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Epoxidation of glycals with oxone–acetone–tetrabutylammonium hydrogen sulfate: a convenient access to simple β-D-glycosides and to α-D-mannosamine and D-talosamine donors

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ABSTRACT

The addition of a phase transfer catalyst during the epoxidation of perbenzylated glycals with oxone–acetone under biphasic conditions allows their complete epoxidation. The epoxides were readily transformed into methyl 1,2-*trans*-β-D-glycosides or 1,2-*trans*-β-D-glycopyranosyl azides (D-*gluco* and-D-*galacto* configurations) bearing a free hydroxyl group at the 2-position. These glycosyl azides were converted to alkyl 1,2-*trans*-2-acetamido-2-deoxy-α-D-pyranosides or alkyl 2-allyloxycarbonylamino-2-deoxy-α-D-pyranosides (D-*manno* and D-*talo* configurations) by a Staudinger reaction and a double inversion of configuration at *C*-1 and *C*-2.

1. Introduction

There has been sustained interest in 1,2-anhydrosugars over the last 20 years due to their application in oligosaccharide synthesis.[1] Danishefsky et al. in particular have extensively developed the use of 1,2-anhydrosugars in oligosaccharide synthesis since 1989, by epoxidation of glycals and reaction with another glycal,[2] although examples of disaccharide synthesis from Brigl's anhydride (3,4,6-tri-*O*-acetyl-1,2-anhydro-α-D-glucopyranose) were reported earlier.[3] 1,2-Anhydrosugars have since been extensively used in the synthesis of *O*-glycosides and oligosaccharides,[2,4,5] as well as for glycosyl donors, such as glycosyl fluorides,[6,7] thioglycosides,[6,8] and glycosyl phosphate[5,8f,h,9] Access to *C*-glycosides have also been described in the literature,[10] and a few examples of *N*-glycosyl derivatives were reported by this route.[6,8a,11]

While other methods have been reported,[12–14] 1,2-anhydrosugars are synthesized for the most part by the direct oxidation of glycals with a solution of dimethyldioxirane (DMDO) in acetone.[15] This method gives high yields and very clean reactions, but presents a number of practical drawbacks, in particular for the synthesis of relatively simple precursors on larger scales, such as the preparation and manipulation of organic peroxides, the low concentration of the dimethyldioxirane solutions, and the difficulty in storing such solutions over long periods of time. The use of dioxiranes formed in situ from alternative ketones, such as trifluoroacetone, has been reported.[16] In 2006, Dondoni and co-workers[17] described a practical, multi-gram epoxidation of 3,4,6-tri-*O*-benzyl-D-glucal and D-galactal with dimethyldioxirane generated in situ from oxone/acetone under biphasic conditions by adapting the procedure reported in 1980 by Curci et al. to alkenes.[18] An improved, more robust procedure adding a phase transfer catalyst is reported herein.

We investigated the nucleophilic ring-opening with an azide anion, to obtain the *C*-2 unprotected 1,2-*trans*-β-D-glycopyranosyl azides, followed by transformation into a sulfonate and a Staudinger reaction in the presence of an alcohol as a practical route to the protected alkyl 2-amino-2-deoxy-α-D-*manno*- and *talo*-pyranosides. Access to glycosaminyl donors based on the migration of a nitrogen atom from *C*-1 to *C*-2, via aziridine intermediates with concomitant double inversion of stereochemistry has already been described by us[19] and Danishefsky[20] for the preparation of glycosides in a D-glucosamine series. More recently, Gin and co-workers expanded upon the *C*-2 acetamidoglycosylation reaction with glycal donors, initially described in the D-*gluco* series,[21] (transfer of an anomeric acetamidate to the *C*-2 position with the formation of an oxazoline intermediate) to the D-*manno* series with the preparation of α-glycosides of the *N*-acetyl-D-mannosamine.[22] Glycosyl azides[23] have been used for the synthesis of glycomimetics[24] and glyclusters[25] and are typically prepared by the nucleophilic displacement of glycosyl bromides under biphasic conditions.[26] *N*-Acetyl-D-mannosamine and its analogs are constituents of oligosaccharides of Gram-positive and Gram-negative bacteria,[27] as well as precursors of sialic acid and analogs,[28] while talosamine and talosaminuronic acid have been identified as components of cell walls of bacteria such as *Methanobacterium thermoautotrophicum*,[29] *Pseudoalteromonas nigrifaciens*,[30] *Pneumococcus* type V[31] and others.[32] Classical methods for the incorporation of the D-mannosamine motif into various oligosaccharide chains[33]

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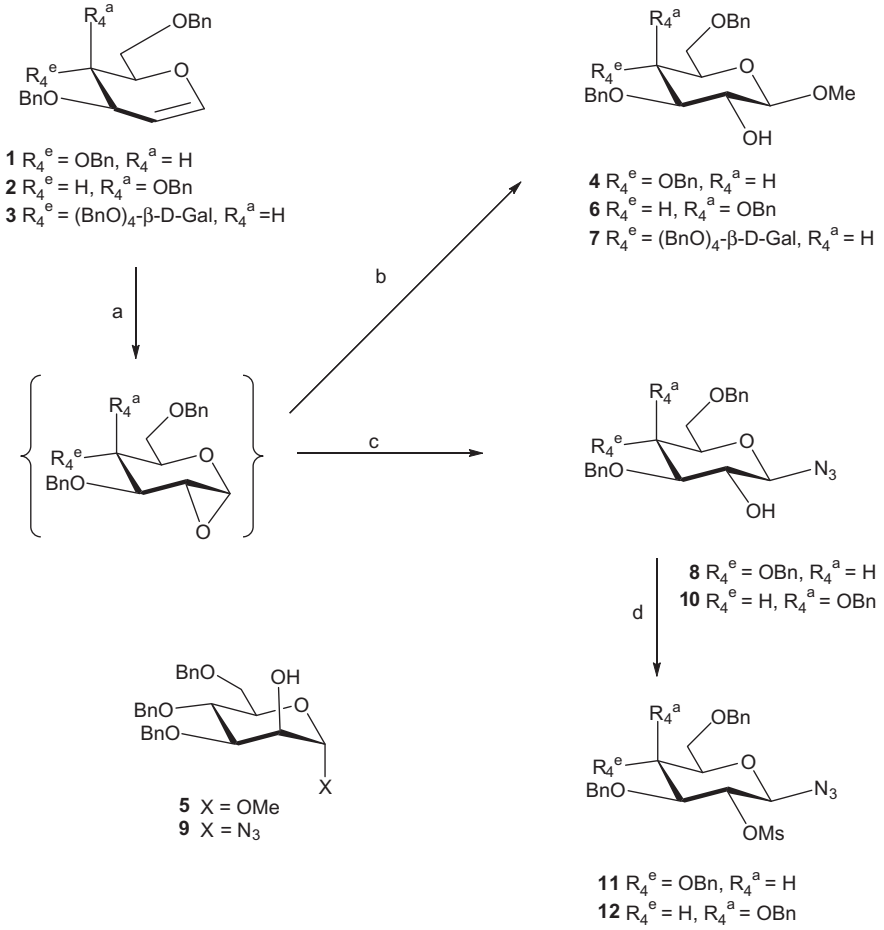
include epimerization reactions at the *C*-2 carbon atom of furanosidic *N*-acetyl-D-glucosamine derivatives,[34] reductions of a *C*-2 oxime,[35] nucleophilic intra- or intermolecular substitutions on the *C*-2 leaving group of a β-D-glucopyranoside,[36] or cyclization of glucal 3-*N*-arylcarbamates, orchestrated by *o*-iodobenzoic acid[37] or via rhodium(II)-catalyzed oxidative cyclizations.[38] Rojas and co-workers thus prepared the pentenyl glycosides of *N*-benzyloxycarbonyl-α-D-mannosamine, which were used as donors in glycosylation reactions. There are only a few examples of *N*-acetyl-D-talosamine syntheses in the literature, which include nucleophilic substitutions on a *C*-2 sulfonate,[39] stereoselective reductions of a *C*-2 oxime,[40] or dihydroxylation reactions on a 2-amino-3,4-glycal.[41]

2. Results and discussion

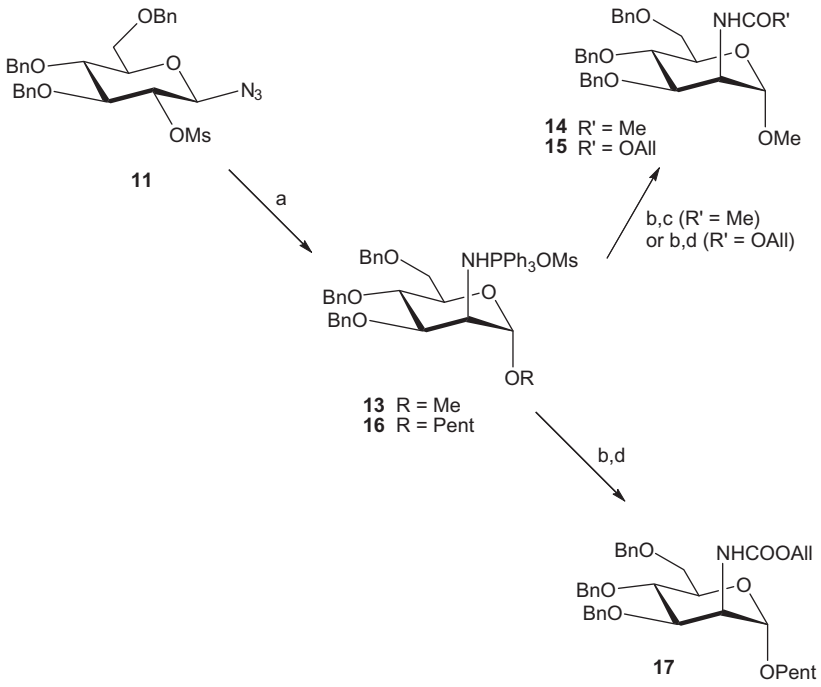
During the epoxidation of 3,4,6-tri-*O*-benzyl-D-glucal according to Dondoni and co-workers,[17] [oxone (2 equiv), acetone, dichloromethane, saturated $NaHCO_3$ solution], we had some difficulty in obtaining consistent results, and observed that the reaction seemed to depend upon a number of factors, including the speed of the magnetic stirring. Since this reaction occurs under biphasic conditions, we thought that the addition of a phase transfer catalyst might facilitate the reaction. Thus, the presence of tetrabutylammonium hydrogen sulfate accelerated the reaction, as observed by Curci[18] in the case of cyclohexene, and the epoxide formation was complete in 2 h; after ring opening with methanol, methyl glycosides **4**, **6**, and **7** were obtained in good yields and stereoselectivity from perbenzylated glycals **1**–**3**. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside **4** was obtained in high overall yield from 3,4,6-tri-*O*-benzyl-D-glucal **1** as an 8:1 mixture of the β-D-*gluco* **4** and α-D-*manno* **5** stereoisomers (75% isolated yield of the pure-β-D-glucopyranoside along with 15% of a 1:2 mixture). Similarly, methyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside **6** and methyl 3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-β-D-Glucopyranoside **7** were obtained in 83% and 80% yield from glycals **2** and **3**, respectively (Scheme 1).

The epoxide ring opening by an azido group has been described previously in the literature: various 1,2-anhydrosugars have been converted into the corresponding D-glycopyranosyl azides in good yields by treatment with lithium azidohydridodiisobutylaluminate in tetrahydrofuran[11] and 3,4,6-tri-*O*-benzyl-β-D-gluco- and galacto-pyranosyl azides **8** and **10** were thus obtained in 73% and 78% yield, respectively. Compound **8** has been previously synthesized from the intermediate epoxide using tetrabutylammonium azide in tetrahydrofuran[6] or sodium azide and lithium perchlorate in acetonitrile.[42]

In order to find a simpler method that would be applicable on a gram-scale, we attempted to open directly the crude epoxide in dichloromethane solution under the biphasic conditions described by Roy and co-workers[26] for the transformation of peracetylated glycopyranosyl bromides into peracetylated glycopyranosyl azides [tetrabutylammonium hydrogen sulfate (1 equiv), sodium azide (4 equiv), dichloromethane, saturated $NaHCO_3$ solution]:



Scheme 1. Synthetic route to β-D-1,2-*trans*-2-hydroxy (mesyloxy) glycosides and glycosyl azides. Reagents and conditions: (a) oxone (2 equiv), acetone, Bu_4NHSO_4 (0.33 equiv), $NaHCO_3$, CH_2Cl_2, H_2O; (b) MeOH, rt; (c) NaN_3 (4 equiv), Bu_4NHSO_4 (1 equiv), CH_2Cl_2, $NaHCO_3$, H_2O; (d) MsCl, pyridine.



Scheme 2. Synthetic route to 2-acetamido or 2-allyloxycarbonylamino-2-deoxy-α-D-mannopyranosides. Reagents and conditions: (a) MeOH (10 equiv) or Pent-4-en-1-ol (1.5 equiv), PPh_3 (1.15 equiv), CH_2Cl_2, 0 °C to rt; (b) 1.5 N NaOH, MeOH, rt; (c) Ac_2O, pyridine; (d) AllOCOCl, $NaHCO_3$, CH_2Cl_2, H_2O.

compounds **8** and **10** were thus obtained in 77% and 83% yield from the corresponding perbenzylated glycals **1** and **2**.

Starting from 3,4,6-tri-*O*-benzyl-D-glucal **1**, as expected a more polar compound was isolated [3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl azide **9**, 9%], resulting from the minor formation of the epoxide on the β-face; nevertheless, the separation of isomers **8** and **9** by column chromatography was relatively easy.

Since it was possible to obtain 1,2-*trans*-D- (and L-) glucosamine derivatives from 2-deoxy-2-iodo-α-D- (and L-)mannopyranosyl azides,[19,43] by Staudinger reaction and intramolecular attack of the iminophosphorane intermediate on the *C*-2 carbon–iodine bound, formation of an aziridine and ring opening by an alcohol, we assumed that the same reaction would also be possible from 3,4,6-tri-*O*-benzyl-2-*O*-mesyl-β-D-glucopyranosyl azide **11** and 3,4,6-tri-*O*-benzyl-2-*O*-mesyl-β-D-galactopyranosyl azide **12**, which were obtained in 92 and 95% yield from **8** and **10**, respectively.

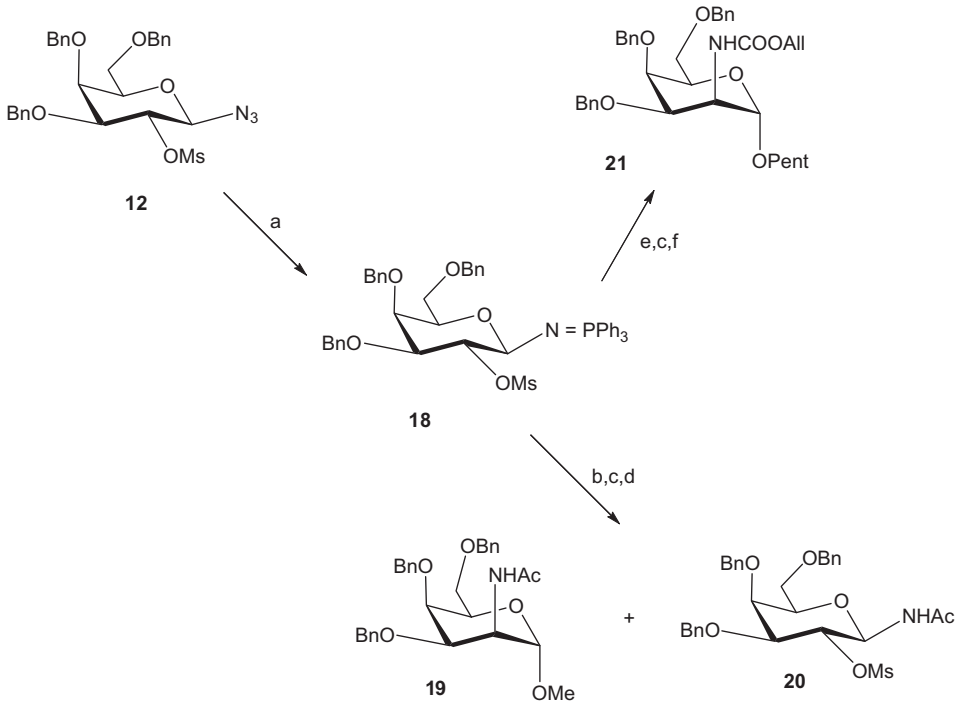
If compound **11** was treated with triphenylphosphine (1.1 equiv) and methanol (10 equiv) in dichloromethane, between 0 and 20 °C, salt **13** was obtained in high yield; the α-*manno* configuration was characterized by ^{1}H NMR (δ H-1 = 4.74 ppm, $J_{1,2}$ = 1.9 Hz, δ H-2 = 3.2 ppm, $J_{2,3}$ = 3.7 Hz, $J_{2,P}$ = 11.0 Hz), ^{13}C NMR (δ C-1 = 101.3 ppm, $J_{1,P}$ = 5.3 Hz, δ C-2 = 55.0 ppm, δ C-3 = 78.41 ppm, $J_{3,P}$ = 2.3 Hz), coupled ^{1}H–^{13}C NMR ($J_{H1\text{-}C1}$ = 170.6 Hz)[44] and 2D experiments (COSY, HSQC). Treatment of the salt **13** with 1.5 M sodium hydroxide and methanol, followed by acetylation afforded the known methyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside **14** in 91% yield[45] (Scheme 2). Similarly, treatment of salt **13** with 1.5 M sodium hydroxide, and allyloxycarbonylation of the free NH_2 derivative under biphasic conditions (allyl chloroformate, dichloromethane, saturated $NaHCO_3$ solution) afforded the methyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside **15** in 88% yield. Knowing that the transformation of the aminophosphonium salt **13** into the carbamate **15** could be achieved in high yield, we investigated the synthesis of the corresponding pentenyl glycoside: the pentenyl group was introduced in 1988 by Fraser-Reid et al. as a leaving group at the anomeric center of a glycosyl donor.[46,47]

Furthermore, the pentenyl glycosides of *N*-benzyloxycarbonyl- and *N*-allyloxycarbonyl-D-glucosamine have been shown to be efficient donors in glycosylation reactions.[38,43]

When methanol was replaced by 4-penten-1-ol, the expected pentenyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside **17** was prepared from **11**, via the intermediate salt **16**, which was also characterized by ^{1}H and ^{13}C NMR; furthermore, since 4-penten-1-ol was expensive and more difficult to eliminate than methanol, only 2 equiv were used; product **17** was obtained in 77% yield.

If 3,4,6-tri-*O*-benzyl-2-*O*-mesyl-β-D-galactopyranosyl azide **12** was treated with triphenylphosphine and methanol, in dichloromethane as described for **11**, the only reaction product was the iminophosphorane **18**, which was recovered in quantitative yield: the result was the same in the absence of methanol (Scheme 3).

Product **18** was also characterized by ^{1}H and ^{13}C NMR data. This could be due to steric problems (the presence of the benzyl group at *C*-4) which hinder the formation of the boatlike conformation necessary for the formation of the transient glycosyl aziridine. Even after refluxing the salt **18** in methanol for 12 h, followed by treatment with sodium hydroxide and reacetylation, methyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-talopyranoside **19** was obtained in only 51% yield. A second product *N*-acetyl-3,4,6-tri-*O*-benzyl-2-deoxy-2-*O*-mesyl-β-D-galactopyranosyl amine **20**, probably resulting from the hydrolysis of the iminophosphorane, was isolated in 21% yield. These results indicated that a higher reaction temperature would be necessary to realize the rearrangement of salt **18**: in the presence of 10 equiv of 4-penten-1-ol, after 4 h at 100 °C in toluene and treatment as described for compound **17**, pentenyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-talopyranoside **21** was isolated in 69% yield. With a smaller excess of 4-penten-1-ol (2 equiv), the yield decreased to 59%. The α-stereochemistry for compound **19** and **21** was ascertained from the ^{1}H and ^{13}C NMR data, and also from the $J_{C1\text{-}H1}$ value in the coupled ^{13}C NMR spectrum (J = 170.9 Hz for **21**).



Scheme 3. Synthetic route to 2-acetamido- or 2-allyloxycarbonylamino-2-deoxy-α-D-talopyranosides. Reagents and conditions: (a) PPh_3 (1.15 equiv), CH_2Cl_2, 0 °C to rt; (b) MeOH, 12 h, reflux; (c) 1.5 N NaOH, MeOH, rt; (d) Ac_2O, pyridine; (e) Pent-4-en-1-ol (2–10 equiv), toluene, 100 °C; (f) AllOCOCl, $NaHCO_3$, CH_2Cl_2, H_2O.

3. Conclusion

In conclusion, the addition of tetrabutylammonium hydrogen sulfate during the epoxidation of perbenzylated glycals with oxone and acetone under biphasic conditions led reproducibly to complete conversions: epoxides were formed quantitatively and could be transformed directly in the presence of methanol to methyl 1,2-*trans*-β-D-glycopyranosides or under biphasic conditions to 1,2-*trans*-β-D-glycopyranosyl azides bearing a free hydroxyl group at the *C*-2 position. After mesylation, the β-D-gluco- and β-D-galacto-pyranosyl azides were subjected to a Staudinger reaction in the presence of 4-penten-1-ol, giving in a few steps, and after double inversion of configuration at *C*-1 and *C*-2, pentenyl 1,2-*trans*-2-allyloxycarbonylamino-2-deoxy-α-D-*manno*- and *talo*-pyranosides, which could in turn be used as donors in glycosylation reactions.

4. Experimental

4.1. General

The dichloromethane used for the Staudinger reactions was washed twice with water, dried with $CaCl_2$ and distilled from CaH_2. Methanol was distilled from magnesium. CH_2Cl_2 was stored over 4 Å molecular sieves; and MeOH over 3 Å molecular sieves. Thin layer chromatography was performed on aluminum sheets coated with Silica Gel 60 F254 (E. Merck). Compounds were visualized by spraying the TLC plates with dilute 15% aqueous H_2SO_4, followed by charring at 150 °C for a few min. Column chromatography was performed on Silica-gel Silicycle P60 (230–400 mesh). ^1H and ^{13}C NMR spectra were recorded with Bruker DRX300 or ALS300 spectrometers working at 300 and 75 MHz, respectively with Me_4Si or residual solvent peaks as internal standard, ESI high resolution measurements were obtained with a MAT 95XL (ThermoFinnigan) electromagnetic mass spectrometer. Elemental analyses were performed by the 'Laboratoire Central d'Analyses du CNRS' (Vernaison, France).

CAUTION: sodium azide may react with dichloromethane to form explosive diazidomethane: experiments must be conducted behind a safety shield.[48]

4.2. Synthesis of methyl 1,2-*trans*-glycosides by epoxidation of glycals and ring opening with methanol: general procedure

A solution of oxone (1.475 g, 2.40 mmol) in water (5.8 mL) was added dropwise at 0 °C for 15 min to a vigorously stirred biphasic mixture of benzylated glycal (1.20 mmol), tetrabutylammonium hydrogen sulfate (0.136 g, 0.40 mmol), acetone (0.5 mL), CH_2Cl_2 (5 mL) and a saturated $NaHCO_3$ solution (8.3 mL). Stirring was maintained for 30 min at 0 °C, and 2 h at room temperature. The aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic phases were washed with water (10 mL) and dried over sodium sulfite (Na_2SO_3). After filtration, the solution was concentrated in the presence of methanol (10 mL) and the residue was stirred overnight in methanol (30 mL). Methanol was evaporated in vacuo and the crude product was purified by column chromatography.

4.2.1. Methyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside 4

Compound **4** was obtained in 75% yield from 3,4,6-tri-*O*-benzyl-D-glucal **1** after purification by column chromatography (1:2 ethyl acetate–petroleum ether). 0.362 g, R_f 0.60 (2:3 ethyl acetate–petroleum ether); Mp = 71–72 °C (ethanol), $[\alpha]_D = -4.7$ (*c* 1.0, $CHCl_3$) {lit.[49] Mp = 72–75 °C, $[\alpha]_D = -5.0$ (*c* 1.0, $CHCl_3$)}; ^1H NMR ($CDCl_3$): δ 7.44–7.20 (m, 15H, $3C_6H_5$), 4.97 and 4.90 (dd, 2H, *J* 11.3 Hz, CH_2Ph), 4.88 and 4.59 (dd, 2H, *J* 10.8 Hz, CH_2Ph), 4.68 and 4.60 (dd, 2H, *J* 12.2 Hz, CH_2Ph), 4.23 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1), 3.81 (dd, 1H, $J_{5,6a}$ 2.1, $J_{6a,6b}$ 10.8 Hz, H-6a), 3.75 (dd, 1H, $J_{5,6a}$ 4.3 Hz, H-6b), 3.70–3.57 (m, 3H, H-2, H-3, H-4), 3.61 (s, 3H, CH_3O), 3.53 (ddd, 1H, $J_{4,5}$ 9.9 Hz, H-5), 2.50 (s, 1H, O*H*).

Further elution gave a 1:2 β-D-*gluco* **4**/α-D-*manno* **5** mixture (0.085 g, 15%): α-*manno* isomer: R_f = 0.56 (2:3 ethyl acetate–petroleum ether). Selected ^1H NMR data for **5**: δ 4.05 (dd, 1H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.0 Hz, H-2), 3.39 (s, 3H, CH_3O).

4.2.2. Methyl 3,4,6-tri-*O*-benzyl-β-D-galactopyranoside 6

Compound **6** was obtained in 83% yield from 3,4,6-tri-*O*-benzyl-D-galactal **2** after purification by column chromatography (2:3 ethyl acetate–petroleum ether). 0.462 g, R_f = 0.51 (2:3 ethyl acetate–petroleum ether), Mp 98–99 °C (ethanol), $[\alpha]_D = -6.4$ (*c* 1.0, $CHCl_3$) {lit.[50] Mp = 99–99.5 °C, $[\alpha]_D = -6.4$ (*c* 1.0, $CHCl_3$)}. ^{1}H NMR ($CDCl_3$): δ 7.42–7.28 (m, 15H, $3C_6H_5$), 4.90 and 4.63 (dd, 2H, *J* 11.6 Hz, CH_2Ph), 4.75 and 4.66 (dd, 2H, *J* 11.8 Hz, CH_2Ph), 4.51 and 4.45 (dd, 2H, *J* 11.7 Hz, CH_2Ph), 4.20 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), 3.96 (dd, 1H, $J_{2,3}$ 9.7 Hz, H-2), 3.96 (br d, 1H, $J_{3,4}$ 2.8 Hz, H-4), 3.67–3.58 (m, 3H, H-5, H-6a, H-6b), 3.55 (s, 3H, CH_3O), 3.45 (dd, 1H, H-3); ^{13}C NMR ($CDCl_3$): δ 138.60, 138.15, 137.95, 128.59–127.64 (C_6H_5), 104.23 (C-1), 82.06 (C-3), 76.76 (C-4), 74.58, 73.64, 72.48 (CH_2Ph), 72.92, 71.36 (C-2, C-5), 68.78 (C-6), 57.04 (CH_3O).

4.2.3. Methyl 3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-β-D-glucopyranoside 7

Compound **7** was obtained from 3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucal **3** (0.424 g, 0.50 mmol) according to the general procedure. The pure glycoside was recovered in 80% yield after purification by column chromatography (2:3 ethyl acetate–petroleum ether). 0.358 g, oily material; R_f 0.53 (2:3 ethyl acetate–petroleum ether) $[\alpha]_D$ = +9.6 (*c* 1.0, $CHCl_3$) {lit.[5a] $[\alpha]_D$ = +12 (*c* 1.0, $CHCl_3$)}; ^{1}H NMR ($CDCl_3$): δ 7.42–7.28 (m, 30H, $6C_6H_5$), 5.28 and 4.90 (dd, 2H, *J* 11.1 Hz, CH_2Ph), 5.15 and 4.73 (dd, 2H, *J* 11.5 Hz, CH_2Ph), 5.01 and 4.96 (dd, 2H, *J* 11.2 Hz, CH_2Ph), 4.87 (s, 2H, CH_2Ph), 4.73 and 4.57 (dd, 2H, *J* 12.1 Hz, CH_2Ph), 4.63 (d, 1H, $J_{1',2'}$ 7.7 Hz, H-1′), 4.55 and 4.49 (dd, 2H, *J* 11.9 Hz, CH_2Ph), 4.38 (d, 1H, $J_{1,2}$ 7.6 Hz, H-1), 4.16 (dd, 1H, $J_{3,4}$ 9.0, $J_{4,5}$ 9.0 Hz, H-4), 4.09 (br d, 1H, $J_{3',4'}$ 3.1, $J_{4',5'}$ 0.5 Hz, H-4′), 4.02 (dd, 1H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.97 (dd, 1H, $J_{2',3'}$ 9.5 Hz, H-2′), 3.91 (dd, 1H, $J_{5,6b}$ 1.5 Hz, H-6b), 3.77–3.53 (m, H, H-2, H-3, H-3′, H-5, H-5′, H-6′a, H-6′b), 3.70 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$): δ 139.01, 138.79, 138.50, 138.32, 138.03, 128.38–127.27 (C_6H_5), 103.62 (C-1), 102.75 (C-1′), 82.69, 82.42, (C-3, C-3′), 79.93 (C-2′), 76.23 (C-4), 75.40 (C-5), 75.28, 74.69, 74.64 (CH_2Ph), 73.60 (C-4′), 73.49 (C-2), 73.41, 73.10 (CH_2Ph), 73.01 (C-5′), 72.53 (CH_2Ph), 68.15 (C-6, C-6′), 56.91 (CH_3O).

4.3. Synthesis of 1,2-*trans* glycopyranosyl azides by epoxidation of glycals and ring opening with sodium azide: general procedure

The crude epoxide was prepared as described in Section 4.2. from perbenzylated glycal **1** or **2** (1.20–2.40 mmol) and oxone (2.40–4.80 mmol). After treatment, the organic phase was partially concentrated in vacuo to 6–12 mL (at room temperature or below). A saturated $NaHCO_3$ solution (6–12 mL), sodium azide (0.312–0.624 g, 4.80–9.60 mmol, 4 equiv) and tetrabutylammonium hydrogen sulfate (1.20–2.40 mmol, 1 equiv) were added successively to the organic solution and the mixture was vigorously stirred for 4 h. After the addition of ethyl acetate (60 mL), the organic phase was washed with a saturated $NaHCO_3$ solution (10 mL), then with brine (10 mL), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography.

4.3.1. 3,4,6-Tri-*O*-benzyl-β-D-glucopyranosyl azide 8

Compound **8** was obtained from 3,4,6-tri-*O*-benzyl-D-glucal **1** (1.00 g, 2.40 mmol) in 77% yield as a solid after purification by column chromatography (2:5 ethyl acetate–petroleum ether). 0.880 g, R_f 0.42 (1:3 ethyl acetate–petroleum ether), Mp 67 °C, $[\alpha]_D = -5.0$ (*c* 1.0, $CHCl_3$) {lit.[6] Mp 64–67 °C, $[\alpha]_D = -4.7$ (*c* 1.15, $CHCl_3$)}; ^{1}H NMR ($CDCl_3$): δ 7.40–7.20 (m, 15H, $3C_6H_5$), 5.05 and 5.01 (dd, 2H, *J* 11.5 Hz, CH_2Ph), 4.97 and 4.71 (dd, 2H, *J* 10.9 Hz, CH_2Ph), 4.77 and 4.68 (dd, 2H, *J* 12.2 Hz, CH_2Ph), 4.63 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1), 3.90–3.83 (m, 2H, H-6a, H-6b), 3.80 (dd, 1H, $J_{3,4}$ 8.9, $J_{4,5}$ 9.3 Hz, H-4), 3.69 (dd, 1H, $J_{2,3}$ 8.9 Hz, H-3), 3.68–3.63 (m, 1H, H-5), 3.60 (dd, 1H, H-2); ^{13}C NMR ($CDCl_3$): δ 138.39, 137.86, 137.86, 128.47–127.69 (C_6H_5), 90.23 (C-1), 84.57 (C-3), 77.09, 77.04 (C-4, C-5), 75.22, 74.94, 73.46 (CH_2Ph), 73.93 (C-2), 68.29 (C-6).

Further elution afforded 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl azide **9**[42] as an oil: 0.103 g, 9% yield. R_f 0.22 (1:3 ethyl acetate–petroleum ether); $[\alpha]_D$ = +180.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.45–7.20 (m, 15H, $3C_6H_5$), 5.53 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 4.90 and 4.60 (dd, 2H, *J* 10.9 Hz, CH_2Ph), 4.73 and 4.60 (dd, 2H, *J* 12.1 Hz, CH_2Ph), 4.72 (s, 2H, CH_2Ph), 4.03–3.77 (m, 6H, H-2, H-3, H-4, H-5, H-6a, H6b), 2.82 (s, 1H, O*H*); ^{13}C NMR ($CDCl_3$): δ 138.24, 137.99, 137.72, 128.53–127.88 (C_6H_5), 89.56 (C-1), 79.27 (C-3), 75.27, 73.64, 72.34 ($PhCH_2$), 73.75, 73.36 (C-4, C-5), 68.63 (C-6), 68.36 (C-2).

4.3.2. 3,4,6-Tri-*O*-benzyl-β-D-galactopyranosyl azide 10[11]

Compound **10** was obtained from 3,4,6-tri-*O*-benzyl-D-galactal **2** (1.00 g, 2.40 mmol) in 83% yield after purification by column chromatography (2:5 ethyl acetate–petroleum ether). 0.948 g, R_f 0.66 (1:2 ethyl acetate–petroleum ether); Mp = 78–79 °C, $[\alpha]_D = -10.7$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.45–7.20 (m, 15H, $3C_6H_5$), 4.93 and 4.66 (dd, 2H, *J* 13.6 Hz CH_2Ph), 4.78 and 4.65 (dd, 2H, *J* 11.8 Hz CH_2Ph), 4.57 and 4.50 (dd, 2H, *J* 11.8 Hz CH_2Ph), 4.56 (d, 1H, $J_{1,2}$ 8.5 Hz, H-1), 4.06 (dd, 1H, $J_{3,4}$ 2.7, $J_{4,5}$ 0.6 Hz, H-4), 3.95 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2), 3.76–3.66 (m, 3H, H-5, H-6a, H-6b), 3.48 (dd, 1H, H-3); ^{13}C NMR ($CDCl_3$): δ 138.39, 137.83, 137.77, 128.72–127.80 (C_6H_5), 90.67 (C-1), 82.21 (C-3), 75.84 (C-4), 74.71, 73.73, 72.48 (CH_2Ph), 72.64 (C-5), 70.70 (C-2), 68.44 (C-6).

4.4. Synthesis of 1,2-*trans*-2-*O*-mesyl glycopyranosyl azides: general procedure

A solution of mesyl chloride (0.286 mL, 3.70 mmol) in dry CH_2Cl_2 (2 mL) was added dropwise to a cooled solution of alcohol **8** or **10** (1.00 g, 2.10 mmol) in pyridine (7 mL). The mixture was allowed to reach room temperature and stirring was maintained overnight. The mixture was poured into ice-water and extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with a saturated $NaHCO_3$ solution (20 mL), brine (10 mL) and dried (Na_2SO_4). After concentration, the residue was purified by column chromatography.

4.4.1. 3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-β-D-glucopyranosyl azide 11

Compound **11** was obtained from 3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl azide **8** (1.00 g, 2.40 mmol) after purification by column chromatography (2:5 ethyl acetate–petroleum ether). 1.070 g (92% yield), oily material, R_f 0.72 (1:2 ethyl acetate–petroleum ether), $[\alpha]_D = -36.9$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.20 (m, 15H, $3C_6H_5$), 4.99–4.82 (m, 3H, CH_2Ph), 4.73–4.58 (m, 3H, CH_2Ph), 4.62 (d, 1H, $J_{1,2}$ 8.3 Hz, H-1), 4.50 (dd, 1H, $J_{2,3}$ 9.6 Hz, H-2), 3.85–3.73 (m, 4H, H-3, H-4, H-6a, H-6b), 3.63 (ddd, 1H, $J_{4,5}$ 9.4, $J_{5,6a}$ 2.4, $J_{5,6b}$ 3.4 Hz, H-5), 3.09 (s, 3H, CH_3SO_2).; ^{13}C NMR ($CDCl_3$): δ 138.17, 137.93, 137.81, 128.94–128.39 (C_6H_5), 87.75 (C-1), 82.52 (C-3), 80.57, 77.57, 77.43 (C-2, C-4, C-5), 75.88, 75.32, 73.49 (CH_2Ph), 68.06 (C-6), 39.56 (CH_3SO_2). Anal. Calcd for $C_{28}H_{31}N_3O_7S$ (553.63): C, 60.74; H, 5.64; N, 7.59. Found: C, 60.68; H, 5.46; N, 7.42.

4.4.2. 3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-β-D-galactopyranosyl azide 12

Compound **12** was obtained from 3,4,6-tri-*O*-benzyl-β-D-galactopyranosyl azide (**10**) (1.00 g, 2.40 mmol) after purification by column chromatography (1:2 ethyl acetate–petroleum ether). 1.070 g, R_f 0.77 (1:2 ethyl acetate–petroleum ether), 95% yield. Mp 87–88 °C, $[\alpha]_D = -33.1$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$):

δ 7.50–7.26 (m, 15H, $3C_6H_5$), 4.96 and 4.64 (dd, 2H, J 11.6 Hz, CH_2Ph), 4.86 (dd, 1H, $J_{1,2}$ 8.7, $J_{2,3}$ 9.7 Hz, H-2), 4.77 and 4.68 (dd, 2H, J 11.5 Hz, CH_2Ph), 4.65 (d, 1H, H-1), 4.07 (br d, 1H, $J_{3,4}$ 3.4, $J_{4,5}$ 1.0 Hz, H-4), 3.76–3.62 (m, 4H, H-3, H-5, H-6a, H-6b), 3.04 (s, 3H, CH_3SO_2); ^{13}C NMR ($CDCl_3$): δ 138.07, 137.66, 137.05, 128.72–127.90 (C_6H_5), 88.12 (C-1), 80.11, 79.16, 77.44, 72.90 (C-2, C-3, C-4, C-5), 74.86, 73.69, 72.61 (CH_2Ph), 68.07 (C-6), 39.24 (CH_3SO_2). Anal. Calcd for $C_{28}H_{31}N_3O_7S$ (553.63): C, 60.74; H, 5.64; N, 7.59. Found: C, 61.24; H, 5.60; N, 7.47.

4.5. Methyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside 14

Triphenylphosphine (0.087 g, 0.33 mmol) was added to a cooled solution (0 °C) of azidomesylate **11** (0.166 g, 0.30 mmol) and MeOH (121 μL, 3.0 mmol, 10 equiv) in CH_2Cl_2 (1.5 mL) under an argon atmosphere and the mixture was allowed to reach room temperature. Stirring was maintained overnight. Concentration of the mixture gave the crude aminophosphonium salt **13**, which was characterized by NMR: ^{1}H NMR ($CDCl_3$): δ 7.80–6.95 (m, 30H, $6C_6H_5$), 4.83 and 4.72 (dd, 2H, J 11.0 Hz, CH_2Ph), 4.72 and 4.62 (dd, 2H, J 12.1 Hz, CH_2Ph), 4.67 and 4.31 (dd, 2H, J 11.6 Hz, CH_2Ph), 4.74 (d, 1H, $J_{1,2}$ 1.9 Hz, H-1), 4.40 (dd, 1H, $J_{3,4}$ 9.1, $J_{4,5}$ 9.5 Hz, H-4), 4.18 (dd, 1H, $J_{5,6a}$ 8.0, $J_{6a,6b}$ 10.6 Hz, H-6a), 3.92 (dd, 1H, $J_{5,6b}$ 2.0 Hz, H-6b), 3.86 (ddd, 1H, H-5), 3.78 (dd, 1H, $J_{2,3}$ 3.5 Hz, H-3), 3.29 (s, 3H, OCH_3), 3.20 (dddd, 1H, $J_{2,NH}$ 11.0, $J_{2,P}$ 11.0 Hz H-2), 2.41 (s, 3H, CH_3SO_2); ^{13}C NMR ($CDCl_3$): δ 138.27, 138.01, 137.50 (C-quat. C_6H_5), 134.45 (J 2.6 Hz, C_{para}), 133.78 (J 11.1 Hz, C_{ortho}), 133.50, 133.34, 129.39 (J 13.3 Hz, C_{meta}), 128.27–127.08 (C_6H_5), 100.33 ($J_{1,P}$ 5.3 Hz, C-1), 78.41 ($J_{3,P}$ 2.3 Hz, C-3), 75.20 (C-4), 74.52, 73.19, 72.91 (CH_2Ph), 72.15 (C-5), 69.43 (C-6), 55.05 (C-2), 54.40 (OCH_3), 38.83 (CH_3SO_2); ^{31}P NMR ($CDCl_3$): δ 41.14. Salt **13** was stirred for 8 h in a mixture of 1.5 M sodium hydroxide (1 mL, 5 equiv) and methanol (3 mL). After neutralization with acetic acid (69 μL, 1.20 mmol) and concentration to dryness, the free-amino derivative was acetylated overnight in a 1:2 acetic anhydride–pyridine mixture (10 mL). The mixture was concentrated again and the product was purified by column chromatography (6:1 ethyl acetate–acetone). The pure product was recovered as an oil in 91% yield. 138 mg, R_f 0.71 (6:1 ethyl acetate–acetone), $[\alpha]_D$ = +33.6 (c 1.0, $CHCl_3$) {lit.[45] $[\alpha]_D$ = +30.4 (c 1.0, $CHCl_3$)}; ^{1}H NMR ($CDCl_3$): δ 7.45–7.20 (m, 15H, $3C_6H_5$), 6.04 (d, 1H, $J_{2,NH}$ 8.9 Hz, H-2), 4.90 and 4.47 (dd, 2H, J 10.8 Hz, CH_2Ph), 4.77 (d, 1H, $J_{1,2}$ 1.6 Hz, H-1), 4.75 and 4.49 (dd, 2H, J 10.6 Hz, CH_2Ph), 4.71 (ddd, 1H, $J_{2,3}$ 4.3 Hz, H-2), 4.66 and 4.50 (dd, 2H, J 11.9 Hz, CH_2Ph), 4.07 (ddd, 1H, $J_{4,5}$ 8.6, $J_{5,6a}$ 1.6, $J_{5,6b}$ 4.7 Hz, H-5), 3.85–3.65 (m, 4H, H-3, H-4, H-6a, H-6b), 3.38 (s, 3H, OCH_3), 2.05 (s, 3H, CH_3CON); ^{13}C NMR ($CDCl_3$): δ 170.47 (CH_3CON), 138.42, 137.96, 137.88, (C-quat. C_6H_5), 128.40–127.73 (C_6H_5), 100.42 (C-1), 77.73 (C-3), 74.03 (C-4), 75.16, 71.63, 71.22 (CH_2Ph), 70.43 (C-5), 68.70 (C-6), 55.06 (OCH_3), 49.12 (C-2), 23.50 (CH_3CON).

4.6. Methyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside 15

Triphenylphosphine (0.135 g, 0.515 mmol) was added to a cooled solution (0 °C) of azidomesylate **11** (0.260 g, 0.47 mmol) and MeOH (190 μL, 4.7 mmol, 10 equiv) in CH_2Cl_2 (1.5 mL) under an argon atmosphere and the mixture was allowed to reach room temperature. Stirring was maintained overnight and the solution was concentrated; the residue was stirred for 8 h in a mixture of 1.5 M sodium hydroxide (1.42 mL, 5 equiv) and methanol (4.5 mL). After neutralization with acetic acid (98 μL, 1.71 mmol) and concentration to dryness the residue was dissolved in CH_2Cl_2 (5 mL), after which water (2 mL), $NaHCO_3$ (0.079 g, 0.94 mmol) and allyl chloroformate (75 μL, 0.705 mmol) were successively added and the mixture was vigorously stirred for 4 h. After dilution with CH_2Cl_2 (40 mL), the organic phase was washed with a saturated $NaHCO_3$ solution (10 mL), dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (1:2 ethyl acetate–petroleum ether). Pure product **15** was recovered in 88% yield: 0.226 g; R_f 0.47 (1:3 ethyl acetate–petroleum ether), $[\alpha]_D$ = +20.0 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.46–7.30 (m, 15H, C_6H_5), 5.95 (m, 1H, C*H*=), 5.35 (br d, 1H, J 17.2 Hz, $0.5CH_2$=), 5.24 (d, 1H, J 10.5 Hz, $0.5CH_2$=), 5.19 (d, 1H, $J_{2,NH}$ 9.0 Hz, NH), 4.88 and 4.45 (dd, 2H, J 10.8 Hz, CH_2Ph), 4.83 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.79 and 4.52 (dd, 2H, J 11.1 Hz, CH_2Ph), 4.66 and 4.51 (dd, 2H, J 12.1 Hz, CH_2Ph), 4.63–4.59 (m, 2H, CH_2-CH=CH_2), 4.39 (br dd, 1H, $J_{2,3}$ 4.6 Hz, H-2), 4.05 (dd, 1H, $J_{3,4}$ 8.9 Hz, H-3), 3.80–3.64 (m, 4H, H-4, H-5, H-6a, H-6b), 3.37 (s, 3H, CH_3O); ^{13}C NMR ($CDCl_3$): δ 156.25 (NHCOO), 138.39, 138.08, 138.01, 128.35–127.67 (C_6H_5), 132.83 (CH=), 117.85 (CH_2=), 100.41 (C-1), 77.86 (C-3), 74.04 (C-4), 70.53 (C-5), 75.15, 73.52, 71.13 (CH_2Ph), 68.64 (C-6), 65.82 (allyl CH_2), 54.97 (CH_3), 50.97 (C-2). Anal. Calcd for $C_{32}H_{37}NO_7$ (547.64): C, 70.18; H, 6.81; N, 2.56. Found: C, 69.31; H, 6.82; N, 2.34.

4.7. Pentenyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-mannopyranoside 17

Triphenylphosphine (0.175 g, 0.67 mmol) was added to a cooled solution (0 °C) of azidomesylate **11** (0.330 g, 0.60 mmol) and pent-4-en-1-ol (124 μL, 1.20 mmol) in CH_2Cl_2 (1.5 mL) under an argon atmosphere and the mixture was allowed to reach room temperature and stirred for 16 h. Concentration gave the crude aminophosphonium salt **16** characterized by NMR. ^{1}H NMR δ 7.80–7.05 (m, 30H, $6C_6H_5$), 5.74 (dddd, 1H, pentenyl C*H*), 4.99–4.90 (m, 2H, pentenyl CH_2), 4.86 and 4.76 (dd, 2H, J 11.0 Hz, $C_6H_5CH_2$), 4.73 and 4.60 (dd, 2H, J 12.1 Hz, $C_6H_5CH_2$), 4.70 and 4.36 (dd, 2H, J 11.6 Hz, $C_6H_5CH_2$), 4.71 (d, 1H, $J_{1,2}$ 2.0 Hz, H-1), 4.45 (dd, 1H, $J_{3,4}$ 9.7, $J_{4,5}$ 9.0 Hz, H-4), 4.21 (dd, 1H, $J_{5,6a}$ 7.5, $J_{6a,6b}$ 10.6 Hz, H-6a), 3.94 (dd, 1H, $J_{5,6b}$ 1.9 Hz, H-6b), 3.89 (ddd, 1H, H-5), 3.83 (ddd, 1H, $J_{2,3}$ 3.8, $J_{3,P}$ 0.9 Hz, H-3), 3.68 (ddd, 1H, J 6.6, J 6.6, J 9.7 Hz, 0.5 pentenyl OCH_2), 3.28 (ddd, 1H, J 6.6, J 6.6, J 9.7 Hz, 0.5 pentenyl OCH_2), 3.18 (dddd, 1H, $J_{2,NH}$ 9.7, $J_{2,P}$ 12.0 Hz, H-2), 2.33 (s, 3H, CH_3SO_2), 2.05–1.94 (m, 2H, pentenyl CH_2), 1.58–1.48 (m, 2H, pentenyl CH_2); ^{13}C NMR ($CDCl_3$): δ 137.88, 137.79, 137.32, (C-quat. C_6H_5), 137.52 (pentenyl *C*H), 134.47 (J 2.4 Hz, C_{para}), 133.60 (J 11.1 Hz, C_{ortho}), 129.30 (J 13.3 Hz, C_{meta}), 128.32–127.02 (C_6H_5), 120.90 (J 104.1 Hz, C_{ipso}), 114.51 (pentenyl=CH_2), 99.33 ($J_{1,P}$ 4.9 Hz, C-1), 78.221 ($J_{3,P}$ 2.6 Hz, C-3), 74.99 (C-4), 74.48, 73.05, 72.83 (CH_2Ph), 71.82 (C-5), 69.28 (C-6), 66.59 (pent OCH_2), 55.05 (C-2), 38.74 (CH_3SO_2), 29.71, 27.91 ($OCH_2CH_2CH_2$); ^{31}P NMR ($CDCl_3$): δ 40.92. Salt **16** was dissolved in a mixture of 1.5 M NaOH (2.1 mL, 3.15 mmol) and methanol (6 mL) and the mixture was stirred overnight before neutralization with acetic acid (145 μL, 2.55 mmol). The crude mixture was concentrated and the residue was dissolved in dichloromethane (6 mL) and water (2.5 mL) containing sodium bicarbonate (100 mg). Allyl chloroformate (96 μL, 0.90 mmol) was added and the mixture was stirred vigorously for 4 h. The aqueous phase was extracted with CH_2Cl_2, then the combined organic phases were washed with water, dried (Na_2SO_4) and concentrated. The crude product was purified by column chromatography (1:3 ethyl acetate–petroleum ether). Pure product **17** was recovered in 77% yield: 0.276 g; R_f 0.65 (1:3 ethyl acetate–petroleum ether), $[\alpha]_D$ = +21.7 (c 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.46–7.30 (m, 15H, C_6H_5), 6.02 (m, 1H, allyl CH_2), 5.88 (m, 1H, pentenyl C*H*=), 5.45–5.27 (m, 3H, allyl CH_2=, N*H*), 5.15–5.00 (m, 2H, pentenyl CH_2), 4.99 (d, 1H, $J_{1,2}$ 1.0 Hz, H-1), 4.97 and 4.54 (dd, 2H, J 10.8 Hz, CH_2Ph), 4.90–4.62 (dd, 2H, J 11.8 Hz, CH_2Ph), 4.73–4.57 (dd, 2H, J 11.5 Hz, CH_2Ph), 4.72–4.66 (m, 2H, allyl CH_2), 4.50 (ddd, 1H, $J_{2,3}$ 4.4, $J_{2,NH}$ 8.9 Hz, H-2), 4.16 (dd, 1H, $J_{3,4}$ 9.0 Hz, H-3), 3.90–3.82 (m, 2H, H-4, H-6a), 3.80–3.72 (m, 3H, H-4, H-6b,

pentenyl OC*H*), 3.51 (ddd, 1H, *J* 6.5, 6.5, 9.6 Hz, pentenyl OC*H*), 2.20 (m, 2H, OCH_2CH_2), 1.76 (m, 2H, $OCH_2CH_2CH_2$). ^{13}C NMR ($CDCl_3$): δ 156.21 (N*H*COO), 138.32, 138.06, 137.96, 137.86 (pentenyl *C*H=), 128.29–127.63 (C_6H_5), 132.80 (allyl *C*H=), 117.74 (allyl CH_2=), 115.02 (pentenyl CH_2=), 99.35 (C-1), 77.93 (C-3), 74.07 (C-4), 75.16, 73.45, 71.12 (CH_2Ph), 70.63 (C-5), 68.61 (C-6), 67.16 (pentenyl OCH_2), 65.74 (allyl CH_2), 54.97 (CH_3), 51.11 (C-2), 30.21, 28.51 ($OCH_2CH_2CH_2$). Anal. Calcd for $C_{36}H_{43}NO_7$ (601.73): C, 71.86; H, 7.20; N, 2.33. Found; C, 71.90; H, 7.04; N, 2.11.

4.8. *N*-(3,4,6-Tri-*O*-benzyl-2-*O*-mesyl-β-D-galactopyranosyl)triphenylphosphine imide 18

Triphenylphosphine (0.175 g, 0.67 mmol) was added to a cooled solution (0 °C) of azidomesylate **12** (0.330 g, 0.60 mmol) in CH_2Cl_2 (2.0 mL) under an argon atmosphere and the mixture was allowed to reach room temperature and stirred for 16 h. Concentration gave the crude imide salt **18** characterized by NMR. ^1H NMR ($CDCl_3$): δ 7.80–7.25 (m, 30H, C_6H_5), 5.14 (dd, 1H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.7 Hz, H-2), 5.04 and 4.67 (dd, 2H, *J* 11.7 Hz, CH_2Ph), 4.80 and 4.76 (dd, 2H, *J* 12.3 Hz, CH_2Ph), 4.60 (dd, 1H, $J_{1,P}$ 18.9 Hz, H-1), 4.44 and 4.39 (dd, 2H, *J* 12.2 Hz, CH_2Ph), 3.99 (br d, 1H, $J_{3,4}$ 2.7 Hz, H-4), 3.62 (dd, 1H, H-3), 3.61–3.52 (m, 3H, H-5, H-6a, H-6b), 3.04 (s, 3H, CH_3SO_2). ^{13}C NMR ($CDCl_3$): δ 138.76, 138.02, 137.94 C-quat.C_6H_5), 133.54 (*J* 9.6 Hz, C_{ortho}), 132.04 (*J* 2.6 Hz, C_{para}), 131.40 (*J* 97.6, C_{ipso}), 128.29–127.57 (C_{meta}, C_6H_5), 88.93 ($J_{1,P}$ 3.8 Hz, C-1), 85.25 ($J_{2,P}$ 23.1 Hz, C-1), 81.31 ($J_{3,P}$ 3.7 Hz, C-1), 74.23 (C-4), 74.27, 73.28, 72.50 (CH_2Ph), 73.80 (C-5), 69.30 (C-6), 39.65 (CH_3SO_2). ^{31}P NMR ($CDCl_3$): δ 30.37. HRMS [M+H$^+$] $C_{46}H_{47}NO_7PS$: calcd 788.2805, found 788.2810.

4.9. Methyl 2-acetamido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-talopyranoside 19 and *N*-acetyl-3,4,6-tri-*O*-benzyl-2-*O*-mesyl-β-D-galactopyranosyl amine 20

Salt **18** [obtained by reaction of azidomesylate **12** (0.250 g, 0.45 mmol) and triphenylphosphine (0.137 g, 0.52 mmol) in dichloromethane (2 mL)] was refluxed for 12 h in methanol (5 mL). After dilution with methanol (5 mL), 1.5 M sodium hydroxide (1.6 mL, 2.4 mmol) was added and the mixture was stirred for 6 h. After neutralization with acetic acid and concentration, the residue was acetylated overnight with a 2:1 pyridine–acetic anhydride mixture (10 mL). The mixture was concentrated to dryness and the products were recovered after purification by column chromatography (2:3 ethyl acetate–petroleum ether). Compound **19** was obtained as an oily material in 51% yield: 0.119 mg, R_f 0.46 (1:1 ethyl acetate–petroleum ether), $[\alpha]_D$ = +13.5 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.41–7.29 (m, 15H, $3C_6H_5$), 7.24 (d, 1H, $J_{2,NH}$ 8.7 Hz, N*H*), 4.90 and 4.55 (dd, 2H, *J* 10.3 Hz, CH_2Ph), 4.73 (d, 1H, $J_{1,2}$ 1.3 Hz, H-1), 4.73 and 4.50 (dd, 2H, *J* 11.6 Hz, CH_2Ph), 4.65 and 4.53 (dd, 2H, *J* 11.7 Hz, CH_2Ph), 4.60 (ddd, 1H, $J_{2,3}$ 4.3 Hz, H-2), 4.03–3.96 (m, 2H, H-4, H-5), 3.93 (dd, 1H, $J_{3,4}$ 4.3 Hz, H-3), 3.78 (dd, 1H, $J_{5,6a}$ 7.3, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.66 (dd, 1H, $J_{5,6b}$ 5.8 Hz, H-6b), 3.37 (s, 3H, OCH_3), 1.77 (s, 3H, CH_3CON); ^{13}C NMR ($CDCl_3$): δ 170.46 (CH_3CON), 138.22, 138.14, 137.98, (C-quat. C_6H_5), 128.59–127.69 (C_6H_5), 101.12 (C-1), 75.76 (C-4), 75.51, 69.99, 68.82 (CH_2Ph), 72.19 (C-3), 69.20 (C-5), 68.82 (C-6), 55.05 (C-2), 54.24 (OCH_3), 48.53 (C-2), 23.37 (CH_3CON). HMRS [M+H$^+$] $C_{30}H_{36}NO_6$: calcd 506.2537, found 506.2546.

*Further elution afforded compound **20** as an oil*: 0.053 g, 21% yield. R_f 0.30 (1:1 ethyl acetate-petroleum ether), $[\alpha]_D$ = +24.8 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.40–7.25 (m, 15H, $3C_6H_5$), 6.55 (d, 1H, $J_{1,NH}$ 9.0 Hz, N*H*), 5.22 (dd, 1H, $J_{1,2}$ 9.1 Hz, H-1), 4.91 and 4.64 (dd, 2H, *J* 11.3 Hz, CH_2Ph), 4.75 and 4.56 (dd, 2H, *J* 11.3 Hz, CH_2Ph), 4.71 (dd, 1H, $J_{2,3}$ 9.8 Hz, H-2), 4.50 and 4.44 (dd, 2H, *J* 11.7 Hz, CH_2Ph), 4.14 (br d, 1H, $J_{3,4}$ 2.8, $J_{4,5}$ 0.5 Hz, H-4), 3.78 (ddd, 1H, $J_{5,6a}$ 6.8, $J_{5,6b}$ 6.8 Hz, H-5), 3.75 (dd, 1H, H-3), 3.62 (d, 2H, H-6a, H-6b), 2.89 (s, 3H, CH_3SO_2), 2.02 (s, 3H, CH_3CON); ^{13}C NMR ($CDCl_3$): δ 170.87 (CH_3CON), 138.24, 137.70, 137.02, (C-quat. C_6H_5), 128.86–128.01 (C_6H_5), 80.56 (C-3), 78.74 (C-2), 78.21 (C-1), 75.24, 73.72, 72.62 (CH_2Ph), 74.75 (C-5), 73.33 (C-4), 67.55 (C-6), 38.58 (SO_2CH_3), 23.45 (CH_3CON). HMRS [M+H$^+$] $C_{30}H_{36}NO_8S$: calcd 570.2156, found 570.2148.

4.10. Pentenyl 2-allyloxycarbonylamino-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-talopyranoside 21

A mixture of salt **18** [obtained by reaction of azidomesylate **12** (0.250 g, 0.45 mmol) and triphenylphosphine (0.137 g, 0.52 mmol) in dichloromethane (2 mL)] and 4-penten-1-ol (0.50 mL, 10 equiv) was stirred for 4 h in toluene (1 mL) at 100 °C. The solution was concentrated in vacuo and the crude product was treated overnight with 1.5 M sodium hydroxide (1.5 mL) and methanol (8 mL). After neutralization (AcOH), the solution was concentrated again; the free-amino derivative was dissolved in dichloromethane (5 mL), after which water (2 mL), sodium bicarbonate (72 mg) and allyl chloroformate (70 μL, 0.66 mmol) were successively added and the biphasic mixture was stirred vigorously for 4 h. The aqueous phase was extracted with dichloromethane (2 × 10 mL), the combined organic phases were washed with a saturated sodium bicarbonate solution (5 mL), dried and concentrated. The crude residue was purified by column chromatography (1:3 ethyl acetate–petroleum ether), affording the pure glycoside **21** in 69% yield: 0.170 g, oily material; R_f 0.73 (1:3 ethyl acetate–petroleum ether), $[\alpha]_D$ = +16.3 (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.45–7.30 (m, 15H, $3C_6H_5$), 6.51 (d, 1H, $J_{2,NH}$ 9.1 Hz, N*H*), 5.97–5.85 (m, 1H, allyl *C*H=), 5.81 (m, 1H, pentenyl *C*H=), 5.30–5.16 (m, 2H, allyl CH_2=), 4.97 and 4.52 (dd, 2H, *J* 10.8 Hz, CH_2Ph), 4.86 (d, 1H, $J_{1,2}$ 1.2 Hz, H-1), 4.77 and 4.51 (dd, 2H, *J* 11.7 Hz, CH_2Ph), 4.60–4.52 (m, 2H, allyl CH_2), 4.55 and 4.46 (dd, 2H, *J* 11.5 Hz, CH_2Ph), 4.31 (ddd, 1H, $J_{2,3}$ 4.3 Hz, H-2), 3.97 (br dd, 1H, $J_{4,5}$ 0.8, $J_{5,6a}$ 7.1, $J_{5,6b}$ 6.0 Hz, H-5), 3.94 (br d, 1H, $J_{3,4}$ 2.9 Hz, H-4), 3.90 (dd, 1H, H-3), 3.66 (dd, 1H, $J_{5,6a}$ 7.1, $J_{6a,6b}$ 9.2 Hz, H-6a), 3.69–3.62 (m, 1H, pentenyl OC*H*), 3.58 (dd, 1H, $J_{5,6b}$ 6.0 Hz, H-6b), 3.46–3.38 (ddd, 1H, *J* 9.6, 9.4, 6.4 Hz, pentenyl OC*H*), 2.16–2.07 (m, 2H, pentenyl CH_2), 1.71–1.60 (m, 2H, pentenyl CH_2); ^{13}C NMR ($CDCl_3$): δ 156.45 (NCOO), 138.22, 138.17, 138.09 (C-quat. C_6H_5), 138.14 (pentenyl *C*H=), 133.12 (allyl *C*H=), 128.64–127.61 (C_6H_5), 117.06 (allyl CH_2=), 115.02 (pentenyl CH_2=), 100.45 (C-1), 75.54 (C-4), 75.39, 73.63, 70.02 (CH_2Ph), 72.58 (C-3), 69.46 (C-5), 69.03 (C-6), 67.30 (pentenyl OCH_2), 65.42 (allyl OCH_2), 50.50 (C-2), 30.41 (pentenyl CH_2), 48.53 (C-2), 28.73 (pentenyl CH_2), 48.53 (C-2). HRMS [M+H$^+$] $C_{36}H_{44}NO_7$: calcd 602.3112, found 602.3117.

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