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Indium-promoted Barbier-type allylations in aqueous media: a convenient approach to 4-*C*-branched monosaccharides and (1→4)-*C*-disaccharides

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Abstract—Starting from methyl 6-bromo-4,6-dideoxy-α-D-*threo*-4-enopyranoside, 4-*C*-branched sugars have been prepared through indium-promoted Barbier-type allylation of various aldehydes in aqueous media followed by hydroboration of the resulting double bond. The intermediate unsaturated monosaccharides were shown to rearrange in acidic media to give 4-*C*-acetyl-5-*C*-alkyl pyranose compounds. From β-1-formyl sugars the corresponding β-(1→4)-*C*-disaccharides were obtained.

Keywords: Organic synthesis in water; Indium-mediated allylations; *C*-branched sugars; *C*-disaccharides

1. Introduction

The stereospecific formation of carbon–carbon bonds is currently the subject of intense research. In carbohydrate chemistry, the regio- and stereoselective synthesis of branched sugars has mainly been stimulated by their occurrence in a large variety of natural products.[1] Moreover, relatively few methods of general preparative significance are available for the synthesis of such compounds.[2]

Recently, we reported a very convenient protocol for the preparation of *C*-branched monosaccharides and *C*-disaccharides under indium promoted Barbier-type allylations in aqueous media.[3] Indeed because indium-mediated reactions can be carried out in such media, they were shown to be particularly suited for carbohydrates and their analogues.[4]

In order to extend our preliminary approach, which started from 2-bromo-3-enopyranoside and 4-bromo-2-enopyranoside derivatives, we now apply this methodology to 6-bromo-4-enopyranoside, which allows access to various 4-*C*-branched monosaccharides and (1→4)-*C*-disaccharides.

2. Results and discussion

The synthesis of the key compound for the allylation reaction, 6-bromo-4,6-dideoxy-α-D-*threo*-4-enopyranoside **7** is summarized in Scheme 1. We started from commercial methyl α-D-glucopyranoside **1**. After quantitative acetylation under standard conditions (acetic anhydride in pyridine, overnight), the peracetylated derivative **2** was treated with lipase from *Candida cylindracea* in a mixture of phosphate buffer (0.1 M; pH 7.0) and di-*n*-butyl ether, to give methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranoside **3** in 97% yield.[5] In the latter reaction, we observed, as reported, complete and regioselective hydrolysis of the primary acetyl ester. Then, PCC oxidation[6] gave directly the unsaturated aldehyde **4**[7] in 78% yield provided that the reaction was performed on a small scale. On a larger scale, we preferred the Swern oxidation (dimethyl sulfoxide/oxalyl chloride/triethylamine), which gave **4** in 91% reproducible yield.[8]

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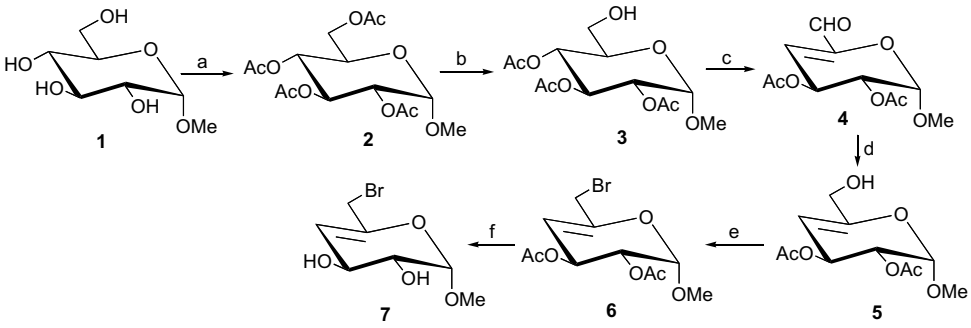


Scheme 1. Reagents and conditions: (a) Ac_2O, pyridine (quantitative yield); (b) lipase from *C. cylindracea*, phosphate buffer (0.1 M, pH 7.0)/Bu_2O (97%); (c) Me_2SO, $(CO)_2Cl_2$, Et_3N, CH_2Cl_2 (91%); (d) $NaBH_4$, MeOH (91%); (e) CBr_4, $(C_6H_5)_3P$, CH_2Cl_2 (93%); (f) LiOH, MeOH/water (97%, overall yield 72%).

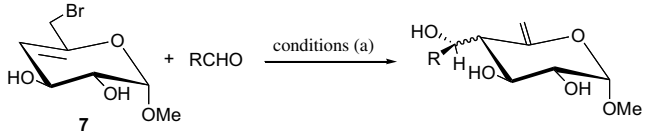
Then, the unsaturated aldehyde **4** was reduced with $NaBH_4$ in MeOH to provide the allyl alcohol **5** in 91% yield. Finally, under standard bromination conditions (triphenylphosphine, carbon tetrabromide) followed by deacetylation with lithium hydroxide in a 3:1 mixture of MeOH–water (97%), we obtained the desired 6-bromo-4-enopyranoside **7** (72% overall yield for the six steps from **1**).

Then we tested the allylation reactions with various aldehydes under indium-promoted Barbier-type conditions. All the results are summarized in Table 1.

First, we tried the reaction with benzaldehyde. It took place in a mixture of 2:1 THF–phosphate buffer (0.11 M; pH 7.0) at rt for 1.5 h to give the adduct **8** in 86% yield as a unique stereoisomer resulting from complete regio- and diastereoselectivity (Table 1, entry 1). The structure of **8** was deduced from NMR analysis. The ^{1}H NMR spectrum notably exhibits a doublet of doublet ($J_{3,4}$ 8.5 Hz and $J_{4,7}$ 4.0 Hz) for H-4, indicating equatorial alkylation at C-4. In ^{13}C NMR spectroscopy, the presence of a quaternary carbon atom and a secondary carbon atom in the olefinic shift area are in good agreement with an exocyclic double bond in C-5,6 position. We obtained along with compound **8**, a small amount (9%) of **26**, which resulted from the reduction in water of the starting bromide with indium. Indeed, when **7** was treated with indium(0), alone without any aldehyde in a 1:1 THF–phosphate buffer (0.05 M; pH 7.0)/THF mixture, we obtained in 1 h **26** in 73% yield. The ^{13}C NMR spectrum of **26** shows clearly an exocyclic double bond at C-5 (97.2 and 153.1 ppm) and a methylene group at C-4 (36.2 ppm). It is noteworthy that this reduction, which occurred to a small extent in the case of the primary bromide **7**, did not occur at all when using a secondary bromide.[3]

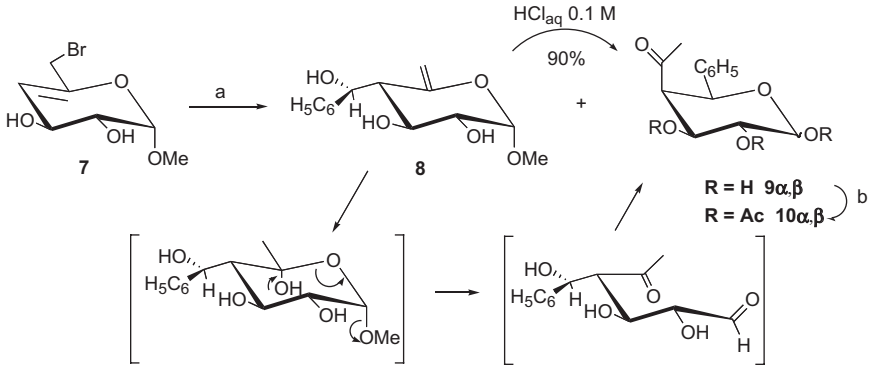
If the reaction is conducted in pure water, in the absence of the phosphate buffer, the 4-*C*-adduct **8** is slowly transformed (30% after 1.5 h) into two new products **9α,β** as a 1:3 mixture of the two α and β anomers. These compounds **9α,β** were fully characterized by spectral analysis. For both compounds, ^{1}H and ^{13}C NMR spectroscopy indicates the presence of the 5-*C*-phenyl moiety in equatorial orientation instead of the H-6 and H-6′ protons and a 4-*C*-acetyl group in axial orientation. Acetylation of **9α,β** led to **10α,β** whose NMR data confirmed the structure. Indeed, we observed a

Table 1. Reactions of **7** with various aldehydes



Entry	RCHO	Products	Cond[b]	Yield[c] (%)	Eq./ax.[d]	Dr: *S*/*R*[d]
1	PhCHO	**8**	1.5	86	1/0	~100/0
2	HCHO	**11a,b**	3	73	0.66/0.34	—
3	**13**	**14**	1.5	57	1/0	~100/0
4	**18**	**19a,b**	2	45	0.64/0.36	~100/0

[a] RCHO (3 equiv), In (2 equiv), 2:1 THF–phosphate buffer (0.11 M, pH 7.0).
[b] Conditions: reaction time (h); rt.
[c] Isolated yields.
[d] Diastereomeric ratio determined within the accuracy of ^{1}H and ^{13}C NMR spectra.



Scheme 2. Reagents and conditions: (a) water, PhCHO (3 equiv), In (2 equiv); **8**, 5%; **9α,β** (α/β: 1:3, 30%) or 2:1 THF–phosphate buffer (0.11 M, pH 7), PhCHO (3 equiv), In (2 equiv); **8**, 86%; **9α,β**, 0%; (b) Ac_2O, py.

doublet of doublet for H-3 ($J_{3,4}$ 6 Hz), which confirmed the 4-*C*-acetyl group in axial orientation and a doublet for H-5 ($J_{3,5}$ 3.5 Hz) indicating the presence of the phenyl group in equatorial orientation.

In fact, without buffering the reaction mixture, **9α,β** arise from the acid hydrolysis of the labile enol ether derivative **8** as shown in Scheme 2. After electrophilic addition of water followed by opening of the ring with elimination of the anomeric methoxy group, the cyclization of the C-7 hydroxyl group onto the aldehyde led to the keto-derivatives **9α,β**. In order to confirm these results, compound **8** was treated by 0.1 M aq HCl. Effectively, in these conditions, **9α,β** was obtained in 90% yield in 5 min as a mixture of anomers (α/β, 1:3).

Interestingly, the 4-*C*-5-*C*-substituted D-*galacto*-like structure of **9α,β** confirms the alkylation at C-4 in equatorial orientation and the configuration of the second new stereogenic center at C-7 in **8**. Indeed, C-4 in **9α,β** (or **10α,β**) arises from C-7 in **8**. On the basis of these results, configuration at C-7 was assigned as (*S*).

From a mechanistic point of view, our results can be explained by the formation of the currently accepted six-membered cyclic transition state between the carbonyl compound and the allylindium sugar moiety. Moreover, in this case, two six-membered transition states seem to be possible, a '*trans*-decalin' state A and a '*cis*-decalin' state B (Chart 1). Generally, *trans*-decalin is more stable than its *cis*-isomer; accordingly, the alkylation at C-4 in equatorial orientation in **8** is in favor of the formation of the '*trans*-decalin' state A. Moreover, the C-7 (*S*) configuration indicates that the phenyl group is in the more favorable equatorial orientation in the transition state as depicted in Chart 1A.

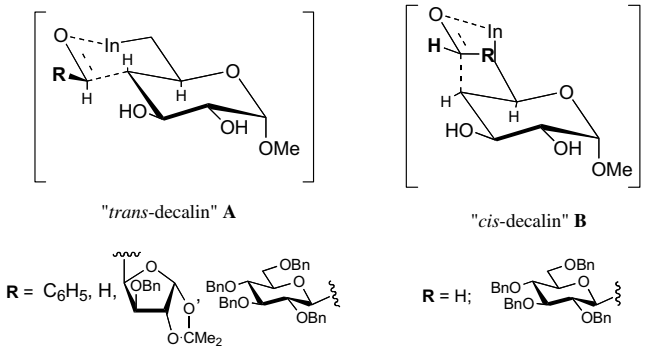
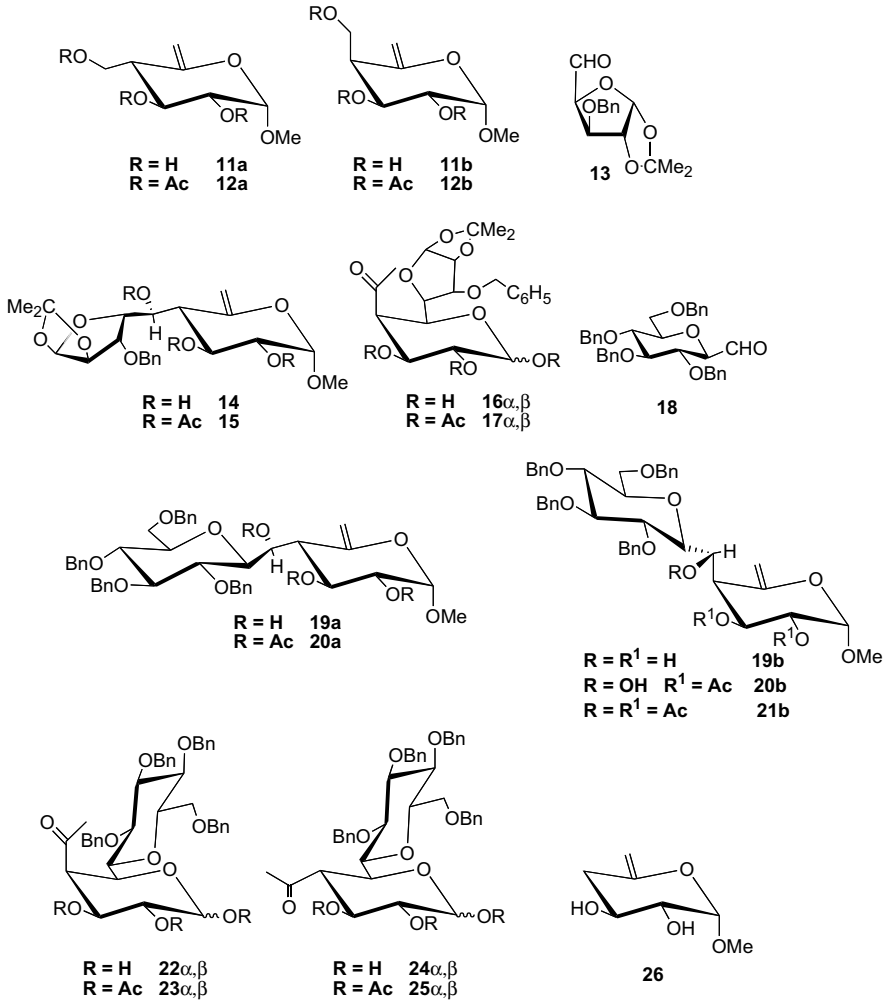


Chart 1. Transition states between the carbonyl compound and the allylindium sugar moiety.

Then in a second step, the reaction was extended to others aldehydes. In the case of formaldehyde (Table 1, entry 2), we obtained at rt in 3 h, a mixture of axial and equatorial C-4 adducts **11a,b** (73% yield in a 2:1 ratio in favor of the equatorial adduct) and the reduced compound **26** (7%). Compound **11a,b** were fully characterized after peracetylation to **12a,b**. The presence of the two epimers at C-4 in **11a,b** can be explained by the formation of the two six-membered cyclic transition states A and B (Chart 1) and certainly reflects the low energy difference between these two states in the case of formaldehyde, resulting from a decrease in the steric hindrance compared with the reaction with benzaldehyde.

Next, we examined the reaction between **7** and 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-*xylo*-dialdose **13**.[9] In this case, the reaction was less efficient than with benzaldehyde and the C-4 equatorial adduct was obtained at rt in 1.5 h as a single diastereoisomer **14** in 57% yield (Table 1, entry 3) along with the reduced derivative **26** (18%). Compound **14** was fully characterized after peracetylation. Treatment of **14** by aq HCl followed by acetylation gave a 11:9 mixture of the two anomers **17α,β** in 81% yield, which confirmed that the configuration of the new stereogenic center C-7 in the starting compound **14** was (*S*). These results indicate clearly that in this case, as previously with benzaldehyde, the bulky substituent (furanose ring) is in the more favorable equatorial orientation in a '*trans*-decalin'-like six-membered transition state.

Finally, to obtain analogues of *C*-oligosaccharides, we turned our attention to the reaction between the



6-bromo-enopyranoside derivative **7** and the β-C-linked 2,3,4,6-tetra-*O*-benzyl-β-D-glucosyl aldehyde **18**.[10] The reaction gave an inseparable 16:9 mixture of the two adducts **19a**,**b** in 45% yield along with **26** (30%). It is difficult at this stage to deduce the stereochemistry at C-4 from the ^{1}H NMR spectrum of the **19a**,**b** mixture as the coupling constants $J_{3,4}$ (6 Hz) were the same for both compounds. Therefore, the mixture was acetylated (16 h, Ac_2O–pyridine) at rt to give the fully acetylated compound **20a** and **20b** in which the tertiary hydroxyl group remained unchanged, which allowed the separation at this stage. Then, **20b** was fully acetylated at 40 °C for 24 h to give **21b**. However, it is still difficult to deduce from the ^{1}H NMR spectrum the stereochemistry at C-4 in **20a** ($J_{3,4}$ 5.5 Hz) and **21b** ($J_{3,4}$ 6 Hz). Compounds **20a** and **21b** were separately treated with 0.1 N aq HCl to give the rearranged products **22α**,**β** and **24α**,**β**, respectively, which were acetylated to **23α**,**β** and **25α**,**β** in which the perbenzyl glucosyl moiety was in equatorial orientation indicating a C-7 (*S*) configuration for both **20a** and **21b**. However, in **23α**,**β** the coupling constant $J_{3,4}$ 6 Hz for both anomers still did not allow to assign the configuration at C-4. However, a NOESY experiment showed clearly a strong NOE effect between H-4 and both H-3 and H-5 but not with H-2, which implied an equatorial H-4 and an axial methylketone. In **25α**,**β**, the coupling constants $J_{3,4}$ 8 Hz for the α anomer and 10.5 Hz for the β anomer indicate an equatorial orientation for the methylketone substituent. This was confirmed through NOESY experiments, which showed strong effects between H-4 and H-2 but not with H-3 and H-5. From these correlations, it can be concluded that for the major stereoisomer **19a**, the alkylation operated at C-4 in equatorial orientation with C-7 (*S*) configuration. As previously, the bulkier substituent (pyranosidic ring) is in more favorable equatorial orientation with a '*trans*-decalin' transition state. For the minor isomer **19b**, the alkylation operated in C-4 axial position with C-7 (*S*) configuration, which implied a *cis*-decalin transition state in which the pyranosidic ring is in axial orientation. This could be explained by a chelation of the indium atom with an oxygen atom in **18**

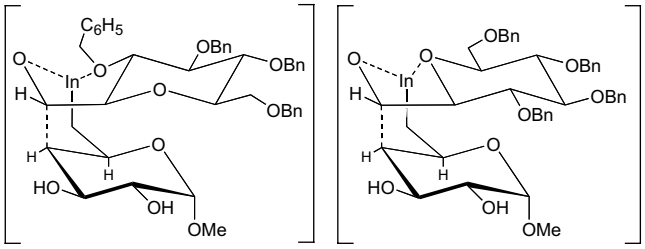
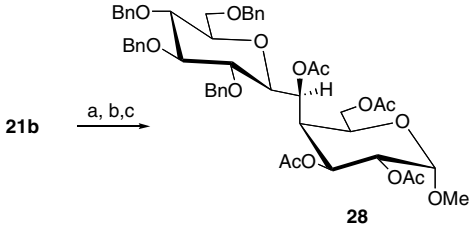


Chart 2. Possible transition states with chelation of indium atom in the reaction with **18**.



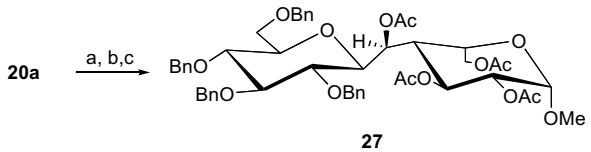
Scheme 4. Reagents and conditions: (a) BH_3, THF; (b) H_2O_2, phosphate buffer (0.5 M, pH 7.0); (c) Ac_2O, pyridine; 83% overall yield.

(either O-3′ or endocyclic oxygen), which cannot operate if the sugar is in equatorial orientation (Chart 2). We have in fact, already found such chelation in previous cases.[3] This axial orientation of the bulkier substituent in the transition state can be correlated with the moderate yield (45%) obtained with the β-C-linked 2,3,4,6-tetra-*O*-benzyl-β-D-glucosyl aldehyde **18** in comparison to that of previous aldehydes.

In fact, all these allylation reactions led to unsaturated analogues of *C*-branched sugars or *C*-disaccharides, which need further elaboration to saccharides by hydroboration of the exocyclic double bond. As an example, we focused on the functionalization of **20a** and **21b** to disaccharides. Thus, hydroboration of **20a** with diborane–tetrahydrofuran followed by oxidation with hydrogen peroxide[11] in phosphate buffer (0.5 M; pH 7.0) and acetylation (Ac_2O–pyridine) led to a protected *C*-disaccharide derivative [D-Glc-β-(1→4)-*C*-L-Ido] **27** as a single diastereoisomer, in 91% overall yield (Scheme 3).

The stereochemistry of the *C*-disaccharide **27** resulted from the attack of the electrophile onto the double bond on the opposite side of the C-1 and C-4 substituents. Moreover, steric hindrance of the 2,3,4,6-tetra-*O*-benzyl-β-D-glucosyl moiety could explain the complete diastereoselectivity of this reaction.

In the same way, hydroboration of compound **21b** with diborane–tetrahydrofuran followed by oxidation with hydrogen peroxide in phosphate buffer (0.5 M; pH 7.0) and then acetylation gave the protected *C*-disaccharide derivative [D-Glc-β-(1→4)-*C*-D-Gal] **25** in 83% yield as a single diastereoisomer (Scheme 4). Here the formation of **25** could be explained by attack of the electrophile at C-5 on the opposite side of the 2,3,4,6-tetra-*O*-benzyl-β-D-glucosyl moiety located at the axial C-4 position.



Scheme 3. Reagents and conditions: (a) BH_3, THF; (b) H_2O_2, phosphate buffer (0.5 M, pH 7.0); (c) Ac_2O, pyridine; 91% overall yield.

In conclusion, we have reported an efficient synthesis of 4-*C*-branched monosaccharides and (1→4)-*C*-disaccharides in aqueous media through indium-promoted Barbier-type allylations. Particularly, we have described an effective access to protected Glc-β-(1→4)-*C*-Ido and Glc-β-(1→4)-*C*-Gal derivatives from methyl α-D-glucopyranoside. The synthesis of these new compounds exemplifies the application of this recently developed method.

3. Experimental

3.1. General methods and materials

All moisture sensitive reactions were performed under argon using oven-dried glassware. If necessary, solvents were dried and distilled prior to use. Reactions were monitored on E. Merck Silica Gel 60 F_{254} plates. Detection was performed using UV light, iodine and/or 5% H_2SO_4 in EtOH, followed by heating. Flash chromatography was performed on Silica Gel 6–35 μm. ^1H and ^{13}C NMR spectra were recorded at rt with Bruker AC 200, 250, or AM 400 spectrometers. Chemical shifts are reported in δ relative to Me_4Si for ^1H and ^{13}C NMR spectra (external reference for D_2O) and relative to the $CDCl_3$ resonance at 77.00 ppm for ^{13}C NMR spectra in $CDCl_3$. Melting points were measured on a Reichert apparatus and were uncorrected. Optical rotations were measured on an Electronic Digital Jasco DIP-370 Polarimeter. Mass spectra were recorded in positive mode on a Finnigan MAT 95 S spectrometer using electrospray ionization. Elemental analyses were performed at the Service Central de Microanalyses du CNRS (Gif-sur-Yvette, France).

3.2. Methyl 2,3-di-*O*-acetyl-4-deoxy-α-D-*threo*-hex-4-enopyranoside (5)

Sodium borohydride (0.120 g, 3.2 mmol) was added to a cooled (0 °C) soln of **4** (0.816 g, 3.2 mmol) in MeOH (20 mL). The mixture was stirred at 0 °C for 10 min, then

quenched with water, and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$), then concentrated. Flash chromatography of the residue (1:1 petroleum ether–EtOAc) gave **5** (0.750 g, 91%) as a colorless oil. $[\alpha]_D$ +277 (*c* 1.0, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.34 (m, 1H, H-3), 5.06 (dd, 1H, $J_{2,1}$ 2.5, $J_{2,3}$ 7 Hz, H-2), 4.98–4.92 (br s, 2H, H-1, H-4), 3.99 (m, 2H, H-6, H-6′), 3.47 (s, 3H, CH_3O), 2.07, 2.01 (2s, 6H, acetyl); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.0 (C=O), 169.9, 152.6 (C-5), 97.2, 94.8 (C-1, C-4), 68.9, 66.6 (C-2, C-3), 60.8 (C-6), 56.0 (CH_3O), 20.5, 20.3 (acetyl). Anal. Calcd for $C_{11}H_{16}O_7$: C, 50.77; H, 6.20; O, 43.03. Found: C, 50.48; H, 6.17; O, 43.49.

3.3. Methyl 2,3-di-*O*-acetyl-6-bromo-4,6-dideoxy-α-D-*threo*-hex-4-enopyranoside (6)

PPh_3 (0.906 g, 3.46 mmol) and CBr_4 (1.05 g, 3.17 mmol) were added to a cooled (−78 °C) soln of **5** (0.750 g, 2.9 mmol) in CH_2Cl_2 (30 mL). The suspension was stirred at 0 °C for 2 h, then quenched with satd aq $NaHCO_3$, and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) then concentrated. Flash chromatography of the crude residue (1:4 petroleum ether–EtOAc) gave **6** (0.872 g, 93%) as white crystals: mp 89 °C (Et_2O); $[\alpha]_D$ +265 (*c* 1.1, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.45 (dd, 1H, $J_{3,4}$ 2.9, $J_{3,2}$ 7.5 Hz, H-3), 5.13 (m, 2H, H-4, H-2), 5.04 (d, 1H, $J_{1,2}$ 2.5 Hz, H-1), 3.84 (m, 2H, H-6, H-6′), 3.58 (s, 3H, CH_3O), 2.12, 2.07, (2s, 6H, acetyl); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.3 (C=O), 170.2, 148.9 (C-5), 99.8, 98.0 (C-1, C-4), 69.0, 66.9 (C-2, C-3), 56.8 (CH_3O), 29.5 (C-6), 21.0, 20.8 (acetyl). Anal. Calcd for $C_{11}H_{15}BrO_6$: C, 40.89; H, 4.68; O, 29.71. Found: C, 40.76; H, 4.55; O, 29.96.

3.4. Methyl 6-bromo-4,6-dideoxy-α-D-*threo*-hex-4-enopyranoside (7)

LiOH (0.453 g, 10.8 mmol) was added to a soln of **6** (0.872 g, 2.7 mmol) in a 3:1 mixture of MeOH–water (24 mL). The suspension was stirred at rt for 5 min, then quenched with aq HCl (1.5 M), and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) then concentrated. Flash chromatography of the residue (EtOAc) gave **7** (0.626 g, 97%) as a colorless oil, which decomposed slowly when kept at rt. ^1H NMR (250 MHz, $CDCl_3$): δ 5.09 (d, 1H, $J_{1,2}$ 2.5 Hz, H-1), 4.98 (d, 1H, $J_{4,3}$ 3.0 Hz, H-4), 4.27 (dd, 1H, $J_{3,4}$ 3.0, $J_{3,2}$ 7.5 Hz, H-3), 3.85 (m, 2H, H-6, H-6′), 3.71 (dd, 1H, $J_{2,1}$ 2.5, $J_{2,3}$ 7.5 Hz, H-2), 3.59 (s, 3H, CH_3O), 2.85 (br s, 2H, OH); ^{13}C NMR (63 MHz, $CDCl_3$): δ 147.2 (C-5), 103.5, 100.1 (C-1, C-4), 71.3, 67.0 (C-2, C-3), 59.6 (CH_3O), 30.2 (C-6). ESIHRMS (positive ion mode): calcd for $C_7H_{11}O_4BrNa$: 260.97385, found: *m*/*z* 260.97411.

3.5. Methyl 4-*C*-[(*S*)-1-phenyl-1-hydroxymethyl]-4,6-dideoxy-α-D-*xylo*-hex-5-enopyranoside (8) and methyl 4,6-deoxy-α-L-*threo*-hex-5-enopyranoside (26)

Indium powder (115 mg, 1 mmol) was added to a soln of **7** (120 mg, 0.5 mmol) and benzaldehyde (153 μL, 1.5 mmol) in a mixture of THF (1 mL) and phosphate buffer (pH 7, 0.11 M, 0.5 mL). After stirring for 1.5 h, the mixture was neutralized with satd aq $NaHCO_3$. The suspension was filtered over Celite, washed with EtOH, and the filtrate was concentrated. Flash chromatography (1:4 petroleum ether–EtOAc) of the residue gave **8** (0.114 g, 86%) as white crystals followed by **26** (7 mg, 9%) as a colorless oil.

Compound **8**: mp 98 °C (Et_2O); $[\alpha]_D$ +99 (*c* 1.1, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): δ 7.52–7.14 (m, 5H, Ar), 5.25 (br s, 1H, H-1), 4.81 (d, 1H, $J_{7,4}$ 4.0 Hz, H-7), 4.68 (s, 1H, H-6′), 4.39 (s, 1H, H-6), 4.20 (t, 1H, $J_{3,2} = J_{3,4}$ 8.5 Hz, H-3), 3.71 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 8.5 Hz, H-2), 3.44 (s, 3H, CH_3O), 2.82 (dd, 1H, $J_{4,7}$ 4.0, $J_{4,3}$ 8.5 Hz, H-4); ^{13}C NMR (63 MHz, $CDCl_3$): δ 152.0 (C-5), 142.2, 128.2, 126.9, 125.9 (Ar), 100.2, 99.7 (C-1, C-6), 72.8, 70.0, 69.1 (C-2, C-3, C-7), 55.7 (CH_3O), 51.4 (C-4). Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81; O, 30.04. Found: C, 63.21; H, 6.92; O, 30.25.

Compound **26**: $[\alpha]_D^{29}$ +84 (*c* 0.8, MeOH); ^1H NMR (250 MHz, $CDCl_3$): δ 4.86 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.54 (d, 1H, $J_{6',5}$ 1.0 Hz, H-6′), 4.37 (d, 1H, $J_{6,5}$ 1.0 Hz, H-6), 3.89 (ddd, 1H, $J_{3,4'}$ 5.5, $J_{3,2}$ 8.5, $J_{3,4}$ 10.5 Hz, H-3), 3.55 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 8.5 Hz, H-2), 3.47 (s, 3H, CH_3O), 2.69 (dd, 1H, $J_{4',3}$ 5.5, J_{gem} 13.5 Hz, H-4′), 2.25 (tdd, 1H, $J_{4,6} = J_{4,6'}$ 1.0, $J_{4,3}$ 10.5, J_{gem} 13.5 Hz, H-4); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 153.06 (C-5), 100.18 (C-1), 97.22 (C-6), 73.73, 68.22 (C-2, C-3), 55.56 (CH_3O), 36.17 (C-4); ESIMS (positive ion mode): calcd for $C_7H_{12}O_4$: ($M+Na^+$), 183.0; found: *m*/*z* 183.0. Anal. Calcd for $C_7H_{12}O_4$: C, 51.49; H, 7.55. Found: C, 51.78; H, 7.53.

3.6. 4-*C*-Acetyl-5-(*S*)-*C*-phenyl-4-deoxy-α,β-L-arabino-pyranose (9α,β)

A soln of **8** (0.053 g, 0.199 mmol) was stirred at rt in aq HCl (0.1 M, 3 mL) for 5 min, then quenched with satd aq $NaHCO_3$, and extracted with CH_2Cl_2. The organic phase was dried ($MgSO_4$) and concentrated. Flash chromatography of the residue (EtOAc) gave a 1:3 mixture of the two adducts **9α,β** (0.045 g, 90%) as a colorless oil.

Compound **9α** (25%): ^1H NMR (250 MHz, $CDCl_3$): δ 7.46–7.21 (m, 5H, Ar), 5.44 (d, 1H, $J_{5,4}$ 3.0 Hz, H-5), 5.37 (d, 1H, $J_{1,2}$ 3.0 Hz, H-1), 4.33–4.20 (m, 2H, H-2, H-3), 3.82 (m, 1H, H-4), 1.64 (s, 3H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 217.3 (C=O), 140.2, 131.6, 131.0, 128.3 (Ar), 95.6 (C-1), 76.8, 74.8, 72.3 (C-2, C-3, C-5), 61.3 (C-4), 37.8 (CH_3CO).

Compound **9β** (75%): ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.46–7.21 (m, 5H, Ar), 4.91 (d, 1H, $J_{5,4}$ 2.9 Hz, H-5), 4.66 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), 4.10–3.94 (m, 2H, H-2, H-3), 3.74 (m, 1H, H-4), 1.61 (s, 3H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 216.1 (C=O), 140.2, 131.6, 131.0, 128.3 (Ar), 100.0 (C-1), 75.0, 74.8, 71.2 (C-2, C-3, C-5), 61.4 (C-4), 37.3 (CH_3CO).

3.7. 1,2,3-Tri-*O*-acetyl-4-*C*-acetyl-5-(*S*)-*C*-(phenyl)-4-deoxy-α,β-L-arabinopyranose (10α,β)

A soln of **9α,β** (45 mg, 0.18 mmol) in a mixture of 1:2 Ac_2O–pyridine (1 mL) was kept overnight at rt and concentrated. Flash chromatography of the residue (1:4 petroleum ether–EtOAc) gave **10α,β** (66 mg, 98%) as a 1:3 mixture of α and β anomers. Anal. Calcd for $C_{19}H_{22}O_8$: C, 60.31; H, 5.86; O, 33.83. Found: C, 60.29; H, 5.89; O, 33.17.

Compound **10α** (25%): ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H, Ar), 6.84 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 6.08 (dd, 1H, $J_{2,1}$ 4.0, $J_{2,3}$ 10.0 Hz, H-2), 5.54 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 10.0 Hz, H-3), 5.36 (d, 1H, $J_{5,4}$ 3.5 Hz, H-5), 3.81 (dd, 1H, $J_{4,5}$ 3.5, $J_{4,3}$ 6.0 Hz, H-4), 2.35, 2.04, 2.03, 1.51 (4s, 12H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 204.8, 170.3, 169.6, 168.8 (C=O), 136.3, 128.2, 125.5 (Ar), 90.1 (C-1), 71.4, 68.7, 66.6 (C-2, C-3, C-5), 55.8 (C-4), 34.0 (CH_3CO), 20.9, 20.7, 20.5 (CH_3COO). Compound **10β** (75%): ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.40–7.22 (m, 5H, Ar), 6.00 (dd, 1H, $J_{1,2}$ 8.5, $J_{2,3}$ 9.5 Hz, H-2), 5.79 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 5.27 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 9.5 Hz, H-3), 5.00 (d, 1H, $J_{5,4}$ 3.5 Hz, H-5), 3.72 (dd, 1H, $J_{4,5}$ 3.5, $J_{4,3}$ 6.0 Hz, H-4), 2.15, 2.06, 2.02, 1.55 (4s, 12H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 204.2, 170.2, 169.3 (C=O), 136.0, 128.6, 125.3 (Ar), 92.8 (C-1), 74.6, 72.2, 68.4 (C-2, C-3, C-5), 55.8 (C-4), 33.7, 20.8, 20.6 (CH_3CO).

3.8. Methyl 2,3-di-*O*-acetyl-4-*C*-[acetoxymethyl]-4,6-dideoxy-α-D-*xylo*-hex-5-enopyranoside (12a) and methyl 2,3-di-*O*-acetyl-4-*C*-[acetoxymethyl]-4,6-dideoxy-β-L-*arabino*-hex-5-enopyranoside (12b)

Indium powder (115 mg, 1 mmol) was added to a soln of **7** (120 mg, 0.5 mmol) and formaldehyde (37% in water, 120 μL, 1.5 mmol) in a mixture of THF (1 mL) and phosphate buffer (pH 7, 0.15 M, 0.38 mL). After stirring for 3 h, the mixture was neutralized with satd aq $NaHCO_3$. The suspension was filtered over Celite, washed with EtOH and the filtrate was concentrated. Flash chromatography (EtOAc) of the residue gave a mixture of **11a,b** (65 mg, 73%) as a colorless oil, which was dissolved in 1:2 Ac_2O–pyridine (3 mL). After 15 h, the solvents were coevaporated with toluene, then flash chromatography (3:1 petroleum ether–EtOAc) of the residue gave an inseparable 16:9 mixture of **12a** and **12b** (111 mg, 96%) as a colorless oil followed by **26** (6 mg, 7%) as a colorless oil. Anal. Calcd for $C_{14}H_{20}O_8$: C, 53.16; H, 6.37; O, 40.47. Found: C, 52.86; H, 6.42; O, 40.48.

Compound **12a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.39 (dd, 1H, $J_{3,4}$ 9.0, $J_{3,2}$ 10.2 Hz, H-3), 5.05–4.94 (m, 2H, H-1, H-2), 4.79 (d, 1H, H-6′), 4.59 (m, 1H, H-6), 4.29 (dd, 1H, $J_{7',4}$ 6.0, J_{gem} 12.5 Hz, H-7′), 4.21 (dd, 1H, $J_{7,4}$ 4.0, J_{gem} 12.5 Hz, H-7), 3.45 (s, 3H, CH_3O), 2.72 (m, 1H, H-4), 2.11–2.07 (m, 9H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.7, 170.2, 169.7, 152.0 (C-5), 98.4 (C-6), 97.6 (C-1), 71.8, 66.9 (C-2, C-3), 60.1 (C-7), 55.4 (CH_3O), 43.2 (C-4), 20.7 (CH_3CO).

Compound **12b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.43 (dd, 0.5H, $J_{3,4}$ 6.5, $J_{3,2}$ 10.0 Hz, H-3), 5.11 (dd, 0.5H, $J_{2,1}$ 6.0, $J_{2,3}$ 10.0 Hz, H-2), 5.05–4.94 (m, 2.5H, H-1), 4.70 (m, 1H, H-6′), 4.50 (m, 1H, H-6), 4.27 (m, 2H, H-7, H-7′), 3.45 (s, 3H, CH_3O), 3.22 (m, 1H, H-4), 2.11–2.07 (m, 12H, CH_3CO); ^{13}C NMR (63 MHz, $CDCl_3$): δ 169.7, 170.1, 170.5 (C=O), 151.9 (C-5), 99.9 (C-6), 97.7 (C-1), 68.3, 67.6 (C-2, C-3), 61.3 (C-7), 55.5 (CH_3O), 42.0 (C-4), 20.7 (CH_3CO).

3.9. Methyl 2,3-di-*O*-acetyl-4-*C*-[1-(*S*)-1-acetoxymethyl-1-(3′-*O*-benzyl-1′,2′-di-*O*-isopropylidene-4′-(*S*)-*C*-α-D-threofuranosyl)]-4,6-dideoxy-α-D-*xylo*-hex-5-enopyranoside (15)

Indium powder (69 mg, 2 mmol) was added to a soln of **7** (72 mg, 0.3 mmol) and aldehyde **13** (0.25 g, 0.9 mmol) in a mixture of THF (0.6 mL) and phosphate buffer (pH 7, 0.11 M, 0.3 mL). After stirring for 1.5 h, the mixture was neutralized with satd aq $NaHCO_3$. The suspension was filtered over Celite, washed with EtOH and the filtrate was concentrated. Flash chromatography (3:1–1:3 petroleum ether–EtOAc) gave starting aldehyde **13** (170 mg) along with **14** (75 mg, 57%) as a colorless oil followed by **26** (9 mg, 18%) as a colorless oil. Compound **14** was dissolved in 1:2 Ac_2O–pyridine (3 mL) and stirred overnight. The solvents were coevaporated with toluene, then flash chromatography (3:1 petroleum ether–EtOAc) of the residue gave **15** (96 mg, 99%) as a colorless oil; $[\alpha]_D$ +52 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.48–7.32 (m, 5H, Ar), 5.97 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.69 (dd, 1H, $J_{7,4}$ 3.0, $J_{7,4'}$ 9.0 Hz, H-7), 5.20 (t, 1H, $J_{3,2} = J_{3,4}$ 10.0 Hz, H-3), 4.93 (br s, 1H, H-6′), 4.87 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.81 (br s, 1H, H-6), 4.79 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.0 Hz, H-2), 4.74 (d, 1H, J_{gem} 11.5 Hz, $PhCH_2$), 4.69 (d, 1H, $J_{2',1'}$ 4.0 Hz, H-2′), 4.62 (dd, 1H, $J_{4',3'}$ 3.5, $J_{4',7}$ 9.0 Hz, H-4′), 4.41 (d, 1H, J_{gem} 11.5 Hz, $PhCH_2$), 3.89 (d, 1H, $J_{3',4'}$ 3.5 Hz, H-3′), 3.42 (s, 3H, CH_3O), 2.38 (dd, 1H, $J_{4,7}$ 3.0, $J_{4,3}$ 10.0 Hz, H-4), 2.07, 2.03, 1.99 (3s, 9H, CH_3CO), 1.48, 1.33 (2s, 6H, $C(CH_3)_2$); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.3, 169.8, 169.5 (CH_3CO), 149.9 (C-5), 136.3, 128.6, 128.3 (Ar), 111.6 ($C(CH_3)_2$), 104.8 (C-1′), 102.0 (C-1), 98.0 (C-6), 81.7, 80.6, 78.5 (C-2′, C-3′, C-4′), 72.7 ($PhCH_2$),

71.4, 66.5, 65.7 (C-2, C-3, C-7), 55.6 (CH_3O), 44.9 (C-4), 26.6, 26.1 ($C(CH_3)_2$), 20.9, 20.7, 20.6 (CH_3CO). Anal. Calcd for $C_{28}H_{36}O_{12}$: C, 59.57; H, 6.43; O, 34.00. Found: C, 59.32; H, 6.53; O, 34.28.

3.10. 4-*C*-Acetyl-5-(*S*)-*C*-[3′-*O*-benzyl-1′,2′-di-*O*-isopropylidene-4′-(*S*)-*C*-α-D-threofuranosyl]-4-deoxy-α,β-L-arabinopyranose (17α,β)

A soln of **14** (0.092 g, 0.21 mmol) was stirred at rt in aq HCl (0.1 M, 2 mL) for 30 min, then quenched with a satd aq $NaHCO_3$ and extracted with CH_2Cl_2. The organic phase was then dried ($MgSO_4$) and concentrated. Flash chromatography (1:4 petroleum ether–EtOAc) of the residue gave **16α,β** (11:9, 77 mg, 86%) as a colorless oil. This oil was then dissolved in 1:2 Ac_2O–pyridine (1.5 mL), stirred overnight and coevaporated with toluene. Flash chromatography (4:1–3:2 petroleum ether–EtOAc) of the residue gave a 11:9 mixture of α and β anomers **17α,β** (0.093 g, 94%) as a colorless oil. Anal. Calcd for $C_{27}H_{34}O_{12}$: C, 58.90; H, 6.22; O, 34.88. Found: C, 58.96; H, 6.41; O, 34.73.

Compound **17α**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.48–7.34 (m, 5H, H-Ar), 6.45 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 5.90 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.61 (dd, 1H, $J_{2,1}$ 4.0, $J_{2,3}$ 10.5 Hz, H-2), 5.38 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 10.5 Hz, H-3), 4.73 (d, 1H, J_{gem} 11.5 Hz, $CH_2C_6H_5$), 4.69 (dd, 1H, $J_{2',3'}$ 1.0, $J_{2',1'}$ 4.0 Hz, 2′-H), 4.44 (d, 1H, J_{gem} 11.5 Hz, $CH_2C_6H_5$), 4.34 (dd, 1H, $J_{5,4}$ 2.5, $J_{5,4'}$ 7.0 Hz, H-5), 4.19 (dd, 1H, $J_{4',3'}$ 4.5, $J_{4',5}$ 7.0 Hz, H-4′), 3.89 (dd, 1H, $J_{3',2'}$ 1.0, $J_{3',4'}$ 4.5 Hz, H-3′), 3.28 (dd, 1H, $J_{4,5}$ 2.5, $J_{4,3}$ 6.0 Hz, H-4), 2.06, 1.98, 1.91 (3s, 12H, CH_3 acetyl), 1.45 (s, 3H, CH_3), 1.33 (s, 3H, CH_3). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 205.3 (CO, ketone), 169.8, 169.6, 168.9 (CO, acetyl), 136.3, 129.1–128.3 (Ar), 112.7 ($(CH_3)_2C$), 105.0 (C-1′), 89.8 (C-1), 82.3, 81.0, 79.1 (C-2′, C-3′, C-4′), 71.5 ($CH_2C_6H_5$), 70.2, 68.0, 66.7 (C-2, C-3, C-5), 50.8 (C-4), 33.3 (CH_3, ketone), 27.1, 26.7 (isopropyl), 20.8, 20.7, 20.5 (acetyl).

Compound **17β**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.48–7.34 (m, 5H, Ar), 5.94 (d, 1H, $J_{1',2'}$ 4.0 Hz, H-1′), 5.72 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 5.55 (dd, 1H, $J_{2,1}$ 8.5, $J_{2,3}$ 10.0 Hz, H-2), 5.17 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 10.0 Hz, H-3), 4.72 (d, 1H, J_{gem} 11.5 Hz, $CH_2C_6H_5$), 4.64 (d, 1H, $J_{2',1'}$ 4.0 Hz, H-2′), 4.43 (d, 1H, J_{gem} 11.5 Hz, $CH_2C_6H_5$), 4.13 (dd, 1H, $J_{3',4'}$ 3.5, $J_{4',5}$ 8.5 Hz, H-4′), 4.01 (dd, 1H, $J_{5,4}$ 2.5, $J_{5,4'}$ 8.5 Hz, H-5), 3.92 (d, 1H, $J_{4',3'}$ 3.5 Hz, H-3′), 3.08 (dd, 1H, $J_{4,5}$ 2.5, $J_{4,3}$ 6.0 Hz, H-4), 2.10, 2.09, 2.03, 2.02 (4s, 12H, CH_3CO), 1.44 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); ^{13}C NMR (63 MHz, $CDCl_3$): δ 205.0 (CO ketone), 169.5, 168.8 (acetyl), 136.5, 128.4–128.7 (Ar), 112.2 ($(CH_3)_2C$), 105.2 (C-1′), 92.7 (C-1), 81.8, 81.0, 79.0 (C-2′, C-3′, C-4′), 73.0 ($CH_2C_6H_5$), 71.7, 71.2, 69.0 (C-2, C-3, C-5), 51.8 (C-4), 32.9 (CH_3 ketone), 26.9, 26.4 (CH_3), 20.9, 20.6 (acetyl).

3.11. Methyl 2,3-di-*O*-acetyl-4-*C*-[(*S*)-1-*O*-acetyl-1-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-methyl]-4,6-dideoxy-α-D-*xylo*-hex-5-enopyranoside (20a), methyl 2,3-di-*O*-acetyl-4-*C*-[(*S*)-1-hydroxy-1-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-methyl]-4,6-dideoxy-α-D-*arabino*-hex-5-enopyranoside (21b)

Indium powder (53 mg, 0.46 mmol) was added to a soln of **7** (55 mg, 0.23 mmol) and aldehyde **18** (0.38 g, 0.69 mmol) in a mixture of THF (0.46 mL) and phosphate buffer (pH 7, 0.11 M, 0.23 mL). After stirring for 2 h, the mixture was neutralized with satd aq $NaHCO_3$. The suspension was filtered over Celite, washed with EtOH, and the filtrate was concentrated. Flash chromatography (3:1–1:3 petroleum ether–EtOAc) of the residue gave the starting aldehyde (248 mg, 0.45 mmol) followed by a 16:9 mixture of **19a** and **19b** (74 mg, 45%), and finally by **26** (11 mg, 30%) as a colorless oil.

Compounds **19a**,**b** (64:36): ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.07 (t, 0.55H, $J_{4,3} = J_{4,7}$ 6.0 Hz, H-4(b)), 2.67 (t, 1H, $J_{4,3} = J_{4,7} = 6.0$ Hz, H-4(a)); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 154.5 (C-5(b)), 153.5 (C-5(a)), 138.5–137.0, 128.9–127.2 (Ar), 100.6 (C-1(a)), 100.2–100.0 (C-1(b), C-6(b)), 98.7 (C-6(a)), 87.2 (C-1′(b)), 87.1 (C-1′(a)), 75.5, 75.4, 75.3, 75.0, 74.9, 73.4, 73.3 (CH_2 benzyl (a,b)), 72.15, 72.0, 70.5, 69.3, 69.2, 68.65 (C-2(a,b), C-3(a,b), C-7(a,b), C-6′(a,b)), 56.0 (OCH_3 (a)), 55.8 (OCH_3 (b)), 48.3 (C-4(a)), 48.0 (C-4(b)).

An aliquot of the 19:9 mixture of **19a**,**b** (50 mg, 0.07 mmol) was added to a mixture of Ac_2O (0.5 mL) and pyridine (1 mL). After 16 h at rt, the reaction mixture was concentrated and flash chromatography of the residue (4:1–3:2 petroleum ether–EtOAc) gave first **20a** (51 mg, 89%) followed by the partially acetylated compound **20b** (25 mg, 81%). This latter was then fully acetylated in 2:1 pyridine–Ac_2O (1.5 mL) at 40 °C for 12 h. The mixture was concentrated, and flash chromatography of the residue (3:1 petroleum ether–EtOAc) gave **21b** (25 mg, 95%) as a colorless oil.

Compound **20a**: $[\alpha]_D$ +33 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45–7.15 (m, 20H, H-Ar), 5.63 (dd, 1H, $J_{7,1}$ 3.0, $J_{7,4}$ 8.5 Hz, H-7), 5.37 (dd, 1H, $J_{3,4}$ 5.5, $J_{3,2}$ 9.0 Hz, H-3), 5.05–4.50 (m, 11H, 1-H, 2-H, H-6b, CH_2 benzyl), 4.37 (s, 1H, H-6a), 3.85–3.37 (m, 10H, CH_3O, H-1′, H-2′, H-3′, H-4′, H-5′, 2H-6′), 3.04 (dd, 1H, $J_{4,3}$ 5.5, $J_{4,7}$ 8.5 Hz, H-4), 2.06, 1.91, 1.82 (3s, 9H, Ac); ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.2, 169.5 (CO), 151.5 (C-5), 138.4–138.1, 128.3–127.5 (Ar), 98.5 (C-6), 97.7 (C-1), 87.4 (C-1′), 79.3, 79.2, 78.3, 76.5 (C-2′, C-3′, C-4′, C-5′), 75.6, 75.0, 74.4, 73.2 (CH_2 benzyl), 71.8, 70.9, 66.9 (C-2, C-3, C-7), 68.6 (C-6′), 56.0 (CH_3O), 46.2 (C-4), 20.9, 20.7, 20.6 (CH_3 acetyl). Anal. Calcd for $C_{48}H_{54}O_{13}$: C, 68.72; H, 6.49; O, 24.79. Found: C, 68.37; H, 6.55; O, 24.16.

Compound **20b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.49 (dd, 1H, $J_{2,3}$ 10.0, $J_{2,1}$ 3.0 Hz, H-2), 5.43 (dd, 1H, $J_{3,2}$

10.0, $J_{3,4}$ 5.0 Hz, H-3), 5.04 (d, 1H, $J_{1,2}$ 3.0 Hz, H-1), 3.15 (t, 1H, $J_{4,7} = J_{4,3}$ 5.0 Hz, H-4), 2.08 (s, 3H, CH_3), 1.88 (s, 3H, CH_3). ESIMS (positive ion mode): calcd for $C_{46}H_{52}O_{12}$: ($M+Na^+$), 819.3; found: *m*/*z* 819.4.

Compound **21b**: $[\alpha]_D^{29}$ +63 (*c* 0.9, CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$): δ 7.45–7.15 (m, 20H, Ar), 5.78 (d, 1H, *J* 8.5 Hz, H-7), 5.48 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 10.5 Hz, H-3), 5.35 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ 10.5 Hz, H-2), 5.01 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 4.99–4.51 (m, 10H, H-6a, H-6b, CH_2 benzyl), 3.80–3.32 (m, 11H, CH_3O, H-1′, H-2′, H-3′, H-4′, H-5′, H-6a′, H-6b′, H-4), 2.11, 2.08, 1.90 (3s, 9H, acetyl); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.2–169.8 (acetyl), 151.4 (C-5), 138.4–138.0, 128.5–127.5 (Ar), 102.3 (C-6), 98.0 (C-1), 87.7 (C-1′), 79.5, 78.35, 78.1 (C-2′, C-3′, C-4′, C-5′), 75.6, 75.0, 74.9, 73.6 (CH_2 benzyl), 69.0, 68.15 (C-2, C-3), 68.5 (C-6′), 66.5 (C-7), 55.5 (CH_3O), 44.7 (C-4), 21.05, 20.75, 20.7 (CH_3CO). ESIMS (positive ion mode): calcd for $C_{48}H_{54}O_{13}$: ($M+Na^+$), 861.3; found: *m*/*z* 861.0.

3.12. 1,2,3-Tri-*O*-acetyl-4-*C*-acetyl-(*S*)-5-*C*-[2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl]-4-deoxy-α,β-L-arabinopyranose (23α,β)

LiOH (16 mg, 0.4 mmol) was added to a soln of compound **20a** (55 mg, 65 μmol) in 2:1 MeOH–water (1.5 mL). After 30 min at rt, aq HCl (0.5 M) was added until neutrality and the mixture was extracted with CH_2Cl_2 then concentrated. Aq HCl (0.1 M, 1 mL) was added and the mixture was stirred for 2 h at rt. After neutralization with sat aq $NaHCO_3$, the mixture was extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated. A mixture of pyridine–Ac_2O (2:1, 3 mL) was then added and after 16 h at rt, the reaction mixture was concentrated. Flash chromatography of the residue (4:1–2:1 petroleum ether–EtOAc) gave a 12:8 mixture of α and β anomers **23α,β** (44 mg, 82%) as a colorless oil. ^1H NMR (250 MHz, $CDCl_3$): δ 7.42–7.10 (m, 32.8H, Ar), 6.46 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1(α)), 5.76 (dd, 1H, $J_{2,1}$ 4.0, $J_{2,3}$ 10.5 Hz, H-2(α)), 5.62 (dd, 0.64H, $J_{2,1}$ 8.5, $J_{2,3}$ 10.0 Hz, H-2(β)), 5.52 (d, 0.64H, $J_{1,2}$ 8.5 Hz, H-1(β)), 5.22 (dd, 1H, $J_{3,4}$ 6.0, $J_{3,2}$ 10.5 Hz, H-3(α)), 4.93–4.41 (m, 13.8H, H-3(β), CH_2Ph), 4.39 (t, 1H, $J_{5,4} = J_{5,1'}$ 2.5 Hz, H-5(α)), 3.78 (t, 0.64H, $J_{5,4} = J_{5,1'}$ 2.5 Hz, H-5(β)), 3.74–3.33 (m, 11.4H, H-1′(α,β), H-2′(α,β), H-3′(α,β), H-4′(α,β), H-5′(α,β), H-6a′(α,β), H-6b′(α,β)), 3.21 (dd, 1H, $J_{4,5}$ 2.5, $J_{4,3}$ 6.0 Hz, H-4(α)), 2.91 (dd, 0.64H, $J_{4,5}$ 2.5, $J_{4,3}$ 6.0 Hz, H-4(β)), 2.12, 2.11, 2.03, 2.00, 1.97, 1.96 (8s, 20H, CH_3COO and CH_3CO); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 205.15 (CO ketone (α)), 204.73 (CO ketone (β)), 169.87, 169.54, 169.25 (CO ester (β)), 169.69, 169.39, 168.77 (CO ester(α)), 138.16–137.55, 128.70–127.62 (Ar), 92.64 (C-1(β)), 90.33 (C-1(α)), 86,65 (C-1′(β)), 86.43 (C-1′(α)), 78.81, 78.45, 78.39, 78.41, 78.37, 77.68, 77.55, 77.46 (C-2′(α,β), C-3′(α,β), C-4′(α,β), C-5′(α,β)), 75.43, 74.83, 74.41, 74.27, 73.24 (CH_2Ph(α,β)), 74.22, 71.89, 71.08, 68.90, 68.77, 66.96, (C-2(α,β), C-3(α,β), C-5(α,β)), 68.60 (C-6′(β)), 68.43 (C-6′(α)), 49.17 (C-4(β)), 49.00 (C-4(α)), 34.08 (CH_3CO(α)), 33.69 (CH_3CO(β)), 20.74, 20.71, 20.66 (CH_3COO(β)), 20.79, 20.63, 20.51 (CH_3COO(α)). Anal. Calcd for $C_{47}H_{52}O_{13}$ (434.54): C, 68.43; H, 6.35; O, 25.21. Found: C, 68.58; H, 6.59; O, 25.21.

3.13. 1,2,3-Tri-*O*-acetyl-4-*C*-acetyl-(*S*)-5-*C*-[2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl]-4-deoxy-α,β-L-arabinopyranose (25α,β)

LiOH (11 mg, 0.27 mmol) was added to a soln of compound **21b** (37 mg, 44 μmol) in 2:1 MeOH–water (1.5 mL). After 30 min at rt, aq HCl (0.5 M) was added until neutrality and the mixture extracted with CH_2Cl_2 then concentrated. Aq HCl (0.1 M, 1 mL) was added and the mixture was stirred for 2 h at rt. After neutralization with satd aq $NaHCO_3$, the mixture was extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated. Pyridine–Ac_2O (2:1, 3 mL) was then added and after 16 h at rt, the reaction mixture was concentrated. Flash chromatography of the residue (4:1–2:1 petroleum ether–EtOAc) gave a 4:5 mixture of α and β anomers **25α,β** (24 mg, 77%) as a colorless oil. Anal. Calcd for $C_{47}H_{52}O_{13}$: C, 68.43; H, 6.35; O, 25.21. Found: C, 68.46; H, 6.61; O, 24.89.

Compound **25α**: ^1H NMR (250 MHz, $CDCl_3$): δ 7.42–7.15 (m, 20H, Ar), 6.21 (d, 1H, $J_{1,2}$ 3.5 Hz, H-1), 6.00 (t, 1H, $J_{3,2} = J_{3,4}$ 8.0 Hz, H-3), 4.98 (dd, 1H, $J_{2,1}$ 3.5, $J_{2,3}$ = 8.0 Hz, H-2), 4.94.52 (m, 9H, H-5, CH_2Ph), 3.81–3.51, 3.31–3.21 (m, 7H, H-1′, H-2′, H-3′, H-4′, H-5′, H-6a′, H-6b′), 3.08 (dd, 1H, $J_{4,5}$ 6.5, $J_{4,3}$ 8.0 Hz, H-4), 2.16, 2.09, 2.05, 1.91 (4s, 12H, acetyl); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 202.71 (CO ketone), 170.19, 169.74, 169.41 (CO acetyl), 138.79, 138.66, 138.26, 138.19, 128.35, 127.19 (Ar), 91.07 (C-1), 86.75 (C-1′), 79.90, 79.25, 77.96, 77.19 (C-2′, C-3′, C-4′, C-5′), 75.40, 75.10, 74.97, 73.49 (CH_2Ph), 72.18, 71.03, 69.29 (C-2, C-3, C-5), 68.78 (C-6′), 55.10 (C-4), 29.71 (CH_3 ketone), 20.84, 20.79, 20.30 (acetyl).

Compound **25β**: ^1H NMR (250 MHz, $CDCl_3$): δ 7.40–7.12 (m, 20H, Ar), 6.32 (dd, 1H, $J_{3,4}$ 10.5, $J_{3,2}$ 9.5 Hz, H-3), 4.95 (dd, 1H, $J_{2,1}$ 8.5, $J_{2,3}$ 9.5 Hz, H-2), 4.91–4.58 (m, 9H, H-5, CH_2Ph), 4.12 (t, 1H, *J* 9.5 Hz), 3.92–3.77 (m, 3H), 3.63 (t, 1H, *J* 9.5 Hz), 3.25 (dd, 1H, $J_{4,3}$ 10.5, $J_{4,5}$ 7.5 Hz H-4), 3.39–3.17 (m, 2H), 2.18, 2.12, 1.97, 1.69 (4s, 12H, acetyl); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 203.98 (CO ketone), 168.86, 168.11, 167.64 (acetyl), 138.28, 138.11, 137.66, 137.50, 128.45–127.25 (Ar), 90.07 (C-1), 85.96 (C-1′), 79.53, 79.34, 78.88, 78.44 (C-2′, C-3′, C-4′, C-5′), 74.96, 74.46, 74.04, 73.79 (CH_2Ph), 72.15, 71.18, 69.38, (C-2, C-3, C-5), 68.68 (C-6′), 55.05 (C-4), 29.78 (CH_3 ketone), 20.65, 20.59, 20.30 (acetyl).

3.14. Methyl 2,3,6-tri-*O*-acetyl-4-*C*-[(*S*)-1-*O*-acetyl-1-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-methyl]-α-L-idopyranoside (27)

A 1 M soln of BH_3–THF complex in THF (0.20 mL, 0.2 mmol) was added to a cooled (0 °C) soln of **20a** (34 mg, 40 μmol) in THF (0.5 mL). The temperature was then raised to rt and after 1 h, a mixture of H_2O_2 (37% v/v, 0.2 mL) and phosphate buffer (0.5 M, pH 7, 1 mL) was added and the resulting mixture stirred for 1 h at rt. CH_2Cl_2 (10 mL) was then added and the mixture was washed with water, dried ($MgSO_4$), and concentrated. Then, 1:2 Ac_2O–pyridine (3 mL) was added and after stirring for 12 h, the reaction mixture was concentrated. Flash chromatography of the residue (4:1 petroleum ether–EtOAc) gave **27** (33 mg, 91%) as a colorless oil. $[\alpha]_D^{29}$ +36 (*c* 1.1, CH_2Cl_2); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.41–7.08 (m, 20H, Ar), 5.54 (dd, 1H, $J_{7,1'}$ 4.0, $J_{7,4}$ 3.5 Hz, H-7), 5.41 (dd, 1H, $J_{3,2}$ 10.5, $J_{3,4}$ 10.0 Hz, H-3), 5.03–4.36 (m, 13H, H-1, H-2, H-5, 2H-6, CH_2Ph), 3.44 (s, 3H, OMe), 3.78–3.37 (m, 7H, H-1′, H-2′, H-3′, H-4′, H-5′, 2H-6′), 2.53 (ddd, 1H, $J_{4,3}$ 10.0, $J_{4,5}$ 5.0, $J_{4,7}$ 3.5 Hz, H-4), 2.03, 1.98, 1.88, 1.87 (4s, 12H, acetyl), ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.75, 170.38, 170.18, 169.92 (CO), 138.17–137.92, 128.44–127.44 (Ar), 98.90 (C-1), 87.06 (C-1′), 79.05, 78.73, 78.36, 77.90 (C-2′, C-3′, C-4′, C-5′), 75.42, 74.93, 74.17, 73.21, 72.69 (CH_2Ph, C-5), 68.77 (C-6′), 67.27 (C-7), 65.85, 64.73, 63.73 (C-2, C-3, C-6), 56.76 (OMe), 43.21 (C-4), 20.94, 20.73, 20.57 (CH_3 acetyl). Anal. Calcd for $C_{50}H_{58}O_{15}$: C, 66.80; H, 6.50; O, 26.70. Found: C, 66.82; H, 6.66; O, 26.61.

3.15. Methyl 2,3,6-tri-*O*-acetyl-4-*C*-[(*S*)-1-*O*-acetyl-1-(2′,3′,4′,6′-tetra-*O*-benzyl-β-D-glucopyranosyl)-methyl]-α-D-galactopyranoside (28)

A 1 M soln of BH_3–THF complex in THF (0.1 mL, 0.1 mmol) was added to a cooled (0 °C) soln of **21b** (18 mg, 21 μmol) in THF (0.5 mL). The temperature was then raised to rt and after 1 h, a mixture of H_2O_2 (37% v/v, 0.1 mL) and phosphate buffer (0.5 M, pH 7, 1 mL) was added and the resulting mixture stirred for 1 h at rt. CH_2Cl_2 (10 mL) was then added and the mixture was washed with water, dried ($MgSO_4$), and concentrated. Then, Ac_2O–pyridine (1:2, 3 mL) was added and after stirring for 12 h, the reaction mixture was concentrated. Flash chromatography of the residue (4:1 petroleum ether–EtOAc) gave **28** (16 mg, 83%) as a colorless oil. $[\alpha]_D^{28}$ +88 (*c* 1.0, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.45–7.08 (m, 20H, Ar), 5.87 (d, 1H, $J_{7,4}$ 3.0 Hz, H-7), 5.49 (dd, 1H, $J_{1,2}$ 4.0, $J_{2,3}$ 10.5 Hz, H-2), 5.25 (dd, 1H, $J_{3,2}$ 10.5, $J_{3,4}$ 5.5 Hz, H-3), 5.01–4.36 (m, 12H, H-1, H-5, 2H-6, CH_2Ph), 3.34 (s, 3H, OCH_3), 3.75–3.29 (m, 6H, H-2′, H-3′, H-4′, H-5′, 2H-6′), 2.91 (d, 1H, $J_{1',2'}$ 9.5 Hz, H-1′), 2.81 (m, 1H, H-4), 2.17, 2.10, 2.02, 1.74 (4s, 12H, acetyl); ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 170.47, 170.35, 170.13, 169.87 (CO), 138.42, 138.35, 138.05, 137.96, 128.61–127.45 (Ar), 97.11 (C-1), 87.31 (C-1′), 81.91, 79.08, 78.25 (C-2′, C-3′, C-4′, C-5′), 75.66, 75.13, 75.00, 73.34 (CH_2Ph, C-5), 70.20, 69.46, 68.31, 65.88, 65.20 (C-2, C-3, C-6, C-7, C-6′), 54.82 (OCH_3), 42.30 (C-4), 21.26, 20.92, 20.83, 20.47 (CH_3 acetyl). Anal. Calcd for $C_{50}H_{58}O_{15}$: C, 66.80; H, 6.50; O, 26.70. Found: C, 66.81; H, 6.76; O, 26.66.

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