

Ready access to 3-amino-2,3-dideoxysugars *via* regio- and stereo-selective tandem hydroamination–glycosylation of glycols†

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Received 13th January 2011, Accepted 2nd March 2011

DOI: 10.1039/c1ob05068k

A highly stereoselective $\text{BF}_3 \cdot \text{OEt}_2$ -promoted tandem hydroamination–glycosylation on a glycol scaffold has been developed to form 3-amino-2,3-dideoxysugars in a one-pot procedure. This efficient multicomponent reaction protocol offers simplicity and general applicability to a broad range of variations on each component.

Structurally-defined aminosugars such as 3-amino-2,3-dideoxy sugars are of great importance and have stimulated tremendous research interest, due to their prevalence in pharmaceuticals such as anthracycline antibiotics,¹ and natural products such as L-ristosamine,² L-daunosamine,³ nocardicyclins⁴ and L-vancosamine.⁵ For example, L-ristosamine is the essential carbohydrate motif in the structure of ristomycin, which is a member of the antibiotic vancomycin family and plays a pivotal role in platelet aggregation and diagnosis of von Willebrand's disease.² Appendage of L-vancosamine to the antibiotic vancomycin transforms it into a potent drug for the treatment of methicillin-resistant *Staphylococcus aureus*.⁶ The medicinal and glycobiological studies of the intriguing activities of this class of aminosugars and derivatives hinge on the synthetic ease of preparation of 3-amino-2,3-dideoxyhexapyranoses.

Unfortunately, current syntheses are complicated due to the inherent challenges associated with carbohydrate chemistry.⁷ It is extremely cumbersome to achieve exclusive stereoselectivity in the synthesis of 3-amino-2,3-dideoxyglycosides due to the non-availability of a neighbouring participating group at the C-2 position that usually directs the glycosylation stereochemistry. Such reactions normally provide a mixture of anomers. Moreover, the synthesis of 3-amino-2,3-dideoxy sugars requires lengthy synthetic routes resulting in diminished overall yields. Therefore, many groups have been making great efforts on various synthetic strategies to achieve more efficient syntheses of 3-amino-2,3-dideoxysugars.^{8–11} For example, Smiatacz and co-workers synthesized methyl and ethyl 3-amino-2,3-dideoxyhexapyranoses through 1,4-addition of hydrazoic acid to pseudoglycols and subsequent hydrogenation of the azide.⁸ Lowary and co-workers developed an alternative method which comprise photo-induced acylnitrene aziridination reaction and hydrogenolytic aziridine opening which finally furnished methyl 3-amino-2,3-dideoxyglycosides.^{9e}

Colinas's group reported an elegant β -stereoselective sulfonamidoglycosylation of D-glycol, in which the replacement of $\text{HBr} \cdot \text{PPh}_3$ with $\text{BF}_3 \cdot \text{OEt}_2$ led to 3-amino derivatives.¹⁰ In another multistep method, pseudoglycol was initially oxidized with stoichiometric $\text{PhI}(\text{OH})\text{OTf}$ to the corresponding α,β -unsaturated ketone. Conjugate addition of a nucleophile to the resultant α,β -unsaturated ketone and subsequent reductive amination completed the synthesis of 3-amino-2,3-dideoxyglycosides.¹¹ Although results from most of the reports are encouraging, poor stereoselectivities, low yields and multiple synthetic steps are the major impediments of the reported strategies to widespread use.

In continuation of our strong interest in the synthesis of biologically active aminosugars and glycosaminoglycans,¹² herein, we report a concise and robust synthetic approach that provides 3-amino-2,3-dideoxysugars with not only exclusive anomeric stereoselectivity but also with a plethora of structural derivatives. Specifically, we envisioned a straightforward synthesis of 3-amino-2,3-dideoxyglycosides by a three-component reaction of 3,4,6-tri-O-acetyl-D-glycol with two (*N*-, and *O*-, or *S*-containing) nucleophiles in a one-pot manner. This methodology involves regio- and stereoselective glycosylation and C-3 amination on the protected glycol scaffold (Fig. 1).

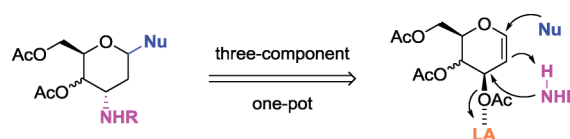


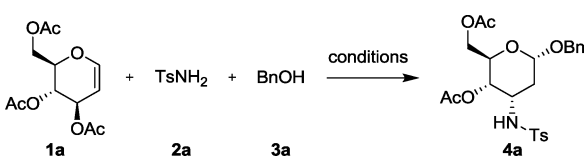
Fig. 1 Our plan for quick access to 3-amino-2,3-dideoxysugars *via* regio- and stereoselective tandem hydroamination/glycosylation of glycols.

Results and discussion

We first determined whether our proposed one-pot three-component reaction was a viable strategy to form the desired products. In fact, when 3,4,6-tri-O-acetyl-D-glucal (**1a**), *p*-toluenesulfonamide (**2a**) and benzyl alcohol (**3a**) were subjected to a one-pot reaction in the presence of 1.1 equiv of triflic acid

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† Electronic supplementary information (ESI) available: NMR spectra for compounds **4a–4z**. See DOI: 10.1039/c1ob05068k

Table 1 Optimization of the one-pot three-component tandem hydroamination/glycosylation reaction^a


Entry	Promoter	Solvent	Time (min)	Yield (%) ^b
1	TfOH (1.1)	toluene	30	31
2	Amberlyst-15 (1.1)	toluene	180	—
3	TFA (1.1)	toluene	120	trace
4	H ₃ PO ₄ (1.1)	toluene	180	—
5	CSA (1.1)	toluene	180	—
6	<i>p</i> -TsOH (1.1)	toluene	180	—
7	Cu(OTf) ₂ (1.1)	toluene	180	—
8	ZnCl ₂ (1.1)	DCM	180	—
9	(C ₆ F ₅) ₃ B (1.1)	toluene	180	—
10	BF ₃ ·OEt ₂ (1.1)	toluene	120	45
11	BF ₃ ·OEt ₂ (2.2)	toluene	30	90
12	BF ₃ ·OEt ₂ (2.2)	DMF	30	—
13	BF ₃ ·OEt ₂ (2.2)	THF	30	—
14	BF ₃ ·OEt ₂ (2.2)	MeCN	30	trace
15	BF ₃ ·OEt ₂ (2.2)	DCM	30	91
16	BF ₃ ·OEt ₂ (2.2)	DCE	30	93
17	TMSOTf (2.2)	DCE	30	90
18	SnCl ₄ (2.2)	DCE	30	92

^a Reactions were carried out with 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), TsNH₂ **2a** (1.1 equiv), BnOH **3a** (1.1 equiv) in 2 mL of solvent.

^b Isolated yields. DCE = 1, 2-dichloroethane.

(TfOH) in toluene at room temperature for 30 min, the desired aminoglycoside **4a** was obtained with exclusive α -stereoselectivity but in a low yield of 31% (Table 1, entry 1). The structural and stereochemical characterization of **4a** was determined by extensive NMR experiments (¹H, ¹³C, COSY, HMQC, HMBC, NOESY, see supporting information†).

To further optimize this process, we conducted a series of experiments to evaluate various promoters and solvents. The results of the preliminary screening are listed in Table 1. For different Brønsted acids tested, such as Amberlyst-15, TFA, H₃PO₄, *p*-TsOH and CSA, the desired product was not detected even after prolonged reaction times (Table 1, entries 2–6). We started to try Lewis acids such as Cu(OTf)₂, ZnCl₂, and (C₆F₅)₃B, but also failed to transform starting materials into the desired 3-amino-2,3-dideoxysugars (Table 1, entries 7–9). However, it is worthy of note that the reaction was found to proceed with the strong Lewis acid BF₃·OEt₂ (1.1 equiv), albeit with extended reaction time and with a moderate yield of 45% (Table 1, entry 10). However, an increase in the promoter loading (2.2 equiv) was found to improve the yield to 90% (Table 1, entry 11). Amongst different solvents screened, 1,2-dichloroethane (DCE) was found to be superior to other solvents in terms of reaction time, percentage yield and activity profile (entry 16). When the reaction was carried out with other strong Lewis acids TMSOTf (2.2 equiv) and SnCl₄ (2.2 equiv), the product could also be obtained in comparable yields (Table 1, entries 17 and 18). It is noteworthy that this tandem hydroamination–glycosylation reaction is operationally simple, easy to carry out and more importantly, devoid of by-products. When we tested the crude reaction mixture by NMR, there was no indication of a double bond, suggesting that there is no formation of a Ferrier product. Thus, the optimized reaction

conditions for the one-pot synthesis were found to be 2.2 equiv of BF₃·OEt₂, at room temperature with DCE as solvent under nitrogen for 30 min (Table 1, entry 16).

With the optimized reaction conditions in hand, we investigated the substrate scope by carrying out the reaction with various nucleophiles. As shown in Table 2, a wide range of aromatic and aliphatic alcohols and thiols gave the desired aminoglycosides with exclusive α -stereoselectivities in high yields. A series of 3-amino-2,3-dideoxyglucosides **4b–4p** were prepared in good to excellent yields (66–95%) (Table 2, entries 1–12). It was observed that long chain alcohols, alcohols bearing an electron withdrawing group, aromatic and hindered aliphatic thiols gave products in slightly lower yields (Table 2, entries 1, 7, 11 and 12, **4d**, **4k**, **4o** and **4p**). With this expedited protocol, we synthesized L-menthol glucoside **4q** in 77% yield (Table 2, entry 13), which is a commonly seen 3-amino-2,3-dideoxysugar motif appended to biologically important natural products.¹³ To our delight, all of the glycosylation products were obtained as pure diastereomers.

In our protocol, aromatic and aliphatic sulfonamides achieve the best results (Table 2, entries 14 and 15). For instance, TsNH₂, NsNH₂ and MsNH₂ proved to be excellent nucleophiles, providing the corresponding products in high yields and anomeric selectivities. Likewise, the reaction with benzyl carbamate (CbzNH₂) gave the corresponding 3-amino-2,3-dideoxyglucoside **4t** in moderate yield (Table 2, entry 16). The benzyloxycarbonyl (Cbz) group in the resulting product could be easily transformed into free amino group. Interestingly, when 3,4,6-tri-*O*-acetyl-D-glucal **1a** was treated with *tert*-butyl carbamate (BocNH₂) under the same reaction conditions, the deprotected product **4u** was isolated after purification (Table 2, entry 17). In contrast, reaction of trimethylsilyl azide (TMSN₃) with tri-*O*-acetyl-D-glucal **1a** proved to be unsuccessful. Finally, the analogous reaction of tri-*O*-acetyl-D-galactal **1b** with TsNH₂ and aromatic or aliphatic alcohols also afforded the corresponding 3-amino-2,3-dideoxygalactosides **4v–4z** in good to excellent yields with exclusive α anomeric selectivity (Table 2, entries 18–21).

We felt that the investigation of the mechanisms would be worthwhile due to the diastereoselectivity of the reaction, even in the absence of a neighbouring directing group at C-2. To gain insight into the mechanism by which BF₃·OEt₂ promotes this reaction, we performed simple ¹⁹F NMR spectroscopic studies. Careful scrutiny of the NMR data suggests that BF₃·OEt₂ is coordinated to the oxygen atom of the glycal. In our control NMR experiments, BnOH and TsNH₂ were combined with BF₃·OEt₂, and as predicted, BF₃·OEt₂ did not show any observable shift from the original ¹⁹F NMR signal, suggesting negligible or no interaction between these nucleophiles and BF₃·OEt₂.¹⁴ However, upon the addition of glycal to the remaining nucleophiles, shifts of the ¹⁹F signal were observed, which indicates the formation of the boron–sugar complex (Fig. 2). This result implies that BF₃·OEt₂ is coordinated to the glycal. Though a detailed mechanism of the present protocol awaits further studies, a simple plausible pathway is postulated (Scheme 1). Our proposed mechanism involves formation of intermediary allyloxocarbenium ion **6** as a result of expulsion of the acetoxy group. Initial diastereofacial selective attack of the N-nucleophile at C3 of the more stable twisted boat conformation is followed by a rapid proton transfer to generate oxocarbenium ion **7**. Finally, preferential axial attack of the alcohol nucleophile at the anomeric position, as a result of

Table 2 Substrate scope studies for $\text{BF}_3 \cdot \text{OEt}_2$ -promoted one-pot three-component α -selective tandem hydroamination–glycosylation reaction^a

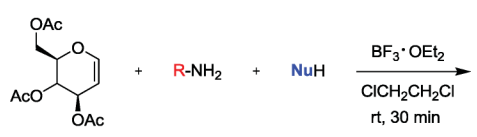
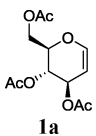
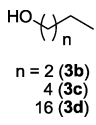
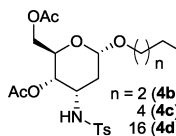
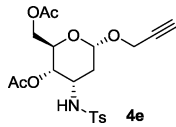
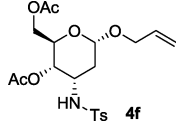
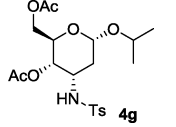
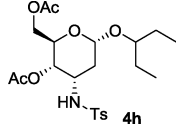
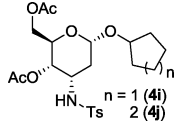
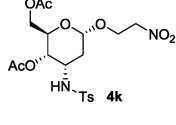
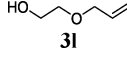
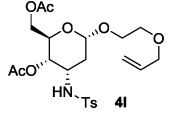
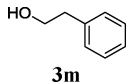
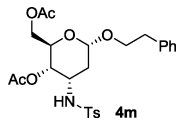
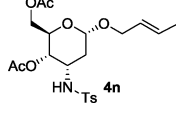
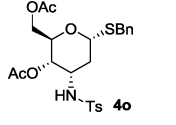
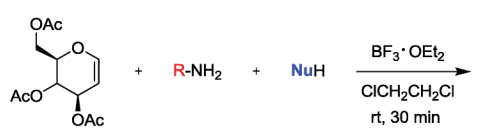
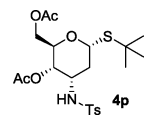
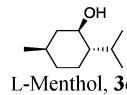
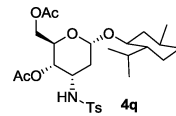
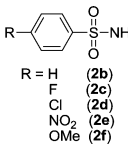
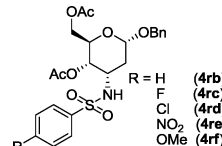
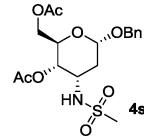
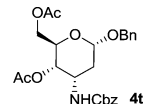
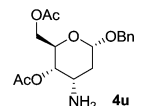
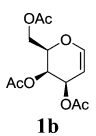
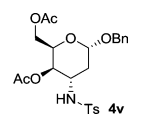
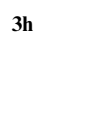
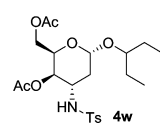
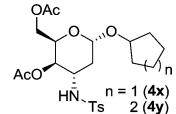
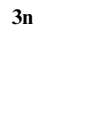
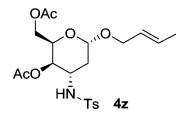
					
Entry	1	R–NH ₂	NuH	Product ^b	Yield (%) ^c
1		TsNH ₂ 2a	 n = 2 (3b) 4 (3c) 16 (3d)	 n = 2 (4b) 4 (4c) 16 (4d)	88 (4b) 84 (4c) 66 (4d)
2	1a	2a			95
3	1a	2a			82
4	1a	2a			85
5	1a	2a			90
6	1a	2a	 n = 1 (3i) 2 (3j)	 n = 1 (4i) 2 (4j)	85 (4i) 88 (4j)
7	1a	2a			76
8	1a	2a			76
9	1a	2a			91
10	1a	2a			83
11	1a	2a			71

Table 2 (Contd.)

					
Entry	1	2	3	Product ^b	Yield (%) ^c
12	1a	2a	3p 		75
13	1a	2a	L-Menthol, 3q 		77
14	1a		3a		85 (4rb) 91 (4rc) 85 (4rd) 88 (4re) 74 (4rf)
15	1a	2g 	3a		92
16	1a	CbzNH ₂ 2h	3a		72
17	1a	BocNH ₂ 2i	3a		54
18	1b 	2a	3a		87
19	1b	2a	3h 		83
20	1b	2a			78 (4x) 77 (4y)
21	1b	2a	3n 		87

^a Reaction conditions: **1** (0.18 mmol, 1.0 equiv), **2** (1.1 equiv), **3** (1.1 equiv), BF₃·OEt₂ (2.2 equiv), DCE (2 mL). ^b All new products were characterized by IR, HRMS, ¹H NMR and ¹³C NMR. ^c Isolated yields. DCE = 1, 2-dichloroethane.

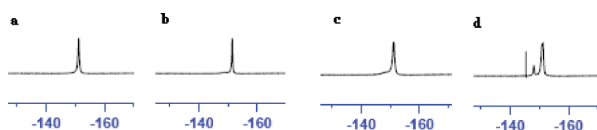
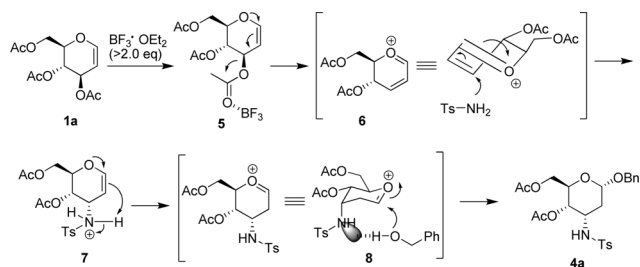


Fig. 2 ^{19}F NMR spectra of (a) $\text{BF}_3\cdot\text{OEt}_2$, (b) $\text{BF}_3\cdot\text{OEt}_2$ and BnOH , (c) $\text{BF}_3\cdot\text{OEt}_2$ and TsNH_2 , and (d) $\text{BF}_3\cdot\text{OEt}_2$, BnOH , TsNH_2 , and tri-*O*-acetyl-D-glucal in CD_2Cl_2 .



Scheme 1 Proposed reaction mechanism.

possible hydrogen bonding between the incoming O-nucleophile and sulfonamido group as shown in structure **8**,¹⁵ provided solely the thermodynamically favoured 1,3-*cis* α -isomer.

Conclusions

In summary, a highly stereoselective $\text{BF}_3\cdot\text{OEt}_2$ -promoted aminoglycosylation of glucals has been developed in a one-pot manner. This efficient multicomponent reaction protocol offers simplicity and general applicability to a broad range of variations on each component. Because of the aforementioned advantages, the present methodology is believed to be able to find broad applications in glycochemistry.

Experimental

General

All reactions were performed under an argon atmosphere. Unless specified, all reagents and starting materials were purchased from commercial sources and used as received. Solvents were purified following standard literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plate. Visualization was achieved by UV light (254 nm) and/or KMnO_4 stain. Flash chromatography was performed using silica gel and a gradient solvent system (EtOAc–hexane as eluent). NMR spectra were recorded at room temperature on Bruker ACF 300, Bruker DPX 400, Bruker AMX 500, and JEOL ECA 400 NMR spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported in Hz. Solid samples were examined as a thin film between NaCl salt plates. High resolution mass spectra (HRMS) were recorded on Waters Q-ToF premierTM mass spectrometer.

General procedure for synthesis of 3-amino-2,3-dideoxysugars

To a solution of 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol) and nitrogen nucleophiles **2** (1.1 equiv) in DCE (2 mL) was added oxygen or sulfur nucleophiles **3** (1.1 equiv) under N_2 atmosphere. $\text{BF}_3\cdot\text{OEt}_2$ (50 μL , 0.4 mmol, 2.2 equiv) was then added to this mixture. The reaction mixture was stirred for 30 min at room temperature, quenched with saturated NaHCO_3 (3 mL) and subsequently extracted with CH_2Cl_2 (5 mL). The extract was dried and concentrated. The residue was subjected to column chromatography (silica gel, hexane–EtOAc) to obtain pure 3-amino-2,3-dideoxysugar **4**.

Benzyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4a). Compound **4a** (82 mg, 93% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +41.9$ (*c* 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.27–7.41 (m, 7H), 6.03 (d, *J* = 9.2 Hz, 1H), 4.88 (d, *J* = 2.8 Hz, 1H), 4.72 (d, *J* = 12 Hz, 1H), 4.64 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.51 (d, *J* = 12 Hz, 1H), 4.28–4.33 (m, 1H), 4.13–4.28 (m, 2H), 3.92 (q, *J* = 3.6 Hz, 1H), 2.41 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H), 1.81 (dt, *J* = 9.6, 3.6 Hz, 1H), 1.47 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.3, 138.0, 136.4, 129.8, 128.7, 128.3, 127.9, 126.9, 96.2, 69.7, 67.0, 64.6, 62.7, 48.0, 32.9, 21.5, 20.9, 20.8; IR (CHCl_3): 3280, 1738, 1539, 1367, 1236, 1170, 1031, 743 cm^{-1} ; HRMS (ESI) *m/z* [*M* + *H*]⁺ calcd for $\text{C}_{24}\text{H}_{30}\text{NO}_8\text{S}$ 492.1692, found 492.1701.

Butyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4b). Compound **4b** (72 mg, 88% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and n-butanol **3b** (18 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +54.8$ (*c* 0.5 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.08 (d, *J* = 9.2 Hz, 1H), 4.81 (d, *J* = 3.6 Hz, 1H), 4.62 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.31 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.11–4.21 (m, 2H), 3.89 (q, *J* = 3.6 Hz, 1H), 3.71–3.73 (m, 1H), 3.38–3.40 (m, 1H), 2.43 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.78 (dt, *J* = 14.8, 3.6 Hz, 1H), 1.24–1.45 (m, 5H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.5, 143.3, 138.0, 129.8, 126.9, 97.1, 68.1, 67.0, 64.4, 62.8, 48.1, 32.8, 31.4, 21.5, 21.0, 20.8, 19.4, 13.8; IR (CHCl_3): 3420, 1740, 1643, 1229, 1161, 1055, 754 cm^{-1} ; HRMS (ESI) *m/z* [*M* + *Na*]⁺ calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_8\text{SNa}$ 480.1668, found 480.1676.

Hexyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4c). Compound **4c** (73 mg, 84% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 1-hexanol **3c** (25 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +54.7$ (*c* 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.00 (d, *J* = 8.8 Hz, 1H), 4.72 (d, *J* = 3.2 Hz, 1H), 4.53 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.23 (dd,

$J = 12.0, 4.8$ Hz, 1H), 4.03–4.09 (m, 2H), 3.81 (q, $J = 3.6$ Hz, 1H), 3.59–3.64 (m, 1H), 3.27–3.32 (m, 1H), 2.34 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.71 (dt, $J = 14.8, 3.6$ Hz, 1H), 1.25–1.54 (m, 9H), 0.84 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.3, 138.0, 129.7, 126.8, 97.1, 68.4, 67.0, 64.4, 62.8, 48.1, 32.8, 31.4, 29.7, 25.9, 22.6, 21.5, 21.0, 20.8, 14.0; IR (CHCl_3): 3327, 2926, 1742, 1342, 1240, 1163, 1055, 735 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{36}\text{NO}_8\text{S}$ 486.2162, found 486.2161.

Octadecyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4d). Compound **4d** (77 mg, 66% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 1-octadecanol **3d** (66 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +44.9$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 6.08 (d, $J = 8.8$ Hz, 1H), 4.81 (d, $J = 2.8$ Hz, 1H), 4.62 (dd, $J = 10.4, 4.0$ Hz, 1H), 4.29 (dd, $J = 12.0, 4.8$ Hz, 1H), 4.17–4.30 (m, 2H), 3.85 (q, $J = 3.6$ Hz, 1H), 3.69–3.71 (m, 1H), 3.36–3.38 (m, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.77 (dt, $J = 14.8, 3.6$ Hz, 1H), 1.25–1.54 (m, 33H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.3, 138.1, 129.7, 126.8, 97.1, 68.4, 67.0, 64.4, 62.8, 48.1, 36.6, 32.8, 31.9, 29.7, 29.66, 29.65, 29.61, 29.5, 29.4, 29.3, 26.2, 24.7, 22.7, 21.5, 21.0, 20.8, 14.1; IR (CHCl_3): 3421, 2924, 1741, 1342, 1240, 1163, 1055, 756, 498 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{35}\text{H}_{59}\text{NO}_8\text{SNa}$ 676.3859, found 676.3857.

Propargyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4e). Compound **4e** (75 mg, 95% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and propargyl alcohol **3e** (12 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +51.5$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 5.82 (d, $J = 8.8$ Hz, 1H), 5.05 (d, $J = 3.2$ Hz, 1H), 4.65 (dd, $J = 10.4, 4.0$ Hz, 1H), 4.32 (dd, $J = 12.0, 4.4$ Hz, 1H), 4.09–4.27 (m, 3H), 3.91 (q, $J = 3.6$ Hz, 1H), 3.38–3.40 (m, 1H), 2.46 (s, 1H), 2.42 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 1.87 (dt, $J = 14.8, 4.0$ Hz, 1H), 1.50 (dd, $J = 18.4, 2.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.4, 137.8, 129.8, 126.9, 95.7, 78.1, 75.5, 66.8, 64.7, 62.6, 54.8, 47.8, 32.7, 21.5, 21.0, 20.8; IR (CHCl_3): 3306, 2922, 1738, 1339, 1242, 1161, 1042, 758 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{25}\text{NO}_8\text{SNa}$ 462.1199, found 462.1201.

Allyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4f). Compound **4f** (65 mg, 82% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and allyl alcohol **3f** (14 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +115.5$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.72 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.02 (d, $J = 9.2$ Hz, 1H), 5.87–5.93 (m, 1H), 5.25–5.31 (m, 2H), 4.87 (d, $J = 3.2$ Hz, 1H), 4.64 (dd, $J = 10.4, 4.0$ Hz, 1H), 4.32 (dd, $J = 12.0, 4.4$ Hz, 1H), 4.14–4.23 (m, 3H), 3.98 (dd, $J = 12.8, 6.0$ Hz, 1H), 3.91 (q, $J = 3.6$ Hz, 1H), 2.42

(s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.82 (dt, $J = 14.8, 4.0$ Hz, 1H), 1.47 (dd, $J = 18.4, 2.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.4, 138.0, 133.0, 129.8, 126.9, 118.2, 96.3, 68.6, 66.9, 64.5, 62.7, 48.0, 32.8, 21.5, 21.0, 20.8; IR (CHCl_3): 3265, 2955, 1742, 1339, 1238, 1163, 1035, 656 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{27}\text{NO}_8\text{SNa}$ 464.1355, found 464.1367.

Isopropyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4g). Compound **4g** (68 mg, 85% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 2-propanol **3g** (15 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +53.9$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.4$ Hz, 2H), 6.16 (d, $J = 8.8$ Hz, 1H), 4.94 (d, $J = 3.2$ Hz, 1H), 4.61 (dd, $J = 10.8, 4.0$ Hz, 1H), 4.31 (dd, $J = 12.0, 4.8$ Hz, 1H), 4.16–4.22 (m, 2H), 3.87–3.92 (m, 2H), 2.42 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.78 (dt, $J = 14.8, 3.6$ Hz, 1H), 1.38 (dd, $J = 10.8, 2.4$ Hz, 1H), 1.30 (d, $J = 6.0$ Hz, 3H), 1.16 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.3, 138.0, 129.7, 126.9, 95.3, 70.6, 67.2, 64.5, 62.8, 48.1, 33.2, 23.4, 21.5, 21.4, 21.0, 20.8; IR (CHCl_3): 3323, 2970, 1741, 1369, 1230, 1163, 1091, 987, 665 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_8\text{SNa}$ 466.1512, found 466.1501.

Isopentanyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4h). Compound **4h** (76 mg, 90% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 3-pentanol **3h** (22 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +47.2$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 6.18 (d, $J = 8.8$ Hz, 1H), 4.92 (d, $J = 3.2$ Hz, 1H), 4.60 (dd, $J = 10.4, 3.6$ Hz, 1H), 4.17–4.31 (m, 3H), 3.89 (q, $J = 3.6$ Hz, 1H), 3.50–3.53 (m, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.76 (dt, $J = 14.8, 4.0$ Hz, 1H), 1.63–1.66 (m, 2H), 1.48–1.54 (m, 2H), 1.39 (dd, $J = 14.4, 2.8$ Hz, 1H), 0.98 (q, $J = 7.2$ Hz, 3H), 0.85 (q, $J = 7.2$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.5, 143.3, 138.0, 129.7, 126.9, 96.1, 81.4, 67.2, 64.7, 62.9, 48.1, 33.1, 26.7, 25.0, 21.5, 21.0, 20.8, 9.9, 9.0; IR (CHCl_3): 3304, 2935, 1742, 1342, 1229, 1163, 989 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_8\text{SNa}$ 494.1825, found 494.1811.

Cyclopentyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4i). Compound **4i** (72 mg, 85% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and cyclopentanol **3i** (18 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +43.6$ (c 0.5 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.70 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.15 (d, $J = 9.2$ Hz, 1H), 4.89 (d, $J = 3.2$ Hz, 1H), 4.62 (dd, $J = 10.4, 3.6$ Hz, 1H), 4.32 (dd, $J = 12.4, 4.8$ Hz, 1H), 4.16–4.21 (m, 3H), 3.86–3.91 (m, 1H), 2.42 (s, 3H), 2.08 (s, 3H), 2.06 (s, 3H), 1.61–1.86 (m, 9H), 1.36 (dd, $J = 14.4, 2.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.7, 170.4, 143.3, 138.1, 129.7, 126.9, 95.9, 79.9, 67.1, 64.6, 62.8, 48.2, 33.5,

33.1, 31.8, 23.4, 23.0, 21.5, 21.0, 20.8; IR (CHCl₃): 3422, 1740, 1340, 1228, 1161, 485 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₂H₃₁NO₈SNa 492.1668, found 492.1669.

Cyclohexyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4j). Compound **4j** (76 mg, 88% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and cyclohexanol **3j** (21 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +63.4 (*c* 0.25 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.26 (d, *J* = 8.8 Hz, 1H), 4.89 (d, *J* = 3.2 Hz, 1H), 4.61 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.18–4.24 (m, 2H), 3.89 (q, *J* = 3.6 Hz, 1H), 3.60–3.65 (m, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 1.90–1.92 (m, 1H), 1.70–1.80 (m, 4H), 1.41–1.55 (m, 2H), 1.23–1.38 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 143.3, 138.1, 129.7, 126.9, 95.3, 76.0, 67.2, 64.6, 62.8, 48.2, 33.3, 33.2, 31.3, 25.5, 23.9, 23.5, 21.5, 21.0, 20.8; IR (CHCl₃): 3419, 1638, 1340, 1230, 1163, 517 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₃H₃₃NO₈SNa 506.1825, found 506.1830.

2'-Nitroethyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4k). Compound **4k** (65 mg, 76% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 2-nitroethanol **3k** (15 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +34.2 (*c* 0.5 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.66 (d, *J* = 9.2 Hz, 1H), 4.88 (d, *J* = 3.2 Hz, 1H), 4.62–4.69 (m, 3H), 4.22–4.27 (m, 3H), 4.09–4.13 (m, 1H), 3.88–3.99 (m, 2H), 2.42 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.85 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.38 (dd, *J* = 14.2, 2.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.3, 143.4, 138.0, 129.8, 126.8, 97.7, 74.8, 66.7, 65.0, 63.9, 62.6, 47.7, 32.7, 21.5, 20.9, 20.8; IR (CHCl₃): 3421, 1734, 1638, 1558, 1340, 1230, 1161, 497 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₁₉H₂₆N₂O₁₀SNa 497.1206, found 497.1193.

2'-(Allyloxy)ethyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4l). Compound **4l** (64 mg, 76% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 2-(allyloxy)ethanol **3l** (22 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +49.9 (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.20 (d, *J* = 9.2 Hz, 1H), 5.91–6.02 (m, 1H), 5.32 (dd, *J* = 16.4 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 4.89 (d, *J* = 3.2 Hz, 1H), 4.64 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.30 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.16–4.21 (m, 2H), 4.07–4.09 (m, 2H), 3.93 (q, *J* = 3.6 Hz, 1H), 3.83–3.85 (m, 1H), 3.62–4.65 (m, 2H), 3.57–3.58 (m, 1H), 2.41 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.80 (dt, *J* = 10.8, 4.0 Hz, 1H), 1.54 (dd, *J* = 14.2, 2.8 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 143.2, 138.3, 134.5, 129.8, 126.8, 117.5, 96.9, 72.4, 68.6, 67.0, 66.4, 64.4, 62.7, 48.1, 32.7, 21.5, 20.9, 20.8; IR (CHCl₃): 3325, 2924, 1740, 1340,

1240, 1163, 1057, 499 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₁H₂₉NO₈SNa 494.1461, found 494.1435.

Phenethyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4m). Compound **4m** (81 mg, 91% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 2-phenylethanol **3m** (24 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +48.2 (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27–7.38 (m, 7H), 5.85 (d, *J* = 9.2 Hz, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 4.55 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.18 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.94–4.06 (m, 2H), 3.82–3.84 (m, 1H), 3.65–3.69 (m, 2H), 2.91–2.94 (m, 2H), 2.41 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.71 (dt, *J* = 9.6, 3.6 Hz, 1H), 1.39 (dd, *J* = 14.4, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 143.3, 138.6, 138.1, 129.7, 128.8, 128.3, 126.9, 126.6, 97.0, 68.9, 68.5, 66.7, 62.6, 47.9, 36.1, 32.9, 21.5, 20.9, 20.8; IR (CHCl₃): 3421, 1740, 1647, 1340, 1240, 1163, 752, 492 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₅H₃₁NO₈SNa 528.1668, found 528.1664.

Phenethyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4n). Compound **4n** (81 mg, 91% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 2-phenylethanol **3n** (24 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +48.2 (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.27–7.38 (m, 7H), 5.85 (d, *J* = 9.2 Hz, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 4.55 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.18 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.94–4.06 (m, 2H), 3.82–3.84 (m, 1H), 3.65–3.69 (m, 2H), 2.91–2.94 (m, 2H), 2.41 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.71 (dt, *J* = 9.6, 3.6 Hz, 1H), 1.39 (dd, *J* = 14.4, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 143.3, 138.6, 138.1, 129.7, 128.8, 128.3, 126.9, 126.6, 97.0, 68.9, 68.5, 66.7, 62.6, 47.9, 36.1, 32.9, 21.5, 20.9, 20.8; IR (CHCl₃): 3421, 1740, 1647, 1340, 1240, 1163, 752, 492 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₅H₃₁NO₈SNa 528.1668, found 528.1664.

(*E*)-But-2-enyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4n). Compound **4n** (68 mg, 83% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and (*E*)-but-2-en-1-ol **3n** (17 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). [α]_D²⁰ = +118.4 (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 7.71 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.04 (d, *J* = 8.7 Hz, 1H), 5.70–5.75 (m, 1H), 5.54–5.57 (m, 1H), 4.86 (d, *J* = 3.3 Hz, 1H), 4.63 (dd, *J* = 10.5, 3.9 Hz, 1H), 4.32 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.11–4.20 (m, 3H), 3.88–3.94 (m, 2H), 2.42 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 1.82 (dt, *J* = 10.8, 3.9 Hz, 1H), 1.76 (d, *J* = 6.9 Hz, 3H), 1.44 (dd, *J* = 14.4, 2.1 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.8, 170.5, 143.4, 138.0, 131.2, 129.8, 126.9, 125.9, 95.8, 68.4, 67.1, 64.4, 62.8, 48.1, 32.9, 21.6, 21.1, 20.9, 17.9; IR (neat): 3419, 1741, 1643, 1240, 1163, 1091, 669 cm⁻¹; HRMS (ESI) m/z [M + Na]⁺ calcd for C₂₁H₂₉NO₈SNa 478.1512, found 478.1526.

Benzylthio 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4o). Compound **4o** (65 mg, 71% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and benzylthiol **3o** (20 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +8.8$ (*c* 0.5 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.27–7.32 (m, 7H), 5.18 (d, *J* = 10.0 Hz, 1H), 4.74–4.84 (m, 2 H), 3.99 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.68–3.78 (m, 3H), 3.33–3.48 (m, 1H), 2.70–2.75 (m, 1H), 2.41 (s, 3H), 2.27 (dt, *J* = 6.4, 2.4 Hz, 1H), 2.07 (s, 3H), 2.04 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.01 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.6, 169.8, 143.8, 138.4, 137.2, 129.4, 128.9, 128.7, 127.4, 127.3, 81.6, 75.9, 68.3, 62.6, 44.6, 38.5, 34.7, 21.5, 20.8, 20.7; IR (CHCl₃): 3420, 1637, 1238, 1163, 524 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₄H₂₉NO₇S₂Na 530.1283, found 530.1285.

tert-Butyl hydrosulfide 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4p). Compound **4p** (64 mg, 75%) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and *tert*-butyl hydrosulfide **3p** (23 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +54.9$ (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.17–5.19 (m, 2H), 4.68 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.03 (dd, *J* = 12.0, 4.4 Hz, 1H), 3.70–3.82 (m, 2H), 3.41 (q, *J* = 3.6 Hz, 1H), 2.41 (s, 3H), 2.12 (dt, *J* = 6.4, 2.4 Hz, 1H), 2.09 (s, 3H), 2.04 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.01 (s, 3H), 1.27 (s, 9H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.5, 170.1, 143.6, 138.5, 129.3, 127.3, 79.5, 76.7, 72.4, 68.4, 62.7, 44.1, 40.3, 40.2, 21.5, 21.1, 20.7; IR (CHCl₃): 3421, 1740, 1636, 1334, 1238, 1163, 1057, 492 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₁H₃₁NO₇S₂Na 496.1440, found 496.1436.

L-menthol 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4q). Compound **4q** (75 mg, 77% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and L-menthol **3q** (32 mg, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +38.9$ (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.14 (d, *J* = 9.0 Hz, 1H), 4.88 (d, *J* = 3.3 Hz, 1H), 4.61 (dd, *J* = 10.5, 3.6 Hz, 1H), 4.18–4.32 (m, 3H), 3.89 (q, *J* = 3.6 Hz, 1H), 3.28 (td, *J* = 4.5 Hz, 1H), 2.42 (s, 3H), 2.17–2.21 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.87–1.90 (m, 1H), 1.63–1.75 (m, 4H), 1.04–1.39 (m, 5H), 0.97 (d, *J* = 7.2 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.69 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.9, 170.5, 143.4, 138.2, 129.7, 126.8, 99.4, 82.8, 67.3, 64.7, 48.8, 43.0, 34.1, 33.1, 31.7, 26.1, 23.2, 22.3, 21.6, 21.3, 21.1, 20.9, 16.2; IR (neat): 3419, 1743, 1653, 1230, 1172, 1042, 561 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₇H₄₁NO₈SNa 562.2451, found 562.2471.

Benzyl 3-benzenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4rb). Compound **4rb** (73 mg, 85% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a**

(50 mg, 0.18 mmol), benzenesulfonamide **2b** (32 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +70.1$ (*c* 0.25 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.80 (d, *J* = 10.0 Hz, 2H), 7.27–7.41 (m, 8H), 6.03 (d, *J* = 9.2 Hz, 1H), 4.88 (d, *J* = 2.8 Hz, 1H), 4.72 (d, *J* = 12 Hz, 1H), 4.64 (dd, *J* = 10.4, 4.0 Hz, 1H), 4.51 (d, *J* = 12 Hz, 1H), 4.28–4.33 (m, 1H), 4.13–4.28 (m, 2H), 3.92 (q, *J* = 3.6 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.81 (dt, *J* = 9.6, 3.6 Hz, 1H), 1.47 (dd, *J* = 14.4, 2.0 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 143.3, 138.0, 136.4, 129.8, 128.7, 128.3, 127.9, 126.9, 96.2, 69.7, 67.0, 64.6, 62.7, 48.0, 32.9, 21.0, 20.8; IR (CHCl₃): 3420, 1740, 1647, 1217, 1165, 505 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₃H₂₇NO₈SNa 500.1355, found 500.1354.

Benzyl 3-*p*-fluorophenylsulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4rc). Compound **4rc** (81 mg, 91% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-fluorobenzenesulfonamide **2c** (35 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +69.1$ (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.79–7.82 (m, 2H), 7.30–7.40 (m, 7H), 6.10 (d, *J* = 8.8 Hz, 1H), 4.91 (d, *J* = 3.2 Hz, 1H), 4.73 (d, *J* = 12 Hz, 1H), 4.65 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.52 (d, *J* = 12 Hz, 1H), 4.31 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.13–4.17 (m, 2H), 3.95 (q, *J* = 3.6 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.86 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.49 (dd, *J* = 14.4, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.8, 170.5, 136.4, 129.6, 129.5, 128.9, 128.5, 128.0, 116.5, 116.4, 96.2, 69.9, 67.0, 64.7, 62.7, 48.2, 33.0, 21.0, 20.9; IR (CHCl₃): 3404, 1740, 1494, 1344, 1234, 1169, 1051, 754, 498 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₃H₂₆NO₈SFNa 518.1261, found 518.1253.

Benzyl 3-*p*-chlorophenylsulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4rd). Compound **4rd** (78 mg, 85% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-chlorobenzenesulfonamide **2d** (38 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +64.3$ (*c* 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.29–7.40 (m, 5H), 6.11 (d, *J* = 8.8 Hz, 1H), 4.91 (d, *J* = 2.8 Hz, 1H), 4.73 (d, *J* = 12 Hz, 1H), 4.65 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.51 (d, *J* = 12 Hz, 1H), 4.30 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.11–4.16 (m, 2H), 3.94 (q, *J* = 3.6 Hz, 1H), 2.08 (s, 3H), 2.05 (s, 3H), 1.85 (dt, *J* = 14.4, 4.0 Hz, 1H), 1.49 (dd, *J* = 14.8, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 139.6, 139.1, 136.3, 129.5, 128.8, 128.4, 128.3, 127.9, 96.1, 69.8, 66.9, 64.6, 62.6, 48.2, 32.9, 20.9, 20.8; IR (CHCl₃): 3422, 1740, 1647, 1344, 1240, 1165, 1051, 754, 497 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₃H₂₆NO₈SClNa 534.0965, found 534.0958.

Benzyl 3-*p*-nitrophenylsulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-glucopyranoside (4re). Compound **4re** (82 mg, 88% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-nitrobenzenesulfonamide **2e** (41 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μ L, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1).

$[\alpha]_D^{20} = +68.4$ (c 0.5 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 8.33 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H), 7.29–7.43 (m, 5H), 6.28 (d, *J* = 8.8 Hz, 1H), 4.93 (d, *J* = 3.2 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.68 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.31 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.13–4.18 (m, 2H), 4.01 (q, *J* = 4.0 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.90 (dt, *J* = 14.8, 4.0 Hz, 1H), 1.50 (dd, *J* = 14.8, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.3, 147.6, 147.0, 136.2, 128.9, 128.6, 128.0, 127.9, 124.5, 96.0, 69.9, 66.8, 64.6, 62.5, 48.5, 33.0, 20.9, 20.8; IR (CHCl₃): 3323, 1740, 1529, 1350, 1240, 1166, 503 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₃H₂₆N₂O₁₀SNa 545.1206, found 545.1207.

Benzyl 3-*p*-methoxyphenylsulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glucopyranoside (4rf). Compound 4rf (67 mg, 74% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *p*-methoxybenzenesulfonamide **2f** (38 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +102.4$ (c 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.32–7.41 (m, 5H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.00 (d, *J* = 8.8 Hz, 1H), 4.89 (d, *J* = 3.2 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.65 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.32 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.13–4.16 (m, 2H), 3.91 (q, *J* = 4.0 Hz, 1H), 3.89 (s, 3H), 2.09 (s, 3H), 2.07 (s, 3H), 1.90 (dt, *J* = 14.8, 3.6 Hz, 1H), 1.48 (dd, *J* = 14.8, 2.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.4, 162.8, 136.4, 132.6, 128.9, 128.8, 128.3, 127.9, 114.3, 96.2, 69.8, 67.0, 64.6, 62.7, 55.6, 48.0, 32.9, 21.0, 20.8; IR (CHCl₃): 3335, 1740, 1597, 1499, 1257, 1157 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₄H₂₉NO₉SNa 530.1461, found 530.1454.

Benzyl 3-methylsulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glucopyranoside (4s). Compound 4s (69 mg, 92% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), methanesulfonamide **2g** (19 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +58.6$ (c 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.32–7.39 (m, 5H), 5.84 (d, *J* = 8.4 Hz, 1H), 5.01 (d, *J* = 3.2 Hz, 1H), 4.77 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.73 (d, *J* = 12.4 Hz, 1H), 4.52 (d, *J* = 11.6 Hz, 1H), 4.32 (dd, *J* = 12.0, 4.4 Hz, 1H), 4.11–4.15 (m, 3H), 2.94 (s, 3H), 2.05–2.17 (m, 8H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.7, 170.1, 136.3, 128.8, 128.4, 128.1, 95.8, 69.7, 67.2, 64.5, 62.6, 48.4, 41.6, 34.0, 21.0, 20.8; IR (CHCl₃): 3421, 1740, 1647, 1327, 1232, 1153, 1049, 754, 499 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₁₈H₂₅NO₈SNa 438.1199, found 438.1193.

Benzyl 3-benzyloxycarbonylamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glucopyranoside (4t). Compound 4t (61 mg, 72% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), benzyl carbamate **2h** (31 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +43.3$ (c 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.31–7.35 (m, 10H), 6.23 (d, *J* = 8.8 Hz, 1H), 5.07 (q, *J* = 12.4 Hz, 2H), 4.99 (d, *J* = 3.2 Hz, 1H), 4.82 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H),

4.54 (d, *J* = 12.0 Hz, 1H), 4.42–4.45 (m, 1H), 4.43 (dd, *J* = 10.8, 4.0 Hz, 1H), 4.09–4.16 (m, 2H), 2.10 (s, 3H), 1.95–2.06 (m, 2H), 1.93 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.8, 170.0, 156.2, 136.8, 136.7, 128.7, 128.5, 128.1, 128.0, 127.9, 127.8, 96.0, 69.4, 67.7, 66.5, 64.4, 62.9, 45.2, 33.0, 20.8, 20.7; IR (CHCl₃): 3420, 1734, 1638, 1508, 1223, 1047, 752, 513 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₅H₂₉NO₈Na 494.1791, found 494.1795.

Benzyl 3-amido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-glucopyranoside (4u). Compound 4u (33 mg, 54% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1a** (50 mg, 0.18 mmol), *tert*-Butyl carbamate **2i** (23 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +82.0$ (c 1.0 CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.28–7.37 (m, 5H), 5.75–5.95 (m, 2H), 5.35 (d, *J* = 9.2 Hz, 1H), 5.15–5.31 (m, 2H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.12–4.31 (m, 3H), 2.10 (s, 3H), 2.06 (s, 3H), 1.28–1.44 (m, 1H), 0.87–0.99 (m, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.8, 170.3, 137.6, 129.3, 128.3, 128.1, 127.9, 127.8, 93.7, 70.3, 67.1, 65.3, 62.9, 41.4, 21.0, 20.9; IR (CHCl₃): 3443, 1742, 1643, 1369, 1231, 1153, 1038 cm⁻¹; HRMS (ESI) *m/z* [M + H]⁺ calcd for C₁₇H₂₄NO₆ 338.1604, found 338.1605.

Benzyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-galactopyranoside (4v). Compound 4v (77 mg, 87% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1b** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and benzyl alcohol **3a** (21 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +41.6$ (c 0.5 CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.31–7.75 (m, 7H), 6.06 (d, *J* = 8.1 Hz, 1H), 4.92 (d, *J* = 3.0 Hz, 1H), 4.78 (d, *J* = 2.7 Hz, 1H), 4.74 (d, *J* = 12 Hz, 1H), 4.51 (d, *J* = 12 Hz, 1H), 4.26–4.30 (m, 1H), 3.99–4.10 (m, 2H), 3.63 (q, *J* = 2.7 Hz, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.95–2.04 (m, 1H), 1.18–1.27 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 170.5, 169.5, 143.5, 137.8, 136.5, 129.8, 128.7, 128.3, 128.1, 127.1, 95.7, 69.4, 67.9, 63.4, 62.9, 47.6, 28.6, 21.6, 20.8, 20.7; IR (neat): 3417, 1643, 1214, 1175, 1042, 665 cm⁻¹; HRMS (ESI) *m/z* [M + Na]⁺ calcd for C₂₄H₂₉NO₈SNa 514.1512, found 514.1516.

Isopentanyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-galactopyranoside (4w). Compound 4w (70 mg, 83% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1b** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and 3-pentanol **3h** (22 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20} = +38.0$ (c 0.5 CHCl₃); ¹H NMR (CDCl₃, 300 MHz): δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 8.1 Hz, 1H), 4.98 (d, *J* = 3.0 Hz, 1H), 4.75 (d, *J* = 3.0 Hz, 1H), 4.32–4.37 (m, 1H), 4.01–4.04 (m, 2H), 3.61 (q, *J* = 3.3 Hz, 1H), 3.49–3.57 (m, 1H), 2.42 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.96–2.04 (m, 1H), 1.49–1.66 (m, 4H), 1.39 (d, *J* = 14.1, 1H), 1.00 (q, *J* = 7.2 Hz, 1H), 0.88 (q, *J* = 7.2 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz): δ 170.5, 169.6, 143.5, 137.9, 129.8, 127.1, 95.9, 81.0, 68.0, 63.5, 63.1, 47.7, 28.9, 26.7, 25.0, 21.6, 20.8, 20.7, 9.9, 9.1; IR (neat): 3419, 1635,

1230, 1161, 1025, 748 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_8\text{SNa}$ 494.1825, found 494.1815.

Cyclopentyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-galactopyranoside (4x). Compound **4x** (66 mg, 78% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1b** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and cyclopentanol **3i** (18 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +29.7$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.77 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.17 (d, $J = 8.4$ Hz, 1H), 4.94 (d, $J = 3.2$ Hz, 1H), 4.76 (d, $J = 3.2$ Hz, 1H), 4.27 (t, $J = 6.0$ Hz, 1H), 4.18–4.20 (m, 1H), 4.03–4.06 (m, 2H), 3.58–3.63 (m, 1H), 2.43 (s, 3H), 2.07 (s, 3H), 2.05 (d, $J = 1.6$ Hz, 1H), 2.03 (s, 3H), 1.71–1.98 (m, 8H), 1.34 (dd, $J = 13.2$, 1.2 Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.5, 169.6, 143.4, 137.9, 129.8, 127.0, 95.9, 79.9, 68.0, 63.3, 62.9, 47.8, 33.4, 31.9, 28.9, 23.4, 23.0, 21.6, 20.8, 20.7; IR (neat): 3419, 1745, 1227, 1161, 1047, 665 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{31}\text{NO}_8\text{SNa}$ 492.1668, found 492.1659.

Cyclohexyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-galactopyranoside (4y). Compound **4y** (67 mg, 77% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1b** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and cyclohexanol **3j** (21 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +34.5$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 400 MHz): δ 7.77 (d, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.27 (d, $J = 8.0$ Hz, 1H), 5.02 (d, $J = 2.8$ Hz, 1H), 4.76 (d, $J = 2.8$ Hz, 1H), 4.28–4.36 (m, 1H), 4.02–4.16 (m, 2H), 2.41 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.90–1.92 (m, 1H), 1.29–2.03 (m, 11H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.6, 170.4, 143.5, 138.0, 129.8, 127.1, 95.4, 76.1, 68.1, 63.4, 63.1, 47.9, 33.4, 31.5, 29.0, 25.5, 24.1, 23.5, 21.6, 20.9, 20.8; IR (neat): 3415, 1742, 1230, 1164, 1032, 714 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_8\text{SNa}$ 506.1825, found 506.1815.

(*E*)-But-2-enyl 3-*p*-toluenesulfonamido-4,6-di-*O*-acetyl-2,3-dideoxy- α -D-galactopyranoside (4z). Compound **4z** (71 mg, 87% yield) was prepared according to the general procedure for synthesis of 3-amino-2,3-dideoxysugars from 3,4,6-tri-*O*-acetyl-D-glucal **1b** (50 mg, 0.18 mmol), *p*-toluenesulfonamide **2a** (34 mg, 0.2 mmol), and (*E*)-but-2-en-1-ol **3n** (17 μL , 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_{\text{D}}^{20} = +32.2$ (c 1.0 CHCl_3); ^1H NMR (CDCl_3 , 300 MHz): δ 7.78 (d, $J = 8.4$ Hz, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 6.08 (d, $J = 8.1$ Hz, 1H), 5.58–5.75 (m, 1H), 5.52–5.57 (m, 1H), 4.91 (d, $J = 3.0$ Hz, 1H), 4.76 (d, $J = 2.7$ Hz, 1H), 4.11–4.15 (m, 1H), 3.98–4.09 (m, 3H), 3.88–3.94 (m, 1H), 3.59 (q, $J = 2.7$ Hz, 1H), 2.42 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H), 1.97–2.00 (m, 1H), 1.76 (d, $J = 5.4$ Hz, 3H), 1.42 (d, $J = 14.4$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.5, 169.5, 143.5, 137.8, 131.1, 129.8, 127.1, 126.0, 95.6, 68.2, 68.0, 63.2, 62.9, 47.6, 28.6, 21.6, 20.8, 20.7, 17.8; IR (neat): 3419, 1744, 1645, 1228, 1161, 1091, 645 cm^{-1} ; HRMS (ESI) m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{29}\text{NO}_8\text{SNa}$ 478.1512, found 478.1518.

Acknowledgements

We thank Prof. Narasaka Koichi for invaluable discussion on mechanism. We gratefully acknowledge Nanyang Technological University (RG50/08) and the Ministry of Education, Singapore (MOE 2009-T2-1-030) for the funding support of this research.

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