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Chemical synthesis of β-D-psicofuranosyl disaccharides

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ABSTRACT

Disaccharides composed of a β-D-psicofuranosyl unit were prepared by the glycosylation reaction of monosaccharide acceptors including three 2,3,4,6-tetra-*O*-protected hexopyranoses with a D-psicofuranosyl benzyl phthalate derivative (**4**). A β-D-psicofuranosidic bond was formed by the TMSOTf-promoted reaction with high selectivity. Removal of the O-protecting groups from the resulting α-D-hexopyranosyl β-D-psicofuranosides furnished the first chemical synthesis of α-D-gluco-, α-D-galacto-, and α-D-mannopyranosyl β-D-psicofuranosides. The common β-D-psicofuranosyl donor **4** was derived efficiently from D-psicose in five steps.

1. Introduction

D-Psicose (Fig. 1) and D-fructose are diastereoisomers at the C-3 chiral center on the furanose ring. Although D-fructose is a component of (+)-sucrose and is widely found in fruits, D-psicose appears in nature only rarely.[1] Therefore, the chemistry and biology of D-psicose have not been extensively investigated in recent decades. Because D-psicose has recently been prepared in large amounts by biotransformation from D-fructose,[2] as well as by chemical transformation,[3,4] biological investigations of D-psicose have gradually increased.[5] These studies have revealed novel properties of D-psicose such as suppression of postprandial blood glucose elevation,[5a–c] α-glucosidase inhibitory activity,[5d] antioxidant,[5e] neuroprotective effect,[5f] prevention of arteriosclerosis,[5g] and diet sugar.[5h] However, except for the enzymatic production of α-D-glucopyranosyl β-D-psicofuranoside (**1**),[6] no oligosaccharides containing D-psicofuranosides have been reported. Herein, we report the synthesis of β-D-psicofuranosyl saccharides including non-reducing disaccharides **1**–**3** via β-selective O-glycosylation using D-psicofuranose derivative **4** as the glycosyl donor.

2. Results and discussion

Although N- and C-glycosidation reactions of D-psicose have been reported,[7,8] these reactions showed variable stereoselectivities depending on both the N- and C-glycosyl acceptors. However, we have found excellent β-selectivity and chemical yield in the case of D-psicofuranosyl donor **4** with O-glycosyl acceptors[9,10] including primary and secondary alcohols, phenols, and aminoalcohols. An example with ceramide is illustrated in Scheme 1. The high β-selectivity appears to arise from the steric influence of the acetonide in **4**. Thus, one of the two methyl groups blocks the attack of the glycosyl acceptor from α-side and results selectively in β-glycosylation.[11]

Yamanoi et al. has recently reported that in the $Sc(OTf)_3$-promoted glycosidation of 2-*O*-acetyl-1,3,4,6-tetra-*O*-benzoyl-D-psi-

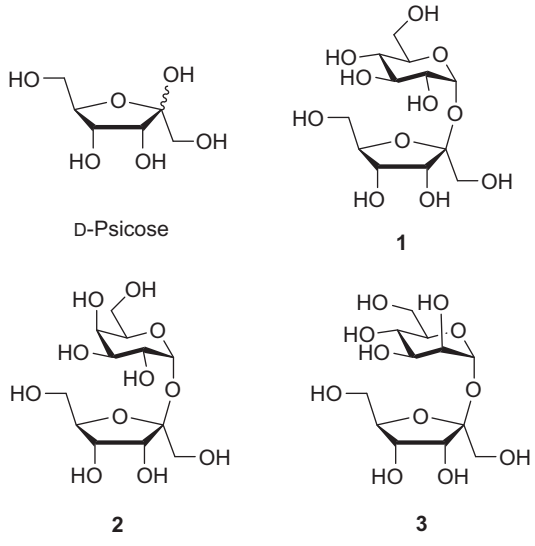

Figure 1. D-Psicose and β-D-psicofuranosyl disaccharides **1**–**3**.

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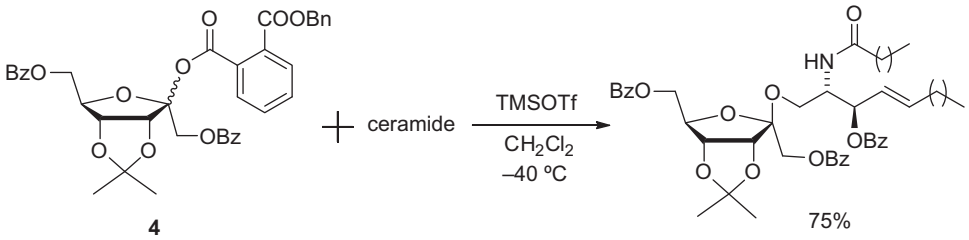
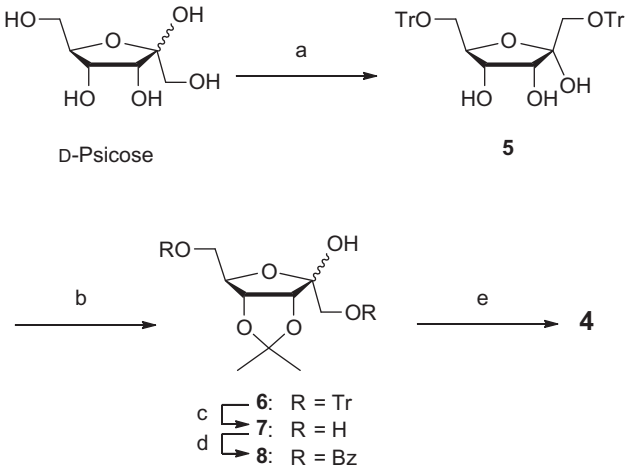


Scheme 1. TMSOTf-promoted glycosylation of ceramide with donor **4**.[10]

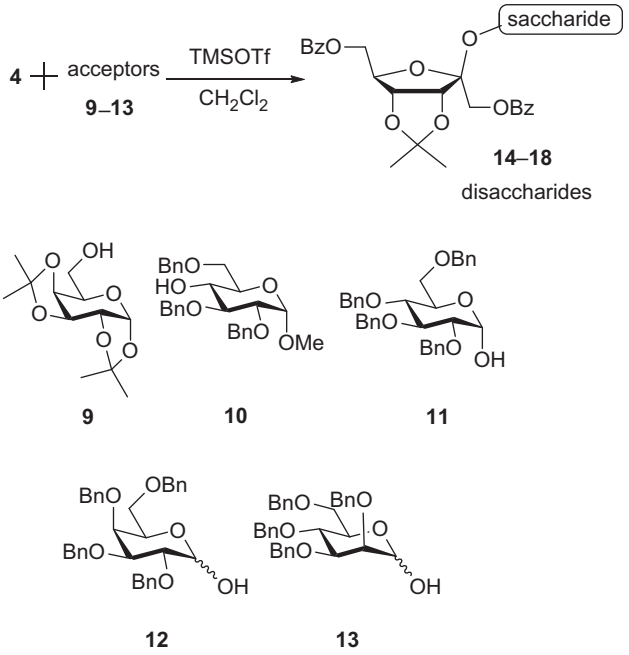
cofuranose with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose, four diastereomeric 2,1′-disaccharides were formed in a 20:8:28:44 ratio.[12] Because donor **4** appears to be suitable for stereoselective O-psicofuranosylation reactions, we considered that this glycosylation reaction could be a good synthetic approach to provide various disaccharides including non-reducing disaccharides. The donor **4** was prepared from D-ribose in nine steps as described in our previous paper.[9] As D-psicose is sufficiently available from D-fructose due to the efficient improvements in enzymatic transformation technology,[2] we have exploited an alternative synthesis of **4** from D-psicose (Scheme 2).

First, ditritylation of D-psicose with an excess of trityl chloride in pyridine proceeded smoothly to give triol **5** in 88% yield. Protection of the C-3 and C-4 hydroxy groups of **5** with 2,2-dimethoxypropane in the presence of PPTS gave the corresponding acetonide **6** in 89% yield. Removal of the two *O*-trityl groups under Birch conditions and the successive benzoylation of the resulting two hydroxy groups with benzoyl chloride gave D-psicofuranose **8** in 54% overall yield in four steps from D-psicose. The conversion of **8** to **4** was performed by the dicyclohexylcarbodiimide-mediated condensation with benzyl hydrogen phthalate[13] in 95% yield.[9]

Psicosyl donor **4** was subjected to glycosidation with five monosaccharides **9**–**13** (Scheme 3). The reactions were conducted in dichloromethane in the presence of TMSOTf at −40 to −20 °C. The results are shown in Table 1. The reaction with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**9**) possessing a primary hydroxy group at the C-6 position proceeded smoothly to give β-glycoside **14** exclusively in 94% yield (entry 1). Acceptor **10**[14] was less reactive and required longer reaction time than **9** due to the sterical reason, but gave **15** in 57% yield with exclusive β-selectivity (entry 2).



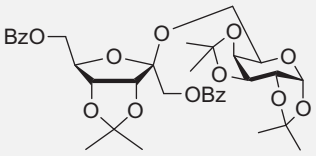
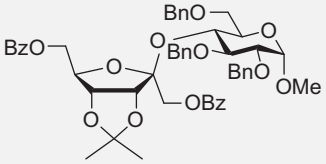
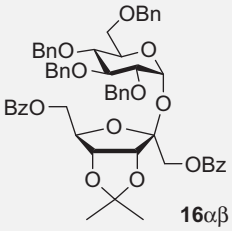
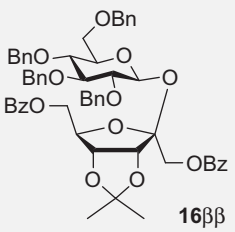
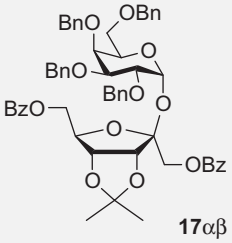
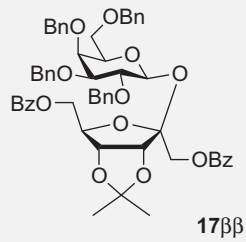
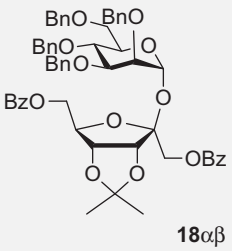
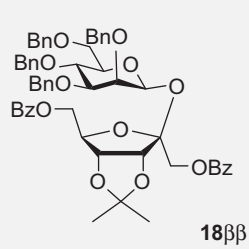
Scheme 2. Conversion of D-psicose into D-psicofuranosyl donor **4**. Reagents and conditions: (a) TrCl, DMAP, pyridine, 50 °C, 8 h, 88%; (b) PPTS, 2,2-dimethoxypropane, 50 °C, 5 h, 89% (α:β = 1:2); (c) Na–NH_3, THF, −78 °C, 10 min, 76% (α:β = 1:3); (d) BzCl, pyridine, 0 °C, 30 min, 87% (α:β = 1:3); (e) benzyl hydrogen phthalate, DCC, DMAP, CH_2Cl_2, rt, 20 h, 95% (α:β = 6:94).[9]



Scheme 3. TMSOTf-promoted glycosylation of acceptors **9**–**13** with donor **4**.

For the stereocontrolled synthesis of non-reducing disaccharides, assembling two saccharides at the anomeric centers by glycosylation reaction is generally quite a difficult task,[15,16] compared to other standard glycosylation reactions, because both glycosylating positions are anomeric centers and may be isomerized during the reaction. Nonetheless, this direct glycosylation is straightforward for the synthesis of a non-reducing disaccharide. To overcome this problem, several synthetic efforts such as neighboring group participation,[17] the use of an α-side protected glycosyl donor,[18] and using an *exo*-glycal donor for the synthesis of trehalose type disaccharides[19] have been reported. Keeping this in mind, a glycosylation approach using **4** for the synthesis of β-D-psicofuranosyl non-reducing disaccharides would be promising. In fact, the reaction of **4** with *O*-benzyl-protected hexopyranose acceptors **11**–**13** gave β-D-psicofuranosides exclusively (entries 3–5). In spite of the expectation of an anomeric effect for these compounds, a mixture of α- and β-D-hexopyranosides was obtained. For example, glycosylation of **11** (α-isomer only) with **4** provided 26% of the ββ-isomer **16ββ** and 58% of αβ-isomer **16αβ** (entry 3). The reaction of galactose acceptor **12** (α:β isomer ratio, 4:3) with **4** gave **17αβ** and **17ββ** in 33% and 41% yields, respectively (entry 4), while that of mannose acceptor **13** (α:β isomer ratio, 9:2) afforded **18αβ** and **18ββ** in 27% and 39% yields, respectively (entry 5). These results indicate that the anomeric stereocontrol for psicosides is satisfactory, although that for hexopyranoside is unsatisfactory, due to an epimerization of the anomeric center even when an excess of α-isomers were used.

Table 1
Glycosidation of D-psicofuranosyl donor **4** with D-hexopyranose acceptors

Entry	Glycosyl acceptor	Temp (°C)	Time (min)	Product (yield, %)	Structure
1	**9**	−40	50	**14** (94%)	
2	**10**	−40 to −20	120	**15** (57%)	
3[a]	**11**	−40 to −20	30	**16αβ** (58%) **16ββ** (26%)	 **16αβ**  **16ββ**
4	**12**	−40 to −20	20	**17αβ** (33%) **17ββ** (41%)	 **17αβ**  **17ββ**
5	**13**	−40 to −20	30	**18αβ** (27%) **18ββ** (39%)	 **18αβ**  **18ββ**

[a] See Ref. 9.

The stereochemistry of **16** was determined by the conversion of the less polar isomer **16αβ** to (+)-sucrose.[9] The structures of **17** and **18** were determined by ^{1}H NMR spectroscopy. NOE studies on these compounds clearly indicated that the glycosidic bond of psicoside was assigned as β. Thus, NOE relations were observed between the H-1 proton and the endo Me group of the acetonide, as well as H-5 proton and the same Me group in each of the isomers **17** and **18**. Stereochemistry of gluco- and galacto-type hexopyranoses is assigned by a coupling constant of the anomeric proton. The values of chemical shift and vicinal coupling constant of the H-1′ proton for the pyranose unit of disaccharides **16**–**24** are listed in Table 2. It is obvious that α-pyranosides **16αβ** and **17αβ** possess smaller coupling constants (~3.5 Hz) than those of **16ββ** and **17ββ** (~7.3 Hz). However, it is difficult to determine an anomeric structure for the mannopyranosides. Indeed, the vicinal coupling constants of the anomeric protons of **18αβ** and **18ββ** showed similar *J*-values (2.0 Hz vs br s). However, the NOE experiment was effective in determining the structures. The more polar isomer **18ββ** indicated clear NOE relationships between the anomeric proton H-1′ and the three protons H-2′, H-3′, and H-5′ (Fig. 2). On the other hand, no NOE relationship was observed between the anomeric proton H-1′ and the two protons H-3′ and H-5′ in the less polar isomer, which was identical to the **18αβ** isomer.

Table 2
Chemical shifts and coupling constants of the H-1′ proton for **16**–**24**

Entry	Compound	Chemical shift (ppm)	*J*-value (Hz)
1	**16αβ**[a]	5.42	3.5
2	**16ββ**[a]	5.14	7.3
3	**17αβ**[a]	5.44	br s
4	**17ββ**[a]	5.09	7.7
5	**18αβ**[a]	5.77	2.0
6	**18ββ**[a]	4.94	br s
7	**19**[b]	5.52	3.5
8	**20**[b]	5.60	3.7
9	**21**[b]	5.48	1.3
10	**22**[c]	5.39	3.7
11	**23**[c]	5.32	3.7
12	**24**[c]	5.56	2.0

[a] In C_6D_6.
[b] In $CDCl_3$.
[c] In CD_3OD.

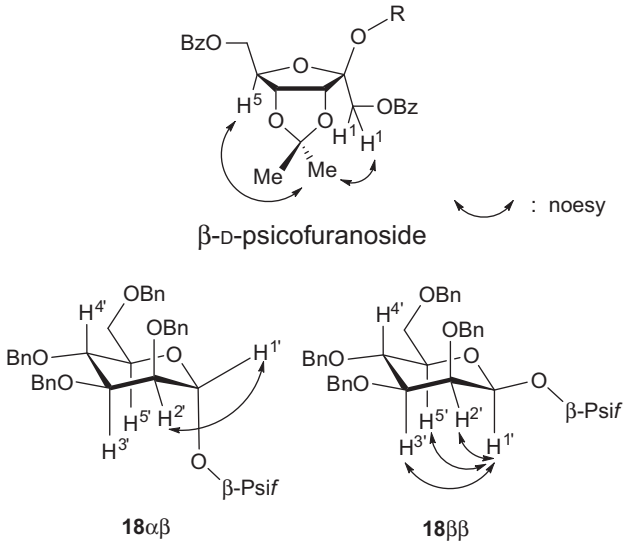


Figure 2. NOESY experiments for β-D-psicofuranosyl disaccharides and mannopyranosides **18**.

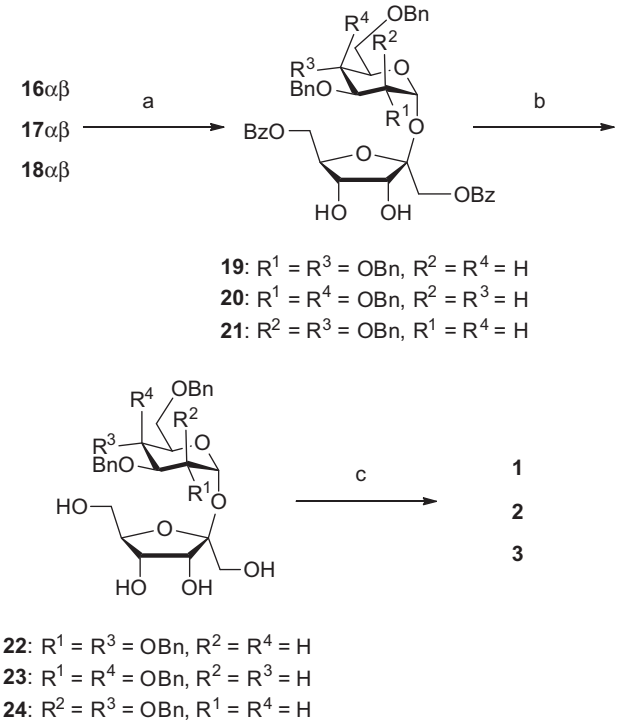
Completion of the synthesis for β-D-psicofuranosyl non-reducing disaccharides was achieved in three-step sequence of different deprotection procedures (Scheme 4). First, disaccharides **16αβ**, **17αβ**, and **18αβ** were treated with *p*-toluenesulfonic acid in MeOH to give diols **19**,[9] **20**, and **21** in 68%, 61%, and 63% yields, respectively. Exposure of diols **19**, **20**, and **21** to methanolic potassium carbonate resulted in debenzoylation to provide tetraols **22**, **23**, and **24** with excellent yields. After successive deprotection of the benzyl groups by hydrogenation in the presence of Pearlman's catalyst, non-reducing disaccharides **1**, **2**, and **3** were obtained in quantitative yields. Because disaccharides **1**–**3** are diastereomeric isomers of (+)-sucrose, we will examine them for biological properties such as sweet taste and inhibitory activity against α-glycosidases. In fact, in initial qualitative experiments, these compounds exhibited a sweet taste.

In conclusion, we have accomplished the first chemical synthesis of non-reducing disaccharides **1**–**3**. β-Selective D-psicofuranosylation of saccharide acceptors **9**–**13** with donor **4** was carried out in CH_2Cl_2 using TMSOTf as a promoter of the glycosylation reaction. β-Psicofuranosyl donor **4** was derived from D-psicose in five steps in excellent yield. The synthetic pathway described in this paper provides short access to β-D-psicofuranosyl saccharides including non-reducing disaccharide.

3. Experimental

3.1. General methods

Melting points were taken on a Yanaco micromelting apparatus and were uncorrected. Specific rotations were measured on a JASCO P-2200 polarimeter using $CHCl_3$, MeOH, or H_2O as a solvent. ^{1}H NMR and ^{13}C NMR spectra were measured on JEOL JNM-AL-300 (300 MHz and 75 MHz) or Varian UNITY INOVA 400 NB (400 MHz and 100 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to the resonance of the solvent or to tetramethylsilane (0.00 ppm) for ^{1}H NMR spectra and ppm relative to the resonance of the solvent or to acetonitrile (1.47 ppm) when D_2O was used, for ^{13}C NMR spectra. For the assignment of protons in ^{1}H NMR spectra, protons of pyranoside ring are numbered as 1′, 2′, etc. IR spectra were recorded on a JASCO FT/IR-410 spectrophotometer. Low- and high-resolution mass spectra (LRMS and HRMS) were obtained on a JEOL JMS 303HF spectrometer using fast atom bombardment (FAB) ionization. Silica gel (230–400 mesh) was used for flash chromatography. Analytical thin-layer chromatography (TLC) was performed on glass pre-coated with silica gel (0.25 mm thickness). Compounds were observed in UV-light at 254 nm and then visualized with *p*-anisaldehyde/sulfuric acid in EtOH stain or molybdatephosphoric acid in EtOH stain. High performance liquid chromatography (HPLC) was carried out on a UV spectrophotometric detector (254 nm) to which a 20 × 250 mm size column packed with silica gel was attached or an RI spectrophotometric detector to which a 10 × 200 mm size Chemco pak® (Kromasol 5NH_2) column. All moisture-sensitive reactions were carried out under an argon atmosphere. THF was dried over sodium/benzophenone ketyl, and CH_2Cl_2 was dried over P_2O_5, and they were distilled prior to use.



Scheme 4. Synthesis of disaccharides **1**–**3**. Reagents and conditions: (a) *p*-TsOH, MeOH, rt, 45 h; (b) K_2CO_3, MeOH, rt, 1 h; (c) H_2, $Pd(OH)_2$–C, MeOH, rt, overnight.

3.2. 1,6-Di-*O*-trityl-α-D-psicofuranose (5)

A mixture of D-psicose (100 mg, 0.56 mmol), 4-(dimethylamino)pyridine (34 mg, 0.28 mmol), and trityl chloride (772 mg, 2.78 mmol) in pyridine (4 mL) was heated at 50 °C for 8 h. The reaction was quenched with water (20 mL) and the reaction mixture was extracted with $CHCl_3$ (15 mL × 3). The combined organic extracts were washed with water (10 mL) and dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The residual oil was purified by flash column chromatography on silica gel eluted with 30% EtOAc in hexane to give **5** (322 mg) in 88% yield. Colorless oil. R_f = 0.21 (40% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45–7.18 (30H, m), 4.21 (1H, ddd, $J_{5,6b}$ = 4.1, $J_{5,6a}$ = 3.7, $J_{4,5}$ = 3.3 Hz, H-5), 4.09 (1H, ddd, $J_{4,OH}$ = 5.9, $J_{3,4}$ = 5.7, $J_{4,5}$ = 3.3 Hz, H-4), 4.03 (1H, s, 2-O*H*), 4.02 (1H, d, $J_{3,OH}$ = 7.0, $J_{3,4}$ = 5.7 Hz, H-3), 3.35 (1H, d, $J_{1a,1b}$ = 9.5 Hz, H-1a), 3.31 (1H, dd, $J_{6a,6b}$ = 10.1, $J_{5,6a}$ = 3.7 Hz, H-6a), 3.29 (1H, d, $J_{1a,1b}$ = 9.5 Hz, H-1b), 3.21 (1H, dd, $J_{6a,6b}$ = 10.1, $J_{5,6b}$ = 4.1 Hz, H-6b), 2.92 (1H, d, $J_{4,OH}$ = 7.0 Hz, 4-O*H*), 2.67 (1H, d, $J_{3,OH}$ = 5.9 Hz, 3-O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.6, 143.4, 128.6, 127.9, 127.8, 127.1, 127.0, 102.7, 87.0, 86.8, 82.7, 72.4 (2C), 66.3, 63.9. IR (film): 3443, 3058, 1730, 1489, 1447, 1078, 748, 701 cm^{-1}. MS (FAB) *m*/*z*: 687 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_{44}H_{40}O_6Na$, 687.2723; found, 687.2726.

3.3. 3,4-*O*-Isopropylidene-1,6-di-*O*-trityl-D-psicofuranose (6)

A mixture of **5** (129 mg, 0.19 mmol) and pyridinium *p*-toluenesulfonate (146 mg, 0.58 mmol) in 2,2-dimethoxypropane (2 mL) was heated at 50 °C for 5 h. Satd aq $NaHCO_3$ (4 mL) was added to the reaction mixture and extracted with EtOAc (2 × 20 mL). The organic layer was washed with water, brine (10 mL each), and dried over $MgSO_4$. Solvent was removed and the residual oil was purified by flash chromatography on silica gel eluted with 10% EtOAc in hexane to give **6** (119 mg) in 89% yield as a 1:2 mixture of α- and β-isomers. Colorless oil. R_f = 0.25 (10% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (β-anomer): 7.49–7.40 (12H, m), 7.31–7.18 (18H, m), 4.63 (1H, dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 1.3 Hz, H-4), 4.42 (1H, d, $J_{3,4}$ = 5.9 Hz, H-3), 4.34 (1H, ddd, $J_{5,6b}$ = 7.3, $J_{5,6a}$ = 5.9, $J_{4,5}$ = 1.3 Hz, H-5), 4.16 (1H, s, O*H*), 3.41 (1H, dd, $J_{6a,6b}$ = 9.5, $J_{5,6a}$ = 5.9 Hz, H-6a), 3.37–3.30 (2H, m, H-1a, 1b), 3.22 (1H, dd, $J_{6a,6b}$ = 9.5, $J_{5,6b}$ = 7.3 Hz, H-6b), 1.31 (3H, s), 1.25 (3H, s); δ (α-anomer): 7.49–7.40 (12H, m), 7.31–7.18 (18H, m), 4.60–4.53 (2H, m, H-3, 4), 4.35–4.30 (1H, m, H-5), 3.33–3.18 (2H, m, H-6a, 6b), 3.27 (1H, d, $J_{1a,1b}$ = 9.5 Hz, H-1a), 3.18 (1H, d, $J_{1a,1b}$ = 9.5 Hz, H-1b), 1.60 (3H, s), 1.36 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (β-anomer): 143.8, 143.5, 128.7–126.9 (Ar), 112.4, 106.0, 85.7, 85.3, 82.8, 81.7, 81.3, 65.1, 65.0, 26.4, 25.4; δ (α-anomer): 143.8, 143.7, 128.7–126.9 (Ar), 115.5, 102.2, 87.0, 86.8, 86.6, 86.6, 81.3, 66.5, 63.9, 26.5, 25.2. IR (film): 3444, 1490, 1448, 1215, 1075, 754, 703 cm^{-1}. MS (FAB) *m*/*z*: 727 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_{47}H_{44}O_6Na$, 727.3036; found, 727.3042.

3.4. 3,4-*O*-Isopropylidene-D-psicofuranose (7)

To a dark blue solution of sodium (ca. 30 mg) in liquid ammonia (5 mL) was added dropwise a solution of compound **6** (84.4 mg, 0.120 mmol) in THF (1 mL) at −78 °C. The mixture was stirred vigorously for 10 min at the same temperature, and then the reaction was carefully quenched by the addition of powdered NH_4Cl (300 mg). After disappearance of dark blue color, MeOH (3 mL) was added and the reaction was allowed to warm up to room temperature to evaporate solvents. EtOAc (20 mL) was added to the residual white solid and the whole was filtered through 1 cm of silica gel pad. The filtrate was concentrated under vacuum. The residue was purified by silica gel flash chromatography eluted with 80% EtOAc in hexane to give triol **7** (20 mg) in 76% yield as a 1:3 mixture of α- and β-isomers. Colorless syrup. R_f = 0.21 (80% EtOAc in hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ (β-anomer): 4.85 (1H, dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 0.9 Hz, H-4), 4.60 (1H, d, $J_{3,4}$ = 5.9 Hz, H-3), 4.33 (1H, ddd, $J_{5,6b}$ = 4.2, $J_{5,6a}$ = 2.9, $J_{4,5}$ = 0.9 Hz, H-5), 3.81 (1H, d, $J_{1a,1b}$ = 12.3 Hz, H-1a), 3.78 (1H, d, $J_{1a,1b}$ = 12.3 Hz, H-1b), 3.74 (1H, dd, $J_{6a,6b}$ = 12.3, $J_{5,6a}$ = 2.9 Hz, H-6a), 3.70 (1H, dd, $J_{6a,6b}$ = 12.3, $J_{5,6b}$ = 4.2 Hz, H-6b), 1.48 (3H, s), 1.31 (3H, s); δ (α-anomer): 4.79 (1H, dd, $J_{3,4}$ = 7.0, $J_{4,5}$ = 3.8 Hz, H-4), 4.74 (1H, d, $J_{3,4}$ = 7.0 Hz, H-3), 4.24 (1H, ddd, $J_{4,5}$ = 3.8, $J_{5,6b}$ = 3.3, $J_{5,6a}$ = 2.7 Hz, H-5), 3.85 (1H, dd, $J_{6a,6b}$ = 12.2, $J_{5,6a}$ = 2.7 Hz, H-6a), 3.70 (1H, d, $J_{1a,1b}$ = 11.5 Hz, H-1a), 3.68 (1H, dd, $J_{6a,6b}$ = 12.2, $J_{5,6b}$ = 3.3 Hz, H-6b), 3.59 (1H, d, $J_{1a,1b}$ = 11.5 Hz, H-1b), 1.60 (3H, s), 1.40 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ (β-anomer): 112.7, 106.2, 86.6, 86.1, 82.0, 64.4, 63.6, 26.2, 24.6; δ (α-anomer): 115.3, 102.9, 82.8, 80.9, 80.6, 65.4, 62.3, 26.4, 24.8. IR (film): 3398, 2940, 1644, 1376, 1212, 1161, 1074, 869 cm^{-1}. MS (FAB) *m*/*z*: 243 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_9H_{16}O_6Na$, 243.0845; found, 243.0848.

3.5. 1,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-D-psicofuranose (8)

To a mixture of **7** (42 mg, 0.19 mmol) and 4-(dimethylamino)pyridine (11.7 mg, 0.096 mmol) in a mixture of pyridine (0.5 mL) and CH_2Cl_2 (3 mL) was dropped benzoyl chloride (0.22 mL, 1.92 mmol) at 0 °C. The mixture was stirred for 30 min at the same temperature. Then, MeOH (0.5 mL) was added and the mixture was further stirred for 20 min. Water was added and the mixture was extracted with EtOAc (15 mL × 2). The organic extract was washed with water and brine (10 mL each), dried over $MgSO_4$ and evaporated. The crude product was purified by flash column chromatography on silica gel eluted with 25% EtOAc in hexane to give **8** (71 mg) in 87% yield as a 1:3 mixture of α- and β-anomers. Colorless oil. Spectral data fully matched with the data reported previously.[9]

3.6. General procedure for the psicofuranosylation of compounds 9–13

A mixture of glycosyl donor **4** (1 mmol, α:β = 6:94) and glycosyl acceptor **9**–**13** (1.2–1.5 mmol) was predried azeotropically by coevaporation with dry toluene (10 mL × 3), which was further dried under reduced pressure over the presence of P_4O_{10}. The dried mixture was dissolved in dry CH_2Cl_2 (20 mL), to which was added TMSOTf (1.5 mmol) at −40 °C. The reaction was continued under the conditions indicated in Table 1. Satd aq $NaHCO_3$ (10 mL) and CH_2Cl_2 (20 mL) were added to the reaction mixture, and organic layer was washed with water and brine, dried (Na_2SO_4), and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel eluted with 15% of EtOAc in hexane for **14**–**18**, respectively. Separation of anomers for **17** and **18** were performed by HPLC under the following conditions; **17**, eluent, 10% EtOAc in hexane, flow rate, 10 mL/min, retention time, 31.3 min (**17αβ**), and 35.3 min (**17ββ**); **18**, eluent, 20% EtOAc in hexane, flow rate, 15 mL/min, retention time, 11.8 min (**18αβ**), and 13.5 min (**18ββ**). Chemical yields are indicated in Table 1 and physical and spectroscopic data are following.

3.6.1. 6-*O*-(1,6-Di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (14)

Colorless oil. R_f = 0.42 (30% EtOAc in hexane). $[\alpha]_D^{23}$ −37.4 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.09–8.06 (4H, m), 7.60–7.52 (2H, m), 7.48–7.39 (4H, m), 5.42 (1H, d, $J_{1',2'}$ = 5.0 Hz, H-1′), 4.83 (1H, dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 1.1 Hz, H-4), 4.76 (1H, d, $J_{3,4}$ = 5.9 Hz, H-3), 4.69 (1H, d, $J_{1a,1b}$ = 11.9 Hz, H-1a), 4.57–4.50 (3H, m, H-4′, 5, 6a), 4.53 (1H, d, $J_{1a,1b}$ = 11.9 Hz, H-1b), 4.41 (1H, dd, $J_{6a,6b}$ = 13.4, $J_{5,6b}$ = 9.9 Hz, H-6b), 4.24 (1H, dd, $J_{1',2'}$ = 5.0, $J_{2',3'}$ = 2.4 Hz, H-2′), 4.21 (1H, dd, $J_{3',4'}$ = 7.9, $J_{4',5'}$ = 1.8 Hz, H-4′), 3.88 (1H, td, $J_{5',6'}$ = 6.6, $J_{4',5'}$ = 1.8 Hz, H-5′), 3.76 (2H, d, $J_{5',6'}$ = 6.6 Hz, H-6′), 1.51 (3H, s), 1.37 (3H, s), 1.33 (3H, s), 1.33 (3H, s), 1.28 (3H, s), 1.26 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.9, 165.7, 133.1, 132.8, 130.0, 129.8, 129.6, 128.3, 128.1, 113.2, 109.3, 109.2, 108.4, 96.1, 85.3, 84.4, 82.3,70.7, 70.4, 70.4, 66.5, 65.0, 60.5, 60.0, 26.5, 25.8, 25.7, 25.1, 24.8, 24.3. IR (KBr): 2987, 1725, 1452, 1381, 1273, 1212, 1071, 870, 711 cm^{-1}. MS (FAB) *m*/*z*: 693 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_{35}H_{42}O_{13}Na$, 693.2523; found, 693.2528.

3.6.2. Methyl 4-*O*-(1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (15)

Colorless oil. R_f = 0.42 (30% EtOAc in hexane). $[\alpha]_D^{22}$ +28.3 (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, C_6D_6) δ: 8.34–8.30 (2H, m), 8.19–8.16 (2H, m), 7.45–7.42 (2H, m), 7.29–6.89 (19H, m), 5.41 (1H, d, J = 7.0 Hz), 5.33 (1H, d, $J_{1a,1b}$ = 12.1 Hz, H-1a), 5.02 (1H, d, J = 10.8 Hz, C*H*HPh), 4.91 (1H, d, J = 10.8 Hz, C*H*HPh), 4.62 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.59 (1H, d, $J_{1a,1b}$ = 12.1 Hz, H-1b), 4.51–4.17 (11H, m), 3.85 (1H, t, J = 9.2 Hz), 3.69 (1H, dd, J = 11.1, 8.7 Hz), 3.37 (1H, dd, $J_{2',3'}$ = 9.7, $J_{1',2'}$ = 3.7 Hz, H-2′), 3.25 (3H, s), 1.39 (3H, s), 0.91 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.1, 165.9, 138.4, 138.3, 138.0, 133.1, 132.9, 130.0, 129.7, 129.6, 129.4, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.5, 127.0, 126.9, 114.8, 107.9, 97.2, 83.9, 80.6, 80.2, 80.0, 79.3, 75.8, 73.2, 72.8, 71.8, 70.0 (2C), 64.1, 63.9, 54.9, 26.2, 24.6. IR (KBr):

2935, 1721, 1601, 1496, 1452, 1376, 1261, 1094, 863, 803, 711 cm^{-1}. MS (FAB) *m*/*z*: 897 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{51}H_{54}O_{13}Na$, 897.3462; found, 897.3470.

3.6.3. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl 1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranoside (17αβ)

Colorless oil. R_f = 0.59 (30% EtOAc in hexane). $[\alpha]_D^{25}$ +32.1 (*c* 1.0, $CHCl_3$). ^1H NMR (300 MHz, C_6D_6) δ: 8.35–8.31 (2H, m), 8.14–8.11 (2H, m), 7.48–7.44 (2H, m), 7.38–7.34 (2H, m), 7.22–6.96 (22H, m), 5.44 (1H, br s, H-1′), 5.06–5.02 (3H, m), 4.83 (1H, d, *J* = 11.4 Hz), 4.82 (1H, d, $J_{3,4}$ = 5.8 Hz, H-3), 4.69–4.55 (7H, m), 4.44–4.40 (1H, m, H-5), 4.27 (1H, d, *J* = 11.0 Hz), 4.17–4.13 (3H, m), 4.07 (1H, d, *J* = 11.9 Hz), 3.99 (1H, br s), 3.72 (1H, dd, *J* = 8.5, 8.0 Hz), 3.53 (1H, dd, *J* = 8.8, 5.7 Hz), 1.39 (3H, s), 1.11 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.0, 165.9, 138.7, 138.6, 138.3, 137.9, 133.0, 132.7, 130.2, 129.8, 129.7, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 113.5, 109.0, 92.5, 84.5, 84.2, 81.9, 79.2, 75.7, 74.9, 74.8, 73.9, 73.2, 72.8, 70.2, 68.3, 64.7, 64.2, 26.5, 24.9. IR (film): 3032, 1723, 1453, 1272, 1099, 711 cm^{-1}. MS (FAB) *m*/*z*: 973 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{57}H_{58}O_{13}Na$, 973.3775; found, 973.3779.

3.6.4. 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl 1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranoside (17ββ)

Colorless oil. R_f = 0.59 (30% EtOAc in hexane). $[\alpha]_D^{25}$ −14.3 (*c* 0.96, $CHCl_3$). ^1H NMR (300 MHz, C_6D_6) δ: 8.32–8.28 (2H, m), 8.16–8.11 (2H, m), 7.36–7.00 (26H, m), 5.24 (1H, d, *J* = 11.6 Hz), 5.09 (1H, d, $J_{1',2'}$ = 7.7 Hz, H-1′), 5.00 (1H, d, *J* = 11.6 Hz), 4.94–4.85 (3H, m), 4.82–4.73 (2H, m), 4.71–4.65 (1H, m), 4.58 (1H, dd, $J_{3,4}$ = 5.7, $J_{4,5}$ = 1.8 Hz, H-4), 4.48–4.37 (2H, m), 4.46 (1H, d, *J* = 12.3 Hz), 4.36 (1H, d, *J* = 11.7 Hz), 4.29 (1H, d, *J* = 11.7 Hz), 4.15 (1H, dd, *J* = 9.5, 8.0 Hz), 4.08 (1H, d, *J* = 11.7 Hz), 3.72 (1H, d, *J* = 2.4 Hz), 3.59–3.49 (2H, m), 3.37–3.32 (2H, m), 1.36 (3H, s), 1.14 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.2, 165.7, 138.8, 138.4, 138.3, 137.8, 132.9, 132.5, 130.6, 130.0, 129.8, 129.7, 128.3, 128.1, 128.0, 128.0, 127.9, 127.6, 127.5, 127.5, 127.4, 127.2, 113.4, 109.3, 95.7, 85.8, 85.3, 82.8, 82.1, 79.1, 75.5, 74.4, 73.6, 73.4, 73.2, 72.7, 68.2, 64.7, 63.5, 26.6, 25.3. IR (film): 2870, 1724, 1602, 1453, 1274, 1097, 711 cm^{-1}. MS (FAB) *m*/*z*: 973 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{57}H_{58}O_{13}Na$, 973.3775; found, 973.3771.

3.6.5. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl 1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranoside (18αβ)

Colorless oil. R_f = 0.58 (30% EtOAc in hexane). $[\alpha]_D^{20}$ +6.3 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6) δ: 8.21–8.18 (2H, m), 8.17–8.15 (2H, m), 7.37–7.33 (2H, m), 7.29–7.20 (6H, m), 7.15–6.93 (18H, m), 5.77 (1H, d, $J_{1',2'}$ = 2.0 Hz, H-1′), 5.01 (1H, d, *J* = 11.4 Hz, C*H*HPh), 4.86 (1H, d, *J* = 11.9 Hz, C*H*HPh), 4.73 (1H, d, $J_{3,4}$ = 5.9 Hz, H-3), 4.68 (1H, dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 2.1 Hz, H-4), 4.68–4.39 (10H, m, 5 × C*H*HPh, H-1a, 1b, 5, 6a, 6b), 4.41 (1H, dd, $J_{4',5'}$ = 9.9, $J_{3',4'}$ = 9.3 Hz, H-4′), 4.40 (1H, d, *J* = 11.9 Hz, C*H*HPh), 4.26 (1H, ddd, $J_{4',5'}$ = 9.9, $J_{5',6'b}$ = 4.8, $J_{5',6'a}$ = 1.6 Hz, H-5′), 4.22 (1H, dd, $J_{3',4'}$ = 9.3, $J_{2',3'}$ = 2.9 Hz, H-3′), 4.07 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'a}$ = 1.6 Hz, H-6′a), 4.00 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'b}$ = 4.8 Hz, H-6′b), 3.98 (1H, dd, $J_{2',3'}$ = 2.9, $J_{1',2'}$ = 2.0 Hz, H-2′), 1.35 (3H, s), 1.09 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.0, 165.4, 138.4, 138.3, 138.2, 138.0, 133.2, 133.1, 129.8, 129.8, 129.7, 128.4, 128.4, 128.3, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.5, 127.4, 127.4, 127.3, 113.8, 108.7, 91.9, 85.4, 84.7, 81.9, 80.2, 75.1, 74.5, 74.3, 73.4, 73.1, 72.7, 71.8, 69.0, 64.7, 62.8, 26.6, 25.1. IR (film): 3031, 2936, 1729, 1602, 1496, 1453, 1374, 1275, 1112, 870, 699 cm^{-1}. MS (FAB) *m*/*z*: 973 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{57}H_{58}O_{13}Na$, 973.3775; found, 973.3781.

3.6.6. 2,3,4,6-Tetra-*O*-benzyl-β-D-mannopyranosyl 1,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-psicofuranoside (18ββ)

Colorless oil. R_f = 0.53 (30% EtOAc in hexane). $[\alpha]_D^{20}$ −10.1 (*c* 1.0, $CHCl_3$). ^1H NMR (400 MHz, C_6D_6) δ: 8.33–8.30 (2H, m), 8.14–8.11 (2H, m), 7.60 (2H, d, *J* = 7.3 Hz), 7.45 (2H, d, *J* = 7.3 Hz), 7.22–6.95 (22H, m), 5.08 (1H, d, *J* = 12.1 Hz, C*H*HPh), 5.07 (1H, d, *J* = 11.5 Hz, C*H*HPh), 4.99 (1H, d, *J* = 12.1 Hz, C*H*HPh), 4.97 (1H, d, *J* = 11.5 Hz, C*H*HPh), 4.94 (1H, br s, H-1′), 4.87 (1H, d, *J* = 11.2 Hz, C*H*HPh), 4.86 (1H, d, $J_{3,4}$ = 5.9 Hz, H-3), 4.73 (1H, d, *J* = 11.9 Hz, C*H*HPh), 4.63 (1H, ddd, $J_{5,6a}$ = 7.9, $J_{5,6b}$ = 6.0, $J_{4,5}$ = 1.3 Hz, H-5), 4.60 (1H, d, *J* = 11.9 Hz, C*H*HPh), 4.52 (1H, d, *J* = 11.2 Hz, C*H*HPh), 4.42 (1H, dd, $J_{3,4}$ = 5.9, $J_{4,5}$ = 1.3 Hz, H-4), 4.38 (1H, d, $J_{1a,1b}$ = 11.7 Hz, H-1a), 4.25 (1H, dd, $J_{4',5'}$ = 9.7, $J_{3',4'}$ = 9.4 Hz, H-4′), 4.22 (1H, dd, $J_{6a,6b}$ = 11.4, $J_{5,6a}$ = 7.9 Hz, H-6a), 4.13 (1H, d, $J_{1',2'}$ = 2.6 Hz, H-2′), 4.05 (1H, d, $J_{1a,1b}$ = 11.7 Hz, H-1b), 3.93 (1H, dd, $J_{6a,6b}$ = 11.4, $J_{5,6h}$ = 6.0 Hz, H-6b), 3.69 (1H, dd, $J_{6'a,6'b}$ = 11.1, $J_{5',6'a}$ = 4.1 Hz, H-6′a), 3.55 (1H, dd, $J_{6'a,6'b}$ = 11.1, $J_{5',6'b}$ = 1.3 Hz, H-6′b), 3.49 (1H, dd, $J_{3',4'}$ = 9.4, $J_{2',3'}$ = 2.7 Hz, H-3′), 3.10 (1H, ddd, $J_{4',5'}$ = 9.7, $J_{5',6'a}$ = 4.1, $J_{5',6'b}$ = 1.3 Hz, H-5′), 1.40 (3H, s), 1.13 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.1, 165.9, 139.0, 138.4, 138.3, 138.2, 133.5, 132.7, 130.4, 129.8, 129.7, 129.3, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 113.5, 109.9, 93.8, 85.5, 84.9, 83.0, 81.7, 75.8, 75.1 (2C), 74.2, 74.1, 73.2, 71.8, 68.9, 65.0, 62.8, 26.5, 25.8. IR (film): 3031, 2869, 1716, 1602, 1496, 1453, 1374, 1274, 1106, 712 cm^{-1}. MS (FAB) *m*/*z*: 973 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{57}H_{58}O_{13}Na$, 973.3775; found, 973.3769.

3.7. Removal of 3,4-*O*-isopropylidene group of 17αβ and 18αβ

A mixture of **17αβ** or **18αβ** (48 mg, 50 μmol) and *p*-toluenesulfonic acid monohydrate (28 mg, 0.15 mmol) was stirred in MeOH (2.2 mL) at room temperature for 45 h. The reaction was quenched with satd aq $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (15 mL × 3). Combined organic layers were washed with water and brine (10 mL each), dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel eluted with 30% EtOAc in hexane to give diol **20** or **21**.

3.7.1. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl 1,6-di-*O*-benzoyl-β-D-psicofuranoside (20)

Colorless oil. 61% yield. R_f = 0.30 (40% EtOAc in hexane). $[\alpha]_D^{24}$ +48.2 (*c* 0.8, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ: 8.05–8.00 (4H, m), 7.53–7.46 (2H, m), 7.39–7.16 (24H, m), 5.60 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.93 (1H, d, *J* = 11.4 Hz), 4.85 (1H, d, *J* = 11.9 Hz), 4.68 (1H, d, *J* = 11.7 Hz), 4.63 (1H, d, *J* = 11.6 Hz), 4.57–4.24 (12H, m), 4.11 (1H, ddd, $J_{5',6'a}$ = 8.0, $J_{5',6'b}$ = 4.1, $J_{4',5'}$ = 1.1 Hz, H-5′), 4.00 (1H, dd, $J_{2',3'}$ = 9.9, $J_{1',2'}$ = 3.7 Hz, H-2′), 3.81 (1H, dd, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 2.8 Hz, H-3′), 3.78 (1H, dd, $J_{3',4'}$ = 2.8, $J_{4',5'}$ = 1.1 Hz, H-4′), 3.57 (1H, dd, $J_{6'a,6'b}$ = 9.6, $J_{5',6'a}$ = 8.0 Hz, H-6′a), 3.33 (1H, dd, $J_{6'a,6'b}$ = 9.6, $J_{5',6'b}$ = 4.1 Hz, H-6′b), 2.55 (1H, d, *J* = 5.5 Hz, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.1, 166.3, 138.8, 138.5, 138.3, 137.3, 133.0, 132.9, 130.0, 129.9, 129.7, 129.7, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.6, 127.4, 127.3, 107.2, 90.3, 81.2, 78.9, 75.7, 75.5, 74.4, 73.6, 73.5, 73.4, 72.5, 71.1, 70.4, 70.2, 65.4, 63.8. IR (film): 3453, 2926, 1723, 1602, 1495, 1453, 1374, 1276, 1098, 713 cm^{-1}. MS (FAB) *m*/*z*: 933 $[M+Na]^+$. HRMS (FAB) *m*/*z*: calcd for $C_{54}H_{54}O_{13}Na$, 933.3462; found, 933.3474.

3.7.2. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl 1,6-di-*O*-benzoyl- β-D-psicofuranoside (21)

Colorless oil. 63% yield. R_f = 0.37 (40% EtOAc in hexane). $[\alpha]_D^{20}$ +44.6 (*c* 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.10–8.07 (2H, m), 7.92–7.89 (2H, m), 7.56–7.48 (2H, m), 7.44–7.39 (2H, m), 7.34–7.21 (18H, m), 7.18–7.12 (4H, m), 5.48 (1H, d, $J_{1',2'}$ = 1.3 Hz, H-1′), 4.84 (1H, d, *J* = 10.8 Hz, C*H*HPh), 4.71 (1H, d, *J* = 12.5 Hz, C*H*HPh), 4.67 (1H, d, *J* = 12.6 Hz, C*H*HPh), 4.63 (1H, d, *J* = 12.6 Hz, C*H*HPh), 4.60 (1H, dd, $J_{6a,6b}$ = 11.9, $J_{5,6a}$ = 6.0 Hz, H-6a), 4.57 (1H, d,

J = 11.5 Hz, C*H*HPh), 4.54 (1H, dd, $J_{6a,6b}$ = 11.9, $J_{5,6b}$ = 3.1 Hz, H-6b), 4.49 (1H, d, J = 11.5 Hz, C*H*HPh), 4.47 (1H, d, J = 10.8 Hz, C*H*HPh), 4.33–4.19 (7H, m, C*H*HPh, H-1a, 1b, 3, 4, 5, O*H*), 3.96 (1H, ddd, $J_{4',5'}$ = 9.5, $J_{5',6'b}$ = 6.8, $J_{5',6'a}$ = 1.5 Hz, H-5′), 3.83 (1H, dd, $J_{5',5'}$ = 9.5, $J_{3',4'}$ = 8.8 Hz, H-4′), 3.79–3.75 (2H, m, H-2′, 3′), 3.78 (1H, dd, $J_{6'a,6'b}$ = 10.1, $J_{5',6'a}$ = 1.5 Hz, H-6′a), 3.64 (1H, dd, $J_{6'a,6'b}$ = 10.1, $J_{5',6'b}$ = 6.8 Hz, H-6′b), 2.69 (1H, d, J = 5.5 Hz, O*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 166.6, 166.4, 138.2, 138.1, 138.0, 137.7, 133.4, 133.0, 129.8, 129.7, 129.6, 129.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.5, 127.3, 107.0, 90.8, 81.6, 79.9, 75.0, 74.6, 74.0, 73.7, 73.4, 72.4, 72.3, 71.8, 71.6, 69.5, 66.0, 62.8. IR (film): 3444, 3031, 2915, 1714, 1602, 1496, 1454, 1279, 1109, 847, 697 cm^{-1}. MS (FAB) m/z: 933 [M+Na]$^+$. HRMS (FAB) m/z: calcd for $C_{54}H_{54}O_{13}Na$, 933.3462; found, 933.3457.

3.8. Removal of benzoyl protecting groups for 19, 20, and 21

A mixture of **19**,[9] **20**, or **21** (16 mg, 50 μmol) and K_2CO_3 (69 mg, 0.5 mmol) in MeOH (6.6 mL) was stirred for 1 h at room temperature. The reaction mixture was filtered through a Celite pad (1 cm) and concentrated under vacuum. The crude material was purified by flash column chromatography on silica gel eluted with EtOAc to afford tetraol **22**, **23**, or **24**.

3.8.1. 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl β-D-psicofuranoside (22)

White amorphous solid. 92% yield. R_f = 0.65 (EtOAc). $[\alpha]_D^{20}$ +32.4 (c 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.36–7.23 (18H, m), 7.16–7.14 (2H, m), 5.39 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.88–4.75 (5H, m, 5 × C*H*HPh), 4.56 (1H, d, J = 12.1 Hz, C*H*HPh), 4.52 (1H, d, J = 11.4 Hz, C*H*HPh), 4.46 (1H, d, J = 12.1 Hz, C*H*HPh), 4.16 (1H, dd, $J_{4,5}$ = 8.4, $J_{3,4}$ = 4.6 Hz, H-4), 4.04 (1H, d, $J_{3,4}$ = 4.6 Hz, H-3), 4.00 (1H, ddd, $J_{4,5}$ = 8.4, $J_{5,6a}$ = 6.4, $J_{5,6b}$ = 2.7 Hz, H-5), 3.90 (1H, dd, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.87 (1H, ddd, $J_{4',5'}$ = 10.0, $J_{5',6'a}$ = 3.7, $J_{5',6'b}$ = 2.2 Hz, H-5′), 3.79 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 6.4 Hz, H-6a), 3.76 (1H, d, $J_{1a,1b}$ = 12.5 Hz, H-1a), 3.70 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6b}$ = 2.7 Hz, H-6b), 3.68 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'a}$ = 3.7 Hz, H-6′a), 3.64 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'b}$ = 2.2 Hz, H-6′b), 3.61 (1H, dd, $J_{2',3'}$ = 9.9, $J_{1',2'}$ = 3.7 Hz, H-2′), 3.58 (1H, dd, $J_{4',5'}$ = 10.0, $J_{3',4'}$ = 9.2 Hz, H-4′), 3.49 (1H, d, $J_{1a,1b}$ = 12.5 Hz, H-1b). ^{13}C NMR (75 MHz, CD_3OD) δ: 140.0, 139.5, 139.3, 138.5, 129.9, 129.6, 129.4, 129.4, 129.3, 129.2, 128.9, 128.8, 128.8, 128.7, 128.6, 110.8, 91.5, 85.8, 83.2, 80.8, 79.2, 76.5, 76.0, 75.7, 75.6, 74.4, 72.7, 71.9, 69.6, 63.9, 61.4. IR (KBr): 3405, 2932, 1454, 1066, 978, 755, 699 cm^{-1}. MS (FAB) m/z: 725 [M+Na]$^+$. HRMS (FAB) m/z: calcd for $C_{40}H_{46}O_{11}Na$, 725.2938; found, 725.2944.

3.8.2. 2,3,4,6-Tetra-*O*-benzyl-α-D-galactopyranosyl β-D-psicofuranoside (23)

White amorphous solid. 84% yield. R_f = 0.71 (EtOAc). $[\alpha]_D^{20}$ +27.8 (c 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.41–7.24 (20H, m), 5.32 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.82 (1H, d, J = 11.0 Hz, C*H*HPh), 4.82 (1H, d, J = 10.1 Hz, C*H*HPh), 4.78 (1H, d, J = 11.5 Hz, C*H*HPh), 4.75 (1H, d, J = 10.1 Hz, C*H*HPh), 4.70 (1H, d, J = 11.5 Hz, C*H*HPh), 4.51 (1H, d, J = 11.0 Hz, C*H*HPh), 4.51 (1H, d, J = 11.9 Hz, C*H*HPh), 4.44 (1H, d, J = 11.9 Hz, C*H*HPh), 4.15 (1H, dd, $J_{4,5}$ = 8.6, $J_{3,4}$ = 4.4 Hz, H-4), 4.08–4.05 (2H, m, H-4′, 5′), 4.05 (1H, dd, $J_{2',3'}$ = 10.2, $J_{1',2'}$ = 3.7 Hz, H-2′), 3.98 (1H, d, $J_{3,4}$ = 4.4 Hz, H-3), 3.98 (1H, ddd, $J_{4,5}$ = 8.6, $J_{5,6a}$ = 6.8, $J_{5,6b}$ = 2.6 Hz, H-5), 3.95 (1H, dd, $J_{2',3'}$ = 10.2, $J_{3',4'}$ = 2.7 Hz, H-3′), 3.77 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 6.8 Hz, H-6a), 3.74 (1H, d, $J_{1a,1b}$ = 12.3 Hz, H-1a), 3.63 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6b}$ = 2.6 Hz, H-6b), 3.54 (1H, dd, $J_{6'a,6'b}$ = 12.0, $J_{5',6'a}$ = 6.8 Hz, H-6′a), 3.51 (1H, dd, $J_{6'a,6'b}$ = 12.0, $J_{5',6'b}$ = 6.2 Hz, H-6′b), 3.46 (1H, d, $J_{1a,1b}$ = 12.3 Hz, H-1b). ^{13}C NMR (75 MHz, CD_3OD) δ: 140.0, 139.9, 139.4, 138.7, 129.9, 129.6, 129.5, 129.3, 129.2, 129.1, 128.8, 128.8, 128.7, 128.7, 110.6, 92.2, 85.7, 80.4, 77.0, 76.1, 76.0, 75.7, 75.6, 74.5, 73.4, 72.1, 71.4, 69.9, 64.1, 61.1. IR (KBr): 3397, 2920, 1560, 1455, 1088, 735, 698 cm^{-1}. MS (FAB) m/z: 725 [M+Na]$^+$. HRMS (FAB) m/z: calcd for $C_{40}H_{46}O_{11}Na$, 725.2938; found, 725.2935.

3.8.3. 2,3,4,6-Tetra-*O*-benzyl-α-D-mannopyranosyl β-D-psicofuranoside (24)

White amorphous solid. Quantitative yield. R_f = 0.55 (EtOAc). $[\alpha]_D^{20}$ +1.1 (c 0.60, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ: 7.42–7.39 (2H, m), 7.36–7.23 (16H, m), 7.19–7.15 (2H, m), 5.56 (1H, d, $J_{1',2'}$ = 2.0 Hz, H-1′), 4.80 (1H, d, J = 11.0 Hz, C*H*HPh), 4.71 (1H, d, J = 12.5 Hz, C*H*HPh), 4.68 (1H, d, J = 12.5 Hz, C*H*HPh), 4.61 (1H, d, J = 12.1 Hz, C*H*HPh), 4.58 (1H, d, J = 11.7 Hz, C*H*HPh), 4.54 (1H, d, J = 11.7 Hz, C*H*HPh), 4.50 (1H, d, J = 11.0 Hz, C*H*HPh), 4.47 (1H, d, J = 12.1 Hz, C*H*HPh), 4.17 (1H, dd, $J_{4,5}$ = 7.7, $J_{3,4}$ = 4.8 Hz, H-4), 4.05 (1H, d, $J_{3,4}$ = 4.8 Hz, H-3), 4.00 (1H, ddd, $J_{4,5}$ = 7.7, $J_{5,6a}$ = 5.9, $J_{5,6b}$ = 3.1 Hz, H-5), 3.95 (1H, dd, $J_{2',3'}$ = 2.6, $J_{1',2'}$ = 2.0 Hz, H-2′), 3.93 (1H, dd, $J_{3',4'}$ = 8.2, $J_{4',5'}$ = 7.9 Hz, H-4′), 3.90 (1H, dd, $J_{3',4'}$ = 8.2, $J_{2',3'}$ = 2.6 Hz, H-3′), 3.83 (1H, ddd, $J_{4',5'}$ = 7.9, $J_{5',6'a}$ = 4.2, $J_{5',6'b}$ = 2.0 Hz, H-5′), 3.78 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 5.9 Hz, H-6a), 3.72 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6b}$ = 3.1 Hz, H-6b), 3.70 (1H, d, $J_{1a,1b}$ = 11.9 Hz, H-1a), 3.70 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'a}$ = 4.2 Hz, H-6′a), 3.65 (1H, dd, $J_{6'a,6'b}$ = 11.0, $J_{5',6'b}$ = 2.0 Hz, H-6′b), 3.59 (1H, d, $J_{1a,1b}$ = 11.9 Hz, H-1b). ^{13}C NMR (75 MHz, CD_3OD) δ: 139.8 (2C), 139.8, 139.5, 129.4, 129.3, 129.1, 129.0, 128.7, 128.6, 110.2, 92.5, 85.8, 80.6, 76.6, 76.4, 75.9, 75.8, 74.4, 73.8, 73.4, 72.7, 71.8, 70.1, 63.8, 63.1. IR (KBr): 3448, 2920, 1455, 1091, 737, 698 cm^{-1}. MS (FAB) m/z: 725 [M+Na]$^+$. HRMS (FAB) m/z: calcd for $C_{40}H_{46}O_{11}Na$, 725.2938; found, 725.2943.

3.9. Removal of benzyl-protecting groups for 22, 23, and 24

To a solution of compound **22**, **23**, or **24** (17 mg, 24.2 μmol) in MeOH (2 mL) was added 10% $Pd(OH)_2$ on carbon (4 mg) and stirred overnight under hydrogen atmosphere (1 atm) at room temperature. After filtration of the reaction mixture and evaporation of the filtrate, the crude product was purified by HPLC under the following conditions; column, Chemco pak® (Kromasil 5NH$_2$), flow rate, 5 mL/min, eluent, 25% H_2O in MeCN. Retention time, 14.8 min for **1**, 15.3 min for **2**, and 19.6 min for **3**. Evaporation of the corresponding fractions gave compound **1**, **2**, or **3**.

3.9.1. α-D-Glucopyranosyl β-D-psicofuranoside (1)

White solid. Quantitative yield. R_f = 0.55 (25% H_2O in MeCN). Mp 168 °C dec. $[\alpha]_D^{20}$ +78.8 (c 0.4, H_2O), lit.[6] $[\alpha]_D^{20}$ +74.36. ^{1}H NMR (400 MHz, D_2O) δ: 5.38 (1H, d, $J_{1',2'}$ = 3.7 Hz, H-1′), 4.26 (1H, dd, $J_{4,5}$ = 8.3, $J_{3,4}$ = 4.8 Hz, H-4), 4.21 (1H, d, $J_{3,4}$ = 4.8 Hz, H-3), 4.08 (1H, ddd, $J_{4,5}$ = 8.3, $J_{5,6b}$ = 6.6, $J_{5,6a}$ = 3.5 Hz, H-5), 3.86–3.75 (4H, m, H-6b, 5′, 6′a, 6′b), 3.84 (1H, dd, $J_{6a,6b}$ = 12.3, $J_{5,6a}$ = 3.5 Hz, H-6a), 3.83 (1H, d, $J_{1a,1b}$ = 12.8 Hz, H-1a), 3.71 (1H, dd, $J_{2',3'}$ = 9.9, $J_{3',4'}$ = 9.2 Hz, H-3′), 3.68 (1H, d, $J_{1a,1b}$ = 12.8 Hz, H-1b), 3.58 (1H, dd, $J_{2',3'}$ = 9.9, $J_{1',2'}$ = 3.7 Hz, H-2′), 3.46 (1H, dd, $J_{4',5'}$ = 9.5, $J_{3',4'}$ = 9.2 Hz, H-4′). ^{13}C NMR (100 MHz, D_2O) δ: 107.5, 90.4, 81.9, 72.7, 71.2, 71.0, 69.4, 69.1, 67.5, 61.0, 58.6, 58.2. IR (KBr): 3385, 2935, 1654, 1420, 1071, 988 cm^{-1}. MS (FAB) m/z: 365 [M+Na]$^+$. HRMS (FAB) m/z: calcd for $C_{12}H_{22}O_{11}Na$, 365.1060; found, 365.1055.

3.9.2. α-D-Galactopyranosyl β-D-psicofuranoside (2)

White solid. Quantitative yield. R_f = 0.52 (25% H_2O in MeCN). Mp 170 °C dec. $[\alpha]_D^{20}$ +63.7 (c 0.3, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 5.40 (1H, d, $J_{1',2'}$ = 3.1 Hz, H-1′), 4.27 (1H, dd, $J_{4,5}$ = 8.2, $J_{3,4}$ = 4.8 Hz, H-4), 4.21 (1H, d, $J_{3,4}$ = 4.8 Hz, H-3), 4.08 (1H, ddd, $J_{5',6'b}$ = 7.0, $J_{5',6'a}$ = 5.3, $J_{4',5'}$ = 1.3 Hz, H-5′), 4.07 (1H, ddd, $J_{4,5}$ = 8.2, $J_{5,6a}$ = 7.0, $J_{5,6b}$ = 3.5 Hz, H-5), 4.01 (1H, dd, $J_{3',4'}$ = 2.6, $J_{4',5'}$ = 1.3 Hz, H-4′), 3.89–3.83 (2H, m, H-2′, 3′), 3.86 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6a}$ = 7.0 Hz, H-6a), 3.83 (1H, d,

$J_{1a,1b}$ = 12.6 Hz, H-1a), 3.82 (1H, dd, $J_{6a,6b}$ = 12.1, $J_{5,6b}$ = 3.5 Hz, H-6b), 3.75 (1H, dd, $J_{6'a,6'b}$ = 11.9, $J_{5',6'a}$ = 5.3 Hz, H-6′a), 3.71 (1H, dd, $J_{6'a,6'b}$ = 11.9, $J_{5',6'b}$ = 7.0 Hz, H-6′b), 3.68 (1H, d, $J_{1a,1b}$ = 12.6 Hz, H-1b). ^{13}C NMR (100 MHz, D_2O) δ: 107.4, 90.5, 81.9, 72.6, 70.0, 69.1, 67.7, 67.5, 66.4, 61.0, 59.4, 58.3. IR (KBr): 3376, 2935, 1637, 1074, 961 cm^{-1}. MS (FAB) *m*/*z*: 365 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_{12}H_{22}O_{11}Na$, 365.1060; found, 365.1055.

3.9.3. α-D-Mannopyranosyl β-D-psicofuranoside (3)

White solid. Quantitative yield. R_f = 0.50 (25% H_2O in MeCN). Mp 173 °C dec. $[\alpha]_D^{20}$ +24.7 (*c* 0.3, H_2O). ^{1}H NMR (400 MHz, D_2O) δ: 5.31 (1H, d, $J_{1',2'}$ = 2.0 Hz, H-1′), 4.26 (1H, dd, $J_{4,5}$ = 8.1, $J_{3,4}$ = 4.8 Hz, H-4), 4.19 (1H, d, $J_{3,4}$ = 4.8 Hz, H-3), 4.06 (1H, ddd, $J_{4,5}$ = 8.1, $J_{5,6a}$ = 6.4, $J_{5,6b}$ = 3.7 Hz, H-5), 3.91 (1H, dd, $J_{2',3'}$ = 3.3, $J_{1',2'}$ = 2.0 Hz, H-2′), 3.87 (1H, dd, $J_{3',4'}$ = 7.9, $J_{2',3'}$ = 3.3 Hz, H-3′), 3.86–3.66 (8H, m, H-1a, 1b, 6a, 6b, 4′, 5′, 6′a, 6′b). ^{13}C NMR (100 MHz, D_2O) δ: 107.4, 91.9, 81.8, 72.8, 71.8, 69.4, 68.9, 68.7, 64.9, 60.9, 59.1, 58.7. IR (KBr): 3388, 2938, 1637, 1419, 1064, 976 cm^{-1}. MS (FAB) *m*/*z*: 365 [M+Na]$^+$. HRMS (FAB) *m*/*z*: calcd for $C_{12}H_{22}O_{11}Na$, 365.1060; found, 365.1064.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2010.05.030.

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