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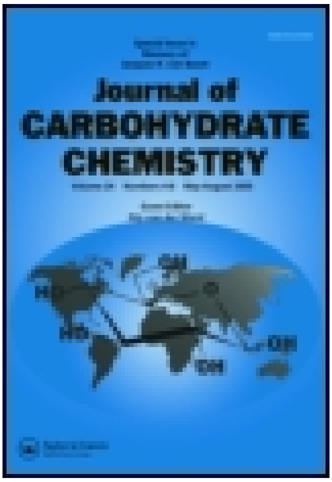

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SYNTHESIS AND GLYCOSIDIC REACTION OF 1,2-ANHYDROMANNO-, LYXO-, GLUCO-, AND XYLOFURANOSE PERBENZYL ETHERS

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ABSTRACT

Stereospecific synthesis of 1,2-anhydromanno-, lyxo-, gluco-, and xylofuranose perbenzyl ethers was successfully achieved *via* intramolecular S_N2 reaction of the corresponding C-1 alkoxide with C-2 bearing tosyloxy group. The key intermediates, furanose 2-sulfonates, were prepared from the corresponding 1,2-diols and tosyl chloride under phase transfer conditions in good yields. Condensation of the anhydro sugars with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose or *N*-benzyloxycarbonyl L-serine methyl ester in the absence of catalyst gave 1,2-*trans*-linked glycofuranosides in high yield.

INTRODUCTION

The ability to couple carbohydrate entities to produce glycosides or higher oligomers is one of the important goals of synthetic organic chemistry.[1] The roles of oligosaccharides as energy storage sources, as structural building blocks, as modifiers of protein folding, as immunological determinants, and as apparent accessories (conjugating agents) to various steroidal hormones and antibiotics are well known.[2-4] Until now, not much attention has been focused on the preparation of non-ribose furanose derivatives

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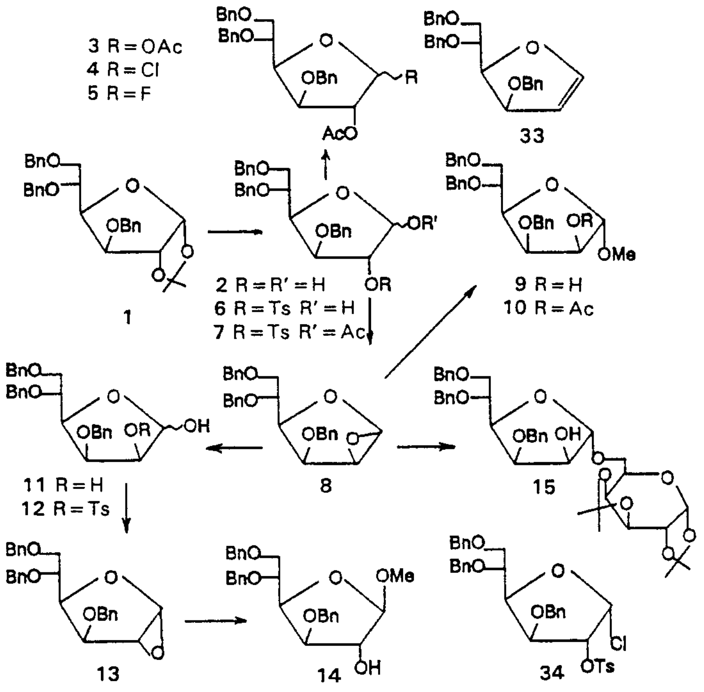
or oligosaccharides, although non-ribose furanose units are widely distributed in the cell-wall and intercellular-matrix polysaccharides of higher plants. Recent reports[5,6] showed that some furanans, like xylofuranan have high anti-HIV activity and low anticoagulant activity as well as low *in vivo* toxicities, and are considered to be potential AIDS drugs. It has also been shown that α-(1→5)-D-arabinofuranose oligomers, existing as terminals of the polysaccharide side chains are responsible for the serological activity.[7,8] In this regard it is of interest to investigate new and effective methods for stereoselective formation of glycofuranosidic linkages. 1,2-Anhydrofuranose sugars would be valuable intermediates for the synthesis of the corresponding 1,2-*trans*-related glycofuranosides and 1→2-linked furanose polysaccharides as well. To our best knowledge, there are only very limited reports dealing with 1,2-anhydrofuranose sugars in contrast to well documented studies on 1,2-anhydropyranose analogues.[9] Danishefsky's group described the synthesis of 1,2-anhydrogalacto-,[10] arabino-, and ribofuranose derivatives[11] by oxidative conversion of the corresponding furanose glycals with 3,3-dimethyldioxirane. However, the method is convenient only for the synthesis of 1,2-anhydro sugar derivatives with the epoxide and C-3 substituent existing on different sides of the furanose ring. Furthermore, it is difficult to carry out the epoxidation on a large scale, and in some cases it is difficult to isolate pure anhydride derivatives[11] by this method. In our previous communication[12] we reported a facile and general method for the synthesis of benzylated 1,2-anhydroglycofuranoses by intramolecular S_N2 reaction of the corresponding C-1 alkoxide with C-2 bearing tosyloxy group. Here we wish to give full accounts on the synthesis of the title anhydro sugars, and on their reactivity and stereoselectivity as glycosyl donors in the synthesis of oligosaccharides and glycopeptides.

RESULTS AND DISCUSSION

Two compounds that can be considered models for 1,2-anhydroglycofuranoses are 2,6-dioxabicyclo[3.1.0]hexane (2,3-epoxytetrahydrofuran), first synthesized by Decor and Descotes,[13] and 5-methyl-2,6-dioxabicyclo[3.1.0]hexane (2,3-epoxy-5-methyloxolane), synthesized by Birkofer and Drutz[14] via ring closure of the corresponding C-2 alkoxide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4 R = Cl
5 R = F
BnO
OBn
R
AcO
33
1
2 R = R' = H
6 R = Ts R' = H
7 R = Ts R' = Ac
OR'
OR
9 R = H
10 R = Ac
OMe
11 R = H
12 R = Ts
OH
8
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OH
OMe
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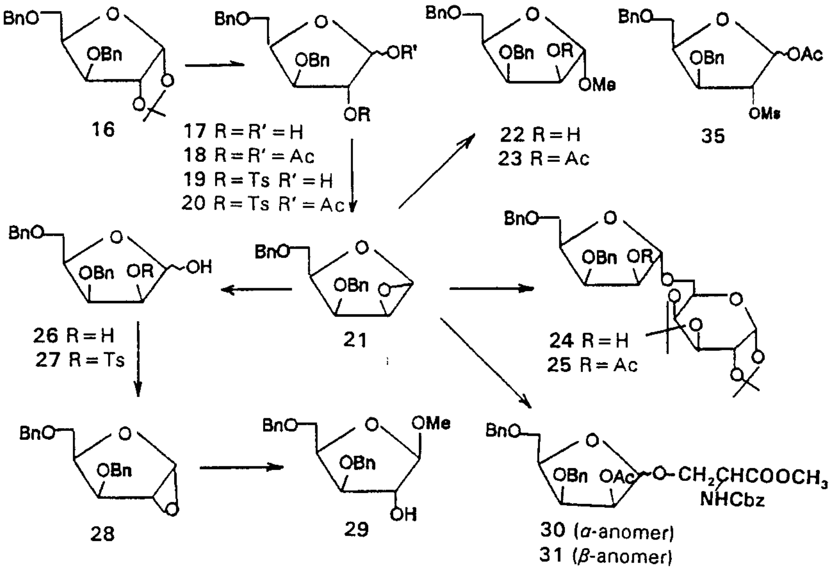
OTs


16
17 R = R' = H
18 R = R' = Ac
19 R = Ts R' = H
20 R = Ts R' = Ac
OR'
OR
22 R = H
23 R = Ac
OMe
35
OAc
OMs
26 R = H
27 R = Ts
OH
21
24 R = H
25 R = Ac
28
29
OMe
OH
O-CH$_2$CHCOOCH$_3$
NHCbz
OAc
30 (α-anomer)
31 (β-anomer)

displacing a chlorine at C-3. The model anhydrides were each synthesized as a racemic mixture. Marzabadi and Spilling reported[9b] the synthesis of 1,2-anhydroglycopyranose derivatives from the corresponding bromohydrins. However, they found that hydrobromination of tri-*O*-benzyl-D-glucal gave a diastereoisomeric mixture of bromohydrins containing α-gluco-, β-gluco-, α-manno-, and β-mannopyranose configurations. The authors also indicated that base catalyzed epimerization at C-2 occurred during cyclization. To avoid the tedious separation of sugar bromohydrins, and the possible epimerization at C-2 during ring closure, the method of hydrobromination of furanose glycals was not used in the present studies. Our attention thus was focused on an intramolecular S_N2 reaction of C-2 alkoxide with C-1 bearing a halide as reported for the synthesis of a series of 1,2-anhydroglycopyranoses.[3,9f-h] For this purpose, a *trans* relationship between C-2 alkoxide and C-1 halide was needed. Thus, 3,5,6-tri-*O*-benzyl-D-glucofuranose (**2**), prepared by hydrolysis of 3,5,6-tri-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (**1**)[15] in 1 M sulfuric acid, was acetylated with acetic anhydride in pyridine to give 1,2-di-*O*-acetyl-3,5.6-tri-*O*-benzyl-D-glucofuranose (**3**). Chlorination of **3** with hydrogen chloride in cold diethyl ether gave 2-*O*-acetyl-3,5,6-tri-*O*-benzyl-α-D-glucofuranosyl chloride (**4**) in low yield (25%). When dry $CaCl_2$ was added to the reaction mixture, the yield of the chloride **4** could be increased to 38%. ^{1}H NMR spectroscopy proved that the fast moving spot was the α-linked chloride **4** (δ 6.41, d, $J_{1,2}$ 4.6 Hz, H-1). Fluorination of **4** with silver fluoride afforded 2-*O*-acetyl-3,5,6-tri-*O*-benzyl-β-D-glucofuranosyl fluoride (**5**) in good yield (63%). The doublet at δ 5.75 ($J_{1,F}$ 63.0, $J_{1,2}$ 0.0 Hz, H-1) indicated that the product was the β fluoride.[9h] It was found, however, that the pure furanosyl α-chloride and β-fluoride compounds were easily transformed into their α and β mixture in the workup of the reaction mixture, and ring closure of the mixture with base gave a product containing the corresponding 1,2-anhydrofuranose and another by-product. To obtain pure title compounds, our attention turned to "inverse" ring closure,[12] i.e., reaction of C-1 alkoxide with C-2 bearing a leaving group. Our earlier study on the synthesis of 1,2-anhydrolyxo- and ribopyranose perbenzyl ethers by the "inverse" ring closure with C-2 bearing a tosyloxy group revealed that no epimerization occurred at C-2 during cyclization, and that the 1,2-anhydropyranoses could be isolated in pure form.[9i] We tried the same strategy for the synthesis of 1,2-anhydrofuranose analogues, i.e., using 3,5,6-tri-*O*-benzyl-2-*O*-tosyl-D-gluco- (**6**) and 3,5-di-*O*-benzyl-2-*O*-tosyl-D-xylofuranose (**19**) as the key intermediates, with **6** being obtained from the corresponding 1,2-diol **2** and **19** from 3,5-di-*O*-benzyl-D-xylofuranose (**17**). When tosylation of **2** or **17** was carried out with tosyl chloride in anhydrous pyridine[9i] for about 4 days, only a small amount of **6** or **19** (20%) was obtained. The main product in the synthesis of **6** gave a fast moving spot on TLC and was identified from ^{1}H NMR spectroscopy data as 3,5,6-tri-*O*-benzyl-2-*O*-tosyl-α-D-glucofuranosyl chloride (**34**, 75%). A similar result was reported for tosylation of the pyranose analogues.[16] We supposed that the chloride formation was caused by the occurrence of hydrogen chloride produced *in situ* from tosylation of the sugar. Consequently, if the tosylation was carried out under phase transfer conditions, the hydrogen chloride would be trapped by base immediately. The experimental results confirmed our hypothesis affording an easily accessible method for the preparation of fully benzylated 1-hydroxy-2-*O*-tosylate of glycofuranoses. The reaction conditions were quite mild, and the 2-*O*-tosylate was the sole product. Furthermore, unreacted starting material could be recovered and reused. Thus, when **2** or **17** was treated with 5% NaOH, about 1.5 equiv of *p*-toluenesulfonyl chloride, and tetrabutylammonium hydrogensulfate (TBAHS) in dichloromethane at room temperature (22-27 °C), **6** (57%) or **19** (70%) was obtained respectively.

The preparation of **6** or **19** was also achieved by an alternative method. Treatment of **2** or **17** with about 3.5 equiv of TsCl and 1 equiv of potassium carbonate in dry pyridine gave a fair yield of **6** (45%) or **19** (60%). Further efforts were tried to improve the yield of furanose 2-sulfonates, but the results were not satisfactory. For example, when **2** was treated with TsCl, triethylamine and potassium carbonate in dichloromethane, the main product was proved from ^{1}H NMR data to be the glycal **33**. Sulfonation of **17** with methanesulfonyl chloride in pyridine followed by acetylation gave 1-*O*-acetyl-3,5-di-*O*-benzyl-2-*O*-methanesulfonyl-D-xylofuranose (**35**) in low yield with poor reproducibility. Both **6** and **19** were α/β mixtures. Ring closure of the mixtures with potassium *tert*-butoxide in oxolane (THF) at room temperature gave quantitatively 1,2-anhydro-3,5,6-tri-*O*-benzyl-β-D-manno- (**8**) or 1,2-anhydro-3,5-di-*O*-benzyl-β-D-lyxofuranose (**21**) respectively. The anhydrides **8** and **21** were identified from their ^{1}H

NMR spectra showing an upfield peak for H-2 at δ 3.63 or 3.58 ppm respectively characteristic of a proton on an epoxide ring carbon. Methanolysis of **8** or **21** quantitatively gave the corresponding methyl α-furanoside **9** or **22**, confirming further the structure of the 1,2-anhydrosugar.

For the preparation of 1,2-anhydro-3,5,6-tri-*O*-benzyl-α-D-gluco- (**13**) or 1,2-anhydro-3,5-di-*O*-benzyl-α-D-xylofuranose (**28**) analogue, "double inverse" ring closure was conducted as described below. Hydrolysis of **8** or **21** (dissolved in a small amount of 1,4-dioxane) with 0.05 N HCl at 0 °C gave the corresponding 1,2-diol **11** or **26**. It was found that the yield of the hydrolysis reaction depended on the solution concentration, and hydrolysis in diluted condition was preferred. Tosylation of **11** or **26** in the same way as described for tosylation of **2** or **17**, followed by quantitative ring closure of **12** or **27** gave the anhydro sugar **13** or **28**. Similarly, the ^{1}H NMR spectrum of **13** or **28** contained the characteristic upfield signal for H-2 at δ 3.60 (dd, $J_{1,2}$ 1.6, $J_{2,3}$ 6.7 Hz) or δ 3.53 (dd, $J_{1,2}$ 1.9, $J_{2,3}$ 6.0 Hz). The structure of **13** or **28** was also confirmed by quantitative methanolysis to give methyl 3,5,6-tri-*O*-benzyl-β-D-glucofuranoside (**14**) or methyl 3,5-di-*O*-benzyl-β-D-xylofuranoside (**29**).

To investigate the reactivity of the anhydro sugars as glycosyl donors, condensation of **8** or **21** with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose was carried out. It was gratifying to note that the condensation, in the absence of catalyst, yielded α-linked disaccharide as the sole product in high yield (83% for **15**, 85% for **24**). Furthermore, the coupling reaction of **21** with *N*-benzyloxycarbonyl L-serine methyl ester (**32**) in dry dichloromethane without catalyst and subsequent acetylation gave a good yield (78.3%) of glycopeptides (**30**,**31**) in high stereoselectivity (α:β = 12:1). When the same coupling reaction was conducted in the presence of $ZnCl_2$ and 4A molecular sieves, the reaction gave an excellent yield of glycopeptide (92%) with high stereoselectivity (α:β = 9:1).

Encouraged by the high reactivity and stereoselectivity of the anhydrofuranose sugars, we have started to study the synthesis of oligosaccharides on solid phase using the furanose 1,2-anhydride as the glycosyl donor. The results will be published elsewhere.

EXPERIMENTAL

General Methods. Optical rotations were determined at 25 °C with a Perkin-Elmer Model 241-MC automatic polarimeter. Melting points were determined with a "Mel-Temp" apparatus and are uncorrected. ^{1}H NMR spectra were recorded with Varian XL-400 or Varian XL-200 spectrometer for solutions in $CDCl_3$. Chemical shifts are given in ppm downfield from the internal Me_4Si. For conformational analysis, the ^{1}H NMR spectra of the title anhydrides were fully assigned by the use of single frequency decoupling. Analytical LC was carried out in stainless steel columns packed with silica gel (10 x 150 mm or 4.6 x 250 mm) or Lichrosorb-NH_2 (4.6 x 250 mm) with peak detection by a differential refractometer (Perkin-Elmer LC-25 RI Detector). Ethyl acetate-petroleum ether (bp 60-90 °C) was used as the eluent at a flow rate of 1 to 4 mL min^{-1}. TLC was performed on silica gel HF, detection being affected either by charring with 30% (v/v) H_2SO_4 in MeOH or by UV light. Preparative chromatography was performed on columns (16 x 240, 18 x 300, and 35 x 400 mm) of silica gel (120-200 mesh). Solutions were concentrated below 50 °C under diminished pressure.

3,4,6-Tri-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1). To a solution of 1,2-*O*-isopropylidene-α-D-glucofuranose[15] (3.0 g, 13.6 mmol) in anhydrous oxolane (60 mL) was added, with vigorous stirring in ice-cold water bath, sodium hydride (80%, 1.65 g, 55 mmol) and benzyl bromide (5.6 mL, 41.6 mmol). Then the mixture was stirred and boiled under reflux for 4 h, when TLC (3:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was directly subjected to steam distillation to remove excess benzyl bromide and dibenzyl ether, and then extracted with dichloromethane. The organic layer was concentrated to a syrup that was purified by column chromatography with 4:1 petroleum ether-EtOAc to give 1 (5.73 g, 85.7%): $[\alpha]_D$ -33° (*c* 9.3, $CHCl_3$); Lit.[15] $[\alpha]_D$ -28° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 7.50-7.20 (m, 15H, 3 Ph*H*), 5.90 (d ,1H, $J_{1,2}$ = 3.7 Hz, H-1), 4.78, 4.42 (2d, 2H, J = 11.7 Hz, PhCH_2), 4.59, 4.42 (2d, 2H, J = 11.5 Hz, PhCH_2), 4.54 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-2), 4.53 (t, 2H, J = 12.2 Hz, PhCH_2), 4.26 (dd, 1H, $J_{3,4}$ = 2.8, $J_{4,5}$ = 9.0 Hz, H-4), 4.23 (d, 1H, $J_{2,3}$ = 0.0, $J_{3,4}$ = 2.8 Hz, H-3), 4.07-4.00 (m, 1H, $J_{4,5}$ = 9.0, $J_{5,6}$ = 1.8, $J_{5,6'}$ = 5.7 Hz, H-5), 3.88 (dd, 1H, $J_{5,6}$ = 1.8 Hz, $J_{6,6'}$ = 11.1 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 5.7, $J_{6,6'}$ = 11.1 Hz, H-6'), 1.42 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3).

Anal. Calcd for $C_{30}H_{34}O_6$: C, 73.47; H, 6.94. Found: C, 73.51; H, 6.90.

3,5,6-Tri-*O*-benzyl-D-glucofuranose (2). To a solution of **1** (5.0 g, 0.2 mmol) in 1,4-dioxane (100 mL) was added 1 M sulfuric acid (15 mL), and the mixture was boiled under reflux with stirring for 4 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was carefully neutralized with powdered sodium bicarbonate, concentrated and partitioned between water and dichloromethane. The organic layer was dried over sodium sulfate and concentrated. Purification of the residue by column chromatography with 2:1 petroleum ether-EtOAc furnished syrupy **2** (3.99 g, 86.9%) as an α,β mixture (1:1): $[\alpha]_D$ -18° (*c* 8.3, $CHCl_3$, for the anomeric mixture); ^1H NMR: δ 7.42-7.18 (m, 15H, 3Ph*H*), 5.44 (d, 0.5H, $J_{1,2}$ = 3.8 Hz, H-1 of α anomer), 5.11 (s, 0.5H, H-1 of β anomer), 4.79, 4.74 (2d, 2 x 0.5 H, J = 10.0, J = 10.5 Hz, one proton of PhCH_2 for α,β anomer respectively), 4.60-4.32 (m, 5H, PhCH_2), 4.10-3.60 (m, 7H, H-2-6,6'), 2.40-2.80 (bs, 2H, 2O*H*).

Anal. Calcd for $C_{27}H_{30}O_6$ (α,β mixture): C, 72.09; H,6.67. Found: C, 71.85; H, 6.75.

1,2-Di-*O*-acetyl-3,5,6-tri-*O*-benzyl-D-glucofuranose (3). Acetylation of **2** (1.2 g, 2.25 mmol) in pyridine (6 mL) and acetic anhydride (4 mL) at room temperature for 4 h gave **3** in quantitative yield as a syrup consisting of α and β anomers in a ratio of 1:1: $[\alpha]_D$ +13° (*c* 1.5, $CHCl_3$, for the anomeric mixture); ^1H NMR: δ 7.42-7.18 (m, 15H, 3Ph*H*), 6.40 (d, 0.5H, $J_{1,2}$ = 4.2 Hz, H-1 of α anomer), 6.14 (s, 0.5H, H-1 of β anomer), 5.35 (dd, 0.5H, $J_{1,2}$ = 4.2, $J_{2,3}$ = 2.1 Hz, H-2 of α anomer), 5.26 (s, 0.5H, H-2 of β anomer), 4.80, 4.76, 4.71, 4.69 (4d, 4 x 0.5H, J = 11.4, J = 11.4, J = 11.1, J = 11.9 Hz, PhCH_2), 4.59, 4.53 (2d, 2 x 0.5H, J = 12.7 Hz, PhCH_2), 4.57 (s, 1H, PhCH_2), 4.50-4.41 (m, 4 x 0.5H, PhCH_2), 4.40-4.30 (m, 1.5H, H-3 of β anomer, and H-4), 4.20 (m, 0.5H, H-3 of α anomer), 4.12-4.00 (m, 1H, H-5), 3.88-3.82 (m, 1H, H-6), 3.70-3.61 (m, 1H, H-6'), 2.09 (s, 1.5H, COCH_3 of α anomer), 2.08 (s, 1.5H, COCH_3 of β anomer), 2.06 (s, 2 x 1.5H, overlapped COCH_3 of α,β anomer).

Anal. Calcd for $C_{31}H_{34}O_8$ (α,β mixture): C, 69.66; H, 6.37. Found: C, 69.69; H, 6.32.

2-*O*-Acetyl-3,5,6-tri-*O*-benzyl-α-D-glucofuranosyl Chloride (4). A solution of **3** (512 mg, 0.81 mmol) containing $CaCl_2$ (200 mg) in dry diethyl ether (15 mL) was saturated at 0 °C with hydrogen chloride gas under a nitrogen atmosphere. Then the solution was kept at room temperature in a sealed bottle for 2.5 h, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material disappeared. The solution was concentrated under reduced pressure to a syrupy residue which was dissolved in dichloromethane (2 mL), and the solution was concentrated. This procedure was repeated several times to remove the hydrogen chloride. Purification of the product by column chromatography (3:1 petroleum ether-EtOAc) gave **4** as a syrup (186 mg, 38%); ^{1}H NMR: δ 7.40-7.15 (m, 15H, 3Ph*H*), 6.41 (d, 1H, $J_{1,2}$ = 4.6 Hz, H-1), 5.15 (dd, 1H, $J_{1,2}$ = 4.6, $J_{2,3}$ = 3.4 Hz, H-2), 4.80-4.44 (m, 7H, 3PhCH_2 and H-4), 4.31 (dd, 1H, $J_{2,3}$ = 3.4, $J_{3,4}$ = 5.7 Hz, H-3), 4.12-4.03 (m, 1H, H-5), 3.82 (dd, 1H, $J_{5,6}$ = 2.2, $J_{6,6'}$ = 10.7 Hz, H-6), 3.64 (dd, 1H, $J_{5,6'}$ = 5.5, $J_{6,6'}$ = 10.7 Hz, H-6'), 2.10 (s, 3H, COCH_3).

2-*O*-Acetyl-3,5,6-tri-*O*-benzyl-β-D-glucofuranosyl Fluoride (5). To a solution of **4** (150 mg, 0.29 mmol) in 2:5 acetonitrile-benzene (5 mL) was added silver fluoride (52 mg, 0.41 mmol). The mixture was stirred vigorously for 16 h in the dark at room temperature, then centrifugated, and the filter cake was washed repeatedly with dichloromethane. The supernatant liquor and combined washings were concentrated. Purification of the syrup by column chromatography (4:1 petroleum ether-EtOAc) yielded **5** as a syrup (91 mg, 63%): $[\alpha]_D$ -58° (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ 7.40-7.22 (m, 15H, 3Ph*H*), 5.75 (d, 1H, $J_{1,F}$ = 63.0, $J_{1,2}$ = 0.0 Hz, H-1), 5.38 (d, 1H, $J_{2,3}$ = 4.8 Hz, H-2), 4.86, 4.45 (2d, 2H, J = 11.0 Hz, PhCH_2), 4.68, 4.56 (2d, 2H, J = 11.4 Hz, PhCH_2), 4.64, 4.58 (2d, 2H, J = 12.3 Hz, PhCH_2), 4.59-4.52 (m, 1H, H-4), 4.13 (dd, 1H, $J_{2,3}$ = 4.8, $J_{3,4}$ = 0.0 Hz, H-3), 4.12-4.08 (m, 1H, H-5), 3.88 (dd, 1H, $J_{5,6}$ = 2.0, $J_{6,6'}$ = 10.2 Hz, H-6), 3.72 (dd, 1H, $J_{5,6'}$ = 4.2, $J_{6,6'}$ = 10.2 Hz, H-6'), 2.13 (s, 3H, COCH_3).

Anal. Calcd for $C_{29}H_{31}FO_6$: C, 70.45; H, 6.28. Found: C, 70.33; H, 6.12.

3,5,6-Tri-*O*-benzyl-2-*O*-tosyl-D-glucofuranose (6). Method A: To a solution of **2** (1.35 g, 3 mmol) in pyridine (10 mL) was added TsCl (2.0 g, 10.5 mmol) and powdered K_2CO_3 (415 mg, 3 mmol). The mixture was stirred at room temperature for about 48 h, and the reaction mixture was poured into ice-cold water, extracted with dichloromethane (50 mL). The organic layer was washed with cold 1 N HCl (3 x 50 mL), then dried over Na_2SO_4. The solution was concentrated under diminished pressure to give **6** (0.81 g, 45%) as an α:β mixture in a ratio of 1:4.

Method B: To a solution of **2** (1.6 g, 3.56 mmol) in dichloromethane (30 mL) was added *p*-toluenesulfonyl chloride (960 mg, 5.05 mmol), TBAHS (150 mg, 0.44 mmol) and 5% aqueous sodium hydroxide (7.0 mL). The solution was stirred at room temperature (27 °C) for 24 h, and then diluted with dichloromethane, washed with cold water. The organic phase was dried over Na_2SO_4, then concentrated under diminished pressure to give **6** (1.03 g, 57%) as an α,β (1:6) mixture which was separated by analytical LC with 3:1 petroleum ether-EtOAc as the eluent. For β isomer: $[\alpha]_D$ -29° (*c* 8.9, $CHCl_3$); ^{1}H NMR: δ 7.75 (d, 2H, PH*H* of Ts), 7.49-7.20 (m, 17H, Ph*H*), 5.07 (d, 1H, $J_{1,2}$ = 0.0, $J_{H1,OH}$ = 11.1 Hz, H-1), 4.79 (s, 1H, H-2), 4.76, 4.42 (2d, 2H, J = 11.3 Hz, PhCH_2), 4.59, 4.52 (2d, 2H, J = 11.6 Hz, PhCH_2), 4.56, 4.46 (2d, 2H, J = 11.5 Hz, PhCH_2), 4.30 (dd, 1H, $J_{3,4}$ = 3.4, $J_{4,5}$ = 9.2 Hz, H-4), 4.25 (d, 1H, $J_{2,3}$ = 0.0, $J_{3,4}$ = 3.4 Hz, H-3), 3.92-3.87 (m, 1H, H-5), 3.83 (dd, 1H, $J_{5,6}$ = 2.4, $J_{6,6'}$ = 11.3 Hz, H-6), 3.63 (dd, 1H, $J_{5,6'}$ = 4.9, $J_{6,6'}$ = 11.3 Hz, H-6'), 3.38 (d, 1H, $J_{H1,OH}$ 11.1 Hz, O*H*), 2.39 (s, 3H, PHCH_3).

Anal. Calcd for $C_{34}H_{36}O_8S$ (α,β mixture): C, 67.53; H, 6.00. Found: C, 67.74; H, 6.05.

1-*O*-Acetyl-3,5,6-tri-*O*-benzyl-2-*O*-tosyl-D-glucofuranose (7). Acetylation of **6** (138 mg, 0.23 mmol) in acetic anhydride (2 mL) and pyridine (3 mL) at room temperature for 4 h afforded **7** quantitatively as a syrup (α:β = 1:2) which was separated by analytical LC with 4:1 petroleum ether-EtOAc as the eluent: For α anomer, $[\alpha]_D$ -8.8° (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ 7.80 (d, 2H, J = 8.4 Hz, Ph-*H* of Ts), 7.45-7.15 (m, 17H, Ph-*H*), 6.25 (d, 1H, $J_{1,2}$ = 4.4 Hz, H-1), 5.00 (d, 1H, $J_{1,2}$ = 4.4 Hz, $J_{2,3}$ = 0.0 Hz, H-2), 4.71, 4.42 (2d, 2H, J = 11.3 Hz, PhCH_2), 4.60, 4.48 (2d, 2H, J = 12.0 Hz, PhCH_2), 4.56, 4.53 (2d, 2H, J = 10.7 Hz, PhCH_2), 4.39 (dd, 1H, $J_{3,4}$ = 5.0, $J_{4,5}$ = 7.8 Hz, H-4), 4.25 (d, 1H, $J_{2,3}$ = 0.0, $J_{3,4}$ = 5.0 Hz, H-3), 4.22-4.17 (m, 1H, H-5), 3.81 (dd, 1H, $J_{5,6}$ = 2.7, $J_{6,6'}$ = 11.2 Hz, H-6), 3.61 (dd, 1H, $J_{5,6'}$ = 5.8, $J_{6,6'}$ = 11.2 Hz, H-6'), 2.49 (s, 3H, PHCH_3), 2.01 (s, 3H, COCH_3). For β anomer, $[\alpha]_D$ -39° (*c* 0.3, $CHCl_3$); ^{1}H NMR: δ 7.75 (d, 2H, J = 8.3 Hz, Ph-*H* of Ts), 7.45-7.15 (m, 17H, Ph-*H*), 6.00 (s, 1H, H-1), 5.01 (s, 1H, H-2), 4.72, 4.52 (2d, 2H, J = 11.2 Hz, PhCH_2), 4.58, 4.49 (2d, 2H, J = 12.5 Hz, PhCH_2), 4.51 (t, 2H, J = 10.5 Hz, PhCH_2), 4.41 (d, 1H, $J_{3,4}$ = 4.6, H-3), 4.31 (dd, 1H, $J_{3,4}$ = 4.6, $J_{4,5}$ = 6.7 Hz, H-4), 4.00-3.93 (m, 1H, H-5), 3.78 (dd, 1H, $J_{5,6}$ = 3.0, $J_{6,6'}$ = 11.0 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 5.4, $J_{6,6'}$ = 11.0 Hz, H-6'), 2.48 (s, 3H, PHC*H*$_3$), 2.00 (s, 3H, COC*H*$_3$).

Anal. Calcd for $C_{38}H_{38}O_9S$ (α,β mixture): C, 66.87; H, 5.88. Found: C, 66.90; H, 5.81.

1,2-Anhydro-3,5,6-tri-*O*-benzyl-β-D-mannofuranose (8). To a solution of **6** (466 mg, 0.77 mmol) in dry oxolane was added potassium *tert*-butoxide (135 mg, 1.2 mmol), and the mixture was stirred at room temperature for 30 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts yielded **8** as a syrup (319 mg, 96%): ^{1}H NMR: δ 7.45-7.25 (m, 15H, 3Ph*H*), 5.11 (d, 1H, $J_{1,2}$ = 2.0 Hz, H-1), 4.69 (s, 2H, PhC*H*$_2$), 4.67, 4.51 (2d, 2H, J = 11.7 Hz, PhC*H*$_2$), 4.60, 4.56 (2d, 2H, J = 12.3 Hz, PhC*H*$_2$), 4.48 (dd, 1H, $J_{3,4}$ = 7.5, $J_{4,5}$ = 8.3 Hz, H-4), 4.40 (dd, 1H, $J_{2,3}$ = 2.0, $J_{3,4}$ = 7.5 Hz, H-3), 4.01 (ddd, 1H, $J_{4,5}$ = 8.3, $J_{5,6}$ = 2.6, $J_{5,6'}$ = 5.5 Hz, H-5), 3.80 (dd, 1H, $J_{5,6}$ = 2.6, $J_{6,6'}$ = 10.4 Hz, H-6), 3.66 (dd, 1H, $J_{5,6'}$ = 5.5, $J_{6,6'}$ = 10.4 Hz, H-6'), 3.63 (t, 1H, $J_{1,2}$ = 2.0, $J_{2,3}$ = 2.0 Hz, H-2).

Methyl 3,5,6-tri-*O*-benzyl-α-D-mannofuranoside (9). Compound **8** (93 mg, 0.21 mmol) was dissolved in anhydrous methanol (6 mL) and kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **9** quantitatively as a syrup; $[\alpha]_D$ +8.7° (*c* 2.3, $CHCl_3$); ^{1}H NMR: δ 7.46-7.20 (m, 15H, 3Ph*H*), 4.85, 4.47 (2d, 2H, J = 12.5 Hz, PhC*H*$_2$), 4.82 (s, 1H, H-1), 4.63, 4.61 (2d, 2H, J = 11.4 Hz, PhC*H*$_2$), 4.51, 4.50 (2d, 2H, J = 11.5 Hz, PhC*H*$_2$), 4.37-4.34 (m, 1H, H-3), 4.29 (m, 1H, H-4), 4.01 (m, 1H, H-5), 3.90-3.70 (m, 2H, H-6,6'), 3.35 (s, 3H, OC*H*$_3$).

Methyl 2-*O*-acetyl-3,5,6-tri-*O*-benzyl-α-D-mannofuranoside (10). Compound **9** (85 mg, 0.18 mmol) was dissolved in acetic anhydride (1 mL) in pyridine (1.5 mL) at room temperature for 4 h to afford **10** (91 mg, 98%) as a syrup: $[\alpha]_D$ +47.8° (*c* 1.8, $CHCl_3$); ^{1}H NMR: δ 7.40-7.18 (m, 15H, 3 Ph*H*), 5.04 (dd, 1H, $J_{1,2}$ = 2.2, $J_{2,3}$ = 4.4 Hz, H-2), 5.01 (d, 1H, $J_{1,2}$ = 2.2 Hz, H-1), 4.81, 4.49 (2d, 2H, J = 11.3 Hz, PhC*H*$_2$), 4.57 (t, 2H, J = 11.0 Hz, PhC*H*$_2$), 4.51, 4.48 (2d, 2H, J = 10.8 Hz, PhC*H*$_2$), 4.40 (t, 1H, $J_{2,3}$ = 4.4, $J_{3,4}$ = 4.4 Hz, H-3), 4.28 (dd, 1H, $J_{3,4}$ = 4.4, $J_{4,5}$ = 7.7 Hz, H-4), 4.07-

4.02 (m, 1H, H-5), 3.85 (dd, 1H, $J_{5,6}$ = 2.5, $J_{6,6'}$ = 11.2 Hz, H-6), 3.70 (dd, 1H, $J_{5,6'}$ = 5.8, $J_{6,6'}$ = 11.2 Hz, H-6'), 3.37 (s, 3H, OC*H*$_3$), 2.00 (s, 3H, COC*H*$_3$).

Anal. Calcd for $C_{30}H_{34}O_7$: C, 71.15; H, 6.72. Found: C, 70.88; H, 6.67.

3,5,6-Tri-*O*-benzyl-2-*O*-tosyl-D-mannofuranose (12). To a solution of **8** (49 mg, 0.11 mmol) in 1,4-dioxane (1 mL) was added 0.05 N HCl (10 mL) in an ice-cold water bath and the reaction mixture was stirred at this temperature for about 1 h, then neutralized with solid sodium bicarbonate, extracted with dichloromethane (5 x 5 mL), dried over Na_2SO_4. The organic solvent was evaporated under diminished pressure to give 3,5,6-tri-*O*-benzyl-D-mannofuranose (**11**) (42 mg, 84%) as a syrup. To a solution of **11** (200 mg, 0.44 mmol) in pyridine (5 mL) was added TsCl (295 mg, 1.54 mmol), DMAP (10 mg), and powdered K_2CO_3 (61 mg, 0.44 mmol). The mixture was stirred at room temperature for about 48 h, then the reaction mixture was poured into ice-cold water, extracted with dichloromethane (20 mL). The organic layer was washed with cold 1 N HCl (3 x 20 mL), then dried over Na_2SO_4. The solution was concentrated under diminished pressure to give **12** (83 mg, 31%) as an α:β (8:1) mixture which was separated by analytical LC with 3:1 petroleum ether-EtOAc as the eluent. Besides, 88 mg of **11** was recovered. For α isomer of **12**: $[\alpha]_D$ +16.4 (*c* 0.7, $CHCl_3$); δ 7.75(d, 2H, PH-*H* of Ts), 7.40-7.18 (m, 17H, Ph*H*), 5.09 (t, 1H, $J_{1,2}$ = 2.9, $J_{2,3}$ = 2.9 Hz, H-1), 5.01 (dd, 1H, $J_{H1,OH}$ = 10.7, $J_{1,2}$ = 2.9 Hz, H-1), 4.80, 4.53 (2d, 2H, J = 11.3 Hz, PhC*H*$_2$), 4.62, 4.61 (2d, 2H, J = 12.6 Hz, PhC*H*$_2$), 4.56, 4.49 (2d, 2H, J = 11.7 Hz, PhC*H*$_2$), 4.41 (dd, 1H, $J_{2,3}$ = 2.9, $J_{3,4}$ = 4.1 Hz, H-3), 4.30 (dd, 1H, $J_{3,4}$ = 4.1, $J_{4,5}$ = 6.9 Hz, H-4), 4.05-4.00 (m, 1H, H-5), 3.89 (dd, 1H, $J_{5,6}$ = 2.7, $J_{6,6'}$ = 11.5 Hz, H-6), 3.81 (dd, 1H, $J_{5,6'}$ = 5.8, $J_{6,6'}$ = 11.5 Hz, H-6'), 3.11 (d, 1H, $J_{H1,OH}$ = 10.7 Hz, O*H*), 2.37 (s, 3 H, PHC*H*$_3$).

Anal. Calcd for $C_{34}H_{36}O_8S$ (α,β mixture): C, 67.53; H, 6.00. Found: C, 67.85; H, 6.09.

1,2-Anhydro-3,5,6-tri-*O*-benzyl-α-D-glucofuranose (13). To a solution of **12** (50 mg, 0.08 mmol) in dry oxolane was added potassium *tert*-butoxide (15 mg, 0.13 mmol), and the mixture was stirred at room temperature for 30 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts yielded **13** as a syrup

(34 mg, 96%): ^{1}H NMR: δ 7.45-7.24 (m, 15H, 3Ph*H*), 5.26 (d, 1H, $J_{1,2}$ = 1.6 Hz, H-1), 4.79, 4.42 (2d, 2H, J = 10.6 Hz, PhCH_2), 4.60, 4.45 (2d, 2H, J = 11.7 Hz, PhCH_2), 4.55, 4.52 (2d, 2H, J = 11.5 Hz, PhCH_2), 4.30 (dd, 1H, $J_{3,4}$ = 3.2, $J_{4,5}$ = 7.5 Hz, H-4), 4.25 (dd, 1H, $J_{2,3}$ = 6.7, $J_{3,4}$ = 3.2 Hz, H-3), 4.10-4.04 (m, 1H, H-5), 3.90 (dd, 1H, $J_{5,6}$ = 2.0, $J_{6,6'}$ = 11.3 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 8.1, $J_{6,6'}$ = 11.3 Hz, H-6'), 3.60 (dd, 1H, $J_{1,2}$ = 1.6, $J_{2,3}$ = 6.7 Hz, H-2).

Methyl 3,5,6-tri-*O*-benzyl-β-D-glucofuranoside (14). Compound **13** (25 mg, 0.058 mmol) was dissolved in anhydrous methanol (2 mL) and kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **14** quantitatively as a syrup; $[\alpha]_D$ -38° (*c* 0.5, $CHCl_3$); ^{1}H NMR: δ 7.38-7.20 (m, 15H, 3Ph*H*), 4.78 (s, 1H, H-1), 4.74, 4.49 (2d, 2H, J = 11.3 Hz, PhCH_2), 4.61, 4.58 (2d, 2H, J = 12.4 Hz, PhCH_2), 4.59, 4.52 (2d, 2H, J = 11.7 Hz, PhCH_2), 4.39 (dd, 1H, $J_{3,4}$ = 5.1, $J_{4,5}$ = 8.9 Hz, H-4), 4.17 (s, 1H, H-2), 4.09-4.02 (m, 1H, H-5), 3.96 (d, 1H, $J_{3,4}$ = 5.1 Hz, H-3), 3.88 (dd, 1H, $J_{5,6}$ = 1.7, $J_{6,6'}$ = 10.2 Hz, H-6), 3.72 (dd, 1H, $J_{5,6'}$ = 5.4, $J_{6,6'}$ = 10.2 Hz, H-6'), 3.36 (s, 3H, OCH_3), 1.80 (bs, 1H, O*H*).

Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.41; H, 6.90. Found: C, 72.15; H, 6.87.

***O*-(3,5,6-Tri-*O*-benzyl-α-D-mannofuranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (15).** The 1,2-anhydro sugar **8** (110 mg, 0.26 mmol) was dissolved in anhydrous dichloromethane (6 mL) containing molecular sieves (1 g). To the mixture was added a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (75 mg, 0.29 mmol) in dichloromethane (1.5 mL) in one portion. The mixture was stirred at room temperature for 2 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that **8** disappeared. The solution was concentrated to a syrup that was subjected to separation by analytical LC with 2:1 petroleum ether-EtOAc as the eluent. Compound **15** was obtained as a syrup (146 mg, 83%): $[\alpha]_D$ +0.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.40-7.20 (m, 15H, 3Ph*H*), 5.50 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 4.98 (d, 1H, $J_{1',2'}$ = 1.4 Hz, H-1'), 4.82, 4.48 (2d, 2H, J = 11.4 Hz, PhCH_2), 4.63, 4.60 (2d, 2H, J = 10.2 Hz, PhCH_2), 4.57 (dd, 1H, $J_{2,3}$ = 2.5, $J_{3,4}$ = 7.7 Hz, H-3), 4.51, 4.49 (2d, 2H, J = 10.9 Hz, PhCH_2), 4.38 (dd, 1H, $J_{2',3'}$ = 6.4 Hz, $J_{3',4'}$ = 4.6 Hz, H-3'), 4.32 (d, 1H, $J_{3',4'}$ = 4.6 Hz, $J_{4',5'}$ = 0.0 Hz, H-4'), 4.30 (dd, 1H, $J_{1,2}$ = 4.8, $J_{2,3}$ = 2.5 Hz, H-2), 4.21 (dd, 1H, $J_{3,4}$ = 7.7, $J_{4,5}$ = 2.0 Hz, H-4), 4.12-4.08 (m, 1H, H-5'), 4.02-3.92 (m, 3H, H-

5,6a,6b), 3.80 (dd, 1H, $J_{5',6'a}$ = 3.0, $J_{6'a,6'b}$ = 10.7 Hz, H-6'a), 3.72 (dd, 1H, $J_{5',6'b}$ = 5.7, $J_{6'a,6'b}$ = 10.7 Hz, H-6'b), 3.69 (dd, 1H, $J_{2',3'}$ = 6.4 Hz, H-2'), 1.55, 1.46, 1.35 and 1.34 (4s, 12H, 2 $C(CH_3)_2$).

Anal. Calcd for $C_{39}H_{48}O_{11}$: C, 67.63; H, 6.94. Found: C, 67.58; H, 7.01.

3,5-Di-*O*-benzyl-D-xylofuranose (17). To a solution of **16**[17] (5.0 g, 13.5 mmol) in 50% acetic acid (30 mL) was added concentrated hydrochloric acid (1.2 mL), and the mixture was stirred at 80 °C for 1.5 h, at the end of which time TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The mixture was carefully neutralized with powdered sodium bicarbonate, concentrated and partitioned between water and dichloromethane. The organic layer was dried over sodium sulfate and concentrated. Purification of the residue by column chromatography with 2:1 petroleum ether-EtOAc furnished syrupy **17** (3.92 g, 88%) as an α,β mixture (1:1): $[\alpha]_D$ -5.0° (*c* 1.3, $CHCl_3$, for the anomeric mixture); ^1H NMR: δ 7.40-7.25 (m, 10H, 2Ph*H*), 5.50 (d, 0.5H, $J_{1,2}$ = 5.3 Hz, H-1 of α anomer), 5.12 (d, 0.5H, $J_{1,2}$ = 11.6 Hz, H-1 of β anomer), 4.83-3.60 (m, 9H, H-2,3,4,5,5', $2PhCH_2$), 2.90-2.55 (bs, 2H, 2 O*H*).

Anal. Calcd for $C_{19}H_{22}O_5$ (α,β mixture): C, 69.09; H, 6.67. Found: C, 69.04; H, 6.75.

1,2-Di-*O*-acetyl-3,5-di-*O*-benzyl-D-xylofuranose (18). Acetylation of **17** (100 mg, 0.3 mmol) in pyridine (5 mL) and acetic anhydride (4 mL) at room temperature for 4 h gave **18** in quantitative yield as a syrup consisting of α and β anomers in a ratio of 2.2:1: $[\alpha]_D$ +15° (*c* 2.1, $CHCl_3$, for the anomeric mixture); ^1H NMR: δ 7.40-7.20 (m, 10H, 2Ph*H*), 6.41 (d, 0.69H, $J_{1,2}$ = 4.7 Hz, H-1 of α anomer), 6.14 (s, 0.31H, H-1 of β anomer), 5.30 (t, 0.69H, $J_{1,2}$ = 4.7, $J_{2,3}$ = 4.7 Hz, H-2 of α anomer), 5.24 (s, 0.31H, H-2 of β anomer), 4.76-4.50 (m, 4H, 2 $PhCH_2$), 4.48-4.40 (m, 1H, H-4), 4.24 (dd, 0.69H, $J_{2,3}$ = 4.7, $J_{3,4}$ = 5.8 Hz, H-3 of α anomer), 4.00 (d, 1H, $J_{3,4}$ = 4.9 Hz, H-3 of β anomer), 3.86-3.62 (m, 2H, H-5,5'), 2.05, 2.04 (2s, 4.14H, $2COCH_3$ of α anomer), 2.08, 2.07 (2s, 1.86H, $2COCH_3$ of β anomer).

Anal. Calcd for $C_{23}H_{26}O_7$ (α, β mixture): C, 66.67; H, 6.28. Found: C, 66.86; H, 6.53.

3,5-Di-*O*-benzyl-2-*O*-tosyl-D-xylofuranose (19). Method A: To a solution of **17** (1.32 g, 4 mmol) in pyridine (15 mL) was added TsCl (1.9 g, 10 mmol) and powder K_2CO_3 (552 mg, 4 mmol). The mixture was stirred at room temperature for about 48 h, and then the reaction mixture was poured into ice-cold water, extracted with dichloromethane (50 mL). The organic layer was washed with cold water (50 mL), 1 N HCl (4 x 40 mL), then dried over Na_2SO_4. The solution was concentrated under diminished pressure to give **19** (1.16 g, 60%) as an α:β mixture in a ratio of 1:4.

Method B: To a solution of **17** (1.32 g, 4 mmol) in dichloromethane (30 mL) was added *p*-toluenesulfonyl chloride (970 mg, 5.1 mmol), TBAHS (100 mg, 0.3 mmol) and 5% aqueous sodium hydroxide (7.2 mL). The mixture was stirred at room temperature (22-27 °C) for 24 h, and then diluted with dichloromethane, washed with cold water. The organic phase was dried over Na_2SO_4, then concentrated under diminished pressure. Separation of the residue by column chromatography gave **19** (1.35 g, 69%) as an α,β (1:7) mixture which was separated by analytical LC with 3:1 petroleum ether-EtOAc as the eluent, and **17** (290 mg). For β isomer: $[\alpha]_D$ -22.8° (*c* 1.6, $CHCl_3$); δ 7.76 (d, 2H, Ph*H* of Ts), 7.46-7.20 (m, 12H, Ph*H*), 5.12 (d, 1H, $J_{H1,OH}$ = 11.9 Hz, H-1), 4.84 (d, 1H, $J_{2,3}$ = 2.5 Hz, H-2), 4.65, 4.49 (2d, 2H, J = 11.5, PhCH_2), 4.59, 4.54 (2d, 2H, J = 11.8, PhCH_2), 4.34-4.30 (m, 1H, H-4), 4.22 (dd, 1H, $J_{2,3}$ = 2.5, $J_{3,4}$ = 5.5 Hz, H-3), 3.90 (d, 1H, $J_{H1,OH}$ = 11.9 Hz, O*H*), 3.69 (dd, 1H, $J_{4,5}$ = 4.7, $J_{5,5'}$ = 10.2 Hz, H-5), 3.64 (dd, 1H, $J_{4,5'}$ = 4.0, $J_{5,5'}$ = 10.2 Hz, H-5'), 2.47 (s, 3H, $PhCH_3$).

Anal. Calcd for $C_{26}H_{28}O_7S$ (α,β mixture): C, 64.46; H, 5.79. Found: C, 64.27; H, 5.74.

1-*O*-Acetyl-3,5-tri-*O*-benzyl-2-*O*-tosyl-D-xylofuranose (20). Compound **19** (50 mg, 0.1 mmol) was acetylated with acetic anhydride (1 mL) in pyridine (1.5 mL) at room temperature for 4 h to afford **20** (53 mg, 98%) as a syrup (α:β = 3:1): $[\alpha]_D$ -10.3° (*c* 4.5, $CHCl_3$, for the anomeric mixture); ^1H NMR: δ 7.77 (d, 2 x 0.25 H, Ph*H* of Ts for β anomer), 7.76 (d, 2 x 0.75H, Ph*H* of Ts for α anomer), 7.45-7.10 (m, 12H, Ph*H*), 6.20 (d, 0.75H, $J_{1,2}$ = 4.7 Hz, H-1 of α anomer), 6.01 (s, 0.25H, H-1 of β anomer), 5.04 (t, 0.75H, $J_{1,2}$ = 4.7, $J_{2,3}$ = 4.7 Hz, H-2 of α anomer), 5.00 (s, 0.25H, H-2 of β anomer), 4.62, 4.48 (2d, 2 x 0.25H, J = 12.4 Hz, PhCH_2 of β anomer), 4.55, 4.49 (2d, 2 x 0.75H, PhCH_2 of α anomer), 4.52, 4.43 (2d, 2 x 0.75H, PhCH_2 of α anomer), 4.51 (s, 2 x 0.25H, PhCH_2 of β anomer), 4.46-4.38 (m, 1.75H, H-3 of α anomer and H-4), 4.21 (d, 0.25H, $J_{3,4}$ = 5.5 Hz, H-3 of β anomer), 3.72 (dd, 0.25H, $J_{4,5}$ = 4.9, $J_{5,5'}$ = 10.3 Hz, H-5 of β anomer), 3.68 (dd, 0.25H, $J_{4,5'}$ = 3.0, $J_{5,5'}$ = 10.3 Hz, H-5' of β anomer), 3.65 (dd, 0.75H, $J_{4,5}$ = 4.1, $J_{5,5'}$ = 10.7 Hz, H-5 of α anomer), 3.57 (dd, 0.75H, $J_{4,5'}$ = 4.1, $J_{5,5'}$ = 10.7 Hz, H-5' of α anomer), 2.48 (s, 3 x 0.25H, PhC*H*$_3$ of β anomer), 2.47 (s, 3 x 0.75H, PhC*H*$_3$ of α anomer), 2.01 (s, 3 x 0.75H, COC*H*$_3$ of α anomer), 1.99 (s, 3 x 0.25H, COC*H*$_3$ of β anomer).

Anal. Calcd for $C_{28}H_{30}O_8S$ (α,β mixture): C, 63.88; H, 5.70. Found: C, 63.90; H, 5.72.

1,2-Anhydro-3,5-di-*O*-benzyl-β-D-lyxofuranose (21). To a solution of **19** (430 mg, 0.89 mmol) in dry oxolane (12 mL) was added potassium *tert*-butoxide (150 mg, 1.3 mmol), and the mixture was stirred at room temperature for 30 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts yielded **21** as a syrup (270 mg, 97%): ^{1}H NMR: δ 7.40-7.20 (m, 10H, 2Ph*H*), 5.18 (d, 1H, $J_{1,2}$ = 1.7 Hz, H-1), 4.69, 4.65 (2d, 2H, J = 11.9 Hz, PhC*H*$_2$), 4.64, 4.50 (2d, 2H, J = 12.7 Hz, PhC*H*$_2$), 4.52-4.48 (m, 1H, H-4), 4.40 (dd, 1H, $J_{2,3}$ = 1.7, $J_{3,4}$ = 8.2 Hz, H-3), 3.83 (dd, 1H, $J_{4,5}$ = 4.0, $J_{5,5'}$ = 10.6 Hz, H-5), 3.68 (dd, 1H, $J_{4,5'}$ = 7.1, $J_{5,5'}$ = 10.6, H-5'), 3.58 (t, 1H, $J_{1,2}$ = 1.7, $J_{2,3}$ = 1.7 Hz, H-2).

Methyl 3,5-di-*O*-benzyl-α-D-lyxofuranoside (22). Compound **21** (20 mg, 0.064 mmol) was dissolved in anhydrous methanol (2 mL) and kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **22** quantitatively as a syrup: $[\alpha]_D$ +9.2 (*c* 1.5, CHCl$_3$); ^{1}H NMR: δ 7.37-7.20 (m, 10H, 2 Ph*H*), 4.86 (s, 1H, H-1), 4.72, 4.50 (2d, 2H, J = 11.7 Hz, PhC*H*$_2$), 4.64, 4.54 (2d, 2H, J = 12.3, PhC*H*$_2$), 4.40 (dd, 1H, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 6.7 Hz, H-3), 4.34-4.31 (m, 1H, H-4), 4.06 (d, 1H, $J_{2,3}$ = 5.0 Hz, H-2), 3.65 (dd, 1H, $J_{4,5}$ = 3.5, $J_{5,5'}$ = 10.3 Hz, H-5), 3.60 (dd, 1H, $J_{4,5'}$ = 2.7, $J_{5,5'}$ = 10.3 Hz, H-5'), 3.34 (s, 3H, OC*H*$_3$).

Methyl 2-*O*-acetyl-3,5-di-*O*-benzyl-α-D-lyxofuranoside (23). Compound **22** (70 mg, 0.2 mmol) was acetylated with acetic anhydride (1.5 mL) in pyridine (3 mL) at room temperature for 4 h to afford **23** (76 mg, 98%) as a syrup: $[\alpha]_D$ +48.3° (*c* 4.6, CHCl$_3$); ^{1}H NMR: δ 7.50-7.20 (m, 10H, 2Ph*H*), 5.08 (dd, 1H, $J_{1,2}$ = 1.8, $J_{2,3}$ = 4.6 Hz, H-2), 4.95 (d, 1H, $J_{1,2}$ = 1.8 Hz, H-1), 4.62, 4.50 (2d, 2H, J = 12.1 Hz, PhC*H*$_2$), 4.49, 4.45 (2d, 2H, J = 11.6 Hz, PhC*H*$_2$), 4.40-4.35 (m, 2H, H-3,4), 3.72 (dd, 1H, $J_{4,5}$

= 4.0, $J_{5,5'}$ = 10.6 Hz, H-5), 3.68 (dd, 1H, $J_{4,5'}$ = 7.3, $J_{5,5'}$ = 10.6 Hz, H-5'), 3.38 (s, 3H, OCH_3), 2.0 (s, 3H, $COCH_3$).

Anal. Calcd for $C_{22}H_{26}O_6$: C, 68.39; H, 6.74. Found: C, 68.43; H, 6.70.

***O*-(3,5-Di-*O*-benzyl-α-D-lyxofuranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (24).** The 1,2-anhydro sugar **21** (130 mg, 0.42 mmol) was dissolved in anhydrous methylene chloride (6 mL) containing 4A molecular sieves (1.0 g). To the mixture was added a solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (130 mg, 0.5 mmol) in dichloromethane (1.5 mL) in one portion. The mixture was stirred at room temperature for 2 h, at which time TLC (2:1 petroleum ether-EtOAc) indicated that **21** disappeared. The solution was concentrated to a syrup that was subjected to separation by analytical LC with 2:1 petroleum ether-EtOAc as the eluent. Compound **24** was obtained as a syrup (202 mg, 85%): $[\alpha]_D$ +0.5° (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 7.40-7.20 (m, 10H, 2Ph*H*), 5.49 (d, 1H, $J_{1,2}$ = 4.8 Hz, H-1), 5.01 (s, 1H, H-1'), 4.72, 4.47 (2d, 2H, J = 11.7 Hz, $PhCH_2$), 4.64, 4.53 (2d, 2H, J = 12.3 Hz, $PhCH_2$), 4.58 (dd, 1H, $J_{2,3}$ = 2.2, $J_{3,4}$ = 7.6 Hz, H-3), 4.43 (dd, 1H, $J_{2',3'}$ = 5.5, $J_{3',4'}$ = 8.0 Hz, H-3'), 4.37-4.28 (m, 3H, H-2,2',4'), 4.20 (dd, 1H, $J_{3,4}$ = 7.6, $J_{4,5}$ = 1.5 Hz, H-4), 4.13 (dd, 1H, $J_{4',5'a}$ = 5.7, $J_{5'a,5'b}$ = 10.6 Hz, H-5'a), 3.97-3.91 (m, 1H, H-5), 3.75 (dd, 1H, $J_{4',5'b}$ = 6.4, $J_{5'a,5'b}$ = 10.6 Hz, H-5'b), 3.72-3.58 (m, 2H, H-6a,6b), 1.51, 1.49, 1.47, 1.46 (4s, 12H, $2C(CH_3)_2$).

***O*-(2-*O*-Acetyl-3,5-di-*O*-benzyl-α-D-lyxofuranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (25).** Acetylation of **24** (100 mg, 0.17 mmol) with acetic anhydride (2 mL) in pyridine (3 mL) gave **25** as a syrup (101 mg, 94%): $[\alpha]_D$ +4.4° (*c* 1.4, $CHCl_3$); δ 7.46-7.25 (m, 10H, 2Ph*H*), 5.51 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 5.18 (dd, 1H, $J_{1',2'}$ = 1.5, $J_{2',3'}$ = 4.6 Hz, H-2'), 5.15 (d, 1H, $J_{1',2'}$ = 1.5 Hz, H-1'), 4.60, 4.48 (2d, 2H, J = 12.0 Hz, $PhCH_2$), 4.58 (dd, 1H, $J_{2,3}$ = 2.6, $J_{3,4}$ = 7.9 Hz, H-3), 4.53, 4.51 (2d, 2H, J = 12.1 Hz, $PhCH_2$), 4.42 (m, 1H, H-4'), 4.41 (dd, 1H, $J_{2',3'}$ = 4.6, $J_{3',4'}$ = 6.4 Hz, H-3'), 4.30 (dd, 1H, $J_{1,2}$ = 5.1, $J_{2,3}$ = 2.6 Hz, H-2), 4.22 (dd, 1H, $J_{3,4}$ = 7.9, $J_{4,5}$ = 1.6 Hz, H-4), 3.95 (m, 1H, H-5'a), 3.80-3.61 (m, 4H, H-5,6a,6b,5'b), 2.01 (s, 3H, $COCH_3$), 1.52, 1.50, 1.48, 1.47 (4s, 12H, $2C(CH_3)_2$).

Anal. Calcd for $C_{33}H_{42}O_{11}$: C, 64.50; H, 6.84. Found: C, 64.61; H, 6.85.

3,5-Di-*O*-benzyl-2-*O*-tosyl-D-lyxofuranose (27). Compound **27** was obtained from hydrolysis of **21** (→**26**) followed by tosylation under phase transfer conditions as an α:β

(5:1) mixture (yield 51%, for two steps). The mixture was separated by analytical LC with 3:1 petroleum ether-EtOAc as the eluent. For α isomer: $[\alpha]_D$ +21.8° (*c* 0.9, $CHCl_3$); δ 7.70 (d, 2H, Ph*H* of Ts), 7.45-7.20 (m, 12H, Ph*H*), 5.08 (dd, 1H, $J_{1,2}$ = 1.6, $J_{2,3}$ = 4.3 Hz, H-2), 5.05 (dd, 1H, $J_{H1,OH}$ = 9.8, $J_{1,2}$ = 1.6 Hz, H-1), 4.60, 4.43 (2d, 2H, J = 12.0 Hz, $PhCH_2$), 4.50, 4.45 (2d, 2H, J = 11.4 Hz, $PhCH_2$), 4.40-4.33 (m, 2H, H-3,4), 3.70 (dd, 1H, $J_{4,5}$ = 3.9, $J_{5,5'}$ = 10.5 Hz, H-5), 3.65 (dd, 1H, $J_{4,5'}$ = 6.1, $J_{5,5'}$ = 10.5 Hz, H-5'), 3.46 (d, 1H, $J_{H1,OH}$ = 9.8 Hz, O*H*), 2.47 (s, 3H, $PhCH_3$).

Anal. Calcd for $C_{26}H_{28}O_7S$ (α,β mixture): C, 64.46; H, 5.79. Found: C, 64.30; H, 6.01.

1,2-Anhydro-3,5-di-*O*-benzyl-α-D-xylofuranose (28). To a solution of **27** (50 mg, 0.1 mmol) in dry oxolane (6 mL) was added potassium *tert*-butoxide (17 mg, 0.15 mmol), and the mixture was stirred at room temperature for 30 min, at the end of which time TLC (3:1 petroleum ether-EtOAc) indicated that the starting material disappeared. The mixture was concentrated to dryness, and the residue was repeatedly extracted with 3:1 petroleum ether-EtOAc. Concentration of the combined extracts yielded **28** as a syrup (31 mg, 97%): ^1H NMR: δ 7.43-7.20 (m, 10H, 2Ph*H*), 5.29 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 4.66, 4.50 (2d, 2H, J = 11.0 Hz, $PhCH_2$), 4.59, 4.55 (2d, 2H, J = 12.5 Hz, $PhCH_2$), 4.34 (dd, 1H, $J_{3,4}$ = 3.7, $J_{4,5}$ = 7.2 Hz, H-4), 4.23 (2d, 2H, $J_{2,3}$ = 6.0, $J_{3,4}$ = 3.7 Hz, H-3), 3.70 (dd, 1H, $J_{4,5}$ = 4.3, $J_{5,5'}$ = 10.5 Hz, H-5), 3.65 (dd, 1H, $J_{4,5'}$ = 6.7, $J_{5,5'}$ = 10.5, H-5'), 3.53 (dd, $J_{1,2}$ = 1.9, $J_{2,3}$ = 6.0 Hz, H-2).

Methyl 3,5-di-*O*-benzyl-β-D-xylofuranoside (29). Compound **28** (20 mg, 0.064 mmol) was dissolved in anhydrous methanol (2 mL) and kept for 1 h at room temperature. TLC (2:1 petroleum ether-EtOAc) indicated that the reaction was complete. The solution was concentrated to afford **29**[15] quantitatively as a syrup; $[\alpha]_D$ -43° (*c* 0.9, $CHCl_3$); Lit.[15] $[\alpha]_D$ -39° (*c* 2, $CHCl_3$); ^1H NMR: δ 7.40-7.20 (m, 10H, 2Ph*H*), 4.75 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 4.75, 4.60 (2d, 2H, J = 10.9 Hz, $PhCH_2$), 4.65, 4.54 (2d, 2H, J = 12.0 Hz, $PhCH_2$), 4.39-4.33 (m, 1H, $J_{3,4}$ = 5.8, $J_{4,5}$ = 4.0 Hz, H-4), 4.17 (dd, 1H, $J_{1,2}$ = 1.9, $J_{2,3}$ = 3.0 Hz, H-2), 3.91 (dd, 1H, $J_{2,3}$ = 3.0, $J_{3,4}$ = 5.8 Hz, H-3), 3.77 (dd, 1H, $J_{4,5}$ = 4.0, $J_{5,5'}$ = 11.2 Hz, H-5), 3.67 (dd, 1H, $J_{4,5'}$ = 2.7, $J_{5,5'}$ = 11.2 Hz, H-5'), 3.40 (s, 3H, OCH_3).

***O*-(2-*O*-Acetyl-3,5-di-*O*-benzyl-α-D-lyxofuranosyl)-*N*-benzyloxycarbonyl-L-serine Methyl Ester (30) and *O*-(2-*O*-Acetyl-3,5-di-*O*-benzyl-β-D-lyxofuranosyl)-*N*-**

benzyloxycarbonyl-L-serine Methyl Ester (31). Method A: To a solution of *N*-benzyloxycarbonyl-L-serine methyl ester (**32**, 116 mg, 0.46 mmol) in dry dichloromethane (12 ml) was added powdered 4A molecular sieves (1 g). The mixture was stirred for 15 min, and then **21** (94 mg, 0.3 mmol) was added with cooling. The mixture was stirred overnight at 0 °C to room temperature. After filtering, the solvent was evaporated under diminished pressure to give a syrup. Purification and separation by analytical LC with 2:1 petroleum ether-EtOAc as the eluent furnished pure **30** and **31** as colourless syrups in a ratio of 12:1 with a total yield of 78.3%;

Method B:[18] To a solution of *N*-benzyloxycarbonyl-L-serine methyl ester (**32**, 71 mg, 0.28 mmol) in dry dichloromethane (8 ml) was added powdered 4A molecular sieves (1 g). The mixture was stirred for 15 min, and then **21** (70 mg, 0.22 mmol) was added with cooling under N_2 atmosphere. The mixture was stirred for 4 h at room temperature. After working up, **30**, **31** were obtained in a ratio of 9:1 with a total yield of 92%. For **30**: $[\alpha]_D$ +18.7° (*c* 1.3, $CHCl_3$); δ 7.35-7.15 (m, 15H, 3Ph*H*), 6.38 (d, 1H, J = 9.0 Hz, N*H*), 5.19 (dd, 1H, $J_{1,2}$ = 1.4, $J_{2,3}$ = 4.5 Hz, H-2), 5.05 (d, 1H, $J_{1,2}$ = 1.4 Hz, H-1), 5.14, 5.08 (2d, 2H, J = 12.0 Hz, $PhCH_2OCO$), 4.68-4.38 (m, 5H, $2PhCH_2$ and CH_2CH), 4.35 (dd, 1H, $J_{2,3}$ = 4.5, $J_{3,4}$ = 7.0 Hz, H-3), 4.30-4.26 (m, 1H, H-4), 4.12, 3.93 (2dd, 2H, 'J = 10.8, "J = 3.0 Hz, OCH_2), 3.72 (s, 3H, OCH_3), 3.68 (dd, 1H, $J_{4,5}$ = 3.5, $J_{5,5'}$ = 10.9 Hz, H-5), 3.60 (dd, 1H, $J_{4,5'}$ = 3.1, $J_{5,5'}$ = 10.9 Hz, H-5'), 2.14 (s, 3H, $COCH_3$).

Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.67; H, 6.28. Found: C, 66.86; H, 6.60.

For **31**: $[\alpha]_D$ +3.9° (*c* 1.2, $CHCl_3$); δ 7.35-7.20 (m, 15H, 3Ph*H*), 6.10 (d, 1H, J = 8.2 Hz, N*H*), 5.22 (dd, 1H, $J_{1,2}$ = 3.4, $J_{2,3}$ = 4.7 Hz, H-2), 5.11, 5.09 (2d, 2H, J = 12.6 Hz, $PhCH_2OCO$), 4.90 (d, 1H, $J_{1,2}$ = 3.4 Hz, H-1), 4.65-4.40 (m, 5H, 2 $PhCH_2$ and CH_2CH), 4.32-4.28 (m, 1H, H-4), 4.07 (dd, 1H, 'J = 10.4, "J = 3.9 Hz, OCH_2), 4.00 (dd, 1H, $J_{2,3}$ = 4.7, $J_{3,4}$ = 6.7 Hz, H-3), 3.74 (dd, 1H, 'J = 10.4, "J = 3.9 Hz, OCH_2), 3.67 (s, 3H, OCH_3), 3.65 (dd, 1H, $J_{4,5}$ = 3.2, $J_{5,5'}$ = 10.8 Hz, H-5), 3.58 (dd, 1H, $J_{4,5'}$ = 4.5, $J_{5,5'}$ = 10.8 Hz, H-5'), 2.15 (s, 3H, $COCH_3$).

1,4-Anhydro-2-deoxy-3,5,6-tri-*O*-benzyl-D-*xylo*-hex-1-enitol (33). To a solution of **2** (100 mg, 0.21 mmol) in dichloromethane (1 mL) was added triethylamine (2 mL), TsCl (80 mg, 0.42 mmol) and powdered potassium carbonate (30 mg, 0.21 mmol). The mixture was stirred at room temperature for 3 days and then poured into ice-cold water, extracted with dichloromethane (15 mL). The organic phase was washed with 1 N HCl (3 x 15 mL), dried over Na_2SO_4, then the solvent was evaporated under diminished pressure to give a syrup. The residue was purified by chromatography on a silica gel column with 1:4 EtOAc-petroleum ether as the eluent. The first fraction with larger Rf value was confirmed by ^{1}H NMR as glycal **33** (34 mg, 40%). From the second fraction, starting material **2** was recovered. The last one was not identified. For **33**, ^{1}H NMR: δ 7.40-7.25 (m, 15H, 3Ph*H*), 6.20 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-1), 4.90 (d, 1H, $J_{1,2}$ = 4.9 Hz, H-2), 4.79, 4.48 (2d, 2H, J = 11.0 Hz, PhCH_2), 4.60 (s, 2H, PhCH_2), 4.56, 4.54 (2d, 2H, J = 12.1 Hz, PhCH_2), 4.33 (dd, 1H, $J_{3,4}$ = 3.3, $J_{4,5}$ = 9.2 Hz, H-4), 4.27 (d, 1H, $J_{3,4}$ 3.4 Hz, H-3), 4.07-4.03 (m, 1H, H-5), 3.85 (dd, 1H, $J_{5,6}$ = 2.5, $J_{6,6'}$ = 11.1 Hz, H-6), 3.62 (dd, 1H, $J_{5,6'}$ = 5.1, $J_{6,6'}$ = 11.1 Hz, H-6').

3,5,6-Tri-*O*-benzyl-2-*O*-tosyl-α-D-glucofuranosyl Chloride (34). To a solution of **2** (110 mg, 0.18 mmol) in pyridine (5 mL) was added TsCl (170 mg, 0.9 mmol). The mixture was stirred at room temperature for about 5 days and then worked up as described for **6**. Purification by column chromatography with 2:1 petroleum ether-EtOAc as the eluent gave three components. The main product gave faster moving spot on TLC which was identified by ^{1}H NMR spectroscopy as the chloride **34** (85 mg, 75%). The second fraction was **6** (17 mg). The third one was the starting material **2**. For **34**, ^{1}H NMR: δ 7.78 (d, 2H, Ph*H* of Ts), 7.42-7.20 (m, 17H, Ph*H*), 6.54 (d, 1H, $J_{1,2}$ = 3.6 Hz, H-1), 5.23 (dd, 1H, $J_{1,2}$ = 3.6, $J_{2,3}$ = 4.3 Hz, H-2), 4.80-4.44 (m, 7H, 3PhCH_2 and H-4), 4.30 (dd, 1H, $J_{2,3}$ = 4.3, $J_{3,4}$ = 2.7 Hz, H-3), 4.15-4.05 (m, 1H, H-5), 3.85 (dd, 1H, $J_{5,6}$ = 2.2, $J_{6,6'}$ = 11.0 Hz, H-6), 3.67 (dd, 1H, $J_{5,6'}$ = 5.0, $J_{6,6'}$ = 11.0 Hz, H-6'), 2.46 (s, 3H, PhCH_3).

1-*O*-Acetyl-3,5-di-*O*-benzyl-2-*O*-methanesulfonyl-D-xylofuranose (35). Preparation method was the same as for **17**, but the sulfonation reagent was methanesulfonyl chloride instead of *p*-toluenesulfonyl chloride. The product was an α,β mixture (1:1). ^{1}H NMR (CDCl$_3$): δ 7.39-7.21 (m, 10H, 2Ph*H*), 6.40 (d, 0.5H, $J_{1,2}$ = 4.1 Hz, H-1 of α anomer), 6.18 (s, 0.5H, H-1 of β anomer), 5.20 (t, 0.5H, $J_{1,2}$ = 4.1, $J_{2,3}$ = 4.1 Hz, H-2 of α anomer), 5.08 (s, 0.5H, H-2 of β anomer), 4.78-4.54 (m, 4H, 2PhCH_2), 4.50 (d, 0.5H, $J_{3,4}$ = 5.3 Hz, H-3 of β anomer), 4.46-4.36 (m, 1H, H-4), 4.26 (dd, 0.5H, $J_{2,3}$ = 4.1, $J_{3,4}$ = 1.4 Hz, H-3 of α anomer), 3.80-3.60 (m, 2H, H-5,5'), 3.09, 2.98 (2s, 3H, SO_2CH_3 of α,β anomer), 2.11, 2.08 (2s, 3H, $COCH_3$ of α,β anomer).

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