the above-mentioned general procedure using **6a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.140 g, 75%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.9) +41.4; IR (cm^{-1}, $CHCl_3$) 3293, 3062, 2925, 1728, 1595, 1453, 1268, 1102, 705; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 2.42 (t, J = 2.3 Hz, 1H), 3.54−3.69 (m, 2H), 3.74−3.85 (m, 2H), 4.00 (t, J = 9.3 Hz, 1H), 4.05 (dd, J = 11.2, 3.6 Hz, 1H), 4.26 (ddd, J = 18.5, 15.9, 2.3 Hz, 2H), 4.56 (dd, J = 11.5, 5.5 Hz, 1H), 4.61 (dd, J = 11.6, 6.7 Hz, 1H), 4.66 (d, J = 10.7 Hz, 1H), 4.71 (d, J = 10.0 Hz, 2H), 4.77 (dd, J = 12.0, 6.2 Hz, 1H), 4.82 (d, J = 10.9 Hz, 1H), 4.93 (d, J = 10.7 Hz, 1H), 5.00 (d, J = 10.9 Hz, 1H), 5.04 (d, J = 3.6 Hz, 1H), 5.41 (d, J = 0.9 Hz, 1H), 5.67 (dd, J = 5.3, 1.1 Hz, 1H), 6.02 (t, J = 5.6 Hz, 1H), 7.19−7.42 (m, 21H), 7.43−7.58 (m, 3H), 7.84 (dd, J = 8.3, 1.1 Hz, 2H), 7.90 (dd, J = 8.3, 1.1 Hz, 2H), 7.94 (dd, J = 8.0, 1.0 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.5, 63.4, 70.5, 71.7, 73.1, 74.8, 74.8, 75.2, 75.7, 75.8, 75.9, 78.9, 79.5, 81.8, 95.2, 105.0, 127.6, 127.8, 127.8, 127.9, 127.9, 127.9, 127.9, 128.2, 128.2, 128.2, 128.2, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.7, 129.0, 129.5, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 133.0, 133.4, 133.4, 137.9, 138.1, 138.7, 165.1, 165.2, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$ 955.3306, found 955.3326.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-glucopyranoside (21a). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.150 g, 79%); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.9) +52.8; IR (cm^{-1}, $CHCl_3$) 3062, 2944, 1727, 1588, 1449, 1274, 1103, 710; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.47 (s, 3H), 3.74 (dd, J = 11.6, 6.7 Hz, 1H), 3.96 (dd, J = 11.5, 2.2 Hz, 1H), 4.24 (ddd, J = 9.2, 6.6, 2.0 Hz, 1H), 4.46−4.57 (m, 1H), 4.65−4.72 (m, 2H), 5.22 (t, J = 3.9 Hz, 1H), 5.25 (dd, J = 9.9, 3.6 Hz, 1H), 5.36 (s, 1H), 5.50 (t, J = 9.9 Hz, 1H), 5.75 (d, J = 4.9 Hz, 1H), 5.86

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(dd, J = 6.9, 4.9 Hz, 1H), 6.12 (t, J = 9.7 Hz, 1H), 7.22−7.64 (m, 18H), 7.87 (ddd, J = 8.6, 7.4, 1.2 Hz, 6H), 7.96−8.04 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.6, 64.7, 66.9, 68.9, 69.5, 70.4, 72.1, 72.2, 75.4, 79.1, 96.7, 106.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.8, 128.9, 129.0, 129.2, 129.6, 129.6, 129.6, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 129.8, 129.8, 129.9, 129.9, 133.0, 133.1, 133.3, 133.3, 133.3, 133.4, 165.1, 165.3, 165.3, 165.7, 165.7, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{46}O_{16}+Na]^+$ 973.2684, found 973.2690.

(Pent-4-enyl) 2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranoside (21b). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.095 g, 90%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.1) +41.0; IR (cm^{-1}, $CHCl_3$) 3070, 2927, 1728, 1596, 1450, 1269, 1113, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.63 (tq, J = 13.8, 6.9, 6.3 Hz, 2H), 2.08 (q, J = 7.1 Hz, 2H), 3.45 (dt, J = 9.4, 6.8 Hz, 1H), 3.78 (dt, J = 9.3, 6.5 Hz, 1H), 4.51 (dd, J = 12.9, 6.6 Hz, 1H), 4.69−4.74 (m, 2H), 4.91−4.97 (m, 1H), 4.97−5.04 (m, 1H), 5.24 (s, 1H), 5.68 (d, J = 4.7 Hz, 1H), 5.75 (ddt, J = 16.8, 10.3, 6.6 Hz, 1H), 5.87 (dd, J = 6.4, 5.0 Hz, 1H), 7.29−7.43 (m, 6H), 7.48−7.58 (m, 3H), 7.87−7.89 (m, 2H), 8.00−8.07 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.5, 30.1, 64.9, 67.8, 72.5, 75.5, 78.7, 105.5, 115.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.9, 129.2, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.1, 133.3, 133.4, 137.8, 165.2, 165.4, 166.1; HRMS (ESI-TOF) m/z calcd for $[C_{31}H_{30}O_8+Na]^+$ 553.1838, found 553.1836.

Benzyl 2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranoside (21c). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.094 g, 85%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +12.1; IR (cm^{-1}, $CHCl_3$)) 3068, 2930, 1727, 1595, 1453, 1268, 1112, 706; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 4.53−4.59 (m, 1H), 4.59 (d, J = 11.8 Hz, 1H), 4.74 (dd, J = 15.3, 3.5 Hz 1H), 4.75−4.78(m, 1H), 4.82 (d, J = 11.8 Hz, 1H), 5.35 (s, 1H), 5.78 (d, J = 4.8 Hz, 1H), 5.94 (dd, J = 7.0, 4.8 Hz, 1H), 7.26−7.35 (m, 10H), 7.41 (t, J = 7.7 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H), 7.88 (d, J = 7.3 Hz, 2H), 8.03 (dd, J = 12.3, 7.3 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 64.6, 69.6, 72.3, 75.6, 79.0, 104.4, 127.8, 127.9, 127.9, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.8, 129.1, 129.5, 129.6, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 136.7, 165.2, 165.3, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{33}H_{28}O_8+Na]^+$ 575.1682, found 575.1697.

Cholesteryl 2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranoside (21d). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.136 g, 82%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) −1.5; IR (cm^{-1}, $CHCl_3$) 3071, 2942, 1729, 1591, 1455, 1269, 1111, 709; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 0.66 (s, 3H), 0.85 (dd, J = 6.6, 1.5 Hz, 6H), 0.88−1.66 (m, 25H), 1.73−2.03 (m, 6H), 2.21 (t, J = 11.1 Hz, 1H), 2.38 (ddd, J = 13.0, 4.5, 1.9 Hz, 1H), 3.55 (dq, J = 11.1, 5.6, 4.4 Hz, 2H), 4.52 (q, J = 13, 6.8 Hz 1H), 4.64−4.74 (m, 2H), 5.33 (d, J = 5.1 Hz, 1H), 5.41 (s, 1H), 5.63 (d, J = 4.8 Hz, 1H), 5.88 (dd, J = 6.4, 4.9 Hz, 1H), 7.27−7.45 (m, 6H), 7.45−7.61 (m, 3H), 7.88 (d, J = 7.6 Hz, 2H), 8.03 (dd, J = 15.8, 7.5 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 12.0, 18.8, 19.4, 21.1, 22.7, 22.9, 23.9, 24.4, 28.1, 28.3, 29.6, 31.9, 32.0, 35.9, 36.3, 36.8, 37.2, 38.6, 39.6, 39.9, 42.4, 50.2, 56.2, 56.8, 65.2, 72.8, 76.2, 78.1, 78.6, 103.9, 122.1, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6, 129.1, 129.4, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 133.2, 133.4, 133.5, 140.4, 165.4, 165.5, 166.3; HRMS (ESI-TOF) m/z calcd for $[C_{53}H_{66}O_8+Na]^+$ 853.4655, found 853.4664.

Benzyl-*N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)-L-serinate (21e). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.136 g, 88%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) +12.1; IR (cm^{-1}, $CHCl_3$) 3371, 3061, 2947, 1725, 1596, 1504, 1453, 1267, 1114, 703; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.82 (dd, J = 10.1, 3.2 Hz, 1H), 4.30 (dd, J = 10.1, 3.2 Hz, 1H), 4.44 (qd, J = 11.6, 5.7 Hz, 2H), 4.57−4.73 (m, 2H), 5.12 (s, 2H), 5.23 (ABq, J = 12.23 Hz, 2H), 5.25 (s, 1H), 5.59 (t, J = 5.20 Hz, 1H), 5.64 (d, J = 5.0 Hz, 1H), 5.79 (d, J = 8.6 Hz, 1H), 7.23−7.43 (m, 16H), 7.46−7.53 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.88 (d, J = 7.3 Hz, 2H), 7.97 (d, J = 7.5 Hz, 2H), 8.01 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.2, 65.5, 67.1, 67.6, 68.4, 72.7, 75.3, 79.3, 106.0, 128.0, 128.0, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.6, 128.6, 128.8, 129.0, 129.5, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.1, 133.4, 133.5, 135.1, 136.1, 155.9, 165.1, 165.2, 166.0, 169.6; HRMS (ESI-TOF) m/z calcd for $[C_{44}H_{39}O_{12}N+Na]^+$ 796.2370, found 796.2360.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)-*α*-D-glucopyranoside (21f). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.162 g, 89%); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.9) +50.5; IR (cm^{-1}, $CHCl_3$) 3022, 2940, 1728, 1602, 1453, 1270, 1106, 761; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.32 (s, 3H), 3.51 (t, J = 9.3 Hz, 1H), 3.56 (dd, J = 9.7, 3.5 Hz, 1H), 3.61 (dd, J = 10.8, 4.7 Hz, 1H), 3.72 (dd, J = 10.0, 4.2 Hz, 1H), 3.97 (t, J = 11.0 Hz, 2H), 4.54 (dd, J = 11.5, 6.0 Hz, 1H), 4.58 (s, 1H), 4.60 (d, J = 7.3 Hz, 1H), 4.62−4.72 (m, 3H), 4.80 (dd, J = 11.3, 9.3 Hz, 2H), 4.87 (d, J = 11.2 Hz, 1H), 4.99 (d, J = 10.9 Hz, 1H), 5.14 (s, 1H), 5.63 (d, J = 4.9 Hz, 1H), 5.82 (t, J = 5.6 Hz, 1H), 7.15−7.60 (m, 24H), 7.82−7.89 (m, 2H), 7.96−8.05 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.3, 65.4, 66.7, 69.8, 72.8, 73.5, 75.0, 75.5, 75.8, 77.4, 79.1, 80.2, 82.2, 97.9, 105.9, 127.6, 127.8, 128.0, 128.0, 128.0, 128.0, 128.0, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.6, 129.0, 129.1, 129.3, 129.8, 129.8, 129.8, 129.9, 129.9, 129.9, 133.2, 133.5, 133.6, 138.3, 138.4, 138.9, 165.2, 165.4, 166.3; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3313.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)-*α*-D-glucopyranoside (21g). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.136 g, 75%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.1) +34.2; IR (cm^{-1}, $CHCl_3$) 3072, 2923, 1728, 1602, 1453, 1268, 1106, 700; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.52 (dd, J = 9.2, 3.5 Hz, 1H), 3.62−3.71 (m, 2H), 3.79 (dd, J = 10.9, 3.6 Hz, 1H), 3.85−3.99 (m, 2H), 4.43−4.52 (m, 1H), 4.55 (d, J = 5.9 Hz, 2H), 4.57 (d, J = 5.4 Hz, 1H), 4.60 (d, J = 6.2 Hz, 2H), 4.56−4.64 (m, 1H), 4.75 (d, J = 12.2 Hz, 1H), 4.88 (d, J = 10.5 Hz, 1H), 5.00 (d, J = 10.5 Hz, 1H), 5.59 (dd, J = 4.8, 1.9 Hz, 1H), 5.64 (d, J = 1.9 Hz, 1H), 5.75 (t, J = 5.4 Hz, 1H), 7.09−7.45 (m, 21H), 7.47−7.62 (m, 3H), 7.87 (dd, J = 8.3, 1.1 Hz, 2H), 7.93 (dd, J = 8.2, 1.1 Hz, 2H), 8.02 (dd, J = 8.2, 1.2 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.3, 64.6, 68.4, 69.4, 72.0, 73.3, 73.4, 75.3, 75.4, 77.2, 78.6, 79.7, 80.6, 98.1, 106.7, 127.3, 127.4, 127.5, 127.5, 127.9, 127.9, 127.9, 128.1, 128.1, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.9, 129.1, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7. 129.7. 133.0, 133.4, 133.4, 137.9, 138.0, 138.8, 165.1, 165.3, 166.0; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3286.

(Pent-4-enyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)-*α*-D-mannopyranoside (21h). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.144 g, 75%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.3) +35.2; IR (cm^{-1}, $CHCl_3$) 3072, 2926, 1728, 1599, 1453, 1268, 1109, 705; ^{1}H NMR (399.78 MHz, $CDCl_3$) δ 1.59 (quintet, J = 6.9 Hz, 2H), 2.04 (q, J = 7.0 Hz, 2H), 3.31 (dt, J = 9.7, 6.4 Hz, 1H), 3.62 (dt, J = 9.7, 6.6 Hz, 1H), 3.68−3.79 (m, 3H), 3.82−3.93 (m, 2H), 4.03 (d, J = 9.1 Hz, 1H), 4.62 (s, 2H), 4.57−4.72 (m, 5H), 4.74 (s, 1H), 4.81 (d, J = 1.5 Hz, 1H), 4.91 (s, 1H), 4.92−5.01 (m, 2H), 5.32 (s, 1H), 5.70 (d, J = 4.9 Hz, 1H), 5.72−5.84 (m, 2H), 7.09−7.67 (m, 24H), 7.86 (d, J = 7.4 Hz, 2H), 7.97−8.09 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.5, 30.2, 65.7, 66.9, 67.1, 71.5, 72.0, 72.4, 72.9, 74.5, 74.7, 75.0, 75.4, 79.0, 80.2, 97.6, 105.7, 114.8, 127.5, 127.5, 127.6, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 129.0, 129.3, 129.7, 129.7, 129.8, 129.8, 132.9, 132.9, 133.2, 133.4, 138.1, 138.3, 138.4, 138.5, 165.1, 165.2, 166.2; HRMS (ESI-TOF) m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$ 985.3775, found 985.3776.

(Prop-2-ynyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-*β*-D-ribofuranosyl)-*α*-D-glucopyranoside (21i). This compound is prepared using the above-mentioned general procedure using **7a**

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(0.100 g, 0.2 mmol) as the starting material. Yield: (0.160 g, 86%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +70.0; IR (cm^{-1}, $CHCl_3$) 3293, 3072, 2927, 1727, 1595, 1453, 1268, 1107, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.42 (t, *J* = 2.1 Hz, 1H), 3.55 (t, *J* = 9.5 Hz, 1H), 3.62 (td, *J* = 10.1, 9.3, 4.1 Hz, 2H), 3.80 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.95 (d, *J* = 9.4 Hz, 1H), 4.00 (t, *J* = 9.3 Hz, 1H), 4.24 (d, *J* = 2.0 Hz, 2H), 4.55 (dd, *J* = 11.6, 5.9 Hz, 1H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.63−4.73 (m, 2H), 4.75 (d, *J* = 3.2 Hz, 2H), 4.81 (d, *J* = 10.9 Hz, 1H), 4.89 (d, *J* = 11.2 Hz, 1H), 5.01 (d, *J* = 10.9 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 5.15 (s, 1H), 5.64 (d, *J* = 4.9 Hz, 1H), 5.82 (t, *J* = 5.5 Hz, 1H), 7.14−7.46 (m, 20H), 7.44−7.54 (m, 3H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 2H), 8.00 (d, *J* = 7.8 Hz, 2H), 8.04 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.6, 65.2, 66.3, 70.4, 72.6, 73.0, 74.7, 74.9, 75.34, 75.6, 77.2, 79.0, 79.0, 79.6, 81.9, 95.1, 105.7, 127.5, 127.6, 127.8, 127.9, 127.9, 127.9, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.9, 129.1, 129.7, 129.7, 129.7, 129.7, 129.7, 129.7, 133.0, 133.3, 133.4, 137.9, 138.2, 138.7, 165.1, 165.3, 166.1; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{56}H_{52}O_{13}+Na]^+$ 955.3306, found 955.3303.

(Prop-2-ynyl) 3,5-di-*O*-benzyl-2-*O*-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-α-D-arabinofuranoside (21j). This compound is prepared using the above-mentioned general procedure using **7a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.107 g, 66%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.8) +31.7; IR (cm^{-1}, $CHCl_3$) ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.30 (t, *J* = 2.3 Hz, 1H), 3.54 (dd, *J* = 10.7, 5.6 Hz, 1H), 3.57 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.07 (dd, *J* = 6.4, 2.7 Hz, 1H), 4.22−4.27 (m, 1H), 4.28 (dd, *J* = 2.3, 1.4 Hz, 2H), 4.49 (s, 2H), 4.53 (ABq, *J* = 11.8 Hz, 2H), 4.62 (dd, *J* = 6.1, 4.1 Hz, 2H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.96 (q, *J* = 5.5 Hz, 1H), 5.38 (d, *J* = 17.6 Hz, 2H), 5.57 (s, 1H), 5.83 (dd, *J* = 5.4, 1.7 Hz, 1H), 7.16−7.72 (m, 19H), 7.98 (ddd, *J* = 8.3, 2.8, 1.2 Hz, 4H), 8.06 (dd, *J* = 8.3, 1.3 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.1, 69.5, 72.4, 72.5, 73.4, 74.7, 75.6, 76.9, 77.1, 79.2, 81.7, 83.8, 86.9, 104.2, 105.4, 127.7, 127.7, 127.7, 127.7, 127.7, 127.8, 127.8, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.5,, 129.7, 129.7, 129.7, 129.7, 129.7, 129.8, 129.8, 133.2, 133.4, 133.5, 137.6, 137.9, 138.1, 165.1, 165.3, 166.0; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{48}H_{44}O_{12}+Na]^+$ 835.2730, found 835.2735.

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (22a). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.152 g, 80%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +33.3; IR (cm^{-1}, $CHCl_3$) 3074, 2929, 1727, 1596, 1457, 1268, 1105, 709; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.39 (s, 3H), 3.79 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.07 (d, *J* = 11.3 Hz, 1H), 4.25−4.32 (m, 1H), 4.55−4.71 (m, 2H), 4.95 (q, *J* = 5.4 Hz, 1H), 5.22 (d, *J* = 9.5 Hz, 1H), 5.25 (s, 1H), 5.32 (s, 1H), 5.60 (d, *J* = 10.0 Hz, 1H), 5.63 (s, 1H), 5.87 (d, *J* = 5.2 Hz, 1H), 6.16 (t, *J* = 9.4 Hz, 1H), 7.18−7.68 (m, 18H), 7.85 (d, *J* = 7.5 Hz, 2H), 7.93 (t, *J* = 7.5 Hz, 4H), 7.99 (d, *J* = 7.5 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.5, 63.5, 66.6, 68.9, 69.3, 70.5, 72.2, 75.2, 79.0, 81.0, 96.8, 106.5, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.6, 128.6, 128.9, 129.0, 129.1, 129.2, 129.6, 129.6, 129.6, 129.6, 129.6, 129.6, 129.8, 129.8, 129.9, 129.9, 129.9, 129.9, 130.0, 130.0, 133.0, 133.0, 133.3, 133.3, 133.5, 133.6, 164.8, 165.2, 165.3, 165.7, 165.8, 166.0; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{54}H_{46}O_{16}+Na]^+$ 973.2684, found 973.2707.

Pent-4-enyl 2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (22b). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.100 g, 94%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +14.2; IR (cm^{-1}, $CHCl_3$) 3074, 2927, 1725, 1594, 1453, 1262, 1108, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 1.75 (quintet, *J* = 6.7 Hz, 2H), 2.18 (q, *J* = 7.1 Hz, 2H), 3.54 (dt, *J* = 9.3, 6.4 Hz, 1H), 3.87 (dt, *J* = 9.3, 6.5 Hz, 1H), 4.64 (dABq, *J* = 11.4, 6.3 Hz, 2H), 4.93−4.99 (m, 2H), 4.97 (s, 1H), 5.24 (s, 1H), 5.64 (d, *J* = 0.8 Hz, 1H), 5.81 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.87 (dd, *J* = 5.8, 1.4 Hz, 1H), 7.34−7.69 (m, 9H), 7.96−8.02 (m, 2H), 8.03−8.09 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.7, 30.2, 63.6, 67.6, 75.3, 78.6, 81.1, 106.1, 114.9, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.5, 129.0, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.0, 165.1, 165.3, 166.1; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{31}H_{30}O_8+Na]^+$ 553.1838, found 553.1837.

Benzyl 2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (22c). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.094 g, 84%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.7) +6.7; IR (cm^{-1}, $CHCl_3$) 3067, 2923, 1725, 1595, 1450, 1262, 1106, 700; ^1H NMR (399.78 MHz, $CDCl_3$) δ 4.57−4.66 (m, 2H), 4.67−4.74 (m, 1H), 4.93 (d, *J* = 11.5 Hz, 1H), 5.01 (q, *J* = 5.8 Hz, 1H), 5.37 (s, 1H), 5.61 (s, 1H), 5.90 (d, *J* = 5.6 Hz, 1H), 7.40 (m, 12H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.98 (t, *J* = 7.6 Hz, 4H), 8.06 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 63.6, 69.5, 75.1, 79.1, 81.0, 105.2, 127.8, 128.0, 128.0, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 129.6, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.1, 133.5, 133.6, 137.1, 165.0, 165.2, 166.1; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{33}H_{28}O_8+Na]^+$ 575.1682, found 575.1693.

Cholesteryl 2,3,5-tri-*O*-benzoyl-β-D-xylofuranoside (22d). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.130 g, 78%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.6) −25.5; IR (cm^{-1}, $CHCl_3$) 2940, 1728, 1601, 1453, 1263, 1107, 708; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.68 (s, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 1.01 (s, 3H), 1.06−2.09 (m, 26H), 2.28 (ddd, *J* = 13.3, 4.5, 1.7 Hz, 1H), 2.43 (ddd, *J* = 13.2, 4.3, 1.7 Hz, 1H), 3.65 (tt, *J* = 11.1, 4.5 Hz, 1H), 4.64 (qd, *J* = 11.4, 6.4 Hz, 2H), 4.95 (q, *J* = 6.2 Hz, 1H), 5.34 (d, *J* = 4.9 Hz, 1H), 5.42 (s, 1H), 5.52 (d, *J* = 1.1 Hz, 1H), 5.88 (dd, *J* = 5.9, 1.5 Hz, 1H), 7.32−7.64 (m, 9H), 7.96−8.00 (m, 2H), 8.07 (d, *J* = 8.2 Hz, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 11.8, 18.6, 19.3, 21.0, 22.5, 22.8, 23.7, 24.2, 27.9, 28.2, 29.5, 31.8, 31.9, 35.7, 36.1, 36.7, 37.2, 38.3, 39.4, 39.7, 42.2, 50.0, 56.0, 56.7, 63.7, 75.3, 77.0, 78.4, 81.5, 103.9, 121.9, 128.2, 128.2, 128.4, 128.4, 128.4, 128.4, 129.0, 129.0, 129.5, 129.6, 129.6, 129.8, 129.8, 129.9, 129.9, 133.0, 133.4, 133.5, 140.2, 165.1, 165.2, 166.1; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{53}H_{66}O_8+Na]^+$ 853.4655, found 853.4667.

Benzyl *N*-(benzyloxycarbonyl)-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-L-serinate (22e). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.136 g, 88%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +23.7; IR (cm^{-1}, $CHCl_3$) 3431, 3365, 3030, 2933, 1724, 1591, 1447, 1262, 1107, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.85 (dd, *J* = 10.0, 3.3 Hz, 1H), 4.40 (dd, *J* = 10.0, 2.8 Hz, 1H), 4.51 (ddd, *J* = 16.8, 11.4, 6.6 Hz, 2H), 4.66 (dt, *J* = 8.7, 3.0 Hz, 1H), 4.94 (q, *J* = 6.1 Hz, 1H), 5.10 (d, *J* = 4.3 Hz, 2H), 5.13 (d, *J* = 11.0 Hz, 1H), 5.21 (s, 1H), 5.25 (d, *J* = 12.2 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 5.70−6.09 (m, 2H), 7.16−7.72 (m, 19H), 7.95 (dd, *J* = 8.2, 1.2 Hz, 2H), 8.00−8.06 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.2, 63.3, 67.3, 67.4, 68.0, 74.3, 79.1, 81.1, 106.8, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.6, 128.6, 128.6, 128.7, 129.4, 129.6, 129.6, 129.6, 129.9, 129.9, 129.9, 129.9, 133.1, 133.7, 133.7, 135.1, 136.1, 156.0, 165.1, 165.2, 165.9, 169.7; HRMS (ESI-TOF) *m*/*z* calcd for $[C_{44}H_{39}O_{12}N+Na]^+$ 796.2370, found 796.2371.

Methyl-2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (22f). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.160 g, 88%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +35.7; IR (cm^{-1}, $CHCl_3$) 3068, 2925, 1725, 1594, 1457, 1263, 1103, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.27 (s, 3H), 3.51 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.63 (t, *J* = 9.4 Hz, 1H), 3.71 (dd, *J* = 10.5, 4.2 Hz, 1H), 3.77 (dd, *J* = 10.0, 2.9 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 4.03 (dd, *J* = 9.7, 0.9 Hz, 1H), 4.56 (dd, *J* = 11.5, 5.8 Hz, 1H), 4.65 (d, *J* = 6.3 Hz, 2H), 4.67 (s, 2H), 4.75 (d, *J* = 12.1 Hz, 1H), 4.85 (dd, *J* = 11.0 Hz, 2H), 4.91−5.04 (m, 2H), 5.17 (s, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 5.85 (dd, *J* = 6.0, 1.4 Hz, 1H), 7.11−7.74 (m, 24H), 7.95 (dd, *J* = 8.1, 1.1 Hz, 2H), 8.00−8.06 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.0, 63.8, 66.4, 69.7, 73.2, 75.0, 75.2, 75.7, 77.4, 78.8, 80.2, 81.2, 82.1, 97.8, 106.0, 127.5, 127.6, 127.8, 127.9, 127.9, 127.9, 127.9, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 128.9, 129.6, 129.6, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.2, 138.3, 138.7, 165.0, 165.2, 166.1;

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HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3309.

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (22g). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.140 g, 77%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.6) +29.0; IR (cm^{-1}, $CHCl_3$) 3071, 2924, 1725, 1595, 1443, 1262, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.36 (s, 3H), 3.53 (dd, *J* = 9.4, 3.6 Hz, 1H), 3.59 (d, *J* = 9.2 Hz, 1H), 3.65−3.77 (m, 2H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.99 (t, *J* = 9.1 Hz, 1H), 4.38 (s, 2H), 4.52 (dd, *J* = 11.6, 6.4 Hz, 1H), 4.56 (s, 1H), 4.58 (d, *J* = 7.4 Hz, 1H), 4.63 (dd, *J* = 11.5, 5.3 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.81 (q, *J* = 5.6 Hz, 1H), 4.91 (d, *J* = 10.5 Hz, 1H), 5.10 (d, *J* = 10.5 Hz, 1H), 5.51 (s, 1H), 5.57 (s, 1H), 5.76 (dd, *J* = 5.1, 1.8 Hz, 1H), 7.06−7.68 (m, 24H), 7.95 (d, *J* = 7.4 Hz, 2H), 7.98 (d, *J* = 7.4 Hz, 2H), 8.02 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.3, 63.0, 68.4, 69.5, 73.2, 73.5, 74.91, 75.2, 77.7, 78.4, 79.7, 80.7, 80.8, 98.1, 107.9, 127.3, 127.3, 127.4, 127.4, 127.7, 127.7, 127.8, 128.1, 128.1, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.8, 128.9, 129.5, 129.7, 129.7, 129.9, 129.9, 129.9, 129.9, 133.0, 133.6, 133.6, 137.8, 138.1, 138.9, 164.9, 165.2, 166.0; HRMS (ESI-TOF) m/z calcd for $[C_{54}H_{52}O_{13}+Na]^+$ 931.3306, found 931.3311.

Pent-4-enyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-mannopyranoside (22h). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.150 g, 78%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +26.3; IR (cm^{-1}, $CHCl_3$) 3074, 2926, 1726, 1595, 1450, 1264, 1108, 710; ^1H NMR (399.78 MHz, $CDCl_3$) δ 1.49 (quintet, *J* = 6.9 Hz, 2H), 1.89−1.99 (m, 2H), 3.22 (dt, *J* = 9.8, 6.4 Hz, 1H), 3.54 (dt, *J* = 9.7, 6.5 Hz, 1H), 3.73−3.79 (m, 2H), 3.84 (dd, *J* = 10.8, 5.8 Hz, 1H), 3.90 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.97 (t, *J* = 9.4 Hz, 1H), 4.08 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.58−4.62 (m, 1H), 4.62 (s, 2H), 4.64 (d, *J* = 2.6 Hz, 1H), 4.67 (d, *J* = 2.3 Hz, 2H), 4.73 (dd, *J* = 11.5, 7.1 Hz, 1H), 4.79 (d, *J* = 1.6 Hz, 1H), 4.88 (s, 1H), 4.91 (s, 1H), 4.89−4.99 (m, 2H), 5.32 (s, 1H), 5.57 (d, *J* = 1.2 Hz, 1H), 5.69 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.85 (dd, *J* = 6.2, 1.5 Hz, 1H), 7.10−7.69 (m, 24H), 7.97 (dd, *J* = 8.0, 1.0 Hz, 2H), 8.02−8.15 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 28.5, 30.1, 63.8, 66.8, 67.5, 71.5, 72.1, 72.3, 74.5, 74.8, 75.1, 75.5, 78.7, 80.2, 81.3, 97.6, 106.4, 114.7, 127.5, 127.5, 127.6, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.2, 128.2, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.5, 128.5, 128.5, 128.5, 128.9, 129.1, 129.7, 129.7, 129.8, 129.9, 129.9, 130.0, 130.0, 132.9, 133.4, 133.5, 138.0, 138.2, 138.4, 138.5, 164.9, 165.4, 166.1.; HRMS (ESI-TOF) m/z calcd for $[C_{58}H_{58}O_{13}+Na]^+$ 985.3775, found 985.3779.

(Prop-2-ynyl) 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-glucopyranoside (22i). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 1 mmol) as the starting material. Yield: (0.160 g, 86%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +38.0; IR (cm^{-1}, $CHCl_3$) 3293, 3065, 3034, 2926, 1726, 1596, 1453, 1264, 1105, 706; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.38 (t, *J* = 2.3 Hz, 1H), 3.56 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.83 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.01 (t, *J* = 9.4 Hz, 2H), 4.19 (dABq, *J* = 16.0, 2.4 Hz, 2H), 4.58 (dd, *J* = 11.5, 5.7 Hz, 1H), 4.63−4.69 (m, 2H), 4.72 (s, 2H), 4.86 (ABq, *J* = 11.0 Hz, 2H), 4.93−5.03 (m, 2H), 5.12 (d, *J* = 3.6 Hz, 1H), 5.18 (s, 1H), 5.51 (d, *J* = 1.1 Hz, 1H), 5.86 (dd, *J* = 6.0, 1.4 Hz, 1H), 7.06−7.71 (m, 24H), 7.98 (dd, *J* = 8.2, 1.0 Hz, 2H), 8.01−8.08 (m, 4H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.3, 63.8, 66.2, 70.3, 72.8, 74.7, 75.0, 75.2, 75.7, 78.8, 79.0, 79.7, 81.1, 81.1, 81.9, 95.0, 105.9, 127.5, 127.6, 127.8, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 128.9, 129.6, 129.6, 129.9, 129.9, 129.9, 129.9, 133.0, 133.5, 133.6, 138.0, 138.2, 138.7, 165.0, 165.2, 166.0; HRMS (ESI-TOF) m/z calcd for $[C_{56}H_{52}O_{13}+Na]^+$ 955.3306, found 955.3308.

(Prop-2-ynyl) 3,5-di-*O*-benzyl-2-*O*-(2,3,5-tri-*O*-benzoyl-β-D-xylofuranosyl)-α-D-arabinofuranoside (22j). This compound is prepared using the above-mentioned general procedure using **8a** (0.100 g, 0.2 mmol) as the starting material. Yield: (0.109 g, 67%); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) +38.8; IR (cm^{-1}, $CHCl_3$) 3074, 2929, 1727, 1596, 1457, 1268, 1105, 709; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.30 (t, *J* = 2.3 Hz, 1H), 3.53−3.61 (m, 2H), 4.07 (dd, *J* = 6.4, 2.7 Hz, 1H), 4.22−4.27 (m, 1H), 4.28 (dd, *J* = 2.3, 1.4 Hz, 2H), 4.49 (s, 2H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.62 (dd, *J* = 6.1, 4.1 Hz, 2H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.96 (q, *J* = 5.5 Hz, 1H), 5.36 (s, 1H), 5.40 (s, 1H), 5.57 (d, *J* = 1.5 Hz, 2H), 5.83 (dd, *J* = 5.4, 1.7 Hz, 1H), 7.03−7.77 (m, 19H), 7.79−8.32 (m, 6H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.1, 63.3, 69.7, 72.3, 73.3, 74.6, 74.9, 79.0, 79.1, 80.9, 81.6, 83.9, 86.5, 104.3, 105.9, 127.6, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.5, 128.5, 128.5, 128.5, 128.8, 129.4, 129.7, 129.7, 129.8, 129.9, 129.9, 129.9, 133.2, 133.6, 133.7, 137.6, 137.9, 164.9, 165.2, 166.0, HRMS (ESI-TOF) m/z calcd for $[C_{48}H_{44}O_{12}+Na]^+$ 812.2833, found 812.2830.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl β-D-ribofuranosyl) α-D-glucopyranoside (23a).[12] This compound is prepared using the above-mentioned general procedure using **7b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.263 g, 80% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) δ 1.5; IR (cm^{-1}, $CHCl_3$) 3456, 3073, 3031, 2923, 2862, 1594, 1455, 1059, 740; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.71 (d, *J* = 2.7 Hz, 1H), 3.33 (s, 3H), 3.46 (t, *J* = 9.2 Hz, 1H), 3.51 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.55 (d, *J* = 5.6 Hz, 2H), 3.55 (dd, *J* = 10.9, 5.0 Hz, 1H), 3.70 (ddd, *J* = 10.0, 4.8, 1.5 Hz, 1H), 3.89 (dd, *J* = 10.9, 1.7 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 4.00−4.12 (m, 2H), 4.22 (q, *J* = 5.5 Hz, 1H), 4.50 (ABq, *J* = 12.0 Hz, 2H), 4.56 (s, 3H), 4.57 (d, *J* = 9.8 Hz, 1H), 4.67 (d, *J* = 12.2 Hz, 1H), 4.80 (t, *J* = 10.8 Hz, 2H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.95 (s, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 7.19−7.43 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.0, 66.3, 69.9, 71.6, 72.7, 73.2, 73.3, 73.3, 74.9, 75.7, 77.6, 79.6, 79.9, 80.7, 82.1, 97.9, 107.8, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 128.1, 128.1, 128.1, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 137.1, 138.1, 138.1, 138.1, 138.6; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3470.

Menthyl 3,5-di-*O*-benzyl β-D-ribofuranoside (23b).[12] This compound is prepared using the above-mentioned general procedure using **7b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.155 g, 78% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) −73.8; IR (cm^{-1}, $CHCl_3$) 3414, 3043, 2924, 2861, 1591, 1457, 1111, 691; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.70 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H), 0.70−1.05 (m, 2H), 0.89 (d, *J* = 6.5 Hz, 3H), 1.08−1.21 (m, 1H), 1.21−1.44 (m, 2H), 1.60 (d, *J* = 14.7 Hz, 2H), 1.96−2.26 (m, 2H), 2.64 (d, *J* = 2.7 Hz, 1H), 3.42 (td, *J* = 10.6, 4.2 Hz, 1H), 3.55 (d, *J* = 5.7 Hz, 2H), 3.90−4.05 (m, 2H), 4.22 (q, *J* = 5.6 Hz, 1H), 4.51 (d, *J* = 12.0 Hz, 1H), 4.54−4.64 (m, 3H), 5.16 (s, 1H), 6.90−7.67 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 16.0, 21.1, 22.3, 23.0, 25.1, 31.3, 34.4, 39.9, 47.9, 72.0, 72.7, 73.0, 74.1, 75.4, 79.7, 80.2, 103.8, 127.6, 127.7, 127.7, 127.9, 127.9, 128.2, 128.4, 128.4, 128.6, 128.6, 137.2, 138.1; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2775.

Methyl 2,3,4-tri-*O*-benzyl 6-*O*-(3,5-di-*O*-benzyl β-D-arabinofuranosyl)-α-D-glucopyranoside (24a).[12] This compound is prepared using the above-mentioned general procedure using **23a** (0.100 g, 0.13 mmol) as the starting material. Yield: (0.093 g, 93% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) +2.0; IR (cm^{-1}, $CHCl_3$) 3421, 3063, 3033, 2926, 2866, 1588, 1454, 1106, 1063, 735, 692; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.59 (s, 1H), 3.31 (s, 3H), 3.33−3.40 (m, 2H), 3.49 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.50 (d, *J* = 5.9 Hz, 2H), 3.54 (dd, *J* = 11.1, 5.8 Hz, 1H), 3.74 (ddd, *J* = 10.1, 5.8, 1.9 Hz, 1H), 3.80 (t, *J* = 5.8 Hz, 1H), 3.94 (d, *J* = 2.1 Hz, 1H), 3.97 (t, *J* = 9.3 Hz, 1H), 4.09 (q, *J* = 5.7 Hz, 1H), 4.15−4.24 (m, 1H), 4.48 (ABq, *J* = 12.0 Hz, 2H), 4.53 (dd, *J* = 7.3, 3.8 Hz, 1H), 4.58 (d, *J* = 11.9 Hz, 1H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.77 (d, *J* = 7.3 Hz, 1H), 4.80 (d, *J* = 6.0 Hz, 1H), 4.87 (dd, *J* = 7.9, 3.2 Hz, 2H), 4.98 (d, *J* = 10.7 Hz, 1H), 7.02−7.65 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.2, 67.3, 69.9, 71.8, 72.0, 73.2, 73.4, 75.0, 75.8, 77.9, 78.2, 79.9, 80.8, 82.0, 84.6, 97.9, 102.2, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 128.0, 128.0, 128.0, 128.1, 128.1, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 137.9, 138.0,

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138.0, 138.0, 138.5; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3438.

Menthyl 3,5-di-*O*-benzyl β-D-arabinofuranoside (24b).[12] This compound is prepared using the above-mentioned general procedure using **23b** (0.100 g, 0.21 mmol) as the starting material. Yield: (0.092 g, 92% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) −89.3; IR (cm^{-1}, $CHCl_3$) 3529, 3083, 3036, 2926, 2864, 1591, 1456, 1117, 1029, 732, 685; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.74 (d, J = 6.9 Hz, 3H), 0.86 (d, J = 7.0 Hz, 3H), 0.69−1.11 (m, 2H), 0.90 (d, J = 6.5 Hz, 3H), 1.15−1.28 (m, 1H), 1.28−1.42 (m, 2H), 1.58−1.73 (m, 2H), 2.01−2.25 (m, 2H), 2.70 (d, J = 8.8 Hz, 1H), 3.48−3.61 (m, 3H), 3.80 (t, J = 5.9 Hz, 1H), 4.09 (q, J = 5.9 Hz, 1H), 4.21 (dt, J = 8.8, 5.4 Hz, 1H), 4.53 (ABq, J = 12.0 Hz, 2H), 4.62 (d, J = 11.9 Hz, 1H), 4.78 (d, J = 11.9 Hz, 1H), 5.20 (d, J = 5.0 Hz, 1H), 7.06−7.55 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 15.8, 21.0, 22.2, 22.9, 25.2, 31.4, 34.3, 40.4, 47.8, 71.9, 72.2, 73.3, 76.8, 77.1, 79.9, 84.9, 98.2, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 128.3, 128.3, 128.3, 128.3, 138.0, 138.0; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2773.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-α-D-arabinofuranosyl)-α-D-glucopyranoside (25a). This compound is prepared using the above-mentioned general procedure using **5b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.270 g, 82% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +47.1; IR (cm^{-1}, $CHCl_3$) 3425, 30683, 3039, 2929, 1591, 1450, 1106, 1065, 735; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.45 (dd, J = 10.4, 2.1 Hz, 1H), 3.51 (dd, J = 9.8, 3.7 Hz, 2H), 3.58 (ddd, J = 10.9, 4.9, 2.0 Hz, 2H), 3.60−3.71 (m, 1H), 3.74 (dd, J = 9.9, 2.3 Hz, 2H), 3.86 (d, J = 2.4 Hz, 1H), 3.95 (t, J = 9.3 Hz, 1H), 4.16 (dd, J = 7.8, 2.6 Hz, 2H), 4.18 (d, J = 2.6 Hz, 1H), 4.26 (d, J = 10.7 Hz, 1H), 4.42 (d, J = 11.7 Hz, 1H), 4.46 (d, J = 11.8 Hz, 1H), 4.60 (t, J = 12.0 Hz, 1H), 4.64 (d, J = 3.7 Hz, 1H), 4.68 (s, 2H), 4.79 (d, J = 11.4 Hz, 2H), 4.95 (d, J = 10.9 Hz, 1H), 5.10 (s, 1H), 7.10−7.44 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.1, 65.5, 69.7, 69.7, 72.0, 73.3, 73.7, 74.8, 75.6, 77.2, 77.4, 79.7, 82.0, 84.0, 85.4, 98.2, 109.5, 127.4, 127.4, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.1, 128.1, 128.2, 128.2, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.5, 128.5, 136.8, 137.6, 138.1, 138.6, 138.9; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3450.

Menthyl 3,5-di-*O*-benzyl-α-D-arabinofuranoside (25b). This compound is prepared using the above-mentioned general procedure using **5b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.165 g, 83% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.1) +62.3; IR (cm^{-1}, $CHCl_3$) 3357, 3071, 2970, 1591, 1453, 1368, 1105, 741; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.76 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 4.3 Hz, 3H), 0.89 (d, J = 3.7 Hz, 3H), 0.96 (dd, J = 12.7, 3.1 Hz, 1H), 1.00−1.08 (m, 1H), 1.08−1.16 (m, 1H), 1.22−1.32 (m, 1H), 1.38 (ddq, J = 11.9, 6.4, 3.3 Hz, 1H), 1.55−1.67 (m, 2H), 2.08−2.20 (m, 2H), 3.22−3.40 (m, 2H), 3.49 (dd, J = 10.4, 2.3 Hz, 1H), 3.66 (dd, J = 10.4, 2.3 Hz, 1H), 3.85 (d, J = 3.1 Hz, 1H), 4.12 (d, J = 10.4 Hz, 1H), 4.30 (q, J = 2.4 Hz, 1H), 4.49 (t, J = 12.4 Hz, 2H), 4.61 (d, J = 11.8 Hz, 1H), 4.67 (d, J = 12.2 Hz, 1H), 5.08 (s, 1H), 7.04−7.53 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 16.2, 21.1, 22.3, 23.2, 25.3, 31.6, 34.3, 42.9, 48.3, 69.8, 71.8, 73.7, 77.9, 79.1, 83.0, 85.3, 110.2, 127.6, 127.6, 127.8, 127.8, 128.0, 128.0, 128.3, 128.3, 128.5, 128.5, 137.0, 138.0; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2776.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-α-D-ribofuranosyl)-α-D-glucopyranoside (26a). This compound is prepared using the above-mentioned general procedure using **25a** (0.100 g, 0.13 mmol) as the starting material. Yield: (0.087 g, 87% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.6) +23.7; IR (cm^{-1}, $CHCl_3$) 3457, 3069, 2927, 1455, 1269, 1109, 744; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.32 (s, 3H), 3.33−3.44 (m, 3H), 3.48−3.53 (m, 1H), 3.61 (t, J = 9.3 Hz, 1H), 3.66 (dd, J = 11.0, 1.7 Hz, 1H), 3.71−3.77 (m, 1H), 3.79 (dd, J = 6.9, 2.8 Hz, 1H), 3.96 (t, J = 9.3 Hz, 1H), 4.12 (d, J = 3.7 Hz, 1H), 4.10−4.21 (m, 2H), 4.38−4.52 (m, 3H), 4.58−4.70 (m, 4H), 4.75−4.84 (m, 3H), 4.96 (d, J = 10.9 Hz, 1H), 5.06 (d, J = 4.7 Hz, 1H), 7.00−7.63 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.1, 66.2, 69.8, 70.0, 72.0, 72.9, 73.4, 75.0, 75.8, 76.9, 77.2, 77.7, 80.0, 82.0, 82.2, 98.0, 101.8, 127.6, 127.6, 127.7, 127.7, 127.7, 127.7, 127.9, 127.9, 127.9, 128.0, 128.0, 128.0, 128.0, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.5, 137.8, 137.8, 138.2, 138.4, 138.8; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3454.

Menthyl 3,5-di-*O*-benzyl-α-D-ribofuranoside (26b). This compound is prepared using the above-mentioned general procedure using **25b** (0.100 g, 0.21 mmol) as the starting material. Yield: (0.090 g, 90% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.9) +48.2; IR (cm^{-1}, $CHCl_3$) 3554, 3030, 2930, 1643, 1454, 1264, 1097, 764; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.77 (d, J = 7.0 Hz, 3H), 0.89 (d, J = 4.3 Hz, 2H), 0.79−1.03 (m, 3H), 0.91 (d, J = 3.8 Hz, 2H), 1.03−1.20 (m, 1H), 1.27−1.50 (m, 2H), 1.55−1.70 (m, 3H), 2.10−2.28 (m, 2H), 2.94 (d, J = 10.2 Hz, 1H), 3.37 (dd, J = 10.6, 4.4 Hz, 1H), 3.48 (dABq, J = 10.4, 4.0 Hz, 2H), 3.78 (dd, J = 7.0, 3.5 Hz, 1H), 4.10 (bs, 1H), 4.19 (q, J = 4.0 Hz, 1H), 4.52 (ABq, J = 12.1 Hz, 2H), 4.56 (d, J = 12.3 Hz, 1H), 4.73 (d, J = 12.3 Hz, 1H), 5.09 (d, J = 4.7 Hz, 1H), 7.12−7.42 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 15.9, 21.2, 22.3, 23.0, 25.3, 31.6, 34.3, 43.2, 48.5, 70.1, 72.0, 72.5, 73.4, 76.5, 80.0, 81.3, 102.7, 127.6, 127.6, 127.6, 127.6, 127.6, 127.6, 128.3, 128.3, 128.3, 128.3, 137.9, 138.2; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2759.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-β-D-xylofuranosyl)-α-D-glucopyranoside (27a). This compound is prepared using the above-mentioned general procedure using **8b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.266 g, 81% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) −6.1; IR (cm^{-1}, $CHCl_3$) 3420, 3029, 2925, 1600, 1454, 1361, 1065, 741; ^1H NMR (399.78 MHz, $CDCl_3$) δ 2.15 (bs, 1H), 3.28 (s, 3H), 3.43−3.54 (m, 2H), 3.58 (dd, J = 10.8, 5.5 Hz, 1H), 3.68 (dd, J = 10.3, 7.1 Hz, 1H), 3.76 (dd, J = 10.4, 4.6 Hz, 2H), 3.94 (dd, J = 6.1, 3.1 Hz, 1H), 3.96−4.02 (m, 2H), 4.14−4.26 (m, 1H), 4.41−4.49 (m, 2H), 4.49 (d, J = 15.4 Hz, 1H), 4.53−4.61 (m, 4H), 4.63 (d, J = 12.1 Hz, 1H), 4.76 (d, J = 12.1 Hz, 1H), 4.81 (d, J = 10.9 Hz, 1H), 4.85 (dd, J = 6.4, 4.6 Hz, 2H), 4.97 (d, J = 10.9 Hz, 1H), 6.80−7.70 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.0, 66.9, 69.7, 69.9, 72.1, 73.3, 73.3, 74.8, 75.7, 77.8, 79.3, 79.8, 79.9, 82.0, 83.5, 97.8, 108.5, 127.4, 127.4, 127.5, 127.6, 127.6, 127.6, 127.7, 127.8, 127.8, 127.8, 127.9, 127.9, 128.0, 128.0, 128.2, 128.2, 128.3, 128.3, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 131.5, 137.8, 138.1, 138.2, 138.3, 138.7; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3442.

Menthyl 3,5-di-*O*-benzyl-β-D-xylofuranside (27b). This compound is prepared using the above-mentioned general procedure using **8b** (0.200 g, 1 mmol) as the starting material. Yield: (0.165 g, 83% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.5) −15.1; IR (cm^{-1}, $CHCl_3$) 3554, 3030, 2930, 1643, 1454, 1264, 1097, 764; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.70 (d, J = 6.9 Hz, 3H), 0.80 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H), 0.62−1.07 (m, 3H), 1.09−1.48 (m, 2H), 1.55−1.72 (m, 2H), 2.08−2.17 (m, 2H), 2.21−2.34 (m, 1H), 3.48 (td, J = 10.6, 4.1 Hz, 1H), 3.68 (dd, J = 10.0, 6.6 Hz, 1H), 3.79 (dd, J = 10.1, 4.9 Hz, 1H), 3.95 (dd, J = 5.5, 3.1 Hz, 1H), 4.24 (s, 1H), 4.40−4.50 (m, 1H), 4.50 (dd, J = 11.9, 1.8 Hz, 2H), 4.59 (d, J = 12.1 Hz, 1H), 4.63 (d, J = 11.8 Hz, 1H), 5.12 (d, J = 1.7 Hz, 1H), 6.74−7.79 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 15.9, 21.0, 22.3, 23.0, 24.8, 31.3, 34.5, 39.6, 48.0, 69.5, 72.1, 73.4, 74.7, 79.1, 79.9, 83.1, 104.0, 127.4, 127.4, 127.5, 127.5, 127.7, 127.7, 128.2, 128.3, 128.3, 128.3, 138.0, 138.3; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2770.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-β-D-lyxofuranosyl)-α-D-glucopyranoside (28a). This compound is prepared using the above-mentioned general procedure using **27a** (0.100 g, 0.13 mmol) as the starting material. Yield: (0.082 g, 82% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) −16.7; IR (cm^{-1}, $CHCl_3$) 3450, 3070, 2929, 1455, 1270, 1109, 740; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.24 (s, 3H), 3.40−3.47 (m, 1H), 3.49 (dd, J = 9.6, 3.5 Hz, 1H), 3.58 (dd, J = 10.9, 6.1 Hz, 1H), 3.64 (dd, J = 9.8, 6.3 Hz, 1H), 3.73−3.82 (m, 2H), 3.94−4.04 (m, 3H), 4.13 (t, J = 5.3 Hz, 1H), 4.19−4.30 (m, 1H), 4.48 (ABq, J = 11.8 Hz, 2H), 4.56 (dd, J = 10.6, 4.1 Hz, 2H), 4.64 (d, J = 12.1 Hz, 1H), 4.68 (d, J = 11.8 Hz, 2H), 4.75 (s, 1H), 4.79 (d, J = 5.3 Hz, 1H), 4.83 (d, J = 3.1 Hz, 1H), 4.82−4.91 (m, 1H), 4.97 (ABq, J = 10.8 Hz, 1H), 6.72−7.72 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 54.9, 67.6, 69.8, 70.1, 73.0, 73.3, 73.5, 74.4, 75.0, 75.7, 78.2, 79.3,

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80.0, 82.1, 97.7, 101.4, 127.3, 127.3, 127.6, 127.6, 127.6, 127.6, 127.7, 127.7, 127.8, 127.8, 127.8, 128.0, 128.0, 128.0, 128.0, 128.3, 128.3, 128.3, 128.3, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 138.0, 138.1, 138.1, 138.2, 138.7; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3457.

Menthyl 3,5-di-*O*-benzyl-*β*-D-lyxofuranoside (28b). This compound is prepared using the above-mentioned general procedure using **27b** (0.100 g, 0.21 mmol) as the starting material. Yield: (0.090 g, 90%); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.5) −138.1; IR (cm^{-1}, $CHCl_3$) 3427, 2939, 1584, 1454, 1148, 1027, 740; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.70 (d, J = 6.9 Hz, 3H), 0.80 (d, J = 7.2 Hz, 3H), 0.75−0.96 (m, 2H), 0.90 (d, J = 6.5 Hz, 3H), 1.07−1.44 (m, 2H), 1.54−1.73 (m, 3H), 2.07 (dd, J = 12.1, 4.0 Hz, 1H), 2.22−2.43 (m, 1H), 3.02 (d, J = 11.4 Hz, 1H), 3.47 (td, J = 10.6, 4.2 Hz, 1H), 3.63 (dd, J = 9.4, 6.2 Hz, 1H), 3.79 (dd, J = 9.4, 6.5 Hz, 1H), 3.94−4.05 (m, 1H), 4.08−4.27 (m, 2H), 4.47 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 11.8 Hz, 1H), 4.63 (d, J = 11.6 Hz, 1H), 4.75 (d, J = 11.7 Hz, 1H), 5.13 (d, J = 5.2 Hz, 1H), 7.10−7.73 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 15.9, 21.1, 22.3, 22.8, 24.7, 31.3, 34.4, 39.9, 48.0, 69.4, 73.0, 73.5, 74.4, 75.1, 77.7, 78.8, 96.5, 127.0, 127.0, 127.3, 127.6, 127.9, 127.9, 128.2, 128.2, 128.3, 128.3, 138.0, 138.5; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2774.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(3,5-di-*O*-benzyl-*α*-D-lyxofuranosyl)-*α*-D-glucopyranoside (29a). This compound is prepared using the above-mentioned general procedure using **6b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.266 g, 85% over two steps); $[\alpha]_D^{25}$ ($CHCl_3$, c 0.7) +48.1; IR (cm^{-1}, $CHCl_3$) 3386, 3032, 2923, 1597, 1454, 1271, 1057, 703; ^1H NMR (399.78 MHz, $CDCl_3$) δ 3.34 (s, 3H), 3.64−3.45 (m, 5H), 3.75−3.68 (m, 1H), 3.96 (t, J = 9.2 Hz, 1H), 4.01 (dd, J = 11.1, 3.3 Hz, 1H), 4.13 (dd, J = 10.2, 4.9 Hz, 1H), 4.22−4.17 (m, 1H), 4.64−4.36 (m, 7H), 4.69 (t, J = 12.4 Hz, 2H), 4.86−4.77 (m, 3H), 4.98 (d, J = 10.8 Hz, 1H), 5.04 (s, 1H), 7.49−7.02 (m, 25H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 55.2, 65.8, 67.7, 69.7, 71.9, 72.4, 73.3, 73.8, 75.0, 75.8, 77.2, 77.5, 77.6, 79.8, 82.0, 98.1, 107.5, 127.7, 127.7, 127.7, 127.8, 127.8, 127.8, 127.8, 127.8, 127.9, 127.9, 127.9, 128.0, 128.0, 128.1, 128.1, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128. 4, 137.0, 137.7, 138.1, 138.2, 138.7; HRMS (ESI-TOF) m/z calcd for $[C_{47}H_{52}O_{10}+Na]^+$ 799.3458, found 799.3453.

Menthyl 3,5-di-*O*-benzyl-*α*-D-lyxofuranoside (29b). This compound is prepared using the above-mentioned general procedure using **6b** (0.200 g, 0.42 mmol) as the starting material. Yield: (0.163 g, 82%); $[\alpha]_D^{25}$ ($CHCl_3$, c 1.0) +58.1; IR (cm^{-1}, $CHCl_3$) 3429, 2927, 1594, 1455, 1150, 1028, 741; ^1H NMR (399.78 MHz, $CDCl_3$) δ 0.77 (d, J = 6.9 Hz, 3H), 0.82 (dd, J = 12.3, 3.2 Hz, 1H), 0.87 (d, J = 5.3 Hz, 3H), 0.89 (d, J = 5.7 Hz, 3H), 0.89−1.00 (m, 1H), 1.08−1.21 (m, 1H), 1.30−1.46 (m, 1H), 1.52−1.72 (m, 3H), 1.96−2.15 (m, 2H), 3.29 (td, J = 10.6, 4.4 Hz, 1H), 3.61 (dd, J = 10.5, 2.1 Hz, 1H), 3.66 (dd, J = 10.5, 3.2 Hz, 1H), 4.08 (dd, J = 9.9, 4.7 Hz, 1H), 4.29−4.42 (m, 2H), 4.45 (d, J = 4.8 Hz, 1H), 4.48 (d, J = 11.4 Hz, 1H), 4.54 (d, J = 11.8 Hz, 1H), 4.64 (d, J = 11.8 Hz, 1H), 4.72 (d, J = 11.3 Hz, 1H), 5.04 (s, 1H), 7.03−7.67 (m, 10H); ^{13}C NMR (100.53 MHz, $CDCl_3$) δ 16.2, 21.1, 22.2, 23.2, 25.5, 31.6, 34.3, 43.2, 48.7, 67.9, 72.0, 72.4, 73.9, 77.0, 78.0, 79.1, 108.5, 127.7, 127.7, 127.7, 127.8, 127.9, 127.9, 128.4, 128.4, 128.4, 128.4, 137.2, 137.9; HRMS (ESI-TOF) m/z calcd for $[C_{29}H_{40}O_5+Na]^+$ 491.2773, found 491.2767.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H, ^{13}C and DEPT NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org

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Notes

The authors declare no competing financial interest.

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