112. Radical Rearrangements of 2-*O*-(Diphenoxyphosphoryl)glycosyl Bromides

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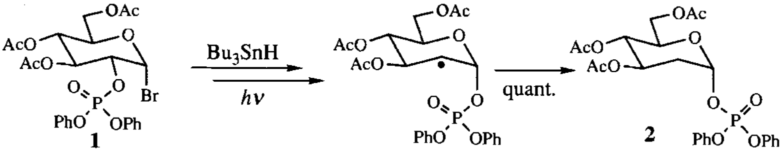
A variety of 2-deoxy-1-*O*-diphenoxylphosphoryl-hexopyranoses were generated *in situ* by a radical 2→1 migration of the phosphate group. The structures of the reactive rearrangement products were fully elucidated by NMR spectroscopy. Rate constants for this new rearrangement were determined for a variety of substrates.

Introduction. – The radical 2→1 migration of acyloxy groups in glycosyl radicals is a well known reaction [1]. Recently, we and *Crich* and *Yao* published studies [2] on the hitherto unknown radical rearrangement of diphenoxyphosphoryl groups. As radical precursors, 3,4,6-tri-*O*-acetyl-2-*O*-(diphenoxyphosphoryl)-α-D-glucopyranosyl bromide (**1**; →**2**, see *Scheme 1*) and 3,5-di-*O*-benzoyl-2-*O*-(diphenoxyphosphoryl)-D-ribofuranosyl bromide were examined. The full extent of this new rearrangement has now been demonstrated by studies on other pyranose radical precursors.

Scheme 1

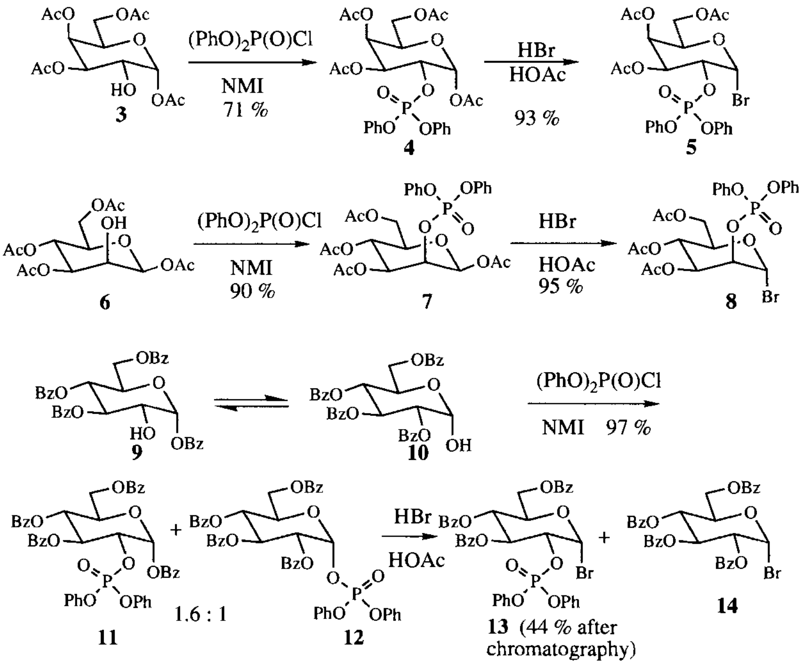


Synthesis of Phosphorylated Glycosyl Bromides. – The partially acetylated carbohydrate derivatives 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose [3] (**3**) and 1,3,4,6-tetra-*O*-acetyl-β-D-mannopyranose [4] (**6**) are available by known literature procedures. Diphenyl phosphorochloridate and 1-methyl-1*H*-imidazole (NMI) were used to introduce the phosphate ester at C(2) (→**4** and **7**, respectively) prior to generation of the glycosyl bromides **5** and **8**, respectively, by treatment with a solution of HBr in AcOH (66 and 86% yield, respectively; *Scheme 2*).

The 1,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranose [5] (**9**) is known to isomerize and thus to be in equilibrium with 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose (**10**) in solution. Nevertheless, the mixture was phosphorylated, and after treatment with HBr in AcOH 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranosyl bromide [6] (**14**) and the desired phosphoryl derivative **13** were separated by chromatography (*Scheme 2*).

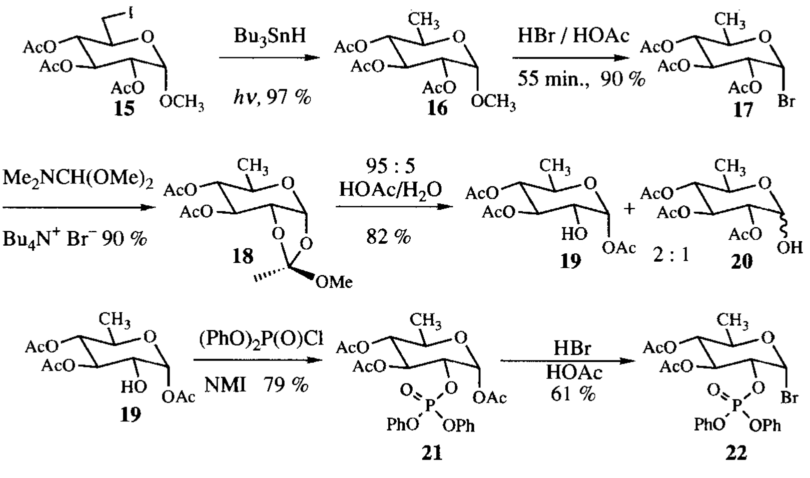
The synthesis of phosphorylated 6-deoxy-sugar **22** was of particular interest, as it would allow to study the influence of the AcO group at C(6) on the different reaction

Scheme 2



steps. The synthesis of its precursor **19** has not been reported. Since 6-deoxy-D-glucopyranose is rather expensive, we chose the following reaction sequence for the synthesis of **19**: methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside [7] (**15**) was reduced quantitatively to methyl 2,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranoside (**16**) by irradiation in the presence of Bu_3SnH (*Scheme 3*). The unstable glucopyranosyl bromide **17** was

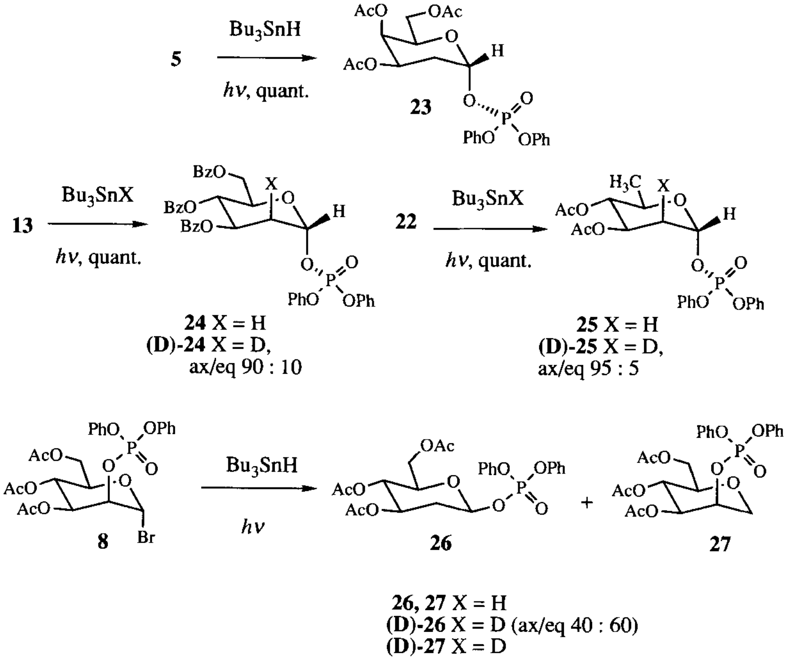
Scheme 3



then generated and subsequently treated with *N,N*-dimethylformamide dimethyl acetal in the presence of Bu_4NBr [8] to yield, after aqueous workup and purification by chromatography orthoester **18**. According to the procedure of *Lemieux* and *Driguez* [9], **18** was hydrolyzed with $AcOH/H_2O$ 95:5. The desired 1,3,4-tri-*O*-acetyl-6-deoxy-α-D-glucopyranose (**19**) was separated by fractional crystallization from Et_2O/pentane (yield over four steps 44%) and converted to **22**.

Rearrangements. – Irradiation of the glycosyl bromides **5**, **13**, and **22** in the presence of 1.1 equiv. of Bu_3SnH resulted in a radical chain reaction producing quantitatively the 1-*O*-phosphorylated hexopyranoses **23**, **24**, and **25**, respectively (*Scheme 4*). In the first step, the Br-atom was abstracted at C(1), then the 2→1 migration of the diphenoxyphosphoryl group occurred. The radical at C(2) was trapped by H-transfer from Bu_3SnH, thereby regenerating the stannyl radical for halogen abstraction. Due to the sensitivity of the products **23**–**25** to elimination of diphenyl hydrogen phosphate on heating and to hydrolysis of the phosphate group at C(1) on chromatography, they could only be examined in solution1), and ^1H-, ^{13}C-, and ^{31}P-NMR spectroscopy were used for structure elucidation [12].

Scheme 4



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1) We have recently shown that 2-deoxy-D-glycosyl phosphates are labile compounds [2], whereas thio derivatives can be isolated [10] [11].

The two α-D-*arabino*-hexopyranoses **24** and **25** were observed in a $^4C_1$-configuration [13] of the pyranose ring. The coupling constant ^3J(C(2),P) [14] indicated a *trans*-orientation of the phosphate group and C(2), in accordance with a *W*-configuration [15] derived from $^4J(H_{ax}$–C(2),P). *J*(*H*–C(1),P) allowed calculation of the dihedral angle H–C(1)–C(1)–O–P; the values of 40 and 30° for **24** and **25**, respectively, correspond to a slight rotation around the C(1)–O bond of the phosphate group towards the O-atom of the pyranose ring. The coupling constants ^2J(C(1),P) = 5.7 and ^3J(C(2),P) = 8.2 Hz observed for the α-D-*lyxo*-hexopyranose **23** show that the diphenoxyphosphoryl group is orientated in an identical manner to the aforementioned compounds. The axial AcO group at C(4) causes only a minor distortion of the $^4C_1$-configuration of the pyranose ring. The conformation of the phosphorylated 2-deoxy-sugars is in accordance with predictions for the orientation of the O-substituent derived from the *exo*-anomeric effect [16]. A recently published crystal structure of α-D-glucopyranosyl potassium hydrogen phosphate [17] reveals an almost identical dihedral angle for the H–C(1)–C(1)–O–P segment, and the angle for H–C(2)–C(2)–C(1)–O–P is given to be 174.6°.

By carrying out the reaction with a deuterated radical mediator, Bu_3SnD, the radical nature of the rearrangement was proved by quantitative incorporation of a D-atom at C(2). The ratio axial/equatorial D of 90:10 for the benzoyl-protected compound (D)-**24** and of 95:5 for the 6-deoxy-sugar (D)-**25** demonstrates an effective shielding of the bottom face of the pyranose ring during the radical reaction.

From former work on 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide [18], we know that the AcO group at C(2) migrates slower than the equatorial group in the *gluco*-configurated compound. As a result, 1,3,4,6-tetra-*O*-acetyl-β-D-*arabino*-hexopyranose is always produced along with the direct reduction product 2,3,4,6-tetra-*O*-acetyl-1,5-anhydro-D-mannitol. With the phosphorylated mannose derivative **8**, the situation is very similar. The reduction product 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-*O*-(diphenoxyphosphoryl)-D-mannitol (**27**) was formed exclusively at elevated Bu_3SnH concentrations (1.4M). Thanks to its stability, **27** could be isolated and purified by chromatography. In dilute solution (0.19M), **27** was formed in an 1:1 mixture along with the new β-D-configurated 2-deoxy-sugar **26**. Phosphate **26** is a very sensitive and unstable intermediate and, depending on the concentration of the solution, isomerizes [19] to the thermodynamically more stable α-D-anomer **2**.

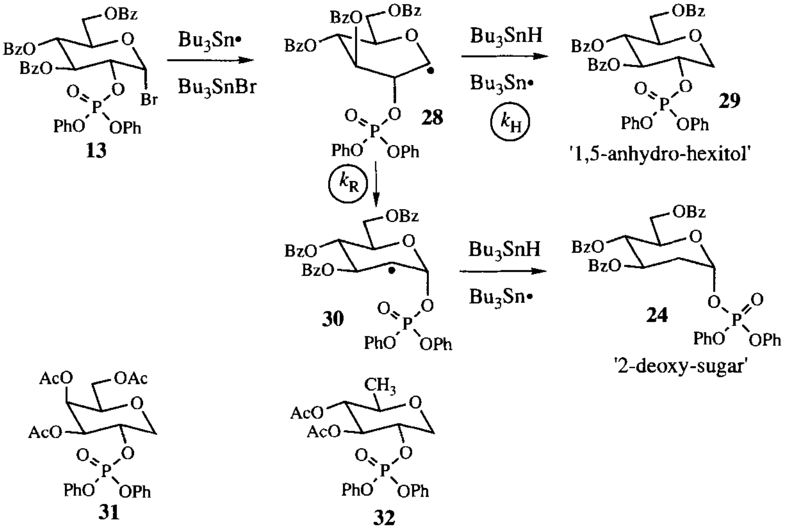
Compound **26** shows as characteristic signals in the ^{1}H-NMR spectrum at 5.40 ppm a *ddd* (*J* = 2.4, 6.9, and 9.3 Hz, H–C(1)) and at 2.04 ppm a *ddd* (*J* = 2.4, 5.2, and 12.5 Hz, H_{eq}–C(2)). The splittings for the signal at 2.04 ppm are characteristic of a 2-deoxy-sugar with an equatorial substituent at C(1), especially the axial-equatorial coupling constant ^3J(H–C(1),H_{eq}–C(2)) of 2.4 Hz. The axial-axial coupling ^3J(H–C(1),H_{ax}–C(2)) of 9.3 Hz is typical for carbohydrates. The coupling constant of 6.9 Hz is a splitting caused by the phosphate ester, and its size clearly proves [12] the location of the diphenoxyphosphoryl group at C(1). Further evidence for the β-D-orientation of the P-group at C(1) was obtained by ^{13}C- and ^{31}P-NMR spectroscopy.

When the irradiation of **8** was carried out with Bu_3SnD, a 2:1 mixture of the deuterated 2-deoxy-sugar (D)-**26** and the deuterated reduction product (D)-**27** was detected. The ^{2}H-NMR spectrum clearly indicated the unspecific incorporation of D at C(2). Thus, an equatorial phosphate group at the anomeric center does not shield the equatorial position at the adjacent radical center in H- or D-abstracting reactions.

All experiments prove that the radical 2→1 migration of the diphenoxyphosphoryl group proceeds exclusively in a stereospecific manner. With the mannose precursor **8**, the migration on the top face of the pyranose ring leads to the β-D-phosphate **26**. The rearrangement products **2** and **23**–**25** with the axial diphenoxyphosphoryl group at C(1) are formed quantitatively from the precursors with equatorial phosphoryl group at C(2).

Kinetic Experiments. – The radical rearrangement of the diphenoxyphosphoryl group appears to be a very fast reaction; on a preparative scale, the rearrangement products

Scheme 5[a])



[a]) Scheme valid for all competition kinetic experiments.

Table. *Rate Constants for the Radical Rearrangement of the Diphenoxyphosphoryl Group at 27°*

Precursor	Hydride	2-Deoxy-sugar	1,5-Anhydro-D-hexitol	k_R/k_H [M]	$k_R \cdot 10^{-5}$ [s^{-1}]
1	Bu$_3$SnH	**2**		3.97	80 [2]
13	Bu$_3$SnH	**24**	**29**	2.07	45
5	Bu$_3$SnH	**23**	**31**	2.23	46
22	PhSH	**25**	**32**	1.9	2000
8	Bu$_3$SnH	**26**	**27**	0.067	1

were formed quantitatively. For a more precise determination of the rate constants, the different steps of the radical process have to be discussed. The radical reaction was initiated by irradiating the mixture of glycosyl bromide and Bu$_3$SnH with a UV lamp. From **13**, radical **28** was generated which could react with the H-donor leading to the 1,5-anhydro-D-hexitol derivative **29** (*Scheme 5*). Alternatively, the phosphate group could migrate from C(2) to C(1), presumably *via* a charge-separated transition state [20]. This secondary radical **30**, subsequently, would react with Bu$_3$SnH to yield 2-deoxy-sugar **24**. In a similar way, glycosyl bromides **5**, **22**, and **8** led to a mixture of rearranged products **23**, **25**, and **26** and unrearranged hexitols **31**, **32**, and **27**, respectively.

The rate constant for the H-transfer from Bu$_3$SnH to cyclohexyl radicals, an adequate model for secondary carbohydrate radicals, is known to be *ca.* $2 \times 10^6 s^{-1}$ at 27° [21]. The competition between reduction of the primary radical (second-order reaction) and the 2→1 rearrangement of the phosphate group (first-order reaction) offers the possibility to determine the rate constant of the rearrangement by competition kinetics. For this purpose, the concentration of Bu$_3$SnH has to be adjusted to allow the required formation of the 2-deoxy-sugars and the 1,5-anhydro-D-hexitols as a mixture. A variation of the concentration of Bu$_3$SnH as H-donor within the range 0.39–1.37M (11–38 equiv.) turned out to be appropriate. Bu_3SnH was used at least in a 10-fold excess (pseudo-first-order conditions). Therefore, the data, which are summarized in the *Table*, could be evaluated by *Eqn. 1*.

$$\frac{[\text{2-deoxy-sugar}]}{[\text{1,5-anhydro-D-hexitol}]} = \frac{k_R}{k_H \cdot [Bu_3SnH]} \tag{1}$$

For the benzoyl-protected glucose derivative **13**, the slope of the plot was 2.07M corresponding to a rate constant of $4.5 \cdot 10^6 s^{-1}$. This was slightly slower than the rate ($8 \cdot 10^6 s^{-1}$) for the acetyl-procted glucose derivative **1**, possibly reflecting a less flexible pyranose ring due to the presence of the bulkier benzoyl groups and the more electron-withdrawing ability of the aromatic ring. The rate constant k_R of $4.6 \cdot 10^6 s^{-1}$ (slope $k_R/k_H = 2.2$M) for the galactose **5** was of the same order of magnitude, reflecting only minor steric interactions of the axial AcO group at C(4) during the rearrangement.

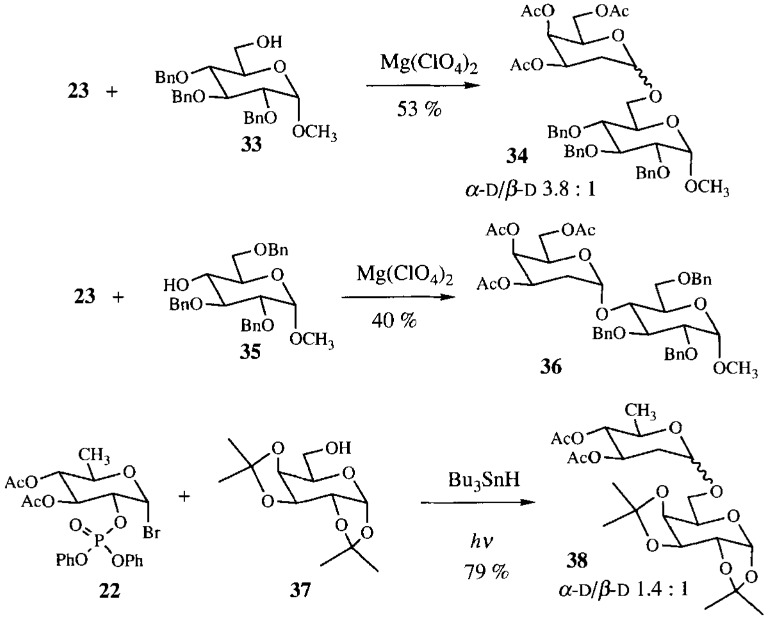
Surprisingly, the reaction with the 6-deoxy-sugar **22** proceeded much faster than expected from the result with glucose **1**. As a consequence, the amount of **32** resulting from reduction with Bu_3SnH was very low, allowing only a rough estimate of the slope to be greater than 8.0M. To determine a precise rate constant, the H-donor had to be changed. The compound of choice was thiophenol. For primary, secondary, and tertiary radicals, the rate constants for H-transfer are known to be in the range of $0.8 \cdot 10^8$ to $1.5 \cdot 10^8 s^{-1}$ at 25° [22]. For our experiments, a mean value of $1.0 \cdot 10^8 s^{-1}$ for the H-transfer to secondary carbohydrate radicals seemed to be appropriate. Variation of thiophenol concentration from 1.26 to 2.5M (33–66 equiv.) gave a good straight-line plot. From the slope of 1.9M, value of $k_R = 2 \cdot 10^8 s^{-1}$ for rearrangement of the diphenoxyphosphoryl group was calculated. This is a 25-fold acceleration in the rate of rearrangement for the 6-deoxy-sugar **22** compared to carbohydrate **1** with identical configuration and an AcO group at C(6). Two effects exist which could explain this observation. The rearrangement is known to proceed through a charge-separated intermediate [23]. A positive charge on the pyranose ring could be disfavored by the electron-withdrawing AcO group at C(6) [24]. A second factor is the increased conformational flexibility of the pyranose ring made possible by the lack of an AcO group at C(6). For the rearrangement of AcO groups [25], it has been proven that halogen abstraction leads primarily to a radical at C(1) that adopts a $B_{2,5}$-conformation. During the course of the rearrangement, the C(1)–C(2) segment succumbs to slight flattening, until the secondary radical adopts the expected $^4C_1$-conformation. This sequence might proceed a little faster in the 6-deoxy case.

The difficulties in carrying out the rearrangement with the axially phosphorylated mannopyranosyl bromide **8** suggested that in this case, the reaction is significantly slower. In the *manno*-series, the primary radical obtained by halogen abstraction from the precursor is stabilized by the coplanar orientation of the singly occupied orbital at C(1) with axial C–O bond at C(2) and the lone pair of the ring O-atom. In addition, the equatorial substituent at C(1) destabilizes the rearrangement product **26**, compared to a product with an axial substituent at C(1).

To tackle the problem of kinetic measurements, the relative rate for H-delivery to the primary radical had to be reduced. The use of the slower H-donor tris(trimethylsilyl)silane [26] was unsuccessful, the only product resulting from *β*-elimination of the phosphate group was 3,4,6-tri-*O*-acetyl-D-*arabino*-hex-1-enitol. Thus, we reverted to the use of Bu_3SnH, but this time in dilute solution. As the reduction is a second-order reaction, the rate constant for H-transfer could be diminished by using Bu_3SnH concentrations of 0.13–0.08M. To ensure pseudo-first-order conditions, the concentration of the *manno*-radical precursor **8** had to be reduced to 0.005M. As the β-D-*arabino*-hexopyranose **26** has only limited stability, the acquisition time for the required ^{31}P-NMR spectra could not be extended to more than 1 h. Despite obtaining only a moderate signal-to-noise ratio, the rate constant was determined to be in the range of $9 \cdot 10^4$ to $1 \cdot 10^5 s^{-1}$. Thus, changing from the glucose series to the axial phosphorylated mannose **8** causes a retardation of the rearrangement by nearly two orders of magnitude. The slower reaction reflects the influence of a better stabilized primary radical and a less stabilized secondary radical on the total gain of stabilizing energy, the driving force for any kind of rearrangement.

Generation 2′-Deoxy-disaccharides. – In our publication restricted to derivatives of the glucose series [2], we stressed the possibilities for synthesizing members of the interesting class of 2′-deoxy-D-*arabino*-hexopyranosyl glycosides using 2-deoxy-D-glycosyl phosphates[2]). As further proof of the synthetic applicability of this new methodology, the two 2′-deoxy-D-*lyxo*-hexopyranosyl glycosides **34** and **36** and the 2′,6′-dideoxy-D-*arabino*-hexopyranosyl glycoside **38** were synthesized (*Scheme 6*). As described for the glucose series [2], the galactosyl bromide **5** was irradiated in THF in the presence of Bu_3SnH. On completion of the diphenoxyphosphoryl migration (→ **23**), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**33**) or methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside [28] (**35**) were reacted with the phosphorylated glycosyl donor **23** in the presence of 0.1 equiv. of anh. $Mg(ClO_4)_2$ to yield **34** and **36**, respectively.

Scheme 6



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[2]) This method complements the known synthetic routes using phosphorothioates and phosphinothioates [11] [27].

The 6-deoxy-2-*O*-(diphenoxyphosphoryl)-α-D-glucopyranosyl bromide (**2**) was irradiated in the presence of Bu_3SnH using 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose [29] (**37**) as nucleophile. Disaccharide **38** was obtained in 79% yield and in an α-D/β-D ratio of 1.4:1. This ratio corresponds exactly to the one observed when the reaction was carried out with the 6-*O*-acetyl-protected compound **1** under identical conditions. Although it has been suggested [30] that ester groups might anchimerically assist the glycosidation step, for the glucose derivatives **1** and **22**, the presence or absence of the AcO group at C(6) has no influence on the stereochemical course of the reaction.

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Experimental Part

General. Flash chromatography (FC): silica gel *C 560 KV*, 35–70 μm, *Chemische Fabrik Uetikon*. TLC Plates: silica gel *60 F*, Art.Nr. 5554, *E. Merck*, Darmstadt; detection by UV fluorescence or by charring with a soln. of $Ce(SO_4)_2 \cdot 4H_2O$ (10 g), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (25 g), and H_2SO_4 (100 ml) in H_2O (900 ml). $[\alpha]_D^{24}$: *Perkin-Elmer-141* polarimeter. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz): *Varian Gemini 300*, TMS as internal standard, $CDCl_3$ or C_6D_6 as solvent; δ in ppm, *J* in Hz. ^{31}P-NMR (121 MHz): *Varian-Gemini-300*; triphenyl phosphate in $CDCl_3$ as external standard for $CDCl_3$ as solvent, H_3PO_4 (85%) in C_6D_6 as external standard for C_6D_6 as solvent. ^{2}H-NMR (61 MHz): *Varian VXR 400*; C_6D_6 as internal standard, C_6H_6 as solvent; *J* in Hz. MS: *VG 70-250*; FAB = fast-atom bombardment.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(diphenoxyphosphoryl)-α-D-galactopyranose* (**4**). After purging of 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose (**3**; 9.0 g, 25.9 mmol) with N_2, dissolution in dry CH_2Cl_2 (100 ml), and cooling in an ice-water bath, diphenyl phosphorochloridate (8.33 g, 31.0 mmol, 1.2 equiv.) and 1-methyl-1*H*-imidazole (2.54 g, 31.0 mmol, 1.2 equiv.) were added within 15 min. Stirring was continued for 16 h with gradual warming to r.t. The CH_2Cl_2 was then evaporated and the oily residue redissolved in CH_2Cl_2 and evaporated a second time to remove traces of 1-methyl-1*H*-imidazole. A soln. of the residue in CH_2Cl_2 (200 ml) was washed successively with ice-water (100 ml), sat. aq. $NaHCO_3$ soln. (2 × 100 ml), and H_2O (100 ml). The org. layer was dried ($MgSO_4$) and evaporated. The oily residue was crystallized from Et_2O and then recrystallized from CH_2Cl_2/Et_2O: **4** (71% yield). White solid. M.p. 80–81°. ^{1}H-NMR ($CDCl_3$): 7.38–7.16 (*m*, 2 Ph); 6.42 (*d*, $J(1,2) = 3.8$, H−C(1)); 5.48 (br. *d*, $J(3,4) = 3.4$, $J(4,5) \leqslant 1.0$, H−C(4)); 5.41 (*dd*, $J(3,4) = 3.4$, $J(2,3) = 10.4$, H−C(3)); 5.03 (*ddd*, $J(1,2) = 3.8$, $J(2,3) = 10.4$, $J(2,P) = 8.5$, H−C(2)); 4.28 (br. *t*, $J(4,5) \leqslant 1.0$, $J(5,6) = 6.8$, H−C(5)); 4.07 (br. *d*, $J(5,6) = 6.8$, 2 H−C(6)); 2.15, 2.06, 2.03, 1.81 (4*s*, 4 Ac). ^{13}C-NMR ($CDCl_3$): 170.6, 170.3, 168.7 (1, 2 and 1 C, Me*C*OO); 150.6, 150.4 (2*d*, $J = 7.4$, 2 C_{ipso}); 130.03, 130.00 (4 C_m); 125.7 (2 C_p); 119.9 (*d*, $J = 4.9$, 4 C_o); 89.5 (*d*, $J = 3.2$, C(1)); 71.5 (*d*, $J = 5.5$, C(2) or C(3)); 68.2 (C(5)); 67.9 (*d*, $J = 5.7$, C(3) or C(2)); 67.3 (C(4)); 60.8 (C(6)); 20.4, 20.3, 20.1 (4 *Me*COO). ^{31}P-NMR ($CDCl_3$): −12.3 (*d*, $J = 8.4$). FAB-MS: 619 ($[M + K]^+$), 521 ($[M - AcO]^+$). Anal. calc. for $C_{26}H_{29}O_{13}P$ (580.48): C 53.81, H 5.04; found: C 53.83, H 5.22.

*3,4,6-Tri-*O*-acetyl-2-*O*-(diphenoxyphosphoryl)-α-D-galactopyranosyl Bromide* (**5**). To a soln. of **4** (6.0 g, 10.3 mmol) in the minimum amount of dry CH_2Cl_2 (20 ml), cooled in an ice-water bath, a cold (4°) soln. of HBr in AcOH (10 ml, 33% by weight) was added. Stirring under N_2 was continued for 16 h with gradual warming to r.t. The mixture was diluted with CH_2Cl_2 (100 ml), ice added, and the org. layer washed successively with H_2O (50 ml), sat. aq. $NaHCO_3$ soln. (2 × 50 ml), and H_2O (50 ml). After drying ($MgSO_4$) and evaporation **5** (93%) was obtained as a white solid. It was used in synthesis without further purification, although FC was possible. Compound **5** was stored at −20° for several weeks without decomposition. TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.34. M.p. 91–92°. ^{1}H-NMR ($CDCl_3$): 7.39–7.20 (*m*, 2 Ph); 6.47 (*d*, $J(1,2) = 4.1$, H−C(1)); 5.50 (br. *d*, $J(3,4) = 3.3$, H−C(4)); 5.44 (*dd*, $J(2,3) = 10.1$, $J(3,4) = 3.3$, H−C(3)); 4.87 (*ddd*, $J(1,2) = 4.1$, $J(2,3) = 10.1$, $J(2,P) = 8.7$, H−C(2)); 4.51 (br. *t*, $J(5,6a) = 6.4$, $J(5,6b) = 6.8$, H−C(5)); 4.17 (*dd*, $J(5,6a) = 6.4$, $J(6a,6b) = 11.4$, H_a−C(6a)); 4.09 (*dd*, $J(5,6b) = 6.8$, $J(6a,6b) = 11.4$, 1 H, H_b−C(6)); 2.14, 2.05, 1.80 (3*s*, 3 Ac). ^{13}C-NMR ($CDCl_3$): 170.6, 170.1, 170.0 (3 Me*C*OO); 150.6, 150.2 (2*d*, $J = 7.5$, 2 C_{ipso}); 130.0 (4 C_m); 126.0, 125.8 (2*d*, $J = 1.5$, 2 C_p); 120.4, 119.9 (2*d*, $J = 4.9$, 4 C_o); 88.2 (*d*, $J = 4.0$, C(1)); 72.0 (*d*, $J = 4.9$, C(3) or C(2)); 71.2 (C(5)); 68.7 (*d*, $J = 5.6$, C(2) or C(3)); 67.0 (C(4)); 60.6 (C(6)); 20.4, 20.3, 20.1 (3 *Me*COO). ^{31}P-NMR ($CDCl_3$): −12.9 (*d*, $J = 8.6$). ^{31}P-NMR (C_6D_6): −11.2 (*d*, $J = 8.1$). FAB-MS: 603, 601 ($[M + 1]^+$), 543, 541 ($[M - AcO]^+$), 521 ($[M - Br]^+$). Anal. calc. for $C_{24}H_{26}BrO_{11}P$ (601.34): C 47.94, H 4.36; found: C 48.17, H 4.46.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(diphenoxyphosphoryl)-β-D-mannopyranose* (**7**). As described for **4**, with 1,3,4,6-tetra-*O*-acetyl-β-D-mannopyranose (**6**), 1.2 equiv. of diphenyl phosphorochloridate and 1.2 equiv. of 1-methyl-1*H*-imidazole: **7** (90%), glassy transparent solid after removal of CH_2Cl_2. TLC (Et_2O): R_f 0.33. ^{1}H-NMR ($CDCl_3$): 7.41–7.18 (*m*, 2 Ph); 5.86 (br. *s*, H–C(1)); 5.42 (*t*, *J*(3,4) = *J*(4,5) = 9.9, H–C(4)); 5.14–5.06 (*m*, H–C(2), H–C(3)); 4.31 (*dd*, *J*(5,6a) = 4.9, *J*(6a,6b) = 12.4, H_a–C(6)); 4.18 (*dd*, *J*(5,6b) = 2.2 *J*(6a,6b) = 12.4, H_b–C(6)); 3.82 (*ddd*, *J*(4,5) = 9.9, *J*(5,6a) = 4.9, *J*(5,6b) = 2.2, H–C(5)); 2.09, 2.07, 1.91, 1.80 (4*s*, 4 Ac). ^{1}H-NMR (C_6D_6): 7.43–6.77 (*m*, 2 Ph); 5.67 (br. *s*, *J*(1,2) ≈ 1.0, H–C(1)); 5.64 (*t*, *J*(3.4) = *J*(4.5) = 10.1, H–C(4)); 5.27 (br. *dd*, *J*(2,3) = 2.9, *J*(2,P) = 9.2, H–C(2)); 5.11 (*ddd*, *J*(2,3) = 2.9, *J*(3,4) = 10.1, *J*(3,P) = 1.8, H–C(3)); 4.25 (*dd*, *J*(5,6a) = 4.6, *J*(6a,6b) = 12.4, H_a–C(6)); 4.06 (*dd*, *J*(5,6b) = 2.1, *J*(6a,6b) = 12.4, H_b–C(6)); 3.35 (*ddd*, *J*(4,5) = 10.1, *J*(5,6a) = 4.6, *J*(5,6b) = 2.1, H–C(5)); 1.68, 1.66, 1.64, 1.47 (4*s*, 4 Ac); ^{4}J(H–C(3),P) in accordance with a W-configuration of these centers. ^{13}C-NMR ($CDCl_3$): 170.8, 170.2, 169.5, 168.6 (4 Me*C*OO); 150.7, 150.5 (2*d*, *J* = 7.6, 2 C_{ipso}); 129.9, 129.8 (4 C_m); 125.5, 125.4 (2 C_p); 120.5, 120.2 (2*d*, *J* = 4.7, 4 C_o); 90.3 (*d*, *J* = 3.4, C(1)); 74.3 (*d*, *J* = 5.0, C(2)); 73.1 (C(4) or C(5)); 70.7 (*d*, *J* = 3.2, C(3)); 64.5 (C(5) or C(4)); 61.6 (C(6)); 20.3, 20.2, 20.1, 19.9 (4 *Me*COO). ^{31}P-NMR ($CDCl_3$): −11.3 (*d*, *J* = 9.4). FAB-MS: 619 ($[M + K]^+$), 581 ($[M + 1]^+$), 521 ($[M - AcO]^+$).

*3,4,6-Tri-*O*-acetyl-2-*O*-(diphenoxyphosphoryl)-α-D-mannopyranosyl Bromide* (**8**). As described for **5**. Yield 95%. TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.44. ^{1}H-NMR ($CDCl_3$): 7.42–7.20 (*m*, 2 Ph); 6.21 (*d*, *J*(1,2) = 1.7, H–C(1)); 5.67 (*dt*, *J*(2,3) = 3.0, *J*(3,4) = 10.1, *J*(3,P) = 2.3, H–C(3)); 5.48 (*t*, *J*(3,4) = *J*(4,5) = 10.1, H–C(4)); 5.15 (*ddd*, *J*(1,2) = 1.7, *J*(2,3) = 3.0, *J*(2,P) = 8.7, H–C(2)); 4.31 (*dd*, *J*(5,6a) = 4.2, *J*(6a,6b) = 12.1, H_a–C(6)); 4.20 (*ddd*, *J*(4,5) = 10.1, *J*(5,6a) = 4.2, *J*(5,6b) = 2.1, H–C(5)); 4.14 (*dd*, *J*(5,6b) = 2.1, *J*(6a,6b) = 12.1, H_b–C(6)); 2.08, 2.07, 1.83 (3*s*, 3 Ac); ^{4}J(H–C(3),P) in accordance with a *W*-configuration of these centers. ^{1}H-NMR ((D_{10})Et_2O): 7.64–7.13 (*m*, Ph); 6.18 (br. *s*, H–C(1)); 5.60 (*ddd*, *J*(2,3) = 2.7, *J*(3,4) = 10.1, *J*(3,P) = 2.1, H–C(3)); 5.52 (*t*, *J*(3,4) = 10.1, *J*(4,5) = 9.8, H–C(4)); 5.09 (*ddd*, *J*(1,2) = 1.8, *J*(2,3) = 2.7, *J*(2,P) = 8.8, H–C(2)); 4.34 (*dd*, *J*(5,6a) = 4.5, *J*(6a,6b) = 12.6, H_a–C(6)); 4.15 (*ddd*, *J*(4,5) = 9.8, *J*(5,6a) = 4.5, *J*(5,6b) = 2.1, H–C(5)); 4.04 (*dd*, *J*(5,6b) = 2.1, *J*(6a,6b) = 12.6, H_b–C(6)); 2.01, 1.95, 1.70 (3*s*, 3 Ac). ^{13}C-NMR ($CDCl_3$): 170.7, 170.2, 169.5 (3 Me*C*OO); 150.4, 150.2 (2*d*, *J* = 7.6, 2 C_{ipso}); 130.1, 130.0 (4 C_m); 126.0, 125.9 (2*d*, *J* = 1.4, 2 C_p); 120.4, 120.2 (2*d*, *J* = 4.8, 4 C_o); 82.8 (*d*, *J* = 4.2, C(1)); 77.0 (*d*, *J* = 5.5, C(2)); 72.8 (C(5)); 68.1 (*d*, *J* = 4.2, C(3)); 64.4 (C(4)); 61.1 (C(6)); 20.4, 20.3, 20.1 (3 *Me*COO); assignments established by a ^{1}H,^{13}C-correlated NMR (HETCOR). ^{31}P-NMR ($CDCl_3$): −12.2 (*d*, *J* = 8.3). FAB-MS: 603, 601 ($[M + 1]^+$), 521 ($[M - Br]^+$). EI-MS: 521 ($[M - Br]^+$). CI-MS (NH_3): 620, 618 ($[M + NH_4]^+$), 538 ($[M + NH_4 - HBr]^+$). Anal. calc. for $C_{24}H_{26}BrO_{11}P$ (601.34): C 47.94, H 4.36; found: C 47.81, H 4.48.

*1,3,4,6-Tetra-*O*-benzoyl-2-*O*-(diphenoxyphosphoryl)- and 2,3,4,6-Tetra-*O*-benzoyl-1-*O*-(diphenoxyphosphoryl)-α-D-glucopyranose* (**11** and **12**, resp.). As described for **4**, with the inseparable mixture of 1,3,4,6- and 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranose (**9/10**; 12.5 g, 20.5 mmol), 1.2. equiv. of diphenyl phosphorochloridate, and 1.2 equiv. of 1-methyl-1*H*-imidazole: inseparable 1.6:1 mixture **11/12** (16.9 g, 97%). TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.38. TLC (Et_2O/pentane 2:1): R_f 0.28. ^{1}H-NMR ($CDCl_3$, data of **11**): 8.18–6.85 (*m*, 6 Ph); 6.66 (*d*, *J*(1,2) = 3.7, H–C(1)); 6.23 (*t*, *J*(2,3) = *J*(3,4) = 9.9, H–C(3)); 5.72 (*t*, *J*(3,4) = *J*(4,5) = 9.9, H–C(4)); 5.19 (*ddd*, *J*(1,2) = 3.7, *J*(2,3) = 9.9, *J*(2,P) = 8.8, H–C(2)); 4.59–4.33 (*m*, H–C(5), 2 H–C(6)). ^{1}H-NMR ($CDCl_3$, data of **12**): 8.18–6.85 (*m*, 6 Ph); 6.39 (*dd*, *J*(1,2) = 3.4, *J*(1,P) = 6.2, H–C(1)); 6.24 (*t*, *J*(2,3) = *J*(3,4) = 10.1, H–C(3)); 5.79 (*t*, *J*(3,4) = *J*(4,5) = 10.1, H–C(4)); 5.49 (*ddd*, *J*(1,2) = 3.4, *J*(2,3) = 10.1, *J*(2,P) = 3.4, H–C(2)); 4.59–4.33 (*m*, H–C(5), 2 H–C(6)).

*3,4,6-Tri-*O*-benzoyl-2-*O*-(diphenoxyphosphoryl)-α-D-glucopyranosyl Bromide* (**13**). As described for **5**, with **12/11** (16.9 g, 20.4 mmol), dry CH_2Cl_2 (40 ml), and HBr/AcOH (30 ml). The mixture of *2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide* (**14**; TLC (Et_2O/pentane 1.5:1): R_f 0.54, and **13**; TLC (Et_2O/pentane 1.5:1): R_f 0.35) was separated by FC: 7.03 (8.93 mmol) of pure **13**. ^{1}H-NMR ($CDCl_3$): 8.05–6.86 (*m*, 5 Ph); 6.51 (*d*, *J*(1,2) = 4.0, H–C(1)); 6.15 (*t*, *J*(2,3) = *J*(3,4) = 9.6, H–C(3)); 5.69 (*t*, *J*(3,4) = 9.6, *J*(4,5) = 9.8, H–C(4)); 4.92 (*ddd*, *J*(1,2) = 4.0, *J*(2,3) = 9.6, *J*(2,P) = 8.9, H–C(2)); 4.70–4.58 (*m*, H–C(5), H_a–C(6)); 4.44 (*dd*, *J*(5,6b) = 4.4, *J*(6a,6b) = 12.5, H_b–C(6)). ^{1}H-NMR (C_6D_6): 8.18–7.90, 7.24–6.58 (2*m*, 5 Ph); 6.51 (*t*, *J*(2,3) = *J*(3,4) = 9.6, H–C(3)); 6.42 (*d*, *J*(1,2) = 4.0, H–C(1)); 5.81 (*t*, *J*(3,4) = 9.6, *J*(4,5) = 10.1, H–C(4)); 4.94 (*ddd*, *J*(1,2) = 4.0, *J*(2,3) = 9.6, *J*(2,P) = 8.6, H–C(2)); 4.61 (*ddd*, *J*(4,5) = 10.1, *J*(5,6a) = 3.0, *J*(5,6b) = 4.6, H–C(5)); 4.47 (*dd*, *J*(5,6a) = 3.0, *J*(6a,6b) = 12.5, H_a–C(6)); 4.29 (*dd*, *J*(5,6b) = 4.6, *J*(6a,6b) = 12.5, H_b–C(6)). ^{13}C-NMR ($CDCl_3$): 165.9, 165.4, 164.9 (3 Ph*C*OO); 149.9, 149.8 (2*d*, *J* = 7.6, 2 C_{ipso} of PhO); 133.6, 133.2, 133.1 (3 C_p of *Ph*COO); 129.9–125.2 (arom. C); 120.3, 119.5 (2*d*, *J* = 4.9, 4 C_o of PhO); 87.0 (*d*, *J* = 3.8, C(1)); 74.8 (*d*, *J* = 5.2, C(2) or C(3)); 72.7 (C(5)); 71.1 (*d*, *J* = 5.6, C(3) or C(2)); 68.0 (C(4)); 61.7 (C(6)). ^{31}P-NMR (C_6D_6): −11.5 (*J* = 8.0). Anal. calc. for $C_{39}H_{32}BrO_{11}P$ (787.55): C 59.48, H 4.10; found: C 59.78, H 4.20.

*Methyl 2,3,4-Tri-*O*-acetyl-6-deoxy-α-*D*-glucopyranoside* (**16**). To a soln. of methyl 2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-α-D-glucopyranoside (**15**; 30.2 g, 70.0 mmol) in dry THF (200 ml) under N_2, Bu_3SnH (20.3 ml, 77.1 mmol) was added and the mixture irradiated with a *Philips-HPR* 125-W mercury high-pressure lamp (TLC monitoring (Et_2O/pentane 2:1)): UV fluorescence for **16**; R_f 0.38 for **15** and **16**. After 45 min (full conversion), the THF was evaporated and the oily residue dissolved in MeCN (150 ml) and extracted with pentane (4 x 150 ml). After removal of the MeCN, the residue was dissolved in Et_2O/CH_2Cl_2 and filtered through a bed of silica gel. Evaporation gave **16** (20.8 g, 97%). Soft, white, large crystals. ^1H-NMR ($CDCl_3$): 5.43 (*t*, *J*(2,3) = *J*(3,4) = 9.6, H–C(3)); 4.90–4.84 (*m*, H–C(1), H–C(2)); 4.80 (*t*, *J*(3,4) = 9.6, *J*(4,5) = 9.9, H–C(4)); 3.88 (*dq*, *J*(4,5) = 9.9, *J*(5,6) = 6.3, H–C(5)); 2.07, 2.04, 2.01 (3*s*, 3 Ac); 1.20 (*d*, *J*(5,6) = 6.3, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 170.1, 170.0, 169.8 (3 Me*C*OO); 96.5 (C(1)); 73.7, 71.2, 70.0, 64.8 (C(2), C(3), C(4), C(5)); 55.2 (MeO); 20.6 (3 *Me*COO); 17.1 (C(6)). FAB-MS: 343 ($[M + K]^+$), 305 ($[M + 1]^+$), 273 ($[M - MeO]^+$). Anal. calc. for $C_{13}H_{20}O_8$ (304.30): C 51.31, H 6.62; found: C 51.25, H 6.51.

*2,3,4-Tri-*O*-acetyl-6-deoxy-α-*D*-glucopyranosyl Bromide* (**17**). A soln. of **16** (20.2 g, 66.4 mmol) in dry CH_2Cl_2 (25 ml) was mixed with 33% HBr/AcOH (90 ml). After 50–55 min at r.t. (longer reaction times led to the formation of numerous by-products), the mixture was worked up as described for **5**. Bromide **17** (90%; needles from CH_2Cl_2) is only moderately stable and should be used for the next step immediately (purification not necessary, substantial loss of product on FC). TLC (Et_2O/pentane 2:1): R_f 0.36. ^1H-NMR ($CDCl_3$): 6.59 (*d*, *J*(1,2) = 4.1, H–C(1)); 5.52 (*t*, *J*(2,3) = *J*(3,4) = 10.0, H–C(3)); 4.89 (*t*, *J*(3,4) = *J*(4,5) = 10.0, H–C(4)); 4.80 (*dd*, *J*(1,2) = 4.1, *J*(2,3) = 10.0, H–C(2)); 4.19 (*dq*, *J*(4,5) = 10.0, *J*(5,6) = 6.3, H–C(5)); 2.10, 2.07, 2.03 (3*s*, 3 Ac); 1.26 (*d*, *J*(5,6) = 6.3, 3 H–C(6)). FAB-MS: 377, 375 ($[M + Na]^+$), 355, 353 ($[M + 1]^+$), 295, 293 ($[M - AcO]^+$).

*3,4-Di-*O*-acetyl-6-deoxy-1,2,*O*-(*exo*-1-methoxyethylidene)-α-*D*-glucopyranose* (**18**) was prepared from **17** and *N,N*-dimethylformamide dimethyl acetal according to [8]. After aq. workup, the oily residue still contained substantial amounts of Bu_4N^+ salts which were separated by FC. TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.43. ^1H-NMR ($CDCl_3$): 5.67 (*d*, *J*(1,2) = 5.3, H–C(1)); 5.15 (*t*, *J*(2,3) = *J*(3,4) = 3.3, H–C(3)); 4.69 (*ddd*, *J*(2,4) = 0.8, *J*(3,4) = 3.3, *J*(4,5) = 9.4, H–C(4)); 4.29 (*ddd*, *J*(1,2) = 5.3, *J*(2,3) = 3.3, *J*(2,4) = 0.8, H–C(2)); 3.82 (*dq*, *J*(4,5) = 9.4, *J*(5,6) = 6.6, H–C(5)); 3.28 (*s*, MeO); 2.10, 2.09 (2*s*, 2 Ac); 1.71 (*s*, $MeCO_3$); 1.25 (*d*, *J*(5,6) = 6.6, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 169.7, 169.2 (2 Me*C*OO); 121.2 (Me*C*O_3); 96.9 (C(1)); 73.6, 73.5, 70.8, 64.7 (C(2), C(3), C(4), C(5)); 50.7 (MeO); 20.74, 20.67, (2 *Me*COO); 20.2 (*Me*CO_3 orthoester); 18.3 (C(6)). FAB-MS: 343 ($[M + K]^+$), 305 ($[M + 1]^+$), 273 ($[M - MeO]^+$).

*1,3,4-Tri-*O*-acetyl-6-deoxy-α-*D*-glucopyranose* (**19**). For 20 min, **18** (20.0 g, 65.8 mmol) was mixed with AcOH/H_2O 95:5 (50 ml). Subsequently ice was added and the mixture extracted with $CHCl_3$ (3×). The org. layer was washed twice with sat. aq. $NaHCO_3$ soln. and once with H_2O, dried ($MgSO_4$), and evaporated. Crystallization from Et_2O/pentane yielded selectively **19**. Additional **19** (most polar fraction) was isolated by FC (Et_2O/pentane/CH_2Cl_2 1:1:1) of the residue resulting from evaporation of the mother liquor. Total yield of **19**, 54%. TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.16. M.p. 137°. ^1H-NMR ($CDCl_3$): 6.17 (*d*, *J*(1,2) = 4.0, H–C(1)); 5.22 (*t*, *J*(2,3) = *J*(3,4) = 9.8, H–C(3)); 4.83 (*t*, *J*(3,4) = *J*(4,5) = 9.8, H–C(4)); 3.95–3.81 (*m*, H–C(5), H–C(2)); 2.19, 2.10, 2.06 (3*s*, 3 Ac); 2.12–2.09 (*d*, *J*(2,OH) = 8.7, OH); 1.18 (*d*, *J*(5,6) = 6.2, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 171.4, 169.7, 169.4 (3 Me*C*OO); 91.4 (C(1)); 73.1, 72.8, 70.1, 67.7 (C(2), C(3), C(4), C(5)); 20.9, 20.8, 20.6 (3 *Me*COO); 17.3 (C(6)). FAB-MS: 329 ($[M + K]^+$), 291 ($[M + 1]^+$), 231 ($[M - AcO]^+$). Anal. calc. for $C_{12}H_{18}O_8$ (290.27): C 49.65, H 6.25; found: C 49.81, H 6.34.

*2,3,4-Tri-*O*-acetyl-6-deoxy-*D*-glucopyranose* (**20**; inseparable α-D/β-D mixture was formed only in minor amounts when the cleavage of **18** was performed in the absence of ammonium salts. ^1H-NMR (α-D/β-D mixture): α-D-anomer: 5.49 (*t*, *J*(2,3) = *J*(3,4) = 10.0, H–C(3)); 5.39 (*m*, (*d*, *J*(1,2) = 3.6, after D_2O exchange), H–C(1)); 4.89 (*dd*, *J*(1,2) = 3.6, *J*(2,3) = 10.0, H–C(2)); 4.16 (*dq*, *J*(4,5) = 10.0, *J*(5.6) = 6.1, H–C(5)); β-D-anomer; 5.21 (*t*, *J*(2,3) = *J*(3,4) = 9.6, H–C(3)); 4.69 (*m*, (*d*, *J*(1,2) = 8.0, after D_2O exchange), H–C(1)); 3.60 (*dq*, *J*(4,5) = 9.7, *J*(5,6) = 6.1, H–C(5)).

*1,3,4-Tri-*O*-acetyl-6-deoxy-2-*O*-(diphenoxyphosphoryl)-α-*D*-glucopyranose* (**21**). As described for **4**, from **19** and diphenyl phosphorochloridate. Yield 79%. ^1H-NMR ($CDCl_3$): 7.34–7.14 (*m*, 2 Ph); 6.30 (*d*, *J*(1,2) = 3.8, H–C(1)); 5.51 (*t*, *J*(2,3) = *J*(3,4) = 9.8, H–C(3)); 4.82 (*t*, *J*(3,4) = *J*(4,5) = 9.8, H–C(4)); 4.75 (*ddd*, *J*(1,2) = 3.8, *J*(2,3) = 9.8, *J*(2,P) = 8.5, H–C(2)); 3.96 (*dq*, *J*(4,5) = 9.8, *J*(5,6) = 6.2, H–C(5)); 2.05, 2.04, 1.84 (3*s*, 3 Ac); 1.18 (*d*, *J*(5,6) = 6.2, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 170.1, 169.4, 168.4 (3 Me*C*OO); 150.2, 150.1 (2*d*, *J* = 7.3, 2 C_{ipso}); 129.8 (4 C_m); 125.5 (2 C_p); 119.9, 119.7 (2*d*, *J* = 5.2, 4 C_o); 88.8 (*d*, *J* = 3.2, C(1)); 74.2 (*d*, *J* = 5.8, C(2) or C(3)); 73.0 (*d*, *J* ≈ 1.0, C(4)); 70.2 (*d*, *J* = 5.7, C(3) or C(2)); 67.4 (C(5)); 20.54, 20.47, 20.41 (3 *Me*OO); 17.1 (C(6)). ^{31}P-NMR ($CDCl_3$): −13.4 (*d*, *J* = 8.5). FAB-MS: 561 ($[M + K]^+$), 523 ($[M + 1]^+$), 463 ($[M - AcO]^+$). Anal. calc. for $C_{24}H_{27}O_{11}P$ (522.44): C 55.18, H 5.21; found: C 55.02, H 5.13.

*3,4-Di-*O*-acetyl-6-deoxy-2-*O*-(diphenoxyphosphoryl)-α-D-glucopyranosyl Bromide* (**22**). As described for **5**. Yield 61%. Purification by FC was possible. TLC (Et_2O/pentane 1:1): R_f 0.24. M.p. 88–89°. ^1H-NMR ($CDCl_3$): 7.38–7.18 (*m*, 2 Ph); 6.37 (*d*, *J*(1,2) = 4.1, H–C(1)); 5.57 (*t*, *J*(2,3) = *J*(3,4) = 9.6, H–C(3)); 4.86 (*t*, *J*(3,4) = *J*(4,5) = 9.6, H–C(4)); 4.62 (*ddd*, *J*(1,2) = 4.1, *J*(2,3) = 9.6, *J*(2,P) = 8.7, H–C(2)); 4.20 *dq*, *J*(4,5) = 9.6, *J*(5,6) = 6.3, H–C(5)); 2.04, 1.83 (2*s*, 2 Ac); 1.24 (*d*, *J*(5,6) = 6.3, 3 H–C(6)). ^1H-NMR (C_6D_6): 7.27–6.76 (*m*, 2 Ph); 6.29 (*d*, *J*(1,2) = 4.1, H–C(1)); 5.88 (*t*, *J*(2,3) = 9.7, *J*(3,4) = 9.5, H–C(3)); 4.85 (*t*, *J*(3,4) = 9.5, *J*(4,5) = 10.1, H–C(4)); 4.65 (*ddd*, *J*(1,2) = 4.1, *J*(2,3) = 9.7, *J*(2,P) = 8.7, H–C(2)); 4.10 (*dq*, *J*(4,5) = 10.1, *J*(5,6) = 6.2, H–C(5)); 1.66, 1.61 (2*s*, 2 Ac); 0.92 (*d*, *J*(5,6) = 6.2, 3 H–C(6)). ^{13}C-NMR ($CDCl_3$): 169.8, 169.5 (2 Me*C*OO); 150.3, 149.9 (2*d*, *J* = 7.4, 2 C_{ipso}); 129.8 (4 C_m); 125.8, 125.6 (2*d*, *J* = 1.4, 2 C_p); 120.2, 119.8 (2*d*, *J* = 4.8, 4 C_o); 87.2 (*d*, *J* = 3.7, C(1)); 74.9 (*d*, *J* = 5.2, C(3) or C(2)); 72.4 (*d*, *J* = 1.3, C(4)); 70.8 (*d*, *J* = 5.6, C(2) or C(3)); 70.5 (C(5)); 20.5, 20.4 (2 *Me*COO); 16.8 (C(6)). ^{31}P-NMR ($CDCl_3$): −12.9 (*d*, *J* = 8.5). ^{31}P-NMR (C_6D_6): −11.5 (*d*, *J* = 7.6). FAB-MS: 583, 581 ($[M + K]^+$), 545, 543 ($[M + 1]^+$), 463 ($[M - Br]^+$). Anal. calc. for $C_{22}H_{24}BrO_9P$ (543.30): C 48.64, H 4.45; found: C 48.50, H 4.47.

*3,4,6-Tri-*O*-acetyl-2-deoxy-1-*O*-(diphenoxyphosphoryl)-α-*D-lyxo*-hexopyranose* (**23**). In a H_2O-cooled jacket flask equipped with a *Heraeus-TQ-150* mercury high-pressure lamp (H_2O-cooled, *Pyrex* tube), **5** (0.6 g, 1.0 mmol) was purged with N_2 and then dissolved in dry THF (20 ml). After addition of Bu_3SnH (35 g, 1.2 mmol) and cooling with H_2O (20°), the mixture was irradiated for 15 min (TLC monitoring: polar hydrolysis products present, *i.e.* 3,4,6-tri-*O*-acetyl-2-deoxy-D-*lyxo*-hexopyranose). This soln. was used for glycosylations (see below). To characterize **23** 0.5–1 ml of the mixture were removed by syringe and evaporated at r.t. The residue was dissolved in deuterated solvent, and the NMR spectra were recorded. ^1H-NMR ($CDCl_3$): 7.40–7.15 (*m*, 2 Ph); 6.17–6.12 (*m*, H–C(1); irrad. at 1.97→*dd*, *J*(1,2ax) = 3.0, *J*(1,P) ≈ 5.6–6.0); 5.38 (br. *s*, H–C(4)); 5.29 (*ddd*, *J*(2a,3) = 12.4, *J*(2eq,3) = 5.0, *J*(3,4) = 3.0, H–C(3)); 4.32 (br. *t*, *J*(4,5) = 1.0, *J*(5,6a) ≈ *J*(5,6a) = 6.6, H–C(5)); 4.07 (*dd*, *J*(5,6a) = 6.5, *J*(6a,6b) = 11.3, H_a–C(6)); 3.92 (*dd*, *J*(5,6b) = 6,7, *J*(6a,6b) = 11.3, H_b–C(6)); 2.19 (*tt*, *J*(2ax,2eq) = 13.1, *J*(2ax,3) = 12.4, *J*(1,2ax) = 3.0, *J*(2ax,P) = 4.1, H_{ax}–C(2)); 1.97 (br. *dd*, *J*(1,2eq) ⩽ 1.0, *J*(2ax,2eq) = 13.1, *J*(2eq,3) = 5.0, H_{eq}–C(2)); 2.13, 2.00, 1.91 (3*s*, 3 Ac). ^1H-NMR (C_6D_6): 7.37–6.81 (*m*, 2 Ph); 6.14–6.10 (*m*, H–C(1)); 5.43 (br. *s*, H–C(4)); 5.34 (*ddd*, *J*(2ax,3) = 12.4, *J*(2eq,3) = 5.1, *J*(3,4) = 2.9, H–C(3)); 4.20 (*dt*, *J*(4,5) ≈ 1.0, *J*(5,6a) = *J*(5,6b) = 6.6, H–C(5)); 4.11 (*dd*, *J*(5,6a) = 6.6, *J*(6a,6b) = 11.0, H_a–C(6)); 3.94 (*dd*, *J*(5,6b) = 6.6, *J*(6a,6b) = 11.0, H_b–C(6)); 1.92 (*tt*, *J*(1,2ax) = *J*(2ax,P) = 3.4, *J*(2ax,2eq) = 13.2, *J*(2ax,3) = 12.4, H_{ax}–C(2)); 1.75 (*ddt*, *J*(2ax,2eq) = 13.2, *J*(2eq,3) = 5.1, *J*(1,2eq) = *J*(2eq,4) = 1.3, H_{eq}–C(2)); 1.67, 1.65, 1.55 (3*s*, 3 Ac); ^4J(H_{eq}–C(2),H–C(4)) in accordance with a W-configuration of these centers. ^{13}C-NMR ($CDCl_3$): 169.8, 169.6, 169.3 (3 Me*C*OO); 150.0, 149.9 (2*d*, *J* = 7.1, 2 C_{ipso}); 129.5 (4 C_m); 125.3, 125.2 (2*d*, *J* = 1.4, 2 C_p); 119.8, 119.7 (2*d*, *J* = 4.9, 2 C_o); 97.6 (*d*, *J* = 5.7, C(1)); 68.8, 65.5, 64.7 (C(3), C(4), C(5)); 61.3 (C(6)); 29.9 (*d*, *J* = 8.2, C(2)); 20.3, 20.15, 20.05 (3 *Me*COO). ^{13}C-NMR (C_6D_6): 169.74, 169.72, 169.3 (3 Me*C*OO); 151.1, 151.0 (2*d*, *J* = 6.9, 2 C_{ipso}); 130.1, 130.0 (4 C_m); 125.7, 125.6 (2*d*, *J* = 1.4, 2 C_p); 120.7, 120.6 (2*d*, *J* = 4.9, 4 C_o); 98.3 (*d*, *J* = 5.6, C(1)); 69.5, 66.1, 65.4 (C(3), C(4), C(5)); 61.6 (C(6)); 30.5 (*d*, *J* = 8.3, C(2)); 20.4, 20.12, 20.10 (3 *Me*COO). ^{31}P-NMR (C_6D_6): −12.5; *J*(1H,^{31}P) not discernible.

*3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-*O*-(diphenoxyphosphoryl)-*D-galacto*-hexitol* (**31**). The ^{13}C-NMR data for the pyranose ring of the reduction product could be derived from the spectra of the kinetic experiments. ^{13}C-NMR (C_6D_6): 74.9 (C(4) or C(5)); 72.5 (*d*, *J* = 6.0, C(2) or C(3)); 72.4 (*d*, *J* = 5.4, C(2) or C(3)); 68.2 (C(5) or C(4)); 68.1 (*d*, *J* = 3.5, C(1)); 61.6 (C(6)); 20.3, 20.2, 19.9 (3 *Me*COO). ^{31}P-NMR (C_6D_6): −11.4 (*d*, *J* = 5.2).

*3,4,6-Tri-*O*-benzoyl-2-deoxy-1-*O*-(diphenoxyphosphoryl)-α-*D-arabino*-hexopyranose* (**24**). A soln. of **13** (79 mg, 0.1 mmol) and Ph_3SnH[3] (33 mg, 0.1 mmol) in C_6D_6 (0.7 ml) in an NMR tube was irradiated for 30 s with the filtered light of a *Hanovia-977-B1* 1-kW Hg-Xe high-pressure lamp. Then the NMR spectra were recorded. ^1H-NMR (C_6D_6): 8.19–7.90, 7.43–6.79 (*m*, 5 Ph); 6.03–6.00 (*m*, H–C(1); irrad. at 2.29→*dd*, *J*(1,2ax) = 3.1, *J*(1,P) = 5.9); 5.91 (*ddd*, *J*(2ax3) = 11.0, *J*(2eq,3) = 5.0, *J*(3,4) = 9.8, H–C(3)); 5.82 (*t*, *J*(3,4) = 9.8, *J*(4,5) = 9.6, H–C(4)); 4.52 (*dd*, *J*(5,6a) = 2.7, *J*(6a,6b) = 12.3, H_a–C(6)); 4.43 (*ddd*, *J*(4,5) = 9.6, *J*(5,6a) = 2.7, *J*(5,6b) = 3.8, H–C(5)); 4.27 (*dd*, *J*(5,6b) = 3.8, *J*(6a,6b) = 12.3, H_b–C(6)); 2.29 (br. *dd*, *J*(1,2eq) ⩽ 1.0, *J*(2ax,2eq) = 12.9, *J*(2eq,3) = 5.0, H_{eq}–C(2)); 1.49 (*ddt*, *J*(2ax,2eq) = 12.9, *J*(2ax,3) = 11.0, *J*(1,2ax) ≈ *J*(2ax,P) = 3.8, H_{ax}–C(2)). ^{13}C-NMR (C_6D_6): 165.8, 165.60, 165.58 (3 Ph*C*OO); 151.1, 151.0 (2*d*, *J* = 6.9, 2 C_{ipso} of PhO); 133.3, 133.2, 132.9 (3 arom. C); 130.5–125.6 (arom. C); 120.9, 120.6 (2*d*, *J* = 4.8, 4 C_o of PhO); 97.6 (*d*, *J* = 5.6, C(1)); 71.2, 69.6, 69.3 (C(3), C(4), C(5)); 62.5 (C(6)); 35.5 (*d*, *J* = 8.2, C(2)). ^{31}P-NMR (C_6D_6): −12.3; *J*(^{1}H,^{31}P) not discernible.

*3,4,6-Tri-*O*-benzoyl-2-deoxy-1-*O*-(diphenoxyphosphoryl)-α-*D-manno*-(2-D)hexopyranose* ((D)-**24**). A soln. of **13** (79 mg, 0.1 mmol) and Bu_3SnD (33 mg, 0.11 mmol) in benzene (0.7 ml) in an NMR tube was irradiated for

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[3] Bu_3SnH could be used in a similar way, but the Bu groups (0.7–1.7 ppm in C_6D_6) obscured part of the CH_2(2) and CH_3(6) group.

30 s with the filtered light of a *Hanovia-977-B1* 1-kW Hg-Xe high-pressure lamp. The soln. was used for recording the ^{2}H-NMR. ^{2}H-NMR (C_6H_6): 2.3–2.0 (br. *s*, 0.1 D); 1.7–1.1 (br. *s*, 0.9 D); *i.e.* axial/equatorial D (*manno*/*gluco*) 90:10. *1,5-Anhydro-3,4,6-tri-*O*-benzoyl-2-*O*-(diphenoxyphosphoryl)-*D*-glucitol* (**29**). ^{31}P-NMR (C_6D_6): –11.5 (*d*, *J* = 7.9).

*3,4-Di-*O*-acetyl-2,6-dideoxy-1-*O*-(diphenoxyphosphoryl)-α-*D-arabino*-hexopyranose* (**25**). A soln. of **22** (55 mg, 0.1 mmol) and Ph$_3$SnH1) (33 mg, 0.1 mmol) in C_6D_6 (0.7 ml) in an NMR tube was irradiated with a *Hanovia-977-B1* 1000-W Hg-Xe high-pressure lamp for 30 s. Dideoxy-sugar **25** is unstable and readily eliminates diphenyl hydrogen phosphate, a process promoted by longer irradiation and by warming of the mixture above 25°. ^{1}H-NMR (C_6D_6): 7.42–6.77 (*m*, 2 Ph); 5.96–5.93 (*m*, H–C(1); irrad. at 2.08→*dd*, *J*(1,2ax) = 3.2, *J*(1,P) = 5.5); 5.44 (*ddd*, *J*(2ax,3) = 11.5, *J*(2eq,3) = 5.2, *J*(3,4) = 9.7, H–C(3)); 4.89 (*t*, *J*(3,4) = *J*(4,5) = 9.7, H–C(4)); 4.00 (*dq*, *J*(4,5) = 9.7, *J*(5,6) = 6.2, H–C(5)); 2.08 (*ddd*, *J*(1,2eq) = 1.4, *J*(2ax,2eq) = 13.6, *J*(2eq,3) = 5.2, H_{eq}–C(2)); 1.65, 1.61, (2*s*, 2 Ac); 1.43–1.32 (*m*, H_{ax}–C(2); irrad. at 5.95→*ddd*, *J*(2ax,2eq) = 13.6, *J*(2ax,3) = 11.5, *J*(2ax,P) = 3.6); 1.01 (*d*, *J*(5,6) = 6.2, 3 H–C(6)). ^{1}H-NMR ($CDCl_3$): 7.40–7.15 (*m*, 2 Ph); 6.19–5.99 (*m*, H–C(1); irrad. at 2.34→*dd*, *J*(1,2ax) = 3.2, *J*(1,P) = 5.6); 5.28 (*ddd*, *J*(2ax,3) = 11.3, *J*(2eq,3) = 5.3, *J*(3,4) = 9.7, H–C(3)); 4.78 (*t*, *J*(3,4) = 9.7, *J*(4,5) = 9.9, H–C(4)); 3.96 (*dq*, *J*(4,5) = 9.9, *J*(5,6) = 6.2, H–C(5)); 2.34 (br. *dd*, *J*(1,2eq) ⩽ 1.0, *J*(2ax,2eq) = 13.5, *J*(2eq,3) = 5.3, H_{eq}–C(2)); 2.05, 2.02 (2*s*, 2 Ac); 1.89 (*ddt*, *J*(2ax,2eq) = 13.5, *J*(2ax,3) = 11.3, *J*(1,2ax) ≈ *J*(2ax,P) = 3.4, H_{ax}–C(2)); 1.07 (*d*, *J*(5.6) = 6.2, 3 H–C(6)). ^{13}C-NMR (C_6D_6): 169.4, 169.3 (2 Me*C*OO); 151.2, 151.0, (2*d*, *J* = 7.0, 2 C_{ipso}); 130.1, 130.0 (4 C_m); 125.6, 125.4 (2*d*, *J* = 1.5, 2 C_p); 120.8, 120.5 (2*d*, *J* = 4.9, 2 C_o); 97.6 (*d*, *J* = 5.6, C(1)); 73.9, 68.7, 68.1 (C(3), C(4), C(5)); 35.5 (*d*, *J* = 8.2, C(2)); 20.4, 20.3 (2 *Me*COO); 17.4 (C(6)). ^{13}C-NMR ($CDCl_3$): rapid decomposition in $CDCl_3$ only characteristic signals could be assigned: 97.3 (*d*, *J* = 6.0, C(1)); 35.5 (*d*, *J* = 8.3, C(2)). ^{31}P-NMR (C_6D_6): –12.4; *J*(^{1}H,^{31}P) not discernible.

*3,4-Di-*O*-acetyl-2,6-dideoxy-1-*O*-(diphenoxyphosphoryl)-α-*D-manno*-(2-D)hexopyranose* ((D)-**25**). As described for (D)-**24**. ^{2}H-NMR (C_6H_6): 2.1–1.8 (br. *s*, 0.05 D); 1.45–1.05 (br. *s*, 0.95 D); *i.e.* axial/equatorial D (*manno*/*gluco*) 95:5.

*3,4-Di-*O*-acetyl-1,5-anhydro-6-deoxy-2-*O*-(diphenoxyphosphoryl)-*D*-glucitol* (**32**). ^{31}P-NMR (C_6D_6): –11.7 (*d*, *J* = 8.7).

*3,4,6-Tri-*O*-acetyl-1,5-anhydro-2-*O*-(diphenoxyphosphoryl)-*D*-mannitol* (**27**). As described for **23**, with **8** (0.30 g, 0.5 mmol) in dry Et_2O (7 ml), and Bu_3SnH (2.80 g, 9.5 mmol; irradiation for 45 min). FC gave 0.20 g (77%) of **27** showing UV fluorescence. Oil. TLC (Et_2O): R_f 0.21. ^{1}H-NMR ($CDCl_3$): 7.37–7.26 (*m*, 2 Ph); 5.36 (*t*, *J*(3,4) = *J*(4,5) = 9.8, H–C(4)); 5.01–4.96 (*m*, H–C(2), H–C(3)); 4.23–4.13 (*m*, 2 H–C(6)); 4.05 (*dd*, *J*(1ax,1eq) = 13.2, *J*(1eq,2) = 1.9, H_{eq}–C(1)); 3.63 (br. *d*, *J*(1ax,1eq) = 13.2, H_{ax}–C(1)); 3.58 (*ddd*, *J*(4,5) = 9.8, *J*(5,6a) = 4.9, *J*(5,6b) = 2.8, H–C(5)); 2.09, 2.06, 1.85 (3*s*, 3 Ac). ^{1}H-NMR (C_6D_6): 7.45–6.76 (*m*, 2 Ph); 5.62 (*t*, *J*(3,4) = *J*(4,5) = 9.9, H–C(4)); 4.94–4.90 (*m*, H–C(2), H–C(3)); 4.23 (*dd*, *J*(5,6a) = 4.9, *J*(6a,6b) = 12.3, H_a–C(6)); 4.05 (*dd*, *J*(5,6b) = 2.2, *J*(6a,6b) = 12.3, H_b–C(6)); 3.60 (*dd*, *J*(1ax,1eq) = 13.3, *J*(1eq,2) = 1.6, H_{eq}–C(1)); 3.06 (*ddd*, *J*(4,5) = 9.9, *J*(5,6a) = 4.9, *J*(5,6b) = 2.2, H–C(5)); 2.70 (*dd*, *J*(1ax,1eq) = 13.3, *J*(1ax,2) = 1.9, H_{ax}–C(1)); 1.72, 1.66, 1.65 (3*s*, 3 Ac). ^{13}C-NMR ($CDCl_3$): 170.5, 170.2, 169.3 (3*s*, 3 Me*C*OO); 150.3, 150.1 (2*d*, *J* = 7.5, 2 C_{ipso}); 129.7 (4 C_m); 125.45, 125.41 (2*d*, *J* = 1.4, 2 C_p); 120.3, 120.1 (2*d*, *J* = 4.8, 4 C_o); 76.6 (C(5)); 74.5 (*d*, *J* = 5.4, C(2) or C(3)); 71.8 (*d*, *J* = 4.0, C(3) or C(2)); 68.2 (*d*, *J* = 3.8, C(1)); 65.4 (C(4)); 62.5 (C(6)); 20.6, 20.5, 20.3 (3 *Me*COO). ^{13}C-NMR (C_6D_6): 77.0 (C(5)); 75.3 (*d*, *J* = 5.4, C(2) or C(3)); 72.3 (*d*, *J* = 3.6, C(3) or C(2)); 68.2 (*d*, *J* = 4.4, C(1)); 65.8 (C(4)); 62.4 (C(6)); from the mixture with **26** in C_6D_6 only the signals of the pyranose ring can be given; signals for the arom. C's and the Ac groups overlap. ^{31}P-NMR ($CDCl_3$): –12.3 (*d*, *J* = 7.5). ^{31}P-NMR (C_6D_6): –10.5 (*d*, *J* = 7.6). FAB-MS: 561 ([*M* + K]$^+$), 523 ([*M* + 1]$^+$).

*Detection of 3,4,6-Tri-*O*-acetyl-2-deoxy-1-*O*-(diphenoxyphosphoryl)-β-*D-arabino*-hexopyranose* (**26**). Irradiation (10–15 s) of **8** (0.1 mmol, 60 mg) and Bu_3SnH (0.12 mmol, 35 mg) in C_6D_6 (0.7 ml) **26**/**27** 1:1. In dilute soln. (0.17 mmol of substrate) the ratio **26**/**27** changed to 3:1. Only the signals of the pyranose ring can be given as the signals of the arom. C's and the Ac groups of **26** and **27** overlap. ^{1}H-NMR (C_6D_6): 5.41 (*ddd*, *J*(1,2ax) = 9.4, *J*(1,2eq) = 2.5, *J*(1,P) = 6.9, H–C(1)); 5.11 (*t*, *J*(3,4) = 9.3, *J*(4,5) = 9.7, H–C(4)); 4.92 (*ddd*, *J*(2ax,3) = 11.4, *J*(2eq,3) = 5.3, *J*(3,4) = 9.3, H–C(3)); 4.26 (*dd*, *J*(5,6a) = 4.1, *J*(6a,6b) = 12.4, H_a–C(6)); 3.93 (*dd*, *J*(5,6b) = 2.4, *J*(6a,6b) = 12.4, H_b–C(6)); 3.12 (*ddd*, *J*(4,5) = 9.7, *J*(5,6a) = 4.1, *J*(5,6b) = 2.4, H–C(5)); 2.09 (*ddd*, *J*(1,2eq) = 2.5, *J*(2ax,2eq) = 12.5, *J*(2eq,3) = 5.3, H_{eq}–C(2)); 1.77–1.71 (*m*, H_{ax}–C(2)); 1.77, 1.68, 1.62 (3*s*, 3 Ac). ^{13}C-NMR (C_6D_6): 96.5 (*d*, *J* = 4.8, C(1)); 72.9, 69.7, 68.3 (C(3), C(4), C(5)); 61.6 (C(6)); 36.3 (*d*, *J* = 9.3, C(2)). ^{31}P-NMR (C_6D_6): –12.8 (*d*, *J* = 7.0). ^{1}H-NMR ((D_{10})Et_2O): 5.51 (*ddd*, *J*(1,2eq) = 2.4, *J*(1,2ax) = 9.3, *J*(1,P) = 6.9, H–C(1)); 5.13–4.89 (*m*, H–C(3), H–C(4)); 4.20 (*dd*, *J*(5,6a) = 2.5, *J*(6a,6b) = 12.3, H_a–C(6)); 3.94 (*dd*, *J*(5,6b) = 4.6, *J*(6a,6b) = 12.3, H_b–C(6)); 3.70 (*ddd*, *J*(9.6, *J*(5,6a) = 2.5, *J*(5,6b) = 4.6, H–C(5)); 2.26 (*ddd*, *J*(1,2eq) = 2.4, *J*(2ax,2eq) = 12.6, *J*(2eq,3) = 5.3, H_{eq}–C(2)); 1.81–1.72 (*m*, H_{ax}–C(2), overlapped by Ac *s*'s).

The deuterated compounds (D)-**26** and (D)-**27** were prepared according to the procedure given for (D)-**24**. In the obtained mixture, the ratio (D)-**26**/(D)-**27** was 2:1, and the axial *vs.* equatorial stereoisomers of (D)-**26** were formed in a 2:3 ratio. (D)-**26**: ^{2}H-NMR (C_6D_6): 2.2–1.8 (br. *s*, 0.40 D); 1.7–1.4 (br. *s*, 0.27 D); (D)-**27**: ^{2}H-NMR (C_6H_6): 2.9–2.5 (br. *s*, 0.33 D).

Kinetic Measurements. A soln. of **5** (90 mg, 0.15 mmol) in C_6D_6 (1.8 ml) was prepared. Identical amounts (0.3 ml) of this soln. were transferred to 6 NMR tubes. Bu_3SnH (80, 120, 160, 200, 240, and 280 µl) was added, then C_6D_6 (320, 280, 240, 200, 160, and 120 µl) up to identical sample volumes of 0.7 ml. The solns. were mixed by shaking for 3 s. Sample by sample was irradiated with the filtered light of a *Hanovia-977-B1* 1-kW Hg-Xe high-pressure lamp for 30 s and the ^{31}P-NMR recorded subsequently. By integration, the ratios **23**/**31** were determined (5.1, 2.8, 2.3, 1.5, 1.2, 1.0) for the 6 different Bu_3SnH concentrations (0.39, 0.59, 0.78, 0.98, 1.17, 1.37M). The slope of a plot **23**/**31** against $[Bu_3SnH]^{-1}$ gave the desired ratio k_R/k_H.

The kinetic measurements with **13** (118 mg, 0.15 mmol) were performed as described for **5**. By integration, the ratios **24**/**29** were determined (5.3, 3.8, 2.9, 2.3, 1.9, 1.4) for the 6 different Bu_3SnH concentrations (0.39, 0.59, 0.78, 0.98, 1.17, 1.37M).

The kinetic measurements with **22** (82 mg, 0.15 mmol) and Bu_3SnH were performed as described for **5**. By integration, the ratio **25**/**32** were determined (21.0, 10.7, 6.7, 7.2, 6.0) for five different Bu_3SnH concentrations (0.59, 0.78, 0.98, 1.17, 1.37M). The slope of a plot **25**/**32** against $[Bu_3SnH]^{-1}$ could only be estimated to be larger than 8.0M.

For the kinetic measurements of **22** (82 mg, 0.15 mmol) with thiophenol as H-donor, **22** was dissolved in C_6D_6 (1.8 ml). Bu_3SnH (60 µl, 0.21 mmol, 1.4 equiv.) was added to this soln.; the Bu_3SnH was necessary to initiate the radical chain reaction by halogen abstraction from the precursor. Identical amounts of 0.3 ml of this soln. were transferred to 4 NMR tubes. Thiophenol (90, 120, 150, and 180 µl) was added, then C_6D_6 (310, 280, 250, and 220 µl) up to identical sample volumes of 0.7 ml. The solns. were mixed by shaking for 3 s. Sample by sample was irradiated with the filtered light of a *Hanovia-977-B1* 1-kW Hg-Xe high-pressure lamp for 30 s and the ^{31}P-NMR recorded subsequently. By integration, the ratios **25**/**32** were determined (1.07, 0.70, 0.42, 0.35) for 4 different thiophenol concentrations (1.26, 1.69, 2.08, and 2.50M). The slope of a plot **25**/**32** against $[PhSH]^{-1}$ gave the desired ratio k_R/k_H.

The kinetic measurements with **8** (12.6 mg, 0.21 mmol) was performed as described for **5**, except for the addition of Bu_3SnH (25, 20, and 15 µl) and C_6D_6 (*ca.* 480 µl; 0.005M **8**; irradiation for 120 s). By integration, the ratios **26**/**27** were determined (7.4, 9.3, 12.4) for 3 different Bu_3SnH concentrations (0.13, 0.11, 0.08M). The slope of a plot **26**/**27** against $[Bu_3SnH]^{-1}$ gave a good estimation of the desired ratio k_R/k_H.

Preparation of the 2-Deoxydisaccharides. To a mixture of the glycosyl acceptor (0.8 mmol) and anh. $Mg(ClO_4)_2$ (18 mg, 0.08 mmol), a soln. of the glycosyl donor **23** in THF was added and the mixture stirred for 15 min. Et_3N (0.5 ml, 5.0 mmol) was added to quench the reaction, then the solvent was evaporated and the residue dissolved in MeCN. After extraction with pentane and removal of MeCN *in vacuo*, the 2-deoxydissacharide was isolated by FC.

*Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D*- and -β-*D-lyxo*-hexopyranosyl)-α-*D*-glucopyranoside* (α-D- and β-D-**34**, resp.). From methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**33**; 360 mg, 0.78 mmol), **23** (1 mmol), and $Mg(ClO_4)_2$ (21 mg): 240 mg (42%) of α-D-**34** and 63 mg (11%) of β-D-**34**. Total yield, 53%. α-D/β-D Ratio, 3.8:1.

α-D-**34**: TLC (Et_2O/pentane 2:1): R_f 0.33. $[\alpha]_D^{24} = +83.1$ (c = 7.27, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.34–7.05 (*m*, 3 Ph); 5.59–5.51 (*m*, H–C(3′), H–C(4′)); 5.04, 5.02 (2*d*, J_{gem} = 1.17, J_{gem} = 11.3, 2 H, PhCH_2O); 4.91 (br. *d*, J(1′,2′ax) = 3.4, J(1′,2′eq) $\leqslant$ 1.0, H–C(1′)); 4.78 (*d*, J_{gem} = 11.3, 1 H, PhCH_2O); 4.67 (*d*, J(1,2) = 3.6, H–C(1)); 4.64 (*d*, J_{gem} = 11.7, 1 H, PhCH_2); 4.54–4.30 (2*d*(*AB*), J_{gem} = 12.0, 2 H, PhCH_2O); 4.27–4.13 (*m*, 4 H); 3.94 (br. *dd*, J(4,5) = 9.9, J(5,6) = 4.2, H–C(5)); 3.84 (*dd*, J(5′,6′a) = 5.5, J(6′a,6′b) = 10.9, H_a–C(6′)); 3.65 (*dd*, J(5′,6′b) = 1.5, J(6′a,6′b) = 10.9, H_b–C(6′)); 3.59–3.52 (*m*, 2 H, H–C(2) and 1 H); 3.23 (*s*, MeOH); 2.07 (*dt*, J(2′ax,2′eq) = J(2′ax,3′) = 13.0, J(1′,2′ax) = 3.4, H_{ax}–C(2′)); 1.84 (br. *dd*, J(1′,2′eq) $\leqslant$ 1.0, J(2′ax,2′eq) = 13.0, J(2′eq,3′) = 4.8, H_{eq}–C(2′)); 1.71, 1.70, 1.63 (3*s*, 3 Ac). ^{13}C-NMR ($CDCl_3$): 170.3, 170.2, 169.9 (3 Me*C*OO); 138.5, 138.2, 138.0 (3 C_{ipso}); 128.4–127.4 (15 C of Ph); 97.8, 97.5 (C(1), C(1′)); 82.1, 79.9, 77.8, 69.7, 66.7, 66.5, 66.0 (C(2), C(3), C(4), C(5), C(3′), C(4′), C(5′)); 75.7, 74.9, 73.2 (3 Ph*C*H_2O); 65.7 (C(6)); 62.3 (C(6′)); 55.1 (MeO); 29.9 (C(2′)); 20.8, 20.60, 20.58 (3 *Me*COO). FAB-MS: 775 ($[M + K]^+$), 735 ($[M - 1]^+$), 645 ($[M - PhCH_2]^+$). Anal. calc. for $C_{40}H_{48}O_{13}$ (736.81): C 65.21, H 6.57; found: C 65.03, H 6.57.

β-D-**34**: TLC (Et_2O/pentane 2:1): R_f 0.24. TLC (Et_2O/pentane/CH_2Cl_2 1:1:1): R_f 0.45. $[\alpha]_D^{24} = +34.6$ (c = 2.12, $CHCl_3$). ^{1}H-NMR (C_6D_6): 7.35–7.06 (*m*, 3 Ph); 5.36 (*d*, J(3′,4′) = 3.1, H–C(4′)); 5.03 (*d*, J_{gem} = 11.2, 1 H, Ph*C*H_2O); 4.95 (*d*, J_{gem} = 11.6, 1 H, PhCH_2O); 4.87 (*ddd*, J(2′ax,3′) = 12.4, J(2′eq,3′) = 4.7, J(3′,4′) = 3.1, H–C(3′)); 4.78 (*d*, J_{gem} = 11.2, 1 H, PhCH_2O); 4.64–4.59 (*m*, 2 H, PhCH_2O, H–C(1)); 4.52, 4.43 (2*d*, J_{gem} = 12.0, 2 H, PhCH_2O); 4.28–4.18 (*m*, H_a–C(6), H_a–C(6′), H–C(3)); 4.16–4.09 (*m*, H–C(1′), H_b–C(6′)); 3.97 (*ddd*, *J*(4,5) = 9.9, *J*(5,6) = 5.0, *J*(5,6) = 1.6, H−C(5)); 3.88–3.60 (*m*, H−C(4), H_b−C(6)); 3.54 (*dd*, *J*(1,2) = 3.4, *J*(2,3) = 9.6, H−C(2)); 3.35 (*dt*, *J*(4′,5′) = 1.0, *J*(5′,6′a) = *J*(5′,6′b) = 6.6, H−C(5)); 3.16 (*s*, MeO); 2.14 (*dt*, *J*(1′,2′ax) = 9.7, *J*(2′ax,2′eq) = *J*(2′ax,3′) = 12.4, H_{ax}−C(2′)); 1.85 (*ddd*, *J*(1′,2′eq) = 2.0, *J*(2′ax,2′eq) = 12.4, *J*(2′eq,3′) = 4.7, H_{eq}−C(2′)); 1.69, 1.67, 1.64 (3*s*, 3 Ac). ^{13}C-NMR (CDCl$_3$): 170.5, 170.3, 170.0 (3 Me*C*OO); 138.6, 138.3, 138.1 (3 C_{ipso}); 128.5–127.6 (15 C of Ph); 100.4 (C(1′)); 98.0 (C(1)); 82.2, 79.8, 77.4, 70.9, 69.7, 68.4, 65.3 (C(2), C(3), C(4), C(5), C(3′), C(4′), C(5′)); 68.0 (C(6)); 61.7 (C(6′)); 55.2 (MeO); 31.7 (C(2′)); 20.8, 20.68, 20.65 (3 *Me*COO). FAB-MS: 775 ($[M + K]^+$), 735 ($[M - 1]^+$), 645 ($[M - PhCh_2]^+$). Anal. calc. for $C_{40}H_{48}O_{13}$ (736.81): C 65.21, H 6.57; found: C 65.22, H 6.60.

*Methyl 2,3,6-Tri-*O*-benzyl-4-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-*D-lyxo*-hexopyranosyl)-α-D-glucopyranoside* (**36**). From methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (**35**; 349 mg, 0.75 mmol), **23** (1 mmol) and Mg(ClO$_4$)$_2$ (19 mg): 220 mg (40%) of **36**. TLC (Et$_2$O/pentane/CH$_2$Cl$_2$ 1:2:1): R_f 0.18. TLC (Et$_2$O/pentane/MeCN 10:10:1): R_f 0.34. $[\alpha]_D^{24}$ = +67.6 (*c* = 2.64, CHCl$_3$). ^{1}H-NMR (CDCl$_3$): 7.36–7.26 (*m*, 3 Ph); 5.48 (br. *d*, *J*(1′,2′eq) ⩽ 1.0, *J*(1′,2′ax) ≈ 3.6, H−C(1′)); 5.20 (br. *s*, H−C(4′)); 5.17 (*ddd*, *J*(2′eq,3′) = 4.8, *J*(2′ax,3′) = 12.4, *J*(3′,4′) = 3.0, H−C(3′)); 5.05 (*d*, J_{gem} = 11.2, 1 H, PhCH_2O); 4.73 (*d*, J_{gem} = 12.0, 1 H, PhCH_2O); 4.69–4.60 (*m*, 4 H, PhCH_2O, H−C(1)); 4.54 (*d*, J_{gem} = 12.2, 1 H, PhCH_2O); 4.01–3.88 (*m* 4 H); 3.77 (*ddd*, *J*(4,5) = 10.0, *J*(5,6) = 2.6, *J*(5,6) = 4.3, H−C(5)); 3.72–3.63 (*m*, 3 H); 3.53 (*dd*, *J*(1,2) = 3.5, *J*(2,3) = 9.6, H−C(2)); 3.42 (*s*, MeO); 2.09, 1.98, 1.97 (3*s*, 3 Ac); 1.91 (*dt*, *J*(1′,2′ax) ≈ 3.6, *J*(2′ax,2′eq) = *J*(2′ax,3′) = 12.4, H_{ax}−C(2′)); 1.71 (br. *dd*, *J*(1′,2′eq) ⩽ 1.0, *J*(2′ax,2′eq) = 12.4, *J*(2′eq,3′) = 4.8, H_{eq}−C(2′)). ^{1}H-NMR (C$_6$D$_6$): 7.40–7.05 (*m*, 3 Ph); 5.71 (br. *d*, *J*(1′,2′eq) ⩽ 1.0, *J*(1′,2′ax) = 3.8, H−C(1′)); 5.56–5.55 (*m*, H−C(4′)); 5.49 (*ddd*, *J*(2′eq,3′) = 4.9, *J*(2′ax,3′) = 12.5, *J*(3′,4′) = 3.0, H−C(3′)); 5.06 (*d*, J_{gem} = 11.5, 1 H, PhCH_2O); 4.65–4.51 (*m*, 4 H, H−C(1), PhCH_2O); 4.43–4.33 (*m*, 2 H, PhCH_2O); 4.23–4.09, 3.93–3.85, 3.80–3.71 (*m*, 4, 2 and 2 H, H−C(5′), H−C(3), H−C(4), H−C(5), H_a−C(6), H_b−C(6), H_a−C(6′), H_b−C(6′)); 3.46 (*dd*, *J*(1,2) = 3.4, *J*(2,3) = 9.6, H−C(2)); 3.21 (*s*, MeO); 2.05 (*dt*, *J*(1′,2′ax) = 3.8, *J*(2′ax,2′eq) = *J*(2′ax,3′) = 12.5, H_{ax}−C(2′)); 1.81 (br. *dd*, *J*(1′,2′eq)′ ⩽ 1.0, *J*(2′ax,2′eq) = 12.5, *J*(2′eq,3′) = 4.9, H_{eq}−C(2′)); 1.71, 1.67, 1.65 (3*s*, 3 Ac). ^{13}C-NMR (CDCl$_3$): 170.3, 170.2, 170.0 (3 Me*C*OO); 138.5, 138.1, 137.8 (3 C_{ipso}); 128.5–127.4 (15 C of Ph): 99.1, 97.7 (C(1), C(1′)); 81.8, 80.1, 76.2, 69.5, 67.2, 66.4, 65.8 (C(2), C(3), C(4), C(5), C(3′), C(4′), C(5′)); 75.3, 73.2, 73.1 (3 Ph*C*H$_2$O); 69.1 (C(6)); 62.3 (C(6′)); 55.2 (MeO); 30.4 (C(2′)); 20.8, 20.68, 20.65 (3 *Me*COO). FAB-MS: 775 ($[M + K]^+$), 737 ($[M + 1]^+$), 736 (M^+), 735 ($[M - 1]^+$), 645 ($[M - PhCH_2]^+$). Anal. calc. for $C_{40}H_{48}O_{13}$ (736.81): C 65.21, H 6.57; found: C 65.06, H 6.65.

*6-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D- and -β-*D-arabino*-hexopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose* (α-D- and β-D-**38**). A soln. of **22** (0.26 g, 0.5 mmol), galactose **37** (0.18 g, 0.69 mmol), and Bu$_3$SnH (0.18 g, 0.62 mmol) in dry Et$_2$O/THF 3:1 (40 ml) was irradiated with the *TQ-150* mercury high-pressure lamp for 15 min (conversion (rearrangement and substitution) complete, no elimination product detectable). Tin compounds were removed by extraction and the residue purified by FC (TLC (Et$_2$O/pentane 2:1): R_f 0.38): 188 mg (79%) of α-D-/β-D-**38** 1.5:1 (not separable by FC).

α-D-**38**: ^{1}H-NMR (CDCl$_3$): 5.52 (*d*, *J*(1,2) = 4.9, H−C(1)); 5.26 (*ddd*, *J*(2′ax,3′) = 11.5, *J*(2′eq,3′) = 5.5, *J*(3′,4′) = 9.6, H−C(3)); 4.93 (br. *d*, *J*(1′,2′eq) = 1.0, *J*(1′,2′ax) = 3.5, H−C(1′)); 4.73 (*t*, *J*(3′,4′) = *J*(4′,5′) = 9.6, H−C(4′)); 4.62 (*dd*, *J*(2,3) = 2.4, *J*(3,4) = 7.9, H−C(3)); 4.32 (*dd*, *J*(1,2) = 4.9, *J*(2,3) = 2.4, H−C(2)); 4.27 (*dd*, *J*(3,4) = 7.9, *J*(4,5) = 1.8, H−C(4)); 3.99–3.92 (*m*, H−C(5)); 3.89 (*dq*, *J*(4′,5′) = 9.6, *J*(5′,6′) = 6.3, H−C(5′)); 3.73 (*dd*, *J*(5,6a) = 5.9, *J*(6a,6b) = 10.0 H_a−C(6)); 3.64 (*dd*, *J*(5,6b) = 7.5, *J*(6a,6b) = 10.0, H_b−C(6)); 2.26 (*ddd*, *J*(1′,2′eq) = 1.0, *J*(2′ax,2′eq) = 12.8, *J*(2′eq,3′) = 5.5, H_{eq}−C(2′)); 2.05, 2.00 (2*s* 2 Ac); 1.84–1.67 (*m*, H_{ax}−C(2′)); 1.56, 1.44, 1.34 (3*s*, 3, 3, and 6 H, Me$_2$C); 1.17 (*d*, *J*(5′,6′) = 6.3, 3 H−C(6′)). ^{1}H-NMR (C$_6$D$_6$): 5.3 (*ddd*, *J*(2′ax,3′) = 11.5, *J*(2′eq,3′) = 5.5, *J*(3′,4′) = 9.6, H−C(3′)); 5.46 (*d*, *J*(1,2) = 5.0, H−C(1)); 4.93 (*t*, *J*(3′,4′) = *J*(4′,5′) = 9.6, H−C(4′)); 4.75 (br. *d*, *J*(1′,2′eq) ⩽ 1.0, *J*(1′,2′ax) = 3.6, H−C(1′)); 4.47 (*dd*, *J*(2,3) = 2.4, *J*(3,4) = 7.9, H−C(3)); 4.19–4.04 (*m*, H−C(2), H−C(4), H−C(5)); 3.99 (*dq*, *J*(4′,5′) = 9.6, *J*(5′,6′) = 6.3, H−C(5′)); 3.91 (*dd*, *J*(5,6a) = 6.2, *J*(6a,6b) = 10.1, H_a−C(6)); 3.74 (*dd*, *J*(5,6b) = 6.9, *J*(6a,6b) = 10.1, H_b−C(6)); 2.19 (br. *dd*, *J*(1′,2′eq) ⩽ 1.0 *J*(2′ax,2′eq) = 12.6, *J*(2′eq,3′) = 5.5, H_{eq}−C(2′)); 1.68, 1.65 (2*s*, 2 Ac); 1.55 (*dt*, *J*(1′,2′ax) = 3.6, *J*(2′ax,2′eq) = 12.6, *J*(2′ax,3′) = 11.5, H_{ax}−C(2′)); 1.43–1.40, 1.14–1.08 (12 H, Me$_2$C); 1.05 (*d*, *J*(5′,6′)–6.3, 3 H−C(6′)).

β-D-**38**: ^{1}H-NMR (CDCl$_3$): 5.53 (*d*, *J*(1,2) = 4.6, H−C(1)); 4.98 (*ddd*, *J*(2′ax,3′) = 12.0, *J*(2′eq,3′) = 5.4, *J*(3′,4′) = 9.6, H−C(3′)); 4.72 (*t*, *J*(3′,4′) = *J*(4′,5′) = 9.6, H−C(4′)); 4.68–4.57 (*m*, H−C(3), H−C(1′)); 4.31 (*dd*, *J*(1,2) = 4.6, *J*(2,3) = 2.4, H−C(2)); 4.21 (*dd*, *J*(3,4) = 7.8, *J*(4,5) = 1.8, H−C(4)); 4.04–3.93 (*m*, H_a−C(6), H−C(5)); 3.74–3.70 (*m*, H_b−C(6)); 3.46 (*dq*, *J*(4′,5′) = 9.6, *J*(5′,6′) = 6.3, H−C(5′)); 2.36 (*ddd*, *J*(1′,2′eq) = 1.9, *J*(2′ax,2′eq) = 12.5, *J*(2′eq,3′) = 5.4, H_{eq}−C(2′)); 2.04, 2.01 (2*s*, 2 Ac); 1.84–1.67 (*m*, H_{ax}−C(2′)); 1.53, 1.45, 1.33 (3*s*, 3, and 6 H, Me$_2$C); 1.22 (*d*, *J*(5′,6′) = 6.3, 3 H−C(6′)). ^{1}H-NMR (C$_6$D$_6$): 5.50 (*d*, *J*(1,2) = 5.0, H−C(1)); 5.00 (*ddd*, *J*(2′ax,3′) = 11.7, *J*(2′eq,3′) = 5.3, *J*(3′,4′) = 9.4, H−C(3′)); 4.85 (*t*, *J*(3′,4′) = *J*(4′,5′) = 9.4, H−C(4′)); 4.43 (*dd*, *J*(2,3) = 2.2, *J*(3,4) = 7.9, H−C(3)); 4.28 (*dd*, *J*(1′,2′eq) = 1.8, *J*(1′,2′ax) = 9.6, H−C(1′)); 4.19–4.04 (*m*, H–C(2), H–C(5), H_a–C(6)); 3.95–3.88 (*m*, H–C(4)); 3.81 (*dd*, *J*(5,6b) = 6.4, *J*(6a,6b) = 10.1, H_b–C(6)); 3.11 (*dq*, *J*(4′,5′) = 9.4, *J*(5′,6′) = 6.3, H–C(5′)); 2.23 (*ddd*, *J*(1′,2′eq) = 1.8, *J*(2′ax,2′eq) = 12.6, *J*(2′,eq,3′) = 5.3, H_{eq}–C(2′)); 1.78–1.64 (*m*, H_{ax}–C(2′)); 1.67, 1.62 (2*s*, 2 Ac); 1.43–1.40, 1.14–1.08 (12 H, Me_2C); 1.05 (*d*, *J*(5′,6′) = 6.3, 3 H–C(6′)). FAB-MS: 513 ([*M* + K]$^+$), 475 ([*M* + 1]$^+$), 473 ([*M* – 1]$^+$), 415 (*M* – AcO).

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