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**PAPER**

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

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A highly stereoselective $BF_3{\cdot}OEt_2$-promoted tandem hydroamination–glycosylation on a glycal 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] nocardicyclins[4] 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-dideoxy- hexapyranoses through 1,4-addition of hydrazoic acid to pseudoglycals 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-glycal, in which the replacement of $HBr{\cdot}PPh_3$ with $BF_3{\cdot}OEt_2$ led to 3-amino derivatives.[10] In another multistep method, pseudoglycal was initially oxidized with stoichiometric PhI(OH)OTs 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-glycal 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 glycal scaffold (Fig. 1).

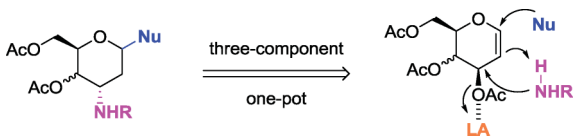


**Fig. 1** Our plan for quick access to 3-amino-2,3-dideoxysugars *via* regio- and stereoselective tandem hydroamination/glycosylation of glycals.

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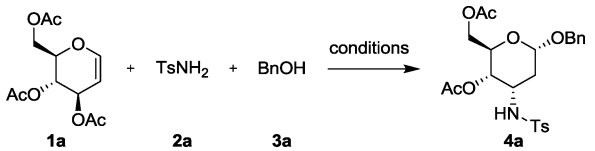
† Electronic supplementary information (ESI) available: NMR spectra for compounds **4a–4z**. See DOI: 10.1039/c1ob05068k

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




1a 2a 3a 4a

| 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 | $H_3PO_4$ (1.1) | toluene | 180 | — |
| 5 | CSA (1.1) | toluene | 180 | — |
| 6 | *p*-TsOH (1.1) | toluene | 180 | — |
| 7 | $Cu(OTf)_2$ (1.1) | toluene | 180 | — |
| 8 | $ZnCl_2$ (1.1) | DCM | 180 | — |
| 9 | $(C_6F_5)_3B$ (1.1) | toluene | 180 | — |
| 10 | $BF_3{\cdot}OEt_2$ (1.1) | toluene | 120 | 45 |
| 11 | $BF_3{\cdot}OEt_2$ (2.2) | toluene | 30 | 90 |
| 12 | $BF_3{\cdot}OEt_2$ (2.2) | DMF | 30 | — |
| 13 | $BF_3{\cdot}OEt_2$ (2.2) | THF | 30 | — |
| 14 | $BF_3{\cdot}OEt_2$ (2.2) | MeCN | 30 | trace |
| 15 | $BF_3{\cdot}OEt_2$ (2.2) | DCM | 30 | 91 |
| 16 | $BF_3{\cdot}OEt_2$ (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), $TsNH_2$ **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 ($^1H$, $^{13}C$, 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, $H_3PO_4$, *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 $Cu(OTf)_2$, $ZnCl_2$, and $(C_6F_5)_3B$, 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 $BF_3{\cdot}OEt_2$ (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 $SnCl_4$ (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 $BF_3{\cdot}OEt_2$, at room temperature with DCE as solvent under nitrogen for 30 min (Table 1, entry 16).

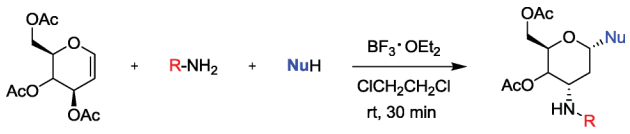
With the optimized reaction conditions in hand, we investigated the substrate scope by carrying out the reaction with various nucleophiles. As shown in Table 2, a wide range of aromatic and aliphatic alcohols and thiols gave the desired aminoglycosides with exclusive α-stereoselectivities in high yields. 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, $TsNH_2$, $NsNH_2$ and $MsNH_2$ proved to be excellent nucleophiles, providing the corresponding products in high yields and anomeric selectivities. Likewise, the reaction with benzyl carbamate ($CbzNH_2$) 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 ($BocNH_2$) under the same reaction conditions, the deprotected product **4u** was isolated after purification (Table 2, entry 17). In contrast, reaction of trimethylsilyl azide ($TMSN_3$) with tri-*O*-acetyl-D-glucal **1a** proved to be unsuccessful. Finally, the analogous reaction of tri-*O*-acetyl-D-galactal **1b** with $TsNH_2$ 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 $BF_3{\cdot}OEt_2$ promotes this reaction, we performed simple $^{19}F$ NMR spectroscopic studies. Careful scrutiny of the NMR data suggests that $BF_3{\cdot}OEt_2$ is coordinated to the oxygen atom of the glycal. In our control NMR experiments, BnOH and $TsNH_2$ were combined with $BF_3{\cdot}OEt_2$, and as predicted, $BF_3{\cdot}OEt_2$ did not show any observable shift from the original $^{19}F$ NMR signal, suggesting negligible or no interaction between these nucleophiles and $BF_3{\cdot}OEt_2$.[14] However, upon the addition of glycal to the remaining nucleophiles, shifts of the $^{19}F$ signal were observed, which indicates the formation of the boron–sugar complex (Fig. 2). This result implies that $BF_3{\cdot}OEt_2$ 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 $BF_3{\cdot}OEt_2$-promoted one-pot three-component α-selective tandem hydroamination–glycosylation reaction[a]




1 2 3 4

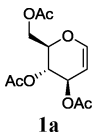
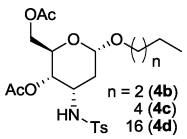
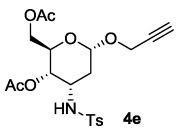
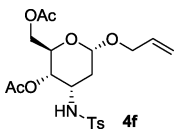
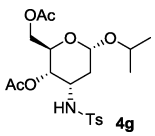
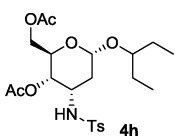
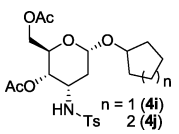
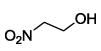
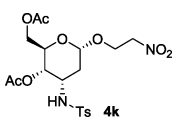
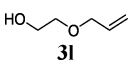
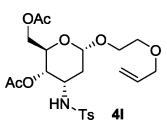
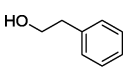
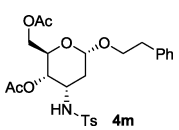
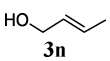
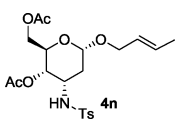
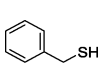
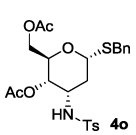
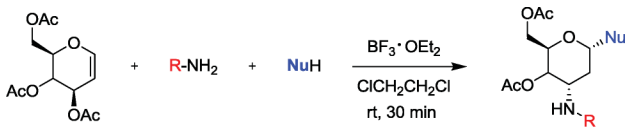
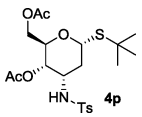
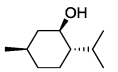
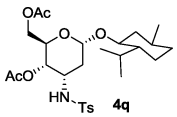
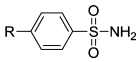
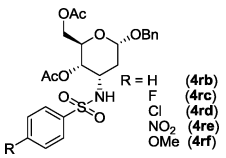
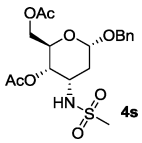
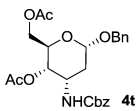
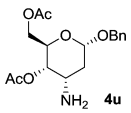
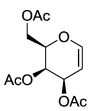
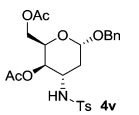
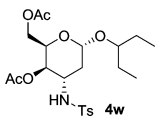
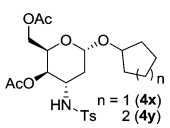
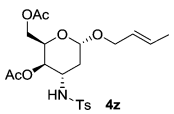
| Entry | 1 | $R–NH_2$ | NuH | Product[b] | Yield (%)[c] |
|---|---|---|---|---|---|
| 1 |  **1a** | $TsNH_2$ **2a** |  n = 2 (**3b**) 4 (**3c**) 16 (**3d**) |  n = 2 (**4b**) 4 (**4c**) 16 (**4d**) | 88 (**4b**) 84 (**4c**) 66 (**4d**) |
| 2 | **1a** | **2a** |  **3e** |  **4e** | 95 |
| 3 | **1a** | **2a** |  **3f** |  **4f** | 82 |
| 4 | **1a** | **2a** |  **3g** |  **4g** | 85 |
| 5 | **1a** | **2a** |  **3h** |  **4h** | 90 |
| 6 | **1a** | **2a** |  n = 1 (**3i**) 2 (**3j**) |  n = 1 (**4i**) 2 (**4j**) | 85 (**4i**) 88 (**4j**) |
| 7 | **1a** | **2a** |  **3k** |  **4k** | 76 |
| 8 | **1a** | **2a** |  **3l** |  **4l** | 76 |
| 9 | **1a** | **2a** |  **3m** |  **4m** | 91 |
| 10 | **1a** | **2a** |  **3n** |  **4n** | 83 |
| 11 | **1a** | **2a** |  **3o** |  **4o** | 71 |

**Table 2** *(Contd.)*




1 2 3 4

| Entry | 1 | R–$NH_2$ | NuH | Product[b] | Yield (%)[c] |
|---|---|---|---|---|---|
| 12 | **1a** | **2a** |  **3p** |  **4p** | 75 |
| 13 | **1a** | **2a** |  L-Menthol, **3q** |  **4q** | 77 |
| 14 | **1a** |  R = H **(2b)**, F **(2c)**, Cl **(2d)**, $NO_2$ **(2e)**, OMe **(2f)** | **3a** |  R = H **(4rb)**, F **(4rc)**, Cl **(4rd)**, $NO_2$ **(4re)**, OMe **(4rf)** | 85 (**4rb**)<br>91 (**4rc**)<br>85 (**4rd**)<br>88 (**4re**)<br>74 (**4rf**) |
| 15 | **1a** |  **2g** | **3a** |  **4s** | 92 |
| 16 | **1a** | $CbzNH_2$ **2h** | **3a** |  **4t** | 72 |
| 17 | **1a** | $BocNH_2$ **2i** | **3a** |  **4u** | 54 |
| 18 |  **1b** | **2a** | **3a** |  **4v** | 87 |
| 19 | **1b** | **2a** | **3h** |  **4w** | 83 |
| 20 | **1b** | **2a** |  n = 1 **(3i)**, 2 **(3j)** |  n = 1 **(4x)**, 2 **(4y)** | 78 (**4x**)<br>77 (**4y**) |
| 21 | **1b** | **2a** | **3n** |  **4z** | 87 |

[a] Reaction conditions: **1** (0.18 mmol, 1.0 equiv), **2** (1.1 equiv), **3** (1.1 equiv), $BF_3{\cdot}OEt_2$ (2.2 equiv), DCE (2 mL). [b] All new products were characterized by IR, HRMS, $^1H$ NMR and $^{13}C$ NMR. [c] Isolated yields. DCE = 1, 2-dichloroethane.

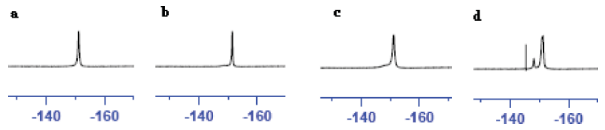
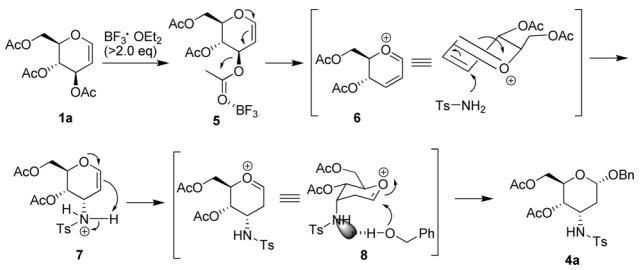



**Fig. 2** $^{19}F$ NMR spectra of (a) $BF_3{\cdot}OEt_2$, (b) $BF_3{\cdot}OEt_2$ and BnOH, (c) $BF_3{\cdot}OEt_2$ and $TsNH_2$, and (d) $BF_3{\cdot}OEt_2$, BnOH, $TsNH_2$, and tri-*O*-acetyl-D-glucal in $CD_2Cl_2$.




**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 $BF_3{\cdot}OEt_2$-promoted amino-glycosylation 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 premier™ 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. $BF_3{\cdot}OEt_2$ (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). $[\alpha]_D^{20}$ = +41.9 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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 $C_{24}H_{30}NO_8S$ 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). $[\alpha]_D^{20}$ = +54.8 (*c* 0.5 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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 $C_{21}H_{31}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +54.7 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + H]$^+$ calcd for $C_{23}H_{36}NO_8S$ 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). $[\alpha]_D^{20}$ = +44.9 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + Na]$^+$ calcd for $C_{35}H_{59}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +51.5 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + Na]$^+$ calcd for $C_{20}H_{25}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +115.5 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + Na]$^+$ calcd for $C_{20}H_{27}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +53.9 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + Na]$^+$ calcd for $C_{20}H_{29}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +47.2 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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) $m/z$ [M + Na]$^+$ calcd for $C_{22}H_{33}NO_8SNa$ 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). $[\alpha]_D^{20}$ = +43.6 (*c* 0.5 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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 ($CHCl_3$): 3422, 1740, 1340, 1228, 1161, 485 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{22}H_{31}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +63.4 (*c* 0.25 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3419, 1638, 1340, 1230, 1163, 517 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{23}H_{33}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +34.2 (*c* 0.5 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3421, 1734, 1638, 1558, 1340, 1230, 1161, 497 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{19}H_{26}N_2O_{10}SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +49.9 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3325, 2924, 1740, 1340, 1240, 1163, 1057, 499 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{21}H_{29}NO_9SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +48.2 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3421, 1740, 1647, 1340, 1240, 1163, 752, 492 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{25}H_{31}NO_8SNa$ 528.1668, found 528.1664.

**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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +48.2 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3421, 1740, 1647, 1340, 1240, 1163, 752, 492 $cm^{-1}$; HRMS (ESI) $m/z$ $[M + Na]^+$ calcd for $C_{25}H_{31}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +118.4 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 $C_{21}H_{29}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +8.8 (*c* 0.5 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3420, 1637, 1238, 1163, 524 cm$^{-1}$; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{24}H_{29}NO_7S_2Na$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +54.9 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3421, 1740, 1636, 1334, 1238, 1163, 1057, 492 cm$^{-1}$; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{21}H_{31}NO_7S_2Na$ 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 $CHCl_3$); $^1$H NMR ($CDCl_3$, 300 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 $C_{27}H_{41}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +70.1 (*c* 0.25 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3420, 1740, 1647, 1217, 1165, 505 cm$^{-1}$; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{27}NO_8SNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +69.1 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3404, 1740, 1494, 1344, 1234, 1169, 1051, 754, 498 cm$^{-1}$; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{26}NO_8SFNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1). $[\alpha]_D^{20}$ = +64.3 (*c* 1.0 $CHCl_3$); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3422, 1740, 1647, 1344, 1240, 1165, 1051, 754, 497 cm$^{-1}$; HRMS (ESI) *m/z* [M + Na]$^+$ calcd for $C_{23}H_{26}NO_8SClNa$ 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 μL, 0.2 mmol) and purified by column chromatography (hexane–ethyl acetate = 5 : 1).

$[\alpha]_D^{20}$ = +68.4 (*c* 0.5 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3323, 1740, 1529, 1350, 1240, 1166, 503 $cm^{-1}$; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{23}H_{26}N_2O_{10}SNa$ 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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3335, 1740, 1597, 1499, 1257, 1157 $cm^{-1}$; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{24}H_{29}NO_9SNa$ 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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3421, 1740, 1647, 1327, 1232, 1153, 1049, 754, 499 $cm^{-1}$; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{18}H_{25}NO_8SNa$ 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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3420, 1734, 1638, 1508, 1223, 1047, 752, 513 $cm^{-1}$; HRMS (ESI) *m/z* $[M + Na]^+$ calcd for $C_{25}H_{29}NO_8Na$ 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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 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 ($CHCl_3$): 3443, 1742, 1643, 1369, 1231, 1153, 1038 $cm^{-1}$; HRMS (ESI) *m/z* $[M + H]^+$ calcd for $C_{17}H_{24}NO_6$ 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-glacal **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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 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 $C_{24}H_{29}NO_8SNa$ 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-glacal **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 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 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); $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ 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* $[M + Na]^+$ calcd for $C_{22}H_{33}NO_8SNa$ 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-glacal **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). $[\alpha]_D^{20}$ = +29.7 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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* $[M + Na]^+$ calcd for $C_{22}H_{31}NO_8SNa$ 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-glacal **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). $[\alpha]_D^{20}$ = +34.5 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 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): $\delta$ 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* $[M + Na]^+$ calcd for $C_{23}H_{33}NO_8SNa$ 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-glacal **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). $[\alpha]_D^{20}$ = +32.2 (*c* 1.0 $CHCl_3$); $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 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): $\delta$ 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* $[M + Na]^+$ calcd for $C_{21}H_{29}NO_8SNa$ 478.1512, found 478.1518.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