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Convenient stereocontrolled amidoglycosylation of alcohols with acetylated glycals and trichloroethoxysulfonamide

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ABSTRACT

A regio- and stereo-controlled, rhodium(II)-catalyzed amidoglycosylation of alcohols has been developed using *O*-acetylated glycals, trichloroethoxysulfonamide, and iodosobenzene. This one-pot amidoglycosylation was applied to a variety of primary and secondary alcohols to afford the β-*O*-glycosides with acceptable yields up to 84%. The reaction would proceed via stereoselective intermolecular aziridination of the glycal from the α-face followed by S_N2 reaction with alcohol at C-1 from the β-face to give 1,2:2,3-di-*trans*-substituted isomer only.

1. Introduction

2-*N*-Acetamido-2-deoxyglycosides, most commonly of the D-glucose and D-galactose series, are widely distributed in living organisms as glycoconjugates (glycolipids, glycoproteins) [1] and glycosaminoglycans (heparin, chondroitin sulfate, hyaluronic acid) [2]. Aminosugars on cell surfaces are assumed to play an important role as receptor ligands for protein molecules such as lectins and antibodies [3]. Except D-glucosamine, most aminosugars, *e.g.*, D-galactosamine, D-mannosamine, disaccharide lactosamine, are rather expensive as starting materials for the chemical synthesis of glycoconjugates and oligosaccharides.

Glycals (1,2-dehydro-sugar derivatives) have proven to be useful synthetic precursors of 2-amino-2-deoxy-*O*-glycosides by way of *N*-functionalization at C-2 accompanied by addition of alcohols to C-1 (aza-glycosylation) (Scheme 1), and a variety of methods have been developed for the nitrogen transfer to glycals over the last few decades [4]. The aza-glycosylation with the glycals might be classified into three types: (1) direct addition of amine precursors such

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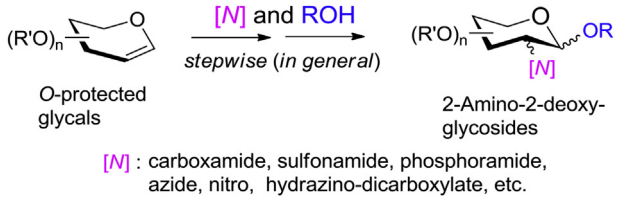


Scheme 1. Aza-glycosylation of alcohols with glycals.

as azide [5–7] and nitro group [8] to the C-2 position along with introduction of leaving groups at C-1 followed by reaction with alcohols; (2) addition of amine precursors to the C-1 position along with addition of halide (usually iodide) to C-2 followed by reaction with alcohols (or alkoxides) to cause rearrangement of the nitrogen to C-2; [9,10] (3) formation of aza-heterocycles followed by ring opening with alcohols [11–14]. Among them, azido-nitration reactions developed by Lemieux and co-workers [5] have been widely used since the reaction of *O*-protected glycals with sodium azide and cerium(IV) ammonium nitrate provides 2-azido-2-deoxy-1-*O*-nitro-glycoses regioselectively. However, the stereoselectivities are dependent on the structure of the glycal substrate; the azidonitrations of acetylated glucal and lactal often proceed non-stereoselectively to give both epimers of the azido group at C-2 (*gluco*-*N* and *manno*-*N* isomers) [15]. In addition, two more steps (C-1 activation and glycosylation) are needed for synthesis of the glycosides.

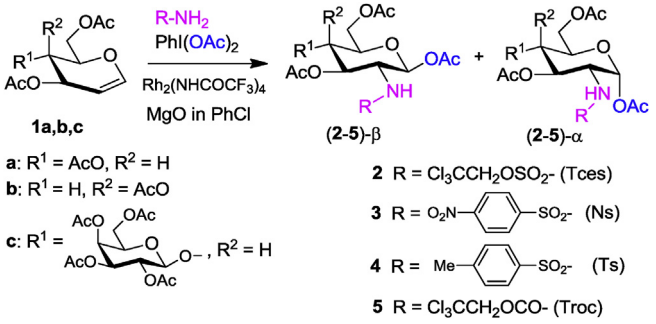
In recent years, transition metal-catalyzed *inter*- and *intra*-molecular aziridinations of alkenes have been developed by using nitrenes as a nitrogen source [16]. The highly reactive nitrene species are generated *in situ* from several types of precursors, *e.g.*, sulfonyliminoiodinanes [17], sulfonamides [18]/sufamate esters [19]/carbamate esters [20]/*N*-substituted hydrazines [21] with iodine(III) compounds, *N*-(sulfonyloxy)carbamates with base [22], chloramine-T [23], and azido-compounds [24]. When the aziridination reactions are applied to glycal derivatives, the corresponding 1,2-aziridines would be formed. The anomeric C-1 position of *N*-sulfonyl or *N*-carbonyl 1,2-aziridino-glycosides would be highly electrophilic to react readily with nucleophiles providing 2-amino-2-deoxy-glycoside derivatives [16c]. There have been several reports on such aminoglycosylation reactions via aziridine intermediates. Rojas and co-workers reported intramolecular aziridinations of 3-*O*-azidoformyl- [25a] and 3-*O*-carbamoyl-D-allal derivatives [25b] and subsequent reactions with alcohols to access 2-amino-2-deoxy-β-D-allopyranosides stereoselectively. Later they applied the reactions to 3-*O*-carbamoyl-D-glucal derivatives to prepare mannosamine derivatives [25c]. Liu and co-workers reported stereoselective synthesis of 1,2-*trans*-2-amino-2-deoxy-1-(*O* or *S*)-glycoside derivatives via rhodium-catalyzed, substrate-controlled aziridination of 4-*O*- or 6-*O*-sulfamoyl-D-glucal derivatives [26]. However, these precedents require preparation of the appropriate substrates for *intramolecular* aziridinations. Stereoselective synthesis of 2-amino-2-deoxy-1-*O*-glycosides from glycals via *intermolecular* aziridination [27] should be more challenging since it would likely afford a mixture of stereoisomers. Indeed, Descotes and co-workers reported that addition of photochemically generated *N*-ethoxycarbonyl-nitrenes to acetylated glycals in methanol gave the methyl 2-amino-glycosides as a mixture of three stereoisomers [28]. Carreira and co-workers reported a stereoselective synthesis of 2-trifluoroacetylamino-sugars by a metal-mediated glycal amination reaction, but minor stereoisomers at C-2 were always detected and the glycosides of alcohols have not been prepared [12].

We report here a regio- and stereo-controlled amidoglycosylation of alcohols via rhodium-catalyzed intermolecular aziridination in a one-pot manner using simple *O*-acetylated glycals (D-glucal, D-galactal, D-lactal), which are readily prepared in 3 steps from the parent sugars [29].

2. Results and discussion

In their research on rhodium-catalyzed olefin aziridination with $PhI(OAc)_2$ and sulfamate esters, Du Bois and co-workers found a stereospecific amido-acetoxylation of tri-*O*-acetyl-D-glucal **1a** to give 2-deoxy-2-(trichloroethoxysulfonyl)amino-glucopyranosyl 1β-*O*-acetate **2a**-β in a regiospecific manner in high yield [30]. However, they have not described the reaction in detail and not presented other sugar-derived substrates. We were interested in this amido-acetoxylation, and confirmed that the reaction of **1a** with $Cl_3CCH_2OSO_2NH_2$ ($TcesNH_2$), $PhI(OAc)_2$, MgO in the presence of a Rh(II) catalyst [$Rh_2(NHCOCF_3)_4$] afforded the β-acetate **2a**-β [31] with a small amount of the α-acetate **2a**-α [32]. The amidoacetoxylation was applied to acetyl-protected galactal **1b** and lactal **1c** under identical conditions. As shown in Table 1, Ac-galactal **1b** gave a 2:1 mixture of the α- and β-acetates (entry 2), whereas Ac-lactal **1c** gave the β-acetate **2c**-β predominantly (entry 3). We tried the amidoacetoxylation with more common sulfonamides and a carbamate ester in place of $TcesNH_2$. The reaction of the glucal **1a** and p-nitrobenzenesulfonamide ($NsNH_2$) gave the product **3a** in lower yield with lower β/α selectivity (entry 4). The reaction of galactal **1b** with $NsNH_2$ gave a comparable result to that with $TcesNH_2$ (entry 5 vs 2). The reaction of **1a** with p-toluenesulfonamide gave the product **4a** in low yield (entry 6). The reaction of **1a**,**b** with 2,2,2-trichloroethyl carbamate ($TrocNH_2$) was also examined. The *N*-trichloroethoxycarbonyl (Troc) glucosamines have been utilized as glycosyl donors because they would give β-glycosides stereoselectively by neighboring group participation and the Troc

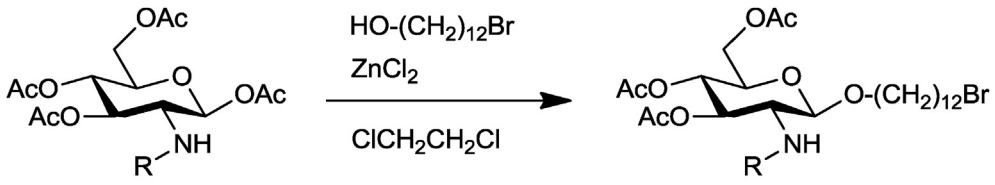
Table 1
Amidoacetoxylation of acetylated glycals **1a,b,c**[a].



Entry	Glycal	R	Product	Yield (%)[b]	β/α ratio[c]	Recovery of 1 (%)
1	**1a**	Tces	**2a**	91	17:1	
2	**1b**	Tces	**2b**	94	1:1.8[d]	
3	**1c**	Tces	**2c**	92	10:1	
4	**1a**	Ns	**3a**	55	5:1	18
5	**1b**	Ns	**3b**	90	1:1.3[d]	
6	**1a**	Ts	**4a**	25	4:1	
7	**1a**	Troc	**5a**	12[e]	6:1	56
8	**1b**	Troc	**5b**	44[f]	3:1	28

[a] Reagents and conditions: R-NH_2 (1.8 equiv.), $PhI(OAc)_2$ (1.8 equiv.), $Rh_2(NHCOCF_3)_4$ (0.1 equiv.), MgO (4 equiv.) in PhCl, 5 °C, 2 h to rt, 10 h.
[b] Isolated yield by silica gel chromatography.
[c] The ratios were determined by ^1H NMR integration of the α/β mixture unless otherwise noted.
[d] The isomers were separated by chromatography.
[e] 1-*O*-Deacetylated **5a** was also obtained in 13% yield.
[f] 1-*O*-Deacetylated **5b** was obtained in 12% yield.

Table 2
Lewis acid-promoted glycosylation with glucosyl β-acetates.



2a R = Tces (β/α = 17:1) **7a**
5a R = Troc (β only) **8a**
6a R = Ac **9a**

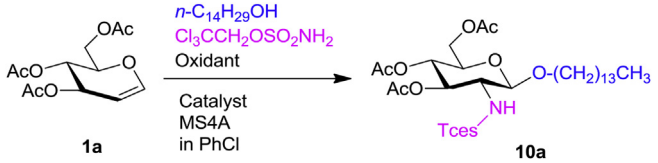
	R	Conditions	Product	Yield(%)[a]
2a	Tces	95 °C, 6 h	**7a**	56[b]
5a	Troc	55 °C, 1 h	**8a**	74[c]
6a	Ac	70 °C, 3 h[d]	**9a**	67

[a] Isolated yield by silica gel chromatography.
[b] Unreacted **2a** was recovered (19%) as an anomeric mixture.
[c] The α-anomer **8a**-α and 1-*O*-deacetylated **5a** were also obtained in 4% and 18% yields, respectively.
[d] The β-acetate **6a** soon disappeared to form the corresponding oxazoline intermediate.

group can be easily and selectively removed under mild conditions (Zn-AcOH) [33]. The reaction of **1a** with $TrocNH_2$ gave the product **5a** in poor yield, and **1b** with $TrocNH_2$ gave **5b** in fair yield. In both cases, substantial amount of glycal remained and the anomeric hydrolyzed products (1-*O*-deacetylated **5a**,**b**) were obtained. In all cases examined, the stereoisomers at C-2 were not detected. Therefore, for the amidoacetoxylation of acetylated glycals under Du Bois' reaction conditions, $TcesNH_2$ showed the highest reactivity. Ac-galactal **1b** would be more reactive than Ac-glucal **1a**, but the β/α-selectivities were lower. The reaction pathway is discussed later.

Glycosyl 1-*O*-β-acetates are more reactive than the corresponding α-acetates, and can be employed as glycosyl donors [34]. With anomerically β-riched (β/α = 17) acetate **2a** in hand, we examined the reactivity in Lewis acid ($ZnCl_2$)-promoted glycosylation with 12-bromododecanol [35]. As shown in Table 2, *N*-Tces-glucosaminyl β-acetate **2a** was found to be much less reactive than

Table 3
Amidoglycosylation of tetradecanol with acetylated glucal **1a** and $TcesNH_2$.

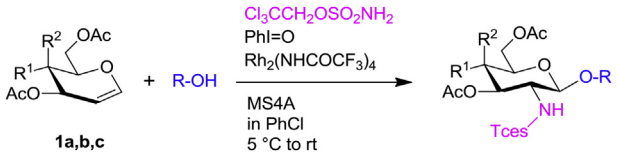


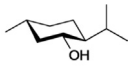
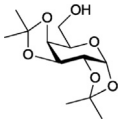
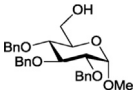
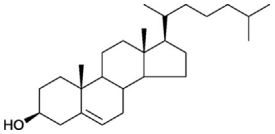
1a **10a**

Entry	Equiv. of $C_{14}H_{29}OH$	Oxidant[a]	Catalyst	Yield (%)[b]
1[c]	4	$PhI(OAc)_2$	$Rh_2(NHCOCF_3)_4$	58[d]
2	4	PhI=O	$Rh_2(NHCOCF_3)_4$	66
3	2	PhI=O	$Rh_2(NHCOCF_3)_4$	78
4	4	PhI=O	$Rh_2(OAc)_4$	45
5	2	PhI=O	$Cu(CH_3CN)PF_6$	17
6	2	PhI=O	$AgNO_3$, tBu_3tpy[e]	25
7[f]	2	PhI=O	$Rh_2(NHCOCF_3)_4$	39

[a] The oxidant (solid, 1.8 equiv.) was added in several portions to the mixture of other reactants for *ca*. 1 h at 5 °C.
[b] Isolated yield by silica gel chromatography.
[c] MgO (4 equiv.) was used in place of MS4A.
[d] 1-Acetate **2a**-β was obtained in 22% yield.
[e] tBu_3tpy: 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine.
[f] The reaction was carried out in toluene.

Table 4
Amidoglycosylation of alcohols with acetylated glycal **1a,b,c** and $TcesNH_2$.[a]



Entry	Glycal	R–OH	Product	Yield (%)[b]
1	**1a**	$Br(CH_2)_{12}$–OH	**7a**	77
2	**1b**	$Br(CH_2)_{12}$–OH	**7b**	84
3	**1c**	$Br(CH_2)_{12}$–OH	**7c**	70
4	**1b**	$AcS(CH_2)_{12}$–OH	**11b**	11
5	**1a**	$Ph(CH_2)_2$–OH	**12a**	75
6	**1b**	$PhCH_2$–OH	**13b**	62
7	**1b**	H_2C=CH–$(CH_2)_3$–OH	**14b**	63
8	**1a**	cyclohexanol	**15a**	57
9	**1b**	cyclohexanol	**15b**	78
10	**1a**	 L(-)-menthol	**16a**	74
11	**1b**	L(−)-menthol	**16b**	76
12	**1c**	L(−)-menthol	**16c**	67
13	**1b**		**17b**	74
14	**1b**		**18b**	21
15	**1b**		**19b**	56

[a] Reagents and conditions: R-OH (2.0 equiv.), $TcesNH_2$ (1.7 equiv.), $PhI(OAc)_2$ (1.8 equiv.), $Rh_2(NHCOCF_3)_4$ (0.1 equiv.), MS4A in PhCl, 5 °C, 2 h to rt.
[b] Isolated yield by silica gel chromatography.

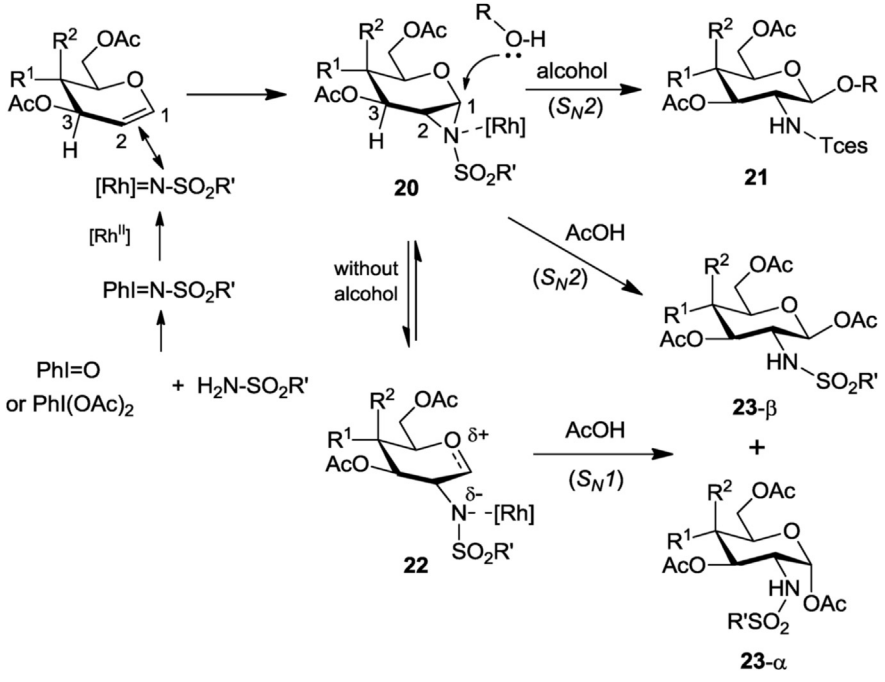
N-Troc derivative **5a** [36] and the yield of β-glycoside **7a** was lower than those of the *N*-Troc **8a** and *N*-Ac **9a** glycosides. Starting material **2a** was recovered (19%) as a 3:1 mixture of α- and β-acetates, indicating that anomerization occurred during the reaction.

Anomeric *O*-acetates can be converted to more reactive leaving groups such as halides and *O*-trichloroacetimidate. Yu and a co-worker reported the conversion of **2a** to the 1-*O*-trichloroacetimidate and the reaction with several alcohols including protected sugars affording the β-glucosides in good yields [31a]. However, the whole process would become lengthy. We next examined a direct synthesis of 2-sulfonamido-1-*O*-glycosides [37] from glycals by adding alcohols in the reaction mixture. As shown in Table 3, the reaction of **1a** and tetradecanol (4 equiv.) with $TcesNH_2$ in the presence of $PhI(OAc)_2$ and catalytic $Rh_2(NHCOCF_3)_4$ in chlorobenzene afforded the desired tetradecyl-β-glucoside **10a** in 58% yield with no α-glucoside. However, the 1-*O*-acetate **2a**-β was also formed (entry 1). Formation of **2a** was suppressed by using iodosobenzene with 4 Å molecular sieves (as dehydration agent) in place of $PhI(OAc)_2$ with MgO (entry 2). Reducing the amount of alcohol improved the yield of **10a** (entry 3). For the aziridination catalyst, $Rh_2(OAc)_4$ was less effective than $Rh_2(NHCOCF_3)_4$, and copper(I) [18a] and silver [17c] catalysts were much less effective (entries 4–6). When the reaction was carried out in toluene, the yield of **10a** decreased and 60% of **1a** was recovered [38] (entry 7).

With the optimized reaction conditions in hand, we investigated the scope and generality of this Rh-catalyzed one-pot amidoglycosylation [39] (amido-alkoxylation of glycals [40]), and the results are summarized in Table 4. Reactions of 12-bromododecanol and 2-phenylethanol with the glycals **1a**,**b**,**c** proceeded smoothly to afford the corresponding β-glycosides **7a**,**b**,**c**, **12a** in good yields (entries 1,2,3,5). In contrast, 12-acetylthio-1-dodecanol gave the galactoside **11b** in poor yield under identical conditions, indicating that the acetylthio group would suppress the reaction (entry 4). Reaction of **1b** with 4-penten-1-ol gave the β-galactoside **14b** in somewhat lower yield along with a byproduct [41] derived from 4-pentenol, indicating that 4-pentenol was also aziridinated, but would be less reactive than **1b** (entry 7). Cyclic secondary alcohols: cyclohexanol and L(−)-menthol reacted with the glycals **1a-c** to give the corresponding β-glycosides in good yields. Ac-galactal **1b** appeared to be more reactive and gave the glycosides in better yields than **1a** and **1c** (entries 8–12 and 1–3). For sugar-derived alcohols, 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose afforded the galactoside **17b** in good yield, whereas methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside gave the galactoside **18b** in low yield, and substantial amounts of some byproducts: de-*O*-benzylated glucoses and benzaldehyde were obtained. The reaction of **1b** with methyl 2,3,6-tri-*O*-benzyl-α-D-glucopyranoside did not give the glycoside (data not shown). In all the cases examined, no α-anomer was detected by ^1H and ^{13}C NMR. Small amounts (3–8%) of hydrolyzed products (1-OH) were formed when using less reactive alcohols.

Danishefsky and co-workers reported a sulfonamido-glycosylation from glycals, and they succeeded in applying the methodology to the syntheses of oligosaccharides and glycoconjugates [10]. Their glycosylation method requires two reaction steps: (1) addition of iodonium reagent [usually I(*sym*-collidine)$_2$-ClO_4] and benzenesulfonamide to glycals to form 1,2-*trans*-2-iodo-1-sulfonamido-glycoses, and (2) reaction with the metal alkoxide of a glycosyl acceptor and silver salt (AgOTf or $AgBF_4$) to cause rearrangement of the sulfonamide to C-2. The latter step usually requires either rather basic alkali-metal (Li, K) alkoxide, with which *O*-acyl protecting groups could be incompatible, or toxic tributyltin alkoxide [42]. In addition, excess amounts (from 1.4 [10a] to 10 [42] equiv.) of expensive silver salts are necessary not only for the abstraction of iodine atom in the latter step but also for the preparation of $I(collidine)_2ClO_4$ (from $AgClO_4$). Our one-pot sulfonamido-glycosylation described above would be more convenient and economical than Danishefsky's method. However, it might be difficult to apply this one-pot glycosylation to oligosaccharide synthesis because secondary alcohols of protected sugars having low nucleophilic and/or steric hindrance did not react well with the adduct of nitrenoid addition to acetylated glycals.

The reaction would proceed via the generation of rhodium-nitrenoid followed by formation of the α-oriented aziridine intermediate (**20**) presumably due to the presence of β-acetoxy group at adjacent C-3 [11–13] (Scheme 2). The aziridine would be opened with the alcohol at C-1 from the β-face (S_N2 reaction) to afford 1,2-



Scheme 2. Proposed reaction pathway.

and 2,3-di-*trans*-product **21** [16c,43]. For the amidoacetoxylation (in the absence of alcohol and the presence of AcOH generated *in situ*), since AcOH is less nucleophilic than alcohol, the aziridine would tend to open to oxocarbenium intermediate **22**. The acetate can add to C-1 from both faces to form a mixture of α- and β-acetates (**23**-α and −β) [43a,b]. β-Acetoxy group at C-4 (R^2) of Ac-galactal **1b** might cover the β-face to give C-1 α-acetate as a major product.

The trichloroethoxysulfonamide in **10a** is converted to either sulfaminic acid or free amine by tuning the reaction conditions (Scheme 3). When **10a** was treated with zinc and acetic acid in methanol, only trichloroethyl group was removed to give the sulfaminic acid **24** in 95% yield. *N*-Sulfated glucosamine is a key structural unit in heparin, a bioactive polysaccharide having anticoagulant and antithrombotic properties [44]. The whole Tces group was removed by treatment with zinc and acetic acid in the presence of $CuSO_4$ in THF to give the amine **25**. This deprotection process might be more convenient than that by zinc-copper couple reported by Du Bois [19a]. The amine **25** reacted with benzoyl chloride to give the benzamide **26**. When the desulfonylation was carried out in the presence of acetic anhydride, the acetamide **27** was obtained in good yield. We previously prepared 12-mercaptododecyl *N*-acetyl-α-lactosaminide via azidonitration of Ac-lactal **1c**, and the synthetic α-lactosaminide showed high binding activity to some galectins evaluated by surface plasmon resonance (SPR) method [15d]. For the synthesis of the β-anomer, bromododecyl β-lactoside **7c** was converted to the acetylthio derivative **28**. Treatment of **28** with zinc and acetic anhydride in the presence of $CuSO_4$ in THF afforded the acetylated β-lactosaminide **29** in good yield.

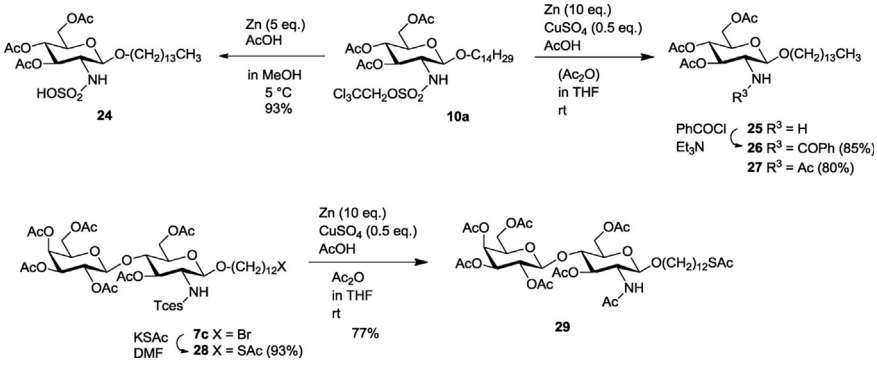
4. Experimental

4.1. General methods

Melting points were determined with a Yanaco melting point apparatus MP-500D. Optical rotations were measured with a JASCO DIP-1000 polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer or on a Bruker Avance III-500 (500 MHz for ^1H and 125.8 MHz for ^{13}C) spectrometer at 25 °C. ^1H chemical shifts (δ) are given in ppm relative to internal $(CH_3)_4Si$ (δ 0.00) in $CDCl_3$ and ^{13}C chemical shifts (δ) are given in ppm relative to $CDCl_3$ (δ 77.0). Elemental analyses and high-resolution mass spectrometry (HRMS) analyses were performed in the analytical section in this Institute (AIST). Mass spectra (MS) were recorded on a Waters micromass ZQ spectrometer with electrospray ionization (ESI) in the positive ion mode. Thin layer chromatography (TLC) and column chromatography were performed on Merck pre-coated silica gel $60F_{254}$ plates and silica gel (Kanto Chemicals, neutral, 100–210 μm, or Wakogel C-300, 45–75 μm), respectively. $Rh_2(NHCOCF_3)_4$ was prepared from $Rh_2(OAc)_4$ and CF_3CONH_2 in chlorobenzene according to ref. [19a]; Supporting information, p. 2. $TcesNH_2$ was obtained commercially from Sigma-Aldrich.

4.2. General procedure for amidoacetoxylation

To a mixture of glycal **1a**,**b**,**c** (0.2 mmol), R-NH_2 (R = Tces, Ns, Ts, or Troc) (0.35 mmol), $Rh_2(NHCOCF_3)_4$ (12 mg, 0.02 mmol), and MgO (32 mg, 0.8 mmol) under nitrogen was added PhCl (3 mL), and the resulting light-purple suspension was cooled with an ice-water bath. $PhI(OAc)_2$ (80 mg, 0.36 mmol) was added in several portions for 1 h, and the resulting light-brown suspension was stirred at 5 °C for 1 h and then at rt for 10 h. The reaction mixture was filtered, washed with CH_2Cl_2, and the combined filtrates were concentrated under reduced pressure. The residue was purified by silica gel chromatography eluting with hexane-EtOAc mixture.



Scheme 3. Conversions of the trichloroethoxysulfonyl group.

3. Conclusions

In conclusion, we have developed a regio- and stereo-selective synthesis of 2-amino-2-deoxy-1-*O*-β-glycosides from acetylated glycals via rhodium(II)-catalyzed intermolecular aziridination with trichloroethoxysulfonamide and iodosobenzene. This amidoglycosylation proceeds smoothly under mild conditions without the use of usual *O*-glycosylation promoters such as Lewis acids, and is applicable to a variety of primary and secondary alcohols with appropriate nucleophilicity. In the absence of alcohol and the presence of diacetoxyiodobenzene, 2-amino-2-deoxy-glycose-1-*O*-acetates are formed as anomeric mixture. On the basis of the stereochemical results, the reaction pathway has been proposed. The *N*-Tces group can be directly converted to either *N*-sulfate, free amine, or acetamide by tuning reaction conditions.

4.2.1. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranose (2a-β)

Obtained in 91% yield (β/α = 17) as a colorless foam: R_f 0.28 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] +9.0 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 2.06 (s, 3H), 2.10 (s, 3H), 2.15 (s, 3H), 2.22 (s, 3H), 3.78 (dt, 1H, *J* = 10.4, 9.0 Hz), 3.87 (ddd, 1H, *J* = 2.2, 4.5, 9.9 Hz), 4.12 (dd, 1H, *J* = 2.2, 12.5 Hz), 4.28 (dd, 1H, *J* = 4.5, 12.5 Hz), 4.61 (d, 1H, *J* = 11.0 Hz), 4.64

(d, 1H, J = 11.0 Hz), 5.11 (t, 1H, J = 9.7 Hz), 5.20 (t, 1H, J = 9.9 Hz), 5.71 (d, 1H, J = 8.7 Hz), 5.81 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.5, 20.7, 20.8, 21.0, 57.9, 61.5, 67.9, 72.4, 72.6, 78.6, 92.0, 93.2, 169.4, 169.7, 170.7, 171.8 ppm. These data are consistent with those reported. [ref. [31b]; Supporting information, p.11].

4.2.2. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-α-D-galactopyranose (2b-α)

Obtained in 61% yield as a colorless foam: R_f 0.24 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] +105.4 (c 1.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.03 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 2.21 (s, 3H), 4.07 (dd, 1H, J = 6.7, 11.2 Hz), 4.10 (dd, 1H, J = 6.7, 11.2 Hz), 4.15 (ddd, 1H, J = 3.6, 9.6, 11.2 Hz), 4.25 (dt, 1H, J = 0.9, 6.7 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.66 (d, 1H, J = 10.8 Hz), 5.14 (d, 1H, J = 9.6 Hz), 5.24 (dd, 1H, J = 3.2, 11.3 Hz), 5.45 (dd, 1H, J = 1.0, 3.1 Hz), 6.40 (d, 1H, J = 3.6 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.57, 20.60, 20.78, 20.84, 52.0, 61.1, 66.9, 67.4, 68.5, 78.3, 90.9, 93.1, 169.0, 170.0, 170.4, 171.0 ppm; MS (ESI): m/z calcd for $C_{16}H_{22}^{35}Cl_3NO_{12}S$ 556.99; found (%) 579.85 ([M($^{35}Cl_3$)+Na]$^+$, 94), 581.96 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 583.95 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 39).

4.2.3. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranose (2b-β)

Obtained in 33% yield as a colorless foam: R_f 0.33 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] +8.3 (c 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 2.05 (s, 3H), 2.11 (s, 3H), 2.17 (s, 3H), 2.23 (s, 3H), 3.95 (dt, 1H, J = 8.9, 11.1 Hz), 4.06 (dt, 1H, J = 0.9, 6.5 Hz), 4.12 (dd, 1H, J = 6.3, 11.2 Hz), 4.16 (dd, 1H, J = 6.7, 11.2 Hz), 4.64 (s, 2H), 5.08 (dd, 1H, J = 3.3, 11.1 Hz), 5.40 (d, 1H, J = 3.3 Hz), 5.67 (d, 1H, J = 9.0 Hz), 5.72 (d, 1H, J = 8.8 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.58, 20.64, 20.78, 21.0, 54.9, 61.2, 66.5, 70.4, 71.7, 78.4, 92.5, 93.3, 169.93, 170.06, 170.5, 171.1 ppm; HRMS (FAB): calcd. for $C_{14}H_{19}^{35}Cl_3NO_{10}S$ [M - OAc]$^+$ 497.9796; found 497.9789.

4.2.4. 1,3,6-Tri-O-Acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranose (2c-β)

Obtained in 92% yield (β/α = 10) as a colorless foam: R_f 0.27 (1:1 hexane/EtOAc); ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 2.13 (s, 3H), 2.17 (s, 6H), 2.18 (s, 3H), 2.23 (s, 3H), 3.73 (q, 1H, J = 8.7 Hz), 3.86 (m, 2H), 3.91 (t, 1H, J = 7.2 Hz), 4.10 (dd, 1H, J = 7.1, 11.2 Hz), 4.14 (m, 1H), 4.18 (dd, 1H, J = 6.3, 11.0 Hz), 4.45 (dd, 1H, J = 1.9, 12 Hz), 4.49 (d, 1H, J = 7.8 Hz), 4.65 (s, 2H), 5.00 (dd, 1H, J = 2.5, 10.5 Hz), 5.10 (dd, 1H, J = 7.8, 10.5 Hz), 5.17 (t, 1H), 5.38 (dd, 1H, J = 0.8, 3.3 Hz), 5.74 (d, 1H, J = 7.8 Hz), 6.02 (d, 1H, J = 9.4 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.49, 20.63 (3C), 20.81, 20.91, 21.01, 57.2, 60.9, 61.9, 66.6, 69.0, 70.7, 70.9, 71.7, 73.5, 74.5, 78.6, 91.9, 93.3, 100.7, 169.2, 169.6, 170.07, 170.13, 170.32, 170.38, 170.9 ppm; MS (ESI): m/z calcd for $C_{28}H_{38}^{35}Cl_3NO_{20}S$ 845.08; found (%) 868.08 ([M($^{35}Cl_3$)+Na]$^+$, 91), 870.07 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 872.00 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 38).

4.2.5. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(p-nitrobenzenesulfonyl)amido-β-D-glucopyranose (3a-β)

Obtained in 55% yield (β/α = 5) as a colorless solid: R_f 0.35 (1:1 hexane/EtOAc); m.p. 155–158 °C; $[\alpha]_D$ [25] +2.8 (c 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H), 1.88 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 3.74 (q, 1H, J = 9.5 Hz), 3.87 (ddd, 1H, J = 2.1, 4.4, 10.0 Hz), 4.10 (dd, 1H, J = 2.1, 12.6 Hz), 4.27 (dd, 1H, J = 4.4, 12.6 Hz), 5.09 (t, 1H, J = 9.7 Hz), 5.20 (t, 1H, J = 9.9 Hz), 5.68 (d, 1H, J = 8.7 Hz), 5.90 (d, 1H, J = 9.4 Hz), 8.06 (m, 2H), 8.36 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.5 (3C), 20.7, 57.3, 61.4, 67.8, 72.5, 72.6, 92.1, 124.2 (2C), 128.2 (2C), 147.0, 150.0, 169.2, 169.3, 170.6, 171.3 ppm; Anal. Calcd for $C_{20}H_{24}N_2O_{13}S$: C, 45.11; H, 4.54; N, 5.26; S, 6.02. Found: C, 44.65; H, 4.49; N,5.11; S, 6.00.

4.2.6. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(p-nitrobenzenesulfonyl)amido-α-D-galactopyranose (3b-α)

Obtained in 51% yield as a colorless foam: R_f 0.29 (1:1 hexane/EtOAc); $[\alpha]_D$ [25] +44.1 (c 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H), 2.01 (s, 3H), 2.13 (s, 3H), 2.17 (s, 3H), 4.04 (m, 3H), 4.21 (dt, 1H, J = 0.6, 6.7 Hz), 5.19 (dd, 1H, J = 3.3, 11.2 Hz), 5.35 (d, 1H, J = 9.0 Hz), 5.39 (dd, 1H, J = 0.6, 3.2 Hz), 6.03 (d, 1H, J = 3.6 Hz), 8.04 (m, 2H), 8.37 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ = 20.5, 20.6, 20.7, 51.4, 61.0, 66.8, 67.4, 68.5, 90.9, 124.5, 128.1, 146.5, 150.2, 168.6, 169.8, 170.3, 170.6 ppm; Anal. Calcd for $C_{20}H_{24}N_2O_{13}S$: C, 45.11; H, 4.54; N, 5.26; S, 6.02. Found: C, 44.87; H, 4.51; N,5.14; S, 5.90.

4.2.7. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(p-nitrobenzenesulfonyl)amido-β-D-galactopyranose (3b-β)

Obtained in 39% yield as a colorless foam: R_f 0.37 (1:1 hexane/EtOAc); $[\alpha]_D$ [25] −2.0 (c 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 3H), 1.86 (s, 3H), 2.03 (s, 3H), 2.18 (s, 3H), 3.88 (dt, 1H, J = 10.8, 9.0 Hz), 4.11 (m, 3H), 5.11 (dd, 1H, J = 3.4, 11.0 Hz), 5.37 (d, 1H, J = 3.3 Hz), 5.71 (d, 1H, J = 8.7 Hz), 5.80 (br, 1H), 8.06 (m, 2H), 8.36 (m, 2H) ppm.

4.2.8. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(p-toluenesulfonyl)amido-β/α-D-glucopyranose (4a-β/α)

Obtained in 25% yield (β/α = 4) as a colorless solid: R_f 0.33 (1:1 hexane/EtOAc); ^{1}H NMR ($CDCl_3$) for β-anomer: δ 1.83 (s, 3H), 1.85 (s, 3H), 2.02 (s, 3H), 2.08 (s, 3H), 2.41 (s, 3H), 3.70 (q, 1H, J = 8.4 Hz), 3.79 (ddd, 1H, J = 2.4, 4.6, 9.6 Hz), 4.08 (dd, 1H, J = 2.2, 12.5 Hz), 4.26 (dd, 1H, J = 4.5, 12.5 Hz), 5.08 (m, 2H), 5.23 (d, 1H, 9.3 Hz), 5.61 (d, 1H, J = 8.6 Hz), 7.30 (m, 2H), 7.72 (m, 2H) ppm.

4.2.9. 1,3,4,6-Tetra-O-Acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl)amido-β/α-D-galactopyranose (5b-β/α)

Obtained in 44% yield (β/α = 3) as a colorless oil: R_f 0.36 (3:2 hexane/EtOAc); ^{1}H NMR ($CDCl_3$) for β-anomer: δ 2.01 (s, 3H), 2.05 (s, 3H), 2.13 (s, 3H), 2.18 (s, 3H), 4.05 (t, 1H, J = 6.6 Hz), 4.11 (m, 1H), 4.13 (dd, 1H, J = 6.4, 11.3 Hz), 4.17 (dd, 1H, J = 6.8, 11.3 Hz), 4.73 (s, 2H), 5.15 (dd, 1H, J = 3.1, 11.2 Hz), 5.15 (1H, NH), 5.41 (d, 1H, J = 3.0 Hz), 5.76 (d, 1H, J = 8.8 Hz) ppm; HRMS (FAB): calcd. for $C_{15}H_{19}^{35}Cl_3NO_9S$ [M - OAc]$^+$ 462.0126; found 462.0120.

4.3. General procedure for $ZnCl_2$-promoted glycosylation

To a mixture of glucosaminyl β-acetate (**2a**-β, **5a**-β, or **6a**) (0.30 mmol), 12-bromo-1-dodecanol (108 mg, 0.4 mmol), and $ZnCl_2$ (56 mg, 0.4 mmol, dried *in vacuo* at 110 °C for 1 h prior to use) was added dichloroethane (4 mL), and the suspension was stirred upon heating with monitoring the reaction by TLC. The resulting mixture was diluted with EtOAc (20 mL) and aq. $NaHCO_3$ (20 mL), and the mixture was stirred for 10 min, filtered through Celite, and washed thoroughly with EtOAc (10 mL). The combined filtrate and washings were successively washed with H_2O and brine. The aqueous phase was extracted with EtOAc (2 × 20 mL), and the combined organic layers were dried over Na_2SO_4. Removal of the solvent gave a residue, which was purified by silica gel column chromatography eluting with hexane-EtOAc mixture.

4.3.1. 12-Bromododecyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (***7a***)

Obtained in 56% yield as a colorless solid: m.p. 71–73 °C; R_f 0.33 (2:1 hexane/EtOAc); $[\alpha]_D$ [25] −17.8 (c 2.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.26 (s-like, 14H), 1.42 (m, 2H), 1.66 (m, 2H), 1.85 (quint, 2H, J = 7.3 Hz), 2.05 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.41 (t, 2H, J = 6.9 Hz), 3.57 (dt, 1H, J = 9.4, 7.0 Hz), 3.58 (q, 1H, J = 9.0 Hz), 3.71 (ddd, 1H, J = 2.3, 4.8, 9.4 Hz), 3.88 (dt, 1H, J = 9.4, 7.3 Hz), 4.14 (dd, 1H, J = 2.3, 12.3 Hz), 4.28 (dd, 1H, J = 4.8, 12.3 Hz), 4.44 (d, 1H, J = 8.2 Hz), 4.68 (d, 1H, J = 10.9 Hz), 4.72 (d, 1H, J = 10.9 Hz), 5.08 (t,

1H, J = 9.5 Hz), 5.13 (t, 1H, J = 9.5 Hz), 5.52 (d, 1H, J = 9.0 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.58, 20.73, 20.85, 25.8, 28.1, 28.7, 29.34, 29.39, 29.47, 29.49, 32.8, 34.1, 59.0, 62.0, 68.4, 70.6, 71.8, 72.9, 78.6, 93.4, 100.7, 169.3, 170.7, 171.6 ppm; Anal. Calcd for $C_{26}H_{43}BrCl_3NO_{11}S$: C, 40.88; H, 5.67; N, 1.83; S, 4.20. Found: C, 41.16; H, 5.63; N, 1.84; S, 4.39.

4.3.2. 12-Bromododecyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonyl)amido-β-D-glucopyranoside (**8a**)

Obtained in 74% yield as a colorless solid: m.p. 75–77 °C; R_f 0.25 (3:1 hexane/EtOAc); $[\alpha]_D$ [25] +0.4 (*c* 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.24–1.34 (m, 14H), 1.42 (m, 2H), 1.57 (m, 2H), 1.85 (quint, 2H, J = 7.2 Hz), 2.029 (s, 3H), 2.032 (s, 3H), 2.09 (s, 3H), 3.41 (t, 2H, J = 6.9 Hz), 3.47 (dt, 1H, J = 9.6, 6.9 Hz), 3.61 (dt, 1H, J = 10.7, 8.6 Hz), 3.70 (m, 1H), 3.88 (dt, 1H, J = 9.6, 6.6 Hz), 4.13 (dd, 1H, J = 2.3, 12.3 Hz), 4.29 (dd, 1H, J = 4.7, 12.3 Hz), 4.64 (d, 1H, J = 8.6 Hz), 4.67 (d, 1H, J = 11.9 Hz), 4.77 (d, 1H, J = 11.9 Hz), 5.07 (t, 1H, J = 9.7 Hz), 5.19 (d, 1H, J = 8.6 Hz), 5.32 (t, 1H, J = 10.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.62, 20.64, 20.75, 25.8, 28.1, 28.7, 29.34, 29.38, 29.41, 29.48, 29.50, 32.8, 34.1, 56.3, 62.1, 68.7, 70.4, 71.7, 71.8, 74.4, 95.4, 100.7, 153.9, 169.5, 170.64, 170.73 ppm; Anal. Calcd for $C_{27}H_{43}BrCl_3NO_{10}$: C, 44.55; H, 5.95; N, 1.92. Found: C, 44.95; H, 5.98; N, 1.67.

4.3.3. 12-Bromododecyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (**9a**)

Obtained in 67% yield as a colorless solid: m.p. 107–109 °C; R_f 0.40 (1:2 hexane/EtOAc); $[\alpha]_D$ [25] −9.9 (*c* 2.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.26 (s-like, 14H), 1.42 (m, 2H), 1.56 (m, 2H), 1.85 (quint, 2H, J = 7.2 Hz), 1.95 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.09 (s, 3H), 3.41 (t, 2H, J = 6.9 Hz), 3.47 (dt, 1H, J = 9.6, 6.9 Hz), 3.70 (ddd, 1H, J = 2.5, 4.7, 10.0 Hz), 3.81 (dt, 1H, J = 10.6, 8.5 Hz), 3.86 (dt, 1H, J = 9.6, 6.5 Hz), 4.13 (dd, 1H, J = 2.5, 12.2 Hz), 4.27 (dd, 1H, J = 4.8, 12.2 Hz), 4.68 (d, 1H, J = 8.3 Hz), 5.07 (t, 1H, J = 9.6 Hz), 5.31 (dd, 1H, J = 9.3, 10.6 Hz), 5.54 (d, 1H, J = 8.7 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.45, 20.53, 20.56, 23.0, 25.7, 27.9, 28.5, 29.16, 29.20, 29.25, 29.30, 29.34, 29.39, 32.6, 33.9, 54.5, 62.1, 68.7, 69.7, 71.4, 72.3, 100.5, 169.3, 170.2, 170.54, 170.59 ppm; Anal. Calcd for $C_{26}H_{44}BrNO_9$: C, 52.52; H, 7.46; N, 2.36. Found: C, 52.85; H, 7.47; N, 2.11.

4.4. General procedure for one-pot amidoglycosylation

To a mixture of glycal **1a**,**b**,**c** (0.2 mmol), alcohol (0.4 mmol), $TcesNH_2$ (80 mg, 0.35 mmol), $Rh_2(NHCOCF_3)_4$ (12 mg, 0.02 mmol), and activated powdered molecular sieves 4 Å (160 mg) under nitrogen was added PhCl (3 mL), and the resulting light-purple suspension was cooled with an ice-water bath. PhIO (80 mg, 0.36 mmol) was added in several portions for 1 h, and the resulting light-brown suspension was stirred at 5 °C for 1 h and then at rt for 5–15 h with monitoring the reaction by TLC. The reaction mixture was filtered, washed with CH_2Cl_2, and the combined filtrates were concentrated under reduced pressure to remove CH_2Cl_2. The residue was purified by silica gel chromatography, usually eluting with hexane-EtOAc mixture.

4.4.1. Tetradecyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**10a**)

Obtained in 78% yield as a colorless foam: R_f 0.35 (2:1 hexane/EtOAc); $[\alpha]_D$ [25] −18.0 (*c* 2.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.88 (t, 3H, J = 6.9 Hz), 1.25 (s-like, 20H), 1.32 (m, 2H), 1.66 (quint, 2H, J = 7.3 Hz), 2.04 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.56 (dt, 1H, J = 9.3, 7.1 Hz), 3.58 (q, 1H, J = 9.0 Hz), 3.69 (ddd, 1H, J = 2.3, 4.9, 8.8 Hz), 3.88 (dt, 1H, J = 9.4, 7.3 Hz), 4.14 (dd, 1H, J = 2.3, 12.3 Hz), 4.27 (dd, 1H, J = 4.9, 12.3 Hz), 4.43 (d, 1H, J = 8.2 Hz), 4.68 (d, 1H, J = 10.9 Hz), 4.72 (d, 1H, J = 10.9 Hz), 5.08 (t, 1H, J = 9.5 Hz), 5.12 (t, 1H, J = 9.5 Hz), 5.36 (d, 1H, J = 8.9 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 14.1, 20.6, 20.7, 20.8, 22.7, 25.8, 29.34, 29.36, 29.49, 29.58, 29.64, 31.9, 59.0, 62.0, 68.4, 70.6, 71.8, 72.8, 78.7, 93.4, 100.8, 169.3, 170.7, 171.6 ppm; MS (ESI): *m/z* calcd for $C_{28}H_{48}^{35}Cl_3NO_{11}S$ 711.20; found (%) 734.21 ([M($^{35}Cl_3$)+Na]$^+$, 97), 736.21 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 738.16 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 43).

4.4.2. 12-Bromododecyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**7b**)

Obtained in 84% yield as a colorless foam: R_f 0.33 (2:1 hexane/EtOAc); $[\alpha]_D$ [25] −35.5 (*c* 1.92, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.27 (s-like, 14H), 1.42 (m, 2H), 1.68 (m, 2H), 1.85 (quint, 2H, J = 7.2 Hz), 2.06 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 3.41 (t, 2H, J = 6.9 Hz), 3.58 (dt, 1H, J = 9.3, 7.2 Hz), 3.73 (q, 1H, J = 9.0 Hz), 3.90 (dt, 1H, J = 9.4, 7.3 Hz), 3.93 (t, 1H, J = 6.6 Hz), 4.12 (dd, 1H, J = 6.7, 11.2 Hz), 4.20 (dd, 1H, J = 6.5, 11.2 Hz), 4.46 (d, 1H, J = 8.4 Hz), 4.71 (s, 2H), 5.07 (dd, 1H, J = 3.5, 10.9 Hz), 5.37 (d, 1H, J = 3.5 Hz), 5.44 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.68 (2C), 20.82, 25.8, 28.1, 28.7, 29.39, 29.47, 29.50, 32.8, 34.0, 56.1, 61.3, 66.9, 70.66, 70.71, 78.6, 93.4, 101.0, 170.2, 170.5, 171.2 ppm; HRMS (FAB): calcd. for $C_{26}H_{44}^{79}Br^{35}Cl_3NO_{11}S$ [M+H]$^+$ 762.0884; found 762.0898.

4.4.3. 12-Bromododecyl 3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**7c**)

Obtained in 70% yield as a colorless foam: R_f 0.24 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] −13.0 (*c* 2.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.24–1.35 (m, 14H), 1.42 (m, 2H), 1.64 (m, 2H), 1.85 (quint, 2H, J = 7.2 Hz), 1.98 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.13 (s, 3H), 2.157 (s, 3H), 2.164 (s, 3H), 3.41 (t, 2H, J = 6.9 Hz), 3.52 (dt, 1H, J = 9.5, 6.9 Hz), 3.55 (dt, 1H, J = 7.5, 9.0 Hz), 3.67 (ddd, 1H, J = 2.5, 5.2, 8.4 Hz), 3.80 (t, 1H, J = 8.5 Hz), 3.83 (dt, 1H, J = 9.5, 7.2 Hz), 3.91 (t, 1H, J = 6.7 Hz), 4.10 (dd, 1H, J = 7.1, 11.1 Hz), 4.14 (dd, 1H, J = 5.2, 12.2 Hz), 4.17 (dd, 1H, J = 6.5, 11.1 Hz), 4.44 (d, 1H, J = 7.6 Hz), 4.49 (dd, 1H, J = 2.5, 12.0 Hz), 4.50 (d, 1H, J = 7.8 Hz), 4.69 (d, 1H, J = 10.9 Hz), 4.72 (d, 1H, J = 10.9 Hz), 4.99 (dd, 1H, J = 3.4, 10.5 Hz), 5.08 (dd, 1H, J = 8.4, 9.4 Hz), 5.10 (dd, 1H, J = 7.8, 10.5 Hz), 5.37 (dd, 1H, J = 0.9, 3.4 Hz), 5.71 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.51, 20.65 (3C), 20.85, 20.97, 25.8, 28.1, 28.7, 29.35, 29.39, 29.47, 32.8, 34.1, 58.3, 60.9, 62.2, 66.6, 69.1, 70.4, 70.7, 70.8, 72.4, 72.6, 75.6, 78.6, 93.4, 100.5, 100.9, 169.5, 170.06, 170.12, 170.36, 170.42, 171.2 ppm; MS (ESI): *m/z* calcd for $C_{38}H_{59}^{79}Br^{35}Cl_3NO_{19}S$ 1049.17; found (%) 1072.16 ([M(^{79}Br+$^{35}Cl_3$)+Na]$^+$, 54), 1074.21 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 1076.13 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 78).

4.4.4. 2-Phenylethyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**12a**)

Obtained in 75% yield as a colorless foam: R_f 0.34 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] −14.4 (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.04 (s, 3H), 2.09 (s, 3H), 2.12 (s, 3H), 2.99 (t, 2H, J = 7.6 Hz), 3.60 (q, 1H, J = 9.0 Hz), 3.69 (ddd, 1H, J = 2.5, 4.9, 9.6 Hz), 3.80 (dt, 1H, J = 10.2, 7.7 Hz), 4.11 (dt, 1H, J = 10.1, 7.6 Hz), 4.13 (dd, 1H, J = 2.5, 12.3 Hz), 4.26 (dd, 1H, J = 4.9, 12.3 Hz), 4.46 (d, 1H, J = 8.2 Hz), 4.64 (d, 1H, J = 10.9 Hz), 4.68 (d, 1H, J = 10.9 Hz), 5.07 (t, 1H, J = 9.4 Hz), 5.12 (t, 1H, J = 9.6 Hz), 5.52 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.6, 20.7, 20.9, 36.0, 58.9, 61.9, 68.4, 70.9, 71.9, 72.8, 78.6, 93.4, 100.7, 126.7, 128.6 (2C), 128.9 (2C), 137.6, 169.4, 170.7, 171.6 ppm; HRMS (FAB): calcd. for $C_{22}H_{28}^{35}Cl_3NO_{11}S$ [M+H]$^+$ 620.0527; found 620.0536.

4.4.5. Benzyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**13b**)

Obtained in 62% yield as a colorless foam: R_f 0.28 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] −44.4 (*c* 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 3H), 2.08 (s, 3H), 2.18 (s, 3H), 3.80 (dt, 1H, J = 10.9, 8.6 Hz), 3.90 (dt,

1H, J = 0.9, 6.6 Hz), 4.15 (dd, 1H, J = 6.5, 11.3 Hz), 4.22 (dd, 1H, J = 6.7, 11.3 Hz), 4.49 (d, 1H, J = 8.3 Hz), 4.56 (s, 2H), 4.68 (d, 1H, J = 11.6 Hz), 4.94 (d, 1H, J = 11.0 Hz), 5.01 (dd, 1H, J = 3.4, 10.9 Hz), 5.21 (d, 1H, J = 8.7 Hz), 5.36 (d, 1H, J = 3.4 Hz), 7.30–7.40 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.7 (2C), 20.8, 56.0, 61.4, 66.9, 70.7, 70.9, 71.0, 78.6, 93.3, 99.2, 128.5, 128.6, 128.7, 135.8, 170.2, 170.5, 171.2 ppm; MS (ESI): *m/z* calcd for $C_{21}H_{26}^{35}Cl_3NO_{11}S$ 605.03; found (%) 627.96 ([M($^{35}Cl_3$)+Na]$^+$, 92), 629.94 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 631.93 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 41).

4.4.6. 4-Pentenyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**14b**)

Obtained in 63% yield as a colorless solid: m.p. 84–86 °C; R_f 0.36 (3:2 hexane/EtOAc); [α]$_D$ [25] −23.1 (*c* 1.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.79 (quint, 2H, J = 7.2 Hz), 2.06 (s, 3H), 2.10 (s, 3H), 2.15 (m, 2H), 2.18 (s, 3H), 3.61 (dt, 1H, J = 9.6, 7.0 Hz), 3.74 (dt, 1H, J = 11.1, 8.4 Hz), 3.91 (t, 1H, J = 7.0 Hz), 3.92 (dt, 1H, J = 9.5, 7.0 Hz), 4.12 (dd, 1H, J = 6.7, 11.3 Hz), 4.19 (dd, 1H, J = 6.7, 11.3 Hz), 4.46 (d, 1H, J = 8.2 Hz), 4.68 (d, 1H, J = 11.0 Hz), 4.71 (d, 1H, J = 11.0 Hz), 4.99 (m, 1H), 5.04 (m, 1H), 5.05 (dd, 1H, J = 3.4, 11.0 Hz), 5.20 (d, 1H, J = 8.4 Hz), 5.37 (d, 1H, J = 3.3 Hz), 5.80 (ddt, 1H, J = 17.0, 10.2, 6.7 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.7 (2C), 20.8, 28.6, 29.9, 56.1, 61.4, 66.9, 69.9, 70.7, 78.6, 93.4, 101.0, 115.2, 137.6, 170.2, 170.5, 171.3 ppm; Anal. Calcd for $C_{19}H_{28}Cl_3NO_{11}S$: C, 39.02; H, 4.83; N, 2.39; S, 5.48. Found: C, 38.83; H, 4.86; N, 2.34; S, 5.39.

4.4.7. Cyclohexyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**15a**)

Obtained in 57% yield as a colorless foam: R_f 0.35 (3:2 hexane/EtOAc); [α]$_D$ [25] −21.8 (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.10–1.50 (m, 5H), 1.57 (m, 1H), 1.78 (m, 2H), 1.98 (m, 2H), 2.05 (s, 3H), 2.09 (s, 3H), 2.13 (s, 3H), 3.57 (q, 1H, J = 9.1 Hz), 3.70 (m, 2H), 4.12 (dd, 1H, J = 2.5, 12.3 Hz), 4.28 (dd, 1H, J = 5.1, 12.3 Hz), 4.58 (d, 1H, J = 8.2 Hz), 4.72 (s, 2H), 5.07 (t, 1H, J = 9.5 Hz), 5.14 (t, 1H, J = 9.7 Hz), 5.55 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.58, 20.73, 20.88, 24.2, 24.3, 25.4, 31.7, 33.5, 59.0, 62.1, 68.6, 71.7, 73.0, 78.4, 78.7, 93.4, 98.7, 169.4, 170.8, 171.7 ppm; MS (ESI): *m/z* calcd for $C_{20}H_{30}^{35}Cl_3NO_{11}S$ 597.06; found (%) 619.95 ([M($^{35}Cl_3$)+Na]$^+$, 100), 622.00 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 97), 623.92 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 39).

4.4.8. Cyclohexyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**15b**)

Obtained in 78% yield as a colorless foam: R_f 0.31 (2:1 hexane/EtOAc); [α]$_D$ [25] −30.2 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.10–1.50 (m, 5H), 1.57 (m, 1H), 1.79 (m, 2H), 2.01 (m, 2H) 2.06 (s, 3H), 2.10 (s, 3H), 2.18 (s, 3H), 3.69 (dt, 1H, J = 3.3, 10.0 Hz), 3.72 (dt, 1H, J = 10.9, 8.6 Hz), 3.93 (t, 1H, J = 6.7 Hz), 4.10 (dd, 1H, J = 6.7, 11.2 Hz), 4.21 (dd, 1H, J = 6.6, 11.3 Hz), 4.60 (d, 1H, J = 8.3 Hz), 4.73 (s, 2H), 5.07 (dd, 1H, J = 3.5, 10.7 Hz), 5.36 (d, 1H, J = 3.5 Hz), 5.53 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.65, 20.71, 20.85, 24.2, 24.4, 25.4, 31.7, 33.6, 56.2, 61.3, 66.9, 70.6, 70.9.1, 78.5, 78.6, 93.4, 99.1, 170.3, 170.5, 171.3 ppm; MS (ESI): *m/z* calcd for $C_{20}H_{30}^{35}Cl_3NO_{11}S$ 597.06; found (%) 620.02 ([M($^{35}Cl_3$)+Na]$^+$, 94), 622.00 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 623.99 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 39).

4.4.9. L-menthyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**16a**)

Obtained in 74% yield as a colorless foam: R_f 0.40 (2:1 hexane/EtOAc); [α]$_D$ [25] −53.4 (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.74 (d, 3H, J = 6.8 Hz), 0.82 (m, 1H), 0.87 (d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 6.5 Hz), 0.98 (m, 1H), 1.00 (q, 1H, J = 11.7 Hz), 1.30 (m, 2H), 1.67 (m, 2H), 2.02 (m, 1H), 2.05 (s, 3H), 2.07 (s, 3H), 2.14 (s, 3H), 2.22 (m, 1H), 3.55 (q, 1H, J = 9.1 Hz), 3.56 (dt, 1H, J = 3.3, 11.0 Hz), 3.70 (ddd, 1H, J = 2.7, 5.3, 9.5 Hz), 4.14 (dd, 1H, J = 2.7, 12.1 Hz), 4.20 (dd, 1H, J = 5.3, 12.1 Hz), 4.54 (d, 1H, J = 8.3 Hz), 4.75 (s, 2H), 5.07 (t, 1H, J = 9.5 Hz), 5.13 (t, 1H, J = 9.5 Hz), 5.38 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 15.3, 20.58, 20.66, 20.80, 20.88, 22.2, 23.1, 25.1, 31.5, 34.2, 40.0, 47.6, 58.9, 62.4, 68.7, 71.5, 73.2, 77.6, 78.8, 93.4, 97.3, 169.4, 170.7, 171.7 ppm.

4.4.10. L-menthyl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**16b**)

Obtained in 76% yield as a colorless foam: R_f 0.40 (2:1 hexane/EtOAc); [α]$_D$ [25] −54.3 (*c* 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.74 (d, 3H, J = 6.8 Hz), 0.82 (m, 1H), 0.88 (d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 6.5 Hz), 0.98 (m, 1H), 1.00 (q, 1H, J = 11.7 Hz), 1.30 (m, 2H), 1.67 (m, 2H), 2.04 (s, 3H), 2.07 (m, 1H), 2.11 (s, 3H), 2.20 (s, 3H), 2.27 (m, 1H), 3.53 (dt, 1H, J = 4.1, 10.7 Hz), 3.66 (q, 1H, J = 9.4 Hz), 3.92 (t, 1H, J = 6.7 Hz), 4.08 (dd, 1H, J = 6.6, 11.2 Hz), 4.20 (dd, 1H, J = 6.8, 11.2 Hz), 4.54 (d, 1H, J = 8.2 Hz), 4.75 (s, 2H), 5.08 (dd, 1H, J = 3.5, 10.7 Hz), 5.35 (d, 1H, J = 3.5 Hz), 5.50 (d, 1H, J = 9.0 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 15.3, 20.64, 20.75, 20.88, 22.2, 23.0, 25.0, 31.5, 34.2, 40.2, 47.6, 56.0, 61.5, 67.1, 70.5, 71.1, 77.9, 78.7, 93.4, 97.9, 170.4, 170.6, 171.4 ppm; MS (ESI): *m/z* calcd for $C_{24}H_{38}^{35}Cl_3NO_{11}S$ 653.12; found (%) 676.09 ([M($^{35}Cl_3$)+Na]$^+$, 95), 678.05 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 680.07 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 40).

4.4.11. L-menthyl 3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**16c**)

Obtained in 67% yield as a colorless foam: R_f 0.30 (3:2 hexane/EtOAc); [α]$_D$ [25] −32.7 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 0.72 (d, 3H, J = 6.8 Hz), 0.80 (m, 1H), 0.86 (d, 3H, J = 7.0 Hz), 0.93 (d, 3H, J = 6.4 Hz), 0.96 (m, 1H), 0.99 (q, 1H, J = 11.6 Hz), 1.30 (m, 2H), 1.66 (m, 2H), 1.98 (s, 3H), 2.05 (m, 1H), 2.05 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.15 (m, 1H), 2.16 (s, 6H), 3.47 (q, 1H, J = 9.2 Hz), 3.53 (dt, 1H, J = 3.9, 10.7 Hz), 3.69 (m, 1H), 3.79 (t, 1H, J = 9.7 Hz), 3.91 (t, 1H, J = 6.7 Hz), 4.10 (dd, 1H, J = 7.0, 10.5 Hz), 4.10 (m, 1H), 4.16 (dd, 1H, J = 6.4, 11.1 Hz), 4.52 (d, 1H, J = 7.8 Hz), 4.55 (d, 1H, J = 8.2 Hz), 4.74 (s, 2H), 5.00 (dd, 1H, J = 3.4, 10.4 Hz), 5.09 (t, 1H, J = 9.0 Hz), 5.10 (dd, 1H, J = 7.8, 10.4 Hz), 5.37 (d, 1H, J = 3.4 Hz), 5.76 (d, 1H, J = 9.1 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 15.3, 20.52, 20.59, 20.63, 20.73, 20.77, 20.98, 22.3, 23.1, 25.1, 31.5, 34.2, 40.0, 47.6, 59.0, 60.9, 62.1, 66.7, 69.1, 70.76, 70.84, 72.3, 73.2, 76.4, 77.3, 78.7, 93.5, 97.0, 101.1, 169.4, 170.1 (2C), 170.35, 170.43, 171.4 ppm; MS (ESI): *m/z* calcd for $C_{36}H_{54}^{35}Cl_3NO_{19}S$ 941.21; found (%) 964.26 ([M($^{35}Cl_3$)+Na]$^+$, 81), 966.27 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 968.27 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 41).

4.4.12. 6-O-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranosyl]-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**17b**)

Obtained in 74% yield as a colorless foam: R_f 0.27 (3:2 hexane/EtOAc); [α]$_D$ [25] −46.4 (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 3H), 1.34 (s, 3H), 1.46 (s, 3H), 1.60 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H), 2.15 (s, 3H), 3.72 (ddd, 1H, J = 7.2, 8.2, 10.9 Hz), 3.92 (dd, 1H, J = 8.8, 12.7 Hz), 3.95 (dt, 1H, J = 0.8, 6.7 Hz), 4.00 (dd, 1H, J = 2.5, 12.6 Hz), 4.12 (dd, 1H, J = 6.7, 11.2 Hz), 4.17 (dd, 1H, J = 2.0, 8.0 Hz), 4.19 (dd, 1H, J = 6.6, 11.2 Hz), 4.34 (dd, 1H, J = 2.3, 5.2 Hz), 4.59 (dd, 1H, J = 2.3, 7.9 Hz), 4.71 (d, 1H, J = 11 Hz), 4.74 (d, 1H, J = 11 Hz), 4.83 (d, 1H, J = 8.4 Hz), 5.04 (dd, 1H, J = 3.3, 10.9 Hz), 5.37 (dd, 1H, J = 0.8, 3.3 Hz), 5.59 (d, 1H, J = 5.2 Hz), 5.82 (d, 1H, J = 8.4 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.60 (2C), 20.65, 24.2, 24.7, 25.87, 25.92, 55.8, 61.2, 66.8, 68.5, 68.8, 70.0, 70.6, 70.84, 70.88, 70.95, 78.7, 93.7, 96.2, 101.2, 109.2, 109.5, 170.1, 170.4, 170.6 ppm; MS (ESI): *m/z* calcd for $C_{26}H_{38}^{35}Cl_3NO_{16}S$ 757.10; found (%) 780.05 ([M($^{35}Cl_3$)+Na]$^+$, 92), 782.04 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 784.02 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 39).

4.4.13. Methyl 6-O-[3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranosyl]-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**18b**)

Obtained in 21% yield as a colorless foam: R_f 0.25 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] +19.5 (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 2.01 (s, 3H), 2.06 (s, 3H), 2.12 (s, 3H), 3.40 (s, 3H), 3.45 (dd, 1H, *J* = 8.9, 9.9 Hz), 3.52 (dd, 1H, *J* = 3.5, 9.7 Hz), 3.65 (dd, 1H, *J* = 5.8, 11.0 Hz), 3.70 (dt, 1H, *J* = 11.0, 7.9 Hz), 3.81 (dt, 1H, *J* = 0.9, 6.7 Hz), 3.86 (ddd, 1H, *J* = 2.1, 5.8, 10 Hz), 4.00 (t, 1H, *J* = 9.2 Hz), 4.10 (m, 3H), 4.28 (d, 1H, *J* = 8.3 Hz), 4.60 (d, 1H, *J* = 3.3 Hz), 4.64 (s, 2H), 4.64 (d, 2H, *J* = 12.1 Hz), 4.79 (d, 1H, *J* = 12.1 Hz), 4.80 (d, 1H, *J* = 11.0 Hz), 4.89 (d, 1H, *J* = 11.6 Hz), 4.96 (dd, 1H, *J* = 3.4, 11.0 Hz), 4.99 (d, 1H, *J* = 11.0 Hz), 5.02 (d, 1H, *J* = 7.6 Hz), 5.34 (dd, 1H, *J* = 0.9, 3.4 Hz), 7.27–7.40 (m, 15H) ppm; ^{13}C NMR ($CDCl_3$): δ 20.6, 20.7, 55.5, 55.6, 61.1, 66.6, 68.9, 69.7, 70.3, 70.7, 73.4, 74.5, 75.6, 77.6, 78.5, 79.8, 81.9, 93.5, 98.0, 101.4, 127.6, 127.82, 127.84, 127.90, 127.93, 128.1, 128.35, 128.44, 138.0, 138.4, 138.6, 170.0, 170.4, 170.9 ppm; MS (ESI): *m/z* calcd for $C_{42}H_{50}^{35}Cl_3NO_{16}S$ 961.19; found (%) 984.18 ([M($^{35}Cl_3$)+Na]$^+$, 100), 986.17 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 95), 988.17 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 32).

4.4.14. Cholest-5-en-3β-yl 3,4,6-tri-O-acetyl-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-galactopyranoside (**19b**)

Obtained in 56% yield as a colorless solid: R_f 0.30 (3:1 hexane/EtOAc); $[\alpha]_D$ [25] −32.0 (*c* 2.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.67 (s, 3H), 0.86 (d, 3H, *J* = 6.6 Hz), 0.87 (d, 3H, *J* = 6.6 Hz), 0.91 (d, 3H, *J* = 6.4 Hz), 1.00 (s, 3H), 0.90–2.05 (m, 26H), 2.05 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 2.33 (m, 1H), 2.39 (ddd, 1H, *J* = 2.1, 4.8, 13.1 Hz), 3.62 (tt, 1H, *J* = 4.7, 11.4 Hz), 3.74 (dt, 1H, *J* = 11.1, 8.5 Hz), 3.90 (t, 1H, *J* = 7.0 Hz), 4.10 (dd, 1H, *J* = 7.0, 11.2 Hz), 4.19 (dd, 1H, *J* = 6.6, 11.2 Hz), 4.57 (d, 1H, *J* = 8.2 Hz), 4.73 (s, 2H), 5.01 (dd, 1H, *J* = 2.4, 8.8 Hz), 5.05 (dd, 1H, *J* = 3.5, 11.0 Hz), 5.37 (d, 1H, *J* = 3.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 11.8, 18.7, 19.3, 20.68, 20.71, 20.9, 21.0, 22.5, 22.8, 23.8, 24.3, 28.0, 28.2, 29.6, 31.8, 31.9, 35.8, 36.2, 36.7, 37.2, 38.5, 39.5, 39.7, 42.3, 50.1, 56.1, 56.7, 61.3, 66.9, 70.7, 70.9, 78.7, 79.7, 93.4, 99.2, 122.5, 139.9, 170.2, 170.4, 171.2 ppm; MS (ESI): *m/z* calcd for $C_{41}H_{64}^{35}Cl_3NO_{11}S$ 883.33; found (%) 906.33 ([M($^{35}Cl_3$)+Na]$^+$, 94), 908.25 ([M($^{35}Cl_2$+^{37}Cl)+Na]$^+$, 100), 910.30 ([M(^{35}Cl+$^{37}Cl_2$)+Na]$^+$, 34).

4.5. Conversions of N-Tces group

4.5.1. Tetradecyl 3,4,6-tri-O-acetyl-2-deoxy-2-sulfoamino-β-D-glucopyranoside (**24**)

To a mixture of **10a** (66 mg, 0.092 mmol) and acetic acid (60 mg, 1.0 mmol) in methanol (1.5 mL) was added zinc (35 mg, 0.5 mmol), and the resulting dark-grey suspension was stirred at 5 °C for 30 min. The reaction mixture was diluted with CH_2Cl_2 (5 mL), filtered and washed with CH_2Cl_2-methanol (10:1). The combined filtrates were concentrated and co-evaporated with heptane (1 mL) to give a residue, which was purified by silica gel chromatography eluting with CH_2Cl_2-methanol (7 → 6) to give **24** (50 mg, 93%) as a colorless solid: m.p. 138–140 °C; R_f 0.30 (6:1 CH_2Cl_2/MeOH); $[\alpha]_D$ [25] +7.7 (*c* 1.1, $CHCl_3$); ^1H NMR (CD_3OD-$CDCl_3$): δ 0.88 (t, 3H, *J* = 6.7 Hz), 1.26 (s-like, 20H), 1.34 (m, 2H), 1.64 (m, 2H), 2.03 (s, 3H), 2.07 (s, 3H), 2.08 (s, 3H), 3.36 (t, 1H, *J* = 9.8 Hz), 3.63 (dt, 1H, *J* = 9.3, 7.2 Hz), 3.75 (ddd, 1H, *J* = 2.3, 4.8, 9.7 Hz), 3.85 (dt, 1H, *J* = 9.0, 7.3 Hz), 4.13 (dd, 1H, *J* = 2.3, 12.2 Hz), 4.27 (dd, 1H, *J* = 4.8, 12.2 Hz), 4.57 (d, 1H, *J* = 8.0 Hz), 4.99 (dd, 1H, *J* = 9.3, 9.7 Hz), 5.24 (t, 1H, *J* = 9.3, 9.8 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 14.1, 20.60, 20.66, 21.3, 22.6, 25.8, 29.35, 29.53, 29.61, 29.67, 29.74, 29.77, 29.80, 29.84, 31.9, 58.2, 62.5, 69.1, 70.4, 71.3, 74.2, 101.0, 169.5, 170.6, 171.5 ppm; Anal. Calcd for $C_{26}H_{47}NO_{11}S$: C, 53.68; H, 8.14; N, 2.41; S, 5.51. Found: C, 53.50; H, 8.25; N, 2.53.

4.5.2. Tetradecyl 3,4,6-tri-O-acetyl-2-benzamido-2-deoxy-β-D-glucopyranoside (**26**)

To a mixture of **10a** (43 mg, 0.06 mmol), powdered anhydrous $CuSO_4$ (5 mg, 0.03 mmol), and acetic acid (0.1 mL) in tetrahydrofuran (1 mL) was added zinc (42 mg, 0.6 mmol) in 1 portion. The resulting dark-grey suspension was stirred at rt for 3 h. The reaction mixture was filtered and washed with EtOAc, and the combined filtrates were mixed with H_2O, and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4), concentrated, and co-evaporated with heptane (1 mL) to give crude **tetradecyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranoside** (**25**) (33 mg) as a colorless solid: R_f 0.50 (EtOAc); ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.25 (s-like, 22H), 1.62 (m, 2H), 2.02 (s, 3H), 2.074 (s, 3H), 2.077 (s, 3H), 2.93 (dd, 1H, *J* = 8.2, 9.7 Hz), 3.51 (dt, 1H, *J* = 9.5, 7.0 Hz), 3.68 (ddd, 1H, *J* = 2.4, 4.9, 9.6 Hz), 3.90 (dt, 1H, *J* = 9.5, 6.7 Hz), 4.11 (dd, 1H, *J* = 2.4, 12.2 Hz), 4.24 (d, 1H, *J* = 8.0 Hz), 4.29 (dd, 1H, *J* = 4.9, 12.2 Hz), 4.98 (t, 1H, *J* = 9.3 Hz), 5.01 (t, 1H, *J* = 9.3 Hz) ppm.

To a solution of the amine **25** in CH_2Cl_2 (1 mL) at 5 °C was added benzoyl chloride (17 mg, 0.12 mmol) in CH_2Cl_2 (0.2 mL) followed by Et_3N (25 mg, 0.25 mmol). The reaction mixture was stirred at 5 °C for 1 h, and then diluted with EtOAc (10 mL) and aq. $NaHCO_3$ (5 mL), and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel chromatography eluting with hexane-EtOAc (3:2) to give **26** (31 mg, 85%) as a colorless solid: m.p. 172–174 °C; R_f 0.30 (3:2 hexane/EtOAc); $[\alpha]_D$ [25] +5.8 (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 7.0 Hz), 1.05–1.35 (m, 22H), 1.52 (m, 2H), 1.99 (s, 3H), 2.04 (s, 3H), 2.10 (s, 3H), 3.47 (dt, 1H, *J* = 9.7, 6.8 Hz), 3.76 (ddd, 1H, *J* = 2.5, 4.8, 9.9 Hz), 3.88 (dt, 1H, *J* = 9.6, 6.3 Hz), 4.10 (q, 1H, *J* = 9.2 Hz), 4.17 (dd, 1H, *J* = 2.4, 12.2 Hz), 4.30 (dd, 1H, *J* = 4.8, 12.2 Hz), 4.78 (d, 1H, *J* = 8.3 Hz), 5.15 (t, 1H, *J* = 9.6 Hz), 5.46 (dd, 1H, *J* = 9.6, 10.4 Hz), 6.22 (m, 1H), 7.41 (m, 2H), 7.50 (m, 1H), 7.70 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ 14.1, 20.63, 20.65, 20.74, 22.6, 25.8, 29.31, 29.40, 29.49, 29.53, 29.60, 29.65, 31.9, 55.0, 62.2, 68.7, 70.0, 71.9, 72.4, 101.0, 126.9 (2C), 128.6 (2C), 131.6, 134.2, 167.5, 169.4, 170.7, 171.1 ppm; Anal. Calcd for $C_{33}H_{51}NO_9$: C, 65.43; H, 8.49; N, 2.31. Found: C, 65.15; H, 8.29; N, 2.07.

4.5.3. Tetradecyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranoside (**27**)

To a mixture of **10a** (43 mg, 0.06 mmol) and powdered anhydrous $CuSO_4$ (5 mg, 0.03 mmol) in tetrahydrofuran (1 mL) was added acetic acid (0.1 mL) and acetic anhydride (0.1 mL). Zinc dust (42 mg, 0.6 mmol) was added in 2 portions for 10 min, and the resulting dark-grey suspension was stirred at rt for 3 h. The reaction mixture was filtered and washed with EtOAc, and the combined filtrates were mixed with H_2O, and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel chromatography eluting with hexane-EtOAc (1:2) to give **27** (26 mg, 80%) as a colorless solid: m.p. 126–129 °C; R_f 0.30 (1:2 hexane/EtOAc); $[\alpha]_D$ [25] −6.3 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.25 (s-like, 22H), 1.57 (m, 2H), 1.95 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.09 (s, 3H), 3.47 (dt, 1H, *J* = 9.6, 6.9 Hz), 3.71 (ddd, 1H, *J* = 2.5, 4.7, 10.0 Hz), 3.82 (dt, 1H, *J* = 10.4, 8.5 Hz), 3.86 (dt, 1H, *J* = 9.6, 6.8 Hz), 4.13 (dd, 1H, *J* = 2.3, 12.3 Hz), 4.27 (dd, 1H, *J* = 4.7, 12.3 Hz), 4.69 (d, 1H, *J* = 8.2 Hz), 5.07 (t, 1H, *J* = 9.6 Hz), 5.32 (dd, 1H, *J* = 9.4, 10.5 Hz), 5.64 (d, 1H, *J* = 8.5 Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 14.1, 20.6, 20.7, 20.8, 22.7, 25.8, 29.34, 29.36, 29.49, 29.58, 29.64, 31.9, 59.0, 62.0, 68.4, 70.6, 71.8,

72.8, 78.7, 93.4, 100.8, 169.3, 170.7, 171.6 ppm; Anal. Calcd for $C_{28}H_{49}NO_9$: C, 61.86; H, 9.08; N, 2.58. Found: C, 61.50; H, 8.95; N, 2.53.

4.5.4. 12-Acetylthiododecyl 3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-deoxy-2-(2,2,2-trichloroethoxysulfonyl)amido-β-D-glucopyranoside (**28**)

To a solution of the lactoside **7c** (105 mg, 0.10 mmol) in DMF (1 mL) at 5 °C was added potassium thioacetate (36 mg, 0.30 mmol). The reaction mixture was stirred at 5 °C for 0.5 h, and then at rt for 3 h. The mixture was diluted with hexane-EtOAc (1:1, 10 mL) and H_2O (5 mL), and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with hexane-EtOAc (1:1). The combined organic extracts were dried (Na_2SO_4) and concentrated to give a brown residue, which was purified by silica gel chromatography eluting with hexane-EtOAc (3:2 to 1:1) to give **27** (98 mg, 93%) as a colorless foam: R_f 0.36 (1:1 hexane/EtOAc); $[\alpha]_D$ [25] −13.2 (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.25 (s-like, 12H), 1.33 (m, 4H), 1.56 (quint, 2H, $J = 7.4$ Hz), 1.63 (quint, 2H, $J = 7.1$ Hz), 1.98 (s, 3H), 2.06 (s, 3H), 2.07 (s, 3H), 2.12 (s, 3H), 2.155 (s, 3H), 2.160 (s, 3H), 2.32 (s, 3H), 2.86 (t, 2H, $J = 7.4$ Hz), 3.53 (dt, 1H, $J = 9.5$, 7.0 Hz), 3.55 (q, 1H, $J = 8.5$ Hz), 3.67 (ddd, 1H, $J = 3.0$, 5.3, 8.4 Hz), 3.81 (t, 1H, $J = 8.0$ Hz), 3.83 (dt, 1H, $J = 9.5$, 7.2 Hz), 3.90 (dt, 1H, $J = 0.8$, 6.8 Hz), 4.10 (dd, 1H, $J = 7.3$, 11.3 Hz), 4.14 (m, 1H), 4.17 (dd, 1H, $J = 6.4$, 11.3 Hz), 4.44 (d, 1H, $J = 7.4$ Hz), 4.48 (dd, 1H, $J = 2.9$, 11.9 Hz), 4.50 (d, 1H, $J = 7.8$ Hz), 4.69 (d, 1H, $J = 10.9$ Hz), 4.72 (d, 1H, $J = 10.9$ Hz), 4.99 (dd, 1H, $J = 3.4$, 10.4 Hz), 5.08 (dd, 1H, $J = 8.2$, 9.1 Hz), 5.11 (dd, 1H, $J = 7.8$, 10.4 Hz), 5.37 (dd, 1H, $J = 0.7$, 3.3 Hz), 5.50 (d, 1H, $J = 9.0$ Hz) ppm.

4.5.5. 12-Acetylthiododecyl 3,6-di-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-2-acetamido-2-deoxy-β-D-glucopyranoside (**29**)

To a mixture of **28** (78 mg, 0.074 mmol) and powdered anhydrous $CuSO_4$ (7 mg, 0.04 mmol) in tetrahydrofuran (1.5 mL) was added acetic acid (0.1 mL) and acetic anhydride (0.1 mL). Zinc dust (60 mg, 0.9 mmol) was added in 2 portions for 10 min, and the resulting dark-grey suspension was stirred at rt for 3 h. The reaction mixture was filtered and washed with EtOAc, and the combined filtrates were mixed with H_2O, and the layers were separated. The organic layer was washed with aq. NaCl, and the combined aqueous layers were extracted with EtOAc. The combined organic extracts were dried (Na_2SO_4) and concentrated to give a residue, which was purified by silica gel chromatography eluting with hexane-EtOAc (1:2) to give **29** (50 mg, 77%) as a colorless solid: m.p. 114–117 °C; R_f 0.24 (1:2 hexane/EtOAc); $[\alpha]_D$ [25] −16.9 (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.25 (s-like, 12H), 1.34 (m, 4H), 1.56 (m, 4H), 1.96 (s, 3H), 1.97 (s, 3H), 2.06 (s, 6H), 2.07 (s, 3H), 2.11 (s, 3H), 2.15 (s, 3H), 2.32 (s, 3H), 2.86 (t, 2H, $J = 7.4$ Hz), 3.41 (dt, 1H, $J = 9.5$, 6.8 Hz), 3.62 (ddd, 1H, $J = 3.0$, 5.2, 8.5 Hz), 3.78 (t, 1H, $J = 8.2$ Hz), 3.81 (dt, 1H, $J = 9.5$, 6.8 Hz), 3.88 (dt, 1H, $J = 0.8$, 6.9 Hz), 4.02 (dt, 1H, $J = 7.5$, 9.4 Hz), 4.09 (dd, 1H, $J = 7.4$, 11.2 Hz), 4.13 (dd, 1H, $J = 5.3$, 11.9 Hz), 4.14 (dd, 1H, $J = 6.4$, 11.2 Hz), 4.44 (d, 1H, $J = 7.5$ Hz), 4.49 (dd, 1H, $J = 2.9$, 11.9 Hz), 4.50 (d, 1H, $J = 8.0$ Hz), 4.98 (dd, 1H, $J = 3.4$, 10.5 Hz), 5.08 (dd, 1H, $J = 8.2$, 9.4 Hz), 5.12 (dd, 1H, $J = 7.9$, 10.5 Hz), 5.36 (dd, 1H, $J = 0.6$, 3.3 Hz), 5.62 (d, 1H, $J = 9.3$ Hz) ppm; ^{13}C NMR ($CDCl_3$): δ 20.4, 20.5, 20.8, 23.1, 25.8, 28.7, 28.97, 29.03, 29.24, 29.32, 29.37, 29.42, 29.47, 30.5, 53.1, 60.7, 62.3, 66.5, 69.0, 69.6, 70.6, 70.7, 72.3, 72.4, 75.7, 100.8, 100.9, 169.3, 169.93, 169.98, 170.02, 170.26, 170.33, 170.5, 196.0; Anal. Calcd for $C_{40}H_{63}NO_{18}S$: C, 54.72; H, 7.23; N, 1.60; S, 3.65. Found: C, 54.55; H, 7.29; N, 1.57; S, 3.60.

Key compounds in this article (Chemical compound viewer)

Compound **7b** (compound7b.mol), **10a** (compound10a.mol), **16c** (compound16c.mol).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.carres.2016.09.001. These data include MOL files and InChiKeys of the most important compounds described in this article.

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