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Synthesis of *C*-glycopyranosyl compounds by a palladium-catalyzed coupling reaction of 1-tributylstannyl-D-glucals with organic halides*,†

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ABSTRACT

1-Tributylstannyl-D-glucals, prepared from the corresponding 1-phenylsulfonyl-D-glucals, were coupled efficiently to various organic halides in the presence of a palladium(0) catalyst. This mild reaction is specially useful for the preparation of 1-*C*-aryl-D-glucals and compatible with unprotected hydroxy groups or hindered aromatic bromides. It has been shown that the resulting 1-*C*-aryl(alkyl)-D-glucals are suited for further synthetic manipulation of the enol ether group, including stereoselective hydrogenation, hydroboration–oxidation, or epoxidation. All compounds formed resulted from the attack of the α-face of the glucal derivatives by the reagent. The reaction, extended to 1,3-, 1,4-di-, and 1,3,5-tri-bromobenzenes, leads to the corresponding symmetrical di-(tri)-*C*-glucosylbenzenes. Finally, a sequential di-*C*-glucosylation of 1,3-dibromobenzene with two different 1-stannylated glucals was obtained.

INTRODUCTION

C-Glucopyranosyl-containing compounds have received considerable attention in the last decade[1–4]. Among the methods that have been developed, stereocontrolled procedures for direct carbon–carbon bond formation at the anomeric center of carbohydrates have emerged, making available a large variety of *C*-glycopyranosyl structures[1]. These structures are not only found in important natural products[2–4], but they can serve as interesting chiral building blocks for the construction of complex polycyclic or acyclic molecules.

Following our interest in evaluating the synthesis of *C*-glycopyranosyl compounds from C-1-anionic intermediates[5–7], we[8] and others[9,10] reported recently the syntheses of 1-substituted glycals by tin–lithium exchange on the corresponding 1-tributylstannylglycals, followed by alkylation with various electrophiles. Similar 1-substituted D-glucals have also been obtained recently by reaction of 1-*C*-lithiated 2-phenylsulfinyl-D-glucals with aldehydes[11,12]. These carbon–carbon bond forming reactions, although practical, all share the inconvenience of having to use strongly basic

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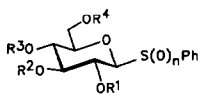
conditions, which forbid the use of base-sensitive protective groups on the coupling partners. A more flexible process, complementary to the aforementioned methods and which tolerates a variety of functional groups including hydroxy groups, would be highly desirable.

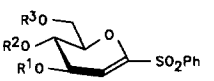
A palladium(0)-catalyzed coupling reaction of 1-tributylstannylglycals with various halides was predicted to be highly versatile on the basis of studies of Beletskaya[13] and Stille[14], a process first described[15] in 1977, demonstrating the ease of cross-coupling of organotin reagents with a variety of organic electrophiles. 1-Alkoxy-1-stannylalkenes have rarely been used in such reactions[16–18] until several reports[19–22] appeared in the course of our studies[23], including a similar investigation[24]. The versatility of Pd (II)-[1,25–27] or Pd(0)-mediated[28–31] *C*-glycosylations have been demonstrated in several instances starting from glycals or hex-2-enopyranosides, reactions in which the carbohydrate derivatives are taken as the electrophilic partner. It was anticipated that the 1-alkyl(aryl)glycals arising from our approach would serve as useful intermediates for the synthesis of *C*-glycopyranosyl compounds by a subsequent stereoselective introduction of functional groups at the enol double-bond, including hydrogenation, hydroboration, or epoxidation. Herein, we describe the details of our preliminary report[23].

RESULTS AND DISCUSSION

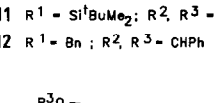
Preparation of 1-tributylstannyl-D-glucals. — The model 1-*C*-stannyl-D-glucals **13**[8], **14**, and **15**, used in this study, were prepared from the corresponding phenyl 1-thio-β-D-glucopyranosides **1**, **4**, and **8** by following a straightforward sequence of reactions previously described[8]. Phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[32–34] was regioselectively *tert*-butyldimethylsilylated at O-3 and methylated in the presence of barium hydroxide[35] to give compound **4**. The latter conditions minimized the migration of the group from O-3 to O-2 (**4** to **5** ratio, 35:1). After treatment with 3-chloroperoxybenzoic acid, sulfone **6** was easily purified from its regioisomer **7**. Base-induced elimination of methanol from **6** furnished the unsaturated sulfone **11**,



1 $R^1 = R^2 = R^3 = R^4 = Bn$; $n = 0$
2 $R^1 = R^2 = R^3 = R^4 = Bn$; $n = 2$
3 $R^1 = H$; $R^2 = Si^tBuMe_2$; R^3, $R^4 = CHPh$; $n = 0$
4 $R^1 = Me$; $R^2 = Si^tBuMe_2$; R^3, $R^4 = CHPh$; $n = 0$
5 $R^1 = Si^tBuMe_2$; $R^2 = Me$; R^3, $R^4 = CHPh$; $n = 0$
6 $R^1 = Me$; $R^2 = Si^tBuMe_2$; R^3, $R^4 = CHPh$; $n = 2$
7 $R^1 = Si^tBuMe_2$; $R^2 = Me$; R^3, $R^4 = CHPh$; $n = 2$
8 $R^1 = R^2 = Bn$; R^3, $R^4 = CHPh$; $n = 0$
9 $R^1 = R^2 = Bn$; R^3, $R^4 = CHPh$; $n = 2$



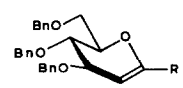
10 $R^1 = R^2 = R^3 = Bn$
11 $R^1 = Si^tBuMe_2$; R^2, $R^3 = CHPh$
12 $R^1 = Bn$; R^2, $R^3 = CHPh$



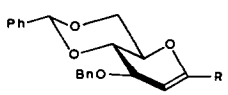
13 $R^1 = R^2 = R^3 = Bn$
14 $R^1 = Si^tBuMe_2$; R^2, $R^3 = CHPh$
15 $R^1 = Bn$; R^2, $R^3 = CHPh$

which was treated with tributylstannane to provide 1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-1-tributylstannyl-2-deoxy-D-*arabino*-hex-1-enitol **14** (71%) together with sulfone **11** (26%). No conditions were found to convert quantitatively the unsaturated sulfone **11** into its stannylated edduct **14**. The structure of the sulfone[36] and the quality of the tributylstannane appear to be, among others, the crucial factors that decide the extent of the conversion. The same sequence of reactions provided stannane **15** from phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*β*-D-glucopyranoside[32] (**8**). Benzylated stannane **13**, previously described by Lesimple *et al.*[8], had also been prepared by Hanessian *et al.*[10] by vinylic deprotonation[8-10] of 1,5-anhydro-3,4,6-tri-*O*-(*tert*-butyldimethyl)silyl-2-deoxy-D-*arabino*-hex-1-enitol, stannylation, and exchange of the protecting groups. The ^{1}H-n.m.r. spectra of stannanes **13**–**15** showed low-field doublets (δ 4.85–5.02, $J_{2,3}$ 2.0–2.5 Hz), flanked by ^{117,119}Sn satellite signals ($J_{2,Sn}$ 26.4–27.0 Hz).

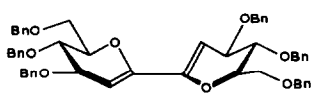
C-*Glycosidation.* — Among the various conditions that we examined to optimize the conversion of stannylated glucals into C-glycosyl compounds, tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] as catalyst in toluene at reflux provided the best conditions for aromatic bromides. McKean *et al.*[37] arrived at the same conclusion in the study of the synthesis of functionalized styrenes. Thus, a refluxing toluene solution of **13** in the presence of bromobenzene (1.5 equiv.) and $Pd(PPh_3)_4$ (0.1 equiv.) furnished, after 3 h, an 88% yield of the desired 1-*C*-arylglycal **16**. Not unexpectedly, a very low conversion (10% after 5 h at reflux) was obtained with chlorobenzene. This observation is in line with the results of Stille[14] who observed that aryl chlorides require activation with electron-withdrawing substituents on the aromatic ring for efficient coupling with tin reagents. This method has been extended to other aryl bromides. Coupling of tin compound **13** with 4-bromoanisole or unprotected 3,5-dibenzyloxy-2-bromophenylmethanol provided the arylated glucals **17** (accompanied by **16**, total yield, 70%) and **18** (70%). The unexpected formation of **16** by loss of the methoxy group in the coupling reaction with 4-bromoanisole is currently under investigation. Similarly, tin reagent **15** was coupled with 2-bromobenzyl or 3,5-dibenzyloxy-2-bromophenylmethanol to give arylglycals **24** and **25**, respectively. As demonstrated with these last examples, the



16 R = Ph
17 R = $C_6H_4OMe(4)$
18 R = (4,6-dibenzyloxy-2-hydroxymethyl) phenylmethyl
19 R = CH_2Ph
20 R = $CH_2CH{=}CH_2$
21 R = $COC_6H_4NO_2(4)$
22 R = I
23 R = $CH{=}CH_2$



24 R = 2-(hydroxymethyl)phenylmethyl
25 R = 4,6-dibenzyloxy-2-(hydroxymethyl) phenylmethyl



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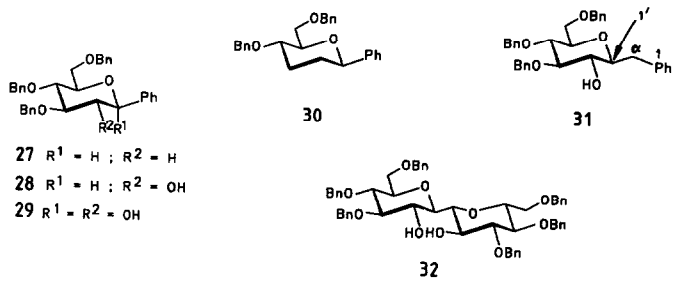
reaction proceeded to completion even with a hindered aryl bromide or in the presence of unprotected hydroxyl groups.

As shown with a wide variety of organotin reagents[14], this reaction is not limited to aryl bromides. Under the same conditions [$Pd(PPh_3)_4$ in toluene], the 1-*C*-benzyl-D-glucal **19** was obtained in 74% yield after a reflux of 1 h in the presence of benzyl bromide. Similarly, the reaction of **13** with allyl bromide in the presence of di(*trans*-4-phenyl-3-buten-2-one)palladium(0) [$Pd(dba)_2$] in oxolane at reflux yielded the 1-substituted glucal **20** (74%). A similar compound was previously obtained[8,9] by vinylic deprotonation of 1,5-anhydro-3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-D-*arabino*-hex-1-enitol and alkylation with allyl bromide or iodide.

In the presence of bis(acetonitrile)dichloropalladium[38] [$PdCl_2(CH_3CN)_2$] as catalyst in dichloroethane (a more active, ligandless catalyst[13]), stannane **13** was coupled with 4-nitrobenzoyl chloride to furnish the 1-*C*-benzoyl-D-glucal **21** in addition to the self-coupled product **26**. This synthetic method was useless with acetylenic or alkenyl iodides or bromides, under the conditions recommended by Stille *et al.*[39,40], for cross-coupling with vinylic or acetylenic tin reagents. Tin–halogen exchange was the major reaction pathway, as in the reaction of stannane **13** with 3-iodo-2-propynol [$PdCl_2(CH_3CN)_2$ in *N,N*-dimethylformamide] which gave 75% of the iodinated glycal **22**. The vinylated compound **23** was obtained, however, in a low yield (33%) by treatment of **13** with vinyl bromide.

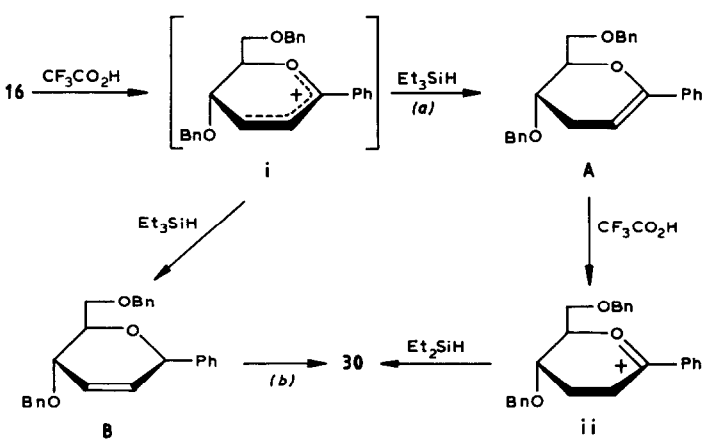
Recently, Friesen and Sturino[24] reported the same arylation of 1,5-anhydro-3,4,6-tri-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-1-tributylstannyl-D-*arabino*-hex-1-enitol[10]. The coupling conditions used in our work with bromobenzene gave only a moderate conversion when used by these authors, a problem that led them to use the procedure of Kosugi *et al.*[17] [bis(triphenylphosphine)palladium dichloride as catalyst in toluene]. Under these conditions, various amounts of self-coupled product were formed[24]. In our experience, no or only a trace of dimer **26** was found, provided that fresh preparations of $Pd(PPh_3)_4$ were used in the arylation reaction. However, treatment of bromobenzene with tin compound **13** in the presence of $PdCl_2(CH_3CN)_2$ in *N,N*-dimethylformamide yielded a significant amount of dimer **26** (39%) with the expected compound **16** (48%). Dimeric compound **26**, also obtained as a side product in the preparation of **19**, was produced in a 85% yield when the electrophilic partner was omitted and $PdCl_2(CH_3CN)_2$ was used as the catalyst at 60° in *N,N*-dimethylformamide. Thus, it appears that $Pd(PPh_3)_4$ in toluene is to be preferred to avoid glycal dimerization in arylation reactions.

Introduction of functional groups at the glycal double-bond. — On the basis of earlier reports[9,12,41] and of our own experience[8], the regioselective introduction of functional groups at the enol ether location of these 1-alkyl(aryl)glucals could proceed stereoselectively. Hydrogenation in the presence of platinum oxide of 1-*C*-phenyl-D-glucal **16**, or hydroboration with borane–dimethyl sulfide complex in oxolane, followed by oxidation under basic conditions or oxidative functionalization by 3-chloroperoxybenzoic acid in the presence of sodium hydrogen carbonate provided, in good yields, the glycosylbenzenes **27**, **28**, or **29**, respectively. All compounds were obtained as single



stereoisomers having the D-*gluco* (or 2-deoxy-D-*arabino*) configuration. Thus, the initial attack of the reagent occurred in all cases from the α-face of the molecule. Treatment of **16** with trifluoroacetic acid (2.5 equiv.) in the presence of triethylsilane (6.0 equiv.) did not lead to the expected glycosylbenzene **27** but rather to the 2,3-dideoxy compound **30** in 80% yield. Acid-catalyzed cleavage of the allylic carbon–oxygen bond would lead to carbocation[42–44] **i**, which is reduced at either C-3 (refs. 45–47) or at C-1 (ref. 48) by triethylsilane to the 3-deoxyglycal **A** (path *a*; see Scheme), or to the 2,3-dideoxyhex-2-enopyranosylbenzene **B** (path *b*). Further reduction would lead to **30**. Any attempts to trap intermediates **A** or **B** failed. The regiospecific reduction at C-1 of 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-1-enitol by triethylsilane–boron trifluoride etherate gave 4,6-di-*O*-acetyl-1,5-anhydro-2,3-dideoxy-D-*erythro*-hex-2-enitol with an excellent yield and no further reduction[48]. By analogy, a hydride attack at C-1 of carbocation **i** would produce **B** (path *b*) as the end-product of the reaction. Instead, path *a* would be preferred since a second carbocation **ii** can be easily formed under the influence of trifluoroacetic acid and reduced to the glycosylbenzene **30**. The stereochemical outcome of the carbocation **ii** reduction (see further), which is similar to that of the pyranose hemiketal reduction[49,50], favors moreover path *a*.

The hydroboration–oxidation sequence was extended to glycals **19** and **26** to provide the corresponding glycosylmethylbenzene **31** and the diglycosyl compound **32** as single stereoisomers, albeit the bis(hydroxylation) of **26** proceeded in a lower yield



(63%). The structure of the compounds obtained was readily assigned by ^{1}H-n.m.r. spectroscopy. Compounds **28**, **31**, and **32** all showed equatorial substituents at C-1 and C-2 ($J_{1,2}$ ~ 9.0, $J_{2,3}$ 8.9–9.8 Hz) in a $^4C_1$(D) conformation expected for β-D-glucosyl residues. Examination of the ^{1}H-n.m.r. data of **29** indicated the structure shown ($J_{2,3}$ 9.0, $J_{2,OH\text{-}2}$ 3.2 Hz), and the long-range coupling constant, $J_{2,OH\text{-}1}$ ~ 1.8 Hz, was diagnostic of the axial orientation of OH-1 (W effect). For the deoxy structure **27**, the coupling constant values were in accordance with an equatorial phenyl substituent at C-1 ($J_{1,2a}$ 11.7, $J_{1,2e}$ 2.2, $J_{2a,3}$ 11.1, and $J_{2e,3}$ 5.0 Hz). The tetrahydropyran ring conformation of **30** could not be ascertained from the ^{1}H-n.m.r. spectrum. The configuration at C-1 of **30** was deduced from the proton–proton n.O.e. measurement using difference spectroscopy, especially from the n.O.e. values observed for H-5 and H-3*a* upon irradiation of H-1.

Di- and tri-C-glycosylations of aromatic compounds. — The ease of the present method for synthesizing *C*-arylglycals prompted us to examine further the reaction with aryl di- or tri-bromides. Coupling of the tin compound **14** (2.0 equiv.) with 1,3-dibromobenzene in the presence of $Pd(PPh_3)_4$ at reflux in toluene gave the symmetrical diglycosylbenzene **34** in excellent yield. The di- (**36**) and tri-glycosylbenzene **37** were likewise obtained by treatment of stannane **13** with 1,4-di- and 1,3,5-tri-bromobenzene, respectively. Moreover, the reaction of **14** with an excess (2.5 equiv.) of 1,3-dibromobenzene gave the monoglycosylbenzene **33**. Further coupling of **33** with tin compound **13** furnished the disymmetrical 1,3-diglycosylbenzene **35** in 79% yield. All symmetrical compounds, **34**, **36**, and **37**, showed only one set of protons in their ^{1}H-n.m.r. spectra for the carbohydrate residues with the expected doublets at δ 5.38–5.60 ($J_{2,3}$ 2.5–3.5 Hz). The signals for the sugar protons in the disymmetrical diglycosylbenzene **35** were differentiated as with H-2″ (δ 5.51, $J_{2'',3''}$ 3.1 Hz) and H-2′ (δ 5.39, $J_{2',3'}$ 2.5 Hz).

The mildness of this palladium-catalyzed *C*-glycosylation should allow its use for a wide variety of sensitive aromatic residues as found in natural substances. Furthermore, the efficient sequential *C*-glycosylation of 1,3-dibromobenzene represents a promising strategic choice for the synthesis of di-*C*-glycosylated antitumor antibiotics,

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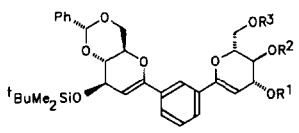
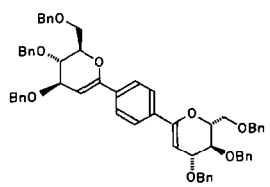


34 R^1 = $SiMe_2{}^tBu$; R^2, R^3 = CHPh
35 R^1 = R^2 = R^3 = Bn



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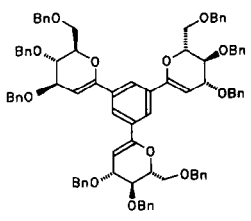

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such as hedamycin,[51,52] kidamycin[53], or pluramycins[54], provided that a differential introduction of functional groups at the glycals double-bond can be devised.

EXPERIMENTAL

General methods. — Melting points were determined for capillary tubes with a Büchi apparatus and are uncorrected. Optical rotations were measured for solutions in $CHCl_3$ with a Perkin–Elmer Model 141 polarimeter at the sodium D-line at $22 \pm 2°$. ^{1}H-N.m.r. spectra were recorded with a Bruker AM-300 WB (300.013 MHz) spectrometer for solutions in C_6D_6 (internal Me_4Si) unless otherwise stated. Locations of atoms in the sugar residues of symmetrical compounds **34**, **36**, and **37** are not primed. Mass spectra were recorded with a Ribermag R-10-10 instrument in the desorption, chemical-ionization mode (d.c.i.) using NH_3 as the reagent gas. T.l.c. was performed on Silica gel 60 F_{254} (Merck) with detection by quenching of fluorescence and by charring with H_2SO_4–EtOH (ratio 10:1). Purification of products was performed by flash chromatography[58] on Silica gel 60 (Merck, 3–63 μm). All solvents and reagents were purified and dried according to standard procedures[55]. The catalysts, $Pd(Ph_3P)_4$[56], $PdCl_2(CH_3CN)_2$[38], and $Pd(dba)_2$[57], were prepared according to the methods described in the literature. Elemental analyses were performed by the Service Central de Micro-Analyse du Centre National de la Recherche Scientifique.

2,3,4,6-Tetra-O-benzyl-β-D-glucopyranosyl phenyl sulfone (**2**). — A solution of phenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[59] (**1**, 16.15 g, 25.5 mmol) in dry dichloromethane (90 mL) was treated at 0° with $NaHCO_3$ (16 g, 200 mmol, 8 equiv.) and 85% 3-chloroperoxybenzoic acid (13.8 g, 64 mmol, 2.5 equiv.), and kept for 4 h at room temperature. The mixture was diluted with dichloromethane and the organic layer was washed with saturated aq. $NaHSO_3$, 0.5M NaOH, and water, dried ($MgSO_4$), and the solvent was evaporated. The residue crystallized from ethanol to give **2** (15.93 g, 94%), white solid, m.p. 136°; lit.[60], m.p. 136–137°.

Phenyl 4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-1-thio-β-D-glucopyranoside (**3**). — A solution of phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[32] (5 g, 13.9 mmol) in dry *N,N*-dimethylformamide (5 mL) was treated under Ar at 0° with *tert*-butyldimethylsilyl chloride (2.30 g, 15.3 mmol, 1.1 equiv.) and imidazole (1.56 g, 22.9 mmol, 1.65 equiv.). After 2 h at room temperature, the mixture was extracted with 1:1 hexane–ether, and the combined extracts were washed with ice-cold water, saturated aq. NH_4Cl, and water. After drying (Na_2SO_4) and concentration *in vacuo*, the residue was purified by column chromatography (1:1 hexane–dichloromethane) to give **3** (6.02 g, 91%) as a colorless syrup, $[\alpha]_D$ −58° (*c* 1.3); ^{1}H-n.m.r.: δ 0.19 (s, 3 H, CH_3), 0.21 (s, 3 H, CH_3), 1.05 (s, 9 H, ^{t}Bu), 2.17 (bs, 1 H, OH), 3.00 (ddd, 1 H, $J_{5,6e}$ 5.5, $J_{4,5}$ 9.5, $J_{5,6a}$ 10.0 Hz, H-5), 3.18 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4), 3.36 (dd, 1 H, $J_{6a,6e}$ 10.0 Hz, H-6*a*), 3.38 (m, 1 H, H-2), 3.68 (dd, 1 H, $J_{2,3}$ 7.5, $J_{3,4}$ 9.5 Hz, H-3), 4.04 (dd, 1 H, $J_{6e,5}$ 5.5, $J_{6e,6a}$ 10.0 Hz, H-6*e*), 4.34 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 5.15 (s, 1 H, C*H*Ph), and 6.95–7.60 (m, 10 H, Ph).

Anal. Calc. for $C_{25}H_{34}O_5SSi$: C, 63.26; H, 7.22. Found: C, 63.50; H, 7.40.

Phenyl 4,6-O-benzylidene-3-O-tert-butyldimethylsilyl-2-O-methyl-1-thio-β-D-glu-

copyranoside (**4**) *and phenyl 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-1-thio-β-*D*-glucopyranoside* (**5**). — A solution of **3** (6 g, 12.6 mmol) in dry *N,N*-dimethylformamide (80 mL) was treated under Ar at 0° with methyl iodide (1.57 mL, 25.3 mmol, 2 equiv.) in the presence of BaO (15.5 g, 101 mmol, 8.0 equiv.) and $Ba(OH)_2 \cdot 8H_2O$ (3.97 g, 12.6 mmol, 1.0 equiv.) and then stirred at 0° for 4 h. After filtration, the solvent was evaporated to dryness, and the residue was diluted with dichloromethane and filtered through a pad of Celite. The filtrate was washed with 15% acetic acid under cooling, saturated aq. $NaHCO_3$, water, dried (Na_2SO_4), and the solvent evaporated to give isomers **4** and **5** (5.80 g, 93.5%; ratio of **4** to **5**, 35:1) as an amorphous powder which was used directly in the next step; ^{1}H-n.m.r. (**4**): δ 0.16 (s, 3 H, CH_3), 0.20 (s, 3 H, CH_3), 1.02 (s, 9 H, ^{t}Bu), 2.92 (ddd, 1 H, $J_{5,6e}$ 5.5, $J_{4,5}$ 10.0, $J_{5,6a}$ 10.5 Hz, H-5), 3.09 (dd, 1 H, $J_{2,3}$ 8.5, $J_{1,2}$ 9.8 Hz, H-2), 3.20 (dd, 1 H, $J_{3,4}$ 9.5, $J_{4,5}$ 10.0 Hz, H-4), 3.39 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ 10.5 Hz, H-6*a*), 3.59 (s, 3 H, OCH_3), 3.71 (dd, 1 H, $J_{2,3}$ 8.5, $J_{3,4}$ 9.5 Hz, H-3), 4.02 (dd, 1 H, $J_{5,6e}$ 5.5, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.28 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 5.15 (s, 1 H, C*H*Ph), and 6.95–7.60 (m, 10 H, 2Ph); ^{1}H-n.m.r. (selected data for **5**): δ 3.50 (s, 3 H, OCH_3), 4.60 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), and 5.20 (s, 1 H, CHPh).

Anal. Calc. for $C_{26}H_{37}O_5SSi$: C, 63.77; H, 7.62. Found: C, 63.79; H, 7.73.

*4,6-*O*-Benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-*O*-methyl-β-*D*-glucopyranosyl phenyl sulfone* (**6**) *and 4,6-*O*-benzylidene-2-*O*-*tert*-butyldimethylsilyl-3-*O*-methyl-β-*D*-glucopyranosyl phenyl sulfone* (**7**). — The mixture of **4** and **5** (6 g, 12.3 mmol), dissolved in dry dichloromethane (60 mL), was treated at 0° with $NaHCO_3$ (7.7 g, 92 mmol, 7.5 equiv.), and 85% 3-chloroperoxybenzoic acid (6 g, 30.6 mmol, 2.5 equiv.), and stirred at 0° for 3 h. The mixture was washed with saturated aq. $NaHSO_3$, saturated aq. NH_4Cl, and water. After drying (Na_2SO_4) and concentration, the residue was purified by column chromatography (1:1 hexane–dichloromethane) to give **7** (180 mg, 2.9%) as a colorless syrup, $[\alpha]_D$ −24° (*c* 1.0); ^{1}H-n.m.r.: δ 0.38 (s, 3 H, CH_3), 0.62 (s, 3 H, CH_3), 1.24 (s, 9 H, ^{t}Bu), 2.73–2.84 (m, 1 H, H-5), 3.12 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ 10.0 Hz, H-6*a*), 3.17–3.28 (m, 2 H, H-3,4), 3.46 (s, 3 H, OCH_3), 3.59 (dd, 1 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.0 Hz, H-6*e*), 4.18 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 4.49 (dd, 1 H, $J_{2,3}$ 8.0, $J_{1,2}$ 9.0 Hz, H-2), 5.08 (s, 1 H, C*H*Ph), and 6.90–7.50 (m, 10 H, 2Ph).

Anal. Calc. for $C_{26}H_{37}O_7SSi$: C, 59.86; H, 7.15. Found: C, 59.99; H, 6.94.

Further elution of the column provided **6** (5.5 g, 85.9%) as a white solid which crystallized from ether–hexane, m.p. 127–128°, $[\alpha]_D$ −47° (*c* 1.3); ^{1}H-n.m.r.: δ 0.12 (s, 3 H, CH_3), 0.18 (s, 3 H, CH_3), 0.91 (s, 9 H, ^{t}Bu), 2.66 (ddd, 1 H, $J_{5,6e}$ 5.5, $J_{4,5}$ 9.6, $J_{5,6a}$ 10.5 Hz, H-5), 3.08 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.6 Hz, H-4), 3.18 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ 10.5 Hz, H-6*a*), 3.64 (dd, 1 H, $J_{5,6e}$ 5.5, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 3.61 (s, 3 H, OCH_3), 3.74 (dd, 1 H, $J_{2,3}$ 8.5, $J_{3,4}$ 9.6 Hz, H-3), 3.93 (dd, 1 H, $J_{2,3}$ 8.5, $J_{1,2}$ 9.5 Hz, H-2), 4.20 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 5.03 (s, 1 H, C*H*Ph), and 6.90–7.95 (m, 10 H, 2Ph); m.s.: *m/z* (%) 521 (M^+ + 1, 100) and 538 (M^+ + 18, 30).

Anal. Calc. for $C_{26}H_{37}O_7SSi$: C, 59.86; H, 7.15. Found: C, 59.97; H, 6.91.

*Phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**8**). — A solution of phenyl 4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside[32] (1 g, 2.77 mmol) in dry *N,N*-dimethylformamide (15 mL) was treated under Ar at 0° with NaH (60%

dispersion in mineral oil; 332 mg, 8.3 mmol, 3 equiv.), benzyl bromide (725 μL, 6.1 mmol, 2.2 equiv.) and stirred at room temperature overnight. The solution was treated at 0° with methanol and concentrated to dryness. The residue was diluted with ether and the organic layer was washed with a saturated NH_4Cl solution and water. After drying ($MgSO_4$) and concentration *in vacuo*, the residue crystallized from ether–hexane to give **8** (1.35 g, 90%) as a white solid, m.p. 154°, $[\alpha]_D$ −25° (*c* 1.0); ^{1}H-n.m.r. ($CDCl_3$): δ 3.47 (ddd, 1 H, $J_{5,6e}$ 5.0, $J_{4,5}$ 9.0, $J_{5,6a}$ 9.5 Hz, H-5), 3.51 (dd, 1 H, $J_{2,3}$ 9.0, $J_{1,2}$ 9.8 Hz, H-2), 3.71 (dd, 1 H, $J_{4,5}$ 9.0, $J_{3,4}$ 9.7 Hz, H-4), 3.80 (dd, 1 H, $J_{5,6a}$ 9.5, $J_{6a,6e}$ 10.5 Hz, H-6*a*), 3.84 (dd, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 9.7 Hz, H-3), 4.39 (dd, 1 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.76 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 4.78 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.80 (d, 1H, *J* 10.0 Hz, C*H*Ph), 4.86 (d, 1 H, *J* 10.0 Hz, C*H*Ph), 4.95 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 5.59 (s, 1 H, C*H*Ph), and 7.20–7.60 (m, 20 H, 4Ph); lit.[32] m.p. 155–157°), $[\alpha]_D$ −31.6° (pyridine).

Anal. Calc. for $C_{33}H_{32}O_5S$: C, 73.31; H, 5.97. Found: C, 73.03; H, 5.89.

*2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-glucopyranosyl phenyl sulfone* (**9**). — Oxidation of **8** (5 g, 9.25 mmol) in dry dichloromethane (60 mL) under the conditions described for the preparation of **2** gave **9** (5.30 g, 90%); m.p. 143° (ether–hexane), $[\alpha]_D$ −4° (*c* 1.1); ^{1}H-n.m.r. ($CDCl_3$): δ 3.38 (ddd, 1 H, $J_{5,6e}$ 5.4, $J_{5,6a}$ 10.3, $J_{4,5}$ 11.5 Hz, H-5), 3.68 (2dd, 2 H, H-4,6*a*), 3.90 (dd, 1 H, $J_{2,3}$ 9.1, $J_{3,4}$ 10.3 Hz, H-3), 4.13 (dd, 1 H, $J_{2,3}$ 9.1, $J_{1,2}$ 9.5 Hz, H-2), 4.15 (dd, 1 H, $J_{5,6e}$ 5.4, $J_{6a,6e}$ 11.5 Hz, H-6*e*), 4.52 (d, 1 H, $J_{1,2}$ 9.5 Hz, H-1), 4.79 and 4.94 (2d, 2 H, *J* 11.4 Hz, 2 C*H*Ph), 4.91 and 5.02 (2 d, 2 H, *J* 10.0 Hz, 2 C*H*Ph), 5.54 (s, 1 H, C*H*Ph), and 7.20–8.00 (m, 20 H, Ph).

Anal. Calc. for $C_{33}H_{32}O_7S$: C, 69.21; H, 5.63. Found: C, 69.02; H, 5.60.

*1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-1-phenylsulfonyl-*D*-*arabino*-hex-1-enitol* (**10**). — A solution of **2** (824 mg, 1.24 mmol) in anhydrous oxolane (5 mL) was treated under Ar at −78° with 1.5M butyllithium in hexane (1.25 equiv.) and stirred for 20 min at −78°. The resulting mixture was treated at −20° with solid NH_4Cl and concentrated to dryness. Dichloromethane was added and the organic layer was washed with saturated aq. NH_4Cl and water, dried (Na_2SO_4), and concentrated *in vacuo*. The residue crystallized from methanol to give **10** (595 mg, 86%) as a white solid, m.p. 84–85°, $[\alpha]_D$ −58° (*c* 1.10); lit.[59] m.p. 85–86°, $[\alpha]_D$ −58°.

*1,5-Anhydro-4,6-*O*-benzylidene-3-*O*-tert-butyldimethylsilyl-2-deoxy-1-phenylsulfonyl-*D*-arabino-hex-1-enitol* (**11**). — Treatment of **6** (4.6 g, 8.87 mmol) in anhydrous oxolane (20 mL) with 1.5M butyllithium in hexane (1.5 equiv.) under the conditions described for the preparation of **10** gave, after crystallization from ether–hexane, **11** (3.48 g, 80%) as a white solid, m.p. 160–161°, $[\alpha]_D$ −54° (*c* 1.3); ^{1}H-n.m.r.: δ 0.04 (s, 3 H, CH_3), 0.06 (s, 3 H, CH_3), 0.94 (s, 9 H, ^{t}Bu), 3.22 (dd, 1 H, $J_{5,6a}$ 10.0, $J_{6a,6e}$ 10.2 Hz, H-6*a*), 3.36 (dd, 1 H, $J_{3,4}$ 7.6, $J_{4,5}$ 10.0 Hz, H-4), 3.42 (ddd, 1 H, $J_{5,6e}$ 4.8, $J_{4,5}$ = $J_{5,6a}$ 10 Hz, H-5), 3.89 (dd, 1 H, $J_{5,6e}$ 4.8, $J_{6a,6e}$ 10.2 Hz, H-6*e*), 4.30 (dd, 1 H, $J_{2,3}$ 2.4, $J_{3,4}$ 7.6 Hz, H-3), 4.99 (s, 1 H, C*H*Ph), 6.27 (d, 1 H, $J_{2,3}$ 2.4 Hz, H-2), and 6.85–8.00 (m, 10 H, 2Ph).

Anal. Calc. for $C_{25}H_{32}O_6SSi$: C, 61.45; H, 6.61. Found: C, 61.39; H, 6.68.

*1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-phenylsulfonyl-*D*-arabino-hex-1-enitol* (**12**). — Treatment of **9** (0.387 g, 0.68 mmol) in anhydrous oxolane (2 mL) with 1.5M butyllithium in hexane (1.2 equiv.) under the conditions described for the

preparation of **10** gave, after column chromatography (15:1 toluene–ethyl acetate containing 0.1% of triethylamine), **12** (229 mg, 73%), which crystallized from dichloromethane–hexane, m.p. 186°, $[\alpha]_D$ −47° (*c* 1.1); ^{1}H-n.m.r.: δ 3.20 (t, 1 H, $J_{5,6a} = J_{6a,6e}$ = 10.2 Hz, H-6*a*), 3.34 (dt, 1 H, $J_{5,6e}$ 5.0, $J_{4,5} = J_{5,6a}$ 10.2 Hz, H-5), 3.54 (dd, 1 H, $J_{3,4}$ 7.8, $J_{4,5}$ 10.2 Hz, H-4), 3.86 (dd, 1 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.2 Hz, H-6*e*), 4.02 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.8 Hz, H-3), 4.48 and 4.53 (2 d, 2 H, *J* 12.0 Hz, 2 C*H*Ph), 5.01 (s, 1 H, C*H*Ph), 6.37 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), and 6.85–8.00 (m, 15 H, 3Ph).

Anal. Calc. for $C_{26}H_{24}O_6S$: C, 67.23; H, 5.21. Found: C, 67.11; H, 5.31.

1,5-Anhydro-3,4,6-tri-O-*benzyl-2-deoxy-1-tributylstannyl*-D-arabino-*hex-1-enitol* (**13**). — Compound **13** was prepared from sulfone **10** according to ref. 8.

1,5-Anhydro-4,6-O-*benzylidene-3*-O-tert-*butyldimethylsilyl-2-deoxy-1-tributylstannyl*-D-arabino-*hex-1-enitol* (**14**). — A solution of **11** (650 mg, 1.35 mmol) in anhydrous toluene (15 mL) was stirred for 3 h at reflux in the presence of tributyltin hydride (1.08 mL, 4.10 mmol, 3 equiv.) and 2,2′-azobis(2-methylpropionitrile) (11 mg, 0.07 mmol, 0.05 equiv.). Evaporation of the solvent and column chromatography (hexane, 2:1 hexane–dichloromethane, and then dichloromethane containing 0.1% of triethylamine) of the residue gave unreacted **11** (170 mg, 26%) and **14** (630 mg, 71%) as a colorless syrup, $[\alpha]_D$ −32° (*c* 1.6); ^{1}H-n.m.r.: δ 0.17 (s, 3 H, CH_3), 0.19 (s, 3 H, CH_3), 0.94 (t, 9 H, Bu), 1.01–1.07 (m, 6 H, Bu), 1.04 (s, 9 H, ^{t}Bu), 1.32–1.44 (m, 6 H, Bu), 1.58–1.69 (m, 6 H, Bu), 3.55–3.69 (m, 1 H, H-6a), 3.83–3.95 (m, 2 H, H-4,5), 4.21–4.27 (m, 1 H, H-6b), 4.62–4.67 (m, 1 H, H-3), 5.02 (d, 1 H, $J_{2,3}$ 2.5 Hz, ^{117,119}Sn satellites, $J_{2,Sn}$ 27.0 Hz, H-2), 5.35 (s, 1 H, C*H*Ph), and 7.10–7.65 (m, Ph).

Anal. Calc. for $C_{32}H_{54}O_4SiSn$: C, 59.17; H, 8.38. Found: C, 59.17; H, 8.49.

1,5-Anhydro-3-O-*benzyl-4,6*-O-*benzylidene-2-deoxy-1-tributylstannyl*-D-arabino-*hex-1-enitol* (**15**). — Treatment of **12** (100 mg, 0.21 mmol) in anhydrous toluene (2 mL) in the presence of tributyltin hydride (170 μL, 0.63 mmol, 3 equiv.) and a catalytic amount of 2,2′-azobis(2-methylpropionitrile) under the conditions described for the preparation of **14** gave, after column chromatography (10:1 hexane–ethyl acetate containing 0.1% of triethylamine), unreacted **12** (45 mg, 45%) and **15** (69 mg, 52%) as a colorless syrup, $[\alpha]_D$ −13.5° (*c* 1.2); ^{1}H-n.m.r.: δ 0.90 (t, 9 H, Bu), 0.93–0.98 (m, 6 H, Bu), 1.25–1.38 (m, 6 H, Bu), 1.46–1.57 (m, 6 H, Bu), 3.74–3.85 (m, 2 H, H-6*a*,6*e*), 3.96–4.03 (m, 1 H, H-4), 4.26–4.37 (m, 2 H, H-3,5), 4.71 and 4.82 (2 d, 2 H, *J* 12.0 Hz, CH_2Ph), 4.89 (d, 1 H, $J_{2,3}$ 2.0 Hz, ^{117,119}Sn satellites, $J_{2,Sn}$ 27.0 Hz, H-2), 5.63 (s, 1H, C*H*Ph), and 7.2–7.6 (m, 10 H, 2 Ph).

Anal. Calc. for $C_{32}H_{46}O_4Sn$: C, 62.66; H, 7.56. Found: C, 62.84; H, 7.68.

1,5-Anhydro-3,4,6-tri-O-*benzyl-2-deoxy-1*-C-*phenyl*-D-arabino-*hex-1-enitol* (**16**). — To a stirred solution of **13** (200 mg, 0.28 mmol) in anhydrous toluene (2.5 mL) under Ar was added bromobenzene (48 μL, 0.42 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (32 mg, 28 μmol, 0.1 equiv.). The yellow solution was heated at 110° for 3 h, and then cooled to room temperature and concentrated to dryness. Column chromatography (8:1 hexane–ethyl acetate containing 0.1% of triethylamine) of the residue gave **16** (122 mg, 88%) as a white solid, which crystallized from ether–hexane, m.p. 65–66°, $[\alpha]_D$ −7° (*c* 1.0); ^{1}H-n.m.r. ($CDCl_3$): δ 3.88 (dd, 1 H, $J_{5,6a}$ 3.1, $J_{6a,6b}$ 11 Hz, H-6a), 3.91 (dd, 1 H, $J_{5,6b}$ 4.8,

$J_{6a,6b}$ 11 Hz, H-6b), 3.96 (dd, 1 H, $J_{3,4}$ 6.0, $J_{4,5}$ 8.2 Hz, H-4), 4.25 (ddd, 1 H, $J_{5,6a}$ 3.1, $J_{5,6b}$ 4.8, $J_{4,5}$ 8.2 Hz, H-5), 4.38 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 6.0 Hz, H-3), 4.6–4.9 (m, 6 H, 3CH_2Ph), 5.42 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2), and 7.2–7.6 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{33}H_{32}O_4$: C, 80.46; H, 6.55. Found: C, 80.41; H, 6.51.

1,5-Anhydro-3,4,6-tri-O-*benzyl-2-deoxy-1*-C-*(4-methoxyphenyl)*-D-arabino-*hex-1-enitol* (**17**). — Treatment of **13** (100 mg, 0.14 mmol) in anhydrous toluene (2 mL) in the presence of 4-bromoanisole (26 μL, 0.21 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (16 mg, 14 μmol, 0.1 equiv.) at reflux for 3 h under the conditions used in the preparation of **16** gave, after column chromatography (10:1 hexane–ethyl acetate containing 0.1% of triethylamine), **16** (26 mg, 37%), identical ($[\alpha]_D$, ^{1}H-n.m.r.) with the compound just described. Further elution provided **17** (24 mg, 33%) as a colorless syrup, $[\alpha]_D$ + 5° (*c* 1.0); ^{1}H-n.m.r.: δ 3.26 (s, 3 H, OMe), 3.85 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.92 (dd, 1 H, $J_{5,6'b}$ 5.0, $J_{6a,6b}$ 10.8 Hz, H-6b), 4.12 (dd, 1 H, $J_{3,4}$ 5.9, $J_{4,5}$ 8.5 Hz, H-4), 4.30 (ddd, 1 H, $J_{5,6a}$ 3.0, $J_{5,6b}$ 5.0, $J_{4,5}$ 8.5 Hz, H-5), 4.43 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 5.9 Hz, H-3), 4.44–4.86 (m, 6 H, 3CH_2Ph), 5.41 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), and 6.75–7.70 (m, 19 H, 4Ph 1 C_6H_4); m.s.: *m/z* (%) 415 (M^+ − OBn, 100) and 523 (M^+ + 1, 18).

Anal. Calc. for $C_{34}H_{34}O_5$: C, 78.14; H, 6.56. Found: C, 78.17; H, 6.53.

1,5-Anhydro-3,4,6-tri-O-*benzyl-2-deoxy-1*-C-*[(4,6-dibenzyloxy-2-hydroxymethyl)phenylmethyl]*-D-arabino-*hex-1-enitol* (**18**). — Treatment of **13** (50 mg, 0.07 mmol) in anhydrous toluene (2 mL) in the presence of Na_2CO_3 (56 mg, 0.53 mmol) with 3,5-dibenzyloxy-2-bromophenylmethanol[60] (42.4 mg, 0.11 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (8 mg, 7 μmol, 0.1 equiv.) at reflux for 4 h under the conditions described for the preparation of **16** gave, after column chromatography (10:1 toluene–ethyl acetate containing 0.1% of triethylamine), syrupy **18** (38 mg, 70%), $[\alpha]_D$ + 3° (*c* 1.2); ^{1}H-n.m.r.: δ 3.75–3.79 (m, 2 H, H-6a,6b), 4.07 (dd, 1 H, $J_{3,4}$ 5.9, $J_{4,5}$ 8.1 Hz, H-4), 4.25–4.82 (m, 14 H, 5 CH_2Ph, CH_2OH, H-3,5), 5.21 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 6.53 (d, 1 H, *J* 2.4 Hz, C_6H_2), 6.83 (d, 1 H, *J* 2.4 Hz, C_6H_2), and 7.04–7.37 (m, 25 H, 5 Ph).

Anal. Calc. for $C_{48}H_{46}O_7$: C, 78.45; H, 6.31. Found: C, 78.29; H, 6.32.

1,5-Anhydro-1-C-*benzyl-3,4,6-tri*-O-*benzyl-2-deoxy*-D-arabino-*hex-1-enitol* (**19**). — Treatment of **13** (50 mg, 0.07 mmol) in anhydrous toluene (2 mL) in the presence of benzyl bromide (13 μL, 0.11 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (4 mg, 3.5 μmol, 0.05 equiv.) at reflux for 1 h under the conditions described for the preparation of **16** gave, after column chromatography (10:1 hexane–ethyl acetate containing 0.1% of triethylamine), **19** (26 mg, 74%) as a colorless syrup, $[\alpha]_D$ − 1° (*c* 1.0); ^{1}H-n.m.r.: ($CDCl_3$): δ 3.39 (bs, 2 H, CH_2Ph), 3.72 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.77 (dd, 1 H, $J_{5,6b}$ 5.0, $J_{6a,6b}$ 11.0 Hz, H-6b), 3.85 (dd, 1 H, $J_{3,4}$ 5.7, $J_{4,5}$ 8.0 Hz, H-4), 4.10 (ddd, 1 H, $J_{5,6a}$ 3.0, $J_{5,6'}$ 5.0, $J_{4,5}$ 8.0 Hz, H-5), 4.17 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 5.7 Hz, H-3), 4.47 (s, 2 H, CH_2Ph), 4.50, 4.57, 4.65, and 4.77 (4 d, 4 H, *J* 11.5 Hz, 2 CH_2Ph), 4.68 (d, 1 H, $J_{2',3}$ 3.0 Hz, H-2), and 7.1–7.4 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{34}H_{34}O_4$: C, 80.60; H, 6.77. Found: C, 80.45; H, 6.94.

1-C-Allyl-1,5-anhydro-3,4,6-tri-O-*benzyl-2-deoxy*-D-arabino-*hex-1-enitol* (**20**). — To a stirred solution of **13** (100 mg, 0.14 mmol) in anhydrous oxolane (2 mL) was added under Ar allyl bromide (48 mg, 0.28 mmol, 2 equiv.), $Pd(dba)_2$ (4.1 mg, 7.2 μmol,

0.05 equiv.), and triphenylphosphine (4.2 mg, 14.2 μmol, 0.1 equiv.). The solution was heated at reflux overnight, cooled to room temperature, and concentrated to dryness. Column chromatography (12:1 hexane–ethyl acetate containing 0.2% of triethylamine) of the residue gave **20** (48 mg, 74%) as a colorless syrup, $[\alpha]_D$ +0.5° (*c* 1.0); ^{1}H-n.m.r.: δ 2.78 (m, 2 H, H_2-1'), 3.75 (dd, 1 H, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 10.5 Hz, H-6b), 3.82 (dd, 1 H, $J_{5',6a}$ 4.5, $J_{6a,6b}$ 10.5 Hz, H-6a), 4.05 (dd, 1 H, $J_{3,4}$ 5.9, $J_{4,5}$ 8.5 Hz, H-4), 4.14 (m, 1 H, H-5), 4.23 (m, 1 H, H-3), 4.35, 4.39, 4.42, and 4.50 (4 d, 4 H, *J* 12.0 Hz, 2 CH_2Ph), 4.63 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.74 (dd, 1 H, $J_{2,1'}$ 0.7, $J_{2,3}$ 2.3 Hz, H-2), 4.81 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 5.01 (m, 1 H, $J_{2',3b'}$ 10.2 Hz, H-3b'), 5.05 (m, 1 H, $J_{2',3a'}$ 17.5 Hz, H-3a'), 5.86 (ddt, 1 H, $J_{1',2'}$ 6.7, $J_{2',3b'}$ 10.2, $J_{2',3a'}$ 17.5 Hz, H-2'), and 7.0–7.5 (m, 15 H, 3 Ph).

Anal. Calc. for $C_{30}H_{32}O_4$: C, 78.92; H, 7.06. Found: C, 78.79; H, 7.18.

Coupling of tin compound **13** *with 4-nitrobenzoyl chloride.* — To a stirred solution of **13** (50 mg, 0.07 mmol) in anhydrous dichloroethane (2 mL) was added under Ar 4-nitrobenzoyl chloride (30 mg, 0.14 mmol, 2 equiv.) and $PdCl_2(CH_3CN)_2$ (1.1 mg, 4.1 μmol, 0.05 equiv.). The yellow solution was heated at reflux for 0.5 h, cooled to room temperature, and concentrated to dryness. Column chromatography (8:1 hexane–ethyl acetate containing 0.2% triethylamine) of the residue gave *1,5-anhydro-3,4,6-tri*-O-*benzyl-2-deoxy*-1-C-(*4-nitrobenzoyl*)-D-arabino-*hex-1-enitol* (**21**; 28 mg, 70%) as a syrup, $[\alpha]_D$ −6° (*c* 1.2); ^{1}H-n.m.r.: δ 3.56 (dd, 1 H, $J_{5,6b}$ 2.8, $J_{6a,6b}$ 10.8 Hz, H-6b), 3.73 (dd, 1 H, $J_{5,6a}$ 5.0, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.96 (dd, 1 H, $J_{3,4}$ 6.0, $J_{4,5}$ 8.2 Hz, H-4), 4.08 (ddd, 1 H, $J_{5,6b}$ 2.8, $J_{5,6a}$ 5.0, $J_{4,5}$ 8.2 Hz, H-5), 4.15 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 6.0 Hz, H-3), 4.23 (s, 2 H, CH_2Ph), 4.28 and 4.40 (2 d, 2 H, *J* 12.0 Hz, CH_2Ph), 4.57 and 4.74 (2 d, 2 H, *J* 11.5 Hz, CH_2Ph), 6.05 (d, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 7.04–7.28 and 7.63–7.73 (m, 19 H, 4 Ph, $C_6H_4NO_2$); m.s.: *m/z* (%) 583 (M^+ + 18, 100.) No correct elemental analysis could be obtained.

Reaction of tin compound **13** *with 3-iodo-2-propyn-1-ol.* — To a stirred solution of **13** (200 mg, 0.28 mmol) in anhydrous *N,N*-dimethylformamide (1 mL) was added under Ar 3-iodo-2-propyn-1-ol[61] (52 mg, 0.42 mmol, 1.5 equiv.) and $PdCl_2(CH_3CN)_2$ (3.8 mg, 14.2 μmol, 0.05 equiv.). The yellow solution was stirred at room temperature for 5 h. After dilution with dichloromethane, the organic layer was washed with aq. $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated. Column chromatography (toluene containing 0.2% of triethylamine) of the residue provided *1,5-anhydro-3,4,6-tri*-O-*benzyl-2-deoxy-1-iodo*-D-arabino-*hex-1-enitol* (**22**; 115 mg, 75%) as a white solid, $[\alpha]_D$ −10° (*c* 1.2), which quickly decomposed at room temperature; ^{1}H-n.m.r. ($CDCl_3$): δ 3.76 (dd, 1 H, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 11.1 Hz, H-6b), 3.83 (dd, 1 H, $J_{5,6a}$ 4.8, $J_{6a,6b}$ 11.1 Hz, H-6a), 3.92 (dd, 1 H, $J_{3,4}$ 5.9, $J_{4,5}$ 8.5 Hz, H-4), 4.11 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 5.9 Hz, H-3), 4.27 (ddd, 1 H, $J_{5,6b}$ 3.0, $J_{5,6a}$ 4.8, $J_{4,5}$ 8.5 Hz, H-5), 4.50, 4.54, 4.58, 4.60, 4.64, and 4.78 (6 d, 6 H, *J* 11.5 Hz, 3 CH_2Ph), 5.44 (d, 1 H, $J_{2,3}$ 3.3 Hz, H-2), and 7.2–7.4 (m, 15 H, 3 Ph); m.s.: *m/z* (%) 91 (100), 435 (M^+ − OBn, 60), and 560 (M^+ + 18, 24). No correct elemental analysis could be obtained.

Coupling of the tin compound **13** *with vinyl bromide.* — Treatment of **13** (50 mg, 0.07 mmol) in anhydrous *N,N*-dimethylformamide (1 mL) with vinyl bromide (10 μL, 0.14 mmol, 2 equiv.) and $PdCl_2(CH_3CN)_2$ (2.1 mg, 3.5 μmol, 0.05 equiv.) at room

temperature for 2 h under the conditions described for the preparation of **22** gave, after column chromatography (5:1 hexane–ethyl acetate containing 0.2% of triethylamine), dimer **26** (15 mg, 52%) and *1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-1-*C*-vinyl-*D-arabino-*hex-1-enitol* (**23**; 10 mg, 33%) as a colorless syrup, $[\alpha]_D$ −23° (*c* 0.5); ^{1}H-n.m.r. ($CDCl_3$): δ 3.75 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.81 (dd, 1 H, $J_{5,6b}$ 4.5, $J_{6a,6b}$ 10.5 Hz, H-6b), 4.03 (dd, 1 H, $J_{3,4}$ 5.9, $J_{4,5}$ 9.0 Hz, H-4), 4.11 (ddd, 1 H, $J_{5,6a}$ 3.0, $J_{5,6b}$ 4.5, $J_{4,5}$ 9.0 Hz, H-5), 4.26 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 5.9 Hz, H-3), 4.36, 4.38, 4.42, and 4.46 (4 d, 4 H, *J* 12.0 Hz, 2 CH_2Ph), 4.61 and 4.79 (2 d, 2 H, *J* 11.8 Hz, CH_2Ph), 4.86 (d, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 5.08 (dd, 1 H, $J_{2a',2b'}$ 2.3 $J_{1',2b'}$ 10.3 Hz, H-2b'), 5.86 (dd, 1 H, $J_{2a',2b'}$ 2.3, $J_{1',2a'}$ 17.4 Hz, H-2b'), 6.03 (dd, 1 H, H-1'), and 7.0–7.4 (m, 15 H, 3 Ph). No correct elemental analysis could be obtained.

*1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-*C*-[(2-hydroxymethyl)-phenylmethyl]-*D-arabino-*hex-1-enitol* (**24**). — Treatment of **15** (700 mg, 1.14 mmol) in anhydrous toluene (14 mL) with *2*-bromophenylmethanol (320 mg, 1.71 mmol, 1.5 equiv.) in the presence of $Pd(PPh_3)_4$ (65 mg, 57 μmol, 0.05 equiv.) at reflux for 6 h under the conditions described for the preparation of **16** gave, after column chromatography (toluene containing 0.1% of triethylamine), **24** (367 mg, 75%) as a white solid, which crystallized from ethyl ether–hexane, m.p. 163–164°, $[\alpha]_D$ −29° (*c* 0.8); ^{1}H-n.m.r.: δ 3.54 (t, 1 H, $J_{5,6a}$ = $J_{6a,6e}$ 10.5 Hz, H-6*a*), 3.76 (ddd, 1 H, $J_{5,6e}$ 5.5, $J_{4,5}$ 10.1, $J_{5,6a}$ 10.5 Hz, H-5), 3.95 (dd, 1 H, $J_{3,4}$ 8.0, $J_{4,5}$ 10.1 Hz, H-4), 4.17 (dd, 1 H, $J_{5,6e}$ 5.5, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.40 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 8.0 Hz, H-3), 4.42 (s, 2 H, CH_2OH), 4.67 and 4.79 (2 d, 2 H, *J* 12.2 Hz, CH_2Ph), 5.28 (s, 1 H, C*H*Ph), 5.57 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), and 6.65–7.61 (m, 14 H, 2 Ph, C_6H_4).

Anal. Calc. for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.18; H, 6.09.

*1,5-Anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-1-*C*-[(4,6-dibenzyloxy-2-hydroxymethyl)phenylmethyl]-*D-arabino-*hex-1-enitol* (**25**). — Treatment of **15** (146 mg, 0.24 mmol) in anhydrous toluene (9 mL) with 4,6-dibenzyloxy-2-bromophenylmethanol[60] (150 mg, 0.36 mmol, 1.5 equiv.) and $Pd(PPh_3)_4$ (15 mg, 12 μmol, 0.05 equiv.) at reflux for 6 h under the conditions described for the preparation of **16** gave, after column chromatography (5:1 hexane–ethyl acetate containing 0.1% of triethylamine), **25** (144 mg, 73%) as a white solid which crystallized from ether–hexane, m.p. 100–101°, $[\alpha]_D$ +2° (*c* 0.8); ^{1}H-n.m.r. ($CDCl_3$): δ 3.55 (dd, 1 H, $J_{5,6a}$ = $J_{6a,6e}$ 10.5 Hz, H-6*a*), 4.03 (ddd, 1 H, $J_{5,6e}$ 5.0, $J_{4,5}$ 10.0, $J_{5,6a}$ 10.5 Hz, H-5), 4.14 (dd, 1 H, $J_{3,4}$ 7.2, $J_{4,5}$ 10.0 Hz, H-4), 4.17 (dd, 1 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.45 (dd, 1 H, $J_{2,3}$ 3.0, $J_{3,4}$ 7.2 Hz, H-3), 4.60–4.80 (m, 6 H, 3CH_2Ph), 4.76 (s, 2 H, CH_2OH), 5.08 (d, 1 H, $J_{2',3'}$ 3.0 Hz, H-2'), 5.31 (s, 1 H, C*H*Ph), 6.53 (d, 1 H, *J* 3.0 Hz, C_6H_2), 6.93 (d, 1 H, *J* 3.0 Hz, C_6H_2), and 7.0–7.7 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{41}H_{38}O_7$: C, 76.62; H, 5.96. Found: C, 76.80; H, 5.71.

*2,6:7,11-Dianhydro-1,3,4,9,10,12-hexa-*O*-benzyl-5,8-dideoxy-*D*-erythro-*L*-gulo-dodeca-5,7-dienitol* (**26**). — Treatment of **13** (100 mg, 0.14 mmol) in anhydrous *N,N*-dimethylformamide (1 mL) with $PdCl_2(CH_3CN)_2$ (3.7 mg, 14 μmol, 0.1 equiv.) under Ar at 60° for 3 h provided, after column chromatography (5:1 hexane–ethyl acetate containing 0.1% of triethylamine), **26** (50 mg, 85%), as a white solid, which crystallized from hexane–ether, m.p. 109°, $[\alpha]_D$ −35° (*c* 0.6); ^{1}H-n.m.r.: δ 3.80 (dd, 2 H, $J_{1a,2(11,12a)}$ 3.1,

$J_{1a,1b(12a,12b)}$ 10.5 Hz, H-1a,12a), 3.83 (dd, 2 H, $J_{1b,2(11,12b)}$ 4.8, $J_{1a,1b(12a,12b)}$ 10.5 Hz, H-1b,12b), 3.89 (dd, 2 H, $J_{3,4(9,10)}$ 5.9, $J_{2,3(10,11)}$ 8.2 Hz, H-3,10), 4.13 (ddd, 2 H, $J_{1a,2(11,12a)}$ 3.1, $J_{1b,2(11,12b)}$ 4.8, $J_{2,3(10,11)}$ 8.2 Hz, H-2,11), 4.29 (dd, 2 H, $J_{4,5(8,9)}$ 3.0, $J_{3,4(9,10)}$ 5.9 Hz, H-4,9), 4.53–4.85 (m, 12 H, 6 C*H*$_2$Ph), 5.53 (d, 2 H, $J_{4,5(8,9)}$ 3 Hz, H-5,8), and 7.2–7.4 (m, 30 H, Ph); m.s.: *m/z* (%) 91 (100), 723 (22), 830 (M^+, 3), and 848 (M^+ + 18, 1).

Anal. Calc. for $C_{54}H_{54}O_8$: C, 78.05, H, 6.55. Found: C, 78.15, H, 6.75.

*(3,4,6-Tri-*O*-benzyl-2-deoxy-β-*D*-*arabino*-hexopyranosyl)benzene* (**27**). — A solution of **16** (60 mg, 0.12 mmol) in dry ethyl acetate (2 mL) containing PtO_2 (10 mg) was stirred under H_2 at room temperature until completion of the reaction. The mixture was filtered through Celite, and the insoluble material was washed with ethyl acetate. Concentration to dryness of the combined filtrate and washings gave a residue, which was purified by column chromatography (10:1 hexane–ethyl acetate) to give **27** (45 mg, 75%) as a colorless syrup, $[\alpha]_D$ +21° (*c* 0.9); ^{1}H-n.m.r.: δ 1.68 (ddd, 1 H, $J_{2a',3'}$ 11.1, $J_{1',2a'}$ 11.7, $J_{2a',2e'}$ 13.0 Hz, H-2*a*′), 2.13 (ddd, 1 H, $J_{1',2e'}$ 2.2, $J_{2e',3'}$ 5.0, $J_{2a',2e'}$ 13 Hz, H-2*e*′), 3.53 (ddd, 1 H, $J_{5',6e'}$ 2.0, $J_{5',6a'}$ 4.5, $J_{4',5'}$ 9.5 Hz, H-5′), 3.63 (ddd, 1 H, $J_{2e',3'}$ 5.0, $J_{2a',3'}$ 11.1, $J_{3',4'}$ 8.9 Hz, H-3′), 3.77 (dd, 1 H, $J_{3',4'}$ 8.9, $J_{4',5'}$ 9.5 Hz, H-4′), 3.80 (dd, 1 H, $J_{5'6b'}$ 2.0, $J_{6a',6b'}$ 10.8 Hz, H-6b′), 3.87 (dd, 1 H, $J_{5',6a'}$ 4.5, $J_{6a',6b'}$ 10.8 Hz, H-6a′), 4.16 (dd, 1 H, $J_{1',2e'}$ 2.2, $J_{1',2a'}$ 11.7 Hz, H-1′), 4.41, 4.46, 4.50, and 4.56 (4 d, 4 H, *J* 12.0 Hz, 2 C*H*$_2$Ph), 4.72 and 5.06 (2 d, 2 H, *J* 11.5 Hz, C*H*$_2$Ph), and 7.04–7.36 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{33}H_{34}O_4$: C, 80.13; H, 6.93. Found: C, 80.32; H, 7.04.

*(3,4,6-Tri-*O*-benzyl-β-*D*-glucopyranosyl)benzene* (**28**). — To a stirred solution of **16** (60 mg, 0.12 mmol) in anhydrous oxolane (2 mL) was added 2M borane–dimethyl sulfide complex in toluene (2 equiv.) under Ar at 0°. After stirring at room temperature for 2 h, 3M NaOH (2 equiv.) and 10M H_2O_2 (6 equiv.) were added at 0°. Stirring was continued overnight at room temperature. The mixture was then diluted with dichloromethane, and the organic layer was washed with 20% $NaHSO_3$, sat. NH_4Cl, and water, dried ($MgSO_4$), and the solvent evaporated. The residue was purified by column chromatography (5:1 to 1:1 hexane–ethyl acetate) to give **28** (52 mg, 82%) as a colorless syrup, $[\alpha]_D$ +35° (*c* 0.7); ^{1}H-n.m.r.: δ 1.45 (d, 1 H, $J_{OH,2'}$ 2.5 Hz, OH), 3.49 (ddd, 1 H, $J_{5',6b'}$ 2.1, $J_{5',6a'}$, $J_{4',5'}$ 9.5 Hz, H-5′), 3.51 (m, 1 H, H-2′), 3.63 (dd, 1 H, $J_{2',3'}$ 8.9, $J_{3',4'}$ 9.0 Hz, H-3′), 3.69 (dd, 1 H, $J_{5',6b'}$ 2.0, $J_{6a',6b'}$ 10.8 Hz, H-6b′), 3.74 (dd, 1 H, $J_{5',6a'}$ 4.2, $J_{6a',6b'}$ 10.8 Hz, H-6a′), 3.90 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{4',5'}$ 9.5 Hz, H-4′), 4.04 (d, 1 H, $J_{1',2'}$ 9.1 Hz, H-1′), 4.39 and 4.51 (2 d, 2 H, *J* 12.0 Hz, C*H*$_2$Ph), 4.70 (d, 1 H, *J* 11.0 Hz, C*H*Ph), 4.86 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.90 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.96 (d, 1 H, *J* 11.0 Hz, C*H*Ph), and 7.0–7.5 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{33}H_{34}O_5$: C, 77.62; H, 6.71. Found: C, 77.68; H, 6.85.

*3,4,6-Tri-*O*-benzyl-1-*C*-phenyl-α-*D*-glucopyranose* (**29**). — To a solution of **13** (84 mg, 0.17 mmol) in anhydrous dichloromethane (1 mL) were added, under Ar, $NaHCO_3$ (43 mg, 0.25 mmol, 1.5 equiv.) and 85% 3-chloroperoxybenzoic acid (52 mg, 0.25 mmol, 1.5 equiv.). The mixture was stirred at 0° for 2 h, and then diluted with dichloromethane and 20% $NaHSO_3$. The organic extract was washed with sat. $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to dryness. The residue was purified by column chromatography (10:1 to 4:1 toluene–ethyl acetate) to give **29** (67 mg, 74%) as a colorless syrup,

$[\alpha]_D$ + 38° (*c* 2.2); ^{1}H-n.m.r.: δ 3.54 (ddd, 1 H, $J_{2,OH-1}$ ~ 1.8, $J_{2,OH-2}$ 3.2, $J_{2,3}$ 9.0 Hz, H-2), 3.71 (dd, 1 H, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 11.0 Hz, H-6b), 3.80 (dd, 1 H, $J_{5,6b}$ 4.3, $J_{6a,6b}$ 11.0 Hz, H-6a), 3.83 (dd, 1 H, $J_{4,5}$ 9.5, $J_{3,4}$ 10.0 Hz, H-4), 3.94 (dd, 1 H, $J_{2,3}$ 9.0, $J_{3,4}$ 10.0 Hz, H-3), 4.25 (ddd, 1 H, $J_{5,6b}$ 2.0, $J_{5,6a}$ 4.3, $J_{4,5}$ 9.5 Hz, H-5), 4.38 and 4.48 (2 d, 2 H, *J* 12.5 Hz, CH_2Ph), 4.67, 4.78, 4.86, and 4.95 (4 d, 4 H, *J* 11.5 Hz, 2 CH_2Ph), and 6.80–7.60 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{33}H_{34}O_6 \cdot H_2O$: C, 72.77; H, 6.66. Found: C, 73.02; H, 6.69.

*(4,6-Di-*O*-benzyl-2,3-dideoxy-β-*D*-*erythro*-hexopyranosyl)benzene* (**30**). — To a solution of **13** (40 mg, 0.08 mmol) in anhydrous dichloromethane (1 mL) were added, under Ar, triethylsilane (78 μL, 0.48 mmol, 6 equiv.) and trifluoroacetic acid (17 μL, 0.2 mmol, 2.5 equiv.) at 0°. The resulting mixture was stirred at room temperature for 2 h, the acid neutralized at 0° with *N,N*-diisopropylethylamine (3 equiv.), and the solvents were evaporated and coevaporated with toluene. The residue was purified by column chromatography (10:1 hexane–ethyl acetate) to provide **30** (26 mg, 81%) as a colorless syrup, $[\alpha]_D$ + 74° (*c* 0.8); ^{1}H-n.m.r. ($CDCl_3$): δ 1.56–1.73 (m, 2 H, H-2*a*,3*a*), 1.94–2.03 (m, 1 H, H-2*e*), 2.31–2.40 (m, 1 H, H-3*e*), 3.54 (ddd, 1 H, $J_{3e,4}$ 4.5, $J_{4,5}$ 9.7, $J_{3a,4}$ 10.2 Hz, H-4), 3.62 (ddd, 1 H, $J_{5,6b}$ 2.7, $J_{5,6a}$ 3.5, $J_{4,5}$ 9.7 Hz, H-5), 3.80 (dd, 1 H, $J_{5,6a}$ 3.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 3.84 (dd, 1 H, $J_{5,6b}$ 2.7, $J_{6a,6b}$ 11.5 Hz, H-6b), 4.42 (dd, 1 H, $J_{1,2e}$ 2.1, $J_{1,2a}$ 10.7 Hz, H-1), 4.49, 4.60, 4.64, and 4.69 (4 d, 4 H, *J* 11.5 Hz, 2 CH_2Ph), and 7.2–7.6 (m, 15 H, 3 Ph); m.s.: *m/z* (%) 106 (100), 389 (M^+ + 1, 47), and 406 (M^+ + 18, 52).

Anal. Calc. for $C_{26}H_{28}O_3$: C, 80.38; H, 7.26. Found: C, 80.21; H, 7.42.

*(3,4,6-Tri-*O*-benzyl-β-*D*-glucopyranosyl)methylbenzene* (**31**). — Treatment of **19** (35 mg, 0.07 mmol) with borane–dimethylsulfide complex in oxolane as described for the synthesis of **28** gave, after column chromatography (5:1 hexane–ethyl acetate), **31** (26 mg, 72%) as a colorless syrup, $[\alpha]_D$ + 24° (*c* 1.8); ^{1}H-n.m.r.: δ 1.87 (s, 1 H, OH), 2.83 (dd, 1 H, $J_{CH,1'}$ 7.1, J_{gem} 14.5 Hz, C*H*Ph), 3.19 (dd, 1 H, $J_{CH,1'}$ 2.5, J_{gem} 14.5 Hz, C*H*Ph), 3.25 (ddd, 1 H, $J_{5',6b'}$ 2.2, $J_{5',6a'}$ 4.0, $J_{4',5'}$ 9.0 Hz, H-5'), 3.33 (dd, 1 H, $J_{1',2'}$ 9.0, $J_{2',3'}$ 9.8 Hz, H-2'), 3.37 (ddd, 1 H, $J_{1',CH}$ 2.5, $J_{1',CH}$ 7.1, $J_{1',2'}$ 9.0 Hz, H-1'), 3.42 (t, 1 H, $J_{3',4'} = J_{4',5'}$ 9.0 Hz, H-4'), 3.60 (dd, 1 H, $J_{5',6b'}$ 2.2, $J_{6a',6b'}$ 11.5 Hz, H-6b'), 3.65 (dd, 1 H, $J_{5',6a'}$ 4.0, $J_{6a',6b'}$ 11.5 Hz, H-6a'), 3.65 (dd, 1 H, $J_{3',4'}$ 9.0, $J_{2',3'}$ 10.0 Hz, H-3'), 4.38 and 4.46 (2 d, 2 H, *J* 12.5 Hz, CH_2Ph), 4.59 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.65 (d, 1 H, *J* 12.0 Hz, C*H*Ph), 4.75 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.87 (d, 1 H, *J* 12.0 Hz, C*H*Ph), and 7.05–7.55 (m, 20 H, 4 Ph).

Anal. Calc. for $C_{34}H_{36}O_5$: C, 77.84; H, 6.92. Found: C, 77.90; H, 7.05.

*2,6:7,11-Dianhydro-1,3,4,9,10,12-hexa-*O*-benzyl-*D*-erythro-*L*-galacto-*L*-gulo-do decitol* (**32**). — Treatment of **26** (50 mg, 0.06 mmol) with borane–dimethyl sulfide complex in oxolane as described for the preparation of **28** gave, after column chromatography (3:2 hexane–ethyl acetate), **32** (32 mg, 62%) as a colorless syrup, $[\alpha]_D$ + 18° (*c* 0.9); ^{1}H-n.m.r.: δ 2.70 (bs, 2 H, OH), 3.42 (m, 2 H, H-2,11), 3.55–3.70 (m, 8 H, H-1a,1b,3,4,9,10,12a,12b), 3.74 (d, 2 H, $J_{5,6(7,8)}$ ~ 9.0 Hz, H-6,7), 4.22 (d, 2 H, $J_{4,5(7,8)} = J_{5,6(8,9)}$ ~ 9.0 Hz, H-5,8), 4.35 and 4.41 (4 d, 4 H, *J* 12.0 Hz, 2 CH_2Ph), 4.54, 4.85, 4.91, and 4.94 (8 d, 8 H, *J* 11.5 Hz, 4 CH_2Ph), and 7.00–7.50 (m, 30 H, 6 Ph); m.s.: *m/z* (%) 91 (58), 884 (M^+ + 18, 100).

Anal. Calc. for $C_{54}H_{58}O_{10} \cdot H_2O$: C, 73.28; H, 6.83. Found: C, 73.37; H, 6.80.

*1,5-Anhydro-4,6-*O*-benzylidene-1-C-(3-bromophenyl)-3-*O*-*tert*-butyldimethyl*

silyl-2-deoxy-D-arabino-*hex-1-enitol* (**33**). — Treatment of **14** (600 mg, 0.92 mmol) in anhydrous toluene (4 mL) with 1,3-dibromobenzene (280 μL, 2.31 mmol, 2.5 equiv.) and $Pd(PPh_3)_4$ (53 mg, 46 μmol, 0.05 equiv.) for 3 h under the conditions described for the preparation of **16** gave, after column chromatography (1:1 hexane–toluene containing 0.1% of triethylamine), **33** (384 mg, 83%) as a colorless syrup, $[\alpha]_D$ − 19° (*c* 1.4): ^{1}H-n.m.r.: δ 0.16 (s, 3 H, CH_3), 0.18 (s, 3 H, CH_3), 1.02 (s, 9 H, ^{t}Bu), 3.52 (dd, 1 H, $J_{5,6a}$ 10.0, $J_{6a,6e}$ 10.5 Hz, H-6*a*), 3.72 (dd, 1 H, $J_{3,4}$ 7.5, $J_{4,5}$ 10.0 Hz, H-4), 3.81 (dt, 1 H, $J_{5,6e}$ 5.0, $J_{4,5}$ = $J_{5,6a}$ 10.0 Hz, H-5), 4.15 (dd, 1 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.5 Hz, H-6*e*), 4.60 (dd, 1 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.5 Hz, H-3), 5.23 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2), 5.29 (s, 1 H, C*H*Ph), and 6.68–7.78 (m, 9 H, 2 Ph); m.s.: *m/z* (%) 279 (100), 503 (M^+ + 1, 38), and 505 (M^+ + 1, 35).

Anal. Calc. for $C_{25}H_{31}BrO_4Si$: C, 59.64; H, 6.21. Found: C, 59.70; H, 6.38.

*1,3-Di-(1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy*-D-arabino-*hex-1-enit-1-yl)benzene* (**34**). — Treatment of **14** (100 mg, 0.15 mmol, 2 equiv.) in anhydrous toluene (2 mL) with 1,3-dibromobenzene (9 μL, 0.075 mmol) and $Pd(PPh_3)_4$ (8 mg, 7.7 μmol, 0.1 equiv.) for 5 h under the conditions described for the preparation of **16** gave, after column chromatography (15:1 hexane–ethyl acetate containing 0.1% triethylamine), **34** (50 mg, 85%) as a white powder, $[\alpha]_D$ − 30.5° (*c* 1.0); ^{1}H-n.m.r.: δ 0.17 (s, 6 H, CH_3), 0.22 (s, 6 H, CH_3), 1.06 (s, 18 H, ^{t}Bu), 3.59 (dd, 2 H, $J_{5,6a}$ 10.0, $J_{6a,6e}$ 10.5 Hz, 2 H-6*a*), 3.80 (dd, 2 H, $J_{3,4}$ 7.2, $J_{4,5}$ 10.0 Hz, 2 H-4), 3.87 (dt, 2 H, $J_{5,6e}$ 5.0, $J_{4,5}$ = $J_{5,6a}$ 10.0 Hz, 2 H-5), 4.25 (dd, 2 H, $J_{5,6e}$ 5.0, $J_{6a,6e}$ 10.5 Hz, 2 H-6*e*), 4.66 (dd, 2 H, $J_{2,3}$ 2.5, $J_{3,4}$ 7.2 Hz, 2 H-3), 5.31 (s, 2 H, 2 C*H*Ph), 5.38 (d, 2 H, $J_{2,3}$ 2.5 Hz, 2 H-2), 6.07–7.25 (m, 7 H, Ph), 7.55 (dd, 2 H, *J* 2.0, 7.5 Hz, C_6H_4), 7.61–7.66 (m, 4 H, Ph), and 8.11 (t, 1 H, *J* 2.0 Hz, C_6H_4).

Anal. Calc. for $C_{44}H_{58}O_8Si_2$: C, 68.54; H, 7.58. Found: C, 68.32; H, 7.72.

*1-(1,5-Anhydro-3,4,6-tri-*O*-benzyl-2-deoxy*-D-arabino-*hex-1-enit-1-yl)-3-(1,5-anhydro-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy*-D-arabino-*hex-1-enit-1-yl)benzene* (**35**). — Treatment of **33** (60 mg, 0.12 mmol) in anhydrous toluene (2 mL) with **13** (101 mg, 0.14 mmol, 1.2 equiv.) and $Pd(PPh_3)_4$ (14 mg, 12 μmol, 0.1 equiv.) for 6 h under the conditions described for the preparation of **16** gave, after column chromatography (20:1 hexane–ethyl acetate containing 0.1% of triethylamine), **35** (78 mg, 78.5%) as a white powder, $[\alpha]_D$ − 16.5° (*c* 1.0); ^{1}H-n.m.r.: δ 0.18 (s, 3 H, CH_3), 0.20 (s, 3 H, CH_3), 1.04 (s, 9 H, ^{t}Bu), 3.58 (dd, 1 H, $J_{5',6a'}$ = $J_{6a',6e'}$ 10.0 Hz, H-6*a'*), 3.78–3.92 (m, 4 H, H-6a",6b",5,4'), 4.08 (dd, 1 H, $J_{3'',4''}$ 5.8, $J_{4'',5''}$ 8.5 Hz, H-4"), 4.23 (dd, 1 H, $J_{5',6e'}$ 5.0, $J_{6a',6e'}$ 10.0 Hz, H-6*e'*), 4.29 (ddd, 1 H, $J_{5'',6b''}$ 3.1, $J_{5'',6a''}$ 4.8, $J_{4'',5''}$ 8.2 Hz, H-5"), 4.35 (dd, 1 H, $J_{2'',3''}$ 3.1, $J_{3'',4''}$ 5.8 Hz, H-3"), 4.42 (d, 1 H, *J* 11.0 Hz, C*H*Ph), 4.45 (s, 2 H, C*H*Ph), 4.48 (d, 1 H, *J* 11.0 Hz, C*H*Ph), 4.64 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 4.68 (dd, 1 H, $J_{2',3'}$ 2.5, $J_{3',4'}$ 7.5 Hz, H-3'), 4.80 (d, 1 H, *J* 11.5 Hz, C*H*Ph), 5.31 (s, 1 H, C*H*Ph), 5.39 (d, 1 H, $J_{2',3'}$ 2.5 Hz, H-2'), 5.51 (d, 1 H, $J_{2'',3''}$ 3.1 Hz, H-2"), and 7.0–8.2 (m, 24 H, 4 Ph, C_6H_4).

Anal. Calc. for $C_{52}H_{58}O_8Si$: C, 74.43; H, 6.98. Found: C, 74.60; H, 7.29.

*1,4-Di-(1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy*-D-arabino-*hex-1-enit-1-yl)benzene* (**36**). — Treatment of **13** (100 mg, 0.14 mmol, 2 equiv.) in anhydrous toluene (2 mL) in the presence of 1,4-dibromobenzene (16.7 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (8 mg, 7.1 μmol, 0.1 equiv.) for 3 h under the conditions described for the preparation of **16** gave,

after column chromatography (10:1 toluene–ethyl acetate), **36** (47.5 mg, 71%) as a white powder, $[\alpha]_D$ −6° (*c* 0.7); ^{1}H-n.m.r.: δ 3.82 (dd, 2 H, $J_{5,6b}$ 3.0, $J_{6a,6b}$ 10.5 Hz, 2 H-6b), 3.88 (dd, 2 H, $J_{5,6a}$ 4.9, $J_{6a,6b}$ 10.5 Hz, 2 H-6a), 4.11 (dd, 2 H, $J_{3,4}$ 6.0, $J_{4,5}$ 8.5 Hz, 2 H-4), 4.25 (ddd, 2 H, $J_{5,6b}$ 3.0, $J_{5,6a}$ 4.9, $J_{4,5}$ 8.5 Hz, 2 H-5), 4.39 (dd, 2 H, $J_{2,3}$ 3.2, $J_{3,4}$ 6.0 Hz, 2 H-3), 4.44 (s, 4 H, 2 CH_2Ph), 4.46 and 4.54 (4 d, 4 H, *J* 12.5 Hz, 2 CH_2Ph), 4.67 and 4.83 (4 d, 4 H, *J* 12.0 Hz, 2 CH_2Ph), 5.49 (d, 2 H, $J_{2,3}$ 3.2 Hz, 2 H-2), 7.0–7.35 (m, 30 H, 6 Ph), and 7.74 (s, 4 H, C_6H_4).

Anal. Calc. for $C_{60}H_{58}O_8$: C, 79.45; H, 6.45. Found: C, 79.31; H, 6.50.

*1,3,5-Tri-(1,5-anhydro-3,4,6-tri-*O*-benzyl-2-deoxy-*D*-arabino-hex-1-enit-1-yl)-benzene* (**37**). — Treatment of **13** (100 mg, 0.14 mmol, 3.3 equiv.) in anhydrous toluene (2 mL) with 1,3,5-tribromobenzene (13.5 mg, 0.04 mmol) and $Pd(PPh_3)_4$ (4.2 mg, 4.3 μmol, 0.1 equiv.) for 4 h under the conditions described for the preparation of **16** gave, after column chromatography (5:1 hexane–ethyl acetate containing 0.1% of triethylamine) **37** (33.3 mg, 59%) as a white powder, $[\alpha]_D$ −22° (*c* 1.0); ^{1}H-n.m.r.: δ 3.83 (dd, 3 H, $J_{5',6b}$ 3.5, $J_{6a,6b}$ 10.5 Hz, 3 H-6b), 3.89 (dd, 3 H, $J_{5,6a}$ 5.0, $J_{6,6b}$ 10.5 Hz, 3 H-6a), 4.11 (dd, 3 H, $J_{3,4}$ 5.9, $J_{4,5}$ 8.0 Hz, 3 H-4'), 4.31–4.39 (m, 6 H, 3 H-3,5), 3.39 (d, 3 H, *J* 12.0 Hz, 3 C*H*Ph), 4.42 (s, 6 H, 3 CH_2Ph), 4.43 (s, 6 H, 6 C*H*Ph), 4.49 (d, 3 H, *J* 12.0 Hz, 3 C*H*Ph), 4.64 and 4.79 (2 d, 6 H, *J* 12.0 Hz, 3 CH_2Ph), 5.60 (dd, 3 H, $J_{2,3}$ 3.4 Hz, 3 H-2), 7.05–7.35 (m, 45 H, 9 Ph), and 8.30 (s, 3 H, C_6H_3).

Anal. Calc. for $C_{87}H_{84}O_{12}$: C, 79.07; H, 6.41. Found: C, 78.88; H, 6.15.

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REFERENCES

1 For recent references on the synthesis of *C*-glycosyl compounds, see *Carbohydr. Res.*, 171 (1987) 1–345.
2 J. G. Buchanan, *Progr. Chem. Org. Nat. Prod.*, 44 (1983) 243–299.
3 U. Hacksell and G. D. Daves, Jr., *Prog. Med. Chem.*, 22 (1985) 1–65.
4 G. D. Daves, Jr., *Acc. Chem. Res.*, 23 (1990) 201–206.
5 J.-M. Beau and P. Sinaÿ, *Tetrahedron Lett.*, 26 (1985) 6185–6188; 6189–6192; 6193–6196.
6 P. Lesimple, J.-M. Beau, and P. Sinaÿ, *J. Chem. Soc., Chem. Commun.*, (1985) 894–895.
7 P. Lesimple, J.-M. Beau, and P. Sinaÿ, *Carbohydr. Res.*, 171 (1987) 289–300.
8 P. Lesimple, J.-M. Beau, G. Jaurand, and P. Sinaÿ, *Tetrahedron Lett.*, 27 (1986) 6201–6204; P. Lesimple and J.-M. Beau, unpublished results; P. Lesimple, Ph.D. dissertation, Université d'Orsay, 1988.
9 K. C. Nicolaou, C.-K. Hwang, and M. E. Duggan, *J. Chem. Soc., Chem. Commun.*, (1986) 925–926.
10 S. Hanessian, M. Martin, and R. C. Desai, *J. Chem. Soc., Chem. Commun.*, (1986) 926–927.
11 R. R. Schmidt, R. Preuss, and R. Betz, *Tetrahedron Lett.*, 28 (1987) 6591–6594.
12 R. Preuss and R. R. Schmidt, *Justus Liebigs Ann. Chem.*, (1989) 429–434.
13 I. P. Beletskaya, *J. Organomet. Chem.*, 250 (1983) 551–564.
14 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 25 (1986) 508–524.
15 M. Kosugi, K. Sasazawa, I. Shimizu, and T. Migita, *Chem. Lett.*, (1977) 301–302.
16 J. A. Soderquist and W.W.-H. Leong, *Tetrahedron Lett.*, 24 (1983) 2361–2362.
17 M. Kosugi, T. Sumiya, Y. Obara, M. Suzuki, H. Sano, and T. Migita, *Bull. Chem. Soc. Jpn.*, 60 (1987) 767–768.

18 V. Farina, S. R. Baker, D. A. Benigni, and C. Sapino, Jr., *Tetrahedron Lett.*, 29 (1988) 5739–5742.
19 S. L. Schreiber, D. Desmaele, and J. A. Porco, Jr., *Tetrahedron Lett.*, 29 (1988) 6689–6692.
20 S. L. Schreiber and J. A. Porco, Jr., *J. Org. Chem.*, 54 (1989) 4721–4723.
21 R. Hambalek and G. Just, *Tetrahedron Lett.*, 31 (1990) 5445–5448.
22 H. B. Kwon, B. H. McKee, and J. K. Stille, *J. Org. Chem.*, 55 (1990) 3114–3118.
23 E. Dubois and J.-M. Beau, *J. Chem. Soc., Chem. Commun.*, (1990) 1191–1192.
24 R. W. Friesen and C. F. Sturino, *J. Org. Chem.*, 55 (1990) 2572–2574.
25 I. Arai and G. D. Daves, Jr., *J. Org. Chem.*, 43 (1978) 4110–4112.
26 S. Czernecki and F. Gruy, *Tetrahedron Lett.*, 22 (1981) 437–440.
27 S. Czernecki and V. Dechavanne, *Can. J. Chem.*, 61 (1983) 533–540.
28 S. Yougai and T. Miwa, *J. Chem. Soc., Chem. Commun.*, (1983) 68–69.
29 T. V. Rajanbabu, *J. Org. Chem.*, 50 (1985) 3642–3644.
30 L. V. Dunkerton, J. M. Enske, and A. J. Serino, *Carbohydr. Res.*, 171 (1987) 89–107; and references cited therein.
31 M. Brakta, P. Lhoste, and D. Sinou, *J. Org. Chem.*, 54 (1989) 1890–1896; and previous work cited therein.
32 A. Lipták, I. Jodál, J. Harangi, and P. Nánási, *Acta Chim. Hung.*, 113 (1983) 415–422.
33 K. C. Nicolaou, J. L. Randall, and G. T. Furst, *J. Am. Chem. Soc.*, 107 (1985) 5556–5558.
34 A. Fernandez-Mayoralas, A. Marra, M. Trumtel, A. Veyrières, and P. Sinaÿ, *Carbohydr. Res.*, 188 (1989) 81–95.
35 R. Kuhn and H. Trischmann, *Chem. Ber.*, 94 (1961) 2258–2263.
36 P. Lesimple and J.-M. Beau, unpublished results.
37 D. R. McKean, G. Parrinello, A. F. Renaldo, and J. K. Stille, *J. Org. Chem.*, 52 (1987) 422–424.
38 J. R. Doyle, P. E. Slade, and H. B. Jonassen, *Inorg. Synth.*, 6 (1960) 216–219.
39 J. K. Stille and B. L. Groh, *J. Am. Chem. Soc.*, 109 (1987) 813–817.
40 J. K. Stille and J. H. Simpson, *J. Am. Chem. Soc.*, 109 (1987) 2138–2152.
41 R. R. Schmidt, W. Frick, B. Haag-Zeino, and S. Apparao, *Tetrahedron Lett.*, 28 (1987) 4045–4048.
42 R. J. Ferrier, *Adv. Carbohydr. Chem. Biochem.*, 20 (1965) 67–137; 24 (1969) 199–266.
43 R. D. Guthrie and R. W. Irvine, *Carbohydr. Res.*, 82 (1980) 207–224.
44 W. Priebe and A. Zamojski, *Tetrahedron*, 36 (1980) 287–297.
45 B. Fraser-Reid and B. Radatus, *J. Am. Chem. Soc.*, 92 (1970) 6661–6663.
46 S. Y.-K. Tam and B. Fraser-Reid, *Tetrahedron Lett.*, (1973) 4897–4901.
47 O. Achmatowicz and B. Szechner, *Tetrahedron Lett.*, (1972) 1205–1209.
48 G. Grynkiewicz, *Carbohydr. Res.*, 128 (1984) c9–c10.
49 M. D. Lewis, J. K. Cha, and Y. Kishi, *J. Am. Chem. Soc.*, 104 (1982) 4976–4978.
50 J.-M. Lancelin, P.-H. Amvam-Zollo, and P. Sinaÿ, *Tetrahedron Lett.*, 24 (1983) 4833–4836.
51 M. Ceroni and U. Sequin, *Helv. Chim. Acta*, 65 (1982) 302–316.
52 I. Takahashi, K.-I. Takahashi, K. Asano, I. Kawamoto, T. Yasuzawa, T. Ashizawa, F. Tomita, and H. Nakano, *J. Antibiot.*, 41 (1988) 1151–1153.
53 M. Furukawa, I. Hayakawa, G. Ohta, and Y. Iitaka, *Tetrahedron*, 31 (1975) 2989–2995.
54 S. Kondo, M. Miyamoto, H. Naganawa, T. Takeuchi, and H. Umezawa, *J. Antibiot.*, 30 (1977) 1143–1145.
55 D. D. Perrin, W. L. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980.
56 D. R. Coulson, L. C. Satek, and S. O. Grim, *Inorg. Synth.*, 13 (1972) 121–123.
57 K. Moseley and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1974) 169–173.
58 W. C. Still, M. Kahn, and A. Mittra, *J. Org. Chem.*, 43 (1978) 2923–2926.
59 R. J. Ferrier, R. H. Furneaux, and P. C. Tyler, *Carbohydr. Res.*, 58 (1977) 397–404.
60 A. K. Sinhababu and R. T. Borchardt, *J. Org. Chem.*, 48 (1983) 2356–2360.
61 T. Ando, S. Shioi, and M. Nakagawa, *Bull. Chem. Soc. Jpn.*, 45 (1972) 2611–2615.