Polymer-Bound Diphenylphosphane Hydrobromide, a Mild Acid for the Activation of Enol Ethers: Applications in Polymer-Assisted Glycosidations

Janis Jaunzems,[a] Dmitri Kashin,[a] Andreas Schönberger,[b] and Andreas Kirschning*[a]

Dedicated to Prof. Dr. A. Zeeck on the occasion of his 65th birthday

Keywords: Baccatin III / Glycosidation / Glycoconjugates / Multistep synthesis / Polymer-bound reagents / Protecting group

Polymer-bound diphenylphosphane hydrobromide **2** shows excellent properties in the activation of enol ethers and glycals, the introduction and cleavage of THP ethers being promoted with excellent yields with this functionalized polymer. Glycosidations of glycals work equally well, with suppression of the formation of undesired Ferrier rearranged products. The reagent is sufficiently mild to leave labile 2-deoxy glycosidic bonds and acid-labile protecting groups intact. It can be employed to transfer disaccharide glycosyl donors onto aglycons and is also selective for the promotion of two glycosidations in one pot. Highly hindered glycosyl donor groups such as the hydroxy group at C-13 of the baccatin III framework can be glycosylated with glycals in the presence of this polymer-bound reagent.

Introduction

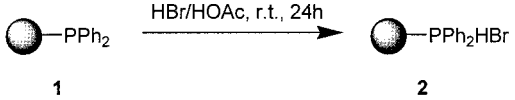
Interest in the development and application of solid-supported reagents[1] and catalysts has recently seen a dramatic increase.[2,3] This hybrid solid-/solution-phase technique possesses all the intrinsic advantages of classical solid-phase techniques: (a) use of excesses of reagents to drive reactions to completion, followed by a simple filtration step to isolate products, and (b) not every active site on the solid phase needs to react. Additionally, all advantages associated with solution-phase chemistry are also exploited here: (a) easy monitoring of the reaction, and (b) no procedures for cleavage from the resin required.

In this context, our group has also been focusing on the evaluation of polymer-bound promoters for glycosidations in order to prepare 2-deoxygenated glycoconjugates with minimum workup. We have demonstrated that glycosyl acetates can be activated by polymer-bound silyl triflate[4] and have also developed thiophilic reagents immobilized on polystyrene, which promote glycosidation of thioglycosides, followed by removal of thiol-containing by-products by scavenging procedures.[5] In a related approach, Ley and coworkers have recently reported polymer-assisted glycosidations relying exclusively on polymer-bound scavenging reagents for removal of by-products originating from conventional solution-phase glycosidations.[6] Much earlier work by Paulsen and Lockhoff[7] and later work by Capillon et al.[8] showed that activation of glycosyl bromides can be achieved with silver cations immobilized on a solid phase.

In this report we disclose "poly-diphenylphosphane hydrobromide" (**2**), a new polymer-bound proton source closely related to the soluble triphenylphosphane hydrobromide studied in detail by Bestmann and later by Falck and co-workers.[9]

Results and Discussion

Polymer-bound reagent **2** (about 1 mmol/g) is conveniently prepared from "poly-diphenylphosphane" (**1**) by treatment with hydrobromic acid (Scheme 1) and is storable under nitrogen for months. In evaluation of the properties of reagent **2**, we first checked its ability to promote the protection of alcohols as THP (tetrahydropyranyl) ethers[10] and their subsequent deprotection to regenerate the starting



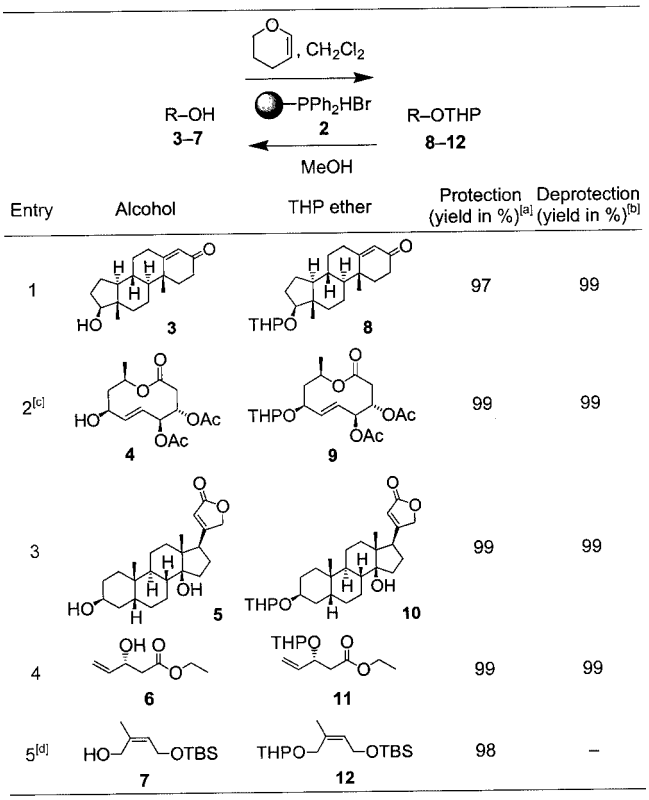
Scheme 1. Preparation of polymer-bound diphenylphosphane hydrobromide **2**

[a] Zentrum für Organische Chemie, Universität Hannover, Schneiderberg 1B, 30167 Hannover, Germany
Fax: (internat.) + 49-511-762-3011
E-mail: andreas.kirschning@oci.uni-hannover.de
[b] Institut für Organische Chemie, Technischen Universität Clausthal,
Leibnizstr. 6, 38678 Clausthal-Zellerfeld, Germany

 DOI: 10.1002/ejoc.200400069

alcohols under protic conditions. As many reagents – including several conventional protic and Lewis acids,[11,12] pyridinium *p*-tosylate (PPTS),[13] Dowex 50 W,[14] and iodotrimethylsilane[15] – are known to promote these simple transformations, we deliberately chose multifunctional alcohols **3**–**7**, which have complexity typical of intermediate alcohols occurring in natural product synthesis. Indeed, this selection should allow evaluation of the mildness of reagent **2** (Table 1). Acid-labile alcohols such as digitoxygenine (**5**, Entry 3), allylic silyl ether **7** (Entry 5) and allylic alcohol **6** (Entry 4) were therefore employed (the lability of the last of these arising from its potential to undergo a retro-aldol reaction).

Table 1. Protection and deprotection of selected alcohols

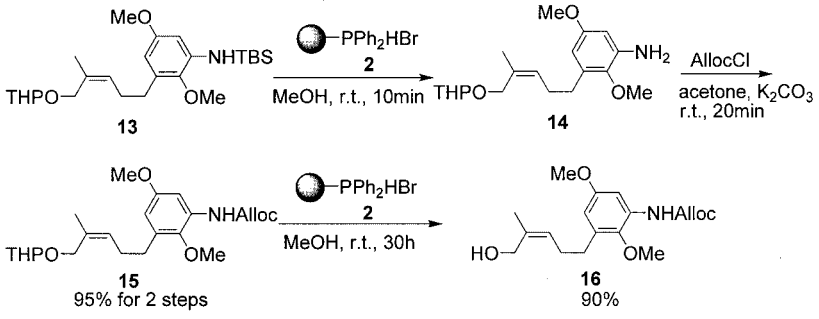


[a] CH_2Cl_2, room temp., 3 h; yields refer to isolated yields. [b] Methanol, room temp. 12 h; yields refer to isolated yields. [c] For preparation of alcohol **4** refer to Scheme 3 and Exp. Sect. [d] When silyl protection was present in the glycoconjugates, Amberlite A-21 was added prior to filtration and concentration. THP = tetrahydropyranyl, Ac = acetate, TBS = *tert*-butyldimethylsilyl.

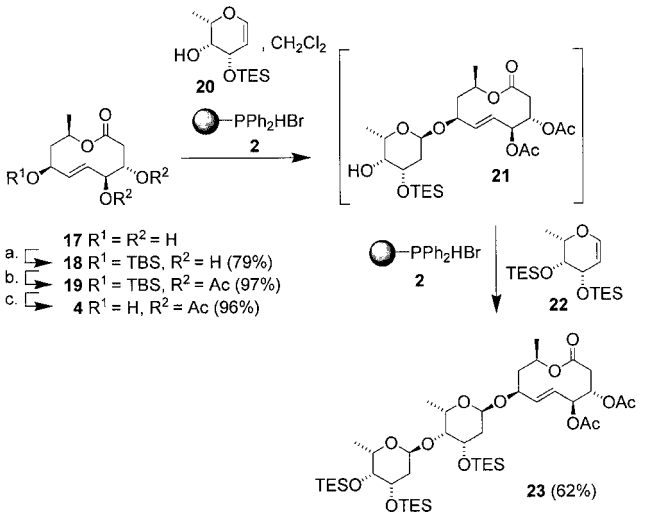
In all these cases, protection of selected alcohols in dichloromethane with use of a catalytic amount of functionalized polymer **2** and 1 equiv. of dihydropyran (DHP) proceeded almost quantitatively within 3 h. The reversed deprotection procedure proceeded under the same conditions, except that methanol was used as a solvent. Here, extended reaction times (12 h) were required in order to provide complete transformation. In all cases, excellent chromatographic and NMR purity was determined for the isolated alcohols, so no additional purification steps relative to other published methods were necessary.

Immobilization of reactive species often leads to a slight to moderate reduction in activity in relation to the parent soluble reagents or catalysts. This can be exploited to enhance the chemoselectivity, as is demonstrated for reagent **2** in a synthetic sequence forming part of a total synthesis approach towards ansamycine antibiotics (Scheme 2). In the presence of an allylic OTHP group in aniline derivative **13**, only the *N*-bound TBS group (*tert*-butyldimethylsilyl) was removed at room temp. in methanol, to yield aniline **14**, while the THP ether remained intact. Finally, after introduction of the allyloxycarbonyl group, the resulting THP ether **15** was selectively cleaved in excellent yield, affording allylic alcohol **16**. Here, reagent **2** showed improved performance over the soluble analogue, which yielded mixtures during the course of the first deprotection.

In the next phase of evaluation of the properties of reagent **2** we directed our focus on the activation of carbohydrate-based enol ether double bonds which are present in glycals.[16] Again, many proton sources, including triphenylphosphane hydrobromide,[9] are known to promote addition of alcohols to the enol ether double bond. The Ferrier rearrangement[17] is a common side reaction, however, resulting in the undesired unsaturated 2,3-dideoxy hexoses. Thus, 3,4-diacylated decarestricine D **4**, obtained by a three-step protection/deprotection sequence from decarestrictine D (**17**)[16k] via intermediates **18** and **19**, was utilized in the first glycosidation procedure (Scheme 3). Decarestrictine D (**17**)[18] was first isolated from the fermentation broth of *Penicillium* species,[19] and is a ten-membered lactone analogue of larger macrolactone antibiotics. When acceptor **4** (1 equiv.) was treated with monosilylated fucal **20** (1 equiv.) in the presence of a catalytic amount of **2**



Scheme 2. Chemoselective deprotection with polymer-bound reagent **2**; Alloc = allyloxycarbonyl

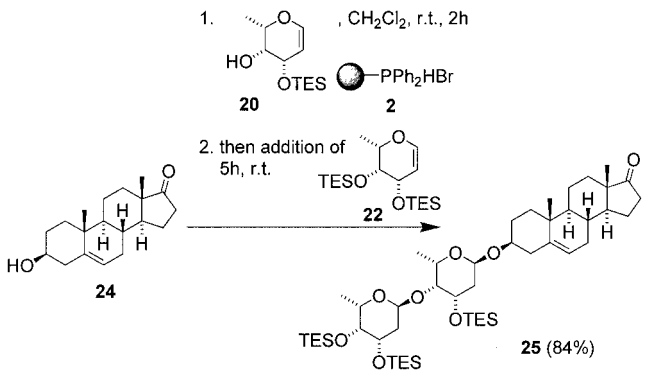


Scheme 3. One-pot diglycosylation of 3,4-diacetoxydecarestrictine D (**4**); reagents and conditions: a) TBSCl (1.5 equiv.), CH_2Cl_2, imidazole, −30 °C, 1 h; b) pyr, Ac_2O (4 equiv.), 50 °C, 7 h; c) TBAF, AcOH, pH = 7, room temp., 5d; TES = triethylsilyl

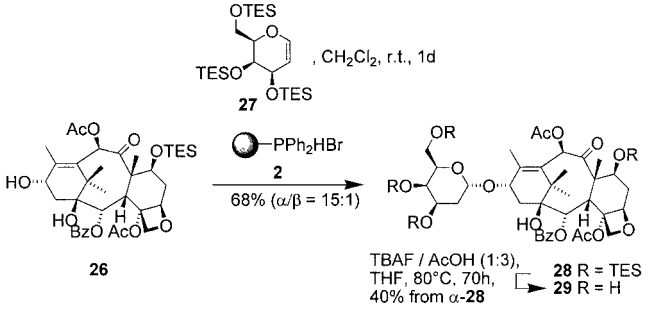
(0.1 mol %), the glycosidation product **21** was quantitatively formed as a single isomer. No formation of the Ferrier product was observed. At this point this product can be isolated, or a second glycosidation can be initiated by addition of glycal **22** (1.2 equiv.) to the reaction mixture. The polymer-attached catalyst **2** again smoothly promotes the addition reaction with similar efficiency and selectivity as seen in the first case, yielding glycoconjugate **23** in a one-pot procedure. This orthogonal glycosidation strategy works so well in this case because the reactivity of the pseudoaxial hydroxy group in glycal **20** is highly reduced relative to that at C-7, this being the most reactive of the three hydroxy groups in decarestrictine. This reactivity difference suppresses the possible dimerization of glycal **20**. It is worth pointing out that the triethylsilyl (TES) protecting groups, including the one attached to the highly reactive allylic hydroxy group at C-3 in glycals **20** and **22**, are not removed under the acidic conditions employed, again a clear indication of the mildness and selectivity of polymer-bound catalysts **2**. In all cases in which the products contained *O*-silyl protection, Amberlite A-21 was added prior to filtration and concentration.

Likewise, dehydro-*epi*-androsterone **24** (1 equiv.) can be treated with glycals **20** (1 equiv.) and **22** (1.2 equiv.) in a similar manner to yield glycosteroid **25** in high yield and with excellent stereoselectivity (only α-anomer for both glycosidation steps) (Scheme 4).

A hydroxy group with a particular lack of reactivity is found at C-13 in baccatin III.[20] This position is typically esterified with *N*-benzoylated isoserine, which is regarded as responsible to a great extent for the excellent antitumor activity of paclitaxel. To the best of our knowledge, no glycoconjugates with carbohydrate moieties attached to C-13 of baccatin III derivatives have been published so far,[21] and so we tested the use of polymer-bound agent **2** in the glycosidation of protected silylated baccatin III **26**[22] with



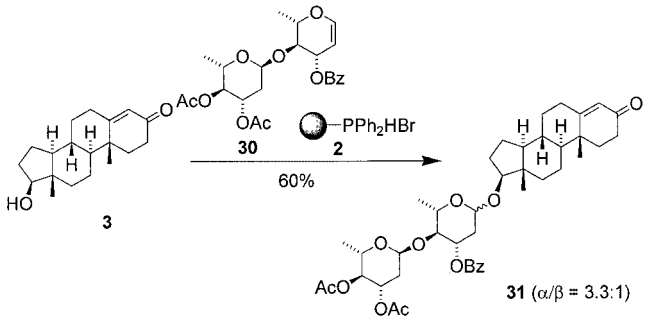
Scheme 4. One-pot diglycosylation of dehydro-*epi*-androsterone **24**



Scheme 5. Glycosylation of 7-TES-protected baccatin III **26**

tri-*O*-silylated galactal **27** (Scheme 5). The glycosyl donor had to be employed in tenfold excess and the reaction time had to be extended to 24 h because of the pronounced lack of accessibility of the 13-hydroxy group in baccatin III **26**. Under these conditions, glycosylated baccatin III **28** was isolated in 68% yield as a mixture of α/β isomers (about 15:1). Workup included chromatographic purification mainly because it was necessary to remove excess galactal **27** and by-products derived from its degradation. Finally, the TES protection on the monosaccharide moiety and on the aglycon were removed by a conventional procedure, furnishing glycosylated baccatin III **29**.[23]

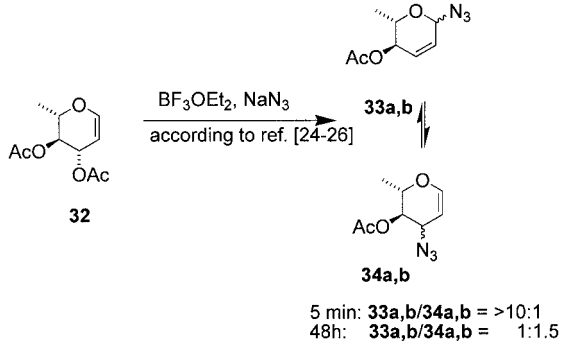
More complex glycosyl donors are deoxygenated disaccharides containing an acid-labile glycosidic bond together with the glycal donor group. Disaccharide glycal **30** was activated with polymer-bound reagent **2** and coupled with testosterone (**3**) (Scheme 6). Disaccharide **31** was isolated as



Scheme 6. Glycosidation of disaccharide glycal **30**

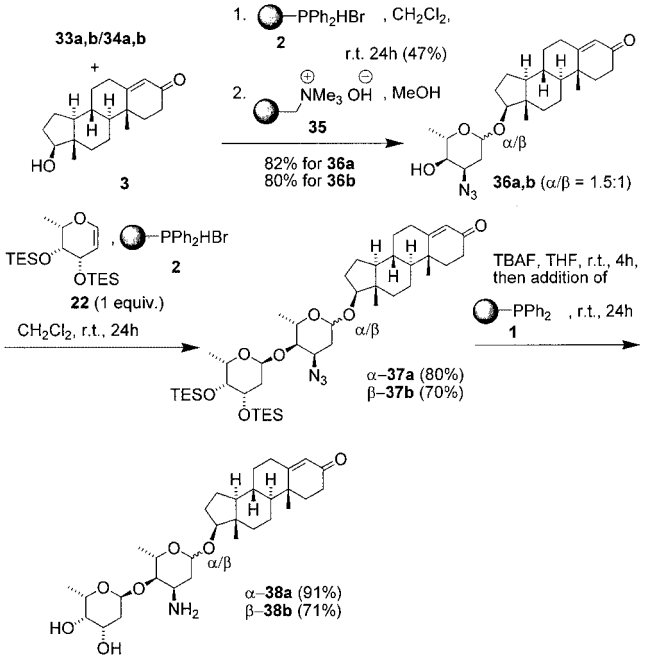
an anomeric mixture, because the *arabino*-configured glycal exerts a lower degree of stereoselection than glycals **20** and **22** containing the stereodirecting pseudoaxial hydroxy or siloxy group at C-4. It should be noted that glycals with electron-withdrawing protecting groups such as **30** show reduced reactivity relative to *O*-silylated glycals in these transformations.

Another complex and difficult to handle glycosyl donor is shown in Scheme 7. Azidodeoxy sugars are ideal precursors for the biologically important class of aminodeoxysaccharides. According to Heyns,[24] Thiem[25] and Monneret,[26] azidodeoxy sugars can be prepared by azidation of glycals with sodium azide as nitrogen source and $BF_3{\cdot}Et_2O$ as Lewis acid promoter. This procedure results in a mixture of α- and β-enopyranosyl azides and 3-azido glycals, existing in equilibrium. It has been suggested that a [3,3]-sigmatropic rearrangement causes this equilibrium.[24−26] So far, these mixtures of azido glycals and enopyranosyl azides have not been utilized in proton-promoted glycosidations.[27] We thus repeated the literature procedure by treating L-rhamnal (**32**) with sodium azide and $BF_3{\cdot}Et_2O$ (Scheme 7). When the reaction was terminated after 5 min and the product mixture was isolated, exclusive formation of the Ferrier-type enopyranosyl azides **33a** and **33b** was noted. The use of longer reaction times (48 h) resulted in rearranged azidoglycals **34a** and **34b**. The product mixture was now a composition of stereoisomeric azidoglycals and enopyranosyl azides in an approximate ratio of 60:40. This crude product mixture was directly subjected to the catalytic glycosidation conditions developed for polymer-bound reagent **2**. We had hoped that the equilibrium depicted in Scheme 7 might be exploited for the exclusive formation of 3-azido-3-deoxy glycosides (Scheme 8).



Scheme 7. Equilibrium of azido glycals and enopyranosyl azides

The glycosidation with testosterone (**3**) was complete within 24 h, and purification afforded an anomeric mixture of *ribo*-configured glycosides, which were directly deacylated with Amberlyst A-26 (hydroxide form) **35** to yield 3-azido-3-deoxy glycosides **36a** and **36b**. The isolated yield was excellent (47% with reference to the starting mixture − in fact about 80% with reference to the *ribo*-configured fraction of the glycals and the enopyranosides derived from them) in view of the observation that the *arabino*-configured azidoglycal and the corresponding β-configured enop-

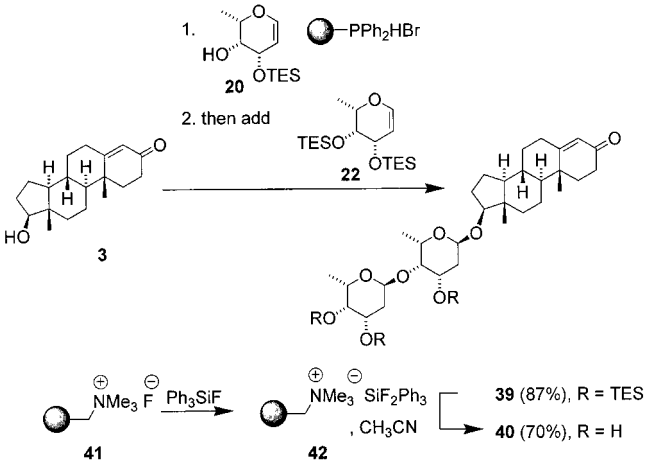


Scheme 8. Polymer-assisted glycosidation of 3-azido glycals

yranosyl azide turned out to be unreactive under the conditions employed and so could be reisolated. At this point the anomeric mixture was separated and the individual isomeric glycosides were further transformed separately. A second glycosidation in the presence of a catalytic amount of reagent **2** and glycal **22** proceeded very smoothly with both glycosides **36a** and **36b**, thereby furnishing disaccharides **37a** and **37b**, respectively. Importantly, no excess of glycosyl donor was required, which allowed simplified purification. Conventional desilylation was achieved with tetrabutylammonium fluoride (TBAF) at room temperature in THF within 4 h, after which polymer-bound diphenylphosphane **1** was added to the reaction mixture. This procedure liberated the amino groups by a Staudinger reaction and gave aminoglycosides **38a** and **38b**, respectively, in very good yield.

Finally, we evaluated polymer-assisted deprotection methods for silyl ethers, which are commonly the final steps in the preparation of glycoconjugates. Protic removal of silyl groups present in glycoconjugates is not a suitable procedure, because of the labile glycosidic linkage present in 2-deoxyhexoses. Here, neutral or basic conditions are more appropriate and can be achieved by use of different fluoride sources.

Disaccharide **39** was prepared in a one-pot fashion by the procedure described in Schemes 3 and 4, with testosterone (**3**) as aglycon (Scheme 9). This per-*O*-silylated product served for testing of different polymer-assisted deprotection methods. DeShong and co-workers developed a new fluoride salt formed from triphenylsilyl fluoride and TBAF.[28] The resulting tetrabutylammonium difluorotriphenylsilicate (TBAT) is stable, compatible with most organic solvents and not hygroscopic. It has mainly been employed because of its non-basic character. Because of these properties we



Scheme 9. Glyconjugate synthesis by polymer-assisted glycosidation and desilylation

prepared the ion-exchange analogue **42** of TBAT. Fluoride exchange resin **41** was prepared as reported by Colonna and co-workers[29] and treated with triphenylsilyl fluoride, with Amberlite A-26 as polymeric source. The functionalized polymer **42** obtained was evaluated as a fluoride source for cleavage of silyl ether protection groups on glycoconjugate **39**.[30] The resin showed good properties as a silyl group cleaving agent in selected systems. In a parallel experiment, fluoride exchange resin **41** was utilized for the deprotection of the same disaccharide **39**, but turned out not to be suited because partial cleavage of the glycosidic bond was observed. Only traces of the desired deprotected triol **40** were formed.

Conclusion

In summary, polymer-bound diphenylphosphane hydrobromide **2** shows excellent properties in the activation of enol ethers and glycals. Introduction and cleavage of THP ethers in excellent yields can be promoted with this functionalized polymer. The mildness of the procedure allows chemoselective manipulations of acid-labile protecting groups (e.g., THP, TES, TBS). Glycosidations of glycals works equally well; formation of undesired Ferrier rearranged products is suppressed. The reagent is sufficiently mild to leave labile 2-deoxy glycosidic bonds intact. It can be employed to transfer disaccharide glycosyl donors onto aglycons and is selective for promotion of two glycosidations in one pot. Studies towards automated solution-phase glycosidations in continuous flow systems are in progress in our laboratories.

Experimental Section

General Remarks and Starting Materials: ^{1}H NMR, ^{13}C NMR and ^{1}H, ^{13}C-COSY and NOESY spectra were measured with Avance 200/DPX (Bruker) 200 MHz (50 MHz), Avance 400/DPX (Bruker) 400 MHz (100 MHz) and Avance 500/DRX (Bruker) instruments, respectively, with use of tetramethylsilane as the internal standard. If not otherwise noted, $CDCl_3$ is the solvent for all NMR experiments. Multiplicities are described with the following abbreviations: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br. = broad. NMR data for oligosaccharides are labelled with a prime (first sugar) and a double prime (second sugar coupled to the first through the anomeric centre). Chemical shift values of ^{13}C NMR spectra are reported as values in ppm relative to residual $CHCl_3$ (δ = 77 ppm) or CD_3OD (49) as internal standards. The multiplicities refer to the resonances in the off-resonance spectra and were elucidated by use of the distortionless enhancement by polarisation transfer (DEPT) spectral editing technique, with secondary pulses at 90° and 135°. Multiplicities are reported with the following abbreviations: s = singlet (due to quaternary C), d = doublet (methine), q = quadruplet (methyl), t = triplet (methylene). Mass spectra were recorded with a type LCT spectrometer (Micromass) and with a type VG autospec (Micromass). Ion mass (*m*/*z*) signals are reported as values in atomic mass units, followed, in parentheses, by the peak intensities relative to the base peak (100%). Optical rotations [α] were collected with a Polarimeter 341 (Perkin−Elmer) at a wavelength of 589 nm and are given in 10^{-1} deg·cm^2·g^{-1}. Combustion analyses were performed at the Institut für Organische Chemie, Universität Hannover. All solvents used were of reagent grade and were further dried. Reactions were monitored by thin layer chromatography (TLC) on silica gel 60 F^{254} (E. Merck, Darmstadt) and spots were detected either by UV absorption or by charring with H_2SO_4/4-methoxybenzaldehyde in methanol. Preparative column chromatography was performed on silica gel 60 (E. Merck, Darmstadt). In most cases this chromatographic step was employed to obtain analytically pure compounds (e.g., for combustion analysis or for the separation of anomeric mixtures). Steroids **3**, **5**, **24** and **27** are commercially available. Reagent **1** was obtained from NovaBiochem. Amberlite A-21 was obtained from Fluka. Glycals **20** and **22** were prepared from L-fucal by partial and exhaustive silylation, respectively, under standard conditions. Similarly, glycals **27** and **32** were obtained from D-galactal and L-rhamnal, respectively, as in ref.[31] Polymer-bound fluoride **41** was prepared as in ref.[29]

Preparation of Polymer-Bound Reagent 2: A suspension of polymer-bound diphenylphosphane (0.5 g, 1.12 mmol/g) in HBr/AcOH (33%, 5 mL) was gently shaken at room temperature for 24 h. The slurry was washed with CH_2Cl_2 (20 × 5 mL) and dried under reduced pressure to afford the dark yellow polymer **2**.[32]

Preparation of Polymer-Bound Tetramethylammonium Difluorotriphenylsilicate TBAT (42): Triphenylsilanol was recrystallized from petroleum ether/ethyl acetate prior to use. Triphenylsilanol (25 g, 90.4 mmol) was dissolved in methanol (90 mL) in a polyethylene bottle and cooled to 5 °C. Aqueous HF (13 mL, 49%, 360 mmol) was slowly added, and the resulting reaction mixture was allowed to warm to room temperature. Stirring was continued for an additional 30 min, resulting in the crystallization of the product as a fine white powder. Distilled water (50 mL) was added to induce further product precipitation. The resulting slurry was filtered in vacuo and washed with water. The crude product was recrystallized (MeOH/water, 15:1) and dried in vacuo to afford pure triphenylsilyl fluoride (23.9 g, 86 mmol; 95%). Polymer-supported fluoride **41** was washed with acetonitrile/ethyl acetate prior to use. A mixture of fluoride exchange resin **41** (2 g, Amberlite A-26) and triphenylsilyl fluoride (3.3 g, 12 mmol; 2 equiv.) in dichloromethane (100 mL) was shaken for 30 min, and the solvent was slowly evaporated under reduced pressure. The resulting polymer was taken up with ethyl acetate (50 mL) and the organic solvent was removed under

reduced pressure. This procedure was repeated three times, and the resulting polymer-bound TBAT (**42**) was filtered, washed with ethyl acetate and dried in high vacuum.

Preparation of 3-*O*-Benzoyl-2,6-dideoxy-4-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-L-*arabino*-hex-1-enitol (30):[5b] Powdered molecular sieves (4 Å, 50 mg) were added to a stirred solution of 3,4-di-*O*-acetyl-2,6-dideoxy-1-phenylthio-α-L-*arabino*-pyranoside (33 mg, 0.1 mmol) and 3-*O*-benzoyl-2,6-dideoxy-L-*arabino*-hex-1-enit (23.4 mg, 0.1 mmol) in acetonitrile (5 mL). The suspension was cooled to 0 °C, and Selectfluor™ (0.105 mmol) was added. The mixture was shaken for 20 min, and the reaction was then terminated by addition of dry Amberlite A-21. The resulting suspension was filtered through a pad of Al_2O_3. The solvent was evaporated under reduced pressure, and the residue was redissolved in 2-propanol (5 mL). After addition of polymer-supported borohydride (100 mg), the mixture was shaken overnight in order to remove thio-derived impurities. The suspension was filtered and concentrated under reduced pressure to afford pure compound **30** (43.4 mg, 97 μmol; 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.3 Hz, 3 H, 6-H′), 1.46 (d, *J* = 6.5 Hz, 3 H, 6-H), 1.75 (ddd, *J* = 13.0, 11.5, 3.7 Hz, 1 H, 2-H′$_{eq}$), 2.04, 1.96 (2s, 6 H, 2 × CH_3CO), 2.15 (dd, *J* = 13.0, 5.2 Hz, 1 H, 2-H′$_{ax}$), 3.94 (dq, *J* = 9.6, 6.3 Hz, 1 H, 5-H′), 3.93 (m, 1 H, 4-H), 4.18 (dq, *J* = 6.7, 6.3 Hz, 1 H, 5-H), 4.71 (dd, *J* = 9.6, 9.6 Hz, 1 H, 4-H′), 4.87 (dd, *J* = 6.1, 3.5 Hz, 1 H, 2-H), 5.23 (ddd, *J* = 11.5, 9.6, 5.2 Hz, 1 H, 3-H′), 5.25 (d, *J* = 3.7 Hz, 1 H, 1-H′), 5.51 (br. dd, *J* = 4.1, 3.5 Hz, 1 H, 3-H), 6.45 (d, *J* = 6.1 Hz, 1 H, 1-H), 7.45 (dd, *J* = 7.1, 7.1 Hz, 2 H, Ph$_{meta}$), 7.57 (dd, *J* = 7.1, 7.1 Hz, 1 H, Ph$_{para}$), 8.01 (d, *J* = 7.1 Hz, 2 H, Ph$_{ortho}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 17.3 (q, C-6), 17.4 (q, C-6′), 20.8, 20.9 (2q, 2 × CH_3CO), 35.4 (t, C-2′), 66.5 (d, C-5′), 68.6 (d, C-3′), 70.8 (d, C-3), 73.3 (d, C-5), 74.7 (d, C-4′), 75.4 (d, C-4), 96.4 (d, C-1′), 98.5 (d, C-2), 128.5 (d, Ph$_{meta}$), 129.6 (d, Ph$_{ortho}$), 129.9 (s, Ph$_{ipso}$), 133.2 (d, Ph$_{ortho}$), 146.0 (d, C-1), 165.9 (s, Ph*C*O), 170.11 (s, CH_3CO), 170.1 (s, CH_3CO) ppm. HRMS ($C_{23}H_{28}O_9$): calcd. 448.1733 [M]$^+$, found 448.1745.

3,4-Di-*O*-acetyl-7-*O*-(*tert*-butyldimethylsilyl)decarestrictine D (19): *tert*-Butyldimethylsilyl chloride (69 mg, 0.46 mmol) was added at −30 °C to a solution of decarestrictine D (**17**) (100 mg, 0.46 mmol) and imidazole (47 mg, 0.69 mmol, 1.5 equiv.) in CH_2Cl_2 (30 mL). The reaction mixture was stirred at this temperature for 1 h, after which the solvent was evaporated under a nitrogen flow while the system was allowed to warm to room temp. Dry pyridine (5 mL) and Ac_2O (187 μL, 4 equiv.) were added, and stirring was continued at 50 °C for 7 h. Pyridine was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 2:1; R_f = 0.53), affording pure **19** (185 mg, 0.446 mmol; 97%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = −0.04, −0.08 [2 s, 6 H, Si(C*H*$_3$)$_2$], 0.79 (s, 9 H, *t*Bu), 1.16 (d, *J* = 6.4 Hz, 1 H, 3 H, 10-H), 1.73 (m, 2 H, CH_2-8), 2.06, 2.05 (2 s, 6 H, 2 × C*H*$_3$CO), 2.54 (m, 2 H, CH_2-2), 4.08 (ddd, *J* = 9.0, 8.4, 5.7 Hz, 1 H, 7-H), 5.20, 5.03 (2 m, 3 H, 9-H, 4-H, 3-H), 5.59 (dd, *J* = 16.2, 3.3 Hz, 1 H, 5-H), 5.70 (dd, *J* = 16.2, 9.0 Hz, 1 H, 6-H) ppm. HRMS ($C_{20}H_{34}O_7Si$): calcd. 415.2152 [M + H]$^+$, found 415.2154.

Preparation of 3,4-Di-*O*-acetyldecarestrictine D (4): *O*-Silylated decarestrictine **19** (160 mg, 0.38 mmol) was dissolved in a minimal amount of THF, added to the buffered THF solution of tetrabutylammonium fluoride[23] (3 mL), and stirred for 5 d. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 2:1; R_f = 0.1) to yield compound **4** (109 mg, 0.363 mmol; 96%) as a semisolid material. $[\alpha]_D^{23}$ = +46.4 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.2 Hz, 3 H, 10-H), 1.83−1.73 (m, 2 H, CH_2-8), 2.08, 2.07 (2 s, 6 H, 2 × C*H*$_3$CO), 2.61, 2.52 (2 ddd, *J* = 14.3, 10.0, 2.6 Hz and *J* = 14.3, 2.6, 2.6 Hz, 2 H, CH_2-2), 2.68 (br. s, 1 H, 7-OH), 4.12 (ddd, *J* = 10.6, 7.9, 3.4 Hz, 1 H, 7-H), 5.08 (m, 1 H, 9-H), 5.22, 5.00 (2 ddd, *J* = 5.2, 2.6, 2.6 Hz and *J* = 10.0, 5.2, 2.6 Hz, 2 H, 4-H, 3-H), 5.66 (dd, *J* = 16.0, 2.6 Hz, 1 H, 5-H), 5.72 (dd, *J* = 16.0, 7.9 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 20.8, 20.9 (2 q, 2 × *C*H_3CO), 21.2 (q, C-10), 33.7 (t, C-2), 42.3 (t, C-8), 68.0 (d, C-9), 70.8, 72.1 (3 d, C-3, C-4, C-7), 123.4 (d, C-5), 136.9 (d, C-6), 169.2, 169.4, 169.8 (3 s, C-1, 2 × CH_3*C*O) ppm. $C_{14}H_{20}O_7$ (300.30): calcd. C 55.99, H 6.71; found C 55.88, H 6.65.

General Procedure for the Introduction of THP Ethers: The alcohol (33 μmol) was dissolved in dry CH_2Cl_2 (3 mL). Dihydropyran (DHP, 2.8 mg, 3.3 μL; 1 equiv.) and a catalytic amount of polymer-bound reagent **2** (0.5 mg, 1.5 mol %) were added, and the suspension was gently shaken at room temperature for 3 h. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure to yield the pure THP-protected product.

17-*O*-(Tetrahydropyran-2′-yloxy)testosterone (8): Testosterone (**3**) (10 mg, 34.7 μmol) was converted into compound **8** (12.5 mg, 33.7 μmol; 97%) by the general procedure for the introduction of THP ethers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.7−2.5 (m, 31 H, THP−H, testosterone−H), 3.5 (m, 1 H, C*H*HOCHO), 3.67 (ddd, 1H *J* = 8.5, 8.1, 4.7 Hz, 1 H, 17-H), 3.91 (ddd, *J* = 10.9, 7.9, 2.9 Hz, 1 H, CH*H*OCHO), 4.65 (br. d, *J* = 3.7 Hz, 1 H, −OC*H*O−), 5.75 (s, 1 H, 4-H) ppm. HRMS ($C_{24}H_{36}O_3$): calcd. 373.2743 [M + H]$^+$, found 373.2748.

3,4-Di-*O*-acetyl-7-*O*-(tetrahydropyran-2′-yloxy)decarestrictine D (9): Diacylated decarestrictine **4** (10 mg, 33 μmol) was converted into compound **9** (12.6 mg, 32.8 μmol; 99%) as a diastereomeric mixture (*dr* = 2:1*) by the general procedure for the introduction of THP ethers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22, (d, *J* = 6.3 Hz, 3 H, CH_3-10), 1.4−2.0 (m, 8 H, THP, CH_2-8), 2.14, 2.12, 2.11 (3 s, 6 H, 2 × C*H*$_3$CO), 2.55 (ddd, *J* = 14.2, 11.6, 2.2 Hz, 1 H, C*H*H-2), 2.66 (ddd, *J* = 14.2, 14.2, 7.0 Hz, 1 H, CH*H*-2), 3.43 (m, 1 H, THP), 3.80 (m, 1 H, THP), 4.12* (ddd, *J* = 10.5, 9.6, 3.2 Hz, 1 H, 7-H), 4.24* (ddd, *J* = 10.5, 9.6, 3.5 Hz, 1 H, 7-H), 4.52* (dd, *J* = 4.5, 2.9 Hz, 1 H, THP), 4.61* (dd, *J* = 4.3, 2.9 Hz, 1 H, THP), 5.03 (m, 1 H, 9-H), 5.13 (2 × ddd, *J* = 21.7, 11.6, 7.0, 2.2 Hz, 1 H, 3-H), 5.32 (dddd, *J* = 16.0, 5.0, 3.5, 1.3 Hz, 1 H, 4-H), 5.63* (ddd, *J* = 16.0, 9.4, 1.3 Hz, 1 H, 5-H), 5.71 (dd, *J* = 16.0, 3.5 Hz, 1 H, 5-H), 5.80* (dd, *J* = 16.0, 3.3 Hz, 1 H, 6-H), 5.87 (ddd, *J* = 16.0, 9.4, 1.3 Hz, 1 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.7 (t, THP), 19.8* (t, THP), 20.9 (q, *C*H_3CO), 20.9 (q, *C*H_3CO), 21.0 (q, C-10), 21.4* (q, C-10), 21.4 (t, THP), 25.2 (t, THP), 25.4* (t, THP), 30.7(d), 30.7* (t, THP), 30.8 (t, THP), 33.4 (t, C-2), 33.9* (t, C-2), 40.1 (t, C-8), 41.1* (t, C-8), 62.7 (t, C-5′), 62.9* (t, C-5′), 68.3 (d, C-9), 68.4* (C-9), 70.9, 72.0, 72.2*, 74.9 (4d, C-3, C-4, C-7), 95.2* (d, THP-1), 97.2 (d, THP-1), 122.9* (d, C-5), 125.7 (d, C-5), 134.7* (d, C-6), 136.1 (d, C-6), 169.1, 169.1, 169.4, 169.5, 169.9 (5 s, C-1, 2 × CH_3*C*O) ppm. HRMS ($C_{19}H_{28}O_8$): calcd. 385.1862 [M + H]$^+$, found 385.1860.

3-*O*-(Tetrahydropyran-2′-yloxy)digitoxygenine (10): Digitoxygenine (**5**) (10 mg, 26.7 μmol) was converted into compound **10** (12.2 mg, 26.5 μmol; 99%) by the general procedure for the introduction of THP ethers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.4−0.7 (m, 33 H, THP, digitoxygenine), 2.80 (m, 1 H, 17-H), 3.50 (m, 1 H, THP), 3.90 (m, 1 H, 3-H), 3.98 (br. s, 1 H, THP), 4.63 (m, 1 H, THP),

4.82 (dd, J = 18.1, 1.6 Hz, 1 H, 21-H), 5.01 (ddd, J = 18.1, 1.6, 1.2 Hz, 1 H5 Hz, 21-H), 5.88 (s, 1 H, 22-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.7 (q, C-18), 19.7 (t, THP), 20.0 (t, THP), 21.2 (t, C-11), 21.4 (t, C-7), 23.7 (q, C-19), 24.1, 25.4, 25.5, 25.6 (4 t, THP), 26.6, 26.7 (2 t, C-16), 26.8 (t, C-6), 26.9 (t, C-2), 29.9, 30.0 (2 t, C-1), 30.4, 30.7 (2 t, C-15), 31.4, 32.2 (2 t, THP), 33.1, 33.2 (2 t, C-4), 35.2 (s, C-10), 35.7 (d, C-9), 36.4, 36.5 (2 d, C-5), 40.0 (t, C-12), 41.9 (d, C-8), 49.6 (s, C-13), 50.9 (d, C-17), 62.8, 62.9 (2 t, THP), 70.8, 71.1 (2 d, C-3), 73.4 (t, C-21), 85.6 (s, C-14), 96.7, 96.9 (2 d, THP-1), 117.6 (d, C-22), 174.5 (s, C-23), 174.6 (s, C-20) ppm. HRMS ($C_{28}H_{42}O_5$): calcd. 459.3111 [M + H]$^+$, found 459.3113.

Ethyl (3*R*)-3-*O*-(Tetrahydropyran-2′-yloxy)pent-4-enoate (11): Ethyl (3*R*)-3-hydroxypent-4-enoate (**6**; 20 mg, 0.139 mmol) was converted into a diastereomeric mixture (*dr* = 2:1*) of THP ethers **11** (31.2 mg, 0.137 mmol; 99%) by the general procedure for the introduction of THP ethers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25, 1.23* (2 t, J = 7.3 Hz, 3 H, CH_2-CH_3), 1.4−1.8 (m, 6 H, THP), 2.47* (dd, J = 15.0, 5.5 Hz, 1 H, 2-H), 2.48 (dd, J = 14.9, 5.7 Hz, 1 H, 2-H), 2.61* (dd, J = 15.0, 8.0 Hz, 1 H, 2-H), 2.64 (dd, J = 14.9, 8.1 Hz, 1 H, 2-H), 3.84, 3.48 (2 m, 2 H, OCHOCH_2), 4.14, 4.12* (2 q, J = 7.3 Hz, 2 H, CH_2-CH_3), 4.50* (ddd, J = 8.0, 6.5, 5.5 Hz, 1 H, 3-H), 4.55 (ddd, J = 8.1, 7.7, 5.7 Hz, 1 H, 3-H), 4.69 (dd, J = 3.1, 3.1 Hz, 1 H, −OC*H*O−), 4.7* (dd, J = 4.1, 3.0 Hz, 1 H, −OC*H*O), 5.11* (ddd, J = 10.5, 1.5, 1.2 Hz, 1 H, 5-H′), 5.21, (dd, J = 10.2, 1.5 Hz, 1 H, 5-H′), 5.25* (d, J = 17.2 Hz, 1 H, 1.2 Hz, 5-H), 5.29 (dd, J = 17.1, 1.5 Hz, 1 H, 5-H), 5.66 (ddd, J = 17.1, 10.2, 7.7 Hz, 1 H, 4-H), 5.91* (ddd, J = 17.2, 10.5, 6.5 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 14.19 (q, CH_2-CH_3), 18.9, 19.5*, 25.3*, 25.5, 30.4*, 30.7 (6t, THP), 40.58 (t, C-2), 41.23* (t, C-2), 60.40* (t, CH_2-CH_3), 61.59 (t, CH_2-CH_3), 72.80 (d, C-3), 74.94 (d, C-3), 94.56 (d, THP-1), 98.68* (d, THP-1), 115.53 (t, −CH=CH_2), 118.37 (t, −CH=CH_2), 136.75 (d, −CH=CH_2), 138.34 (d, −CH=CH_2), 170.79 (s, C=O), 170.92 (s, C=O) ppm. HRMS ($C_{12}H_{20}O_4$): calcd. 229.1440 [M + H]$^+$, found 229.1441.

(*Z*)-4-(*tert*-Butyldimethylsiloxy)-2-methyl-1-(tetrahydropyran-2′-yloxy)-2-butene (12): Dihydropyran (48 μL, 0.53 mmol) and polymer-bound reagent **2** (2 mg) were added to a solution of (*Z*)-4-(*tert*-butyldimethylsiloxy)-2-methyl-2-buten-1-ol (**7**; 0.1 g, 0.44 mmol) in dichloromethane (2 mL). After 10 min, the reaction was terminated by addition of dry Amberlite A-21. After filtration and washing of the solids with methanol (2 × 2 mL), the combined filtrates were concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 6:1), yielding compound **12** (0.13 g, 0.43 mmol; 98%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 [s, 6 H, Si(CH_3)$_2$], 0.89 [s, 9 H, Si(CCH_3)$_3$], 1.86−1.78 and 1.73−1.47 (br. m, 6 H, THP), 1.79 (2 s, 3 H, CH_3), 3.54−3.48 (m, 1 H, THP-5), 3.89−3.83 (m, 1 H, THP-5), 4.04 (dd, J = 11.7, 0.7 Hz, 1 H, CH_2-1), 4.11 (d, J = 11.7 Hz, 1 H, CH_2-1), 4.23 (dq, J = 6.4, 1.1 Hz, 2 H, CH_2-4), 4.57 (dd, J = 3.8, 3.1 Hz, 1 H, THP-1), 5.50 (t, J = 6.4 Hz, 1 H, 3-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.0 ppm): δ = −5.1 [q, Si(CH_3)$_2$], 18.4 [q, Si(CCH_3)$_3$], 19.4 (s, C-3), 21.6 (q, CH_3), 25.5 (s, C-2), 26.0 [q, Si(CCH_3)$_3$], 30.6 (s, C-4), 59.6 (s, C-9), 62.1 (s, C-1), 65.5 (s, C-6), 97.6 (t, C-5), 128.9 (t, C-8), 133.6 (q, C-7) ppm. HRMS ($C_{16}H_{32}O_3Si$): calcd. 301.2199 [M + H]$^+$, found 301.2201.

General Procedure for the Cleavage of THP Ethers: Polymer-bound diphenylphosphane hydrobromide **2** (2 mg, 6 mol %) was added at room temperature to a stirred solution of the THP-protected alcohol (0.033 mmol) in methanol (5 mL). The mixture was gently shaken at room temperature for 12 h, filtered through a pad of Celite and concentrated under reduced pressure. The product was additionally dried under high vacuum to remove remaining traces of THP-methyl ether.

Deprotection of 17-*O*-(Tetrahydropyran-2′-yloxy)testosterone (8): 17-*O*-(Tetrahydropyran-2′-yloxy)testosterone (**8**; 12.5 mg, 33.7 μmol) was deprotected to afford testosterone (**3**) (9.9 mg, 33.4 μmol, 99%) by the general procedure for the cleavage of THP ethers. Spectroscopic and physical data are identical with those of authentic testosterone.

Deprotection of 3,4-Di-*O*-acetyl-7-*O*-(tetrahydropyran-2′-yloxy)decarestrictine D (9): 3,4-Di-*O*-acetyl-7-*O*-(tetrahydropyran-2′-yloxy)decarestrictine D (**9**; 12.6 mg, 32.8 μmol) was deprotected to afford compound **4** (9.75 mg, 32.5 μmol; 99% yield) by the general procedure for the cleavage of THP ethers. Spectroscopic and physical data are mentioned above.

Deprotection of 3-*O*-(Tetrahydropyranyl)digitoxygenine (10): 3-*O*-(Tetrahydropyranyl)digitoxygenine (**10**; 12.2 mg, 26.5 μmol) was deprotected to afford digitoxygenine (**5**; 9.8 mg, 26.2 μmol; 99%) by the general procedure for the cleavage of THP ethers. Spectroscopic and physical data are identical with those of authentic digitoxygenine.

Ethyl (3*R*)-3-Hydroxypent-4-enoate (6): Ethyl (3*R*)-3-*O*-(tetrahydropyran-2′-yloxy)pent-4-enoate (**11**; 31.2 mg, 0.137 mmol) was deprotected to afford compound **6** (19.59 mg, 0.136 mmol; 99%) by the general procedure for the cleavage of THP ethers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.1 Hz, 3 H, CH_2-CH_3), 2.50 (dd, J = 16.1, 8.7 Hz, 1 H, 2-H), 2.57 (dd, J = 16.1, 4.6 Hz, 1 H, 2-H), 3.02 (br. s, 1 H, OH), 4.16 (q, J = 7.1 Hz, 2 H, CH_2-CH_3), 4.53 (ddd, J = 8.7, 4.6, 2.8 Hz, 1 H, 3-H), 5.14 (ddd, J = 10.5, 1.4, 1.4 Hz, 1 H, 5-H), 5.31 (ddd, J = 17.1, 1.4, 1.4 Hz, 1 H, 5-H), 5.87 (ddd, J = 17.1, 10.5, 1.4 Hz, 1 H, 4-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 14.13 (q, CH_3), 41.13 (t, C-2), 60.75 (t, CH_2-CH_3), 68.90 (d, C-3), 115.35 (t, C-5), 138.78 (d, C-4), 172.22 (s, C=O) ppm. $C_7H_{10}O_3$ (144.17): calcd. C 58.32, H 8.39; found C 58.35, H 8.31.

{(*Z*)-2,5-Dimethoxy-3-[4-methyl-5-(tetrahydropyran-2′-yloxy)pent-3-enyl]phenyl}amine (14): Amine **13** (98 mg, 0.22 mmol) was dissolved in methanol (5 mL), and polymer-bound reagent **2** (1 mg) was added. The mixture was stirred for 10 min, and the reaction was terminated by addition of dry Amberlite A-21. After filtration, the solids were washed with methanol (2 × 5 mL) and the combined filtrates were concentrated under reduced pressure. The crude product **14** (74 mg, 0.22 mmol) was directly used in the next step without further purification or analysis.

(Allyloxycarbamoyl){2,5-dimethoxy-3-[(*Z*)-4-methyl-5-(tetrahydropyran-2′-yloxy)pent-3-enyl]phenyl}amine (15): An aqueous solution of potassium carbonate (4.2 м; 94 mg, 30 equiv.) and allyloxycarbonyl chloride (0.25 mL, 10 equiv.) was added to a solution of aniline **14** (74 mg, 0.22 mmol) in acetone (5 mL). The reaction mixture was stirred for 20 min and then diluted with brine. The product was extracted with diethyl ether (3 × 5 mL), the organic phase was separated and dried (Na_2SO_4), and the solvent was removed under reduced pressure. The crude material was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford compound **15** (90 mg, 0.21 mmol; 95% from **13**) as a colourless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.71−1.53 (m, 6 H, 2 × 2-H′, 2 × 3-H′, 2 × 4-H′, −THP), 1.77 (m, 3 H, 2-CH_3), 2.42−2.34 (m, 2 H, 2-H, −pentenyl), 2.69−2.58 (m, 2 H, 1-H, −pentenyl), 3.55−3.44 (m, 1 H, 1-H′), 3.69 (s, 3 H, OCH_3), 3. 77 (s, 3 H, OCH_3), 3.93−3.81 (m, 1 H, 1-H), 4.08 (m, 2 H, 2 × 6′-H), 4.68

(dt, J = 5.7, 1.4 Hz, 2 H, $-CH_2CH=CH_2$), 5.28 (dd, J = 10.4, 2.8 Hz, 1 H, 1.4 Hz, $-CH_2CH=CHH$), 5.38 (ddd, J = 17.2, 2.8, 1.4 Hz, 1 H, $-CH_2CH=CHH$), 5.40−5.47 (m, 1 H, 8-H), 5.99 (dddd, J = 17.2, 10.4, 5.7, 5.7 Hz, 1 H, $-CH_2CH=CH_2$), 6.41 (d, J = 3.1 Hz, 1 H, Ar), 7.22 (s, 1 H, Ar), 7.61 (s, 1 H, N−H) ppm. HRMS ($C_{23}H_{33}NO_6$): calcd. 420.2386 $[M + H]^+$, found 420.2390.

(Allyloxycarbamoyl){3-[(*Z*)-5-hydroxy-4-methyl)pent-3-enyl]-2,5-(dimethoxy)phenyl}amine (16): Polymer-bound reagent **2** (1 mg) was added to a solution of THP ether **15** (90 mg, 0.21 mmol) in methanol (5 mL). After 30 h at room temp., the reaction was terminated by addition of dry Amberlite A-21. After filtration, the solids were washed with methanol (2 × 5 mL) and the combined filtrates were concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1), yielding compound **16** (64 mg, 0.19 mmol; 90%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77 (m, 3 H, 2-CH_3), 2.35 (dd, J = 15.0, 7.6 Hz, 2 H, 2 × 4-H), 2.63 (m, 2 H, 2 × 5-H), 3.69 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.05 (s, 2 H, 1-H and 1-H′), 4.68 (d, J = 5.7 Hz, 2 H, $-CH_2CH=CH_2$), 5.27 (dd, J = 10.5, 1.4 Hz, 1 H, $-CH_2CH=CHH$), 5.32−5.36 (m, 1 H, 3-H), 5.37 (dd, J = 17.2, 1.4 Hz, 1 H, $-CH_2CH=CHH$), 5.98 (dddd, J = 17.2, 10.5, 5.7, 5.7 Hz, 1 H, $-CH_2CH=CH_2$), 6.39 (d, J = 3.0 Hz, 1 H, Ar), 7.20 (s, 1 H, Ar), 7.61 (s, 1 H, N−H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, δ = 77.0 ppm): δ = 21.2 (q, 2-CH_3), 28.3 (s, C-4), 30.1 (s, C-5), 55.5 (q, OCH_3), 61.1 (p, OCH_3), 61.5 (s, C-1), 65.9 (s, $-CH_2CH=CH_2$), 109.7 (t, C-3), 118.3 (s, $-CH_2CH=CH_2$), 127.2 (t, Ar), 131.9 (q, Ar), 132.4 (t, Ar), 134.9 (q, Ar), 135.4 (q, C-2), 140.4 (q, Ar), 153.1 (q, Ar), 156.1 (q, C=O) ppm. HRMS ($C_{18}H_{25}NO_5$): calcd. 358.1630 $[M + Na]^+$, found 358.1636.

3,4-Di-*O*-acetyl-7-*O*-[(2-deoxy-3,4-di-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)-(1→4)-(2-deoxy-3-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)]-decarestrictine D (23): Polymer-bound reagent **2** (1 mg) and LiBr (5 mg) were added to a solution of L-fucal **20** (24 mg, 0.1 mmol) and decarestrictine (**4**) (30 mg, 0.1 mmol) in dry dichloromethane. The reaction mixture was shaken at room temp. for 2 h, after which fully silylated L-fucal **22** (40 mg, 0.12 mmol) in dichloromethane (1 mL) was added. The resulting solution was stirred at room temp. for another 4 h and the reaction was terminated by the addition of Amberlite A-21. Filtration was followed by washing of the solid with ethyl acetate and the concentration of the combined filtrates under reduced pressure. The crude material was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:2), which afforded disaccharide **23** (56 mg, 62 μmol; 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.6 [m, 18 H, 3 × Si(CH_2CH_3)$_3$], 0.9 [m, 27 H, 3 × Si(CH_2CH_3)$_3$], 1.26, 1.23, 1.19 (3 d, J = 6.6, J = 6.5, J = 6.4 Hz, 9 H, 10-H, 6-H′, 6-H′′), 2.1−1.4 (m, 6 H, 2-H, 2-H′, 2-H′′), 2.17, 2.14 (2 s, 6 H, 2 × OAc), 2.51 (dd, J = 14.0, 2.2 Hz, 1 H, 8-H), 2.67 (dd, J = 14.0, 6.6 Hz, 1 H, 8-H), 3.53 (br. s, 1 H, 4-H′′), 3.63 (br. d, J = 2.5 Hz, 1 H, 4-H′), 3.75 (br. q, J = 6.5 Hz, 1 H, 5-H′), 4.15−4.0 (m, 3 H, 7-H, 3-H′, 3-H′′), 4.30 (br. q, J = 6.4 Hz, 1 H, 5-H′′), 4.83 (d, J = 3.1 Hz, 1 H, 1-H′′), 5.02 (ddd, J = 7.2, 5.0, 2.5 Hz, 1 H, 3-H), 5.06 (d, J = 3.0 Hz, 1 H, 1-H′), 5.14 (ddd, J = 9.8, 6.6, 2.2 Hz, 1 H, H-9), 5.33 (m, 1 H, 4-H), 5.60 (ddd, J = 16.0, 9.5, 1.5 Hz, 1 H,, 6-H), 5.77 (ddd, J = 16.0, 8.5, 3.5 Hz, 1 H, 5-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 4.7, 4.9, 5.2, 6.8, 7.0 (3 q, 2 t, 3 × TES), 17.3 (q, C-6′′), 18.0 (q, C-6′), 20.9, 21.0 (2 q, 2 × $COCH_3$), 21.4 (q, C-10), 32.9 (t, C-2′), 33.5 (t, C-2), 33.8 (t, C-2′′), 40.9 (t, C-8), 66.8 (d, C-3′), 67.3 (d, C-3′′), 67.5 (d, C-5′′), 67.7 (d, C-5′), 68.3 (d, C-9), 70.8, 71.8, 71.9 (3 d, C-3, C-4, C-7), 73.8 (d, C-4′′), 74.5 (d, C-4′), 93.5 (d, C-1′), 97.7 (d, C-1′′), 125.9 (d, C-5), 134.0 (d, C-6), 169.0, 169.5, 169.9 (3 s, 2 × $COCH_3$, C-1) ppm. HRMS ($C_{44}H_{82}O_{13}Si_3$): calcd. 903.5142 $[M + H]^+$, found 903.5146.

3-*O*-[(2-Deoxy-3,4-di-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)-(1→4)-(2-deoxy-3-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)]dehydro-*epi*-androsterone (25): Polymer-bound reagent **2** (1 mg) was added to a solution of fucal **18** (24 mg, 0.1 mmol) and dehydro-*epi*-androsterone (**24**) (28 mg, 0.1 mmol) in dichloromethane (5 mL). The reaction mixture was shaken at room temp. for 2 h, after which di-*O*-silylated L-fucal **22** (40 mg, 0.12 mmol) in dichloromethane (1 mL) was added. The solution was shaken for another 5 h, and Amberlite A-21 was then added to terminate the reaction, after which the solvent was removed under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/petroleum ether, 1:3, R_f = 0.62) to yield glycoconjugate **25** (71 mg, 84 μmol; 84%). $[\alpha]_D^{23}$ = −85.6 (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.55−0.7 [m, 18 H, 3 × Si(CH_2CH_3)$_3$], 0.88 (s, 3 H, CH_3-18), 0.93−1.02 [m, 27 H, 3 × Si(CH_2CH_3)$_3$], 1.03 (s, 3 H, CH_3-19), 1.13 (d, J = 6.4 Hz, 3 H, CH_3-6′′), 1.17 (d, J = 6.7 Hz, 3 H, CH_3-6′), 0.9−2.5 (m, 24 H, CH_2-2′′, CH_2-2′, androsterone-H), 3.39 (dddd, J = 11.1, 11.1, 4.6, 4.6 Hz, 1 H, 3-H), 3.56, (br. s, 1 H, 4-H′′), 3.65 (br. d, J = 2.5 Hz, 1 H, 4-H′), 3.86 (br. q, J = 6.7 Hz, 1 H, 5-H′), 4.05−4.15 (m, 2 H, 3-H′, 3-H′′), 4.31 (br. q, J = 6.4 Hz, 1 H, 5-H′′), 5.02 (d, J = 2.5 Hz, 1 H, 1-H′′), 5.09 (d, J = 3.1 Hz, 1 H, 1-H′), 5.35 (br. d, J = 5.1 Hz, 1 H, 6-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.3, 4.9, 4.8 [3 t, 3 × Si(CH_2CH_3)$_3$], 7.0, 6.8 [2 q, 3 × Si(CH_2CH_3)$_3$], 13.5 (q, C-18), 17.6 (q, C-6′′), 18.0 (q, C-6′), 19.4 (q, C-19), 20.4 (t, C-11), 21.9 (t, C-15), 29.6 (t, C-2), 30.8 (t, C-1), 31.5 (t, C-12), 31.6 (d, C-8), 32.9 (t, C-2′′), 34.5 (t, C-2′), 35.8 (t, C-16), 36.9 (s, C-10), 37.3 (t, C-7), 38.7 (t, C-4), 47.5 (s, C-13), 50.3 (d, C-9), 51.8 (d, C-14), 66.9 (d, C-3′), 67.3 (d, C-3′′), 67.5 (d, C-5′′), 67.6 (d, C-5′), 74.0 (d, C-4′′), 74.9 (d, C-4′), 76.1 (d, C-3), 96.0 (d, C-1′′), 97.8 (d, C-1′), 120.7 (d, C-6), 141.2 (s, C-5), 220.9 (s, C-17) ppm. HRMS ($C_{49}H_{90}O_8Si_3$): calcd. 891.6022 $[M + H]^+$, found 891.6018.

13-*O*-Glycosylated Baccatin III 28: 7-*O*-(Triethylsilyl)baccatin III (**26**; 68.5 mg, 98 μmol; prepared according to ref.[22]) and tri-*O*-silylated galactal **27** (479 mg, 0.98 mmol) were dissolved in dry dichloromethane (25 mL), and polymer-bound reagent **2** (50 mg) was added. The reaction mixture was shaken at room temp. for 24 h and the reaction was terminated by the addition of Amberlite A-21. Filtration was followed by washing of the solid with ethyl acetate and the concentration of the combined filtrates under reduced pressure. The crude material was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:8), which afforded glycosylated baccatin α/β-**28**.

α-28: First fraction (R_f = 0.54; ethyl acetate/petroleum ether, 1:4): 74 mg, 62 μmol; 63%. $[\alpha]_D^{22}$ = −2.5 (c = 1.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ(aglycon) = 0.71−0.5 [m, 6 H, Si(CH_2CH_3)$_3$], 0.99−0.87 [m, 9 H, Si(CH_2CH_3)$_3$], 1.01 (s, 3 H, CH_3-16), 1.14 (s, 3 H, CH_3-17), 1.59 (s, 1 H, OH-1), 1.68 (s, CH_3-19), 1.88 (ddd, J = 14.4, 10.6, 2.0 Hz, 1 H, 6-H′), 2.05 (dd, J = 14.6, 9.2 Hz, 1 H, 14-H′), 2.15 (s, 3 H, CH_3-18), 2.16 (s, 3 H, CH_3CO_2− at position 10), 2.25 (dd, J = 14.6, 9.2 Hz, 1 H, 14-H), 2.26 (s, 3 H, CH_3CO_2− at position 4), 2.53 (ddd, J = 14.4, 9.6, 6.8 Hz, 1 H, 6-H), 3.81 (d, J = 7.0 Hz, 1 H, 3-H), 4.15 (d, J = 8.4 Hz, 1 H, 20-H′), 4.30 (d, J = 8.4 Hz, 1 H, 20-H), 4.50 (dd, J = 10.6, 6.8 Hz, 1 H, 7-H), 4.96 (dd, J = 9.6, 2.0 Hz, 1 H, 5-H), 5.04 (dd, J = 9.2, 9.2 Hz, 1 H, 13-H), 5.68 (d, J = 7.0 Hz, 1 H, 2-H), 6.51 (s, 1 H, 10-H), 7.48 (dd, J = 8.4, 7.6 Hz, 2 H, Ph_{meta}), 7.61 (tt, J = 7.6, 1.4 Hz, 1 H, Ph_{para}), 8.08 (dd, J = 8.4, 1.4 Hz, 2 H, Ph_{ortho}) ppm; δ(glycan) = 0.71−0.5 [m, 18 H, Si(CH_2CH_3)$_3$], 0.99−0.87 [m, 27 H, Si(CH_2CH_3)$_3$], 1.62 (dd, J = 12.8, 4.2 Hz, 1 H, 2-H_{eq}), 2.21 (ddd, J = 12.8, 11.7, 3.0 Hz, 1 H, 2-H_{ax}), 3.52 (dt, J = 6.2, 1.0 Hz, 1 H, 5-H), 3.66 (d, J = 6.2 Hz, 2 H, 6-H), 3.86 (dd, J = 2.0, 1.0 Hz, 1

H, 4-H), 4.10 (ddd, J = 11.7, 4.2, 2.0 Hz, 1 H, 3-H), 5.13 (d, J = 3.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ(aglycon) = 5.8−4.2 [t, Si(CH_2CH_3)$_3$], 7.0−6.6 [q, Si(CH_2CH_3)$_3$], 10.1 (q, C-19), 13.9 (q, C-18), 20.8 (q, CH_3CO_2− at position 10), 21.5 (q, C-17), 22.4 (q, CH_3CO_2− at position 4), 26.4 (q, C-16), 33.4 (t, C-14), 37.1 (t, C-6), 43.2 (s, C-15), 46.9 (d, C-3), 58.3 (s, C-8), 67.3 (d, C-13), 72.2 (d, C-7), 75.1 (d, C-2), 75.2 (d, C-10), 76.5 (t, C-20), 79.7 (s, C-1), 80.9, (s, C-4), 84.2 (d, C-5), 128.6 (d, 2 C, Ph$_{meta}$), 129.4 (s, Ph$_{ipso}$), 130.1 (d, 2 C, Ph$_{ortho}$), 131.9 (s, C-11), 133.6 (d, Ph$_{para}$), 143.5 (s, C-12), 167.1 (s, PhCO_2−), 169.2 (s, CH_3CO_2− at position 10), 171.1 (s, CH_3CO_2− at position 4), 202.3. (s, C-9) ppm; δ(glycan) = 5.8−4.2 [t, Si(CH_2CH_3)$_3$], 7.0−6.6 [q, Si(CH_2CH_3)$_3$], 35.1 (t, C-2), 62.9 (t, C-6), 67.4 (d, C-3), 70.4 (d, C-4), 73.7 (d, C-5), 93.8 (d, C-1) ppm. HRMS ($C_{61}H_{104}O_{15}Si_4$): calcd. 1189.6531 [M + H]$^+$, found 1189.6536.

β-28: Second fraction (R_f = 0.37; ethyl acetate/petroleum ether, 1:4): 4.7 mg, 4 μmol; 4.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ(aglycon) = 0.71−0.5 [m, 6 H, Si(CH_2CH_3)$_3$], 0.99−0.87 [m, 9 H, Si(CH_2CH_3)$_3$], 1.39, 1.07 (2s, 6 H, CH_3-16, CH_3-17), 1.68 (s, 1 H, OH), 1.80−1.72 (m, 1 H, 6′-H), 1.87 (s, CH_3-19), 2.17 (s, 3 H, CH_3-10), 2.18 (s, 3 H, CH_3CO_2− at position 18), 2.27−2.05 (m, 2 H, 14-H, 14-H′), 2.26 (s, 3 H, CH_3CO_2− at position 4), 2.50−2.37 (m, 1 H, 6-H), 3.83 (d, J = 7.0 Hz, 1 H, 3-H), 4.15, 4.07 (2d, J = 12.8 Hz, 2 H, 20-H, 20-H′), 4.38 (dd, J = 10.6, 4.4 Hz, 1 H, 7-H), 5.14 (dd, J = 10.4, 2.8 Hz, 1 H, 5-H), 5.20−5.15 (m, 1 H, 13-H), 5.74 (d, J = 7.0 Hz, 1 H, 2-H), 6.47 (s, 1 H, 10-H), 7.48 (dd, J = 8.4, 7.6 Hz, 2 H, Ph$_{meta}$), 7.60 (tt, J = 7.6, 1.4 Hz, 1 H, Ph$_{para}$), 7.79 (dd, J = 8.4, 1.4 Hz, 2 H, Ph$_{ortho}$) ppm; δ(glycan) = 0.70−0.48 [m, 18 H, Si(CH_2CH_3)$_3$], 1.02−0.85 [m, 27 H, Si(CH_2CH_3)$_3$], 1.67−1.60 (m, 1 H, 2-H$_{eq}$), 2.27−2.05 (m, 1 H, 2-H$_{ax}$), 3.68 (d, J = 7.2 Hz, 2 H, 6-H), 3.74 (dt, J = 7.2, 1.0 Hz, 1 H, 5-H), 3.90 (dd, J = 2.0, 1.0 Hz, 1 H, 4-H), 4.02−3.93 (m, 1 H, 3-H), 4.70 (d, J = 7.0 Hz, 1 H, 1-H) ppm. Not all ^{13}C NMR spectroscopic data could be collected, due to the small amount of material available.

13-*O*-Glycosylated Baccatin III 29: Tetrabutylammonium fluoride trihydrate (395 mg, 1.25 mmol) was dissolved under N_2 in THF (12.5 mL), and the mixture was treated with AcOH (0.225 mL, 3.9 mmol; 3.1 equiv. with reference to TBAF). A proportion of this solution (4 mL; 8 equiv.) was taken, glycosylated baccatin III α-**28** (60 mg, 51 μmol) was added, and the mixture was heated under reflux for 70 h. After the mixture had cooled to room temp., neutralization was achieved by addition of an aqueous solution of hydrogencarbonate. After extraction with ethyl acetate and drying of the organic phase ($MgSO_4$), the filtrate was concentrated in vacuo. The crude material was purified by column chromatography on Sephadex (acetone) followed by a second chromatographic step on silica gel (dichloromethane/MeOH, 20:1) and finally on Sephadex again (acetone) to yield α-**29** (14.9 mg, 20.3 μmol; 40.3%). $[\alpha]_D^{22}$ = +121.2 (c = 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ(aglycon) = 1.11 (s, 3 H, CH_3-17), 1.18 (s, 3 H, CH_3-16), 1.65 (s, CH_3-19), 1.90−1.82 (m, 1 H, 6-H′), 1.99 (s, 3 H, CH_3-18), 2.08 (dd, J = 15.0, 8.4 Hz, 1 H, 14-H′), 2.24 (s, 3 H, CH_3CO_2− at position 10), 2.28 (s, 3 H, CH_3CO_2− at position 4), 2.32 (dd, J = 15.0, 8.4 Hz, 1 H, 14-H), 2.54 (ddd, J = 14.4, 9.4, 6.8 Hz, 1 H, 6-H), 3.79 (d, J = 7.2 Hz, 1 H, 3-H), 4.14 (d, J = 8.4 Hz, 1 H, 20-H′), 4.31 (d, J = 8.4 Hz, 1 H, 20-H), 4.44 (dd, J = 10.6, 6.8 Hz, 1 H, 7-H), 4.96 (dd, J = 9.4, 2.4 Hz, 1 H, 5-H), 4.99 (dd, J = 8.4, 8.4 Hz, 1 H, 13-H), 5.66 (d, J = 7.2 Hz, 1 H, 2-H), 6.30 (s, 1 H, 10-H), 7.50 (dd, J = 8.4, 7.6 Hz, 2 H, Ph$_{meta}$), 7.62 (t, J = 7.6 Hz, 1 H, Ph$_{para}$), 8.08 (dd, J = 8.4, 1.4 Hz, 2 H, Ph$_{ortho}$) ppm; δ(glycan) = 1.90−1.82 (m, 1 H, 2-H$_{eq}$), 2.12−2.04 (m, 1 H, 2-H$_{ax}$), 3. 74 (ddd, J = 5.0, 4.2, 1.0 Hz, 1 H, 5-H), 3.85 (dd, J = 12.0, 4.2 Hz, 1 H, 6-H′), 3.89 (dd, J = 12.0, 5.0 Hz, 1 H, 6-H), 4.03 (dd, J = 2.6, 1.0 Hz, 1 H, 4-H), 4.10 (ddd, J = 12.0, 5.0, 2.6 Hz, 1 H, 3-H), 5.16 (d, J = 3.0 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ(aglycon) = 9.6 (q, C-19), 14.9 (q, C-18), 20.9 (q, CH_3CO_2− at position 10), 22.2 (q, C-17), 22.4 (q, CH_3CO_2− at position 4), 26.5 (q, C-16), 35.8, 35.4 (t, 2 C, C-6, C-14), 43.1 (s, C-15), 45.7 (d, C-3), 58.3 (s, C-8), 69.9 (d, C-13), 75.2 (d, C-2), 75.7 (d, C-10), 76.3 (t, C-20), 77.0 (t, C-7), 80.9, 79.9 (2 s, 2 C, C-4, C-1), 84.4 (d, C-5), 128.7 (d, 2 C, Ph$_{meta}$), 129.2 (s, Ph$_{ipso}$), 130.0 (d, 2 C, Ph$_{ortho}$), 131.6 (s, C-11), 133.8 (d, Ph$_{para}$), 145.1 (s, C-12), 171.4, 169.8, 167.0 (3 s, CH_3CO_2− at positions 4 and 10, PhCO_2−), 204.0. (s, C-9) ppm; δ(glycan) = 32.9 (t, C-2), 63.5 (t, C-6), 65.3 (d, C-3), 69.5 (d, C-4), 70.3 (d, C-5), 95.2 (d, C-1) ppm. HRMS ($C_{37}H_{48}O_{15}$): calcd. 733.3071 [M + H]$^+$, found 733.3074.

17-*O*-[4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-(1→4)-(3-*O*-benzoyl-2,6-dideoxy-β-L-*arabino*-hexopyranosyl]testosterone (31b) and 17-*O*-[4-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-(1→4)-(3-*O*-benzoyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)]testosterone (31a): Polymer-bound reagent **2** (2 mg) was added to a mixture of testosterone (**3**) (28 mg, 0.1 mmol) and disaccharide **30** (44 mg, 0.1 mmol) in dry acetonitrile (5 mL). The resulting suspension was shaken at room temp. for 24 h, and the reaction was terminated by addition of Amberlite A-21 (10 mg). The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The anomeric isomers were finally separated by flash column chromatography (ethyl acetate/petroleum ether, 1:5) to afford two fractions.

31b: First fraction: 10.3 mg, 14 μmol, 14%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.7 (m, 43 H, 2 × CH_3CO, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H), 3.44 (dq, J = 9.0, 6.1 Hz, 1 H, 5-H′), 3.59 (dd, J = 9.0, 9.0 Hz, 1 H, 4-H′), 3.69 (t, J = 8.3 Hz, 1 H, 17-H), 3.93 (dq, J = 9.6, 6.2 Hz, 1 H, 5-H′′), 4.56 (dd, J = 9.5, 1.7 Hz, 1 H, 1-H′), 4.65 (dd, J = 9.6, 9.5 Hz, 1 H, 4-H′′), 5.15 (m, 2 H, 3-H′, 3-H′′), 5.23 (d, J = 3.3 Hz, 1 H, 1-H′′), 5.72 (s, 1 H, 4-H), 7.45 (dd, J = 7.5, 7.5 Hz, 2 H, Ph$_{meta}$), 7.58 (dd, J = 7.5, 7.5 Hz, 1 H, Ph$_{para}$), 7.99 (d, J = 7.5 Hz, 2 H, Ph$_{ortho}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 11.6 (q, C-18), 17.3 (q, C-6′′), 17.4 (q, C-19), 18.6 (q, C-6′), 20.6 (t, C-11), 20.8, 20.9 (2 q, 2 × COCH_3), 23.2 (t, C-15), 27.5 (t, C-16), 31.6 (t, C-7), 32.8 (t, C-6), 34.0 (t, C-2), 35.3 (d, C-8), 35.5 (t, C-2′′), 35.7 (t, C-1), 36.6 (t, C-2′), 37.1 (t, C-12), 38.7 (s, C-10), 42.4 (s, C-13), 50.6 (d, C-14), 54.0 (d, C-9), 66.4 (d, C-5′′), 68.5(d, C-3′′), 70.5 (d, C-5′), 74.7 (d, C-4′′), 75.0 (d, C-3′), 79.6 (d, C-4′), 87.2 (d, C-17), 97.7 (d, C-1′′), 98.1 (d, C-1′), 123.8 (d, C-4), 128.6 (d, Ph$_{meta}$), 129.5 (d, Ph$_{ortho}$), 129.7 (d, Ph$_{para}$), 133.3 (s, Ph$_{ipso}$), 165.4 (s, COPh), 170.0, 170.1 (2s, COCH$_3$), 171.3 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{42}H_{56}O_{11}$): calcd. 737.3901 [M + H]$^+$, found 737.3904.

31a: Second fraction: 33.9 mg, 46 μmol; 46%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.7 (m, 43 H, 2 × CH_3CO, 6-H′, 6-H′, 2-H′, 2-H′′, testosterone-H), 3.52 (t, J = 8.5 Hz, 1 H, 8.5 Hz, 17-H), 3.55 (dd, J = 9.3, 9.1 Hz, 1 H, 4-H′), 3.91 (dq, J = 9.3, 6.2 Hz, 1 H, 5-H′), 3.96 (dq, J = 9.5, 6.2 Hz, 1 H, 5-H′′), 4.66 (dd, J = 9.5, 9.2 Hz, 1 H, 4-H′′), 4.91 (d, J = 2.7 Hz, 1 H, 1-H′), 5.19 (ddd, J = 11.4, 9.2, 5.1 Hz, 1 H, 3-H′′), 5.24 (d, J = 3.1 Hz, 1 H, 1-H′′), 5.47 (ddd, J = 11.2, 9.1, 5.1 Hz, 1 H, 3-H′), 5.73 (s, 1 H, 4-H), 7.45 (dd, J = 7.5, 7.5 Hz, 2 H, Ph$_{meta}$), 7.58 (dd, J = 7.5, 7.5 Hz, 1 H, Ph$_{para}$), 8.0 (d, J = 7.5 Hz, 2 H, Ph$_{ortho}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 11.7 (q, C-18), 17.3 (q, C-6′′), 17.4 (q, C-19), 18.4 (q, C-6′), 20.6 (t, C-11), 20.8, 20.9 (2 q, COCH_3), 23.4 (t, C-15), 28.5 (t, C-16), 31.6 (t, C-7), 32.8 (t, C-6), 33.9 (t, C-2), 35.4 (d, C-8), 35.5 (t, C-2′), 35.7 (t, C-2′′), 35.7 (t, C-1), 37.2 (t, C-12), 38.7 (s, C-10), 42.9 (s, C-13), 50.3 (d, C-14),

53.9 (d, C-9), 66.4 (d, C-5′), 66.4 (d, C-5′′), 68.5 (d, C-3′′), 73.4 (d, C-3′), 74.8 (d, C-4′′), 80.6 (d, C-4′), 87.5 (d, C-17), 97.4 (d, C-1′), 97.8 (d, C-1′′), 123.8 (d, C-4), 128.6 (d, Ph_{meta}), 129.5 (d, Ph_{ortho}), 129.9 (d, Ph_{para}), 133.2 (s, Ph_{ipso}), 165.4(s, *C*OPh), 170.0, 170.1 (2 s, 2 × *C*OCH_3), 171.3 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{42}H_{56}O_{11}$): calcd. 737.3901 [M + H]$^+$, found 737.3903.

4-*O*-Acetyl-α-L-*erythro*-hex-2-enopyranosyl Azide (33a), 4-*O*-Acetyl-β-L-*erythro*-hex-2-enopyranosyl Azide (33b), 4-*O*-Acetyl-1,5-anhydro-3-azido-2,3,6-trideoxy-L-*ribo*-hex-1-enitol (34a) and 4-*O*-Acetyl-1,5-anhydro-3-azido-2,3,6-trideoxy-L-*arabino*-hex-1-enitol (34b): 3,4-Di-*O*-acetyl-L-rhamnal (**32**; 1 g, 4.7 mmol) and solid NaN_3 (0.79 g, 12 mmol) were suspended in absol. acetonitrile (10 mL), and powdered molecular sieves (4 Å, 1 g) were added. After the mixture had been cooled to −30 °C, boron trifluoride−diethyl ether (1.35 mL, 10 mmol) was slowly added dropwise over 30 min. The suspension was stirred at the same temperature for another 1 h, and sodium hydrogencarbonate (1 g) was added to the reaction mixture for neutralization. The mixture was allowed to warm to room temp. over 30 min while stirring was continued. The resulting slurry was filtered and washed with ethyl acetate, and the combined filtrates were concentrated. The crude material obtained was dissolved in ethyl acetate and washed with brine. The organic phase was separated, and the solvent was removed under reduced pressure. The crude product mixture was purified by column chromatography (ethyl acetate/petroleum ether, 1:10) to yield **33a**, **33b**, **34a** and **34b** (0.9 g, 4.6 mmol, 98% yield) as a colourless oil, which was directly subjected to the subsequent reaction. The spectroscopic data are identical to those reported in the literature.[24−26]

Testosteryl 3-Azido-2,3,6-trideoxy-α-L-*allo*-pyranoside (36a) and Testosteryl 3-Azido-2,3,6-trideoxy-β-L-*allo*-pyranoside (36b): Polymer-bound reagent **2** (2 mg) was added to a stirred solution of testosterone (**3**) (73 mg, 0.25 mmol) and the azidoglycal mixture **33a/33b/34a/33b** (50 mg, 0.25 mmol) in dry dichloromethane (5 mL). The stirring was continued for 24 h, and was followed by addition of Amberlite A-21 (10 mg). The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The products were finally separated by flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to afford the α-configured glycoconjugate (16 mg, 33 μmol; 13.2%) and the β-glycoconjugate (15 mg, 31 μmol; 12.4%), together with a mixture of the two diastereomers (26 mg, 54 μmol; 21.6%). Both anomeric glycosidation products were separately deacetylated by use of Amberlite A-26 (hydroxide form) with **35** in methanol. This was achieved by dissolving the respective compounds (16 mg, 33 μmol, and 15 mg, 31 μmol) separately in methanol (5 mL) and addition of Amberlite A-26 (hydroxide form; 0.1 g) to each reaction vessel. The resulting suspensions were shaken for 24 h, after which the reaction mixtures were filtered. The filtrates were concentrated under reduced pressure to afford alcohols **36a** (11.2 mg, 25.3 μmol; 82%) and **36b** (11.6 mg, 26.2 μmol, 80% yield).

36a: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.7 (m, 32 H, 6-H′, 2-H′ testosterone-H), 3.45 (dd, *J* = 8.5, 8.5 Hz, 1 H, 17-H), 4.15 (ddd, *J* = 3.4, 3.4, 3.4 Hz, 1 H, 3-H′), 4.22 (dq, *J* = 9.6, 6.2 Hz, 1 H, 5-H′), 4.57 (dd, *J* = 9.6, 3.4 Hz, 1 H, 4-H′), 4.83 (d, *J* = 3.8 Hz, 1 H, 1-H′), 5.72 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 11.6 (q, C-18), 17.1 (q, C-6′), 17.4 (q, C-19), 20.6 (t, C-11), 20.8 (q, CO*C*H_3), 23.4 (t, C-15), 28.6 (t, C-16), 31.5 (t, C-7), 32.3 (t, C-2′), 32.8 (t, C-6), 33.9 (t, C-2), 35.4 (d, C-8), 35.7 (t, C-1), 37.0 (t, C-12), 38.6 (s, C-10), 43.0 (s, C-13), 50.1 (d, C-14), 53.9 (d, C-9), 55.0 (d, C-3), 62.0 (d, C-5′), 73.5 (d, C-4′), 88.4 (d, C-17), 96.3 (d, C-1′), 123.8 (d, C-4), 170.1 (s, C=O), 171.2 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{25}H_{37}N_3O_4$): calcd. 444.2862 [M + H]$^+$, found 444.2865.

36b: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.7 (m, 32 H, 6-H′, 2-H′ testosterone-H), 1.20 (d, *J* = 6.2 Hz, 3 H, 6-H′), 1.68 (ddd, *J* = 14.3, 13.9, 4.8 Hz, 1 H), 2.26 (ddd, *J* = 14.3, 4.0, 2.3 Hz, 1 H), 3.64 (dd, *J* = 8.4, 8.4 Hz, 1 H, 17-H), 3.89 (dq, *J* = 9.3, 6.2 Hz, 1 H, 5-H′), 4.16 (ddd, *J* = 3.5, 3.5, 3.5 Hz, 1 H, 3-H′), 4.65 (dd, *J* = 9.3, 3.5 Hz, 1 H, 4-H′), 4.66 (dd, *J* = 9.2, 2.3 Hz, 1 H, 1-H′), 5.71 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 11.6 (q, C-18), 17.4 (q, C-19), 17.9 (q, C-6′), 20.6 (t, C-11), 20.6 (q, CO*C*H_3), 23.1 (t, C-15), 27.5 (t, C-16), 31.6 (t, C-7), 32.8 (t, C-6), 33.9 (t, C-2), 35.5 (d, C-8), 35.7 (t, C-1), 36.6 (t, C-2′), 37.0 (t, C-12), 38.6 (s, C-10), 42.4 (s, C-13), 50.6 (d, C-14), 53.9 (d, C-9), 58.0 (d, C-3′), 68.0 (d, C-5′), 74.4 (d, C-4′), 87.2 (d, C-17), 96.4 (d, C-1′), 123.8 (d, C-4), 170.1 (s, *C*=O), 171.2 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{25}H_{37}N_3O_4$): calcd. 444.2862 [M + H]$^+$, found 444.2865.

17-*O*-[(2-Deoxy-3,4-di-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)-(1→4)-(3-azido-2,3,6-dideoxy-α-L-*allo*-pyranosyl)]testosterone (37a): Polymer-bound reagent **2** (0.5 mg, 1.5 mol %) was added to a stirred solution of **36a** (11.2 mg, 25.3 μmol) and glycal **22** (10 mg, 2.66 mmol) in dry dichloromethane (5 mL). The stirring was continued for 24 h, and was followed by addition of Amberlite A-21 (5 mg). The mixture was filtered through a pad of Celite, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) to afford **37a** (16.1 mg, 20 μmol; 80%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.5 (m, 67 H, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H, 2 × TES), 3.37 (dd, *J* = 9.0, 3.2 Hz, 1 H, 4-H′), 3.45 (dd, *J* = 8.5, 8.5 Hz, 1 H, 17-H), 3.59 (s, 1 H, 4-H′′), 3.74 (q, *J* = 6.3 Hz, 1 H, 5-H′′), 3.96 (ddd, *J* = 11.6, 2.4, 4.1 Hz, 1 H, 3-H′′), 4.12 (m, 2 H, 3-H′, 5-H′), 4.80 (d, *J* = 3.8 Hz, 1 H, 1-H′), 5.09 (d, *J* = 3.1 Hz, 1 H, 1-H′′), 5.72 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 4.8, 5.2, 6.8, 7.0 (2 t, 2 q, 2 × TES), 11.7 (q, C-18), 17.3 (q, C-6′′), 17.4 (q, C-6′), 17.8 (q, C-19), 20.6 (t, C-11), 23.4 (t, C-15), 28.7 (t, C-16), 31.6 (t, C-7), 32.3 (t, C-2′′), 32.3 (t, C-2′), 32.8 (t, C-6), 33.9 (t, C-2), 35.5 (d, C-8), 35.7 (t, C-1), 37.1 (t, C-12), 38. 7 (s, C-10), 43.0 (s, C-13), 50.2 (d, C-14), 52.9 (d, C-5′), 54.0 (d, C-9), 63.2 (d, C-3′), 67.5 (d, C-3′′), 68.3 (d, C-5′′), 73.4 (d, C-4′′), 74.2 (d, C-4′), 88.2 (d, C-17), 93.4 (d, C-1′′), 96.5 (d, C-1′), 123.8 (d, C-4), 171.2 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{43}H_{75}N_3O_7Si_2$): calcd. 802.5222 [M + H]$^+$, found 802.5218.

17-*O*-[(2-Deoxy-3,4-di-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)-(1→4)-(3-azido-2,3,6-dideoxy-β-L-*allo*-pyranosyl)]testosterone (37b): The β-configured glycoconjugate **36b** (11.6 mg, 26 μmol) was transformed into disaccharide **37b** (14.6 mg, 18.2 μmol; 70%) under conditions identical to those described for glycoside **36a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.5−0.7 (m, 67 H, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H, 2 × TES), 3.37 (dd, *J* = 9.0, 3.2 Hz, 1 H, 4-H′), 1.16 (d, *J* = 6.3 Hz, 3 H, 6-H′′), 1.25 (d, *J* = 6.2 Hz, 3 H, 6-H′), 3.53 (dd, *J* = 8.9, 3.2 Hz, 1 H, 4-H′), 3.60 (br. s, 1 H, 4-H′′), 3.64 (dd, *J* = 8.3, 8.3 Hz, 1 H, 17-H), 3.79 (br. q, *J* = 6.3 Hz, 1 H, 5-H′′), 3.85 (dq, *J* = 8.9, 6.2 Hz, 1 H, 5-H′), 3.95 (ddd, *J* = 11.7, 4.1, 2.4 Hz, 1 H, 3-H′′), 4.17 (ddd, *J* = 3.2, 3.2, 3.2 Hz, 1 H, 3-H′), 4.65 (dd, *J* = 9.0, 1.5 Hz, 1 H, 1-H′), 5.08 (d, *J* = 3.1 Hz, 1 H, 1-H′′), 5.72 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 4.8, 5.2, 6.8, 7.0 (2 t, 2 q, 2 × TES), 11.6 (q, C-18), 17.2 (q, C-6′′), 17.4 (q, C-19), 18.5 (q, C-6′), 20.6 (t, C-11), 23.2 (t, C-15), 27.5 (t, C-16), 31.6 (t, C-7), 31.9 (t, C-2′′), 32.8 (t, C-6), 34.0 (t, C-2), 35.5 (d, C-8), 35.7 (t, C-2′), 35.7 (t, C-1), 36.6 (t, C-12), 38.7 (s, C-10), 42.4 (s, C-13), 50.6 (d, C-14), 54.0 (d, C-9), 55.8

(d, C-3′), 67.4 (d, C-3′′), 68.4 (d, C-5′′), 69.0 (d, C-5′), 73.4 (d, C-4′′), 75.4 (d, C-4′), 87.1 (d, C-17), 94.3 (d, C-1′′), 96.6 (d, C-1′), 123.8 (d, C-4), 171.3 (s, C-5), 199.5 (s, C-3) ppm. HRMS ($C_{43}H_{75}N_3O_7Si_2$): calcd. 802.5222 $[M + H]^+$, found 802.5221.

17-*O*-[(2-Dideoxy-α-L-*fuco*-pyranosyl)-(1→4)-(3-amino-2,3,6-dideoxy-α-L-*allo*-pyranosyl)]testosterone (38a): A solution of TBAF in THF (1 M, 60 μL, 60 μmol) was added to a solution of glycoconjugate **37a** (16.1 mg, 20 μmol) in THF (1 mL). After the solution had been stirred for 4 h at room temp., polymer-bound diphenylphosphane **1** (20 mg, 1.1 mmol/g) was added. The suspension was stirred at room temperature for 24 h and the polymers were filtered off. The resulting filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (ethyl acetate/EtOH, 6:1) to yield glycoconjugate **38a** (10 mg, 18.3 μmol; 91%) as a colourless film. ^{1}H NMR (500 MHz): δ = 2.6−0−7 (m, 37 H, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H), 3.46 (dd, *J* = 9.4, 3.8 Hz, 1 H, 4-H′), 3.52 (dd, *J* = 7.1, 3.8 Hz, 1 H, 3-H′), 3.59 (t, *J* = 8.5 Hz, 1 H, 17-H), 3.61 (br. d, *J* = 2.6 Hz, 1 H, 4-H′′), 3.98 (m, 3 H, 3-H′′, 5′-H, 5′′-H), 4.92 (d, *J* = 2.8 Hz, 1 H, 1-H′), 5.10 (d, *J* = 3.3 Hz, 1 H, 1-H′′), 5.75 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_3OD, δ = 49 ppm): δ = 12.2 (q, C-18), 17.7, 17.1 (2 q, C-6′, C-6′′), 18.6 (q, C-19), 21.7 (t, C-11), 23.0 (q, *C*H_3COO^-),24.3 (t, C-15), 29.8 (t, C-16), 32.8 (t, C-7), 33.0 (t, C-2′′), 33.9 (t, C-6), 34.2 (t, C-2′), 34.7 (t, C-2), 36.7 (d, C-8), 36.8 (t, C-1), 38.3 (t, C-12), 40.0 (s, C-10), 44.0 (s, C-13), 45.6 (d, C-3′′), 51.3 (d, C-14), 55.4 (d, C-9), 63.4 (d, C-5′), 66.8, 68.5 (2 d, C-3′′, C-5′′), 72.1 (d, C-4′′), 76.3 (d, C-4′), 89.7 (d, C-17), 95.4 (d, C-1′′), 99.1 (d, C-1′), 124.2 (d, C-4), 175.0 (s, C-5), 202.3 (s, C-3) ppm. LC-LRMS (ESI): *m*/*z* (%) = 546.34 (60) $[M - H]^-$. HRMS ($C_{31}H_{48}NO_7$): calcd. 546.3431, found 546.3431.

17-*O*-[(2-Dideoxy-α-L-*fuco*-pyranosyl)-(1→4)-(3-amino-2,3,6-dideoxy-β-L-*allo*-pyranosyl)]testosterone (38b): The β-configured glycoconjugate **37b** (14.6 mg, 18.2 μmol) was transformed into disaccharide **38b** (7.1 mg, 13 μmol; 71%) under reaction conditions identical to those described for the preparation of glycoside **38a**. ^{1}H NMR (500 MHz, CD_3OD): δ = 2.5−0.7 (m, 37 H, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H), 3.53 (dd, *J* = 7.0, 3.6 Hz, 1 H, 4-H′), 3.61 (br. s, 1 H, 4-H′′), 3.73 (br. q, *J* = 6.2 Hz, 1 H, 5-H′′), 3.77 (dd, *J* = 8.1, 8.1 Hz, 1 H, H-17), 3.97 (m, 3 H, 3-H′, 3-H′′, 5-H′), 4.93 (dd, *J* = 7.1, 2.6 Hz, 1 H, 1-H′), 5.07 (d, *J* = 3.4 Hz, 1 H, 1-H′′), 5.75 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_3OD, δ = 49 ppm): δ = 12.1 (q, C-18), 17.1 (q, C-6′′), 17.7 (q, C-19), 19.8 (q, C-6′), 21.7 (q, *C*H_3COO^-), 22.7 (t, C-11), 24.2 (t, C-15), 28.3 (t, C-16), 32.9 (t, C-2′′), 33.0 (t, C-7), 33.9 (t, C-6), 34.7 (t, C-2), 35.0 (t, C-2′), 36.7 (d, C-8), 36.8 (t, C-1), 38.1 (t, C-12), 40.0 (s, C-10), 43.6 (s, C-13), 45.5 (d, C-5′), 51.9 (d, C-14), 55.5 (d, C-9), 66.8 (d, C-5′′), 68.5 (d, C-3′′), 70.7 (d, C-3′), 72.1 (d, C-4′′), 77.1 (d, C-4′), 87.3 (d, C-17), 97.0 (d, C-1′), 97.7 (d, C-1′′), 124.1 (d, C-4), 175.1 (s, C-5), 202.3 (s, C-3) ppm. HRMS ($C_{31}H_{49}NO_7$): calcd. 547.3497 $[M + H]^+$, found 547.3512.

17-*O*-[(2-Deoxy-3,4-di-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)-(1→4)-(2-deoxy-3-*O*-triethylsilyl-α-L-*fuco*-pyranosyl)]testosterone (39): Polymer-bound reagent **2** (1 mg) and LiBr (5 mg) were added to a solution of fucal **20** (24 mg, 0.1 mmol) and testosterone (**3**) (28 mg, 0.1 mmol) in dichloromethane (3 mL). The reaction mixture was shaken at room temp. for 2 h, after which di-*O*-silylated L-fucal **22** (40 mg, 0.12 mmol) in dichloromethane (1 mL) was added. The resulting suspension was shaken at room temp. for another 4 h, and the reaction was finally terminated after addition of Amberlite A-21 (10 mg). The polymers were filtered off and washed with ethyl acetate, and the combined filtrates were concentrated under reduced pressure. The crude material was finally purified by column chromatography on silica gel (ethyl acetate/petroleum ether, 1:4) to afford disaccharide **39** (77.5 mg, 87 μmol; 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.5−0.5 (m, 82 H, 3 × TES, 6-H′, 6-H′′, 2-H′, 2-H′′, testosterone-H), 3.45 (t, *J* = 8.2 Hz, 1 H, 17-H), 3.55 (br. s, 1 H, 4-H′′), 3.65 (br. d, *J* = 2.4 Hz, 1 H, 4-H′), 3.80 (br. q, *J* = 6.8 Hz, 1 H, 5-H′), 4.10 (m, 2 H, 3-H′, 3-H′′), 4.30 (br. q, *J* = 6.3 Hz, 1 H, 5-H′′), 4.89 (d, *J* = 2.9 Hz, 1 H, 1-H′′), 5.09 (d, *J* = 2.8 Hz, 1 H, 1-H′), 5.72 (s, 1 H, 4-H), 5.09 (d, *J* = 2.8 Hz, 1 H, 1-H′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, $CDCl_3$, δ = 77 ppm): δ = 4.8 4.9, 5.1, 5.2, 6.7, 6.8, 7.0, (3 × TES), 11.5 (q, C-18), 17.4 (q, C-6′′), 17.5 (q, C-6′), 17.9 (q, C-19), 20.6 (t, C-11), 23.4 (t, C-15), 26.9(t), 28.6 (t, C-16), 31.5 (t, C-7), 32.9 (t, C-6), 33.9 (t, C-2), 34.3 (t, C-2′′), 35.4 (d, C-8), 35.5 (t, C-2′), 35.7 (t, C-1), 37.1 (t, C-12), 38.6 (s, C-10), 42.8 (s, C-13), 50.1 (d, C-14), 53.9 (d, C-9), 66.9, 67.3, 67.6, 67.8, 73.9, 74.9, (6d, C-3′, C-4′, C-5′, C-3′′, C-4′′, C-5′′), 87.5 (d, C-17), 97.7 (d, C-1′), 98.9 (d, C-1′′), 123.8 (d, C-4), 171.1 (s, C-5), 199.4 (s, C-3) ppm. HRMS ($C_{48}H_{86}O_8Si_3$): calcd. 890.5934 $[M + H]^+$, found 890.5937.

17-*O*-[(2-Dideoxy-α-L-*fuco*-pyranosyl)-(1→4)-(2-dideoxy-α-L-*fuco*-pyranosyl)]-testosterone (40): Glycoconjugate **39** (67 mg, 75 μmol) was mixed with polymer-bound TBAT **42** (200 mg, 10 equiv.) in acetonitrile (10 mL). This suspension was shaken at room temp. for 48 h and the polymer was filtered off. The solid was washed with methanol, and the combined filtrates were concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (ethyl acetate; R_f = 0.14) to afford compound **40** (29 mg, 52 μmol; 70%). ^{1}H NMR (500 MHz, CD_3OD): δ = 2.5−0.7 (m, 31 H, 2-H′, 2-H′, testosterone-H), 1.26, 1.21 (2d, *J* = 6.5 and *J* = 6.4 Hz, 6 H, 6-H′, 6-H′′), 3.54 (t, *J* = 8.5 Hz, 1 H, 17-H), 3.59 (br. d, *J* = 2.2 Hz, 1 H, 4-H′′), 3.62 (br. d, *J* = 2.0 Hz, 1 H, 4-H′), 3.95 (br. q, *J* = 6.5 Hz, 1 H, 5-H′), 3.98 (ddd, *J* = 11.8, 4.9, 2.0 Hz, 1 H, 3-H′), 4.04 (ddd, *J* = 11.8, 5.9, 2.2 Hz, 1 H, 3-H′′), 4.28 (br. q, *J* = 6.4 Hz, 5-H′′), 4.95 (d, *J* = 3.7 Hz, 1 H, 1-H′), 4.96 (d, *J* = 4.6 Hz, 1 H, 1-H′′), 5.73 (s, 1 H, 4-H) ppm. ^{13}C NMR (125 MHz, CD_3OD, δ = 49 ppm): δ = 12.1 (q, C-18), 17.1, 17.5 (2 q, C-6′, C-6′′), 17.7 (q, C-19), 21.8 (t, C-11), 24.3 (t, C-15), 29.6 (t, C-16), 32.8 (t, C-7), 33.3 (t, C-2′′), 33.9 (t, C-6), 34.7 (2 t, C-2′, C-2), 36.7 (d, C-8), 36.8 (t, C-1), 38.4 (t, C-12), 40.0 (s, C-10), 44.0 (s, C-13), 51.5 (d, C-14), 55.5 (d, C-9), 66.7, 66.7 (2 d, C-3′′, C-3′), 68.1 (d, C-5′), 68.5 (d, C-5′′), 72.3 (d, C-4′′), 81.7 (d, C-4′), 88.6 (d, C-17), 99.9 (d, C-1′), 101.4 (d, C-1′′), 124.1 (d, C-4), 175.1 (s, C-5), 202.3 (s, C-3) ppm. LCMS (ESI): *m*/*z* (%) = 547.33 (90) $[M - H]^-$, 548.33 (25) [M]. HRMS ($C_{31}H_{47}O_8$): calcd. 547.3271$[M + H]^+$, found 547.3278.

Acknowledgments

This work was supported by the DFG (SFB 416, project B2) and the Fonds der Chemischen Industrie. D. K. thanks the Ministerium für Wissenschaft and Kultur (MWK), Niedersachsen for a scholarship. We thank Markus Kalesse (Hannover) for providing alcohol **6**. We are grateful to AnalytiCon Discovery (Potsdam) for a donation of deacetyl-baccatin III.

[1] [1a] I. R. Baxendale, R. I. Storer, S. V. Ley, in *Polymeric Materials in Organic Synthesis and Catalysis* (Ed.: M. R. Buchmeiser), Wiley-VCH, **2003**, pp. 53−132. [1b]A. Kirschning, H. Monenschein, R. Wittenberg, *Angew. Chem. Int. Ed.* **2001**, *40*, 650−679. [1c] S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer, S. J. Taylor, *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815−4195. [1d] D. H. Drewry, D. M. Coe, S. Poon, *Med. Res. Rev.* **1999**, *19*, 97−148.

[2] For reviews on solid-supported catalysts, see ref.[1] and: [2a] W. Solodenko, T. Frenzel, A. Kirschning, in *Polymeric Materials in Organic Synthesis and Catalysis* (Ed.: M. R. Buchmeiser), Wiley-VCH, **2003**, pp. 201−240. [2b] S. V. Ley, I. R. Baxendale, in *Supported Catalysts and their Applications* (Ed.: D. C. Sherrington, A. P. Kybett), The Royal Society of Chemistry Proceedings, **2001**. [2c]B. Clapham, T. S. Reger, K. D. Janda, *Tetrahedron* **2001**, *57*, 4637−4662. [2d] B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648−2689; *Angew. Chem. Int. Ed.* **1999**, *38*, 2476−2514. [2e] E. Lindner, T. Schneller, F. Auer, H. A. Mayer, *Angew. Chem.* **1999**, *111*, 2288−2309; *Angew. Chem. Int. Ed.* **1999**, *38*, 2154−2174. [2f] J. H. Cameron, in *Solid State Organometallic Chemistry: Methods and Applications* (Eds.: M. Gielen, R. Willem, B. Wrackmeyer), Wiley, Chichester **1999**, pp. 473−519. [2g]J. H. Clark, D. J. Macquarrie, *Chem. Soc. Rev.* **1996**, 303−310. [2h] D. C. Bailey, S. H. Langer, *Chem. Rev.* **1981**, *81*, 109−148.

[3] [3a] Recoverable Catalysts and Reagents, J. A. Gladysz, *Chem. Rev.* **2002**, *102*, 3215−3216. [3b] C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275−3300.

[4] A. Kirschning, M. Jesberger, A. Schönberger, *Org. Lett.* **2001**, *3*, 3623−3626.

[5] [5a] J. Jaunzems, G. Sourkouni-Argirusi, M. Jesberger, A. Kirschning, *Tetrahedron Lett.* **2003**, *44*, 637−639. [5b] J. Jaunzems, E. Hofer, M. Jesberger, G. Sourkouni-Argirusi, A. Kirschning, *Angew. Chem. Int. Ed.* **2003**, *42*, 1166−1170.

[6] R. N. MacCoss, P. E. Brennan, S. V. Ley, *Org. Biomol. Chem.* **2003**, *1*, 2029−2031.

[7] H. Paulsen, O. Lockhoff, *Chem. Ber.* **1981**, *114*, 3102−3114.

[8] J. Capillon, A. Richard, R. Audebert, C. Quivoron, *Polym. Bull.* **1985**, *13*, 185−192.

[9] [9a] M. Schwieter, *Helv. Chim. Acta* **1962**, *45*, 541−549. [9b] H. J. Bestmann, *Justus Liebigs Ann. Chem.* **1967**, *709*, 105−116. [9c] V. Bolitt, C. Mioskowski, d-S. Shin, J. R. Falck, *Tetrahedron Lett.* **1988**, 4583−4586. [9d] V. Bolitt, C. Mioskowski, S.-G. Lee, J. R. Falck, *J. Org. Chem.* **1990**, *55*, 5812−5813.

[10] The first mention of the use of 2,3-dihydropyran can be found in: R. Paul, *Bull. Soc. Chim. Fr.* **1934**, *1*, 971−980. [10a] G. F. Woods, D. N. Kramer, *J. Am. Chem. Soc.* **1947**, *69*, 2246. [10b] W. E. Parham, E. L. Anderson, *J. Am. Chem. Soc.* **1948**, *70*, 4187−4189.

[11] [11a] T. W. Greene, P. G. M. Wuts, in *Protective Groups in Organic Synthesis*, 3rd ed., Wiley-Interscience, New York, **1999**. [11b] P. Kocienski, in *Protecting Groups*, Thieme Verlag, Stuttgart, New York, **2003**.

[12] [12a] B. S. Babu, K. K. Balasubramanian, *Tetrahedron Lett.* **1998**, *39*, 9287−9288. [12b] M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati, *Tetrahedron Lett.* **1988**, *39*, 8159−8162. [12c] A. Sidduri, M. J. Rozema, P. Knochel, *J. Org. Chem.* **1993**, *58*, 2694−2713. [12d] T. Tashiro, K. Aksaka, H. Ohrui, E. Fattorusso, K. Mori, *Eur. J. Org. Chem.* **2002**, *21*, 3659−3665.

[13] [13a] A. P. C. Chen, Y.-H. Chen, H.-P. Liu, Y.-C. Li, C.-T. Chen, P.-H. Liang, *J. Am. Chem. Soc.* **2002**, *124*, 15217−15224. [13b] N. Nishitani, K. Yamakawa, *Tetrahedron Lett.* **1991**, *32*, 387−390.

[14] M. Hoskovec, A. Luxova, A. Svatos, W. Boland, *Tetrahedron* **2002**, *58*, 9193−9201.

[15] G. A. Olah, A. Husain, B. P. Singh, *Synthesis* **1985**, 703−704.

[16] [16a] R. U. Lemieux, S. Levine, *Can. J. Chem.* **1964**, *42*, 1473. [16b] R. U. Lemieux, A. R. Morgan, *Can. J. Chem.* **1965**, *43*, 2190. [16c] J. Thiem, H. Karl, J. Schwenter, *Synthesis* **1978**, *696*. [16d] J. Thiem, H. Karl, *Tetrahedron Lett.* **1978**, 4999. [16e] J. Thiem, P. J. Ossowowski, *Carbohydr. Chem.* **1984**, *3*, 287. [16f] J. Thiem, A. Prahst, T. Wendt, *Liebigs Ann. Chem.* **1986**, 1044. [16g] J. Thiem, W. Klaffke, *J. Org. Chem.* **1989**, *54*, 2006. [16h] R. W. Friesen, S. J. Danishefsky, *J. Am. Chem. Soc.* **1989**, *111*, 6656−6660. [16i] K. Suzuki, G. A. Sulikowski, R. W. Friesen, S. J. Danishefsky, *J. Am. Chem. Soc.* **1990**, *112*, 8895−8902. [16j] K. Tatsuta, K. Fujimoto, M. Kinoshita, S. Umezawa, *Carbohydr. Res.* **1977**, *54*, 85−104. [16k] G. Dräger, A. Garming, C. Maul, M. Noltemeyer, R. Thiericke, M. Zerlin, A. Kirschning, *Chem. Eur. J.* **1998**, *4*, 1324−1333. [16l] S. Sabesan, S. Neira, *J. Org. Chem.* **1991**, *56*, 5468−5472. [16m] V. Bolitt, C. Mioskowsky, S. G. Lee, G. R. Falck, *J. Org. Chem.* **1990**, *55*, 5812−5813. [16n] O. B. Flekhert, L. A. Baltina, G. A. Tolstikov, *J. Nat. Prod.* **2000**, *63*, 992−994.

[17] R. Ferrier, R. Hay, N. Vethaviyasar, *Carbohydr. Res.* **1973**, *27*, 55−61.

[18] [18a] G. Dräger, A. Kirschning, R. Thiericke, M. Zerlin, *Nat. Prod. Rep.* **1996**, *13*, 365−375. [18b] G. Rousseau, *Tetrahedron* **1995**, *51*, 2777−2849.

[19] [19a] S. Grabley, E. Granzer, K. Hütter, D. Ludwig, M. Mayer, R. Thiericke, G. Till, J. Wink, S. Phillips, A. Zeeck, *J. Antibiot.* **1992**, *45*, 56−65. [19b] A. Göhrt, A. Zeeck, K. Hütter, R. Hirsch, H. Kluge, R. Thiericke, *J. Antibiot.* **1992**, *45*, 66−73.

[20] [20a] K. C. Nicolaou, R. K. Guy, P. Potier, *Sci. Am.* **1996**, 84−88. [20b] K. C. Nicolaou, W.-M. Dai, R. K. Guy, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 15−44.

[21] Novel taxoids from the Chinese yew *Taxus yunnanensis*, containing xyloside at position 7 of the taxoid backbone as well as a glucoside at position 10, were reported recently. Indeed, the majority of natural taxoid glycosides have been found to be xylosides, all of them attached to C-7: [21a] S.-H. Li, H.-J. Zhang, X.-M. Niu, P. Yao, H.-D. Sun, H. H. S. Fong, *Tetrahedron* **2003**, *59*, 37−45. [21b] S.-H. Li, H.-J. Zhang, P. Yao, H.-D. Sun, H. H. S. Fong, *Phytochemistry* **2001**, *38*, 369−374. So far only two glucosides have been reported: [21c] X. J. Tong, W. S. Fang, J. Y. Zhou, C. H. He, W. M. Chen, Q. C. Fang, *J. Nat. Prod.* **1995**, *58*, 233−238.

[22] Protected paclitaxel was prepared by the procedure described in: J.-N. Denis, A. E. Greene, D. Guenard, F. Gueritte-Voegelein, L. Mangatal, P. Potier, *J. Am. Chem. Soc.* **1988**, *110*, 5917−5919.

[23] The tetrabutylammonium fluoride (TBAF) buffered solution (pH = 7) for mild silyl ether cleavage consisted of TBAF/AcOH/THF (266 mg/0.151 mL/8.4 mL). Glycobaccatin **29** showed no activity in stabilizing microtubuli, nor did it exert antitumor activity.

[24] [24a] K. Heyns, R. Holweg, *Chem. Ber.* **1978**, *111*, 1632−1645. [24b] K. Heyns, J. Feldmann, D. Hadamczyk, J. Schwentner, J. Thiem, *Chem. Ber.* **1981**, *114*, 232−239.

[25] J. Thiem, D. Springer, *Carbohydr. Res.* **1985**, *136*, 325−334.

[26] J. Boivin, M. Pais, C. Monneret, *Carbohydr. Res.* **1980**, *79*, 193−204.

[27] For recent applications of these azido sugar mixtures, see: [27a] Y. St.-Denis, J. F. Lavallee, D. Nguyen, G. Attardo, *Synlett* **1995**, 272−274. [27b] A. Kirschning, S. Domann, G. Dräger, *Synlett* **1995**, 767−769. [27c] C. Fava, R. Galeazzi, G. Mobbili, M. Orena, *Tetrahedron: Asymmetry* **2001**, *12*, 2731−2741.

[28] [28a] C. J. Handy, Y. Lam, P. DeShong, *J. Org. Chem.* **2000**, *65*, 3542−3543. [28b] A. S. Pilcher, H. L. Ammon, P. DeShong, *J. Am. Chem. Soc.* **1995**, *117*, 5166−5167. [28c] A. S. Pilcher, P. DeShong, *J. Org. Chem.* **1996**, *61*, 6901−6905.

[29] S. Colonna, A. Re, A. Gelbard, E. Cesarotti, *J. Chem. Soc., Perkin Trans. 1* **1979**, 2248−2252.

[30] Examples of polymer-supported reagents as desilylating agents for silyl ethers: [30a] J. Asakura, M. J. Robins, Y. Asaka, T. H. Kim, *J. Org. Chem.* **1996**, *61*, 9026−9027. [30b] E. C. L. Gautier, A. E. Graham, A. McKillop, S. P. Standen, R. J. K. Taylor, *Tetrahedron Lett.* **1997**, *38*, 1881−1884. [30c] C. Li, Y. Li, W. Huang, B. He, *Synth. Commun.* **1991**, *21*, 1315−1320. [30d] N. Tanaka, Y. Masaki, *Synlett* **1999**, 1960−1962.

[31] B. K. Shull, Z. Wu, M. Koreeda, *J. Carbohydr. Chem.* **1996**, *15*, 955−964.

[32] C. A. M. Alfonso, N. M. L. Vieira, W. B. Motherwell, *Synlett* **2000**, 382−384.

Received February 2, 2004

