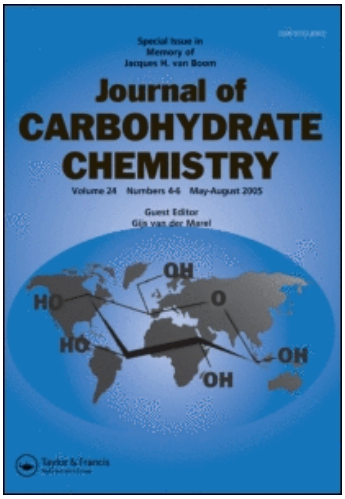

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Preparation of Building Blocks for Carba-Oligosaccharides: Some Protected 5a'-Carba-D-hexopyranosyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitols, and 5a,5a'-Dicarba Congeners Thereof

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Preparation of Building Blocks for Carba-Oligosaccharides: Some Protected 5a′-Carba-D-hexopyranosyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitols, and 5a,5a′-Dicarba Congeners Thereof

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Four configurational types of two protected *O*-linked (5a-carba-D-hexopyranosyl)-D-glucal and carba-D-glucal derivatives were prepared in order to provide versatile synthetic intermediates readily convertible into carba-oligosaccharides of biological interest. These compounds may also find application as donors for elongation of carba-oligosaccharide chains having *O*-linked carbahexopyranose residues at nonreducing ends.

Keywords Carbohydrate mimics, Carbasugars, Carba-oligosaccharides, 5a′-Carba- and 5a,5a′-dicarbadisaccharides, *O*-linked

INTRODUCTION

Recently, 5a-carbasugars[1–3] as well as *N*- and *O*-linked 5a′-carbadisaccharides have been shown to act as substrate analogs[4–6] and/or inhibitors[7] for some

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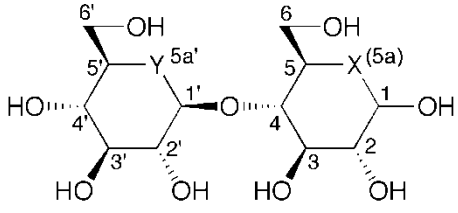
glycosyltransferases involved in oligosaccharide chain synthesis. Therefore, taking advantage of these distinct features of carba-oligosaccharides, much attention has been focused on the development of new glycosyltransferase inhibitors.

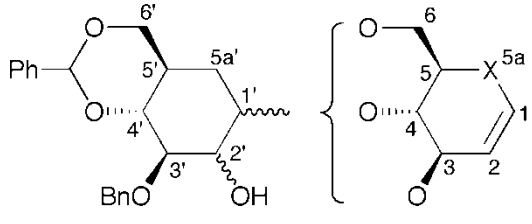
There are three types of carba-disaccharides; taking carbacellobiose as an example, type A is composed of two carbaglucopyranoses, and types B and C consist of one carba- and one true-glucopyranoses (Fig. 1). In the present study, versatile protected intermediates were prepared systematically, aiming at provision of conventional sequences for design of biologically interesting carba-oligosaccharides of types A and B, resistant to enzymatic hydrolysis. For strategic reasons the use of reactive D-glucal and carba-D-glucal as precursors for reducing ends is desirable to minimize the crucial glycosylation steps for elongation of oligosaccharide chains.

Attempts were made to prepare carba-disaccharides by allowing 1,2-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranose[8] (**1**) to couple with some protected glucal and carbaglucal derivatives **2**–**6** (Fig. 2).



Three types of *O*-linked carbadisaccharides:

A: 5a,5a'-Dicarba: X = Y = CH_2
B: 5a'-Carba: X = O, Y = CH_2
C: 5a-Carba: X = CH_2, Y = O



α,β-5aCGlc

α,β-5aCMan

X = O
X = CH_2

Protecting groups:
benzyls or benzylidene

Figure 1: Some protected 5a′-carba- and 5a,5a′-dicarba-disaccharide derivatives synthesized in the present study.

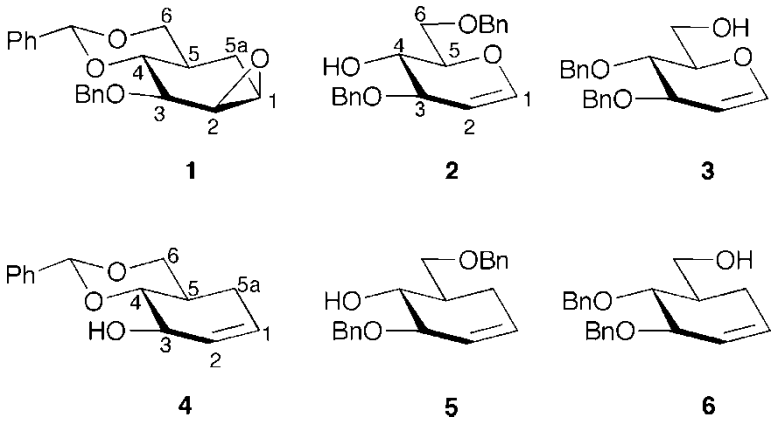


Figure 2: The 5a-carba-D-mannopyranosyl donor **1** and five acceptors **2**–**6**.

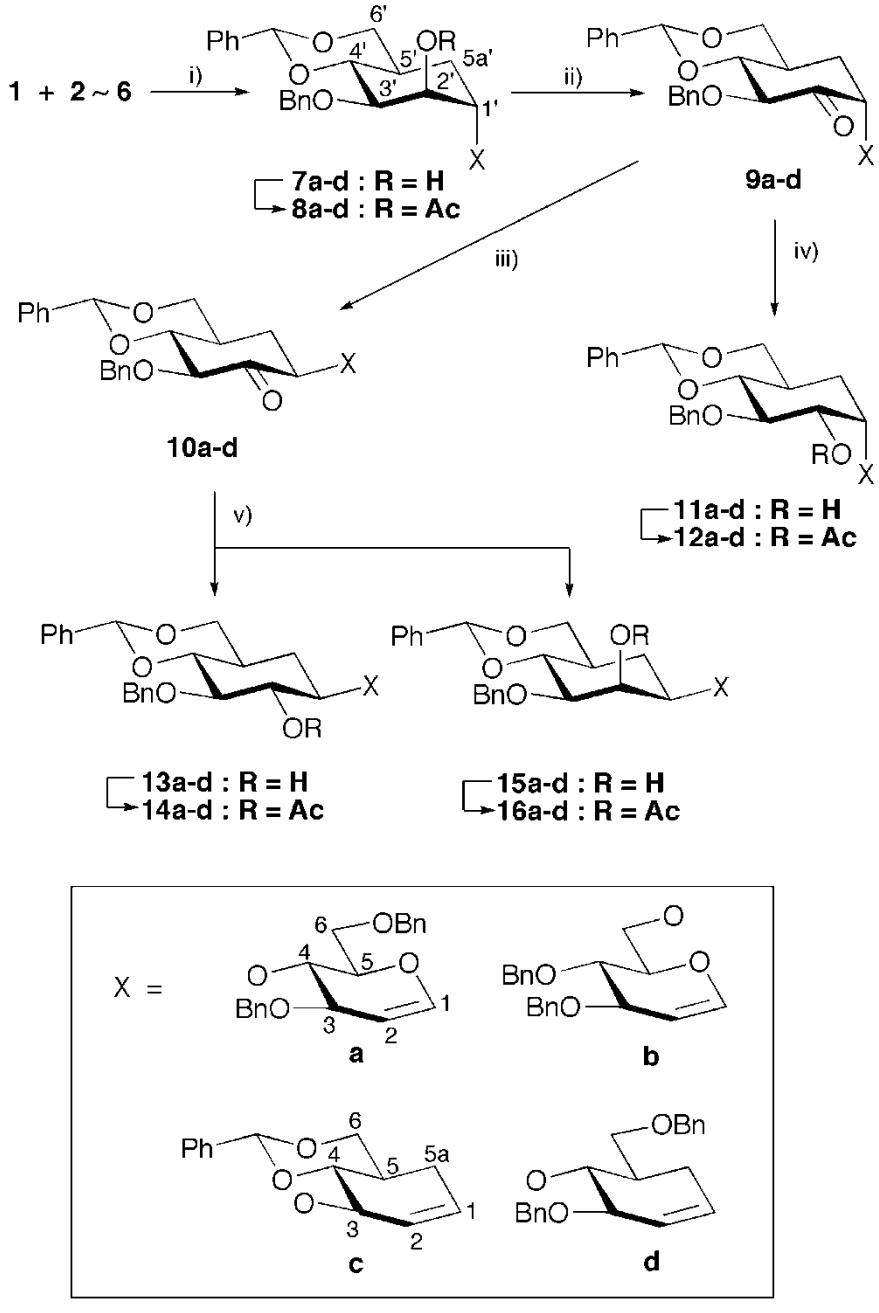
The configurations of 5a-carba-α-D-mannopyranose residues in the obtained condensates were then structurally modified through consecutive steps: first oxidation of the 2′-hydroxyl group, then base-catalyzed epimerization at C-1′, and finally selective reduction, to construct 5a-carba-α- and β-mannosyl and α-and β-glucosyl-glucal derivatives. These protected compounds may find use as acceptors or donors for chemical and/or biochemical preparation of complex carba-oligosaccharides of biological interest.

RESULTS AND DISCUSSION

Preparation of 5a′-Carbadisaccharide Derivatives

First, 4- and 6-*O*-unprotected derivatives of D-glucal were chosen as acceptors for coupling. Thus, 3,6-di-*O*-benzyl-D-glucal (**2**) was prepared from D-glucal under standard conditions.[9] Also 3,4-di-*O*-benzyl-D-glucal[10] (**3**) was generated from 6-*O*-(*tert*-butyldiphenylsilyl)-D-glucal.

Coupling of the epoxide **1** (1.5 molar equiv) and the oxide anion generated from compound **2** by treatment with an excess of NaH in dry DMF was carried out in the presence of 15-crown-5 ether at 60°C (Sch. 1). After treatment of the reaction mixture with acetic anhydride in pyridine, a mixture of products was easily separable by a silica gel column and the major product was isolated as the *O*-acetyl derivative **8a** (44%) in 87% yield based on **2** consumed. *O*-Deacylation of **8a** with a catalytic amount of methanolic sodium methoxide in methanol gave the alcohol **7a** (97%), which was shown to be identical with the major product observed in the coupling reaction mixture by TLC. The assigned structure of **8a** could be confirmed by ^{1}H NMR spectroscopy: resonated broad double doublets were present at δ 4.09 and 4.17 for H-1′ and H-2′ with



Scheme 1: Transformation of the coupled **7a–d** into 5a′-carbadisaccharide derivatives **11a–d**, **13a–d**, and **15a–d**: reagents and conditions: i) NaH, DMF, 15-crown-5 ether; **1** (1.5 molar equiv), acceptors **2** ~ **5**, 60°C (→ **7a–d**); Ac_2O, pyridine, (→ **8a–d**); ii) NaOMe, MeOH; Ac_2O, DMSO, 25°C; iii) DBU (1.5 molar equiv), toluene, 60°C; iv) $NaBH_4$, THF, 0°C; v) $CeCl_3$. $7H_2O$, MeOH, 0°C; $NaBH_4$, 0°C.

$J = \sim 3.0$ Hz, respectively. The alcohol **7a** was then oxidized with acetic anhydride in DMSO at 25°C, giving the 2-keto derivative **9a** (88%). Epimerization of **9a** ($\rightarrow$ **10a**) was carried out under the influence of DBU (1.5 molar equiv) in toluene at 60°C. The equilibrium mixture of products was readily separated on a silica gel column to give the anomer **10a** (37%), together with **9a** (54%). Reduction of **9a** with $NaBH_4$ in THF at 0°C produced the equatorial alcohol **11a** (43%), together with **7a** (28%). Compound **11a** was then converted into the *O*-acetyl derivative **12a** (95%), the *α-gluco* configuration of which was assigned by its ^{1}H NMR spectrum: a doublet of double doublets was present at δ 4.32 for H-1′ with $J = 2.0$, 3.5, and 3.5 Hz.

On the other hand, treatment of **10a** with cerium(III) chloride heptahydrate in methanol, followed by reduction with sodium borohydride at 0°C, gave, after separation on a silica gel column, the *β-gluco* and *β-manno*-carbadisaccharides **13a** (73%) and **15a** (22%), which were further characterized as the acetates **14a** and **16a**, respectively. Their assigned structures were confirmed on the basis of ^{1}H NMR spectra: doublets of doublets appeared at δ 5.00 and 5.64 for H-2′ with $J = \sim 9.5$ and ~ 3.0 Hz, respectively.

Secondly, the 6-*O*-unprotected D-glucal (**3**) was allowed to couple with the epoxide **1** under similar conditions, affording a condensate **7b** (56%), in 91% yield based on **3** consumed, which was also converted into the acetate **8b**. The proposed structures were confirmed similarly on the basis of the ^{1}H NMR spectra. Oxidation of **7b** with acetic anhydride in DMSO gave the ketone **9b** (94%), which underwent epimerization with DBU to afford an approximately 1 : 1 mixture of products. This was fractionated by silica gel chromatography to afford **9b** (44%) and the anomer **10b** (41%). A similar reduction of **10b** with $NaBH_4$ gave the *β-gluco* and *β-manno*-type compounds **13b** (39%) and **15b** (56%), the structures of which were assigned on the basis of the ^{1}H NMR spectra of their *O*-acetyl derivatives **14b** and **16b**, containing doublets of doublets at δ 5.08 ($J = \sim 9.4$ Hz) and δ 5.81 ($J = 2.7$ and 2.9 Hz), respectively.

Preparation of 5a,5a′-Dicarbadisaccharide Derivatives

1,5-Anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol[11] (**4**) was chosen as a 3-OH free 5a-carba-D-glucal acceptor, and the other 4- and 6-*O*-unprotected derivatives were derivatized from **4**. Thus, treatment of **4** with benzyl bromide in DMF in the presence of NaH gave a crystalline benzyl ether (90%), which was reduced with sodium cyanoborohydride in THF in the presence of MS-4A at room temperature to produce, after separation through a silica gel column, the 3,4- and 3,6-di-*O*-benzyl derivatives **5** (63%) and **6** (3%). The ^{1}H NMR spectra of the respective *O*-acetyl derivatives, derived from **5** and **6**, revealed the downfield shifts (~ 1.4 and ~ 0.6 ppm) of the signals due to the protons attached to the carbon atoms bearing the acetoxyl

groups. These data were likely to be related to those observed for the *O*-acetyl derivatives of **2** and **3**.

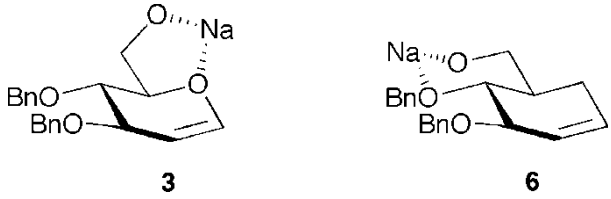
Coupling of the epoxide **1** with compound **4** was conducted under similar conditions as described for **7a** to give the α-mannopyranosyl 5a,5a′-dicarbadisaccharide derivative **7c** (45%) in 66% yield based on **4** consumed. Under the similar conditions, condensation of **1** with compound **5** gave **7d** (17%) in 69% yield based on **5** consumed. The structures of **7c** and **7d** were confirmed on the basis of the respective acetyl derivatives **8c** and **8d**, the ^{1}H NMR spectra of which revealed the narrow signals at δ 5.61 and 5.57 due to the equatorial protons H-2′ attached to the carbon atoms bearing the acetoxyl groups.

Attempted coupling of **1** with the 6-OH free carbaglucal **6**, however, failed under the standard conditions employed throughout in this study. The oxonium ion generated from the primary hydroxyl group of **6** seems not to be stabilized sufficiently (Fig. 3) to undergo nucleophilic attack of **6**, compared to that of the pyranoid congener **3**, conceivably owing to a lack of the pyranoid oxygen atom involved in favorable chelate formation.

Compound **7c,d** could be transformed through a similar sequence of reactions into the α,*β-gluco*- and *β-manno*-5a,5a′-dicarbadisaccharide derivatives **11c**,**d**, **13c,d**, and **15c,d**, respectively. Thus, **7c** was oxidized to the ketone **9c** (99%), which was subjected to the similar epimerization conditions to give the epimer **10c** (49%) and **9c** (36%) recovered. Reduction of **10c** with $NaBH_4$–$CeCl_3$ in MeOH afforded the *β-gluco* and *β-manno* dicarbadisaccharides **13c** (50%) and **15c** (43%). Their structures were confirmed on the basis of ^{1}H NMR spectra of the respective acetyl derivatives **14c** and **16c**, indicating doublets of doublets (δ 5.06, J = 9.4 and 9.4 Hz) and (δ 3.51, J = 2.8 and 9.8 Hz) due to H-2′ and H-3′, respectively.

On the other hand, **9c** was reduced with $NaBH_4$ in THF to give the *α-gluco* dicarbadisaccharide **11c** (64%) together with **7c** (28%). The structure of **11c** was confirmed by the ^{1}H NMR spectrum of its acetyl derivative **12c**, which contained the resonated signals due to H-2′ and H-3′ at δ 4.87 (dd, J = 3.3 and 9.9 Hz) and 4.08 (dd, J = 9.4 and 9.9 Hz), respectively.

Compound **7d** was oxidized to the ketone **9d** (91%), which was subjected to the similar epimerization conditions to give **9d** (36%) and the epimer **10d** (46%). Reduction of **10d** with $NaBH_4$–$CeCl_3$ in MeOH afforded the *β-gluco*



3 **6**

Figure 3: Postulated chelate formation of oxonium ions generated from compounds **3** and **6**.

and β-*manno* dicarbadisaccharides **13d** (47%) and **15d** (38%). Their structures were confirmed on the basis of ^{1}H NMR spectra of the respective acetyl derivatives **14d** and **16d**, revealing doublets of doublets (δ 5.02, $J = 9.4$ and 9.4 Hz) and (δ 3.33, $J = 2.8$ and 9.8 Hz) due to H-2′ and H-3′, respectively.

Reduction of **9c** with $NaBH_4$ in THF gave the α-*gluco* dicarbadisaccharide **11d**, which was acetylated to the *O*-acetyl derivative **12d** (53%) together with **8d** (31%). The ^{1}H NMR spectrum of **12d** contained a signal due to H-2′ at δ 4.89 (dd, $J = 3.6$ and 9.8 Hz), confirming the proposed structure.

Although ^{1}H NMR spectra of the present dicarbadisaccharide derivatives were shown to be rather complex, owing to an overlap of signals due to two cyclitol moieties bonded by way of ether-linkage, the spectra could be interpreted by correlation with those of a series of related carbadisaccharide derivatives.

CONCLUSION

Optimization of coupling reactions of epoxide and oxonium ions generated from glucal and carbaglucal derivatives was not carried out in this study. Nucleophilicity of the oxonium ion may be controlled by the bulkiness of the molecule as well as chemical features of the neighboring functions.[12] Among four acceptors **2**–**5** usable in the couplings, the oxonium ion generated from **5** was shown to be the most inactive toward the epoxide **1**, probably due to considerable steric hindrance. Also, concerning the crucial step of epimerization at the anomeric positions of carba-2′-uronate residues of **9a**–**d**, it appears that stereo-electronic effects of the aglycon moieties, rather than combinations of both bases and solvents, may influence the ratio of α/β-anomers in the range of 1 : 1–1 : 3.

In a synthesis of *O*-linked carba-oligosaccharides having carbasugar moieties at non reducing ends, an important key step is construction of an ether-linkage between a true sugar acceptor and a carbaglycosyl donor. Therefore, desirable building blocks for synthesis of such carba-oligosaccharides may include *O*-linked 5a′-carba-disaccharide derivatives with reactive glucal residues at reducing ends. The 5a-carba- and 5a,5a′-dicarba-disaccharides newly synthesized here can be readily transformed into 5a′-carba-α,β-glucopyranosyl and β-mannopyranosylglucal derivatives, which can then be chemically modified as well as biologically transformed into higher carba-oligosaccharides of biological interest.

EXPERIMENTAL

General Procedures

Melting points: Mel-Temp capillary melting point apparatus, uncorrected. Specific rotations: Jasco DIP-370 polarimeter, 1-dm cells. IR

spectra: Jasco A-202 or FT-IR-200. ^{1}H NMR spectra: Jeol JNM GSX-270 f.t. (270 MHz) and Jeol Lambda-300 (300 MHz); solvent $CDCl_3$ internal standard tetramethylsilane (TMS), D_2O external acetone. Mass spectra: positive-ion electrospray ionization on a Jasco GC-Mass GC-Mare. TLC: SilicaGel 60 GF (E. Merck, Darmstadt); detection by charring with concd H_2SO_4. Column chromatography: silica gel 60 K070 (Katayama Chemicals, Osaka), Wakogel C-33 (silica gel, 300 mesh, Wako Chemical, Osaka), and Disogel sp-60 (silica gel, 60 mesh, Daiso, Osaka). Organic solutions, after drying with anhydrous Na_2SO_4, were concentrated $<50^\circ$C at diminished pressure.

1,5-Anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (2). According to the standard procedure,[9] compound **2** was prepared from 3,4,6-tri-*O*-acetyl-D-glucal in 66% yield as a syrup: $[\alpha]_D^{26}$ -35° (*c* 1.2, $CHCl_3$); ref.[9] $[\alpha]_D^{23}$ -25.0° (*c* 5.7, $CHCl_3$).

Acetylation of **2** (136 mg, 417 mmol) with acetic anhydride (0.7 mL) in pyridine (1.4 mL) for 10 h at rt gave, after chromatography on a column of silica gel (10 g, 1:10 ethyl acetate/hexane), the 4-*O*-acetyl derivative (154 mg, $\sim$100%) as a syrup: $[\alpha]_D^{24}$ -19° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.45 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.2$ Hz, H-1), 5.27 (dd, 1H, $J_{3,4} = 5.1$ Hz, $J_{4,5} = 10.1$ Hz, H-4), 4.88 (ddd, 1H, $J_{2,5} = \sim 1.0$ Hz, $J_{2,3} = 3.9$ Hz, $J_{1,2} = 6.2$ Hz, H-2), 4.61 and 4.54 (ABq, $J_{gem} = 12.2$ Hz), and 4.56 and 4.50 (ABq, $J_{gem} = 12.0$ Hz) (2 × CH_2Ph), 4.27 (dddd, 1H, $J_{2,5} = 1.0$ Hz, $J_{5,6b} = 4.4$ Hz, $J_{5,6a} = 6.8$ Hz, $J_{4,5} = 10.1$ Hz, H-5), 3.93 (ddd, 1H, $J_{1,3} = 1.2$ Hz, $J_{2,3} = 3.9$ Hz, $J_{3,4} = 5.1$ Hz, H-3), 3.74 (dd, 1H, $J_{5,6a} = 6.8$ Hz, $J_{6gem} = 10.6$ Hz, H-6a), 3.64 (dd, 1H, $J_{5,6b} = 4.4$ Hz, $J_{6gem} = 10.6$ Hz, H-6b), 2.02 (s, 3H, Ac). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.79; H, 6.64.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (8a). To a stirred solution of **2** (33.4 mg, 102 μmol) in DMF (0.50 mL) were added in turn NaH (25 mg, 6 molar equiv) and 15-crown-5 ether (0.12 mL, 6 molar equiv) at an interval of 1 h at 0°C. After stirring for a further 1 h, a solution of 1,2-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranose[8] (**1**) (52.0 mg, 1.5 molar equiv) in DMF (0.5 mL) was added to the mixture, and it was heated for 27 h at 60°C. After the addition of a small amount of MeOH, the reaction mixture was diluted with ethyl acetate (30 mL), and the solution was thoroughly washed with water, dried (Na_2SO_4), and evaporated. The residue was treated with acetic anhydride (0.5 mL) and pyridine (1 mL) overnight at rt. Evaporation of the excess reagents and the products were purified by a column of silica gel (8 g, 1:12 → 1:5 ethyl acetate/hexane, v/v) to give **8a** [32 mg (44% yield), 87% based on **2** consumed] as a syrup, along with **2** (16.5 mg) unchanged: $[\alpha]_D^{25}$ -23° (*c* 1.2, $CHCl_3$); ^{1}H NMR

(300 MHz, $CDCl_3$) (*inter alia*): δ 7.52–7.12 (m, 20H, 4 × Ph), 6.40 (dd, 1H, $J_{4',5'} = 8.7$ Hz, $J_{3',4'} = 10.8$ Hz, H-4′), 5.60 (s, 1H, C*H*Ph), 4.84 (dd, 1H, $J_{2,3} = 2.1$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.64 and 4.54 (ABq, $J_{gem} = 11.7$ Hz), and 4.51–4.60 (m, 4H) (3 × CH_2Ph), 4.17 (br d, $J_{1',2'} = \sim 3$ Hz, 1H, H-2′), 4.09 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{1',2'} = \sim 3$ Hz, $J_{1',5a'eq} = 3.2$ Hz, H-1′), 4.07 (br dd, 1H, $J_{1,3} = 0.9$ Hz, $J_{2,3} = 2.1$ Hz, H-3), 4.01 (dd, 1H, $J_{5',6'a} = 4.5$ Hz, $J_{6'gem} = 11.1$ Hz, H-6′a), 3.71 (dd, 1H, $J_{2',3'} = \sim 3$ Hz, $J_{3',4'} = 10.8$ Hz, H-3′), 3.58 (dd, 1H, $J_{6'gem} = 11.1$ Hz, $J_{5',6'b} = 12.0$ Hz, H-6′b), 2.47 (br s, 1H, OH), 2.14 (ddddd, 1H, $J_{5',5a'eq} = 3.2$ Hz, $J_{5',6'a} = 4.5$ Hz, $J_{4',5'} = 8.7$ Hz, $J_{5',6'b} = 12.0$ Hz, $J_{5',5a'ax} = 12.5$ Hz, H-5′), 1.53 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.2$ Hz, $J_{5a'gem} = 13.8$ Hz, H-5a′eq), 1.22 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{5',5a'ax} = 12.5$ Hz, $J_{5a'gem} = 13.8$ Hz, H-5a′ax). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 73.02; H, 6.59.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 4)-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (7a). A solution of **8a** (24.3 mg, 34 μmol) in MeOH (1.0 mL) was treated with 1 M methanolic sodium methoxide (0.2 mL) for 8 h at rt. After neutralization with Amberlite IR-120 (H^+) resin and evaporation, the product was purified by chromatography on silica gel (3 g, 1:5 ethyl acetate/hexane, v/v) to give **7a** (22 mg, 97%) as a syrup: $[\alpha]_D^{26}$ −23° (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.52–7.21 (m, 20H, 4 × Ph), 6.40 (dd, 1H, $J_{1,3} = 0.9$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.60 (s, 1H, C*H*Ph), 4.84 (dd, 1H, $J_{2,3} = 2.1$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.75 and 4.51 (ABq, $J_{gem} = 11.7$ Hz), and 4.62–4.47 (m, 4 H) (3 × CH_2Ph), 4.17 (br dd, 1H, $J_{2',3'} = 2.9$ Hz, $J_{1',2'} = 3.2$ Hz, H-2′), 4.09 (ddd, 2H, $J_{1',5a'ax} = 2.6$ Hz, $J_{1',2'} = J_{1',5a'eq} = 3.2$ Hz, H-1′), 4.01 (dd, 1H, $J_{5',6'a} = 4.5$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 3.58 (dd, 1H, $J_{5',6'b} = J_{6'gem} = 11.0$ Hz, H-6′b), 2.47 (br s, 1H, OH), 2.14 (ddddd, 1H, $J_{5',5a'eq} = 3.2$ Hz, $J_{5',6'a} = 4.5$ Hz, $J_{4'.5'} = 8.7$ Hz, $J_{5',6'b} = 12.0$ Hz, $J_{5',5a'ax} = 12.5$ Hz, H-5′), 1.46 (dd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.2$ Hz, H-5a′eq), 1.38 (ddd, 1H, $J_{1',5a'ax} = 2.6$ Hz, $J_{5',5a'ax} = 12.5$ Hz, $J_{5a'gem} = 13.5$ Hz, H-5a′ax). Anal. Calcd for $C_{41}H_{44}O_8$: C, 74.08; H, 6.67. Found C, 74.28; H, 6.73.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-*arabino*-hex-2-ulopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (9a). To a solution of **7a** (93.7 mg, 141 μmol) in DMSO (3.0 mL) was added acetic anhydride (0.40 mL, 30 molar equiv), and it was stirred for 10 h at 25°C. After treatment with a small amount of methanol, the mixture was diluted with ethyl acetate (100 mL), and the solution was washed thoroughly with water, dried, and evaporated. The product was purified by chromatography (silica gel: 12 g, 1:19 ethyl acetate/toluene, v/v) to give **9a** (82.3 mg, 88%) as a syrup: $[\alpha]_D^{25}$ −58° (*c* 0.28, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.60–7.16 (m, 20H, 4 × Ph), 6.39 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.55 (s, 1H,

C*H*Ph), 4.77 (dd, 1H, $J_{2,3} = 2.7$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.66 and 4.46 (ABq, $J_{gem} = 12.0$ Hz), 4.63 and 4.54 (ABq, $J_{gem} = 12.0$ Hz), and 4.41 and 4.35 (ABq, $J_{gem} = 11.5$ Hz) (3 × CH_2Ph), 4.20 (dd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{1',5a'eq} = 3.2$ Hz, H-1′), 4.14 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 4.08 (ddd, 1H, $J_{1,3} = 1.2$ Hz, $J_{2,3} = 2.7$ Hz, $J_{3,4} = 8.5$ Hz, H-3), 1.75 (ddd, 1H, $J_{1',5a'eq} = 3.2$ Hz, $J_{5',5a'eq} = 3.4$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′eq), 1.12 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{5',5a'ax} = 13.2$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′ax). Anal. Calcd for $C_{41}H_{42}O_8$: C, 74.30; H, 6.39. Found: C, 74.21; H, 6.40.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-*arabino*-hex-2-ulopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (10a). To a solution of **9a** (35.0 mg, 52.8 μmol) in toluene (1.4 mL) was added DBU (12 μL, 1.5 molar equiv), and it was stirred for 8 h at 60°C. The mixture was then diluted with ethyl acetate (50 mL), and the solution was washed thoroughly with water, dried (Na_2SO_4), and evaporated. The products were chromatographed on silica gel (5 g, 1:20 ethyl acetate/toluene, v/v) to give **9a** (16 mg, 54%), along with **10a** (13 mg, 37%), as crystals: mp 123–124°C; $[\alpha]_D^{25}$ −25° (*c* 0.65, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.23 (m, 20H, 4 × Ph), 6.43 (br d, 1H, $J_{1,2} = 6.1$ Hz, H-1), 5.50 (s, 1H, C*H*Ph), 4.87 (dd, 1H, $J_{2,3} = 2.0$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.82 and 4.55 (ABq, $J_{gem} = 12.2$ Hz), 4.61 and 4.54 (ABq, $J_{gem} = 12.0$ Hz,), and 4.66 and 4.40 (ABq, $J_{gem} = 12.0$ Hz) (3 × CH_2Ph), 4.34 (m, 1H, H-1′), 4.24 (dd, 1H, $J_{2,3} = 2.0$ Hz, $J_{3,4} = 7.1$ Hz, H-3), 3.92 (d, 1H, $J_{3',4'} = 10.1$ Hz, H-3′), 3.78 (dd, 1H, $J_{3,4} = 7.1$ Hz, $J_{4,5} = 9.5$ Hz, H-4), 1.12 (ddd, 1H, $J_{1',5a'ax} = 12.6$ Hz, $J_{5',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 13.4$ Hz, H-5a′ax). Anal. Calcd for $C_{41}H_{42}O_8$: C, 74.30; H, 6.39. Found: C, 74.18; H, 6.41.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (11a). To a solution of **9a** (13.0 mg, 19.6 μmol) in THF (1.0 mL) was added sodium borohydride (2.2 mg, 3 molar equiv), and it was stirred for 25 h at 0°C. The mixture was diluted with ethyl acetate (20 mL), and the solution was washed with water, dried (Na_2SO_4), and evaporated. The products were separated by preparative TLC (silica gel) with (2:3 ethyl acetate/hexane, v/v), **7a** (3.7 mg, 28%) and **11a** (5.6 mg, 43%) as syrups: $[\alpha]_D^{19}$ −11° (*c* 0.28, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.53–7.22 (m, 20H, 4 × Ph), 6.40 (dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{1,2} = 5.1$ Hz, H-1), 5.55 (s, 1H, C*H*Ph), 4.85 (dd, 1H, $J_{2,3} = 2.4$ Hz, $J_{1,2} = 6.11$ Hz, H-2), 4.68–4.58 (m, 4 H) and 4.78 and 4.53 (ABq, $J_{gem} = 11.2$ Hz) (3 × CH_2Ph), 4.25 (br ddd, 1H, $J_{1,3} = J_{2,3} = \sim 2.4$ Hz, $J_{3,4} = 6.8$ Hz, H-3), 4.19 (ddd, 1H, $J_{1',5a'ax} = 2.0$ Hz, $J_{1',2'} = J_{1',5a'eq} = 2.5$ Hz, H-1′), 1.58 (ddd, 1H, $J_{1',5a'eq} = \sim 2.5$ Hz, $J_{5',5a'eq} = 3.4$ Hz, $J_{5a'gem} = 14.2$ Hz, H-5a′eq), 0.90 (ddd, 1H, $J_{1',5a'ax} = 2.0$ Hz, $J_{5',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 14.2$ Hz, H-5a′ax).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (12a). Compound **11a** (5.4 mg, 8.1 μmol) was acetylated with acetic anhydride and pyridine in the usual manner to give, after chromatography (silica gel: 2 g, 1:15 ethyl acetate/toluene, v/v) to give **12a** (5.4 mg, 95%) as a syrup: $[\alpha]_D^{21}$ −6° (*c* 0.27, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.46–7.17 (m, 20H, 4 × Ph), 6.38 (br d, 1H, $J_{1,2} = 6.1$ Hz, H-1), 5.51 (s, 1H, C*H*Ph), 4.84 and 4.58 (ABq, $J_{gem} = 11.7$H), 4.55 and 4.48 (ABq, $J_{gem} = 12.0$ Hz), and 4.46 and 4.36 (ABq, $J_{gem} = 11.2$ Hz) (3 × CH_2Ph), 4.32 (br ddd, 1H, $J_{1',5a'ax} = 2.0$ Hz, $J_{1',2'} = J_{1',5a'eq} = 3.5$ Hz, H-1′), 3.65 (dd, 1H, $J_{5,6a} = 3.2$ Hz, $J_{6gem} = 10.7$ Hz, H-6a), 3.54 (dd, 1H, $J_{3',4'} = 9.5$ Hz, $J_{4',5'} = 10.3$ Hz, H-4′), 3.48 (dd, 1H, $J_{5',6'a} = J_{6'gem} = 11.0$ Hz, H-6′a), 1.93 (s, 3H, Ac), 1.74 (ddd, 1H, $J_{1',5a'eq} = 2.0$ Hz, $J_{5',5a'eq} = \sim 3.5$ Hz, $J_{5a'gem} = 14.2$ Hz, H-5a′eq), 0.84 (ddd, 1H, $J_{1',5a'ax} = 2.0$ Hz, $J_{5',5a'ax} = 12.5$ Hz, $J_{5a'gem} = 14.2$ Hz, H-5a′ax). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 72.71; H, 6.59.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (13a) and 3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (15a). A solution of **10a** (12.7 mg, 19.2 μmol) and cerium(III) chloride heptahydrate (0.10 g, 14 molar equiv) in methanol (0.50 mL) was stirred for 30 min at 0°C. Sodium borohydride (10 mg, 14 molar equiv) was added to the mixture, which was then stirred for 47 h at 0°C. The mixture was diluted with ethyl acetate (50 mL), and the solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (2 g, 1:15 ethyl acetate/toluene, v/v) to give **13a** (8.7 mg, 73%) and **15a** (2.8 mg, 22%) as a syrup:

13a: m.p. 116–118°C; $[\alpha]_D^{28}$ −28° (*c* 0.44, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.50–7.24 (m, 20H, 4 × Ph), 6.40 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.51 (s, 1H, C*H*Ph), 4.89 (dd, 1H, $J_{2,3} = 2.4$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.94 and 4.76 (ABq, $J_{gem} = 11.5$ Hz), 4.66 and 4.60 (ABq, $J_{gem} = 12.0$ Hz), and 4.70 and 4.43 (ABq, $J_{gem} = 11.5$ Hz) (3 × CH_2Ph), 4.14 (m, 1H, H-3), 3.97 (br d, 1H, $J_{6gem} = 11.2$ Hz, H-6a), 3.79 (dd, 1H, $J_{5,6b} = 2.0$ Hz, $J_{6gem} = 11.2$ Hz, H-6b), 3.68 (m, 1H, H-1′), 1.74 (ddd, 1H, $J_{1',5a'eq} = 4.9$ Hz, $J_{1',5a'ax} = 11.2$ Hz, $J_{5a'gem} = 12.8$ Hz, H-5a′eq), 0.92 (ddd, 1H, $J_{1',5a'ax} = J_{5',5a'ax} = 11.2$ Hz, $J_{5a'gem} = 12.8$ Hz, H-5a′ax).

15a: $[\alpha]_D^{19}$ +8° (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.28 (m, 20H, 4 × Ph), 6.41 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.57 (s, 1H, C*H*Ph), 4.89 (dd, 1H, $J_{2,3} = 2.0$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.69 and 4.65 (ABq, $J_{gem} = 12.3$ Hz), 4.67–4.54 (m, 2 H), and 4.66 and 4.45 (ABq, $J_{gem} = 11.5$ Hz) (3 × CH_2Ph), 4.30 (br s, 1H, H-2′), 4.23 (dd, 1H, $J_{2,3} = 2.0$ Hz,

$J_{3,4} = 7.1$ Hz, H-3), 3.59 (dd, 1H, $J_{5',6'a} = J_{6'gem} = 10.7$ Hz, H-6′a), 3.32 (dd, 1H, $J_{2',3'} = 3.0$ Hz, $J_{3',4'} = 9.5$ Hz, H-3′), 2.78 (br s, 1H, OH).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (14a). Compound **13a** (8.3 mg, 12.5 μmol) was acetylated conventionally to give, after chromatography (silica gel: 2 g, 1:10 ethyl acetate/toluene, v/v), **14a** (8.6 mg, 98%) as a syrup: $[\alpha]_D^{27}$ −8° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.50–7.22 (m, 20H, 4 × Ph), 6.39 (dd, 1H, $J_{1,3} = 1.2$ Hz. $J_{1,2} = 6.1$ Hz, H-1), 5.52 (s, 1H, C*H*Ph), 5.00 (t, 1H, $J_{1',2'} = J_{2',3'} = 9.5$ Hz, H-2′), 4.86 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.89 and 4.58 (ABq, $J_{gem} = 12.0$ Hz), 4.64 and 4.44 (ABq, $J_{gem} = 12.5$ Hz), and 4.58 and 4.51 (ABq, $J_{gem} = 12.0$ Hz) (3 × CH_2Ph), 3.65–3.55 (m, 1H, H-1′), 1.88 (m, 1H, $J_{5',5a'eq} = 3.4$ Hz, $J_{1',5a'eq} = 4.4$ Hz, $J_{5a'gem} = 13.2$ Hz, H-5a′eq), 0.98 (ddd, 1H, $J_{1',5a'ax} = 11.7$ Hz, $J_{5',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 13.2$ Hz, H-5a′ax). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 72.74; H, 6.65.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-β-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (16a). Compound **15a** (6.0 mg, 9.0 μmol) was acetylated conventionally to give, after chromatography (silica gel: 2 g, 1:10 ethyl acetate/toluene, v/v), **16a** (6.3 mg, 98%) as a syrup: $[\alpha]_D^{19}$ −24° (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.44–7.14 (m, 20H, 4 × Ph), 6.35 (dd, 1H, H-1), 5.64 (m, 1H, $J_{2',3'} = 2.9$ Hz, H-2′), 5.48 (s, 1H, C*H*Ph), 4.82 (dd, 1H, $J_{2,3} = 2.4$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.60 and 4.36 (ABq, $J_{gem} = 11.2$ Hz), 4.58–4.51 (m, 2 H), and 4.58 and 4.36 (ABq, $J_{gem} = 12.9$ Hz) (3 × CH_2Ph), 3.86 (dd, 1H, $J_{5',6'a} = 3.9$ Hz, $J_{6'gem} = 10.6$ Hz, H-6′a), 3.80–3.60 (m, 1H, H-1′), 3.50 (dd, 1H, $J_{5',6'b} = 10.5$ Hz, $J_{6'gem} = 10.6$ Hz, H-6′b), 3.25 (dd, 1H, $J_{2',3'} = 2.9$ Hz, $J_{3',4'} = 9.5$ Hz, H-3′), 2.02 (s, 3H, Ac), 1.57 (ddd, 1H, $J_{1',5a'eq} = 2.7$ Hz, $J_{5',5a'eq} = 3.2$ Hz, $J_{5a'gem} = 11.8$ Hz, H-5a′eq). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 72.55; H, 6.79.

1,5-Anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (3). According to the standard procedure,[10] compound **3** was prepared: syrup, R_f 0.3 (1:3 acetone/hexane); $[\alpha]_D^{26}$ −41° (*c* 1.20, $CHCl_3$); ref.[10] $[\alpha]_D^{20}$ −34.8° (*c* 0.82, $CHCl_3$).

For further characterization, the acetyl derivative was obtained in the usual manner: syrup, R_f 0.46 (1:3 acetone/hexane); $[\alpha]_D^{28}$ +2.4° (*c* 1.10, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37–7.25 (m, 10 H, Ph), 6.39 (br dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 4.92 (dd, 1H, $J_{2,3} = 2.7$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.85 and 4.66 (ABq, $J_{gem} = 11.2$ Hz), and 4.66 and 4.56 (ABq, $J_{gem} = 11.4$ Hz) (2 × CH_2Ph), 4.41 (dd, 1H, $J_{5,6a} = 2.9$ Hz, $J_{gem} = 12.2$ Hz, H-6a), 4.35 (dd, 1H, $J_{5,6b} = 5.1$ Hz, $J_{gem} = 12.2$ Hz, H-6b), 4.23 (br

ddd, 1H, $J_{1,3} = 1.0$ Hz, $J_{2,3} = 2.7$ Hz, $J_{3,4} = 6.1$ Hz, H-3), 4.09 (ddd, 1H, $J_{5,6a} = 2.9$ Hz, $J_{5,6b} = 5.1$ Hz, $J_{4,5} = 8.5$ Hz, H-5), 3.77 (dd, 1H, $J_{3,4} = 6.1$ Hz, $J_{4,5} = 8.5$ Hz, H-4), 2.05 (s, 3H, Ac). Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.53; H, 6.78.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (7b). Coupling of **1** (125 mg, 370 μmol, 1.5 molar equiv) and **3** (80.2 mg, 246 μmol) was carried out similarly as in the preparation of **7a**. The products were chromatographed on silica gel (50 g, 1:30 ethyl acetate/toluene, v/v) to give **7b** [91.5 mg (56% yield), 91% based on **3** consumed], along with **3** (30.5 mg) unchanged: $[\alpha]_D^{26}$ +15° (*c* 0.88, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.21 (m, 20H, 4 × Ph), 6.35 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.61 (s, 1H, C*H*Ph), 4.87 (br dd, $J_{2,3} = 2.4$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.85 and 4.65 (ABq, $J_{gem} = 11.2$ Hz), 4.68 and 4.56 (ABq, $J_{gem} = 11.7$ Hz), and 4.63 (m, 2 H) (3 × CH_2Ph), 4.21 (ddd, 1H, $J_{1,3} = 1.2$ Hz, $J_{2,3} = 2.4$ Hz, $J_{3,4} = 6.1$ Hz, H-3), 4.16 (br dd, 1H, $J = \sim 2.9$ Hz, H-2′), 4.07 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 3.74 (br ddd, 1H, $J = \sim 2.5$ Hz, H-1′), 3.67 (dd, 1H, $J_{5,6a} = 2.7$ Hz, $J_{6gem} = 10.8$ Hz, H-6a), 3.64 (dd, 1H, $J_{5',6'b} = J_{6'gem} = 11.0$ Hz, H-6b′), 2.56 (br s, 1H, OH), 2.21 (m, 1H, H-5′), 1.44 (br ddd, 1H, $J_{1,5a'ax} = \sim 3$ Hz, $J_{5',5a'ax} = J_{5a'gem} = \sim 13$ Hz, H-5a′ax).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (8b). Compound **7b** (17.6 mg, 27 μmol) was acetylated as in the preparation of **8a**. The product was purified by chromatography on silica gel (2 g, 1:9 ethyl acetate/toluene, v/v) to give **8b** (17.5 mg, 94%) as a syrup: $[\alpha]_D^{19}$ +16° (*c* 0.87, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47–7.12 (m, 20H, 4 × Ph), 6.25 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.56 (br s, 1H, C*H*Ph), 5.49 (br t, 1H, $J = \sim 2.0$ Hz, H-2′), 4.79 (dd, 1H, $J_{2,3} = 2.7$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.76 and 4.56 (ABq, $J_{gem} = 11.1$ Hz), 4.60 (s, 2 H), and 4.58 and 4.49 (ABq, $J_{gem} = 11.7$ Hz) (3 × CH_2Ph), 4.13 (br dd, 1H, $J_{2,3} = 2.4$ Hz, $J_{3,4} = 6.3$ Hz, H-3), 4.01 (dd, 1H, $J_{5',6'a} = 4.5$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 3.70 (dd, 1H, $J_{3,4} = 6.3$ Hz, $J_{4,5} = 8.4$ Hz, H-4), 3.66 (dd, 1H, $J_{5,6a} = 2.4$ Hz, $J_{6gem} = 10.5$ Hz, H-6a), 3.57 (t, 1H, $J_{5',6'b} = J_{6'gem} = 11.0$ Hz, H-6′b), 3.56 (ddd, 1H, $J = \sim 2.0$ Hz, H-1′), 2.04 (s, 3H, OAc), 1.51 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = \sim 2.0$ Hz, $J_{5a'gem} = 13.8$ Hz, H-5a′eq), 1.27 (ddd, 1H, $J_{1',5a'ax} = 2.5$ Hz, $J_{5',5a'ax} = J_{5a'gem} = 13.8$ Hz, H-5a′ax). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 73.01; H, 6.69.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-*arabino*-hex-2-ulopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (9b). Compound **7b** (57.2 mg, 86 μmol) was treated with acetic anhydride

(0.25 mL, 30 molar equiv) in DMSO (1.7 mL) for 15 h at 25°C. After usual processing, the product was purified by column chromatography (silica gel: 10 g, 1:15 ethyl acetate/toluene, v/v) to give **9b** (53.7 mg, 94%) as crystals: mp 123–124°C; $[\alpha]_D^{24}$ +15° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.48–7.12 (m, 20H, 4 × Ph), 6.12 (dd, 1H, $J_{1,3} = 1.2$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.48 (s, 1H, C*H*Ph), 4.79 (m, 1H, H-2), 4.59 (m, 1H, H-3′), 4.78 and 4.57 (ABq, $J_{gem} = 11.2$ Hz), 4.74 and 4.56 (ABq, $J_{gem} = 11.4$ Hz), and 4.58 and 4.48 (ABq, $J_{gem} = 11.5$ Hz) (3 × CH_2Ph), 4.15 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 4.12 (m, 1H, H-3), 3.82–3.74 (m, 1H, H-1′), 2.56 (ddddd, 1H, $J_{5',5a'eq} = 3.4$ Hz, $J_{5',6'b} = 4.4$ Hz, $J_{4',5'} = J_{5',6'a} = \sim 10.5$ Hz, $J_{5',5a'ax} = 13.2$ Hz, H-5′), 1.81 (ddd, 1H, $J_{1',5a'eq} = 3.2$ Hz, $J_{5',5a'eq} = 3.4$ Hz, $J_{5a'gem} = 14.5$ Hz, H-5a′eq), 1.18 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{5',5a'ax} = 13.2$ Hz, $J_{5a'gem} = 14.5$ Hz, H-5a′ax). Anal. Calcd for $C_{41}H_{42}O_8$: C, 74.30; H, 6.39. Found: C, 74.24; H, 6.45.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-*arabino*-hex-2-ulopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (10b). Compound **9b** (50.7 mg, 76.5 mmol) was treated with DBU (17 μL, 1.5 molar equiv) in toluene (2.0 mL) for 7 h at 60°C. After usual processing, the product was purified by silica gel chromatography (10 g, 1:20 ethyl acetate/toluene, v/v) to give **9b** (22 mg, 44%) and **10b** (26.3 mg, 41%): $[\alpha]_D^{22}$ –10.4° (*c* 0.78, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.52–7.25 (m, 20H, 4 × Ph), 6.39 (d, 1H, $J_{1,2} = 6.1$ Hz, H-1), 5.55 (s, 1H, C*H*Ph), 4.89 (br d, 1H, $J_{1,2} = 6.1$ Hz, H-2), 4.91 and 4.66 (ABq, $J_{gem} = 12.3$ Hz), 4.89 and 4.80 (ABq, $J_{gem} = 12.1$ Hz), and 4.64 and 4.54 (ABq, $J_{gem} = 11.5$ Hz) (3 × CH_2Ph), 4.11–3.96 (m, 2H, H-5, H-1′), 4.06 (d, 1H, $J_{3',4'} = 10.0$ Hz, H-3′), 3.84–3.77 (m, 1H, H-1′), 1.27 (ddd, 1H, $J_{5',5a'ax} = 12.0$ Hz, $J_{1',5a'ax} = 12.5$ Hz, $J_{5a'gem} = 12.6$ Hz, H-5a′ax). Anal. Calcd for $C_{41}H_{42}O_8$: C, 74.30; H, 6.39. Found: C, 74.29; H, 6.42.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (11b). Compound **9b** (13.1 mg, 19.8 μmol) was treated with $NaBH_4$ (2.2 mg, 3 molar equiv) in THF at 0°C as in the preparation of **11a**. The products were chromatographed on silica gel (3 g, 1:15 ethyl acetate/toluene, v/v), to give **7b** (4.2 mg, 32%) and **11b** (8.7 mg, 66%) as a syrup: $[\alpha]_D^{22}$ +31° (*c* 0.32, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.20 (m, 20H, 4 × Ph), 6.39 (br d, 1H, $J_{1,2} = 6.3$ Hz, H-1), 5.57 (s, 1H, C*H*Ph), 4.90 (br dd, 1H, $J_{2,3} = 3.0$ Hz, $J_{1,2} = 6.3$ Hz, H-2), 4.96 and 4.78 (ABq, $J_{gem} = 11.4$ Hz), 4.85 and 4.65 (ABq, $J_{gem} = 11.4$ Hz), and 4.60 (m, 2 H) (3 × CH_2Ph), 4.09 (dd, 1H, $J_{5,6a} = 4.2$ Hz, $J_{6gem} = 10.5$ Hz, H-6a), 3.94 (dd, 1H, $J_{5,6b} = 5.1$ Hz, $J_{6gem} = 10.5$ Hz, H-6b), 3.58 (dd, 1H, $J_{3',4'} = J_{4',5'} = 11.0$ Hz, H-4′), 2.83 (d, 1H, $J_{2',OH} = 7.5$ Hz, OH), 1.73 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.0$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′eq), 1.01 (br t, 1H, $J_{1',5a'ax} = \sim 3$ Hz, $J_{5',5a'ax} = 13.5$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′ax).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (12b). Compound **11b** (6.4 mg, 9.6 μmol) was acetylated as in the preparation of **12a** to give, after chromatography (silica gel, 2 g, 1:15 ethyl acetate/toluene, v/v) to give **12b** (6.7 mg, 99%) as a syrup: $[\alpha]_D^{22}$ +21° (*c* 0.34, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.53–7.19 (m, 20H, 4 × Ph), 6.35 (br dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{1,2} = 6.0$ Hz, H-1), 5.59 (s, 1H, C*H*Ph), 4.89 and 4.85 (ABq, each 1H, $J_{gem} = 11.0$ Hz, CH_2Ph), 4.88 (dd, 1H, $J_{2,3} = 2.7$ Hz, $J_{1,2} = 6.0$ Hz, H-2), 4.80 (dd, 1H, $J_{1',2'} = 3.0$ Hz, $J_{2',3'} = 10.0$ Hz, H-2′), 4.19 (br dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{2,3} = 2.7$ Hz, $J_{3,4} = 5.7$ Hz, H-3), 3.89 (dd, 1H, $J_{3,4} = 5.7$ Hz, $J_{4,5} = 8.4$ Hz, H-4), 4.01 (dd, 1H, $J_{2',3'} = J_{3',4'} = \sim 10$ Hz, H-3′) 3.64 (br dd, 1H, $J_{3',4'} = J_{4',5'} = \sim 11.0$ Hz, H-4′), 2.01 (s, 3H, Ac), 1.74 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.5$ Hz, $J_{5a'gem} = 14.0$ Hz, H-5a′eq), 1.07 (ddd, 1H, $J_{1',5a'ax} = 1.5$ Hz, $J_{5',5a'ax} = 13.5$ Hz, $J_{5a'gem} = 14.0$ Hz, H-5a′ax). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 72.93; H, 6.80.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (13b) and 3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (15b). Compound **10b** (11.7 mg, 17.7 μmol) was treated with sodium borohydride in the presence of cerium(III) chloride in methanol as in the preparation of **13a** and **15a**. The products were chromatographed on silica gel (2 g, 1:15 ethyl acetate/toluene, v/v) to give **13b** (4.6 mg, 39%) and **15b** (6.5 mg, 56%) as syrups.

13b: $[\alpha]_D^{22}$ −3.4° (*c* 0.23, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.29 (m, 20H, 4 × Ph), 6.41 (dd, 1H, $J_{1,3} = 0.7$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.56 (s, 1H, C*H*Ph), 4.88 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.99 and 4.77 (ABq, $J_{gem} = 11.4$ Hz), 4.85 and 4.73 (ABq, $J_{gem} = 11.2$ Hz), and 4.64 and 4.55 (ABq, $J_{gem} = 11.7$ Hz) (3 × CH_2Ph), 4.19 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{3,4} = 6.1$ Hz, H-3), 4.14 (dd, 1H, $J_{5'6'a} = 4.4$ Hz, $J_{6'gem} = 11.1$ Hz, H-6′a), 4.03 (ddd, 1H, $J_{5,6a} = 3.4$ Hz, $J_{5,6b} = 5.1$ Hz, $J_{4,5} = 8.3$ Hz, H-5), 3.81 (dd, 1H, $J_{3,4} = 6.1$ Hz, $J_{4,5} = 8.3$ Hz, H-4), 3.34 (br d, 1H, $J_{1',2'} = 10.5$ Hz, H-1′), 2.83 (br s, 1H, OH), 1.00 (ddd, 1H, $J_{1',5a'ax} = 11.2$ Hz, $J_{5',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 13.2$ Hz, H-5a′ax).

15b: $[\alpha]_D^{23}$ +24° (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.48–7.25 (m, 20H, 4 × Ph), 6.36 (dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.56 (s, 1H, C*H*Ph), 4.86 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.81 and 4.71 (ABq, $J_{gem} = 12.3$ Hz), 4.79 and 4.65 (ABq, $J_{gem} = 11.6$ Hz), and 4.59 and 4.48 (ABq, $J_{gem} = 11.7$ Hz) (3 × CH_2Ph), 4.24 (br dd, 1H, $J_{1',2'} = 2.2$ Hz, $J_{2',3'} = 2.8$ Hz, H-2′), 3.63 (dd, 1H, $J_{5',6'a} = 10.6$ Hz, $J_{6'gem} = 10.7$ Hz, H-6′a), 3.39 (dd, 1H, $J_{2',3'} = 2.8$ Hz, $J_{3',4'} = 9.6$ Hz, H-3′), 3.30 (m, 1H, $J_{1',2'} = 2.2$ Hz, $J_{1',5a'eq} = 6.6$ Hz, $J_{1',5a'ax} = 9.3$ Hz, H-1′), 2.43 (br s, 1H, OH).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (14b). Compound **13b** (4.6 mg, 6.9 μmol) was acetylated as in the preparation of **13a** to give, after chromatography (silica gel: 2 g, 1:10 ethyl acetate/toluene, v/v), **14b** (4.9 mg, 100%) as a syrup: $[\alpha]_D^{19}$ +11° (*c* 0.25, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.53–7.23 (m, 20H, 4 × Ph), 6.38 (br d, 1H, $J_{1,2} = 6.0$ Hz, H-1), 5.56 (s, 1H, C*H*Ph), 5.08 (dd, 1H, $J_{1',2'} = J_{2',3'} = 9.4$ Hz, H-2′), 4.88 (dd, 1H, $J_{2,3} = 3.0$ Hz, $J_{1,2} = 6.0$ Hz, H-2), 4.13 (dd, 1H, $J_{5',6'eq} = 4.0$ Hz, $J_{6'gem} = 10.8$ Hz, H-6a′eq), 4.12 (dd, 1H, $J_{2,3} = 3.0$ Hz, $J_{3,4} = 7.5$ Hz, H-3), 3.98 (ddd, 1H, $J = \sim 4.0$ Hz, H-5), 3.65 (dd, 1H, $J_{3',4'} = J_{4',5'} = 9.4$ Hz, H-4′), 3.60 (dd, 1H, $J_{5',6'ax} = J_{6'gem} = 10.8$ Hz, H-6′ax), 3.55 (dd, 1H, $J_{3',4'} = 9.0$ Hz, $J_{2',3'} = 9.4$ Hz, H-3′), 3.41 (ddd, 1H, $J_{1',5a'eq} = 4.5$ Hz, $J_{1',2'} = 10.5$ Hz, $J_{1',5a'ax} = 10.8$ Hz, H-1′), 1.95 (s, 3H, Ac), 1.81 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.0$ Hz, $J_{5a'gem} = 12.7$ Hz, H-5a′eq), 1.72 (m, 1H, H-5′), 1.04 (ddd, 1H, $J_{5',5a'ax} = 11.4$ Hz, $J_{1',5a'ax} = 12.0$ Hz, $J_{5a'gem} = 12.7$ Hz, H-5a′ax).

HRMS Calcd for $C_{43}H_{46}O_9$. Found: 706.2947 (M: 0.1%).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 6)-1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-D-*arabino*-hex-1-enitol (16b). Compound **15b** (5.5 mg, 8.3 μmol) was acetylated as in the preparation of **12a** to give, after chromatography (silica gel: 2 g, 1:10 EtOAc/toluene, v/v), **16b** (5.4 mg, 93%) as a syrup: $[\alpha]_D^{22}$ −8.6° (*c* 0.27, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.28 (m, 20H, 4 × Ph), 6.38 (dd, 1H, $J_{1,3} = 1.0$ Hz, $J_{1,2} = 6.1$ Hz, H-1), 5.81 (dd, 1H, $J_{1',2'} = 2.7$ Hz, $J_{2',3'} = 2.9$ Hz, H-2′), 5.60 (s, 1H, C*H*Ph), 4.89 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{1,2} = 6.1$ Hz, H-2), 4.83 and 4.69 (ABq, $J_{gem} = 11.5$ Hz), 4.70 and 4.67 (ABq, $J_{gem} = 10.4$ Hz), and 4.63 and 4.53 (ABq, $J_{gem} = 11.6$ Hz) (3 × CH_2Ph), 4.16 (dd, 1H, $J_{2,3} = 2.9$ Hz, $J_{3,4} = 5.7$ Hz, H-3), 4.12 (dd, 1H, $J_{5',6'a} = 4.3$ Hz, $J_{6'gem} = 10.9$ Hz, H-6′a), 4.02 (dd, 1H, $J_{5,6b} = 3.6$ Hz, $J_{5,6a} = 5.4$ Hz, H-5), 3.89 (dd, 1H, $J_{3',4'} = 9.8$ Hz, $J_{4',5'} = 10.0$ Hz, H-4′), 3.86 (dd, 1H, $J_{5,6a} = 5.4$ Hz, $J_{6gem} = 11.1$ Hz, H-6a), 3.78 (dd, 1H, $J_{3,4} = 5.7$ Hz, $J_{4,5} = 8.1$ Hz, H-4), 3.72 (dd, 1H, $J_{5,6b} = 3.6$ Hz, $J_{6gem} = 11.1$ Hz, H-6b), 3.67 (t, 1H, $J_{5',6'b} = J_{6'gem} = 10.9$ Hz, H-6′b), 3.48 (dd, 1H, $J_{2',3'} = 2.9$ Hz, $J_{3',4'} = 9.8$ Hz, H-3′), 3.44 (br ddd, 1H, $J_{1',2'} = 2.7$ Hz, $J_{1',5a'eq} = 4.5$ Hz, $J_{1',5a'ax} = 11.4$ Hz, H-1′), 2.11 (s, 3H, Ac). Anal. Calcd for $C_{43}H_{46}O_9$: C, 73.07; H, 6.56. Found: C, 72.65; H, 6.77.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (7c): A mixture of 1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol[11] (**4**, 195 mg, 0.84 mmol) in DMF (3.0 mL) was treated with NaH (100 mg, 3 molar equiv) for 1 h at 0°C to rt. To the mixture was added 15-crown-5 ether (0.50 mL, 3 molar equiv), and it was stirred for 1 h at

0°C to rt. After addition of the epoxide **1** (426 mg, 1.5 molar equiv), it was stirred for 16 h at 60°C. The reaction was quenched by addition of methanol, the reaction mixture was diluted with EtOAc, and the solution was washed with water, dried, and evaporated. The residue was chromatographed on a column of silica gel (100 g, 1:30 EtOAc/toluene) to give **7c** [216 mg (45% yield), 66%] as a syrup: R_f 0.5 (1:3 EtOAc/toluene); $[\alpha]_D^{22}$ −67° (*c* 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.46–7.12 (m, 15 H, 3 × Ph), 5.68 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = 2.4$ Hz, $J_{1,5a(eq)} = 4.8$ Hz, $J_{1,2} = 10.2$ Hz, H-1), 5.53 (br s, 2H, 2 × C*H*Ph), 5.51 (br d, 1H, $J_{1,2} = 10.5$ Hz, H-2), 4.49 and 4.20 (ABq, $J_{gem} = 11.5$ Hz, CH_2Ph), 4.06 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 3.96 (m, 1H, $J_{1',5a'eq} = 2.7$ Hz, $J_{1',5a'ax} = 5.6$ Hz, H-1′), 3.86 (dd, 1H, $J_{3',4'} = 9.5$ Hz, $J_{4',5'} = 10.2$ Hz, H-4′), 3.77 (dd, 1H, $J_{2',3'} = 3.2$ Hz, $J_{3',4'} = 9.5$ Hz, H-3′), 2.46 (br s, 1H, OH), 2.23 (m, 1H, H-5′), 2.08 (dddd, 1H, $J_{5,5a(eq)} = J_{5,6a} = \sim 5$ Hz, $J_{5,5a(ax)} = J_{5,6b} = \sim 11$ Hz, H-5), 1.96 [ddd, 1H, $J_{1,5a(eq)} = J_{5,5a(eq)} = \sim 5.0$ Hz, $J_{5agem} = 17.2$ Hz, H-5a(eq)], 1.68 [ddddd, 1H, $J_{2,5a(ax)} = J_{5a(ax),6a} = J_{5a(ax),6b} = 2.8$ Hz, $J_{5,5a(ax)} = 11.2$ Hz, $J_{5agem} = 17.2$ Hz, H-5a(ax)] 1.50–1.44 (m, 2H, 2 × H-5a′).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (8c): Compound **7c** (16 mg, 29 μmol) was acetylated in the usual manner and the product was chromatographed on a column of silica gel (2 g, 1:9 EtOAc/toluene) to give **8c** (17 mg, 97%) as a syrup: R_f 0.57 (1:4 EtOAc/toluene); $[\alpha]_D^{20}$ −52° (*c* 0.88, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.52–7.12 (m, 15 H, 3 × Ph), 5.75 (m, 1H, $J_{1,3} = 1.5$ Hz, $J_{1,5a(ax)} = 2.2$ Hz, $J_{1,5a(eq)} = 2.4$ Hz, $J_{1,2} = 10.3$ Hz, H-1), 5.62 and 5.61 (2 s, each 1H, 2 × C*H*Ph), 5.61 (m, 1H, H-2′), 5.54 (m, 1H, $J_{1,2} = 10.3$ Hz, H-2), 4.30–4.22 (m, 3H, H-3, CH_2Ph), 4.19 (dd, 1H, $J_{5,6a} = 4.9$ Hz, $J_{6gem} = 11.2$ Hz, H-6a), 4.13 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 10.8$ Hz, H-6′a), 3.97 (m, 1H, H-1′), 3.77 (dd, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 11.0$ Hz, H-4), 3.67 (dd, 1H, $J_{5',6'b} = 6.9$ Hz, $J_{6'gem} = 10.8$ Hz, H-6′b), 3.64 (dd, 1H, $J_{5,6b} = 6.9$ Hz, $J_{6gem} = 11.2$ Hz, H-6b), 2.17 [m, 1H, $J_{5,6a} = 4.9$ Hz, $J_{5,5a(eq)} = 5.1$ Hz, $J_{4,5} = 11.0$ Hz, $J_{5,6b} = 11.2$ Hz, H-5], 2.04 [m, 1H, H-5a(eq)], 2.06 (s, 3H, Ac), 1.75 [m, 1H, H-5a(ax)], 1.60 (m, 1H, H-5a′eq), 1.40 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{5',5a'ax} = 13.4$ Hz, $J_{5a'gem} = 13.7$ Hz, H-5a′ax). Anal. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58. Found: C, 72.36; H, 6.76.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-*arabino*-hex-2-ulopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (9c): A solution of **7d** (82 mg, 143 μmol) in DMSO (2.5 mL) was treated with acetic anhydride (0.41 mL, 30 molar equiv) for 15 h at rt. After addition of methanol, the mixture was diluted with EtOAc, and the solution was washed thoroughly with water, dried (Na_2SO_4), and evaporated.

The residue was chromatographed on a column of silica gel (10 g, 1:10 EtOAc/toluene) to give **9d** (81 mg, 99%) as a crystalline solid: $[\alpha]_D^{22}$ −64° (*c* 0.65, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.46–7.08 (m, 15 H, 3 × Ph), 5.73 (dd, 1H, $J_{1,3} = J_{1,5a(ax)} = \sim 2.0$ Hz, $J_{1,5a(eq)} = 4.8$ Hz, $J_{1,2} = 10.0$ Hz, H-1), 5.57 (dd, 1H, $J_{2,3} = 2.7$ Hz, $J_{1,2} = 10.0$ Hz, H-2), 5.56 and 5.47 (2 s, each 1H, 2 × C*H*Ph), 4.79 and 3.51 (ABq, $J_{gem} = 10.0$ Hz, CH_2Ph), 3.97 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{2,3} = 2.7$ Hz, $J_{3,4} = 7.8$ Hz, H-3), 3.80 (d, 1H, $J_{3',4'} = 11.2$ Hz, H-3′), 3.70 (dd, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 10.7$ Hz, H-4), 1.87 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 3.4$ Hz, $J_{5a'gem} = 14.3$ Hz, H-5a′eq), 1.23 (ddd, 1H, $J_{1',5a'ax} = 2.4$ Hz, $J_{5',5a'ax} = 13.4$ Hz, $J_{5a'gem} = 14.3$ Hz, H-5a′ax). Anal. Calcd for $C_{35}H_{36}O_7$: C, 73.92; H, 6.38. Found: C, 73.72; H, 6.45.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-*arabino*-hex-2-ulopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (10c): A solution of **9c** (68 mg, 120 μmol) in toluene (2.7 mL) was treated with DBU (27 μL, 1.5 molar equiv) for 3 h at 60°C. The mixture was then diluted with EtOAc, and the solution was washed with water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a column of silica gel (20 g, 1:15 EtOAc/toluene) to give **10c** (33 mg, 64%) as crystals: R_f 0.6 (1:3 EtOAc/tolurne); $[\alpha]_D^{24}$ −15.5° (*c* 1.23, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.45–7.08 (m, 15H, 3 × Ph), 5.86 (br d, 1H, $J_{1,2} = 10.0$ Hz, H-2), 5.69 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = 2.5$ Hz, $J_{1,5a(eq)} = 4.8$ Hz, $J_{1,2} = 10.0$ Hz, H-1), 5.54 and 5.47 (2 s, each 1H, 2 × C*H*Ph), 4.82 and 4.55 (ABq, $J_{gem} = 12.2$ Hz, CH_2Ph), 4.45 (br dd, 1H, $J_{1',5a'eq} = 6.5$ Hz, $J_{1',5a'ax} = 12.6$ Hz, H-1′), 3.78 (dd, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 10.9$ Hz, H-4), 1.25 (ddd, 1H, $J_{1',5a'ax} = J_{5',5a'ax} = 12.6$ Hz, $J_{5a'gem} = 12.9$ Hz, H-5a′ax). Anal. Calcd for $C_{35}H_{36}O_7$: C, 73.92; H, 6.38. Found: C, 73.63; H, 6.56.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (11c). A solution of compound **10c** (56 mg, 98 μmol) in THF (1.0 mL) was treated with $NaBH_4$ (19 mg, 5 molar equiv) for 3 h at 0°C. After the addition of a small amount of H_2O, the mixture was diluted with EtOAc and the solution was washed with H_2O, dried, and evaporated. The residual product was chromatographed on a column of silica gel (10 g, 1 : 15 EtOAc/toluene) to give **11c** (36 mg, 64%) as crystals, along with **7d** (16 mg, 28%): R_f 0.34 (1:3 EtOAc/toluene); mp 202.5–204°C; $[\alpha]_D^{23}$ −65° (*c* 1.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.55–7.21 (m, 15 H, 3 × Ph), 5.73 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = \sim 2$ Hz, $J_{1,5a(eq)} = 4.8$ Hz, $J_{1,2} = 10$ Hz, H-1), 5.65 (s, 1H, C*H*Ph), 5.58 (br d, 1H, $J_{1,2} = 10$ Hz, H-2), 5.56 (s, 1H, C*H*Ph), 4.61 and 4.40 (ABq, $J_{gem} = 11.2$ Hz, CH_2Ph), 4.43 (br dd, 1H, $J_{1,3} = 2.4$ Hz, $J_{3,4} = 8.2$ Hz, H-3), 4.17 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.2$ Hz, H-6′a), 3.88 (dd, 1H, $J_{3,4} = 8.2$ Hz, $J_{4,5} = 10.7$ Hz, H-4), 3.69 (dd, 1H, $J_{5,6a} = 10.7$ Hz, $J_{6gem} =$

11.4 Hz, H-6a), 1.13 (ddd, 1H, $J_{5',5a'ax} = 13.2$ Hz, $J_{1',5a'ax} = 13.7$ Hz, $J_{5a'gem} = 13.9$ Hz, H-5a′ax).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (12c). Compound **11c** (36 mg, 63 μmol) was acetylated in the usual manner, and the product was chromatographed on a column of silica gel (4 g, 1:10 EtOAc/toluene) to give **12c** (39 mg, ∼100%) as crystals: mp 172–173°C; $[\alpha]_D^{24}$ −30° (*c* 1.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.53–7.22 (m, 15 H, 3 × Ph), 5.76 (br dd, 1H, $J_{1,3} = 2.4$ Hz, $J_{1,2} = 10.0$ Hz, H-1), 5.61 and 5.60 (2 s, each 1H, 2 × C*H*Ph), 5.55 (br d, 1H, $J_{1,2} = 10.0$ Hz, H-2), 4.87 (dd, 1H, $J_{1',2'} = 3.3$ Hz, $J_{2',3'} = 9.9$ Hz, H-2′), 4.89 and 4.63 (ABq, $J_{gem} = 11.7$ Hz, CH_2Ph), 4.08 (dd, 1H, $J_{3',4'} = 9.4$ Hz, $J_{2',3'} = 9.9$ Hz, H-3′), 3.86 (dd, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 10.7$ Hz, H-4), 1.83 (s, 3H, Ac), 1.78 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'ax} = 3.4$ Hz, $J_{5a'gem} = 13.8$ Hz, H-5a′eq), 1.14 (ddd, 1H, $J_{1',5a'ax} = 3.0$ Hz, $J_{5',5a'ax} = 12.6$ Hz, $J_{5a'gem} = 13.8$ Hz, H-5a′ax). Anal. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58. Found: C, 72.17; H, 6.77.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (13c) and 3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (15c). Compound **10d** (17.4 mg, 30.6 μmol) was reduced with $NaBH_4$ in the presence of cerium(III) chloride as in the preparation of **13a** and **15a**. The products were chromatographed on silica gel (4 g, ethyl acetate/toluene, 1:10, v/v) to give **13c** (6.7 mg, 39%) and **15c** (5.7 mg, 33%), along with **10c** (4 mg) unchanged.

13c: mp 201–202.5°C; $[\alpha]_D^{21}$ −37° (*c* 0.33, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.23 (m, 15 H, 3 × Ph), 5.75 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{1,5a(eq)} = 4.4$ Hz, $J_{1,2} = 10.3$ Hz, H-1), 5.70 (br d, 1H, $J_{1,2} = 10.3$ Hz, H-2), 5.62 and 5.56 (2 s, each 1H, 2 × C*H*Ph), 4.98 and 4.75 (ABq, $J_{gem} = 11.4$ Hz, CH_2Ph), 4.21 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{2,3} = 3.4$ Hz $J_{3,4} = 8.1$ Hz, H-3), 4.20 (dd, 1H, $J_{5,6a} = 4.4$ Hz, $J_{6gem} = 11.0$ Hz, H-6a), 4.08 (dd, 1H, $J_{5',6'a} = 4.6$ Hz, $J_{6'gem} = 11.1$ Hz, H-6′a), 3.76 (dd, 1H, $J_{3,4} = 8.1$ Hz, $J_{4,5} = 11.0$ Hz, H-4), 3.68 (dd, 1H, $J_{6gem} = 11.0$ Hz, $J_{5,6b} = 11.5$ Hz, H-6b), 3.60 (dd, 1H, $J_{6'gem} = 11.1$ Hz, $J_{5',6'b} = 11.2$ Hz, H-6′b), 2.82 (br s, 1H, OH), 2,15 (ddddd, 1H, $J_{5,5eq} = J_{5,6a} = \sim 4.5$ Hz, $J_{4,5} = J_{5,5ax} = J_{5,6b} = \sim 11$ Hz, H-5), 1.95 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = \sim 3.5$ Hz, $J_{5a'gem} = 13.0$ Hz, H-5a′eq).

15c: $[\alpha]_D^{21}$ +5.6° (*c* 0.36, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52–7.27 (m, 15 H, 3 × Ph), 5.75 (ddd, 1H, $J_{1,3} = J_{1,5a(ax)} = 2.0$ Hz, $J_{1,5aeq} = 4.5$ Hz, $J_{1,2} = 10.2$ Hz, H-1), 5.62 and 5.60 (2 s, each 1H, 2 × C*H*Ph), 5.57 (br s, 1H,

H-2), 4.85 and 4.73 (ABq, $J_{gem} = 12.1$ Hz, CH_2Ph), 4.35 (dd, 1H, $J_{1',2'} = 2.4$ Hz, $J_{2',3'} = 2.6$ Hz, H-2′), 4.25 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{2,3} = 4.0$ Hz, $J_{3,4} = 7.8$ Hz, H-3), 4.20 (dd, 1H, $J_{5,6a} = 4.5$ Hz, $J_{6gem} = 11.0$ Hz, H-6a), 4.08 (dd, 1H, $J_{5',6'a} = 3.3$ Hz, $J_{6'gem} = 11$ Hz, H-6a′), 4.05 (dd, 1H, $J_{3',4'} = J_{4',5'} = 9.5$ Hz, H-4′), 3.81 (m, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 11.0$ Hz, H-4), 3.77 (m, 1H, $J_{1',2'} = 2.4$ Hz, H-1′), 3.67 (dd, 1H, $J_{5',6'b} = J_{6'gem} = \sim 11$ Hz, H-6′b), 3.47 (dd, 1H, $J_{2',3'} = 2.6$ Hz, $J_{3',4'} = 9.5$ Hz, H-3′), 2.51 (brs, 1H, OH), 2.15 (ddddd, 1H, $J_{5,6a} \sim 5$ Hz, $J_{5,6a} = \sim 5$ Hz, $J_{5,5a(eq)} = 5.1$ Hz, $J_{4,5} = J_{5,5a(ax)} = J_{5,6b} = \sim 9$ Hz, H-5), 2.04 [ddd, 1H, $J_{1,5a(eq)} = 4.4$ Hz, $J_{5,5a(eq)} = 5.1$ Hz, $J_{5agem} = 11.5$ Hz, H-5a(eq)].

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (14c). Compound **13c** (6.7 mg, 12 μmol) was acetylated and purified as in the preparation of **14a** to give **14c** (7.0 mg, 97%) as crystals: mp 199.5–200.5°C; $[\alpha]_D^{21}$ −10° (*c* 0.36, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.26 (m, 15 H, 3 × Ph), 5.45 (br d, 1H, $J_{1,2} = 10.0$ Hz, H-1), 5.06 (t, 1H, $J_{1',2'} = J_{2',3'} = 9.4$ Hz, H-2′), 4.89 and 4.64 (ABq, $J_{gem} = 11.7$ Hz, CH_2Ph), 4.15 (br dd, 1H, $J_{1,3} = 2.2$ Hz, $J_{3,4} = 8.4$ Hz, H-3), 4.04 (dd, 1H, $J_{5',6'a} = 4.4$ Hz, $J_{6'gem} = 11.0$ Hz, H-6′a), 3.60 (t, 1H, $J_{5',6'b} = J_{6'gem} = 11.0$ Hz, H-6′b), 3.52 (t, 1H, $J_{2',3'} = J_{3',4'} = 9.4$ Hz, H-3′), 2.00 (s, 3H, Ac), 1.16 (ddd, 1H, $J_{1',5a'eq} = 11.4$ Hz, $J_{1',5a'ax} = 12.7$ Hz, $J_{5a'gem} = 12.8$ Hz, H-5a′ax). Anal. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58. Found: C, 72.46; H, 6.76.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 3)-1,5-anhydro-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (16c). Compound **15c** (6.2 mg, 11 μmol) was acetylated and purified as in the preparation of **14a** to give **16c** (6.5 mg, 97%) as a syrup: $[\alpha]_D^{20}$ −31° (*c* 0.31, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 4.29 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{2,3} = 3.7$ Hz, $J_{3,4} = 7.6$ Hz, H-3), 4.21 (dd, 1H, $J_{5,6a} = 4.6$ Hz, $J_{6gem} = 11.1$ Hz, H-6a), 3.98 (ddd, 1H, $J_{1',2'} = 2.8$ Hz, $J_{1',5a'eq} = 4.2$ Hz, $J_{1',5a'ax} = 11.2$ Hz, H-1′), 3.92 (dd, 1H, $J_{3',4'} = J_{4',5'} = 9.8$ Hz, H-4′), 3.80 (dd, 1H, $J_{3,4} = 7.8$ Hz, $J_{4,5} = 11.0$ Hz, H-4), 3.51 (dd, 1H, $J_{2',3'} = 2.8$ Hz, $J_{3',4'} = 9.8$ Hz, H-3′), 1.52 (ddd, 1H, $J_{1',5a'ax} = 11.2$ Hz, $J_{5',5a'ax} = J_{5a'gem} = 12.0$ Hz, H-5a′ax). Anal. Calcd for $C_{37}H_{40}O_8$: C, 72.53; H, 6.58. Found: C, 72.50; H, 6.66.

1,5-Anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (5) and 1,5-anhydro-3,4-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (6). To a solution of 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol[11] (**4**, 1.39 g, 4.31 mmol) in THF (56 mL) were added in turn molecular sieves 4A (3.25 g), a trace of methyl orange, and sodium cyanoborohydride (3.25 g, 12 molar equiv), and the mixture was stirred for 30 min at 25°C. Diethyl ether solution saturated with hydrogen chloride was added to it

until the color turned pink. After stirring continued for 3 h and subsequent treatment with Dowex-50 W×2 (H^+) resin, the mixture was filtered through a bed of Celite. The filtrate was diluted with chloroform (300 mL), and the solution was washed with saturated aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (200 g, 1:10 ethyl acetate/hexane, v/v) to give **5** (878 mg, 63%) as crystals and **6** (47 mg, 3%) as a syrup. For further characterization compounds **5** and **6** were converted into the respective acetyl derivatives.

5: m.p. 45–48.5°C; $[\alpha]_D^{19}$ −42° (*c* 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40–7.25 (m, 10 H, 2 × Ph), 4.74 and 4.68 (ABq, $J_{gem} = 11.7$ Hz) and 4.56 and 4.52 (ABq, $J_{gem} = 12.3$ Hz) (2 × C*H*$_2$Ph), 4.02 (dd, 1H, $J_{1,3} = 2.0$ Hz, $J_{3,4} = 7.6$ Hz, H-3), 3.77 (m, 1H, H-4), 3.65 (dd, 1H, $J_{5,6a} = 5.5$ Hz, $J_{6gem} = 9.2$ Hz, H-6a), 3.61 (dd, 1H, $J_{5,6b} = 5.0$ Hz, $J_{6gem} = 9.2$ Hz, H-6b), 3.22 (br s, 1H, OH); the 4-*O*-acetyl derivative: crystals: m.p. 49–50°C; $[\alpha]_D^{24}$ −37° (*c* 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35–7.23 (m, 10 H, 2 × Ph), 5.79 (dd, 1H, $J_{1,3} = 2.3$ Hz, $J_{1,2} = 10.0$ Hz, H-1), 5.67 (dd, 1H, $J_{2,3} = 5.0$ Hz, $J_{1,2} = 10.0$ Hz, H-2), 5.19 (dd, 1H, $J_{3,4} = 7.3$ Hz, $J_{4,5} = 10.5$ Hz, H-4), 4.62 and 4.53 (ABq, $J_{gem} = 11.7$ Hz), and 4.47–4.40 (ABq, $J_{gem} = 12.0$ Hz) (2 × C*H*$_2$Ph), 4.13–4.09 (br ddd, 1H, $J_{1,3} = 2.3$ Hz, $J_{2,3} = 5.0$ Hz, $J_{3,4} = 7.3$ Hz, H-3), 3.48 (dd, 1H, $J_{5,6a} = 4.6$ Hz, $J_{6gem} = 9.2$ Hz, H-6a), 3.38 (dd, 1H, $J_{5,6b} = 6.3$ Hz, $J_{6gem} = 9.2$ Hz, H-6b). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.39; H, 7.21.

6: $[\alpha]_D^{19}$ −21° (*c* = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.24 (m, 10 H, 2 × Ph), 4.98 and 4.74 (ABq, $J_{gem} = 11.2$ Hz), and 4.72 and 4.64 (ABq, $J_{gem} = 11.5$ Hz) (2 × C*H*$_2$Ph), 4.23 (ddd, 1H, $J_{1,3} = 1.5$ Hz, $J_{2,3} = 3.2$ Hz, $J_{3,4} = 7.1$ Hz, H-3), 2.62 (br s, 1H, OH); the 6-*O*-acetyl derivative: $[\alpha]_D^{19}$ +3.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39–7.25 (m, 10H, 2 × Ph), 4.71 and 4.66 (ABq, $J_{gem} = 11.6$ Hz), and 4.91 and 4.63 (ABq, $J_{gem} = 11.0$ Hz) (2 × C*H*$_2$Ph), 3.62 (dd, 1H, $J_{3,4} = 7.3$ Hz, $J_{4,5} = 10.3$ Hz, H-4). Anal. Calcd for $C_{23}H_{26}O_4$: C, 75.38; H, 7.15. Found: C, 75.28; H, 7.28.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (7d). Coupling of **5** (55.3 mg, 170 μmol) and **1** (86.5 mg, 1.5 molar equiv) was carried out as in the preparation of **7a**. The product was purified by chromatography (silica gel: 27 g, 1:9 ethyl acetate/hexane, v/v) to give **7d** [19.7 mg (17%), 69% based on **4** consumed] as a syrup, along with **4** (40 mg) unchanged: $[\alpha]_D^{24}$ −22° (*c* 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.47–7.18 (m, 20H, 4 × Ph), 5.58 (dd, 1H, $J_{1,2} = 10.2$ Hz, H-2), 5.54 (s, 1H, C*H*Ph), 4.70 and 4.46 (ABq, $J_{gem} = 12.0$ Hz), 4.55 and 4.46 (ABq, $J_{gem} = 11.5$ Hz), and 4.46 and 4.37 (ABq, $J_{gem} = 12.2$ Hz) (3 × C*H*$_2$Ph), 4.13 (dd, 1H,

$J_{1',2'} = 2.7$ Hz, $J_{2',3'} = 2.9$ Hz, H-2′), 4.05 (m, 1H, $J_{1',2'} = 2.7$ Hz, H-1′), 3.76 (dd, 1H, $J_{2',3'} = 2.9$ Hz, $J_{3',4'} = 9.6$ Hz, H-3′), 3.41 (dd, 1H, $J_{5,6a} = 3.2$ Hz, $J_{6gem} = 9.0$ Hz, H-6a), 2.35 (br s, 1H, OH).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (8d). Compound **7d** (19 mg, 29 μmol) was acetylated as in the preparation of **8a** to give, after chromatography (silica gel: 2 g, 1:5 ethyl acetate/hexane, v/v), **8d** (21 mg, 99%) as a syrup: $[\alpha]_D^{24}$ −32° (*c* 1.05, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.47–7.18 (m, 20H, 4 × Ph), 5.69 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = \sim 2.3$ Hz, $J_{1,5a(eq)} = 4.5$ Hz, $J_{1,2} = 10.5$ Hz, H-1), 5.57 (br dd, 1H, $J = \sim 3$ Hz, H-2′), 5.55 (s, 1H, C*H*Ph), 4.62–4.47 (m, 4 H), and 4.44 and 4.36 (ABq, $J_{gem} = 12.2$ Hz) (3 × CH_2Ph), 4.01 (br q, 1H, $J = \sim 3$ Hz, H-1′), 3.95 (dd, 1H, $J_{5'.6'a} = 4.5$ Hz, $J_{6'gem} = 10.5$ Hz, H-6′a), 3.87 (dd, 1H, $J_{2',3'} = 3.0$ Hz, $J_{3',4'} = 9.8$ Hz, H-3′), 3.81 (dd, 1H, $J_{4',5'} = 9.5$ Hz, $J_{3',4'} = 9.8$ Hz, H-4′), 3.63 (dd, 1H, $J_{5'.6'b} = 6.9$ Hz, $J_{6'gem} = 10.5$ Hz, H-6′b), 3.58 (dd, 1H, $J_{5,6a} = 2.4$ Hz, $J_{6gem} = 9.7$ Hz, H-6a), 3.36 (dd, 1H, $J_{5,6b} = 2.9$ Hz, $J_{6gem} = 9.7$ Hz, H-6b), 1.88 (m, 1H, H-5), 1.54 (ddd, 1H, $J_{1',5a'eq} = J_{5',5a'eq} = 1.0$ Hz, $J_{5a'gem} = 13.5$ Hz, H-5a′eq), 1.16 (ddd, 1H, $J_{1',5a'ax} = 2.7$ Hz, $J_{5',5a'ax} = J_{5a'gem} = 13.5$ Hz, H-5a′ax). Anal. Calcd for $C_{44}H_{48}O_8$: C, 74.98; H, 6.86. Found: C, 75.09; H, 6.96.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-α-D-*arabino*-hex-2-ulopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (9d). Compound **7d** (20.7 mg, 31.2 μmol) was treated with acetic anhydride (89 μL, 30 molar equiv) in DMSO (0.60 mL) as in the preparation of **9a** to give, after chromatography (silica gel: 4 g, 1:15 ethyl acetate/toluene, v/v), **9d** (18.7 mg, 91%) as a syrup: $[\alpha]_D^{27}$ −51° (*c* 0.80, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.55–7.21 (m, 20H, 4 × Ph), 5.56 (s, 1H, C*H*Ph), 5.49 (br d, 1H, $J_{1,2} = 10.0$ Hz, H-2), 4.84 and 4.51 (ABq, $J_{gem} = 10.3$ Hz), 4.64 and 4.42 (ABq, $J_{gem} = 12.3$ Hz), and 4.54–4.40 (m, 2 H) (3 × CH_2Ph), 4.21 (dd, 1H, $J_{1',5a'ax} = 2.5$ Hz, $J_{1',5a'eq} = 3.2$ Hz, H-1′), 4.06 (ddd, 1H, $J_{1,3} = 2.0$ Hz, $J_{2,3} = 2.2$ Hz, $J_{3,4} = 7.1$ Hz, H-3), 3.43 (dd, 1H, $J_{5,6a} = 3.2$ Hz, $J_{6gem} = 10.9$ Hz, H-6a), 1.80 (ddd, 1H, $J_{1',5a'eq} = 3.2$ Hz, $J_{5',5a'eq} = 3.4$ Hz, $J_{5a'gem} = 14.3$ Hz, H-5a′eq), 1.11 (ddd, 1H, $J_{1',5a'ax} = 2.5$ Hz, $J_{5',5a'ax} = 11.7$ Hz, $J_{5a'gem} = 14.3$ Hz, H-5a′ax). Anal. Calcd for $C_{42}H_{44}O_7$: C, 76.34; H, 6.71. Found: C, 76.28; H, 6.91.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-*arabino*-hex-2-ulopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (10d). Compound **9c** (15.7 mg, 23.8 μmol) was treated with DBU (5.3 μL, 1.5 molar equiv) in toluene (0.60 mL) for 6 h at 65°C as in the preparation of **10a**. After the usual processing, the products were chromatographed on silica

gel (3 g, 1:30 ethyl acetate/toluene, v/v) to give **9d** (5.7 mg, 36%) and **10d** (7.3 mg, 47%) as crystals: mp 138–139°C; $[\alpha]_D^{25}$ −29° (*c* 0.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.20 (m, 20H, 4 × Ph), 5.77 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = \sim 2$ Hz, $J_{1,5a(eq)} = 4.2$ Hz, $J_{1,2} = 9.5$ Hz, H-1), 5.69 (br dd, 1H, $J_{1,3} = 1.9$ Hz, $J_{1,2} = 10.1$ Hz, H-2), 5.48 (s, 1H, C*H*Ph), 4.80 and 4.53 (ABq, $J_{gem} = 12.2$ Hz), and 4.70 and 4.43 (ABq, $J_{gem} = 11.4$ Hz) (2 × CH_2Ph), 4.14 (br d, 1H, $J_{3,4} = 7.6$ Hz, H-3), 3.73 (dd, 1H, $J_{5,6a} = 2.7$ Hz, $J_{6gem} = 9.2$ Hz, H-6a), 1.08 (ddd, 1H, $J_{1',5a'ax} = 12.6$ Hz, $J_{5',5a'ax} = J_{5a'gem} = 12.7$ Hz, H-5a′ax).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-α-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (12d). A solution of **10d** (22 mg, 33 μmol) in THF (1.0 mL) was treated with $NaBH_4$ (3.7 mg, 3 molar equiv) for 3 h at 0°C. After the reaction was quenched by addition of water, the mixture was evaporated to dryness, and the residual product was acetylated in the usual manner. The product was chromatographed by a preparative TLC (1:3 EtOAc/toluene irrigated three times) to give **12d** (12 mg, 53%) and **8d** (7 mg, 31%): $[\alpha]_D^{21}$ −5° (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.54–7.26 (m, 20H, 4 × Ph), 5.66 (br d, 1H, $J_{1,2} = 10.0$ Hz, H-2), 5.59 (s, 1H, C*H*Ph), 4.89 (dd, 1H, $J_{1',2'} = 3.6$ Hz, $J_{2',3'} = 9.8$ Hz, H-2′), 4.53 (m, 1H, H-1′), 4.93 and 4.67 (ABq, $J_{gem} = 11.7$ Hz), 4.61 and 4.47 (ABq, $J_{gem} = 11.5$ Hz), and 4.58 and 4.45 (ABq, $J_{gem} = 12.2$ Hz) (3 × CH_2Ph), 2.09 (dddd, 1H, $J_{5,6b} = 3.6$ Hz, $J_{5,6a} = 3.7$ Hz, $J_{5,5a(eq)} = 4.6$ Hz, $J_{4,5} = 9.0$ Hz, H-5), 2.02 (s, 3H, Ac), 1.83 (ddd, 1H, $J_{1',5a'eq} = 2.9$ Hz, $J_{5',5a'eq} = 3.7$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′eq), 1.00 (ddd, 1H, $J_{1',5a'ax} = 1.6$ Hz, $J_{5',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 14.4$ Hz, H-5a′ax). Anal. Calcd for $C_{44}H_{48}O_8$: C, 74.98; H, 6.86. Found: C, 74.82; H, 7.01.

3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (13d) and 3-*O*-Benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (15d). Compound **10d** (10.0 mg, 15 μmol) was treated with $NaBH_4$ in the presence of cerium(III) chloride in methanol as in the preparation of **13a** and **15a**. The products were chromatographed on silica gel (2 g, 1:25 ethyl acetate/toluene, v/v) to give **13d** (4.5 mg, 47%) and **15d** (3.6 mg, 38%) as crystals.

13d: mp 140–142°C; $[\alpha]_D^{27}$ −51° (*c* 0.23, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.50–7.24 (m, 20H, 4 × Ph), 5.50 (s, 1H, C*H*Ph), 4.92 and 4.80 (ABq, $J_{gem} = 11.5$ Hz), 4.75 and 4.45 (ABq, $J_{gem} = 11.5$ Hz), and 4.62 and 4.49 (ABq, $J_{gem} = 12.2$ Hz) (3 × CH_2Ph), 4.16 (br s, 1H, OH), 3.73 (ddd, 1H, $J_{1',5a'eq} = 4.6$ Hz, $J_{1',2'} = 8.8$ Hz, $J_{1',5a'ax} = 11.2$ Hz, H-1′), 2.33 [dd, 1H, $J_{5agem} = 11.2$ Hz, $J_{5,5a(ax)} = 11.4$ Hz, H-5a(ax)], 2.11 [dd, 1H, $J_{5,5a(eq)} = 4.0$ Hz, $J_{5agem} = 11.2$ Hz, H-5a(eq)], 1.96 (m, 1H, H-5), 1.71 (ddd, 1H,

$J_{5',5a'eq} = 3.2$ Hz, $J_{1',5a'eq} = 4.6$ Hz, $J_{5a'gem} = 12.9$ Hz, H-5a′eq), 1.54 (m, 1H, H-5′), 0.91 (ddd, 1H, $J_{1',5a'ax} = 11.2$ Hz, $J_{5',5a'ax} = J_{5a'gem} = 12.9$ Hz, H-5a′ax).

15d: mp 105.5–108°C; $[\alpha]_D^{26}$ −10° (*c* 0.69, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.51–7.21 (m, 20H, 4 × Ph), 5.76 (m, 1H, $J_{1,3} = J_{1,5a(ax)} = \sim 2.2$ Hz, $J_{1,5a(eq)} = 4.5$ Hz, $J_{1,2} = 10.0$ Hz, H-1), 5.70 (m, 1H, $J_{2,3} = J_{2,5a(eq)} = \sim 1.5$ Hz, $J_{1,2} = 10.0$ Hz, H-2), 5.57 (s, 1H, C*H*Ph), 4.61 and 4.54 (ABq, $J_{gem} = 11.2$ Hz), 4.70 and 4.49 (ABq, $J_{gem} = 12.2$ Hz), and 4.68–4.44 (m, 2 H) (3 × CH_2Ph), 4.32 (dd, 1H, $J_{1',2'} = 2.4$ Hz, $J_{2',3'} = 2.7$ Hz, H-2′), 4.12 (ddd, 1H, $J_{2,3} = \sim 1.5$ Hz, $J_{1,3} = 1.7$ Hz, $J_{3,4} = 7.6$ Hz, H-3), 3.44 (dd, 1H, $J_{5,6a} = 2.9$ Hz, $J_{6gem} = 9.3$ Hz, H-6a), 3.33 (dd, 1H, $J_{2',3'} = 2.7$ Hz, $J_{3',4'} = 9.5$ Hz, H-3′), 2.85 (br s, 1H, OH).

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-glucopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (14d). Compound **13d** (19.3 mg, 29 mmol) was acetylated conventionally to give, after chromatography (silica gel: 2 g, 1:12 ethyl acetate/toluene, v/v), **14d** (19.5 mg, 95%) as a syrup: $[\alpha]_D^{26}$ −14° (*c* 0.95, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ = 7.49–7.22 (m, 20H, 4 × Ph), 5.75 (br d, 1H, $J_{1,2} = 10.3$ Hz, H-1), 5.67 (br d, 1H, $J_{1,2} = 10.3$ Hz, H-2), 5.50 (s, 1H, C*H*Ph), 5.02 (dd, 1H, $J_{1',2'} = J_{2',3'} = 9.4$ Hz, H-2′), 4.89 and 4.61 (ABq, $J_{gem} = 11.7$ Hz), 4.71 and 4.51 (ABq, $J_{gem} = 11.5$ Hz), and 4.51 and 4.44 (ABq, $J_{gem} = 12.0$ Hz) (3 × CH_2Ph), 3.68–3.56 (m, 1H, H-1′), 1.92 (s, 3H, Ac), 1.51 (m, 1H, H-5′), 0.92 (ddd, 1H, $J_{5',5a'ax} = 11.5$ Hz, $J_{1',5a'ax} = 12.9$ Hz, $J_{5a'gem} = 13.2$ Hz, H-5a′ax). Anal. Calcd for $C_{44}H_{48}O_8$: C, 74.98; H, 6.86. Found: C, 74.83; H, 6.90.

2-*O*-Acetyl-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranosyl-(1 → 4)-1,5-anhydro-3,6-di-*O*-benzyl-2-deoxy-5a-carba-D-*arabino*-hex-1-enitol (16d). Compound **15d** (10.8 mg, 16 μmol) was acetylated conventionally to give, after chromatography (silica gel: 2 g, 1 : 10 ethyl acetate/toluene, v/v), **16d** (11 mg, 96%) as a syrup: $[\alpha]_D^{27}$ −28° (*c* 0.37, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) (*inter alia*): δ 7.50–7.22 (m, 20H, 4 × Ph), 5.54 (s, 1H, C*H*Ph), 4.73 and 4.47 (ABq, $J_{gem} = 11.4$ Hz), 4.62 and 4.42 (ABq, $J_{gem} = 12.5$ Hz), and 4.61 and 4.49 (ABq, $J_{gem} = 12.1$ Hz) (3 × CH_2Ph), 4.07 (br dd, 1H, $J_{1,3} = 2.2$ Hz, $J_{3,4} = 7.6$ Hz, H-3), 3.81–3.73 (m, 1H, H-1′), 3.33 (dd, 1H, $J_{2',3'} = 2.8$ Hz, $J_{3',4'} = 9.8$ Hz, H-3′), 2.12 (s, 3H, Ac). Anal. Calcd for $C_{44}H_{48}O_8$: C, 74.98; H, 6.86. Found: C, 74.73; H, 7.07.

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