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Phase transfer catalysis toward the synthesis of O-, S-, Se- and C-glycosides

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Abstract

Phase transfer catalysis (PTC) has been used for the synthesis of anomeric glycosyl derivatives, which included O-, S-, Se- and C- glycosides. These various glycosyl derivatives have been stereospecifically obtained from glycosyl halides **1**, **2**, **3**, **14**, **26**. These reactions proceeded in generally good yields, and were essentially complete within 3 h.

Keywords: PTC; Carbohydrate; Substitution; Thioglycoside; Selenoglycoside; Sialic acid

1. Introduction

Over the years, phase transfer catalysis (PTC) has proven to be a very useful and convenient method for various synthetic transformations. This methodology allows synthetic modifications under mild conditions that were heretofore reserved to very drastic reagents and reaction media. PTC was first devised to permit simple reactions where various reagents had incompatible solubilities. It has now developed into a far reaching field of synthetic transformations with complex substrates, as well as differing reaction media. Many natural products are synthesized with PTC conditions included in their procedures. Among these natural products, carbohydrates have proved to be challenging molecules because of the variety of functional groups, ring sizes, and stereocenters they include. Classical carbohydrate transformations are quite tedious as a result of the various protection and deprotection steps needed. These often require reactive promoters and reagents that can be quite toxic, costly and difficult to manipulate. Also, the use of very polar solvents can prove to be tedious because of the need for drying, purifying and removing them after completion. PTC is well suited for carbohydrate chemistry as the conditions can be quite mild and applicable to large scale synthesis. The use of non-anhydrous, as well as technical grade solvents, can alleviate much of the preparative work. Another important fact is that glycosides are susceptible to hydrolysis under acidic conditions, whereas PTC conditions are generally carried out under neutral or basic conditions.

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Even though this methodology has proven itself quite useful, its practice is not common [1]. Known examples of its use include complete or regioselective protection of hydroxyl groups by acetylation [2], acylation [3], benzylation [4], silylation [5], chain elongation by Wittig reaction [6], oxidation [7] and reduction [8]. Although these transformations are quite useful, the major stereoselective modifications of interest to carbohydrate chemist involve the anomeric center. The ability to control the stereochemistry at this position can be quite challenging and is perhaps the most important to the field of carbohydrate chemistry. So far, PTC conditions have been applied only to a limited number of glycosides [9–11,12a,12b,12c,13,14a,14b,14c, 14d,14e,15–21]. We present herein results demonstrating PTC as an effective and general methodology, as well as expanding the repertoire of glycosides prepared under PTC. It has been previously shown that glycosyl halides in an aqueous/organic two-phase system with tetraalkylammonium salts, can provide a variety of O-, N-, S-, Se- and C-glycosides with clean anomeric halide inversions [1]. The work presented in this paper is an expansion of the library of glycosides that can be prepared using PTC.

2. Results and discussion

2.1. O-glycosides

Several O-glycosides have been previously prepared in our group by using PTC [22,23]. By using anomeric nucleophilic substitutions, under PTC conditions, we synthesized various O-aryl glycosides with different electron donating and withdrawing substituents. The transformations were applied to glucose, galactose, *N*-acetylglucosamine, *N*-acetylgalactosamine, common disaccharides, and to sialic acid. These were prepared in order to probe potential electronic contributions from their binding to a plant lectin [23]. PTC conditions were successfully applied toward the syntheses of α and β napthols (80% for **7**, 70% for **8**), to glycohydrolase substrates 7-hydroxy-4-methylcoumarin (87% for **9**, 48% for **10**, 27% for **11**), to chromogenic substrate Fat Brown B® (30% for **12**), and to estrone pro-drug (65% for **13**) (Fig. 1). The conditions applied for the PTC were for a liquid/liquid biphasic system. Dichloromethane was used as organic solvent and aqueous NaOH as the base. Tetrabutylammonium hydrogen sulfate was used as the phase transfer catalyst since the counter anions avoided the possibility of double halide displacement and possible scrambling of the anomeric configuration that could be observed in the presence of chloride, bromide, or iodide anions. In all cases, complete anomeric inversion occurred, as expected from an S_N2 type mechanism without anchimeric group participation [21].

This synthetic approach was also extended to prepare divalent substrates. Bis(4-hydroxyphenyl)sulfone was an ideal candidate to test the PTC conditions on a bisphenoxide. Peracetylated galactosyl and *N*-acetylglucosaminidyl

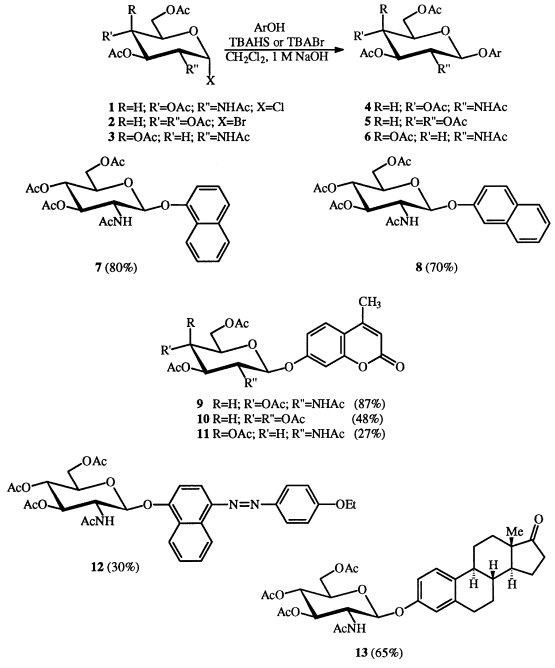


Fig. 1. Synthesis of O-aryl glycosides.

halides were then used for the synthesis of different substrates (**15**, **17**) (Fig. 2). These results showed that bisphenoxides could be glycosylated under PTC conditions, but in poor yields (22% for **15**, 36% for **17**), owing to the inherent difficulties associated with the transfer of dianionic species into the organic phase. Some monosubstituted derivatives could be isolated from these reactions (11% for **16**, 46% for **18**). Compound **15** was prepared according to previous PTC conditions, which included CH_2Cl_2 and NaOH. It was demonstrated afterwards that EtOAc was also effective as the organic phase and the use of Na_2CO_3 provided milder basic conditions for the PTC, preventing partial de-*O*-acetylation occasionally observed with substrates of low reactivity. By examining the results for compound **17**, the higher yield can be explained by the fact that EtOAc has a higher dielectric constant. The higher polarity of the solvent allowed a larger proportion of the dianion to be transferred into the organic phase.

The PTC reaction has already been demonstrated to be general and applicable to many other glycosyl halides. Other O-glycosyl derivatives were similarly prepared using these reaction conditions [24–27]. One such series of derivatives, which was prepared albeit unwill-

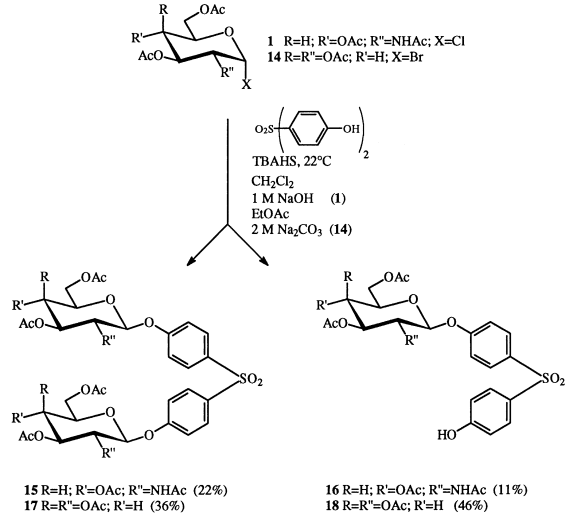


Fig. 2. Synthesis of disubstituted O-aryl glycosides.

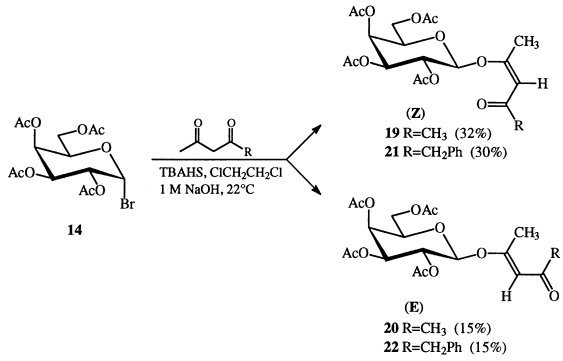
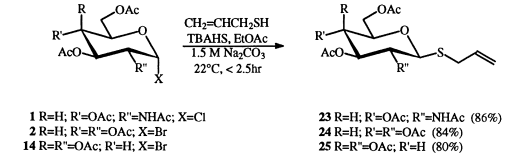


Fig. 3. Synthesis of enol glycosides.

ingly, are the enolate derivatives (**19**–**22**) (Fig. 3). Initially, C-glycosides were the target products desired. Glycosyl halide **14** was treated with 2,4-dione derivatives under PTC conditions, hoping to generate carbanions which could add to form the corresponding C-glycosides. The enolate intermediates reacted to give O-glycosides instead, in yields of 45–47%, and poor *Z*/*E* (2:1) stereoselectivity. This route showed a different approach for generating O-enol glycosides. The aglycons stereochemistry was determined from nuclear Overhauser enhancement (n.O.e.) experiments. Thus, irradiation of the olefinic hydrogen in the aglycon gave an n.O.e. of 16% for the anomeric proton in both *E*-O-enol glycosides (**20** and **22**), while no such n.O.e. could be observed in the *Z*-O-enol glycosides (**19** and **21**).

2.2. Thio- and seleno-glycosides

O-Glycosides, although being naturally occurring, are not hydrolytically stable to the action of glycohydrolase enzymes. The need for more stable glycosides, as well as more potent glycosyl donors in the syntheses of oligosaccharides, has triggered much interest in the preparation of thio- and seleno-glycosides [28,29]. Originally synthesized from peracetalyted sugars, Lewis acids, and the corresponding thiols, the stereochemical outcome of these transformations were not always predictable. By applying PTC conditions, and owing to the higher acidi-



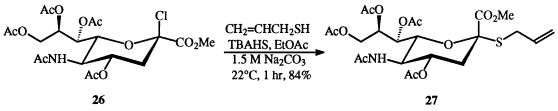


Fig. 4. Synthesis of S-allyl glycosides.

ties and ''softness'' of thiols and selenols, we could obtain various thio- and selenoglycosides in very high yields [30–37]. Because of this increased acidity, milder basic conditions could be used. It has been found that saturated $NaHCO_3$ and 1 M Na_2CO_3, as the aqueous phase, were sufficient with thiols and selenols together with tetrabutylammonium hydrogen sulfate. As for solvent, the original conditions for PTC have included CH_2Cl_2 but this was a poor choice in the case of thiols and selenols. We have previously demonstrated that large proportions of the thiols reacted with dichloromethane to give products such as bis(4-nitrophenylthio)methane [30]. It has since been shown that EtOAc was a much better choice of solvent, which allowed fast and stereospecific routes toward thio- and seleno-glycosides by using stoichiometric amounts of nucleophiles. This is equally applicable to dissaccharides [30,36] and thioether linked dissaccharides [16,17,19]. Since some thiols are more prone to disulfide formation under basic conditions than others, it may be necessary to perform certain of the reactions under a nitrogen atmosphere. We

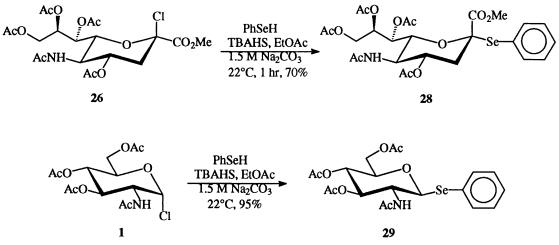


Fig. 5. Synthesis of seleno-glycosides.

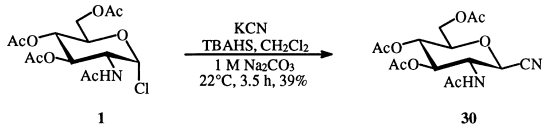


Fig. 6. Synthesis of C-glycosides.

have demonstrated that allyl mercaptan can be added efficiently (86% for **23**, 84% for **24**, 80% for **25**). This entry has been applied to sialic acid **26** [32] to give the corresponding thio-glycosides **27** in 84% yield (Fig. 4).

These conditions have been demonstrated to work with selenols. Representative examples have been benzene selenol and acetochloroneuraminic acid **26** and chloride **1** to give the corresponding seleno-glycosides (**28**, **29**) in 70% and 95% yield, respectively (Fig. 5).

2.3. C-glycosides

The formation of C-glycosides spurred tremendous interest and research in recent years [37]. Their obvious advantages are their stereochemical stability as well as their resistance to glycohydrolase enzymes. Several methods exist for their synthesis but no successful application of PTC has been reported so far [21]. By using chloride **1** and potassium cyanide, we obtained the corresponding glycosyl cyanide (**30**) in 39% yield (Fig. 6). Our previous attempts with compounds containing acidic methylene units ($MeNO_2$, CH_3CN, malonates, etc.) and peracetylated sugars met with failure. It is believed that de-O-acetylation was the major source of difficulties with these nucleophiles. Attempts with diones resulted in O-alkylation products (**19**–**22**), as discussed above. Work is now in progress to attempt these reactions with perbenzylated glycosyl halides instead of peracetylated derivatives.

3. Conclusion

We have demonstrated that PTC can be applied successfully to O-aryl, S-allyl and Se-

phenyl glycosides. The first reported use of PTC for the synthesis of C-glycosides has also been included.

4. Experimental

4.1. General methods

Melting points were determined on a Gallenkamp apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on Varian Gemini-200 and Bruker AMX-500 spectrometers. Proton chemical shifts (δ) are given relative to internal chloroform (δ = 7.24 ppm) for $CDCl_3$ solutions or to methanol (3.30 ppm) for CD_3OD solutions. Carbon chemical shifts are given relative to deuteriochloroform (77.0 ppm) and to CD_3OD (49.0 ppm). Optical rotations were measured at room temperature (23 ± 1°C) in a 1 dm cell on a Perkin-Elmer 241 polarimeter. Mass spectra were recorded on a VG 7070-E spectrometer (CI, ether) and Kratos Concept IIH (FAB-MS, thioglycerol). Thin-layer chromatography (TLC) was performed using silica gel 60 F-254 and column chromatography on silica gel 60 (230–400 mesh, E. Merck No. 9385). All solvents and reagents were reagent grade and were used without further purification.

4.1.1. α-Naphthyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (7)

Chloride **1** (407.2 mg, 1.114 mmol), α-naphthol (332.0 mg, 2.233 mmol) and tetrabutylammonium bromide (359.3 mg, 1.114 mmol) were stirred vigorously in a two-phase system consisting of 4.0 ml of CH_2Cl_2 and 3.0 ml of 1 M NaOH, at room temperature for approximately 30 min after which time TLC (25/5/2, $CHCl_3$/EtOAc/*n*-prOH) indicated complete consumption of the chloride **1**. The reaction was worked up by adding 50 ml of ethyl acetate and successively washing the organic phase with 40 ml of 1 M NaOH and 40 ml of water (2×). The organic phase was then dried with Na_2SO_4, filtered and evaporated to a brownish mass. Compound **7** was recovered in 80% yield (422 mg) after three crystallization crops from isopropanol. Compound **7** has m.p. 212–213°C (*i*-prOH); $[\alpha]_D$ − 66.0° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 8.15 (m, 1H, H_{Ar}), 7.52 (d, 1H, J = 8.4 Hz, H_{Ar}), 7.47 (m, 2H, H_{Ar}), 7.33 (dd, 1H, J = 7.7, J = 8.2, H_{Ar}), 7.02 (dd, 1H, J = 0.9, J = 8.7, H_{Ar}), 5.59 (d, 1H, $J_{2,NH}$ = 9.2, NH), 5.30 (dd, 1H, $J_{2,3}$ = 10.4, $J_{3,4}$ = 9.3, H_3), 5.22 (d, 1H, $J_{1,2}$ = 8.3, H_1), 5.20 (dd, 1H, $J_{4,5}$ = 9.6, H_4), 4.51 (m, 1H, H_2), 4.31 (dd, 1H, $J_{5,6}$ = 5.4, $J_{6,6'}$ = 12.3, H_6), 4.20 (dd, 1H, $J_{5,6'}$ = 2.6, $H_{6'}$), 3.91 (ddd, 1H, H_5), 2.05–2.08 (3s, 9H, 3 OAc), 1.94 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 169.3–170.8 (4 C═O), 153.1 (O–C_{Ar}), 134.1, 127.1, 126.2, 125.5 (2C), 125.3, 122.3, 121.7, 108.8 (9 C_{Ar}), 99.7 (C_1), 72.1 (C_5), 71.4 (C_3), 68.6 (C_4), 61.9 (C_6), 53.4 (C_2), 22.5 (NAc), 20.1 (3 OAc). MS (CI ether, rel. intensity) m/z: 474 ($[M + H]^+$, 34%), 330 ($[M$ – aglycon$]^+$, 100%). Anal. Calcd for $C_{24}H_{27}NO_9$: C, 60.88; H, 5.75; N, 2.96%. Found: C, 60.60; H, 5.83; N, 2.84.

4.1.2. β-Naphthyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (8)

Chloride **1** (430 mg, 1.18 mmol) was stirred with one equivalent of TBA bromide and two equivalents of β-naphthol in the same solvent system and under identical conditions as for **7**. Identical work up and crystallization procedure gave **8** in 70% yield (369 mg). Compound **8** has m.p. 220–221°C (*i*-prOH); $[\alpha]_D$ − 65.8° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.67–7.78 (m, 3H, H_{Ar}), 7.13–7.47 (m, 4H, H_{Ar}), 5.75 (d, 1H, $J_{2,NH}$ = 8.8 Hz, NH), 5.42 (dd, 1H, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.3, H_3), 5.38 (d, 1H, $J_{1,2}$ = 8.2, H_1), 5.14 (dd, 1H, $J_{4,5}$ = 9.8, H_4), 4.54 (dd, 1H, H_2), 4.28 (dd, 1H, $J_{5,6}$ = 5.5, $J_{6,6'}$ = 12.2, H_6), 4.16 (dd, 1H, $J_{5,6'}$ = 2.6, $H_{6'}$), 3.92 (ddd, 1H, H_5), 1.93–2.05 (4s, 12H, 3 OAc, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 169.6–171.0 (4 C═O), 155.0 (O–C_{Ar}), 134.2, 130.1, 129.6, 127.8, 127.1, 126.6, 124.7, 119.0, 111.5 (9 C_{Ar}), 99.0 (C_1), 72.1 (C_5), 71.9 (C_3), 68.8 (C_4), 62.2 (C_6), 54.7 (C_2), 23.0 (NAc), 20.4–20.5 (3 OAc). MS (CI ether, rel. intensity) m/z: 474 ($[M + H]^+$,

30%), 330 ([M - aglycon]$^+$, 100%). Anal. Calcd for $C_{24}H_{27}NO_9$: C, 60.88; H, 5.75; N, 2.96%. Found: C, 60.94; H, 5.66; N, 2.89.

*4.1.3. 7-O-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl) 3-methyl coumarin (**9**)*

Chloride **1** (505 mg, 1.38 mmol), TBAHS (467 mg, 1.38 mmol) and 7-hydroxy-3-methyl coumarin (485 mg, 2.75 mmol) were stirred vigorously in a combination of 5 ml of CH_2Cl_2 and 5 ml of 1 M NaOH at room temperature for 30 min. The reaction was then worked up by adding 50 ml of ethyl acetate and successively washing the organic phase with 50 ml 1 M NaOH (2 ×) and 50 ml H_2O (3 ×). During the extraction procedure, material began to crystallize out of organic phase and settle at the interface. The aqueous phase was removed, and the organic phase evaporated to dryness to yield a white crystalline mass. Recrystallization from $CHCl_3$/EtOH gave, in three crops, **9** in 87% yield (604 mg), pure by TLC and NMR. Compound **9** has m.p. 255–256°C ($CHCl_3$/EtOH); $[\alpha]_D$ − 0.0° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.45 (d, 1H, J = 8.5 Hz, H_{Ar}), 6.12 (d, 1H, $J_{allylic}$ = 1.2, C(O)C*H*═), 6.00 (d, 1H, $J_{2,NH}$ = 8.9, NH), 5.41 (dd, 1H, $J_{2,3}$ = 10.5, $J_{3,4}$ = 9.3, H_3), 5.37 (d, 1H, $J_{1,2}$ = 8.2, H_1), 5.14 (dd, 1H, $J_{4,5}$ = 9.9, H_4), 4.27 (dd, 1H, $J_{5,6}$ = 5.5, $J_{6,6'}$ = 12.2, H_6), 4.18 (m, 1H, H_2), 4.14 (dd, 1H, $J_{5,6'}$ = 2.6, $H_{6'}$), 3.92 (ddd, 1H, H_5), 2.35 (d, 3H, CH_3 coumarin), 1.99–2.08 (3s, 9H, 3 OAc), 1.94 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 169.7–170.3 (4 C═O, Ac), 160.3 (C═O, coumarin), 159.5 (C_7, coumarin), 154.6 (C_9, coumarin), 153.5 (C_4, coumarin), 126.8 (C_5, coumarin), 114.9 (*C*-Me), 113.8 (C_8, coumarin), 112.3 (C_6, coumarin), 103.5 (C(O)–*C*H═), 97.5 (C_1), 72.4 (C_5), 71.2 (C_3), 68.5 (C_4), 61.7 (C_6), 53.1 (C_2), 22.6 (NAc), 20.3–20.4 (3 OAc), 18.0 (CH_3, coumarin). MS (CI ether, rel. intensity) m/z: 506 ([M + H]$^+$, 3%), 330 ([M − aglycon]$^+$, 100%), 177 ([coumarin + H]$^+$, 100%). Anal. Calcd for $C_{24}H_{27}NO_{11}$: C, 57.03; H, 5.38; N, 2.77%. Found: C, 56.80; H, 5.44; N, 2.71.

*4.1.4. 7-O-(β-D-glucopyranosyl) 3-methyl coumarin (**10**)*

Acetobromoglucose **2** (315 mg, 0.766 mmol), TBAHS (260 mg, 0.766 mmol) and 7-hydroxy-3-methyl coumarin (260 mg, 1.48 mmol) were stirred in 1.5 ml of CH_2Cl_2 and 1.5 ml of 1 M NaOH at room temperature for 40 min, until TLC (1/1 EtOAc/hexanes + 1% *n*-prOH) indicated complete consumption of the bromide. The reaction was work up by adding 30 ml EtOAc and successively washing the organic phase with 30 ml 1 M NaOH, 30 ml H_2O (twice) and 15 ml sat. brine. The organic phase was then dried with Na_2SO_4, filtered and evaporated to a clear oil. Purification by preparative TLC gave 60.0 mg (49%) of the known acetoxy glucal (R_f = 0.52) and 88.0 mg (48%) of **10** (R_f = 0.26). The glycoside could be crystallized from ether/hexanes. Compound **10** has m.p. 144–145°C (ether/hexanes); $[\alpha]_D$ − 36.0° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.47 (d, 1H, J = 8.6 Hz, H_5 coumarin), 6.88 (m, 2H, H_{Ar}), 6.13 (d, 1H, $J_{allylic}$ = 1.1, C(O)C*H*═), 5.07–5.34 (m, 4H, H_1, H_2, H_3, H_4), 4.25 (dd, 1H, $J_{5,6}$ = 5.6, $J_{6,6'}$ = 12.4, H_6), 4.12 (dd, 1H, $J_{5,6'}$ = 2.3, $H_{6'}$), 3.89 (ddd, 1H, $J_{4,5}$ = 10.5, H_5), 2.35 (d, 3H, $J_{allylic}$ = 0.8, CH_3 coumarin), 2.06, 2.01, 2.01 (3s, 9H, 3 OAc), 1.99 (s, 3H, NAc).; ^{13}C NMR ($CDCl_3$) δ (ppm): 170.7, 170.3, 169.5, 169.4 (4 C═O, Ac), 160.8 (C═O, coumarin), 159.2 (C_7, coumarin), 154.9 (C_9, coumarin), 152.3 (C_4, coumarin), 125.8 (C_5, coumarin), 115.5 (*C*-Me), 113.9 (C_8, coumarin), 113.1 (C_6, coumarin), 103.5 (C(O)–*C*H═), 98.2 (C_1), 72.4 (C_5), 72.2 (C_3), 70.8 (C_2), 67.9 (C_4), 61.6 (C_6), 20.3–20.5 (4 OAc), 18.4 (CH_3, coumarin). MS (CI ether, rel. intensity) m/z: 507 ([M + H]$^+$, 74%), 331 ([M − aglycon]$^+$, 100%); Anal. Calcd for $C_{24}H_{26}O_{12}$: C, 56.92; H, 5.17%. Found: C, 56.81; H, 5.10.

*4.1.5. 7-O-(2-acetamido-2-deoxy-β-D-galactopyranosyl) 3-methylcoumarin (**11**)*

Chloride **3** (0.453 mmol), TBAHS (153.6 mg, 0.453 mmol) and 7-hydroxy-3-methylcou-

marin (159.5 mg, 0.905 mmol) were added to 2 ml of CH_2Cl_2 and 2 ml of 1 M NaOH. The resulting solution was vigorously stirred at room temperature for 50 min, after which time the reaction was worked up as described for **10**. Purification of the clear oil by preparative TLC (25/5/3 $CHCl_3$/EtOAc/*n*-prOH) gave, after overnight extraction of the silica in 40 ml 2/1 EtOAc/CH_2Cl_2, filtration and evaporation, pure **11** in 27% yield (61.0 mg). Compound **11** has m.p. 219–220°C (ether/hexanes); $[\alpha]_D$ − 5.5° (c 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.48 (dd, 1H, $J_{5,8} = 1.7$ Hz, $J_{5,6} = 7.6$, H_5 coumarin), 6.49 (m, 2H, H_{Ar}), 6.15 (d, 1H, $J_{allylic} = 1.2$, C(O)C*H*═), 5.64 (d, 1H, $J_{2,NH} =$ 8.7, NH), 5.38–5.45 (AB m, 2H, H_3, H_4), 5.39 (d, 1H, $J_{1,2} = 8.3$, H_1), 4.28 (ddd, 1H, $J_{2,3} =$ 10.5, H_2), 4.11–4.18 (m, 3H, H_5, H_6, $H_{6'}$), 2.38 (d, 3H, $J_{allylic} = 1.2$, CH_3 coumarin), 2.16, 2.09, 2.03 (3s, 9H, 3 OAc), 1.96 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.2–170.6 (4 C═O, Ac), 160.9 (C═O, coumarin), 159.6 (C_7, coumarin), 154.7 (C_9, coumarin), 152.4 (C_4, coumarin), 125.6 (C_5, coumarin), 115.2 (*C*-Me), 114.0 (C_8, coumarin), 112.9 (C_6, coumarin), 103.9 (C(O)–*C*H═), 98.5 (C_1), 71.4 (C_5), 69.7 (C_3), 66.6 (C_4), 61.6 (C_6), 51.2 (C_2), 23.4 (NAc), 20.6 (3 OAc), 18.6 (CH_3, coumarin). MS (CI ether, rel. intensity) *m/z*: 506 ($[M + H]^+$, 3%), 330 ($[M -$ aglycon$]^+$, 100%), 177 ($[$Coumarin + H$]^+$, 100%). Anal. Calcd for $C_{24}H_{27}NO_{11}$: C, 57.03; H, 5.38; N, 2.77%. Found: C, 57.19; H, 5.38; N, 2.61.

*4.1.6. [4-(p-ethoxyphenyl)azonaphth-l-yl]2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (**12**)*

Chloride **1** (80.0 mg, 0.219 mmol), TBAHS (74.0 mg, 0.218 mmol) and 4-(*p*-ethoxyphenyl)azonaphth-l-ol (Fat Brown B indicator) (66.0 mg, 0.226 mmol) were stirred vigorously for 45 min in 1.0 ml of CH_2Cl_2 and 1.0 ml of 1 M NaOH, at room temperature. After the usual extractive procedure, evaporation gave a yellow crystalline mass. The product was purified by silica gel chromatography (1:1 $CHCl_3$:EtOAc). Compound **12** was obtained in 30% yield (40.6 mg) after evaporation of solvent. The whole mass was recrystallized from 20 ml EtOH to give floculant yellow needles. FAB (glycerol)- and CI (ether)-MS procedures failed to desorb the sample and thus could not provide an adequate spectrum. Compound **12** has m.p. 274–275°C (EtOH); $[\alpha]_D$ + 22.5° (c 1, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.90 (dd, 1H, $J = 0.6$, $J = 7.7$ Hz, H_{Ar}), 8.21 (dd, 1H, $J = 0.8$, $J = 8.4$, H_{Ar}), 7.99 (d, 2H, $J_{o,p} = 9.1$, H_m to glycoside), 7.75 (d, 1H, $J = 8.4$, H_{Ar}), 7.59 (symmetrical m, 2H, H_{Ar}), 7.06 (d, 1H, $J = 8.5$, H_{Ar}), 7.01 (d, 2H, H_o to glycoside), 5.58 (d, 1H, $J_{2,NH} =$ 9.1, NH), 5.30 (dd, 1H, $J_{2,3} = 10.4$, $J_{3,4} = 9.4$, H_3), 5.25 (d, 1H, $J_{1,2} = 7.6$, H_1), 5.21 (dd, 1H, $J_{4,5} = 9.4$, H_4), 4.55 (ddd, 1H, H_2), 4.31 (dd, 1H, $J_{5,6} = 5.5$, $J_{6,6'} = 12.3$, H_6), 4.20 (dd, 1H, $J_{5,6'} = 2.5$, $H_{6'}$), 4.12 (q, 2H, $J = 7.0$, CH_2), 3.94 (ddd, 1H, H_5), 1.94–2.09 (4s, 12H, 3 OAc, NAc), 1.46 (t, 3H, $J = 7.0$, CH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.6, 170.3, 170.1, 169.3 (C═O), 161.3 (C_{ipso} to glycoside), l55.0 (quat. C_{Ar}), 147.5 (quat. C_{Ar}), 143.4 (quat. C_{Ar}), 132.2 (quat. C_{Ar}), 127.4 (CH_{Ar}), 126.4 (CH_{Ar}), 125.8 (quat. C_{Ar}), 124.9 (C_m to glycoside), 123.2 (CH_{Ar}), 122.0 (CH_{Ar}), 114.7 (C_o to glycoside), 111.8 (CH_{Ar}), 108.3 (CH_{Ar}), 99.7 (C_1), 72.2 (C_5), 72.1 (C_3), 68.3 (C_4), 63.8 (CH_2), 62.1 (C_6), 23.3 (NAc), 20.6–20.7 (3 OAc), 14.8 (CH_3 of aglycon). Anal. Calcd for $C_{32}H_{35}N_3O_{10}$: C, 61.83; H, 5.67; N, 6.76%. Found: C, 61.51; H, 6.03; N, 6.71.

*4.1.7. 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl estrone (**13**)*

Chloride **1** (350 mg, 0.957 mmol), TBAHS (324.9 mg, 0.957 mmol) and estrone (517.4 mg, 1.914 mmol, 2 equiv.) were stirred vigorously at room temperature in a two-phase system comprised of 3.5 ml CH_2Cl_2 and 3.5 ml 0.1 M NaOH for 30 min after which time TLC (2/1 EtOAc/hexane) indicated a complete consumption of **1**. After the usual extractive work up, the

product was purified by radial silica gel chromatography (2/1 EtOAc/hexane). 369.6 mg (65%) of **13**, pure by TLC and NMR, was recovered after solvent evaporation. Compound **13** has m.p. 124°C sinters (ether/hexanes); $[\alpha]_D + 54.6°$ (c 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ (ppm): 7.17 (dd, 1H, $J = 8.7$ Hz, H_m to glycoside), 6.75 (dd, 1H, $J = 1.7$, $J = 8.7$, H_o next to H_m), 6.71 (d, 1H, $J = 1.7$, H_o to glycoside and steroid ring), 5.57 (d, 1H, $J_{2,NH} = 8.8$, NH), 5.38 (dd, 1H, $J_{2,3}$ 10.5, $J_{3,4} = 9.3$, H_3), 5.16 (d, 1H, $J_{1,2} = 8.3$, H_1), 5.11 (dd, 1H, $J_{4,5} = 9.8$, H_4), 4.26 (dd, 1H, $J_{5,6} = 5.4$, $J_{6,6'} =$ 12.2 Hz, H_6), 4.14 (dd, 1H, $J_{5,6'} = 2.4$, $H_{6'}$), 4.08 (ddd, 1H, H_2), 3.84 (ddd, 1H, H_5), 2.85 (m, 2H, steroid), 2.52 (d, 1H, $J = 8.7$, steroid), 2.46 (d, 1H, $J = 7.8$, steroid), 2.01–2.07 (3s, 9H, 3 OAc), 1.94 (s, 3H, NAc), 0.88 (s, 3H, CH_3 steroid), remaining peaks between 1.23 and 2.37 ppm, belonging to the steroid aglycon integrate for 11H. ^{13}C NMR ($CDCl_3$) δ (ppm): 220.7 (C═O steroid), 170.7, 170.5, 170.3, 169.3 (C═O), 154.8 (O–C_{Ar}), 137.8 (quat. C_{Ar}), 126.2 (C_m to glycoside), 116.9 (C_o to glycoside), 114.1 (C_o to glycoside), 98.9 (C_1), 72.1 (C_5), 71.9 (C_3), 68.6 (C_4), 50.4 (CH steroid), 48.0 (quat. steroid), 44.0 (CH steroid), 38.2 (CH steroid), 35.9 (CH steroid), 31.6 (CH_2 steroid), 29.7 (CH_2 steroid), 26.5 (CH_2 steroid), 25.9 (CH_2 steroid), 23.4 (NAc), 21.6 (CH_2 steroid), 20.7–20.8 (3 OAc), 13.9 (CH_3 steroid). MS (FAB glycerol, rel. intensity) m/z: 1189 ($[2M + H]^+$, 2.4%), 600 ($[M + H]^+$, 17%), 330 ($[M$ – aglycon$]^+$, 84%), 269 ([Estrone + H]$^+$, 58%). Anal. Calcd for $C_{32}H_{41}NO_{10}$: C, 64.09; H, 6.89; N, 2.34%. Found: C, 63.97; H, 6.86; N, 2.34.

4.1.8. Bis[4-(2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyloxy)phenyl]sulfone (15)

Chloride **1** (403 mg, 1.10 mmol), tetrabutylammonium hydrogen sulfate (250 mg, 0.73 mmol) and bis(4-hydroxyphenyl)sulfone (92.3 mg, 0.368 mmol) were stirred vigorously at room temperature in CH_2Cl_2 (5 ml) and 1 M NaOH (5 ml) for 2 h. TLC ($CHCl_3$/EtOAc/*i*-prOH, 25:5:2) indicated complete transformation of the chloride **1** ($R_f = 0.54$), unreacted sulfone ($R_f = 0.42$) and two new major products ($R_f = 0.24$ and 0.13). EtOAc was added and the organic phase was washed successively with 1 M NaOH, water and brine. The combined organic extracts were dried (Na_2SO_4), filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using the above eluent. The monosubstituted glycoside **16** was obtained in 11% yield (24.3 mg) followed by the desired bisglycosylated compound **15** in 22% yield (74.6 mg). Compound **15** has m.p. 214–216°C (EtOH); $[\alpha]_D - 0.7°$ (c 1, DMSO); ^1H NMR (DMSO-d_6) δ (ppm): 7.78 (d, 2H, $J_{o,m} = 8.9$ Hz, H_o), 7.02 (d, 2H, H_m), 5.77 (d, 1H, $J_{2,NH} = 8.5$ Hz, NH), 5.39 (dd, 1H, $J_{2,3} =$ 10.3, $J_{3,4} = 9.4$, H_3), 5.38 (d, 1H, $J_{1,2} = 8.1$, H_1), 5.11 (dd, 1H, $J_{4,5} = 9.9$, H_4), 4.24 (dd, 1H, $J_{5,6} = 5.3$, $J_{6,6'} = 12.2$, H_6), 4.13 (dd, 1H, $J_{5,6'} = 2.3$, $H_{6'}$), 4.11 (ddd, 1H, H_2), 3.89 (ddd, 1H, H_5), 2.04, 2.03 (3s, 9H, 3 OAc), 1.89 (s, 3H, NAc); ^{13}C NMR (DMSO-d_6) δ (ppm): 169.7, 169.4, 169.3, 169.0 (4 C═O), 159.9 (C_p), 135.0 (C_{ipso}), 129.7 (C_m), 116.9 (C_o), 96.9 (C_1), 72.1(C_5), 70.9 (C_3), 68.1 (C_4), 61.4 (C_6), 52.9 (C_2), 22.6 (NAc), 20.3, 20.4 ($3CH_3$, OAc). Anal. calcd. for $C_{40}H_{48}N_2O_{20}S$: C 52.72, H 5.32, N 3.02, S 3.29; found: C 52.86, H 5.32, N 3.08, S 3.53.

The monoglycosylated by-product **16** showed ^1H NMR ($CDCl_3$) δ (ppm): 7.76 (d, 2H, $J_{o,m} =$ 8.8 Hz, H_o), 7.72 (d, 2H, $J_{o',m'} = 8.7$ Hz, $H_{o'}$), 6.99 (d, 2H, H_m), 6.87 (d, 2H, $H_{m'}$), 5.95 (d, 1H, $J_{2,NH} = 7.4$ Hz, NH), 5.37 (d, 1H, $J_{1,2} = 8.3$ Hz, H_1), 5.36 (dd, 1H, $J_{2,3} = 10.1$, $J_{3,4} = 9.5$ Hz, H_3), 5.12 (dd, 1H, $J_{4,5} = 9.8$, H_4), 4.24 (dd, 1H, $J_{5,6} = 5.2$, $J_{6,6'} = 12.2$ Hz, H_6), 4. 12 (dd, 1H, $J_{5,6'} = 2.3$ Hz, $H_{6'}$), 4.11 (ddd, 1H, H_2), 3.85 (m, 1H, H_5), 2.04, 2.02 (3s, 9H, OAc), 1.91 (s, 3H, NAc). MS for $C_{26}H_{29}NO_{12}S$ (FAB$^+$glycerol, rel. intensity) m/z: 580.1 ($[M + H]^+$, 1.2%), 330 ($[M$ – aglycon$]^+$, 100%).

*4.1.9. Bis[4-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyloxy)phenyl]sulfone (**17**)*

Acetobromogalactose **14** (400 mg, 0.973 mmol), bis(4-hydroxyphenyl)sulfone (101 mg, 0.405 mmol) and tetrabutylammonium hydrogen sulfate (275 mg, 0.811 mmol) were vigorously stirred in ethyl acetate (4 ml) and 2 M sodium carbonate (8 ml) at room temperature. After 6 h, TLC ($CHCl_3$/MeOH, 25:1) indicated complete transformation of the bromide **14** ($R_f = 0.55$) to give the monoglycosylated product **18** ($R_f = 0.35$) and the desired bisglycosylated product **17** ($R_f = 0.22$) as the major compound. The organic phase was diluted with ethylacetate and washed with saturated $NaHCO_3$, water and brine. The pooled organic extracts were dried (Na_2SO_4), filtered and evaporated under reduced pressure. The residue was then purified by radial chromatography using $CHCl_3$/*i*-prOH (30:1) to provide the monoglycosylated sulfone derivative **18** (109 mg, 46%) and the desired bisglycoside **17** (133 mg, 36%). Compound **17** (foam) $[\alpha]_D + 10.5°$ (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.84 (d, 2H, $J_{o,m} = 8.8$ Hz, H_o), 7.04 (d, 2H, H_m), 5.46 (dd, 1H, $J_{1,2} = 7.8$, $J_{2,3} = 10.4$, H_2), 5.43 (d, 1H, $J_{3,4} = 3.4$, H_4), 5.07–5.08 (m, 2H, H_1 and H_3), 4.03–4.19 (m, 3H, H_5, H_6 and $H_{6'}$), 2.15, 2.03, 2.02, 1.99 (4s, 12H, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.1, 170.0, 169.2 (4 C═O), 160.1 (C_p), 136.1 (C_{ipso}), 129.6 (C_m), 117.0 (C_o), 98.6 (C_1), 71.3 (C_3), 70.6 (C_5), 68.3 (C_4), 66.6 (C_2), 61.3 (C_6), 20.6, 20.5 (OAc). MS for $C_{40}H_{46}O_{22}S$ (FAB$^+$glycerol, rel. intensity) *m*/*z*: 1844.9 $[2M + Na]^+$, 1%), 933.2 ($[M + Na]^+$, 10%), 331.1 ($[M - \text{aglycon}]^+$, 40%). The monogalactosylated sulfone by-product **18**: ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, 2H, $J_{o,m} = 8.8$ Hz, H_o), 7.74 (d, 2H, $J_{o',m'} = 8.9$, $H_{o'}$), 7.02 (d, 2H, H_m), 6.92 (d, 2H, $H_{m'}$), 5.46 (dd, 1H, $J_{1,2} = 7.8$, $J_{2,3} = 10.3$, H_2), 5.44 (d, 1H, $J_{3,4} = 3.4$, H_4), 5.08 (dd, 1H, H_3), 5.07 (d, 1H, H_1), 4.03–4.19 (m, 3H, H_5, H_6 and $H_{6'}$), 2.15, 2.02, 1.99 (3s, 12H, OAc). MS for $C_{26}H_{28}O_{13}S$ (FAB$^-$ glycerol, rel. intensity) *m*/*z*: 579.2 ($[M - H]^-$, 7%), 249 ([aglycon]$^-$, 28%).

4.1.10. PTC galactosylation of 2,4-pentanedione, preparation of enolate glycosides 19 and 20

Acetobromogalactose **14** (2.00 g, 4.86 mmol) and TBAHS (1.65 g, 1 equiv.) were dissolved in 20 ml of 1,2-dichloroethane. 20 ml of 1 M NaOH were then added followed by 750 μl (1.5 equiv.) of 2,4-pentanedione. The reaction was stirred for a total of 11 h at room temperature, after which TLC (1/1 EtOAc/hexane + 0.5% *i*-prOH) showed complete consumption of the bromide **14** ($R_f = 0.17$, Z-O-enol-β-D-galactopyranoside **19**; $R_f = 0.30$, E-O-enol-β-D-galactopyranoside **20**). The reaction was worked up by separating the aqueous phase, diluting the organic phase with EtOAc then successively washing it with sat. $NaHCO_3$, water (2 ×), and sat. brine. Drying (Na_2SO_4), filtration and evaporation under reduced pressure gave an oil. After dissolving in a minimum of CH_2Cl_2, the crude material was applied to silica gel column then eluted with a gradient of EtOAc/hexane (3/4, 1/1, 4/3; v/v) including 0.5% *i*-prOH. 0.31 g (15%) of *E*-enol galactoside **20** was recovered, followed by 0.67 g (32%) of the *Z*-enol galactoside **19**. Compound **19** has m.p. 125–127°C; $[\alpha]_D - 3.2°$ (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 5.41 (dd, 1H, $J_{4,5} = 1.0$ Hz, H_4), 5.40 (dd, 1H, $J_{2,3} = 10.3$, H_2), 5.20 (s, 1H, ═CH), 5.08 (d, 1H, $J_{1,2} = 7.9$, H_1), 5.06 (dd, 1H, $J_{3,4} = 3.5$, H_3), 4.13 (m, 2H, H_6 and $H_{6'}$), 3.98 (ddd, 1H, $J_{5,6'} = 7.2$, $J_{5,6} = 5.6$, H_5), 2.29 (s, 3H, CH_3CO from aglycon), 2.07 (s, 3H, CH_3C═), 1.97–2.14 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 197.7 (C═O), 170.1, 170.0, 169.8, 168.9 (C═O, OAc), 161.4 (O–C═), 112.6 (═CH), 96.3 (C_1), 71.2 (C_5), 70.5 (C_3), 68.1 (C_2), 66.6 (C_4), 61.2 (C_6), 20.6, 20.5, 20.4 (4 OAc), 18.3 (CH_3). Anal. Calcd for $C_{19}H_{26}O_{11}$: C, 53.02; H, 6.09%. Found: C, 53.23; H, 6.12. Compound **20** has m.p. 126–127°C; $[\alpha]_D - 7.3°$ (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 5.69 (s, 1H, ═CH), 5.41 (dd, 1H, $J_{4,5} = 1.0$ Hz, H_4), 5.37 (dd, 1H, $J_{2,3} = 10.5$, H_2), 5.05 (dd, 1H, $J_{3,4} = 3.4$, H_3), 4.97 (d, 1H, $J_{1,2} = 8.0$, H_1), 4.14 (m, 2H, H_6

and $H_{6'}$), 4.03 (ddd, 1H, $J_{5,6'} = 7.3$, $J_{5,6} = 5.5$, H_5), 2.24 (s, 3H, $CH_3C{=}$), 2.15 (s, 3H, CH_3CO from aglycon), 1.97–2.14 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 197.0 (C=O), 170.2, 170.0, 169.9, 169.1 (C=O, OAc), 168.7 (O–C=), 103.8 (=CH), 96.7 (C_1), 71.4 (C_5), 70.4 (C_3), 67.9 (C_2), 66.7 (C_4), 61.5 (C_6), 20.6, 20.5 (4 OAc), 18.5 (CH_3). Anal. Calcd for $C_{19}H_{26}O_{11}$: C, 53.02; H, 6.09%. Found: C, 53.25; H, 6.13.

4.1.11. PTC galactosylation of benzyl 3-keto-butanoate. Preparation of enolate glycosides 21 and 22

Acetobromogalactose **14** (200 mg, 0.486 mmol), TBAHS (165 mg, 1 equiv.), and benzyl 3-keto butanoate (acetobenzyl acetate) (140 μl) were stirred vigorously at room temperature in 2.5 ml of 1,2-dichloroethane and 2.5 ml of 1 M NaOH. After 6 h, TLC (1/1, EtOAc/hexane + 0.5% *i*-prOH) showed a complete consumption of the halide **14** to give two major products ($R_f = 0.25$, Z-O-enol-β-D-galactopyranoside **21**; $R_f = 0.39$, E-O-enol-β-D-galactopyranoside **22**). The reaction was worked up as described for **19**/**20**. The products were simplified by preparative TLC using $CHCl_3$/MeOH (30/1, v/v) as eluent. Extraction of the u.v. active bands with EtOAc gave 73 mg (30%) of **21** and 38 mg (15%) of **22**. All attempts at crystallization failed for both compounds. Compound **21** has $[\alpha]_D$ + 11.4° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.29 (m, 5H, H_{Ar}), 5.43 (dd, 1H, $J_{2,3} = 10.5$, H_2), 5.39 (dd, 1H, $J_{4,5} = 1.0$ Hz, H_4), 5.10 (d, 1H, $J_{1,2} = 7.8$, H_1), 5.09 (s, 1H, =CH), 5.03 (dd, 1H, $J_{3,4} = 3.4$, H_3), 5.03 (s, 2H, CH_2Ph), 4.11 (m, 2H, H_6 and $H_{6'}$), 3.94 (ddd, 1H, $J_{5,6'} = 7.2$, $J_{5,6} = 5.5$, H_5), 2.13 (s, 3H, $CH_3C{=}$), 1.97–2.14 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.2, 170.1, 169.2 (C=O, OAc), 163.7 (C=O), 163.5 (O–C=), 136.6 (C_{ipso}), 128.3 (C_o), 128.0 (C_m), 127.8 (C_p), 100.4 (C_1), 97.7 (=CH), 71.1 (C_5), 70.6 (C_3), 68.1 (C_2), 66.8 (C_4), 65.2 (CH_2), 61.3 (C_6), 20.7, 20.6, 20.5, 20.4 (4 OAc), 19.9 (CH_3). Compound **22** has $[\alpha]_D$ − 16.1° (c 1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.32 (m, 5H, H_{Ar}), 5.39 (dd, 1H, $J_{4,5} = 1.0$ Hz, H_4), 5.32 (dd, 1H, $J_{2,3} = 10.5$, H_2), 5.30 (s, 1H, =CH), 5.09 (s, 2H, CH_2Ph), 5.02 (dd, 1H, $J_{3,4} = 3.6$, H_3), 4.91 (d, 1H, $J_{1,2} = 7.9$, H_1), 4.11 (m, 2H, H_6 and $H_{6'}$), 3.97 (ddd, 1H, $J_{5,6'} = 7.3$, $J_{5,6} = 5.6$, H_5), 2.25 (s, 3H, $CH_3C{=}$), 1.97–2.14 (4s, 12H, OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4, 170.1, 170.0, 169.9 (C=O, OAc), 169.1 (C=O), 166.8 (O–C=), 136.0 (C_{ipso}), 128.5 (C_o), 128.4 (C_m), 128.1 (C_p), 97.0 (C_1), 95.7 (=CH), 71.5 (C_5), 70.5 (C_3), 68.0 (C_2), 66.8 (C_4), 65.7 (CH_2), 61.5 (C_6), 20.6, 20.5, 20.4, 20.3 (4 OAc), 18.3 (CH_3).

4.1.12. Allyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-1-thio-β-D-glucopyranoside (23)

Chloride **1** (100 mg, 0.273 mmol) and TBAHS (82.8 mg, 0.273 mmol) were dissolved in EtOAc (1 ml). A solution of allyl mercaptan (140 μl, 1.37 mmol) in 1.5 M Na_2CO_3 (1 ml) was added to the reaction mixture and stirred vigorously at room temperature. After 2.5 h, TLC showed complete consumption of **1** to give crude **23** as the major product. The reaction was worked up by addition of EtOAc (10 ml) and washed with $NaHCO_3$ (2 × 10 ml), distilled water (2 × 10 ml) and sat. NaCl (8 ml). The organic phase was dried (Na_2SO_4) and the residue obtained after concentration of the organic phase was chromatographed on silica gel column using 3/1 ethyl acetate/hexanes with 0.5% isopropanol as eluant. Pure product **23** was obtained in 86% yield (84.0 mg). Compound **23** has ^{1}H NMR ($CDCl_3$) δ (ppm): 5.70–5.84 (m, 1H, CH=), 5.41 (d, 1H, $J_{2,NH}$ = 9.2 Hz, NH), 5.06–5.15 (m, 4H, H_3, H_4, $=CH_2$), 4.48 (d, 1H, $J_{1,2} = 10.3$ Hz, H_1), 4.20 (dd, 1H, $J_{5,6} = 5.2$, $J_{6,6'} = 12.3$, H_6), 4.13 (m, 1H, H_2), 4.11 (dd, 1H, $J_{5,6'} = 2.4$, $H_{6'}$), 3.60 (m, 1H, H_5), 3.38 (dd, 1H, $J_{vic} = 8.8$, J_{gem} = 13.4, SCH_x), 3.20 (dd, 1H, $J_{vic} = 5.8$, SCH_y), 2.07, 2.01, 2.00 (3s, 8H, 3OAc), 1.94 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 171.5,

171.0, 170.3, 169.6 (C═O), 133.7 (CH═), 118.1 (═CH_2), 83.0 (C_1), 76.1 (C_5), 74.2 (C_3), 68.7 (C_4), 62.7 (C_6), 53.3 (C_2), 33.0 (SCH_2), 23.6 (NAc), 21.0, 20.9 (OAc). MS for $C_{17}H_{25}NO_8S$ (CI ether, rel. intensity) m/z: 404 ($[M + H]^+$, 62.9%), 330 ($[M$ – aglycon$]^+$, 7.5%).

*4.1.13. Allyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (**24**)*

To a solution of α-acetobromoglucose **2** (100 mg, 0.243 mmol) and tetrabutylammonium hydrogen sulfate (82.5 mg, 0.243 mmol) in ethyl acetate (1 ml) was added a solution of allyl mercaptan (138 μl, 1.22 mmol) in 1.5 M sodium carbonate (1 ml). The reaction mixture was stirred at room temperature until TLC indicated complete transformation of the starting material (< 2.5 h). Ethyl acetate (10 ml) was added to the reaction mixture and the organic layer was separated and washed three times with saturated sodium hydrogen carbonate (10 ml each), twice with water (10 ml) and once with saturated sodium chloride (10 ml). The organic phase was then dried using sodium sulfate and evaporated near dryness. The oily residue was purified by silica gel column chromatography using 1/3 ethyl acetate/hexanes containing 0.5% isopropanol as eluant, to obtain pure thioallyl glucoside **24** (82.5 mg) in 84% yield. Compound **24** has ^{1}H NMR ($CDCl_3$) δ (ppm): 5.72–5.78 (m, 1H, CH═), 5.20 (dd, 1H, $J_{3,4} \sim J_{2,3} \sim 9.3$ Hz, H_3), 5.00–5.15 (m, 4H, H_2, H_4, ═CH_2), 4.45 (d, 1H, $J_{1,2} = 10.0$, H_1), 4.20 (dd, 1H, $J_{5,6} = 5.1$, $J_{6,6'} = 12.3$, H_6), 4.10 (dd, 1H, $J_{5,6'} = 2.4$, $H_{6'}$), 3.63 (m, 1H, H_5), 3.38 (dd, 1H, $J_{vic} = 8.5$, $J_{gem} = 13.5$, SCH_x), 3.20 (dd, 1H, $J_{vic} = 6.3$, SCH_y), 2.06, 2.03, 2.00, 1.98 (4s, 12H, 4OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 169.4 (C═O), 133.3 (CH═), 118.0 (═CH_2), 81.9 (C_1), 75.6 (C_5), 73.9 (C_3), 69.9 (C_4), 68.4 (C_2), 62.2 (C_6), 32.9 (SCH_2), 20.8, 20.7,.20.5 (CH_3). MS for $C_{17}H_{24}O_9S$ (CI ether, rel. intensity) m/z: 405 ($[M + H]^+$, 2.3%), 331 ($[M$ – aglycon$]^+$, 100%).

*4.1.14. Allyl 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (**25**)*

Acetobromogalactose **14** (200 mg, 0.486 mmol) and TBAHS (165 mg, 0.486 mmol) were dissolved in EtOAc (2 ml). A solution of allyl mercaptan (276 μl, 2.43 mmol) in 1.5 M Na_2CO_3 (2 ml) was added to the reaction mixture and stirred vigorously at room temperature. After 2.5 h, TLC showed complete consumption of **14** to give crude **25** as the major product. The reaction was worked up by addition of EtOAc (20 ml) and washed with $NaHCO_3$ (2 × 20 ml), distilled water (2 × 20 ml) and sat. NaCl (15 ml). The organic phase was dried (Na_2SO_4) and the residue obtained after concentration of the organic phase was chromatographed on silica gel column using 1/3 ethyl acetate/hexanes with 0.5% isopropanol as eluant. Pure product **25** was obtained in 80% yield (158.0 mg). Compound **25** has ^{1}H NMR ($CDCl_3$) δ (ppm): 5.69–5.89 (m, 1H, CH═), 5.40 (dd, 1H, $J_{3,4} = 3.3$ Hz, $J_{4,5} = 0.9$, H_4), 5.09–5.30 (m, 3H, H_2, ═CH_2), 5.02 (dd, 1H, $J_{2,3} = 10.0$, H_3), 4.45 (d, 1H, $J_{1,2} = 10.0$, H_1), 4.03–4.16 (m, 2H, H_6, $H_{6'}$), 3.86 (ddd, 1H, $J_{5,6} = 7.1$, H_5), 3.39 (dd, 1H, $J_{vic} = 8.3$, J_{gem} 13.5, SCH_x), 3.21 (dd, 1H, $J_{vic} = 6.2$, SCH_y), 2.13, 2.05, 2.03, 1.96 (4s, 12H, 4OAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.2, 170.0, 169.5 (C═O), 133.3 (CH═), 117.8 (═CH_2), 82.3 (C_1), 74.3 (C_5), 71.8 (C_3), 67.3 (C_4), 67.1 (C_2), 61.6 (C_6), 32.7 (SCH_2), 20.7, 20.6,.20.6, 20.5 (CH_3). MS for $C_{17}H_{24}O_9S$ (CI ether, rel. intensity) m/z: 405 ($[M + H]^+$, 1.8%), 331 ($[M$ – aglycon$]^+$, 100%).

*4.1.15. Methyl (allyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-2-thio-D-glycero-α-D-galacto-2-nonulopyranosid) onate (**27**)*

To a solution of chloride **26** (118 mg, 0.232 mmol) and TBAHS (78.8 mg, 0.232 mmol) in ethyl acetate (1.2 ml) was added a solution of allyl mercaptan (75 μl, 0.928 mmol) in 1.0 M Na_2CO_3 (1.2 ml). The reaction mixture was stirred at room temperature until TLC indicated complete transformation of the starting material (1 h). Ethyl acetate (18 ml) was added to the

reaction mixture and the organic phase was separated and washed three times with sat. $NaHCO_3$ (20 ml each), twice with water (20 ml) and once with sat. NaCl (10 ml). The organic layer was then dried using Na_2SO_4 and evaporated near dryness. The oily residue was purified by silica gel chromatography 5/2 EtOAc/hexanes with 0.5% *i*-prOH as eluant. Pure product **27** was obtained in 84% yield (106.4 mg) as white crystals from ether/hexanes. Compound **27** has m.p. 109–111°C (ether/hexanes); $[\alpha]_D$ + 38.9° (c 1.01, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 5.73 (dddd, 1H, J_{cis} = 10.0 Hz, J_{trans} = 17.0, CH═), 5.37 (ddd, 1H, $J_{8,9}$ = 2.7, $J_{8,9'}$ = 5.4, H_8), 5.29 (dd, 1H, $J_{7,8}$ = 8.2, H_7), 5.19 (d, 1H, $J_{5,NH}$ = 9.9, NH), 5.06–5.18 (m, 2H, ═CH_2), 4.83 (ddd, 1H, $J_{4,5}$ = 10.4, H_4), 4.29 (dd, 1H, $J_{9,9'}$ = 12.5, H_9), 4.09 (dd, 1H, $H_{9'}$), 4.02 (ddd, 1H, $J_{5,6}$ = 10.7, H_5), 3.84 (dd, 1H, $J_{6,7}$ = 2.2, H_6), 3.76 (s, 3H, OMe), 3.35 (dd, 1H, J_{gem} = 13.8, J_{vic} = 7.5, SCH_x), 3.26 (dd, 1H, J_{vic} = 6.3, SCH_y), 2.69 (dd, 1H, $J_{3e,4}$ = 4.6, $J_{3e,3a}$ = 12.7, H_{3e}), 2.15, 2.12, 2.01, 2.00 (4s, 12H, 4OAc), 1.96 (dd, 1H, $J_{3a,4}$ = 11.7, H_{3a}), 1.84 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.9, 170.6, 170.1, 170.1 (C═O), 168.3 (C_1), 132.9 (CH═), 118.0 (═CH_2), 82.9 (C_2), 74.1 (C_6), 69.5 (C_4), 68.6 (C_8), 67.3 (C_7), 62.2 (C_9), 52.8 (OMe), 49.3 (C_5), 37.8 (C_3), 31.6 (SCH_2), 23.1 (NAc), 21.1, 20.8, 20.7, 20.6 (OAc). MS (CI ether, rel. intensity) *m/z*: 548 ($[M + H]^+$, 68.4%), 488 ($[M - Co_2Me]^+$ and/or $[M - OAc]^+$, 55.8%), 474 ($[M$ – aglycon$]^+$, 22.1%). Anal. Calcd for $C_{23}H_{33}NO_{12}S$: C, 50.45; H, 6.07; N, 2.56%. Found: C, 50.65; H, 5.97; N, 2.38.

*4.1.16. Methyl [2-(phenylselenyl) 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid) onate (**28**)*

To a solution of chloride **26** (235 mg, 0.462 mmol) and TBAHS (157 mg, 0.462 mmol) dissolved in EtOAc (1.6 ml) was added 1 M NaOH (1.6 ml). Benzeneselenol (110 μl, 0.924 mmol) was added to the mixture while vigorously stirred at room temperature. Within 5 min, a fleeting green color was observed and the reaction was completed in 10 min. The mixture was diluted by adding EtOAc (30 ml) and the organic layer was separated from the aqueous phase. The organic phase was washed with cold 1 M NaOH (2 × 30 ml), water (2 × 30 ml) followed by saturated NaCl solution (25 ml). The organic extract was then dried (Na_2SO_4), filtered and evaporated under reduced pressure. The desired product was recrystallized from EtOAc/petroleum ether or hexanes/benzene to afford 70% yield of **28** (203.5 mg). Compound **28** has m.p. 103–106°C (EtOAc/pet. ether); $[\alpha]_D$ + 18.0° (c 1, MeOH); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.60 (d, 2H, H_o), 7.29–7.40 (m, 3H, H_m, H_p), 5.23–5.26 (m, 2H, H_7, H_8), 5.19 (d, 1H, $J_{5,NH}$ = 10.0 Hz, NH), 4.79 (ddd, 1H, $J_{3e,4}$ = 4.7, H_4), 4.37 (dd, 1H, $J_{8,9}$ = 2.2, H_9), 4.18 (dd, 1H, $J_{9,9'}$ = 12.5, $H_{9'}$), 3.96 (ddd, 1H, $J_{5,6}$ = 10.5, H_5), 3.85 (dd, 1H, $J_{6,7}$ = 1.6, H_6), 3.54 (s, 3H, OMe), 2.83 (dd, 1H, $J_{3e,3a}$ = 12.9, H_{3e}), 2.09, 2.05, 2.02, 1.98 (4s, 12H, 4OAc), 2.04 (dd, 1H, H_{3a}), 1.83 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 170.3, 170.0, 169.8 (C═O), 169.0 (C_1), 137.7 (C_m), 129.6 (C_p), 128.9 (C_o), 125.8 (C_{ipso}), 81.7 (C_2), 74.6 (C_6), 70.0 (C_4), 69.7 (C_8), 67.6 (C_7), 62.0 (C_9), 52.6 (OMe), 49.2 (C_5), 38.9 (C_3), 23.1 (NAc), 21.1, 20.8, 20.7, 20.6 (OAc). MS (CI ether, rel. intensity) *m/z*: 631 ($[M + H]^+$, 76%), 475 ($[M$ – aglycon + H$]^+$, 20%). Anal. Calcd for $C_{26}H_{33}NO_{11}Se$: C, 50.84; H, 5.38; N, 2.28%. Found: C, 50.61; H, 5.49; N, 2.23.

*4.1.17. Phenyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-1-seleno-β-D-glucopyranoside (**29**)*

Chloride **1** (202.0 mg, 0.553 mmol), and TBAHS (187.3 mg, 0.553 mmol) were stirred in 2 ml CH_2Cl_2 and 2 ml 1 M Na_2CO_3 at room temperature for a moment. 100 μl (1.5 equiv) of benzeneselenol was then added to the mixture by syringe. A TLC analysis (25/5/1 $CHCl_3$/EtOAc/n-prOH) of the reaction mixture showed a complete and clean conversion of the halide **1** (R_f = 0.45) had occurred within 10 min. The reaction was work up by diluting with

EtOAc (20 ml) and washing the organic phase with 0.5 M NaOH, water and sat. NaCl. After drying (Na_2SO_4), filtration and evaporation of the organic extracts a yellow oil was obtained. The product **29** was purified by filtration through a short bed of silica gel. Elution with CH_2Cl_2 retained the product and liberated bis(phenylseleno) methane and diphenyl selenide. The product **29** was then eluted from the silica bed with EtOAc. Pure **29** was obtained in 95% yield (258 mg) after solvent removal. The amorphous white solid was then crystallized from warm ethanol. Compound **29** has m.p. 189–190°C (EtOH); $[\alpha]_D$ − 30.9° (c 1.18, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 7.59 (m, 2H, H_m), 7.29 (m, 3H, H_o, H_p), 5.57 (d, 1H, $J_{2,NH} = 9.3$ Hz, NH), 5.12 (dd, 1H, $J_{3,4} = 9.4$, H_4), 5.03 (dd, 1H, H_3), 4.97 (d, 1H, $J_{1,2} = 10.6$, H_1), 4.06–4.21 (m, 3H, H_2, H_6, $H_{6'}$), 3.64 (ddd, 1H, $J_{5,6} = 3.0$, $J_{5,6'} = 4.9$, H_5), 2.05, 2.00, 1.99 (3s, 9H, OAc), 1.95 (s, 3H, NAc). ^{13}C NMR ($CDCl_3$) δ (ppm): 171.2, 170.6, 170.0, 169.3 (C═O), 134.7 (C_m), 129.0 (C_o), 128.3 (C_p), 127.9 (C_{ipso}), 82.7 (C_1), 76.9 (C_5), 73.6 (C_3), 68.3 (C_4), 62.4 (C_6), 54.1 (C_2), 23.3 (NAc), 20.6–20.7 (3 OAc). MS for $C_{20}H_{25}NO_8Se$ (CI ether, rel. intensity) m/z: 490.9 ($[M+5]^+$, 2.8%), 489.9 ($[M+4]^+$, 12.8), 488.8 ($[M+3]^+$, 13.1), 486.6 ($[M+1]^+$, 59.4), 330 ($[M-\text{SePh}]^+$, 100).

*4.1.18. 2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl cyanide (**30**)*

Chloride **1** (250 mg, 0.690 mmol), potassium cyanide (224 mg, 3.45 mmol) and TBAHS (234 mg, 0.690 mmol) were stirred vigorously at room temperature in CH_2Cl_2 (4 ml) and 1 M Na_2CO_3 (4 ml). After 3.5 h, TLC (EtOAc) showed complete consumption of **1** ($R_f = 0.64$) to give **30** ($R_f = 0.53$) as the major product. The reaction was worked up by addition of methylene chloride (20 ml) and washed with distilled water (2 × 20 ml) and sat. NaCl. The organic extracts were dried (Na_2SO_4), filtered and evaporated under reduced pressure to give a white solid. The crude product was purified by silica gel chromatography (EtOAc/Hexanes, 4/1) and recrystallized from ethanol giving analytically pure **30** (98 mg) in 39% yield. Compound **30** has m.p. 173–175°C (EtOH); $[\alpha]_D$ − 44.7° (c 0.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ (ppm): 6.16 (d, 1H, $J_{2,NH} = 8.6$ Hz, NH), 5.34 (dd, 1H, $J_{3,4} = 9.4$, H_3), 5.04 (dd, 1H, $J_{4,5} = 9.9$, H_4), 4.68 (d, 1H, $J_{1,2} = 10.6$, H_1), 4.21 (dd, 1H, $J_{6,6'} = 12.5$, H_6), 4.02 (dd, 1H, $J_{5,6'} = 2.3$, $H_{6'}$), 3.99 (ddd, 1H, $J_{2,3} = 10.3$, H_2), 3.74 (ddd, 1H, $J_{5,6} = 4.6$, H_5), 2.08, 2.03, 2.00 (3s, 9H, 3 OAc), 1.97 (s, 3H, NAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.9, 170.7, 170.6, 169.2 (C═O), 115.1 (C≡N), 76.6 (C_5), 71.7 (C_3), 67.7 (C_4), 66.7 (C_1), 61.6 (C_6), 53.0 (C_2), 23.1 (NAc), 20.7, 20.6, 20.5 (OAc); MS (CI ether, rel. intensity) m/z: 356.9 ($[M+H]^+$, 100%), 329.9 ($[M-\text{HCN}]^+$, 26.6%), 314.9 ($[M-\text{Ac}+H]^+$, 8.8%); Anal. Calcd for $C_{15}H_{20}N_2O_8$: C, 50.54; H, 5.66; N, 7.86%. Found: C, 50.14; H, 5.70; N, 7.63.

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