# Synthesis of Deoxy Glycosides Under Neutral Conditions in $LiClO_4$/Solvent Mixtures

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**Abstract:** 2-Deoxy- and 2,6-dideoxyglycosyl trichloroacetimidates, phosphites and fluorides are efficiently activated in 0.1M metal perchlorate/solvent mixtures, i. e. without the need for an additional promoter like a strong Lewis acid or a heavy metal salt. Under these neutral conditions they react with different glycosyl acceptors to give oligosaccharides, amino acid glycosides and cholesteryl glycosides in high yields and with pronounced stereoselectivity. For 3,4,6-tri-*O*-benzyl protected 2-deoxy glucose the highest yields were observed with the α-imidate, however, the anomer ratio was highest if the corresponding glycosyl fluoride was used. The stereoselectivity was not significantly influenced by the solvent and the metal ion, the yield was highest in 0.1M solutions of $LiClO_4$ in diethyl ether. Under these gentle conditions also 2-deoxy-L-fucosyl fluoride and D-digitoxosyl fluoride react with different *O*-silylated glycosyl acceptors to give sensitive 2,6-dideoxyglycosides with preparatively useful results.

**Key words:** deoxyglycosides, glycosylations, $LiClO_4$/diethyl ether mixtures, carbohydrates, oligosaccharides

## Introduction

Glycosides of 2-deoxy- and 2,6-dideoxycarbohydrates occur in various natural products. For instance they form characteristic structural elements of antitumor drugs like the anthracyclins, aureolic acid, calicheamicin and esperamicin, of antibiotics active against Gram positive bacteria, like the orthosomycins, and of cardiac glycosides used in the treatment of cardiac insufficiency.[1] Whereas the therapeutic effect of these drugs is mediated by the aglycon, the glycosidic part influences the pharmacokinetic properties of the physiologically active compounds. The development of new drugs with altered glycosidic parts or aglycons is actively being pursued. For instance 2-deoxy-L-fucose is employed in the development of so called class II anthracyclin antibiotics.[1,2] Also, digitoxosides in which the aglycons found in the natural *Digitalis* glycosides are replaced by analogs are of great interest as new and safer drugs for the treatment of cardiac insufficiency.[3] Due to this biological relevance the development of methods for the efficient and stereoselective construction of deoxyglycosidic linkages is of great relevance to organic synthesis, medicinal and bioorganic chemistry.[1]

In comparison to the synthesis of other glycosides 2-deoxyglycoside synthesis is particularly challenging, since 2-deoxyglycosides on the one hand are more acid labile. On the other hand a stereodirecting neighboring group adjacent to the anomeric center is lacking that may direct the steric course of the glycosidation reaction.

For the stereoselective synthesis of 2-deoxy-α-glycosides the latter problem mostly is circumvented by electrophile mediated addition of acceptor alcohols to the double bond of glycals followed by reductive removal of the C-2-substituent.[4] For the construction of β-configured 2-deoxyglycosides the use of glycosyl donors with equatorial 2-substituents acting as neighboring group[5] and of 1,2-anhydropyranoses[6] followed by reductive removal of the 2-substituent has provided solutions to the problem. Clearly, the application of direct methods for the efficient and highly stereoselective construction of 2-deoxy- and 2,6-dideoxyglycosides is highly desirable. For this purpose the Koenigs–Knorr reaction employing the insoluble silver silicate,[7] the Lewis acid-mediated activation of glycosyl phosphites and phosphoramidates,[8] and the activation of glycosyl sulfoxides in the presence of a Lewis acid[9] were developed recently. In the light of the pronounced acid-sensitivity of deoxyglycosides and the drawbacks associated with the use of toxic and expensive heavy metal salts, the development of alternative methods that proceed under very mild, preferably neutral conditions and without the use of strong Lewis acids or other promotors is of great interest.

We have recently reported that solutions of $LiClO_4$ in organic reaction media favor the formation of glycosyl cations by detachment of suitable leaving groups from various glycosyl donors and thus are eminently suitable for *O*-glycoside synthesis under very mild conditions.[10] In these solvent systems glycosyl halides, trichloroacetimidates, phosphates and phosphites are activated under neutral conditions and participate as glycosyl donors in glycosylation reactions with different glycosyl acceptors.

In this paper we report on the application of this method for the construction of 2-deoxy- and 2,6-dideoxyglycosides (Scheme 1).[11]

## Results and Discussion

Our previous investigations on the use of $LiClO_4$/solvent mixtures for glycoside synthesis under neutral conditions had revealed that glycosyl trichloroacetimidates and glycosyl fluorides[12] are particularly advantageous glycosyl donors in these reaction media. Therefore, the corresponding glycosyl donors **1–4** derived from benzyl-pro-



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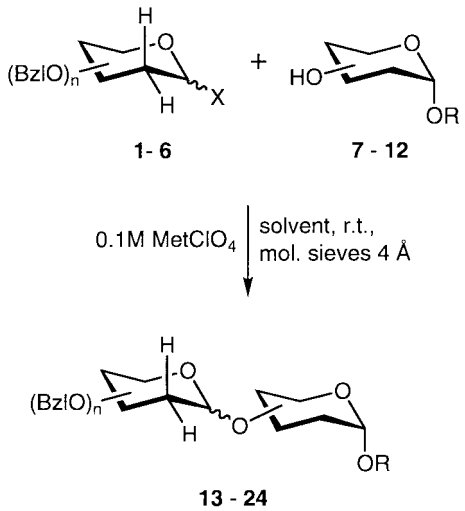


**Scheme 1** Synthesis of 2-deoxyglycosyl saccharides in metal (Met) perchlorate/diethyl ether mixtures

tected 2-deoxyglucose (Figure 1) were employed to determine if deoxyglycosides could be built up in solutions of metal perchlorates in organic solvents. Alcohols **7–12** were used as model glycosyl acceptors. 2-Deoxyglucosyl-α-trichloroacetimidate **1** was synthesized by deprotonation of 3,4,6-tri-*O*-benzyl-2-deoxyglucopyranose[13] with NaH and subsequent treatment with trichloroacetonitrile according to the method introduced by R. R. Schmidt et al.[14] An α/β−mixture with the α-anomer predominating (α:β = 25:1) was obtained in quantitative yield. If $K_2CO_3$ was employed as base the corresponding β-anomer **2** was formed in excess[14] (quantitative yield, α:β = 1:8; see the experimental part).

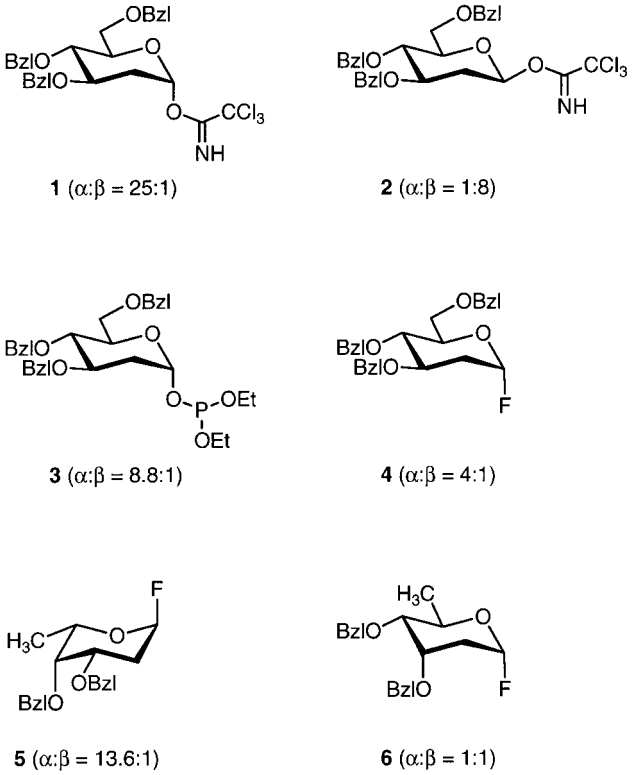


**Figure 1** Glycosyl donors employed in the synthesis of 2-deoxy and 2,6-dideoxyglycosides

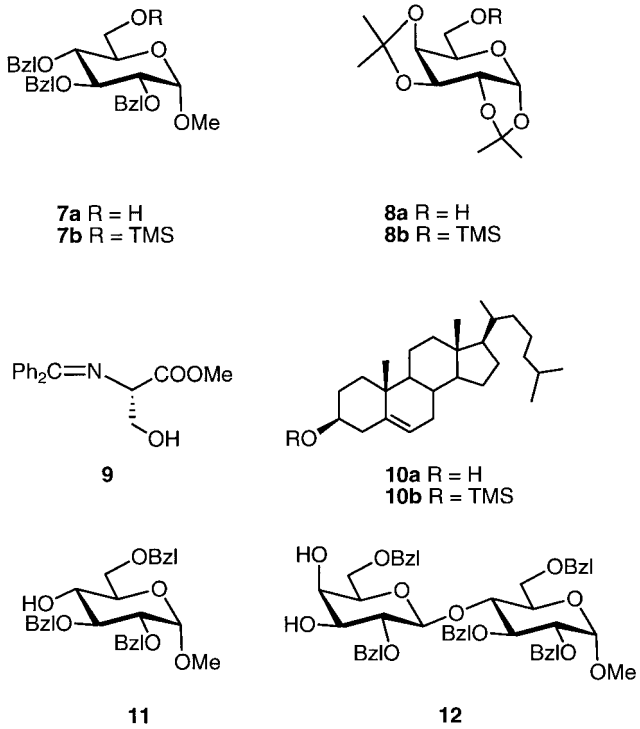


**Figure 2** Glycosyl acceptors employed in the glycosylation reactions

Upon treatment of α-configured glycosyl donor **1** with selectively deprotected glucosyl acceptor **7a** in differently concentrated solutions of $LiClO_4$ in diethyl ether the corresponding disaccharide **13** was formed smoothly and in high yield. Variation ot the $LiClO_4$ concentration between 0.03 M and 0.5 M revealed that the yield was highest in 0.1 M $LiClO_4$/diethyl ether (Table 1, entry 1). Therefore all further glycosylations were conducted in 0.1 M solutions (Table 1). Under these conditions deoxyglucosyl disaccharide **13** was obtained in 89% isolated yield and with an α/β ratio of 1.5:1. Use of the more reactive β-glycosyl donor did not give an improved yield and the α/β ratio was very similar (Table 1, entry 2). Also variation of the solvent and the metal counterion did not significantly change the picture. In toluene, $CH_3CN$ and $CH_2Cl_2$ and also with $Mg(ClO_4)_2$ and $Ba(ClO_4)_2$ the stereoselectivity was very similar. However, the yield was consistently lower (Table 1, entries 3–7). In particular, the finding that in $CH_3CN$ the α/β ratio remains unchanged is surprising. Obviously, the "nitrile-effect"[15] that was observed in the activation of the analogous glucosyl trichloroacetimidate in $LiClO_4$/diethyl ether[10a,b] is not operating in the deoxy case. In order to determine the influence of the perchlorate anion, solutions of $LiN(Tf)_2$,[16] $LiBF_4$ and $LiPF_6$ in diethyl ether were investigated as reaction media. For the



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**Table 1** Results of the Glycosylations in 0.1M Solutions of $MetClO_4$ Employing Donors **1** and **2** and Acceptor **7a** To Give Glycoside **13**

| Entry | Donor[a] | Promoter | Solvent | Yield (%)[b] | Anomer ratio (α:β)[c] |
|---|---|---|---|---|---|
| 1 | **1** | $LiClO_4$ | $Et_2O$ | 89 | 1.5:1 |
| 2 | **2** | $LiClO_4$ | $Et_2O$ | 78 | 1.1:1 |
| 3 | **1** | $LiClO_4$ | toluene | 69 | 1.8:1 |
| 4 | **1** | $LiClO_4$ | $CH_3CN$ | 68 | 1.5:1 |
| 5 | **1** | $LiClO_4$ | $CH_2Cl_2$ | 75 | 1.8:1 |
| 6 | **1** | $Ba(ClO_4)_2$ | $CH_3CN$ | 66 | 1.8:1 |
| 7 | **1** | $Mg(ClO_4)_2$ | $CH_2Cl_2$ | 43 | 1.3:1 |
| 8 | **1** | $LiN(SO_2CF_3)_2$ | $Et_2O$ | 31 | 1.3:1 |
| 9 | **1** | $LiBF_4$ | $Et_2O$ | 75 | 1.6:1 |
| 10 | **1** | $LiPF_6$ | $Et_2O$ | 29 | 3.6:1 |

[a] The donors **1** (α:β = 25:1) and **2** (α:β = 1:8) were used as anomeric mixtures.
[b] Chromatographically purified glycoside **13**.
[c] The ratio was determined by $^1H$ or $^{13}C$ NMR.

hexafluorophosphate the stereoselectivity was significantly higher (Table 1, enty 10), but the yield was inferior in all three cases. Thus, the best results were obtained with α-deoxyglucosyl imidate **1** in 0.1 M solutions of $LiClO_4$ in diethyl ether. Therefore, all further glycoside syntheses with this donor were carried out under these conditions.

In order to determine the scope of this new method, imidate **1** was coupled with glycosyl acceptors **8–11**. In the course of the ensuing reactions galactosyl glycoside **14**, serine glycoside **15** and cholesterol derivative **16** were formed in high yields and with α/β ratios ranging from 2.4:1 to 1:1 (Table 2, entries 1–3). Deoxyglucosyl disaccharide **17** was obtained in lower yield, however, the α−anomer was formed with complete stereoselectivity (Table 2, entry 4). These results demonstrate that 2-deoxyimidate **1** is efficiently activated in 0.1 M solutions of $LiClO_4$ in diethyl ether in the absence of a strong Lewis acid. As already pointed out earlier, the rate-accelerating effect of these reaction media may be attributed to their ability to stabilize polar or ionic transition states or intermediates like glycosyl cations.[10,17]

Although with imidate **1** the desired glycosides were formed in high yields the stereoselectivity remained mostly low. In an attempt to find glycosyl donors that react with higher selectivity the use of deoxyglucosyl phosphite **3** and of deoxyglucosyl fluoride **4** in the glycosidations was investigated. Deoxyglucosyl phosphite **3** was obtained from 3,4,6-tri-*O*-benzyl-2-deoxyglucose according to a published procedure[8b] and fluoride **4** was synthesized from this selectively deprotected deoxyglucose derivative by treatment with diethylaminosulfur trifluoride[18] (DAST; see the experimental part).

Deoxyglycosyl phosphite **3** was also activated in 0.1 M $LiClO_4$/diethyl ether and reacted with glycosyl acceptors **7a** and **8a** to give disaccharides **13** and **14** in 56% and 43% yield and with α/β ratios of 3.5:1 and 4.2:1 respectively. Thus, although a higher preference for the α−anomer could be recorded with this glycosyl donor the situation was not improved to a satisfying degree. The use of 2-deoxyglucosyl fluoride **4**, however, led to significantly higher anomer ratios. Glycosyl donor **4** is also activated in 1M $LiClO_4$ in diethyl ether under very mild conditions. It reacts with selectively deprotected glucose derivative **7a**, galactosyl alcohol **8a** and cholesterol **10a** to give glycosides **13**, **14** and **16** in yields of 41–65% (Table 3). More gratifyingly, a pronounced preference for the α−anomer is observed. Thus, glucosyl disaccharide **13** is formed with an α/β ratio of 13.4:1 whereas with the imidate **1** only a value of 1.5:1 was recorded (compare Table 1, entry 1 and Table 3, entry 1). Similarly for galactosyl disaccharide **14** the anomer ratio raised to 6:1 (as compared to 2:1 for the imidate). Cholesteryl glycoside **16** prepared from fluoride **4** displayed an α/β ratio of 11.4:1 whereas if imidate **1** was used the two anomers were fomed in equal amounts (Table 2, entry 3 and Table 3, entry 3). Thus, although with fluoride **4** yields are lower than with imidate **1**, the higher stereoselectivity overcompensates this loss in reactivity.

In order to extend the scope of the method established as described above, the synthesis of 2,6-dideoxyglycosides in $LiClO_4$/diethyl ether was investigated. Since glycosides of 2-deoxy-L-fucose and of D-digitoxose are targets of current interest (see the Introduction), these two carbohydrates were chosen for further studies. In the light of the finding that 2-deoxyglucosyl fluoride was the most advantageous of the 2-deoxyglucosyl donors investigated, the corresponding fluorides **5** and **6** (Figure 1) of 2-deoxylfucose and D-digitoxose were prepared (Scheme 2). To this end, triacetates **25**[19] and **26**[20] were converted into diacetylated allyl glycosides **27** and **28**. After removal of the acetates, benzyl ether protecting groups were introduced. The allyl glycosides were then cleaved by Rh(I)-mediated isomerisation of the allyl to the 1-propenyl group and subsequent Lewis acid mediated hydrolysis of the enol ethers formed in this process.[21] Finally, the resulting dideoxycarbohydrates selectively deprotected at the

**Table 2** Results of Glycosylations With Glycosyl Imidate **1** in 0.1M Solutions of $LiClO_4$

| Entry | Acceptor | Solvent | Glycoside | Yield (%) | Anomer ratio (α:β) |
|---|---|---|---|---|---|
| 1 | **8a** | $Et_2O$ | **14** | 91 | 2:1 |
| 2 | **9** | $CH_2Cl_2$ | **15** | 57 | 2.4:1 |
| 3 | **10a** | $Et_2O$ | **16** | 78 | 1:1 |
| 4 | **11** | $Et_2O$ | **17** | 37 | only α |

**Table 3** Results of the Glycosylations with Glycosyl Fluoride **4** in 0.1M Solutions of $LiClO_4$ in Diethyl Ether

| Entry | Acceptor | Glycoside | Yield (%) | Anomer ratio (α:β) |
|---|---|---|---|---|
| 1 | **7a** | **13** | 65 | 13.4:1 |
| 2 | **8a** | **14** | 49 | 6:1 |
| 3 | **10a** | **16** | 41 | 11.4:1 |



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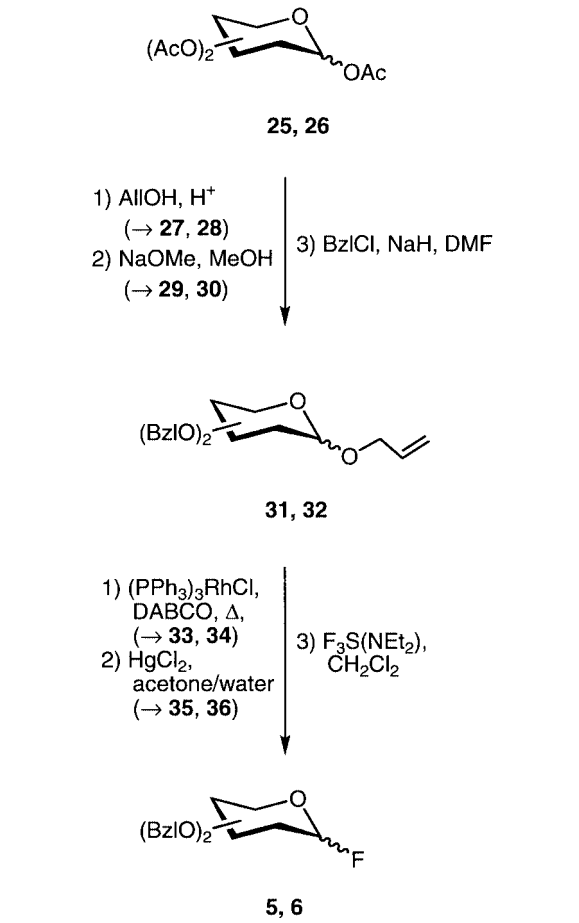
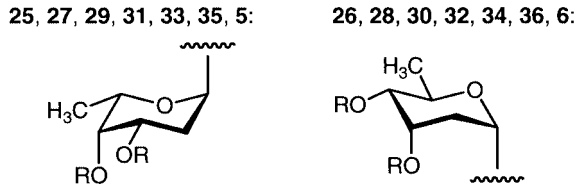
anomeric center were converted into glycosyl fluorides **5** and **6** by treatment with DAST.

As glycosyl acceptors silyl ethers **7b**, **8b** and **10b** were employed to facilitate the reactions by formation of the very stable Si–F bond. Lactose acceptor **12** was used to test if any regioselectivity could be obtained. Upon treatment of benzyl-protected 2-deoxyfucosyl fluoride **5** with glucose derivative **7b**, galactosyl acceptor **8b**, cholesteryl silyl ether **10b** and lactose derivative **12** in 0.1 M $LiClO_4$ in diethyl ether, glycosides **18–21** were smoothly formed in moderate to high yield. In all cases, the anomer ratio was gratifyingly high (Table 4, entries 1–5). Whereas the glucose and the galactose disaccharides were obtained with α/β ratios of 8:1 to 13:1, cholesteryl glycoside **20** and trisaccharide **21** were formed with complete α-selectivity. Furthermore, the glycosylation of lactose acceptor **21** proceeded with complete regioselectivity to deliver exclusively the 4'-deoxyfucosyl trisaccharide. Once more the use of $CH_3CN$ as solvent did not influence the course of the stereoselection. Glycoside **20** was formed in both diethyl ether and acetonitrile with complete α-selectivity (Table 4, entries 3 and 4). Thus, under these reaction conditions glycosides of 2-deoxy-L-fucose can be prepared with high selectivity and the method is applicable to the construction of oligosaccharides.

D-Digitoxosyl fluoride **6** reacted with glucosyl- and galactosyl silyl ethers **7b** and **8b** and silylated cholesterol **10b** also under the mild conditions provided by the $LiClO_4$/ether systems to give the corresponding disaccharides **22** and **23** as well as and the steroid glycoside **24** in satisfying yields (Table 4, entries 6–8). Whereas with glucose acceptor **7b** the anomers were formed nearly in a 1:1 ratio, for galactose disaccharide **23** once more a high α/β ratio was recorded (Table 4, entries 6 and 7). In the case of cholesteryl glycoside **24** unexpectedly the β-isomer was formed in excess (Table 4, entry 8).

In conclusion the results detailed above demonstrate that in 0.1 M $LiClO_4$/diethyl ether mixtures glycosides of 2-deoxy- and 2,6-dideoxycarbohydrates are formed in high yields and with high stereoselectivity. The glycosidation reactions proceed under neutral conditions and without need for an additional promoter usually applied in glycoside synthesis, i.e. a strong Lewis acid, a heavy metal salt or an alkylating reagent.




**Scheme 2.** Synthesis of 2,6-dideoxy fluorides **5** and **6**

The $LiClO_4$/diethyl ether method compares favourably with established methods of 2-deoxyglycoside synthesis. For instance coupling of in situ generated glycosyl phosphates of 2-deoxyglucose with glycosyl acceptors **7a** and **8a** proceeded in 72% and 79% respectively,[22] whereas activation of imidate **1** in $LiClO_4$/diethyl ether delivered disaccharides **13** and **14** in 89% and 91% yield respectively (Table 1 and Table 2). The synthesis of these disaccharides employing a thioglycoside[23] or a pentenyl glycoside[24] as glycosyl donors and methyl iodide or I(collidine)$_2ClO_4$ as promoters proceeded in 68–88% yield. 2-Deoxyfucosyl glucopyranoside **18** could be built up in 91% yield by employing the dibenzylphosphite of 2-de-

**Table 4** Results of the Glycosylations with 2-Deoxyfucosyl Donor **5** and Digitoxosyl Fluoride **6** in 0.1M Solutions of $LiClO_4$ in Organic Solvents

| Entry | Donor | Acceptor | Glycoside | Solvent | Yield | Anomer ratio (α:β) |
|---|---|---|---|---|---|---|
| 1 | **5** | **7b** | **18** | $Et_2O$ | 49 | 8:1 |
| 2 | **5** | **8b** | **19** | $Et_2O$ | 75 | 13:1 |
| 3 | **5** | **10b** | **20** | $Et_2O$ | 66 | only α |
| 4 | **5** | **10b** | **20** | $CH_3CN$ | 51 | only α |
| 5 | **5** | **12** | **21** | $Et_2O$ | 31 | only α |
| 6 | **6** | **7b** | **22** | $Et_2O$ | 52 | 1:1.3 |
| 7 | **6** | **8b** | **23** | $Et_2O$ | 61 | 10:1 |
| 8 | **6** | **10b** | **24** | $Et_2O$ | 39 | 1:4.5 |



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oxyfucose as glycosyl donor and TMSOTf as promotor,[8] whereas it was obtained in $LiClO_4$/diethyl ether in only 49% yield. However in the case of the phosphite donor at α/β ratio was only 2:1, whereas in $LiClO_4$/diethyl ether it was significantly higher (8.1:1).

MPs were recorded on a Büchi 530 melting point apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR were measured on a Bruker AC-250, a Bruker AM-400 or a Bruker DRX-500 spectrometer. Chemical shifts are expressed in ppm downfield relative to TMS as an internal standard. Specific optical rotation values were determined on a Perkin Elmer polarimeter 241. Mass spectra were obtained with a Finnigan MAT 90 spectrometer or a PerSeptive Biosystems Voyager™ spectrometer. Elemental analyses were performed on an Elementar CHN-Rapid Analyzer. For thin-layer chromatography (TLC) Macherey-Nagel silica gel ALUGRAM® SIL G/UV254 layers were used. Flash chromatography was performed with Baker silica gel (40–60μm). $LiPF_6$ and $LiBF_4$ were obtained from Aldrich and Fluka as >98% pure solids. $LiClO_4$ (Acros), $Mg(ClO_4)_2$ (Fluka), $Ba(ClO_4)_2$ (Merck) and $LiN(CF_3SO_2)_2$ (3M-company) were dried extensively in vacuo prior to use. The carbohydrates **3**,[8b] **7a**,[5j,8b] **8a**,[25] **9**,[26] **12**[27] and 3,4,6-tri-*O*-benzyl-2-deoxy-α/β-D-glucopyranose[13] were prepared according to literature procedures.

### Glycosyl Donors

#### 3,4,6-Tri-*O*-benzyl-2-deoxy-α/β-D-glucopyranosyl Trichloroacetimidates (1) and (2)

These compounds were prepared by analogy to the procedures described by R. R. Schmidt et al.[14] and used without further purification.

#### 3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl Trichloroacetimidate (2)

Pale yellow oil; yield quantitative; anomeric ratio α:β = 1:8; $R_f$:0.24 (EtOAc/hexane 1/2). $C_{29}H_{30}NCl_3O_5$.

$^1H$ NMR (250 MHz, $CDCl_3$): δ = 1.90 (q, $J_{1,2} = J_{2,2'} = J_{2,3} = 10.9$ Hz, 1H, 2-H), 2.53 (ddd, $J_{2',3} = J_{2',1} = 2.4$ Hz, $J_{2,2'} = 10.3$ Hz, 1H, 2'-H), 3.63–3.81 (m, 5H, 3-H, 6-H), 4.51–4.72 (m, 5H, OC$H_2$Ph), 4.87 (d, $J_{gem} = 10.8$ Hz, 1H, OC$H_2$Ph), 5.86 (dd, $J_{2',1} = 2.2$ Hz, $J_{1,2} = 9.2$ Hz, 1H, 1-H), 7.19–7.32 (m, 15H, Ph-*H*), 8.56 (s, 1H, NH).

$^{13}C$ NMR (62.5 MHz, $CDCl_3$): δ = 34.27 (1C, $CH_2$, C-2), 68.70 (1C, $CH_2$, C-6), 71.43, 73.28, 74.63 (3C, $CH_2$, O*C*$H_2$Ph), 75.91, 76.49–77.50, 78.15 (3C, CH, C-3, C-4, C-5), 96.10 (1C, CH, C-1), 127.57–128.92 (15C, CH, Ph-*C*H), 138.03–160.88 (5C, $C_{ipso}$).

#### 3,4,6-Tri-*O*-benzyl-2-deoxy-α-D-glucopyranosyl Trichloroacetimidate (1)

Pale yellow oil; yield quantitative; anomeric ratio = 25:1; $R_f$:0.24 (EtOAc/hexane 1/2). $C_{29}H_{30}NCl_3O_5$.

$^1H$ NMR(500 MHz, $CDCl_3$): δ = 1.85 (ddd, $J_{1,2} = 3.2$ Hz, $J_{2,3} = J_{2,2'} = 12.6$ Hz, 1H, 2-H), 2.38 (dd, $J_{2',3} = 4.4$ Hz, $J_{2,2'} = 13.6$ Hz, 1H, 2'-H), 3.54 (t, $J_{4,3} = J_{4,5} = 9.4$ Hz, 1H, 4-H), 3.59–3.65 (m, 2H, 6'-H, 6-H), 3.87–3.90 (m, 1H, 5-H), 3.97–4.02 (m, 1H, 3-H), 4.49–4.52 (m, 3H, OC$H_2$Ph), 4.64–4.68 (m, 2H, OC$H_2$Ph), 4.85 (d, $J_{gem} = 10.9$ Hz, 1H, OC$H_2$Ph), 6.24 (s, 1H, 1-H), 7.12–7.34 (m, 15H, Ph-*H*), 8.52 (s, 1H, NH).

$^{13}C$ NMR(125.7 MHz, $CDCl_3$): δ = 34.03 (1C, $CH_2$, C-2), 68.23 (1C, $CH_2$, C-6), 72.03 (1C, $CH_2$, O*C*$H_2$Ph), 73.28 (1C, CH, C-5), 73.35, 75.11 (2C, $CH_2$, O*C*$H_2$Ph), 76.20 (1C, CH, C-3), 77.37 (1C, CH, C-4), 96.08 (1C, CH, C-1), 96.49 (1C, $C_{ipso}$), 127.59–128.46 (15C, CH, Ph-*C*H), 137.17–137.96 (4C, $C_{ipso}$).

### Glycosyl Fluorides 4, 5 and 6; General Procedure

To a solution of 3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranose, 3,4-di-*O*-benzyl-2-deoxy-L-fucopyranose or 3,4-di-*O*-benzyl-2,6-dideoxy-D-ribohexopyranose (0.1 mmol) in $CH_2Cl_2$ (0.4 mL) at –78 °C was added rapidly under Ar DAST (30.9 mmol) and the solution was stirred for 20 min. The cooling bath was removed and after 15 min stirring at r.t. TLC indicated completion of the reaction. In the cases of the fluorides **4** and **5** stirring was continued at 0 °C. MeOH (0.1 mL) was added to quench the reaction. The solution was diluted with $CH_2Cl_2$ (50 mL), washed with $H_2O$, dried ($Na_2SO_4$) and concentrated in vacuo. The fluorides were used without further purification.

#### 3,4,6-Tri-*O*-benzyl-2-deoxy-α/β-D-glucopyranosyl Fluoride (4)

Yellowish oil; yield quantitative; anomeric ratio α:β = 4:1; $R_f$:0.53 (EtOAc/hexane 1/2).

MS (EI): *m*/*z* = 435 [$M^+$-H]. $C_{27}H_{29}O_4F$.

α-Anomer:

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.75 (dt, $J_{2,3} = J_{2',2} = 13.7$ Hz, $J_{2,F} = 39.8$ Hz, 1H, 2-H), 2.43 (dt, $J_{2',3} = 4.7$ Hz, $J_{2,2'} = J_{2',F} = 13.7$ Hz, 1H, 2'-H), 3.62–3.80 (m, 3H, 4-H, 6'-H, 6-H), 3.92–3.99 (m, 2H, 3-H, 5-H), 4.49–4.64 (m, 5H, OC$H_2$Ph), 4.89 (d, $J_{gem} = 10.8$ Hz, 1H, OC$H_2$Ph), 5.75 (d, $J_{1,F} = 52.0$ Hz, 1H, 1-H), 7.18–7.34 (m, 15H, Ph-*H*).

$^{13}C$ NMR (125.7 MHz, $CDCl_3$): δ = 35.15 (1C, $J_{C2,F} = 26.6$ Hz, $CH_2$, C-2), 68.24 (1C, $CH_2$, C-6), 72.05, 73.48, 75.05 (3C, $CH_2$, O*C*$H_2$Ph), 73.22, 76.39, 77.26 (3C, CH, C-3, C-4, C-5), 106.93 (1C, $J_{C1,F} = 216.4$ Hz, CH, C-1), 127.65–128.43 (15C, CH, Ph-*C*H), 137.89, 138.26, 138.28 (3C, $C_{ipso}$).

Characteristic signals of the β-anomer:

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 5.38 (dd, $J_{1,2} = 6.8$ Hz, $J_{1,F} = 52.0$ Hz, 1H, 1-H).

$^{13}C$ NMR (125.7 MHz, $CDCl_3$): δ = 34.79 (1C, $J_{C2,F} = 21.5$ Hz, $CH_2$, C-2), 106.62 (1C, $J_{C1,F} = 211.7$ Hz, CH, C-1).

#### 3,4-Di-*O*-benzyl-2-deoxy-α/β-L-fucopyranosyl Fluoride (5)

Pale red oil; quantitative yield; anomeric ratio α/β = 13.6:1; $R_f$:0.66 (EtOAc/hexane 1/2).

MS (EI): *m*/*z* = 330 [$M^+$]. $C_{20}H_{23}O_3F$.

α-Anomer:

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, $J_{5,6} = 6.5$ Hz, 3H, 6-C$H_3$), 2.15–2.19 (m, 1H, 2'-H), 2.25–2.30 (m, 1H, 2-H), 3.67 (s, 1H, 4-H), 3.91–3.95 (m, 1H, 3-H), 4.02 (q, $J_{5,6} = 6.5$ Hz, 1H, 5-H), 4.59–4.62 (m, 2H, OC$H_2$Ph), 4.69 (d, $J_{gem} = 11.6$ Hz, 1H, OC$H_2$Ph), 4.98 (d, $J_{gem} = 11.6$ Hz, 1H, OC$H_2$Ph), 5.77 (d, $J_{1,F} = 52.7$ Hz, 1H, 1-H), 7.25–7.39 (m, 10H, Ph-*H*).

$^{13}C$ NMR (125.7 MHz, $CDCl_3$): δ = 17.15 (1C, $CH_3$, C-6), 30.30 (d, $J_{C2,F} = 26.0$ Hz, 1C, C-2), 69.58 (1C, CH, C-5), 70.50 (1C, $CH_2$, O*C*$H_2$Ph), 74.09 (1C, CH, C-3), 74.44 (1C, $CH_2$, O*C*$H_2$Ph), 75.08 (1C, CH, C-4), 107.77 (d, $J_{C1,F} = 213.8$ Hz, 1C, C-1), 127.33–128.76 (10C, CH, Ph-*C*H), 138.21, 138.53 (2C, $C_{ipso}$).

Characteristic signals for the β-anomer:

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.29 (d, $J_{5,6} = 6.4$ Hz, 3H, 6-C$H_3$), 5.25 (ddd, $J_{1,F} = 52.7$ Hz, 1H, 1-H).

#### 3,4-Di-*O*-benzyl-2,6-dideoxy-α/β-D-ribohexopyranosyl Fluoride (6)

Pale yellow oil; yield quantitative; anomeric ratio α:β = 1.1:1; $R_f$:0.61 (EtOAc/hexane 1/2).

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, $J_{5,6} = 6.9$ Hz, 6H, 6α-C$H_3$, 6β-C$H_3$), 1.65 (ddt, $J_{1,2} = J_{2,3} = 3.4$ Hz, $J_{2',2} = 15.4$ Hz, $J_{2,F} = 39.6$ Hz, 1H, 2α-H), 1.83–1.89 (m, 1H, 2β-H), 2.30–2.39 (m, 1H, 2'β-H), 2.44 (ddd, $J_{2',3} = 3.1$ Hz, $J_{2',2} = 15.4$ Hz, $J_{2',F} = 4.9$ Hz, 1H, 2'α-H), 3.16 (dd, $J_{3,4} = 2.8$ Hz, $J_{4,5} = 9.6$ Hz, 1H, 4α-H), 3.40 (dd, $J_{3,4} = 2.6$



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Hz, $J_{4,5}$ = 5.8 Hz, 1H, 4β-H), 3.95 (q, $J_{2',3} = J_{2,3} = J_{3,4}$ = 2.9 Hz, 1H, 3α-H), 4.04 (q, $J_{2',3} = J_{2,3} = J_{3,4}$ = 3.8 Hz, 1H, 3β-H), 4.21–4.26 (m, 1H, 5β-H), 4.43 (d, $J_{gem}$ = 11.9 Hz, 1H, OC*H*$_2$Ph), 4.49–4.52 (m, 1H, 5α-H), 4.55–4.62 (m, 5H, OC*H*$_2$Ph), 4.66 (d, $J_{gem}$ = 12.0 Hz, 1H, OC*H*$_2$Ph), 4.77 (d, $J_{gem}$ = 12.4 Hz, 1H, OC*H*$_2$Ph), 5.57 (dd, $J_{1,2}$ = 3.2 Hz, $J_{1,F}$ = 52.5 Hz, 1H, 1α-H), 5.73 (ddd, $J_{1,2'}$ = 2.6 Hz, $J_{1,2}$ = 5.6 Hz, $J_{1,F}$ = 53.6 Hz, 1H, 1β-H), 7.25–7.40 (m, 20H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 17.98 (1C, $CH_3$, C-6α), 19.30 (1C, $CH_3$, C-6β), 32.02 (d, $J_{C2,F}$ = 25.6 Hz, 1C, $CH_2$, C-2α), 33.05 (d, $J_{C2,F}$ = 23.5 Hz, 1C, $CH_2$, C-2β), 65.30 (1C, CH, C-5α), 68.36 (1C, CH, C-3α), 69.85 (d, $J_{C3,F}$ = 6.1 Hz, 1C, CH, C-3β), 70.81, 70.83, 71.25, 71.88 (4C, $CH_2$, O*C*H$_2$Ph), 71.88 (1C, CH, C-5β), 78.01 (1C, CH, C-4β), 79.44 (1C, CH, C-4α), 105.3 (d, $J_{C1,F}$ = 220.8 Hz, 1C, CH, C-1α), 107.68 (d, $J_{C1,F}$ = 209.1 Hz, 1C, CH, C-1β), 127.55–128.43 (20C, CH, Ph-*C*H), 137.91, 138.06, 138.18, 138.42 (4C, $C_{ipso}$).

MS (EI): *m*/*z* = 330 [M$^+$]. $C_{20}H_{23}O_3F$.

### Allyl Glycosides 27 and 28; General Procedure

1,3,4-Tri-*O*-acetyl-2-deoxy-α/β-L-fucopyranose[20] (**25**) or 1,3,4-tri-*O*-acetyl-2-deoxy-α/β-D-ribohexopyranose[19] (**26**) were dissolved in allyl alcohol (4.1 mL) and sat. HCl in $Et_2O$ (0.7 mL) was added at 0 °C under Ar. After 2 h stirring $K_2CO_3$ was added, the mixture was filtered through Celite and the allyl alcohol was removed in vacuo. In the case of digitoxose a few drops of $Et_3N$ had to be added before removal of the alcohol. The crude product was purified by flash chromatography using hexane/$Et_2O$ 6/1 as eluent.

### Allyl 3,4-Di-*O*-acetyl-2-deoxyα/β-L-fucopyranoside (27)

Yield 76%; anomeric ratio α:β = 1.6:1.

$C_{13}H_{20}O_6$ calcd C 57.34, H 7.40; found C 57.57, H 7.06.

α-Anomer: colorless oil; $R_f$:0.11 (hexane/$Et_2O$ 3/1); $[\alpha]^{22}_D$ = –145.5 (*c* = 0.8 in MeOH).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.13 (d, $J_{5,6}$ = 6.6 Hz, 3H, 6-C*H*$_3$), 1.86 (dd, $J_{2',3}$ = 5.1 Hz, $J_{2',2}$ = 12.6 Hz, 1H, 2'-H), 1.98 (s, 3H, C(O)C*H*$_3$), 2.05 (ddd, $J_{2,1}$ = 3.7 Hz, $J_{2,3} = J_{2',2}$ = 12.5 Hz, 1H, 2-H), 2.16 (s, 3H, C(O)C*H*$_3$), 3.97 (ddt, $^4J$ = 1.3 Hz, $J_{vic}$ = 6.0 Hz, $J_{gem}$ = 13.0 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.08 (q, $J_{5,6}$ = 6.6 Hz, 1H, 5-H), 4.14 (ddt, $^4J$ = 1.4 Hz, $J_{vic}$ = 5.2 Hz, $J_{gem}$ = 13.0 Hz, 1H, OC*H*$_2$CH=CH$_2$), 5.02 (d, $J_{1,2}$ = 3.3 Hz, 1H, 1-H), 5.18–5.20 (m, 2H, 4-H, OCH$_2$CH=C*H*$_2$), 5.27–5.33 (m, 2H, 3-H, OCH$_2$CH=C*H*$_2$), 5.86–5.94 (m, 1H, OCH$_2$C*H*=CH$_2$).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 16.43 (1C, $CH_3$, C-6), 20.67 (1C, C(O)*C*H$_3$), 20.84 (1C, C(O)*C*H$_3$), 29.82 (1C, $CH_2$, C-2), 64.63 (1C, CH, C-5), 66.74 (1C, CH, C-3), 69.97 (1C, $CH_2$, O*C*H$_2$CH=CH$_2$), 69.78 (1C, CH, C-4), 96.57 (1C, CH, C-1), 117.11 (1C, $CH_2$, OCH$_2$CH=*C*H$_2$), 133.95 (1C, CH, OCH$_2$*C*H=CH$_2$), 169.99 (1C, $C_{ipso}$), 170.63 (1C, $C_{ipso}$).

β-Anomer: colorless oil; $R_f$ = 0.07 (hexane/$Et_2O$ 3/1); $[\alpha]^{22}_D$ = –9.9 (*c* = 0.6 in MeOH).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.22 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6-C*H*$_3$), 1.98–1.91 (m, 2H, 2'-H, 2-H), 2.00 (s, 3H, C(O)C*H*$_3$), 2.16 (s, 3H, C(O)C*H*$_3$), 3.68 (dq, $J_{4,5}$ = 0.9 Hz, $J_{5,6}$ = 6.5 Hz, 1H, 5-H), 4.09 (ddt, $^4J$ = 1.3 Hz, $J_{vic}$ = 6.4 Hz, $J_{gem}$ = 12.3 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.40 (ddt, $^4J$ = 1.5 Hz, $J_{vic}$ = 5.1 Hz, $J_{gem}$ = 12.8 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.57 (dd, $J_{1,2'}$ = 2.8 Hz, $J_{1,2}$ = 9.2 Hz, 1H, 1-H), 4.97–5.00 (m, 1H, 3-H), 5.10 (d, $J_{3,4}$ = 3.1 Hz, 1H, 4-H) 5.19 (ddt, $^4J$ = 1.3 Hz, $J_{gem}$ = 1.4 Hz, $J_{cis}$ = 10.4 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.28 (ddt, $^4J = J_{gem}$ = 1.6 Hz, $J_{trans}$ = 18.0 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.89–5.96 (m, 1H, OCH$_2$C*H*=CH$_2$).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 16.39 (1C, $CH_3$, C-6), 20.67 (1C, C(O)*C*H$_3$), 20.76 (1C, C(O)*C*H$_3$), 31.63 (1C, $CH_2$, C-2), 68.61 (1C, CH, C-4), 68.94 (1C, CH, C-3), 69.12 (1C, CH, C-5), 69.67 (1C, $CH_2$, O*C*H$_2$CH=CH$_2$), 98.62 (1C, CH, C-1), 117.47 (1C, $CH_2$, OCH$_2$CH=*C*H$_2$), 133.84 (1C, CH, OCH$_2$*C*H=CH$_2$), 170.01 (1C, $C_{ipso}$), 170.68 (1C, $C_{ipso}$).

### Allyl 3,4-Di-*O*-acetyl-2,6-dideoxy-α/β-D-ribohexopyranoside (28)

This compound was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/8. Yield 81%; anomeric ratio α:β = 1.1:1. $C_{13}H_{20}O_6$•0.25 $H_2O$ calcd C 56.41, H 7.46; found C 56.68, H 6.93.

β-Anomer: white solid; mp 24 °C; $R_f$:0.60 (EtOAc/hexane 1/1); $[\alpha]^{21}_D$ = +4.2 (*c* = 1.1 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.23 (d, $J_{5,6}$ = 6.3 Hz, 3H, 6-C*H*$_3$), 1.89 (ddd, $J_{2,3}$ = 3.0 Hz, $J_{2,1}$ = 9.2 Hz, $J_{2',2}$ = 14.2 Hz, 1H, 2-H), 2.01 (s, 3H, C(O)C*H*$_3$), 2.06 (ddd, $J_{2',1}$ = 2.3 Hz, $J_{2',3}$ = 4.2 Hz, $J_{2',2}$ = 14.2 Hz, 1H, 2'-H), 2.10 (s, 3H, C(O)C*H*$_3$), 3.91–3.97 (m, 1H, 5-H), 4.06 (ddt, $^4J$ = 1.2 Hz, $J_{vic}$ = 6.2 Hz, $J_{gem}$ = 12.7 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.37 (ddt, $^4J$ = 1.4 Hz, $J_{vic}$ = 5.2 Hz, $J_{gem}$ = 12.7 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.60 (dd, $J_{3,4}$ = 3.1 Hz, $J_{4,5}$ = 9.5 Hz, 1H, 4-H), 4.84 (dd, $J_{1,2'}$ = 2.2 Hz, $J_{1,2}$ = 9.2 Hz 1H, 1-H), 5.19 (dd, $J_{gem}$ = 1.4 Hz, $J_{cis}$ = 10.4 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.29 (ddt, $J_{gem}$ = 1.6 Hz, $J_{trans}$ = 17.2 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.45 (ddd, $J_{3,4} = J_{3,2'}$ = 3.2 Hz, $J_{3,2}$ = 3.7 Hz 1H, 3-H), 5.88–5.96 (m, 1H, OCH$_2$C*H*=CH$_2$).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 17.81 (1C, $CH_3$, C-6), 20.68 (1C, C(O)*C*H$_3$), 20.88 (1C, C(O)*C*H$_3$), 35.45 (1C, $CH_2$, C-2), 67.21 (1C, CH, C-5), 68.05 (1C, CH, C-3), 69.57 (1C, $CH_2$, O*C*H$_2$CH=CH$_2$), 72.5 (1C, CH, C-4), 97.07 (1C, CH, C-1), 117.25 (1C, $CH_2$, OCH$_2$CH=*C*H$_2$), 133.97 (1C, CH, OCH$_2$*C*H=CH$_2$), 169.85 (1C, $C_{ipso}$), 169.88 (1C, $C_{ipso}$).

α-Anomer: colorless oil; $R_f$:0.41 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = +187.2 (*c* = 0.5; in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6-C*H*$_3$), 1.99–2.10 (m, 1H, 2-H), 2.04 (s, 3H, C(O)C*H*$_3$), 2.09 (s, 3H, C(O)C*H*$_3$), 2.17 (ddd, $J_{2',1}$ = 1.4 Hz, $J_{2',3}$ = 3.7 Hz, $J_{2',2}$ = 15.05 Hz, 1H, 2'-H), 3.94 (ddt, $^4J$ = 1.4 Hz, $J_{vic}$ = 5.7 Hz, $J_{gem}$ = 13.4 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.19–4.28 (m, 2H, 5-H, OC*H*$_2$CH=CH$_2$), 4.65 (dd, $J_{3,4}$ = 3.2 Hz, $J_{4,5}$ = 9.5 Hz, 1H, 4-H), 4.85 (d, $J_{1,2}$ = 3.6 Hz, 1H, 1-H), 5.17 (dd, $J_{gem}$ = 1.7 Hz, $J_{cis}$ = 10.5 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.26 (q, $J_{3,4} = J_{3,2'} = J_{3,2}$ = 3.5 Hz, 1H, 3-H), 5.33 (ddt, $^4J = J_{gem}$ = 1.7 Hz, $J_{trans}$ = 17.1 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.88–5.96 (m, 1H, OCH$_2$C*H*=CH$_2$).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 17.31 (1C, $CH_3$, C-6), 20.80 (1C, C(O)*C*H$_3$), 21.15 (1C, C(O)*C*H$_3$), 33.18 (1C, $CH_2$, C-2), 62.07 (1C, CH, C-5), 66.42 (1C, CH, C-3), 67.86 (1C, $CH_2$, O*C*H$_2$CH=CH$_2$), 72.32 (1C, CH, C-4), 95.01 (1C, CH, C-1), 116.17 (1C, $CH_2$, OCH$_2$CH=*C*H$_2$), 134.37 (1C, CH, OCH$_2$*C*H=CH$_2$), 169.98 (1C, $C_{ipso}$), 170.68 (1C, $C_{ipso}$).

### Deacetylation of 27 and 28; General Procedure

To a solution of allyl 3,4-di-*O*-acetyl-2-deoxy-α-L-fucopyranoside (**27a**) allyl 3,4-di-*O*-acetyl-2-deoxy-β-L-fucopyranoside **(27b)** allyl 3,4-di-*O*-acetyl-2,6-dideoxy-α-D-ribo-hexopyranoside (**28a**) or allyl 3,4-di-*O*-acetyl-2,6-dideoxy-β-D-ribohexopyranoside (**28b**) in MeOH (1.4 mL) was added 1 M NaOCH$_3$/MeOH (1.4 mL) under Ar at r.t. After stirring for 12 h the solution was neutralized with Amberlite 120 H$^+$, filtered and concentrated in vacuo. In the case of **28a** or **28b** the reaction went to completion within 1 h.

### Allyl 2-Deoxy-α-L-fucopyranoside (29a)

Colorless oil; quantitative yield; $R_f$ = 0.13 (EtOAc/hexane 2/1); $[\alpha]^{23}_D$ = –176.0 (*c* = 0.6 in MeOH).

$^1$H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, $J_{5,6}$ = 6.6 Hz, 3H, 6-C*H*$_3$), 1.75 (dd, $J_{2',3}$ = 5.0 Hz, $J_{2',2}$ = 10.2 Hz, 1H, 2'-H), 1.91 (ddd, $J_{2,1}$ = 3.7 Hz, $J_{2,3} = J_{2',2}$ = 12.4 Hz, 1H, 2-H), 3.56 (d, $J_{3,4}$ = 2.1 Hz, 1H, 4-H), 3.85 (q, $J_{5,6}$ = 6.5 Hz, 1H, 5-H), 3.91–3.99 (m, 2H, 3-H, OC*H*$_2$CH=CH$_2$), 4.10 (dd, $J_{vic}$ = 5.1 Hz, $J_{gem}$ = 13.2 Hz, 1H, OC*H*$_2$CH=CH$_2$), 4.89 (d, $J_{1,2}$ = 3.1 Hz, 1H, 1-H), 5.14 (dd, $^4J = J_{gem}$ = 1.2 Hz, $J_{cis}$ = 10.4 Hz, 1H, OCH$_2$CH=C*H*$_2$), 5.26 (dd,



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$^4J = J_{gem}$ = 1.6 Hz, $J_{trans}$ = 17.4 Hz, 1H, $OCH_2CH=CH_2$), 5.87–5.96 (m, 1H, $OCH_2CH=CH_2$).

$^{13}C$ NMR (100.6 MHz, $CDCl_3$): δ = 17.16 (1C, $CH_3$, C-6), 33.02 (1C, $CH_2$, C-2), 66.58, 67.28, 71.92 (3C, CH, C-3, C-4, C-5), 68.57 (1C, $CH_2$, $OCH_2CH=CH_2$), 97.99 (1C, CH, C-1), 116.77 (1C, $CH_2$, $OCH_2CH=CH_2$), 135.68 (1C, CH, $OCH_2CH=CH_2$).
$C_9H_{16}O_4 \bullet 0.25\ H_2O$ calcd C 56.09, H 8.63; found C 56.31, H 8.47.

**Allyl 2-Deoxy-β-L-fucopyranoside (29b)**

Colorless oil; quantitative yield; $R_f$ = 0.13 (EtOAc/hexane 2/1); $[\alpha]^{23}_D$ = +41.8 (*c* = 0.5 in MeOH).

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.27 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6-$CH_3$), 1.75–1.70 (m, 1H, 2'-H), 1.82–1.89 (m, 1H, 2-H), 3.47–3.52 (m, 2H, 4-H, 5-H), 3.68–3.73 (m, 1H, 3-H), 4.05 (dd, $J_{vic}$ = 5.9 Hz, $J_{gem}$ = 13.0 Hz, 1H, $OCH_2CH=CH_2$), 4.31 (dd, $J_{vic}$ = 5.1 Hz, $J_{gem}$ = 13.0 Hz, 1H, $OCH_2CH=CH_2$), 4.48 (dd, $J_{1,2'}$ = 2.2 Hz, $J_{1,2}$ = 9.7 Hz, 1H, 1-H), 5.14 (dd, $^4J = J_{gem}$ = 1.5 Hz, $J_{cis}$ = 10.4 Hz, 1H, $OCH_2CH=CH_2$), 5.26 (dd, $^4J = J_{gem}$ = 1.7 Hz, $J_{trans}$ = 17.3 Hz, 1H, $OCH_2CH=CH_2$), 5.87–5.97 (m, 1H, $OCH_2CH=CH_2$).

$^{13}C$ NMR (100.6 MHz, $CDCl_3$): δ = 16.93 (1C, $CH_3$, C-6), 35.05 (1C, $CH_2$, C-2), 69.67 (1C, CH, C-3), 70.19 (1C, $CH_2$, $OCH_2CH=CH_2$), 71.01 (1C, CH, C-4), 71.68 (1C, CH, C-5), 100.41 (1C, CH, C-1), 116.85 (1C, $CH_2$, $OCH_2CH=CH_2$), 135.61 (1C, CH, $OCH_2CH=CH_2$). $C_9H_{16}O_4 \bullet 0.25\ H_2O$ calcd C 56.09, H 8.63; found C 56.31, H 8.47.

**Allyl 2,6-Dideoxy-α/β-D-ribohexopyranoside (30)**
This compound used directly in the next protection step without further characterization.

β-Anomer: quantitative yield; colorless oil; $R_f$:0.16 (EtOAc/hexane 1/1), $[\alpha]^{21}_D$ = –39.2 (*c* = 0.7 in MeOH).

α-Anomer: yield 71%; colorless oil; $R_f$:0.11 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = +153.6 (*c* = 0.6 in methanol).

**Protection of 29 and 30 as Benzyl Ethers; General Procedure**
A solution of allyl 2-deoxy-α-L-fucopyranoside (**29a**), allyl 2-deoxy-β-L-fucopyranoside (**29b**), allyl-2,6-dideoxy-α-D-ribohexopyranoside (**30a**), or allyl-2,6-dideoxy-β-D-ribohexopyranoside (**30b**) in DMF (68 mL) was treated in three portions with NaH (25.2 mmol) and stirred for 30 min at 0 °C. A solution of benzyl chloride (48.6 mmol) in DMF (12 mL) was added within 1 h. After stirring for 12 h at r.t. MeOH (2 mL) was added at 0 °C. In the case of **30a** or **30b** the reaction was complete within 1.5 h at 0 °C. After the solvent was removed in vacuo the residue was taken up in $CH_2Cl_2$ (50 mL) and the solution was extracted with water. The organic phase was dried ($MgSO_4$), the solvent was removed in vacuo and the product was isolated by flash chromatography using EtOAc/hexane 1/8 as eluent.

**Allyl 3,4-Di-*O*-benzyl-2-deoxy-α-L-fucopyranoside (31a)**
Colorless oil; yield 80%; $R_f$:0.57 (EtOAc/hexane 1/2),$[\alpha]^{21}_D$ = –80.0 (*c* = 0.6 in $CHCl_3$).

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6-$CH_3$), 2.00 (dd, $J_{2',3}$ = 4.6 Hz, $J_{2',2}$ = 12.6 Hz, 1H, 2'-H), 2.20 (ddd, $J_{2,1}$ = 3.7 Hz, $J_{2,3} = J_{2',2}$ = 12.3 Hz, 1H, 2-H), 3.60 (s, 1H, 4-H), 3.81 (q, $J_{5,6}$ = 6.5 Hz, 1H, 5-H), 3.90–3.96 (m, 2H, 3-H, $OCH_2CH=CH_2$), 4.09 (dd, $J_{vic}$ = 5.2 Hz, $J_{gem}$ = 13.1 Hz, 1H, $OCH_2CH=CH_2$), 4.56–4.62 (m, 2H, $OCH_2Ph$), 4.68 (d, $J_{gem}$ = 11.7 Hz, 1H, $OCH_2Ph$), 4.96 (d, $J_{gem}$ = 11.7 Hz, 1H, $OCH_2Ph$), 4.99 (d, $J_{1,2}$ = 3.5 Hz, 1H, 1-H), 5.14 (d, $J_{cis}$ = 10.4 Hz, 1H, $OCH_2CH=CH_2$), 5.25 (dd, $^4J = J_{gem}$ = 1.5 Hz, $J_{trans}$ = 17.2 Hz, 1H, $OCH_2CH=CH_2$), 5.85–5.92 (m, 1H, $OCH_2CH=CH_2$), 7.22–7.39 (m, 10H, Ph-*H*).

$^{13}C$ NMR (125.7 MHz, $CDCl_3$): δ = 17.27 (1C, $CH_3$, C-6), 30.61 (1C, $CH_2$, C-2), 66.72 (1C, CH, C-5), 67.77 (1C, $CH_2$, $OCH_2CH=CH_2$), 70.36, 74.31 (2C, $CH_2$, $OCH_2Ph$), 75.34 (1C, CH, C-3), 75.76 (1C, CH, C-4), 97.12 (1C, CH, C-1), 116.74 (1C, $CH_2$, $OCH_2CH=CH_2$), 127.22–128.36 (10C, CH, Ph-*C*H), 134.46 (1C, CH, $OCH_2CH=CH_2$), 138.64 (1C, $C_{ipso}$), 138.89 (1C, $C_{ipso}$).

$C_{23}H_{28}O_4$ calcd C 74.97, H 7.66; found C 75.11, H 7.12.

**Allyl 3,4-Di-*O*-benzyl-2-deoxy-β-L-fucopyranoside (31b)**
Colorless oil; yield 71%; $R_f$:0.54 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = +49.0 (*c* = 0.6 in $CHCl_3$).

$^1H$ NMR(500 MHz, $CDCl_3$): δ = 1.21 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6-$CH_3$), 2.06–2.10 (m, 2H, 2'-H, 2-H), 3.35 (q, $J_{5,6}$ = 6.4 Hz, 1H, 5-H), 3.50 (s, 1H, 4-H), 3.51–3.55 (m, 1H, 3-H), 4.02 (dd, $J_{vic}$ = 6.4 Hz, $J_{gem}$ = 12.8 Hz, 1H, $OCH_2CH=CH_2$), 4.36 (ddt, $^4J$ = 1.4 Hz, $J_{vic}$ = 5.0 Hz, $J_{gem}$ = 12.8 Hz, 1H, $OCH_2CH=CH_2$), 4.41 (dd, $J_{1,2'}$ = 3.5 Hz, $J_{1,2}$ = 8.6 Hz, 1H, 1-H), 4.58 (q, $J_{gem}$ = 12.2 Hz, 2H, $OCH_2Ph$), 4.71 (d, $J_{gem}$ = 11.9 Hz, 1H, $OCH_2Ph$), 4.96 (d, $J_{gem}$ = 11.9 Hz, 1H, $OCH_2Ph$), 5.15 (dd, $J_{gem}$ = 1.3 Hz, $J_{cis}$ = 10.4 Hz, 1H, $OCH_2CH=CH_2$), 5.26 (ddt, $^4J$ = 1.5 Hz, $J_{gem}$ = 3.1 Hz, $J_{trans}$ = 17.3 Hz, 1H, $OCH_2CH=CH_2$), 5.87–5.95 (m, 1H, $OCH_2CH=CH_2$), 7.23–7.40 (m, 10H, Ph-*H*).

$^{13}C$ NMR(125.7 MHz, $CDCl_3$): δ = 17.22 (1C, $CH_3$, C-6), 32.31 (1C, $CH_2$, C-2), 69.28 (1C, $CH_2$, $OCH_2CH=CH_2$), 70.19 (1C, $CH_2$, $OCH_2Ph$), 70.79 (1C, CH, C-5), 74.20 (1C, $CH_2$, $OCH_2Ph$), 74.34 (1C, CH, C-4), 77.91 (1C, CH, C-3), 99.13 (1C, CH, C-1), 117.13 (1C, $CH_2$, $OCH_2CH=CH_2$), 127.28–128.48 (10C, CH, Ph-*C*H), 134.41 (1C, CH, $OCH_2CH=CH_2$), 138.39 (1C, $C_{ipso}$), 138.86 (1C, $C_{ipso}$).

$C_{23}H_{28}O_4$ calcd C 74.97, H 7.66; found C 75.11, H 7.12.

**Allyl 3,4-Di-*O*-benzyl-2,6-dideoxy-α/β-D-ribohexopyranoside (32)**
The crude product was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/8.

β-Anomer: yield 89%; colorless oil; $R_f$:0.23 (EtOAc/hexane 1/8); $[\alpha]^{22}_D$ = +53.7 (*c* = 0.5 in $CHCl_3$).

$^1H$ NMR (400 MHz, $CDCl_3$): δ = 1.31 (d, $J_{5,6}$ = 6.3 Hz, 3H, 6-$CH_3$), 1.56 (ddd, $J_{2,3}$ = 2.5 Hz, $J_{2,1}$ = 9.6 Hz, $J_{2',2}$ = 13.7 Hz, 1H, 2-H), 2.21 (ddd, $J_{1,2'}$ = 2.1 Hz, $J_{2',3}$ = 3.8 Hz, $J_{2',2}$ = 13.8 Hz, 1H, 2'-H), 3.11 (dd, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 9.2 Hz, 1H, 4-H), 3.95 (q, $J_{3,2} = J_{3,2'} = J_{3,4}$ = 2.9 Hz, 1H, 3-H), 3.98–4.06 (m, 2H, 5-H, $OCH_2CH=CH_2$), 4.31–4.34 (m, 1H, $OCH_2CH=CH_2$), 4.38 (d, $J_{gem}$ = 11.8 Hz, 1H, $OCH_2Ph$), 4.52 (d, $J_{gem}$ = 11.7 Hz, 1H, $OCH_2Ph$), 4.59–4.67 (2d, $J_{gem}$ = 12.2 Hz, 2H, $OCH_2Ph$), 4.87 (dd, $J_{1,2'}$ = 1.9 Hz, $J_{1,2}$ = 9.5 Hz, 1H, 1-H), 5.14 (dd, $^4J = J_{gem}$ = 1.4 Hz, $J_{cis}$ = 10.9 Hz, 1H, $OCH_2CH=CH_2$), 5.25 (ddt, $^4J = J_{gem}$ = 1.6 Hz, $J_{trans}$ = 17.2 Hz, 1H, $OCH_2CH=CH_2$), 5.58–5.95 (m, 1H, $OCH_2CH=CH_2$), 7.22–7.35 (m, 10H, Ph-*H*).

$^{13}C$ NMR (125.7 MHz, $CDCl_3$): δ = 18.55 (1C, $CH_3$, C-6), 35.37 (1C, $CH_2$, C-2), 69.15 (1C, CH, C-5), 69.71 (1C, $CH_2$, $OCH_2CH=CH_2$), 71.13 (1C, CH, C-3), 71.39, 71.62 (2C, $CH_2$, $OCH_2Ph$), 80.93 (1C, CH, C-4), 97.34 (1C, CH, C-1), 117.15 (1C, $CH_2$, $OCH_2CH=CH_2$), 127.69–128.44 (10C, CH, Ph-*C*H), 134.48 (1C, CH, $OCH_2CH=CH_2$), 138.15 (1C, $C_{ipso}$), 138.69 (1C, $C_{ipso}$).

$C_{23}H_{28}O_4$ calcd C 74.97, H 7.66; found C 74.92, H 7.63.

α-Anomer: yield 77%; colorless oil; $R_f$:0.31 (EtOAc/hexane 1/4); $[\alpha]^{20}_D$ = +162.3 (*c* = 0.5 in $CHCl_3$).

$^1H$ NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6-$CH_3$), 1.66 (dt, $J_{2,3} = J_{2,1}$ = 3.5 Hz, $J_{2',2}$ = 14.8 Hz, 1H, 2-H), 2.32 (ddd, $J_{1,2'}$ = 1.3 Hz, $J_{2',3}$ = 3.6 Hz, $J_{2',2}$ = 14.8 Hz, 1H, 2'-H), 3.14 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 9.0 Hz, 1H, 4-H), 3.90–3.95 (m, 2H, 3-H, $OCH_2CH=CH_2$), 4.20–4.24 (m, 1H, $OCH_2CH=CH_2$), 4.30–4.35 (m, 1H, 5-H), 4.40 (d, $J_{gem}$ = 12.0 Hz, 1H, $OCH_2Ph$), 4.54–4.60 (2d, $J_{gem}$ = 12.0 Hz, 2H, $OCH_2Ph$), 4.77–4.81 (m, 2H, 1-H, $OCH_2Ph$), 5.13 (dd, $J_{gem}$ = 1.5 Hz, $J_{cis}$ = 8.2 Hz, 1H, $OCH_2CH=CH_2$), 5.31 (dd, $J_{gem}$ = 1.7 Hz, $J_{trans}$ = 17.2 Hz, 1H, $OCH_2CH=CH_2$), 5.88–5.96 (m, 1H, $OCH_2CH=CH_2$), 7.23–7.41 (m, 10H, Ph-*H*).

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$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 18.06 (1C, $CH_3$, C-6), 31.67 (1C, $CH_2$, C-2), 63.42 (1C, CH, C-5), 67.83 (1C, $CH_2$, O*C*$H_2$CH=$CH_2$), 68.95 (1C, CH, C-3), 70.11, 70.51 (2C, $CH_2$, O*C*$H_2$Ph), 79.85 (1C, CH, C-4), 95.46 (1C, CH, C-1), 116.14 (1C, $CH_2$, OCH$_2$CH=*C*H$_2$), 127.38–128.28 (10C, CH, Ph-*C*H), 134.71 (1C, CH, OCH$_2$*C*H=CH$_2$), 138.32 (1C, $C_{ipso}$), 138.75 (1C, $C_{ipso}$).

### Isomerization of Allyl Glycosides to Propenyl Glycosides; General Procedure

A suspension of allyl glycoside **31** or **32** (1 mmol), $(PPh_3)_3RhCl$ (0.1 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.3 mmol) in EtOH/$H_2O$ (10/1) (23.3 mL) was stirred for 25 min at 85 °C. The solvent was distilled off in vacuo and the residue was filtered through a short silica gel column with EtOAc/hexane 1/10 as eluent to remove the catalyst.

**Prop-1-enyl 3,4-Di-*O*-benzyl-2-deoxy-α-L-fucopyranoside (33a)**

Colorless oil; yield 90%; *E*/*Z*-ratio:1/1.8; $R_f$:0.38 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.15, 1.16 (2d, $J_{5,6}$ = 6.5 Hz, 6H, 6-C*H*$_3$), 1.53 (dd, $^4J$ = 1.5 Hz, $J_{vic}$ = 6.1 Hz, 3H, OCH=CHC*H*$_3$ E), 1.56 (dd, $^4J$ = 1.7 Hz, $J_{vic}$ = 6.0 Hz, 3H, OCH=CHC*H*$_3$ Z), 2.00–2.08 (m, 2H, 2'-H E, 2'-H Z), 2.17–2.24 (m, 2H, 2-H E, 2-H Z), 3.59 (s, 2H, 4-H E, 4-H Z), 3.78–3.83 (m, 2H, 5-H E, 5-H Z), 3.91–3.99 (m, 2H, 3-H E, 3-H Z), 4.45–4.50 (m, 1H, OCH=C*H*CH$_3$ Z), 4.55–4.63 (m, 4H, OC*H*$_2$Ph), 4.67, 4.68, 4.96, 4.98 (4d, $J_{gem}$ = 11.7 Hz, 4H, OC*H*$_2$Ph), 4.99–5.04 (m, 1H, OCH=C*H*CH$_3$ E), 5.16 (d, $J_{1,2}$ = 3.7 Hz, 2H, 1-H E, 1-H Z), 6.13 (dq, $^4J$ = 1.7 Hz, $J_{cis}$ = 6.3 Hz, 1H, OC*H*=CHCH$_3$ Z), 6.19 (dq, $^4J$ = 1.6 Hz, $J_{trans}$ = 12.3 Hz, 1H, OC*H*=CHCH$_3$ E), 7.15–7.38 (m, 20H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 9.19 (1C, $CH_3$, OCH=CH*C*H$_3$ Z), 12.49 (1C, $CH_3$, OCH=CH*C*H$_3$ E), 17.21 (2C, $CH_3$, C-6 E, C-6 Z), 29.96 (1C, $CH_2$, C-2 Z), 30.04 (1C, $CH_2$, C-2 E), 67.30 (1C, CH, C-5 E), 67.45 (1C, CH, C-5 Z), 70.38–74.39 (4C, $CH_2$, O*C*$H_2$Ph), 74.92 (1C, CH, C-3 Z), 75.08 (1C, CH, C-3 E), 75.64 (2C, CH, C-4 Z, C-4 E), 97.68 (1C, CH, C-1 E), 98.06 (1C, CH, C-1 Z), 102.57 (1C, CH, OCH=*C*HCH$_3$ Z), 103.13 (1C, CH, OCH=*C*HCH$_3$ E), 127.21–128.38 (20C, CH, Ph-*C*H), 138.47–138.81 (4C, $C_{ipso}$), 142.11 (1C, CH, O*C*H=CHCH$_3$ Z), 143.28 (1C, CH, O*C*H=CHCH$_3$ E).

$C_{23}H_{28}O_4$.

**Prop-1-enyl 3,4-Di-*O*-benzyl-2-deoxy-β-L-fucopyranoside (33b)**

Colorless oil; yield 76%; *E*/*Z*-ratio:1/1; $R_f$:0.36 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.23, 1.24 (2d, $J_{5,6}$ = 6.5 Hz, 6H, 6-C*H*$_3$), 1.53 (dd, $^4J$ = 1.4 Hz, $J_{vic}$ = 7.6 Hz, 3H, OCH=CHC*H*$_3$ E), 1.59 (dd, $^4J$ = 1.6 Hz, $J_{vic}$ = 6.9 Hz, 3H, OCH=CHC*H*$_3$ Z), 2.05–2.18 (m, 4H, 2'-H E, 2'-H Z, 2-H E, 2-H Z), 3.40 (q, $J_{5,6}$ = 6.4 Hz,, 2H, 5-H E, 5-H Z), 3.50 (s, 2H, 4-H E, 4-H Z), 3.52–3.56 (m, 2H, 3-H E, 3-H Z), 4.44–4.50 (m, 1H, OCH=C*H*CH$_3$ Z), 4.56–4.63 (m, 6H, 2 x OC*H*$_2$Ph, 1-H E, 1-H Z), 4.69, 4.72 (2d, $J_{gem}$ = 11.8 Hz, 2H, OC*H*$_2$Ph), 4.96 (d, $J_{gem}$ = 11.9 Hz, 2H, OC*H*$_2$Ph), 5.03–5.09 (m, 1H, OCH=C*H*CH$_3$ E), 6.18 (dd, $^4J$ = 1.7 Hz, $J_{cis}$ = 6.3 Hz, 1H, OC*H*=CHCH$_3$ Z), 6.23 (dd, $^4J$ = 1.5 Hz, $J_{trans}$ = 12.3 Hz, 1H, OC*H*=CHCH$_3$ E), 7.21–7.39 (m, 20H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 9.48 (1C, $CH_3$, OCH=CH*C*H$_3$ Z), 12.46 (1C, $CH_3$, OCH=CH*C*H$_3$ E), 17.26 (1C, $CH_3$, C-6 Z), 17.28 (1C, $CH_3$, C-6 E), 31.77 (1C, $CH_2$, C-2 E), 31.79 (1C, $CH_2$, C-2 Z), 70.31 (2C, $CH_2$, O*C*$H_2$Ph), 71.25 (1C, CH, C-5 E), 71.32 (1C, CH, C-5 Z), 74.34–74.41 (4C, 2CH, 2CH$_2$, C-4 Z, C-4 E, 2*O*C*$H_2$Ph), 77.64 (1C, CH, C-3 E), 77.67 (1C, CH, C-3 Z), 99.47 (1C, CH, C-1 E), 99.98 (1C, CH, C-1 Z), 102.73 (1C, CH, OCH=*C*HCH$_3$ Z), 103.56 (1C, CH, OCH=*C*HCH$_3$ E), 127.36–128.54 (20C, CH, Ph-*C*H), 138.35 (2C, $C_{ipso}$), 138.90 (2C, $C_{ipso}$), 142.70 (1C, CH, O*C*H=CHCH$_3$ Z), 143.80 (1C, CH, O*C*H=CHCH$_3$ E).

$C_{23}H_{28}O_4$.

**Prop-1-enyl 3,4-Di-*O*-benzyl-2,6-dideoxy-α/β-D-ribohexopyranoside (34)**

The crude compound was purified by flash chromatography with EtOAc/hexane 1/10 as eluent.

β-Anomer: Yield 93%; *E*/*Z*-ratio:1/1.5; colorless oil; $R_f$:0.63 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.30 (d, $J_{5,6}$ = 6.2 Hz, 6H, 6-C*H*$_3$ E, 6-C*H*$_3$ Z), 1.53 (dd, $^4J$ = 1.4 Hz, $J_{vic}$ = 6.8 Hz, 3H, OCH=CHC*H*$_3$ E), 1.58 (dd, $^4J$ = 1.6 Hz, $J_{vic}$ = 6.8 Hz, 3H, OCH=CHC*H*$_3$ Z), 1.61–1.69 (m, 2H, 2-H E, 2-H Z), 2.22–2.31 (m, 2H, 2'-H E, 2'-H Z), 3.15 (2dd, $J_{3,4}$ = 2.7 Hz, $J_{4,5}$ = 9.4 Hz, 2H, 4-H E, 4-H Z), 3.97–4.01 (m, 2H, 3-H E, 3-H Z), 4.05–4.10 (m, 2H, 5-H E, 5-H Z), 4.42 (d, $J_{gem}$ = 11.7 Hz, 2H, OC*H*$_2$Ph), 4.46–4.50 (m, 2H, OCH=C*H*CH$_3$ Z, OCH=C*H*CH$_3$ E), 4.54–4.57 (m, 2H, OC*H*$_2$Ph), 4.62–4.69 (m, 4H, OC*H*$_2$Ph), 5.04–5.08 (m, 2H, 1-H E, 1-H Z), 6.18 (td, $^4J$ = 0.8 Hz, $J_{cis}$ = 6.3 Hz, 1H, OC*H*=CHCH$_3$ Z), 6.22 (dd, $^4J$ = 1.4 Hz, $J_{trans}$ = 12.3 Hz, 1H, OC*H*=CHCH$_3$ E), 7.21–7.36 (m, 20H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 9.34 (1C, $CH_3$, OCH=CH*C*H$_3$ Z), 12.36 (1C, $CH_3$, OCH=CH*C*H$_3$ E), 18.37 (1C, $CH_3$, C-6 Z), 18.40 (1C, $CH_3$, C-6 E), 34.58 (1C, $CH_2$, C-2 Z), 34.63 (1C, $CH_2$, C-2 E), 69.52 (1C, CH, C-5 E), 69.63 (1C, CH, C-5 Z), 70.79 (1C, CH, C-3 Z), 70.85 (1C, CH, C-3 E), 71.41–71.60 (4C, $CH_2$, O*C*$H_2$Ph), 80.39 (1C, CH, C-4 Z), 80.49 (1C, CH, C-4 E), 97.41 (1C, CH, C-1 E), 97.93 (1C, CH, C-1 Z), 102.47 (1C, CH, OCH=*C*HCH$_3$ Z), 103.22 (1C, CH, OCH=*C*HCH$_3$ E), 127.64–128.36 (20C, CH, Ph-*C*H), 137.96 (2C, $C_{ipso}$), 138.43 (2C, $C_{ipso}$), 142.98 (1C, CH, O*C*H=CHCH$_3$ Z), 144.05 (1C, CH, O*C*H=CHCH$_3$ E).

$C_{23}H_{28}O_4$.

α-Anomer: Yield 49%; *E*/*Z*-ratio:1/1; colorless oil; $R_f$:0.61 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.25, 1.26 (2d, $J_{5,6}$ = 6.4 Hz, 6H, 6-C*H*$_3$ E, 6-C*H*$_3$ Z), 1.54–1.70 (m, 8H, 2-H E, 2-H Z, OCH=CHC*H*$_3$ E, OCH=CHC*H*$_3$ Z), 2.36 (ddd, $J_{1,2'}$ = 1.3 Hz, $J_{2',3}$ = 3.5 Hz, $J_{2',2}$ = 15.9 Hz, 1H, 2'-H E), 2.42 (ddd, $J_{1,2'}$ = 1.0 Hz, $J_{2',3}$ = 3.3 Hz, $J_{2',2}$ = 15.0 Hz, 1H, 2'-H Z), 3.12–3.15 (m, 2H, 4-H E, 4-H Z), 3.90–3.95 (m, 2H, 3-H E, 3-H Z), 4.29–4.36 (m, 2H, 5-H E, 5-H Z), 4.41, 4.42 (2d, $J_{gem}$ = 12.0 Hz, 2H, OC*H*$_2$Ph), 4.47–4.61 (m, 5H, 2 x OC*H*$_2$Ph, OCH=C*H*CH$_3$ Z), 4.79, 4.84 (2d, $J_{gem}$ = 12.3 Hz, 2H, OC*H*$_2$Ph), 4.97 (d, $J_{1,2}$ = 3.7 Hz, 1H, 1-H E), 5.00 (d, $J_{1,2}$ = 4.0 Hz, 1H, 1-H Z), 5.04–5.12 (m, 1H, OCH=C*H*CH$_3$ E), 6.12 (dq, $^4J$ = 1.7 Hz, $J_{cis}$ = 6.2 Hz, 1H, OC*H*=CHCH$_3$ Z), 6.20 (dt, $^4J$ = 1.5 Hz, $J_{trans}$ = 10.7 Hz, 1H, OC*H*=CHCH$_3$ E), 7.21–7.43 (m, 20H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 9.46 (1C, $CH_3$, OCH=CH*C*H$_3$ Z), 12.63 (1C, $CH_3$, OCH=CH*C*H$_3$ E), 18.08 (2C, $CH_3$, C-6 Z, C-6 E), 30.95 (1C, $CH_2$, C-2 Z), 31.19 (1C, $CH_2$, C-2 E), 63.76 (1C, CH, C-5 Z), 63.92 (1C, CH, C-5 E), 68.50 (1C, CH, C-3 Z), 68.87 (1C, CH, C-3 E), 70.09, 70.19, 70.53, 70.55 (4C, $CH_2$, O*C*$H_2$Ph), 79.67 (1C, CH, C-4 E), 79.71 (1C, CH, C-4 Z), 95.92 (1C, CH, C-1 E), 96.27 (1C, CH, C-1 Z), 102.97 (1C, CH, OCH=*C*HCH$_3$ Z), 103.34 (1C, CH, OCH=*C*HCH$_3$ E), 127.45–128.34 (20C, CH, Ph-*C*H), 138.18, 138.29, 138.60, 138.75 (4C, $C_{ipso}$), 142.51 (1C, CH, O*C*H=CHCH$_3$ Z), 143.67 (1C, CH, O*C*H=CHCH$_3$ E).

$C_{23}H_{28}O_4$.



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**Hydrolysis of the Prop-1-enyl Glycosides 33 and 34; General Procedure**

Prop-1-enyl 3,4-di-*O*-benzyl-2-deoxy-α/β-L-fucopyranoside (**33**) or prop-1-enyl 3,4-di-*O*-benzyl-2-deoxy-α/β-D-ribohexopyranoside (**34**) (1 mmol) and $HgCl_2$ (5.05 mmol) were suspended in acetone/$H_2O$ (5/1) (13.0 ml) at r.t. and stirred for 30 min. After removal of acetone in vacuo the mixture was extracted with $CH_2Cl_2$ (50 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed in vacuo. The crude product was purified by flash chromatography with EtOAc/hexane 1/2.

**3,4-Di-*O*-benzyl-2-deoxy-α/β-L-fucopyranose (35)**

White solid; mp 58 °C; yield 73%; anomeric ratio α:β = 2.4:1; $R_f$:0.22 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6a-C$H_3$), 1.24 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6β-C$H_3$), 1.93–1.97 (m, 2H, 2-H), 2.14–2.19 (m, 2H, 2'-H), 2.94 (t, $J_{1,OH=}$2.5 Hz, 1H, 1-OH), 3.44 (q, $J_{5,6}$ = 6.4 Hz, 1H, 5β-H), 3.51 (s, 1H, 4β-H), 3.53–3.57 (m, 1H, 3β-H), 3.61 (s, 1H, 4α-H), 3.73 (d, $J_{1,OH=}$9.12 Hz, 1H, 1-OH), 3.96–3.99 (m, 1H, 3α-H), 4.06 (q, $J_{5,6}$ = 6.5 Hz, 1H, 5α-H), 4.56–4.71 (m, 7H, 3 x OC$H_2$Ph, 1β-H), 4.96 (d, $J_{gem}$ = 11.7 Hz, 2H, OC$H_2$Ph), 5.42 (s, 1H, 1α-H), 7.25–7.39 (m, 20H, Ph-*H*).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 17.21 (1C, $CH_3$, C-6β), 17.36 (1C, $CH_3$, C-6α), 30.52 (1C, $CH_2$, C-2α), 34.48 (1C, $CH_2$, C-2β), 66.89 (1C, CH, C-5α), 71.14 (1C, CH, C-5β), 70.25, 70.43 (2C, $CH_2$, O$CH_2$Ph), 74.31–74.78 (4C, 2$CH_2$, 2CH, 2*O$CH_2$Ph, C-3α, C-4β), 75.67 (1C, CH, C-4α), 77.53 (1C, CH, C-3β), 92.64 (1C, CH, C-1α), 94.75 (1C, CH, C-1β), 127.28–128.48 (20C, CH, Ph-*C*H), 138.22–138.74 (4C, $C_{ipso}$).

MS (EI): *m*/*z* = 328 [$M^+$].

$C_{20}H_{24}O_4$.

**3,4-Di-*O*-benzyl-2,6-dideoxy-α/β-D-ribohexopyranose (36)**

This compound was purified by flash chromatography with EtOAc/hexane 1/8→1/5. Yield 65%; anomeric ratio α/β = 1/1.3; colorless oil; $R_f$:0.18 (EtOAc/hexane 1/2).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.29 (d, $J_{5,6}$ = 6.3 Hz, 3H, 6β-C$H_3$), 1.32 (d, $J_{5,6}$ = 6.2 Hz, 3H, 6α-C$H_3$), 1.48 (ddd, $J_{2,3}$ = 2.4 Hz, $J_{2,1}$ = 9.7 Hz, $J_{2',2}$ = 13.8 Hz, 1H, 2β-H), 1.74 (dt, $J_{1,2}$ = $J_{2,3}$ = 3.1 Hz, $J_{2',2}$ = 14.4 Hz, 1H, 2α-H), 2.18 (dd, $J_{2',3}$ = 3.7 Hz, $J_{2',2}$ = 14.4 Hz, 1H, 2'α-H), 2.27 (ddd, $J_{2',1}$ = 2.1 Hz, $J_{2',3}$ = 3.7 Hz, $J_{2',2}$ = 13.8 Hz, 1H, 2'β-H), 3.11 (dd, $J_{4,3}$ = 2.6 Hz, $J_{4,5}$ = 8.9 Hz, 2H, 4α-H, 4β-H), 3.59 (d, $J_1\beta_{,OH=}$5.8 Hz, 1H, 1β-OH), 3.97 (q, $J_{2',3}$ = $J_{2,3}$ = $J_{3,4}$ = 2.9 Hz, 1H, 3β-H), 4.06–4.12 (m, 2H, 3α-H, 5β-H), 4.29–4.34 (m, 1H, 5α-H), 4.40, 4.47 (2d, $J_{gem}$ = 11.7 Hz, 2H, OC$H_2$Ph), 4.54–4.69 (m, 5H, OC$H_2$Ph), 4.80 (d, $J_{gem}$ = 11.9 Hz, 1H, OC$H_2$Ph), 5.08 (dd, $J_{1,2}$ = 3.6 Hz, $J_{1,OH=}$11.0 Hz, 1H, 1α-H), 5.19 (ddd, $J_{1,2'}$ = 2.0 Hz, $J_{1,OH=}$5.8 Hz, $J_{1,2}$ = 9.5 Hz, 1H, 1β-H), 5.31 (d, $J_1\alpha_{,OH=}$11.0 Hz 1H, 1α-OH), 7.24–7.36 (m, 20H, Ph-*H*).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 18.26 (1C, $CH_3$, C-6α), 18.36 (1C, $CH_3$, C-6β), 34.11 (1C, $CH_2$, C-2α), 36.36 (1C, $CH_2$, C-2β), 62.85 (1C, CH, C-5α), 69.20, 72.43 (2C, CH, C-3α, C-5β), 70.81 (1C, CH, C-3β), 71.29, 71.49, 71.60, 73.08 (4C, $CH_2$, O$CH_2$Ph), 80.57, 80.96 (2C, CH, C-4α, C-4β), 91.79 (1C, CH, C-1α), 92.19 (1C, CH, C-1β), 127.62–128.52 (20C, CH, Ph-*C*H), 137.49, 137.75, 137.90, 138.40 (4C, $C_{ipso}$).

MS (EI):328 [$M^+$].

$C_{20}H_{24}O_4$.

**Glycosidation Reactions**

**Glycosidations with the Fluorides 4, 5 and 6 as Donors; General Procedure**

Pulverized, freshly activated molecular sieves 4Å (70 mg), $LiClO_4$ or $Ba(ClO_4)_2$ (0.2 mmol) and acceptor (0.2 mmol) were stirred in $Et_2O$, $CH_2Cl_2$ or MeCN (1 mL) for 30 min under Ar. To this suspension was added a solution of the donor (0.1 mmol) in the same solvent (1 mL). In the case of acceptors without TMS group, CsF (0.1 mmol) was used as acid scavenger. After stirring for 3 d (2 d with the donors **5** and **6**) at r.t., the mixture was diluted with $CH_2Cl_2$ (50 mL), filtered and washed with $H_2O$. The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography.

**Glycosidations with Phosphite 3 and Trichloracetimidates 1 and 2; General Procedure**

To a mixture of donor (0.1 mmol), acceptor (0.2 mmol), molecular sieves 4Å (70 mg) and metal perchlorate (0.2–2.0 mmol) was added the respective solvent (2 mL) under Ar. After a reaction time of 3 d at r.t. the mixture was diluted with $CH_2Cl_2$ (50 mL), filtered and washed with $H_2O$. The organic layer was dried ($Na_2SO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography.

**3,4,6-Tri-*O*-benzyl-2-deoxy-α/β-D-glucopyranosyl-*N*-diphenylmethylene Serine Methyl Ester (15)**

Colorless oil; yield 57%; anomeric ratio α:β = 2.4:1.

MS (FAB): *m*/*z* = 699 [$M^+$]. $C_{44}H_{45}O_7N$.

α-Anomer: $R_f$:0.35 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = +10.8 (*c* = 0.7 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.67 (ddd, $J_{2,1}$ = 3.1 Hz, $J_{2,2'}$ = $J_{2,3}$ = 12.2 Hz, 1H, 2-H), 2.22 (dd, $J_{2',3}$ = 5.0 Hz, $J_{2',2}$ = 12.8 Hz, 1H, 2'-H), 3.58–3.67 (m, 3H, 4-H, 5-H, 6'-H), 3.68 (s, 3H, COOC$H_3$), 3.73 (dd, $J_{5,6}$ = 3.4 Hz, $J_{6',6}$ = 10.5 Hz, 1H, 6-H), 3.75–3.86 (m, 1H, β-C$H_2$), 3.87–3.90 (m, 1H, 3-H), 4.11 (dd, $J_{vic}$ = 4.7 Hz, $J_{gem}$ = 9.9 Hz, 1H, β-C$H_2$), 4.34 (dd, $J_{cis}$ = 4.7 Hz, $J_{trans}$ = 7.4 Hz, 1H, α-C*H*), 4.48 (d, $J_{gem}$ = 12.1 Hz, 1H, OC$H_2$Ph), 4.51 (d, $J_{gem}$ = 11.0 Hz, 1H, OC$H_2$Ph), 4.61 (q, $J_{gem}$ = 11.5 Hz, 3H, OC$H_2$Ph), 4.88 (d, $J_{gem}$ = 11.0 Hz, 1H, OC$H_2$Ph), 4.95 (d, $J_{1,2}$ = 2.6 Hz, 1H, 1-H), 7.14–7.38 (m, 23H, Ph-*H*), 7.64 (d, *J* = 7.5 Hz, 2H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 35.24 (1C, $CH_2$, C-2), 52.20 (1C, $CH_3$, O$CH_3$), 65.47 (1C, CH, α-*C*H), 68.04 (1C, $CH_2$, β-*C*$H_2$), 68.72 (1C, $CH_2$, C-6), 70.84 (1C, CH, C-5), 71.58, 73.43, 74.78 (3C, $CH_2$, O$CH_2$Ph), 76.78–77.29 (1C, CH, C-3), 78.11 (1C, CH, C-4), 97.75 (1C, CH, C-1), 127.48–130.50 (25C, CH, Ph-*C*H), 135.98, 138.11, 138.59, 138.70, 139.40, 170.56, 172.02 (7C, $C_{ipso}$).

β-Anomer: $R_f$ = 0.42 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = –54.7 (*c* = 0.2 in $CHCl_3$).

$^1$H NMR (250 MHz, $CDCl_3$): δ = 1.58 (q, $J_{2,2'}$ = $J_{2,3}$ = $J_{2,1}$ = 10.7 Hz, 1H, 2-H), 2.28 (dd, $J_{2',3}$ = 5.0 Hz, $J_{2',2}$ = 12.8 Hz, 1H, 2'-H), 3.29–3.38 (m, 1H, 5-H), 3.46–3.74 (m, 4H), 3.71 (s, 3H, COOC$H_3$), 4.07 (d, *J* = 7.2 Hz, 2H), 4.34–4.70 (m, 7H, 1-H, 2.5 x OC$H_2$Ph), 4.87 (d, $J_{gem}$ = 11.5 Hz, 1H, OC$H_2$Ph), 7.15–7.46 (m, 23H, Ph-*H*), 7.60–7.67 (m, 2H, Ph*H*).

**Cholesteryl 3,4,6-Tri-*O*-benzyl-2-deoxy-α/β-D-glucopyranoside (16)**

MS (MALDI): *m*/*z* = 826 [$M^+$+Na].

$C_{54}H_{74}O_5$•$H_2O$ calcd C 78.98, H 9.33; found C 79.15, H 9.00.

α-Anomer: colorless oil; $R_f$ = 0.48 ($CH_2Cl_2$/$Et_2O$ 20/1); $[\alpha]^{21}_D$ = +65.6 (*c* = 2.2 in $CHCl_3$).

$^1$H NMR(500 MHz, $CDCl_3$): δ = 0.67 (s, 3H), 0.85–0.97 (m, 10H), 0.99–1.22 (m, 11H), 1.22–1.60 (m, 12H), 1.73 (ddd, $J_{2,1}$ = 3.3 Hz, $J_{2,3}$ = $J_{2,2'}$ = 12.2 Hz, 1H, 2-H), 1.79–2.02 (m, 5H), 2.24–2.35 (m, 3H, 2'-H), 3.43–3.49 (m, 1H), 3.62 (t, $J_{3,4}$ = $J_{4,5}$ = 9.4 Hz, 1H, 4-H), 3.68 (dd, $J_{5,6'}$ = 1.9 Hz, $J_{6',6}$ = 10.5 Hz, 1H, 6'-H), 3.80 (dd, $J_{5,6}$ = 3.9 Hz, $J_{6',6}$ = 10.5 Hz, 1H, 6-H), 3.85–3.88 (m, 1H, 5-H), 4.00–4.05 (m, 1H, 3-H), 4.49 (d, $J_{gem}$ = 12.0 Hz, 1H, OC$H_2$Ph), 4.51 (d, $J_{gem}$ = 10.7 Hz, 1H, OC$H_2$Ph), 4.63–4.69 (m, 3H, OC$H_2$Ph), 4.89 (d,

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$J_{gem}$ = 10.7 Hz, 1H, OC$H_2$Ph), 5.13 (d, $J_{1,2}$ = 2.9 Hz, 1H, 1-H), 5.28 (d, $J$ = 5.0 Hz, 1H), 7.16–7.36 (m, 15H, Ph-*H*).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 11.85, 18.72, 19.35 (3C, $CH_3$), 21.04 (1C, $CH_2$), 22.57, 22.82 (2C, $CH_3$), 23.82, 24.29, 27.63 (3C, $CH_2$), 28.01 (1C, CH), 28.23 (1C, $CH_2$), 31.88 (1C, CH), 31.92 (1C, $CH_2$), 35.78 (1C, CH), 35.91 (1C, $C_{ipso}$), 36.19, 36.72, 37.07 (3C, $CH_2$, C-2), 39.51, 39.77, 39.96 (3C, $CH_2$), 42.31 (1C, $C_{ipso}$), 50.09, 56.14, 56.76 (3C, CH), 68.98 (1C, $CH_2$, C-6), 70.69 (1C, CH, C-5), 71.75, 73.41, 75.01 (3C, $CH_2$, OC$H_2$Ph), 75.87 (1C, CH), 77.84 (1C, CH, C-3), 78.44 (1C, CH, C-4), 95.01 (1C, CH, C-1), 121.64 (1C, CH), 127.46–129.02 (15C, CH, Ph-*C*H), 138.18, 138.53, 138.82, 140.84 (4C, $C_{ipso}$).

β-Anomer:[28] colorless solid; mp 109 °C; $R_f$:0.42 ($CH_2Cl_2$/$Et_2O$ 20/1); $[\alpha]^{20}_D$ = +139.4 (*c* = 1.8 in $CHCl_3$); [Ref.: [5j] $[\alpha]^{23}_D$ = –30.5 (*c* = 1.7 in $CHCl_3$)].

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.67 (s, 3H), 0.83–1.66 (s, 33H), 1.67 (q, $J_{2,1}$ = $J_{2,3}$ = $J_{2,2'}$ = 11.0 Hz, 1H, 2-H), 1.79–1.86 (m, 2H), 1.95–2.02 (m, 3H), 2.22–2.33 (m, 3H, 2'-H), 3.40 (ddd, $J_{5,6'}$ = 1.8 Hz, $J_{5,6}$ = 5.2 Hz, $J_{4,5}$ = 9.7 Hz, 1H, 5-H), 3.48 (t, $J_{3,4}$ = $J_{4,5}$ = 9.1 Hz, 1H, 4-H), 3.56–3.62 (m, 1H), 3.64–3.70 (m, 1H, 3-H), 3.68 (dd, $J_{5,6}$ = 5.2 Hz, $J_{6',6}$ = 10.8 Hz, 1H, 6-H), 3.76 (dd, $J_{5,6'}$ = 1.7 Hz, $J_{6',6}$ = 10.7 Hz, 1H, 6'-H), 4.54–4.63 (m, 5H, 1-H, 2 x OC$H_2$Ph), 4.68 (d, $J_{gem}$ = 11.7 Hz, 1H, OC$H_2$Ph), 4.90 (d, $J_{gem}$ = 10.9 Hz, 1H, OC$H_2$Ph), 5.34 (d, $J$ = 5.2 Hz, 1H), 7.21–7.35 (m, 15H, Ph-*H*).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 11.84, 18.71, 19.35 (3C, $CH_3$), 21.02 (1C, $CH_2$), 22.57, 22.83 (2C, $CH_3$), 23.79, 24.27 (2C, $CH_2$), 28.00 (1C, CH), 28.22, 29.69 (2C, $CH_2$), 31.85 (1C, CH), 31.93 (1C, $CH_2$), 35.77 (1C, CH), 36.16 (1C, $CH_2$), 36.72 (1C, $C_{ipso}$), 37.20, 37.29 (2C, $CH_2$, C-2), 38.90, 39.50, 39.75 (3C, $CH_2$), 42.29 (1C, $C_{ipso}$), 50.15, 56.10, 56.73 (3C, CH), 69.41 (1C, $CH_2$, C-6), 71.30, 73.34, 74.95 (3C, $CH_2$, OC$H_2$Ph), 75.09 (1C, CH, C-5), 78.12, 78.15 (2C, CH, C-4), 79.55 (1C, CH, C-3), 97.91 (1C, CH, C-1), 121.82 (1C, CH), 127.48–128.41 (15C, CH, Ph-*C*H), 138.33, 138.35, 138.38, 140.65 (4C, $C_{ipso}$).

**Methyl-*O*-(3,4-di-*O*-benzyl-2-deoxy-α/β-L-fucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (18)**
MS (MALDI): *m*/*z* = 797 [$M^+$+Na].

$C_{48}H_{54}O_9$•$H_2O$ calcd C 72.71, H 7.12; found C 72.82, H 6.87.

α-Anomer: colorless oil; $R_f$:0.46 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = –16.2 (*c* = 1.2 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.12 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6b-C$H_3$), 1.91 (dd, $J_{2',3}$ = 4.6 Hz, $J_{2',2}$ = 12.5 Hz, 1H, 2'b-H), 2.14 (dt, $J_{1,2}$ = 3.6 Hz, $J_{2',2}$ = $J_{2,3}$ = 12.3 Hz, 1H, 2b-H), 3.32 (s, 3H, OC$H_3$), 3.42–3.51 (m, 3H, 2a-H, 4a-H, 6a-H), 3.57 (s, 1H, 4b-H), 3.68–3.71 (m, 1H, 5a-H), 3.77–3.81 (m, 2H, 5b-H, 6a-H), 3.86–3.90 (m, 1H, 3b-H), 3.98 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 1H, 3a-H), 4.52–4.58 (m, 4H, 1a-H, 1.5*OC$H_2$Ph), 4.67 (d, $J_{gem}$ = 12.1 Hz, 1H, OC$H_2$Ph), 4.68 (d, $J_{gem}$ = 11.7 Hz, 1H, OC$H_2$Ph), 4.78–4.89 (m, 4H, 1b-H, 1.5 x OC$H_2$Ph), 4.95 (d, $J_{gem}$ = 11.7 Hz, 1H, OC$H_2$Ph), 4.99 (d, $J_{gem}$ = 10.8 Hz, 1H, OC$H_2$Ph), 7.23–7.39 (m, 25H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 17.24 (1C, $CH_3$, C-6b), 30.61 (1C, $CH_2$, C-2b), 54.96 (1C, $CH_3$, OC$H_3$), 66.02 (1C, $CH_2$, C-6a), 66.65 (1C, CH, C-5b), 70.06 (1C, CH, C-5a), 70.24, 73.31, 74.34 (3C, $CH_2$, OC$H_2$Ph), 74.84 (1C, CH, C-3b), 75.04 (1C, $CH_2$, OC$H_2$Ph), 75.63 (1C, CH, C-4b), 75.81 (1C, $CH_2$, OC$H_2$Ph), 77.90 (1C, CH, C-4a), 80.01 (1C, CH, C-2a), 82.16 (1C, CH, C-3a), 97.84 (1C, CH, C-1a), 98.09 (1C, CH, C-1b), 127.33–128.45 (25C, CH, Ph-*C*H), 2 x 138.16, 138.55, 138.69, 138.88 (5C, $C_{ipso}$).

Characteristic signals for the β-anomer:

$^1$H NMR (250 MHz, $CDCl_3$): δ = 1.17 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6b-C$H_3$), 3.36 (s, 3H, OC$H_3$).

**6-*O*-(3,4-Di-*O*-benzyl-2-deoxy-α/β-L-fucopyranosyl)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (19)**
Yield 75%; anomeric ratio α:β = 13:1.

MS (FAB): *m*/*z* = 569 [$M^+$-H]. $C_{32}H_{42}O_9$.

α-Anomer: colorless oil; $R_f$:0.51 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = –16.2 (*c* = 0.9 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.16 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6b-C$H_3$), 1.31, 1.34, 1.43, 1.53 (4s, 12H, C(C$H_3$)), 2.03 (dd, $J_{2',3}$ = 4.5 Hz, $J_{2',2}$ = 12.5 Hz, 1H, 2'b-H), 2.18 (dt, $J_{1,2}$ = 3.7 Hz, $J_{2',2}$ = $J_{2,3}$ = 12.3 Hz, 1H, 2b-H), 3.55 (dd, $J_{6',5}$ = 6.7 Hz, $J_{6,6'}$ = 10.1 Hz, 1H, 6'a-H), 3.59 (s, 1H, 4b-H), 3.77 (dd, $J_{6,5}$ = 6.4 Hz, $J_{6,6'}$ = 10.1 Hz, 1H, 6a-H), 3.85–3.94 (m, 3H, 3b-H, 5b-H, 5a-H), 4.20 (dd, $J_{5,4}$ = 1.7 Hz, $J_{4,3}$ = 7.9 Hz, 1H, 4a-H), 4.31 (dd, $J_{1,2}$ = 2.4 Hz, $J_{2,3}$ = 4.9 Hz, 1H, 2a-H), 4.57–4.64 (m, 3H, 3a-H, OC$H_2$Ph), 4.70, 4.97 (2d, $J_{gem}$ = 11.8 Hz, 2H, OC$H_2$Ph), 5.00 (d, $J_{1,2}$ = 3.2 Hz, 1H, 1b-H), 5.53 (d, $J_{1,2}$ = 5.0 Hz, 1H, 1a-H), 7.24–7.39 (m, 10H, Ph-*H*).

$^{13}$C NMR(125.7 MHz, $CDCl_3$): δ = 17.29 (1C, $CH_3$, C-6b), 24.55, 24.97, 26.00, 26.12 (4C, $CH_3$, C(C$H_3$)), 30.50 (1C, $CH_2$, C-2b), 65.28 (1C, $CH_2$, C-6a), 66.70, 66.76 (2C, CH, C-5a, C-5b), 70.35 (2C, 1CH, 1$CH_2$, C-3a, OC$H_2$Ph), 70.61 (1C, CH, C-2a), 71.16 (1C, CH, C-4a), 74.25 (1C, $CH_2$, OC$H_2$Ph), 75.34 (1C, CH, C-3b), 75.77 (1C, CH, C-4b), 96.31 (1C, CH, C-1a), 97.81 (1C, CH, C-1b), 108.53, 109.22 (2C, $C_{ipso}$, *C*($CH_3$)), 127.33–128.39 (10C, CH, Ph-*C*H), 138.70, 138.98 (2C, $C_{ipso}$).

Characteristic signals for the β-anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6b-C$H_3$), 1.97–2.12 (m, 1H, 2b-H), 5.49 (d, $J_{1,2}$ = 5.0 Hz, 1H, 1a-H).

**Cholesteryl 3,4-Di-*O*-benzyl-2-deoxy-α-L-fucopyranoside (20)**
This compound was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/8→1/4→1/2. White solid; mp 109 °C; $R_f$:0.66 (EtOAc/hexane 1/2); $[\alpha]^{21}_D$ = –72.2 (*c* = 1.0 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.67 (s, 3H), 0.85–1.57 (m, 33H), 1.15 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6-C$H_3$), 1.76–1.84 (m, 3H), 1.93–2.01 (m, 3H, 2'-H, 2H Chol), 2.17–2.21 (m, 2H, 2-H), 2.32 (dd, $J$ = 3.0 Hz, $J$ = 13.2 Hz, 1H), 3.41–3.44 (m, 1H), 3.61 (s, 1H, 4-H), 3.87 (q, $J_{5,6}$ = 6.6 Hz, 1H, 5-H), 3.94–3.96 (m, 1H, 3-H), 4.59–4.64 (m, 2H, OC$H_2$Ph), 4.69, 4.96 (2d, $J_{gem}$ = 11.8 Hz, 2H, OC$H_2$Ph), 5.11 (d, $J_{1,2}$ = 3.3 Hz, 1H, 1-H), 5.32 (d, $J$ = 4.8 Hz, 1H), 7.24–7.39 (m, 10H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 11.85, 18.72, 19.38 (3C, $CH_3$), 17.34 (1C, $CH_3$, C-6), 21.05 (1C, $CH_2$), 22.57, 22.82 (2C, $CH_3$), 23.82, 24.29 (2C, $CH_2$), 28.01 (1C, CH), 28.23, 29.54 (2C, $CH_2$), 31.20 (1C, $CH_2$, C-2), 31.89 (2C, CH, $CH_2$), 35.78 (1C, $C_{ipso}$), 36.19 (1C, CH), 36.74, 37.40, 38.70, 39.51, 39.78 (5C, $CH_2$), 42.31 (1C, $C_{ipso}$), 50.15, 56.13, 56.73 (3C, CH), 66.61 (1C, CH, C-5), 70.42, 74.29 (2C, $CH_2$, OC$H_2$Ph), 75.64 (1C, CH, C-3), 75.88 (1C, CH, C-4), 76.09 (1C, CH), 95.91 (1C, CH, C-1), 121.67 (1C, CH), 127.23–128.36 (10C, CH, Ph-*C*H), 138.76, 138.97, 140.70 (3C, $C_{ipso}$).

MS (MALDI): *m*/*z* = 721 [$M^+$+Na].

$C_{47}H_{68}O_4$ calcd C 80.97, H 9.84; found C 80.46, H 9.53.

**Benzyl-*O*-(3,4-di-*O*-benzyl-2-deoxy-α-L-fucopyranosyl)-(1→4)-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-α/β-D-glucopyranoside (21)**
The crude product was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/10→1/4. Colorless oil; $R_f$:0.12 (EtOAc/hexane 1/4).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.17 (d, $J_{5,6}$ = 6.5 Hz, 3H, 6c-C$H_3$), 1.93 (dd, $J_{2',3}$ = 4.5 Hz, $J_{2,2'}$ = 12.6 Hz, 1H, 2'c-H), 2.16 (ddd, $J_{2,1}$ = 3.7 Hz, $J_{2',2}$ = $J_{2,3}$ = 12.4 Hz, 1H, 2c-H), 3.33 (t, $J$ = 5.9 Hz, 1H), 3.33–3.36 (m, 1H), 3.44–3.62 (m, 6H), 3.63 (bs, 1H, 4c-H), 3.71 (dd, $J$ = 1.4 Hz, $J$ = 10.1 Hz, 1H, 6'-H), 3.80 (dd, $J$ = 4.0 Hz,



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*J* = 10.8 Hz, 1H, 6-H), 3.87 (d, *J* = 3.2 Hz, 1H), 3.89–3.93 (m, 1H, 3c-H), 3.97 (q, $J_{5,6}$ = 6.6 Hz, 1H, 5c-H), 4.00 (t, *J* = 9.3 Hz, 1H), 4.37–4.42 (m, 3H, 1-H, OC*H*$_2$Ph), 4.48 (d, $J_{1,2}$ = 7.7 Hz, 1H, 1-H), 4.58–4.75 (m, 10H, OC*H*$_2$Ph), 4.90 (d, $J_{gem}$ = 10.8 Hz, 1H, OC*H*$_2$Ph), 4.94–4.99 (m, 3H, OC*H*$_2$Ph), 5.25 (d, $J_{1,2}$ = 3.5 Hz, 1H, 1c-H), 7.20–7.41 (m, 40H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 17.42 (1C, $CH_3$, C-6c), 30.82 (1C, $CH_2$, C-2c), 67.30 (1C, CH), 68.04, 68.62 (2C, $CH_2$, C-6a, C-6b), 69.25 (1C, CH), 70.43, 70.94 (2C, $CH_2$, O*C*H$_2$Ph), 72.63 (1C, CH), 73.21, 73.42, 74.43, 75.00 (4C, $CH_2$, O*C*H$_2$Ph), 75.10 (2C, CH), 75.21, 75.36 (2C, $CH_2$, O*C*H$_2$Ph), 75.52, 76.48, 79.43, 79.49, 81.73, 82.95 (6C, CH), 100.13 (1C, CH, C-1c), 102.52, 102.58 (2C, CH, C-1a, C-1b), 127.15–128.43 (40C, CH, Ph-*C*H), 137.54, 138.10, 138.16, 138.41, 138.45, 138.59, 138.74, 139.15 (8C, $C_{ipso}$).

MS (MALDI): *m*/*z* = 1217 [$M^+$+Na]. $C_{74}H_{80}O_{14}$.

**_O_-(3,4-Di-_O_-benzyl-2,6-dideoxy-α/β-D-ribohexopyranosyl)-(1→6)-2,3,4-tri-_O_-benzyl-α-D-glucopyranoside (22)**

The product was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/6→1/2.

MS (MALDI): *m*/*z* = 797 [$M^+$+Na].

$C_{48}H_{54}O_9$•$H_2O$ calcd C 72.71, H 7.12; found C 72.69, H 7.16.

β-Anomer: colorless oil; $R_f$:0.45 (ethyl acetate/hexane 1/2; $[\alpha]^{21}_D$ = +43.0 (*c* = 0.8 in $CHCl_3$).

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.27 (d, $J_{5,6}$ = 6.3 Hz, 3H, 6b-C*H*$_3$), 1.55–1.61 (m, 1H, 2b-H), 2.14 (ddd, $J_{2',1}$ = 2.0 Hz, $J_{2',3}$ = 3.6 Hz, $J_{2',2}$ = 13.6 Hz, 1H, 2'b-H), 3.11 (dd, $J_{4,3}$ = 2.7 Hz, $J_{4,5}$ = 9.2 Hz, 1H, 4b-H), 3.34 (s, 3H, $OCH_3$), 3.51–3.55 (m, 2H, 2a-H, 4a-H), 3.63 (dd, $J_{6',5}$ = 4.5 Hz, $J_{6,6'}$ = 10.9 Hz, 1H, 6'a-H), 3.74–3.76 (m, 1H, 5a-H), 3.96–4.01 (m, 3H, 3a-H, 3b-H, 5b-H), 4.08 (dd, $J_{6,6'}$ = $J_{6,5}$ = 10.1 Hz, 1H, 6a-H), 4.40 (d, $J_{gem}$ = 11.7 Hz, 1H, OC*H*$_2$Ph), 4.67–4.50 (m, 5H, OC*H*$_2$Ph), 4.58 (d, $J_{1,2}$ = 3.5 Hz, 1H, 1a-H), 4.77–4.89 (m, 3H, OC*H*$_2$Ph), 4.84 (dd, $J_{1,2'}$ = 1.8 Hz, $J_{1,2}$ = 9.9 Hz, 1H, 1b-H), 4.98 (d, $J_{gem}$ = 10.9 Hz, 1H, OC*H*$_2$Ph), 7.25–7.36 (m, 25H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 18.33 (1C, $CH_3$, C-6b), 35.19 (1C, $CH_2$, C-2b), 55.09 (1C, $CH_3$, O*C*H$_3$), 67.47 (1C, $CH_2$, C-6a), 69.84 (1C, $CH_2$, C-5a), 69.09, 71.09, 82.12 (3C, CH, C-3a, C-3b, C-5b), 71.37, 71.61, 73.34, 75.10, 75.77 (5C, $CH_2$, O*C*H$_2$Ph), 77.81, 79.76 (2C, CH, C-2a, C-4a), 80.73 (1C, CH, C-4b), 98.00 (1C, CH, C-1a), 98.19 (1C, CH, C-1b), 127.58–128.44 (25C, CH, Ph-*C*H), 138.02, 138.15, 138.27, 138.51, 138.80 (5C, $C_{ipso}$).

Characteristic signals of the α-anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, $J_{5,6}$ = 6.2 Hz, 3H, 6b-C*H*$_3$), 1.55–1.61 (m, 2H, 2b-H, 2'b-H), 3.36 (s, 3H, OC*H*$_3$).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 18.18 (1C, $CH_3$, C-6b), 55.17 (1C, $CH_3$, O*C*H$_3$), 94.88 (1C, CH, C-1a).

**_O_-(3,4-Di-_O_-benzyl-2,6-dideoxy-α/β-D-ribohexopyranosyl)-(1→6)-1,2:3,4-di-_O_-isopropylidene-α-D-galactopyranoside (23)**

The product was purified by flash chromatography with ethyl acetate/hexane (1% $Et_3N$) 1/6→1/4. Colorless oil; $R_f$:0.43 (EtOAc/hexane 1/2).

MS (FAB): *m*/*z* = 569 [$M^+$-H]. $C_{32}H_{42}O_9$.

α-Anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.26 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6b-C*H*$_3$), 1.29, 1.32, 1.44, 1.51 (4s, 12H, C(C*H*$_3$)), 1.63 (dt, $J_{1,2}$ = $J_{2,3}$ = 3.8 Hz, $J_{2',2}$ = 14.9 Hz, 1H, 2b-H), 2.36 (dd, $J_{2',3}$ = 2.6 Hz, $J_{2',2}$ = 14.4 Hz, 1H, 2'b-H), 3.15 (dd, $J_{4,3}$ = 2.9 Hz, $J_{4,5}$ = 9.1 Hz, 1H, 4b-H), 3.65 (t, $J_{6,5}$ = $J_{6,6'}$ = 9.3 Hz, 1H, 6a-H), 3.79 (dd, $J_{5,6'}$ = 5.7 Hz, $J_{6,6'}$ = 9.5 Hz, 1H, 6'a-H), 3.90 (q, $J_{4,3}$ = $J_{3,2a}$ = $J_{3,2e}$ = 3.2 Hz, 1H, 3b-H), 3.99–4.02 (m, 1H, 5a-H), 4.28–4.31 (m, 3H, 2a-H, 4a-H, 5b-H), 4.44 (d, $J_{gem}$ = 11.9 Hz, 1H, OC*H*$_2$Ph), 4.54 (d, $J_{gem}$ = 12.4 Hz, 1H, OC*H*$_2$Ph), 4.55 (dd, $J_{3,4}$ = 3.4 Hz, $J_{2,3}$ = 7.1 Hz, 1H, 3a-H), 4.60 (d, $J_{gem}$ = 11.9 Hz, 1H, OC*H*$_2$Ph), 4.76 (d, $J_{gem}$ = 12.3 Hz, 1H, OC*H*$_2$Ph), 4.82 (d, $J_{1,2}$ = 3.8 Hz, 1H, 1b-H), 5.51 (d, $J_{1,2}$ = 5.0 Hz, 1H, 1a-H), 7.26–7.40 (m, 10H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 18.10 (1C, $CH_3$, C-6b), 24.42, 24.93, 25.99, 26.17 (4C, $CH_3$, C(*C*H$_3$)), 31.47 (1C, $CH_2$, C-2b), 65.47 (1C, $CH_2$, C-6a), 65.78 (1C, CH, C-5a), 69.06 (1C, CH, C-3b), 69.95 (1C, $CH_2$, O*C*H$_2$Ph), 63.56, 70.45, 70.67, 70.88 (4C, CH, C-2a, C-3a, C-4a, C-5b), 70.60 (1C, $CH_2$, O*C*H$_2$Ph), 79.82 (1C, CH, C-4b), 96.26 (1C, CH, C-1a), 96.56 (1C, CH, C-1b), 108.52, 108.97 (2C, $C_{ipso}$, *C*(CH$_3$)), 127.33–128.30 (10C, CH, Ph-*C*H), 138.21, 138.79 (2C, $C_{ipso}$).

Characteristic signals of the β-anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 3.11 (dd, $J_{4,3}$ = 2.9 Hz, $J_{4,5}$ = 9.1 Hz, 1H, 4b-H), 5.56 (d, $J_{1,2}$ = 5.0 Hz, 1H, 1a-H).

**Cholesteryl 3,4-Di-_O_-benzyl-2,6-dideoxy-α/β-D-ribohexopyranoside (24)**

The product was purified by flash chromatography with EtOAc/hexane (1% $Et_3N$) 1/10→1/8. White solid; $R_f$:0.55 (EtOAc/hexane 1/4).

MS (MALDI): *m*/*z* = 720 ($M^+$+Na).

MS (FAB): *m*/*z* = 696 (M–-2H).

$C_{47}H_{68}O_4$•0.25 $H_2O$ calcd C 80.47, H 9.84; found C 80.30, H 9.57.

β-Anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 0.67 (d, *J* = 2.7 Hz, 3H), 0.85–1.18 (m, 21H), 1.22–1.41 (m, 5H), 1.28 (d, $J_{5,6}$ = 6.2 Hz, 3H, 6-C*H*$_3$), 1.43–1.57 (m, 8H, 2a-H, 7H Chol), 1.59–1.85 (m, 2H), 1.91–2.01 (m, 3H), 2.12–2.19 (m, 2H, 2'-H, 1H Chol), 2.29–2.32 (m, 1H), 3.12 (dd, $J_{4,3}$ = 2.8 Hz, $J_{4,5}$ = 9.3 Hz, 1H, 4-H), 3.53–3.55 (m, 1H), 3.97–4.02 (m, 2H, 3-H, 5-H), 4.41 (d, $J_{gem}$ = 11.8 Hz, 1H, OC*H*$_2$Ph), 4.55 (d, $J_{gem}$ = 11.8 Hz, 1H, OC*H*$_2$Ph), 4.67 (bs, 2H, OC*H*$_2$Ph), 4.95 (dd, $J_{1,2'}$ = 1.8 Hz, $J_{1,2}$ = 9.6 Hz, 1H, 1-H), 5.35–5.37 (m, 1H), 7.25–7.44 (m, 10H, Ph-*H*).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 11.86 (1C, $CH_3$), 18.45 (1C, $CH_3$, C-6), 18.72, 19.36 (2C, $CH_3$), 21.04 (1C, $CH_2$), 22.57, 22.83 (2C, $CH_3$), 23.82, 24.29 (2C, $CH_2$), 28.02 (1C, CH), 28.24, 29.67 (2C, $CH_2$), 31.89 (1C, CH), 31.96 (1C, $CH_2$), 35.79 (1C, CH), 35.91 (1C, $C_{ipso}$), 36.19 (1C, $CH_2$, C-2), 36.75, 37.33, 38.92, 39.52, 39.78 (5C, $CH_2$), 42.32 (1C, $C_{ipso}$), 50.18, 56.14, 56.77 (3C, CH), 68.92 (1C, CH, C-3), 71.33 (1C, CH, C-5), 71.37, 71.65 (2C, $CH_2$, O*C*H$_2$Ph), 77.82 (1C, CH), 80.78 (1C, CH, C-4), 95.86 (1C, CH, C-1), 121.69 (1C, CH), 127.29–128.38 (10C, CH, Ph-*C*H), 138.05, 138.15, 138.70 (3C, $C_{ipso}$).

Characteristic signals of the α-anomer:

$^1$H NMR (500 MHz, $CDCl_3$): δ = 1.25 (d, $J_{5,6}$ = 6.4 Hz, 3H, 6-C*H*$_3$), 3.16 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 9.0 Hz, 1H, 4-H), 4.94 (d, $J_{1,2}$ = 4.4 Hz, 1H, 1-H).

$^{13}$C NMR (125.7 MHz, $CDCl_3$): δ = 94.09 (1C, CH, C-1).

The analytical data recorded for 2-deoxyglucosyl disaccharides **13**,[5j,8b] **14**[6] and **17**[7] are in accordance with reported values.

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