JOC The Journal of Organic Chemistry

FEATURED ARTICLE

pubs.acs.org/joc

Synthesis of Sulfonamide-Bridged Glycomimetics

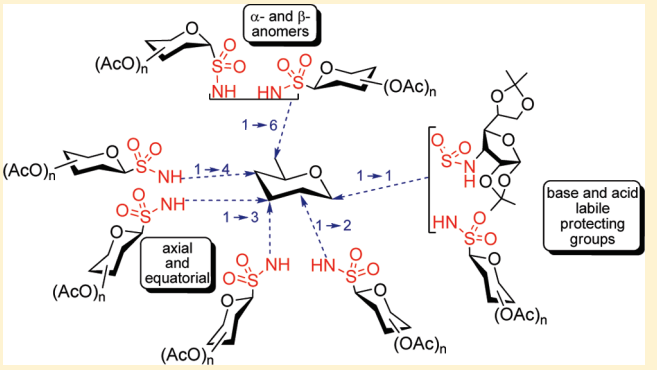
Marie Lopez,[†] Laurent F. Bornaghi,[†] Hugues Driguez,[§] and Sally-Ann Poulsen*[,†]

[†]Eskitis Institute, Griffith University, Nathan Campus, Queensland, 4111, Australia

[§]Centre de Recherche sur les Macromolécules Végétales, UPR-CNRS 5301, BP53, 38041 Grenoble, France

Supporting Information

ABSTRACT: A flexible and short synthesis of sulfonamide-bridged di-, tri-, tetra-, and octasaccharide glycomimetics was accomplished by reaction of glycosyl thioacetates with amino sugar substrates. The chemistry to incorporate the sulfonamide linker in place of a native *O*-glycosidic bond was broadly scoped, allowing access to head-to-head (1↔1) and head-to-tail (1→2), (1→3), (1→4), and (1→6) sulfonamide-bridged glycomimetics. The synthesis proceeds with retention of configuration at the anomeric center and is compatible with variable stereochemical arrangements and with acid- and base-labile protecting groups.



INTRODUCTION

Carbohydrates play an important role in diverse biological events and in principle offer immense opportunities for therapeutic drug development, yet in practice constitute relatively few drugs.[1] Native glycosidic bonds are sensitive to hydrolysis by endogenous glycoside hydrolases, and it is this liability that has led to the avoidance of carbohydrate-based molecules for in vivo applications.[1] Synthetic glycomimetics are designed to circumvent in vivo problems, and recent trends demonstrate that glycomimetics are increasingly emerging as lead compounds for drug discovery and as probes for chemical biology research.[1,2] The rationale is to replace the enzymatically labile glycosidic bond with a covalent, robust, non-native linker to address inherent metabolic instability.

The development of straightforward synthetic methods toward novel, stable, and short linkers between sugar building blocks is needed to support the discovery of new glycomimetics with potential bioactive properties.[2] The structural complexity of natural carbohydrates stems from linking saccharide building blocks in variable arrangements via a glycosidic bond; hence the synthesis of both head-to-head and head-to-tail linkages is ideally sought.[2] Existing replacements for the native glycosidic bond, comprising one or two bridging atoms between the pyranosyl moieties, are summarized in Figure 1. It is apparent that relatively few head-to-head (1↔1) or head-to-tail (1→2), (1→3), (1→4), and (1→6) linkers are known in the literature. Highly significant to this study is that straightforward and general synthetic methodology to link two sugars is not yet available. The *S*- and *C*-glycosides are the most well-documented replacements for the native glycosidic bond.[3]

RESULTS AND DISCUSSION

Given that there is no prior general methodology that provides a common synthetic route to glycomimetics linked via the anomeric center of one glycosyl residue to all positions of the second residue, we decided to target this challenge. Our laboratory recently developed a synthesis of *S*-glycosyl primary sulfonamides,[24,25] a class of molecules that had remained elusive using conventional synthetic routes toward sulfonamides. Herein we expand the utility of our recent synthetic methodology to covalently tether sugar moieties via a sulfonamide bridge. The sulfonamide moiety has not previously been utilized to join carbohydrates to generate either *S*- or *N*-linked carbohydrates of the type $[(\text{sugar})_n\text{-SO}_2\text{-NH-(sugar)}_m, n \geq 1]$. We first explored the synthesis of (1↔1), (1→2), (1→3), (1→4), and (1→6) sulfonamide-bridged disaccharides, Figure 2.

The chemistry we proposed had a requirement for *S*-glycosyl thioacetate and a panel of amino sugar partners as reagents. These carbohydrate reagents are readily available from either commercial sources and/or through chemical synthesis.[26,27] Specifically, we examined the reaction of 1-*S*-acetyl-2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose (**1**) with per-*O*-acetylated glucosylamine (**6**), 2-glucosamine (**7**), 3-aminoglucose (**8**), methyl 4-aminoglucoside (**9**), and methyl 6-aminoglucoside (**10**), Scheme 1. The reaction of thioacetate **1** with amines **6**−**10** in the presence of diethyl bromomalonate generated the corresponding sulfenamide linked disaccharides in all cases (**14a**−**18a**). Oxidation of **14a**−**18a** with excess *m*-CPBA gave the target sulfonamide-linked disaccharide mimetics **14b**−**18b**. The *O*-acetyl groups were removed using

Received: January 18, 2011
Published: March 14, 2011

   dx.doi.org/10.1021/jo2001269 | *J. Org. Chem.* 2011, 76, 2965–2975

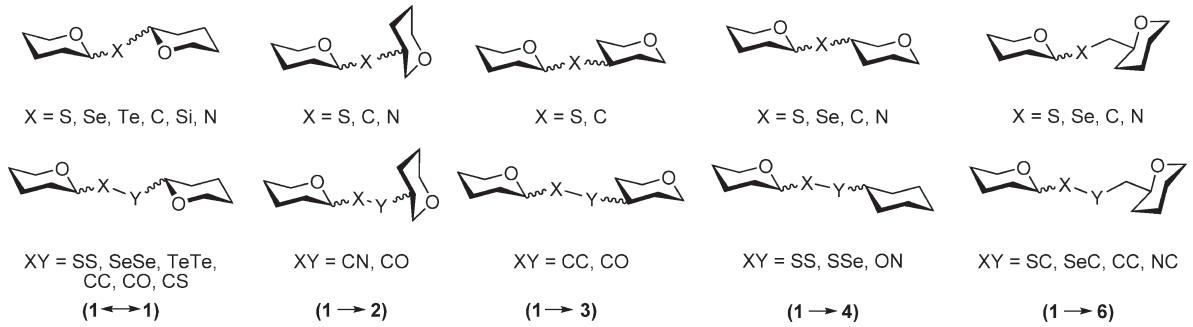


Figure 1. Known head-to-head (1↔1)[4−8] or head-to-tail (1→2),[9−12] (1→3),[13,14] (1→4),[15−18] and (1→6)[19−23] glycomimetic disaccharides.

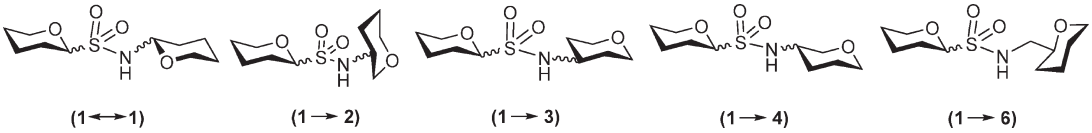
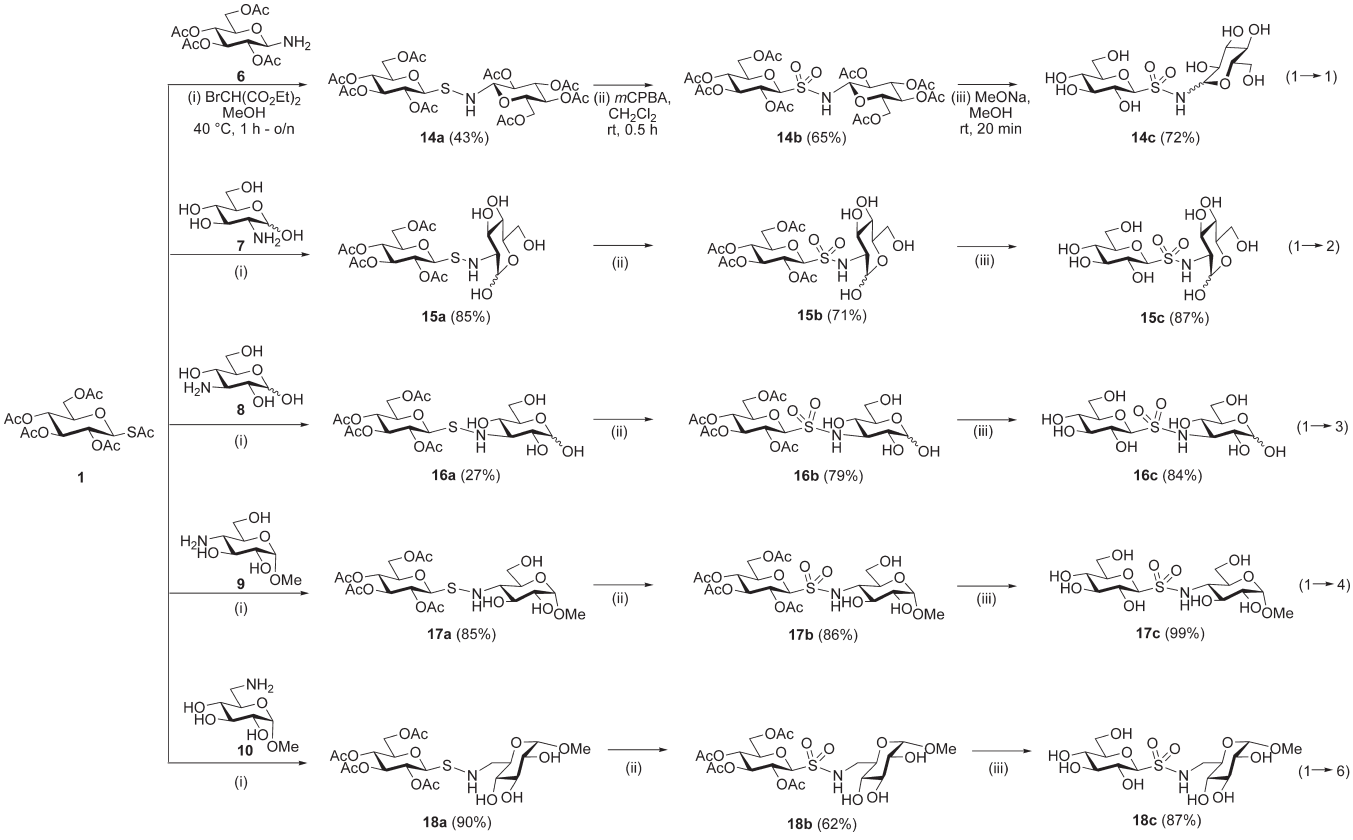


Figure 2. Target sulfonamide-bridged disaccharides.

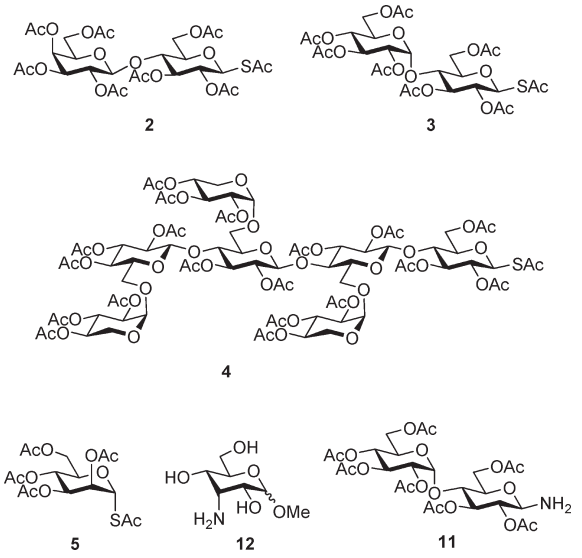
Scheme 1. Synthesis of (1↔1), (1→2), (1→3), (1→4), and (1→6) Sulfonamide-Bridged Disaccharides



standard Zemplén conditions[28] to liberate the fully deprotected, water-soluble sulfonamide-bridged disaccharides **14c**−**18c**. The stereoselectivity of the reactions was evidenced from characteristic $^3J_{1,2}$ coupling constants for each saccharide partner.

Having established that the sulfonamide moiety provides a general linker for glycomimetic disaccharides in just two straightforward synthetic steps, we were encouraged to extend our investigation to the reaction of larger thioacetate substrates, including the thioacetyl disaccharides (**2**, **3**) and heptasaccharide (**4**). The reaction of these thioacetates with monosaccharide amino sugars **7**, **10**, and the disaccharide per-*O*-acetylated maltosyl amine (**11**) proceeded to generate sulfonamide-bridged trisaccharides **19a**−**c**, **20a**−**c**, and **21a**−**c**, tetrasaccharides **22a**−**c**, and octasaccharides **23a**−**b**, respectively, Table 1, entries 1−5. We next explored whether stereochemical characteristics of reagents, such as α-, β-, equatorial, or axial, had implications to the generality of this method.

dx.doi.org/10.1021/jo2001269 |*J. Org. Chem.* 2011, 76, 2965–2975

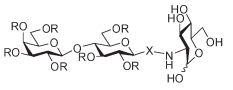
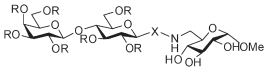
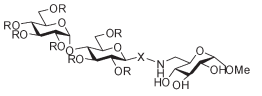
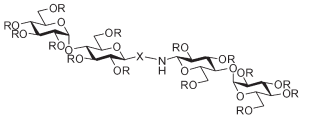
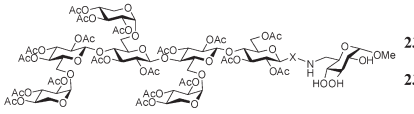
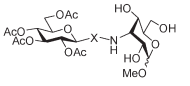
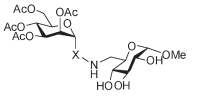


1-*S*-Acetyl-2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranose (**5**) and methyl 3-aminoalloside (**12**) allowed the effect of an α-anomer of the thioacetate and an axial amine to be assessed, respectively. There were no notable differences in reaction behavior of **5** (α-anomer) and **1** (*β*-anomer) or **12** (axial amine) compared to **8** (equatorial amine), Table 1, entries **6** and **7**.

The yield of purified sulfenamides was in general good; however, in cases where the yield was low this could be readily accounted for. The reaction to form sulfenamides **14a** (43%) and **22a** (23%) proceeds with the formation of two side products: (i) a disulfide[29] and (ii) a diglycosylamine (possible only from amino sugars **6** and **11**).[30] The side products were formed in small amounts; however, their chromatographic separation from the target sulfenamides proved difficult owing to similar physical properties. The lower yield for the synthesis of the (1→3) analogue **16a** (27%) and **24a** (39%) may be a result of the possible lower reactivity of the 3-position of reagents **8** and **12**.[31]

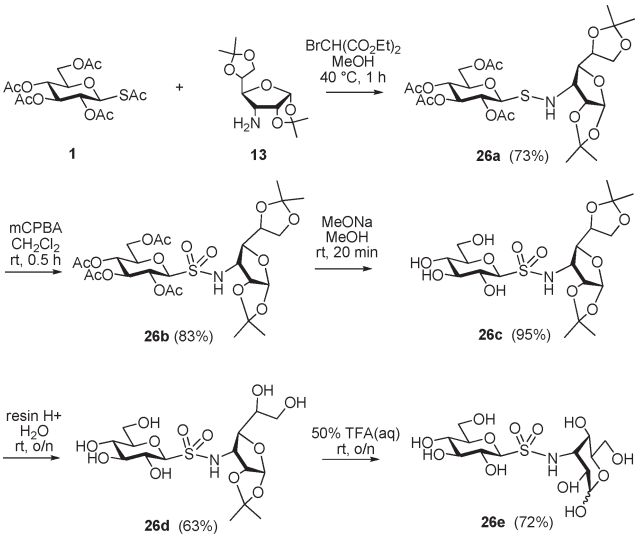
As a further test of the scope of this methodology, we assessed the presence and removal of base- and acid-labile protecting groups, a combination commonly encountered in carbohydrate chemistry. Amine **13**, a furanose derivative synthesized from commercially available 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, comprises two isopropylidene acetal protecting groups. Synthesis of sulfenamide **26a** (from **1** and **13**), oxidation to sulfonamide **26b**, cleavage of the acetates of **26b** to give **26c**, followed by stepwise removal of the acetals of **26c** to give **26d** and **26e**, respectively, confirmed that the sulfonamide glycomimetics are stable to both the base and acid conditions required for the removal of the respective protecting groups, Scheme 2.

Table 1. Investigation of the Scope of the Sulfonamide Moiety as a Glycomimetic Linker

entry	substrate	product[a]	yield[a]
1	**2** and **7**		**19a** (68%) **19b** (53%) **19c** (94%)
2	**2** and **10**		**20a** (84%) **20b** (72%) **20c** (98%)
3	**3** and **10**		**21a** (75%) **21b** (87%) **21c** (98%)
4	**3** and **11**		**22a** (23%) **22b** (53%) **22c** (99%)
5	**4** and **10**		**23a** (60%) **23b** (59%)
6	**1** and **12**		**24a** (39%) **24b** (68%)
7	**5** and **10**		**25a** (76%) **25b** (80%)

[a] Key: (a) X = S, R = Ac; (b) X = SO_2, R = Ac; (c) X = SO_2, R = H.

Scheme 2. Compatibility with Base- And Acid-Labile Protecting Groups



CONCLUSION

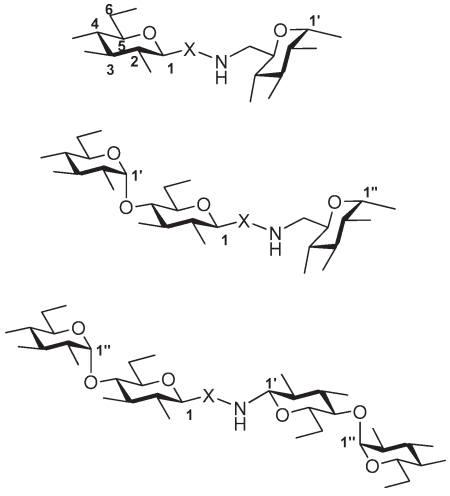
In summary, we have targeted the synthesis of glycomimetics, a challenging area of chemistry with a high and, until now, unmet demand for broadly scoped and general synthetic approaches toward robust glycomimetic linkers. We have synthesized sulfonamide-bridged di-, tri-, tetra-, and octasaccharide glycomimetics using a uniform, straightforward, and short synthesis starting from a selection of readily accessible 1-thioacetyl glycose and amino sugar reagents. The primary limitation identified with this approach is a requirement to use excess reagents. The incorporation of the sulfonamide linker in place of a native *O*-glycosidic bond has allowed access to head-to-head (1↔1) and head-to-tail (1→2), (1→3), (1→4), and (1→6) sulfonamide-bridged glycomimetics. The chemistry is compatible with larger sugars, variable stereochemical arrangements, and acid- and base-labile protecting groups. This chemistry, in combination with the impressive pharmaceutical pedigree of the sulfonamide moiety, featuring in the chemical

dx.doi.org/10.1021/jo2001269 |*J. Org. Chem.* 2011, 76, 2965–2975

structure of >100 marketed drugs,[32] affirms the versatility of the sulfonamide moiety as a synthetically universal linker between carbohydrate building blocks. This implies tremendous future potential for the application of sulfonamide-bridged glycomimetics in drug discovery and glycobiology, wherein it is desirable to introduce an unnatural link in place of the native glycosidic bond.

EXPERIMENTAL SECTION

All starting materials were purchased from commercial suppliers. *S*-Acetyl thioglycoses were synthesized according to literature methods.[27] Amino sugar reagents were either purchased from commercial suppliers or synthesized according to literature methods.[33−39] All reactions were monitored by TLC using silica plates with visualization of product bands by UV fluorescence (λ = 254 nm) and charring with orcinol stain (1 g of orcinol monohydrate in a mixture of EtOH/H_2O/H_2SO_4 72.5:22.5:5). Silica gel flash chromatography was performed using silica gel 60 Å (230−400 mesh). NMR (^{1}H, ^{13}C {^{1}H}, gCOSY and HSQC) spectra were recorded on a 500 MHz spectrometer at 30 °C. Chemical shifts for ^{1}H and ^{13}C NMR acquired in DMSO-d_6 are reported in ppm relative to residual solvent proton (δ = 2.50 ppm) and carbon (δ = 39.5 ppm) signals, respectively. Chemical shifts for ^{1}H NMR acquired in $CDCl_3$ are reported in ppm relative to residual solvent proton (δ = 7.26 ppm). Multiplicity is indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublet); ddd (doublet of doublet of doublet); br (broad). Coupling constants are reported in hertz (Hz). Numbering of di-, tri-, and tetrasaccharides used for NMR assignments is shown below.



Melting points are uncorrected. High- and low-resolution mass spectra were acquired using electrospray as the ionization technique in positive-ion and/or negative-ion modes as stated. All MS analysis samples were prepared as solutions in methanol. Optical rotations were measured at 25 °C with Na-589 nm wavelength and a 100 mm cell and reported as an average of 10 measurements.

General Procedure 1: Synthesis of Glycomimetic Sulfenamides. The thioacetate derivative (1.0 equiv) was solubilized in anhydrous methanol under a nitrogen atmosphere. Diethyl bromomalonate (2.5 equiv) was added and the reaction stirred for 30 min at rt under nitrogen. Next, a solution of amino sugar (5.0 equiv) in methanol (neutralized with diisopropylethylamine (5.0 equiv) if amino sugar is its hydrochloride salt) was added and the reaction stirred overnight at 40 °C under nitrogen. For products **10a**, **19a**, **20a**, and **22a**, the methanol was evaporated and the residue solubilized in CH_2Cl_2 and washed with brine. After back-extraction of each aqueous phase with CH_2Cl_2 the organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated. For the remaining sulfenamide compounds no aqueous wash was performed due to their high water solubility. Instead, these products were purified directly following removal of methanol in the presence of silica gel. The sulfenamides were purified as described for each compound **10a**−**20a** and **22a**.

General Procedure 2: Synthesis of Glycomimetic Sulfonamides. The sulfenamide derivative (1.0 equiv) was solubilized in CH_2Cl_2. *m*-CPBA (7.0 equiv) as a solution in CH_2Cl_2 was added dropwise. The reaction was maintained at rt with stirring until full disappearance of the starting material, typically 1 h. For products **10b**, **19b**, **20b**, and **22b**, the reaction mixture was diluted in CH_2Cl_2 and quenched with saturated $NaHCO_3$. The resulting mixture was filtered through Celite. After extraction with CH_2Cl_2, the organic layer was washed with saturated $NaHCO_3$ and brine. The aqueous phases were back-extracted with CH_2Cl_2. The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated. For the remaining sulfonamide compounds no aqueous wash was performed because of their high water solubility. Instead, the reaction mixture was concentrated at 10 °C prior to purification. The expected sulfonamides were purified as described for each compound **10b**−**20b** and **22b**.

General Procedure 3: Deprotection of Per-*O*-acetylated Glycomimetics.[30] Fully deprotected compounds were prepared by treating a solution of the per-*O*-acetylated compound (1.0 equiv) in MeOH at 0 °C with methanolic sodium methoxide (0.05 M final concentration), pH 12. The reaction was warmed to rt and allowed to stir until full deprotection was evidenced by TLC (30 min to overnight). The reaction mixture was neutralized with Amberlite IR-120 [H^+] and filtered and the resin washed several times with methanol. The filtrate was evaporated under reduced pressure and lyophilized to afford the fully deprotected compounds **10c**−**20c** and **22c**. If needed, compounds were purified by flash chromatography as described.

***N*-(2,3,4,6-Tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosylamine (14a).** Compound **14a** was obtained from compounds **1** and **6** according to the general procedure 1. After purification by flash chromatography (1:1 EtOAc/hexane), **14a** (43% yield) was obtained as a white solid. R_f = 0.24 (1:1 EtOAc/hexane). Mp = 125−127 °C; $[\alpha]^{25}_D$ = +5 (c = 1.0, chloroform); ^{1}H NMR (500 MHz, DMSO-d_6) δ = 5.32 (t, J = 9.5 Hz, 1H, H-3); 5.21 (t, J = 9.5 Hz, 1H, H-3″); 4.96 (t, J = 9.5 Hz, 1H, H-2); 4.94 (m, 1H, N*H*); 4.87 (t, J = 10.0 Hz, 1H, H-4); 4.85 (t, J = 10.0 Hz, 1H, H-4″); 4.83 (t, J = 9.0 Hz, 1H, H-2″); 4.66 (d, J = 10.0 Hz, 1H, H-1); 4.38 (t, J = 9.5 Hz, 1H, H-1″); 4.17 (dd, J = 12.0, 4.0 Hz, 1H, H-6a″); 4.14 (dd, J = 11.5, 4.5 Hz, 1H, H-6a); 4.10 (dd, J = 12.0, 2.0 Hz, 1H, H-6b); 4.05 (dd, J = 12.0, 2.0 Hz, 1H, H-6b″); 3.96 (m, 1H, H-5); 3.89 (m, 1H, H-5″); 2.06, 2.05, 2.02, 2.01, 1.98, 1.97, 1.93, 1.92 (8 × s, 24H, OCOC*H*$_3$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.1, 170.0, 169.5, 169.2 (2C), 169.0, 168.9 (OCOCH$_3$); 91.3 (C-1″); 87.4 (C-1); 74.2 (C-5); 73.3 (C-3); 73.0 (C-3″); 71.5 (C-5″); 70.5 (C-2″); 68.1 (C-4″); 67.9 (C-4); 67.3 (C-2); 61.8, 61.7 (C-6, C-6″); 20.5 (3C), 20.4, 20.3 (4C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 732 [M + Na]$^+$. HRMS: calcd for $C_{28}H_{39}NO_{18}$SNa 732.1780, found 732.1754.

2-Deoxy-2-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-α,β-D-glucopyranose (15a). Compound **15a** was obtained from compound **1** and glucosamine hydrochloride salt **7** according to the general procedure 1. Purification by flash chromatography (2:1 acetone/toluene) afforded **15a** (80% yield) as a mixture of α and β anomers (α/β 80:20) as a light yellow oil. R_f = 0.39 (2:1 acetone/toluene). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.48 (d, J = 6.5 Hz, 0.2H, O*H*-1″$_\beta$); 6.45 (d, J = 4.5 Hz, 0.8H, O*H*-1″$_\alpha$); 5.37 (t, J = 9.5 Hz, 0.8H, H-3$_\alpha$); 5.28 (t, J = 9.0 Hz, 0.2H, H-3$_\beta$); 5.21 (br t, J = 4.0 Hz, 0.8H, H-1″$_\alpha$); 5.06 (t, J = 9.5 Hz, 0.8H, H-2$_\alpha$); 4.98 (t, J = 9.5 Hz, 0.8H, H-4$_\alpha$); 4.93 (t, J = 10.0 Hz, 0.2H, H-2$_\beta$); 4.90 (t, J = 9.0 Hz, 0.2H, H-4$_\beta$); 4.74 (d, J = 5.5 Hz, 0.8H, O*H*-4″$_\alpha$); 4.69 (d, J = 10.5 Hz, 0.2H, H-1$_\beta$); 4.64 (d, J = 5.0 Hz, 0.8H, O*H*-3″$_\alpha$); 4.46 (d, J = 4.5 Hz, 0.2H, O*H*-3″$_\beta$); 4.44 (d, J = 6.5 Hz, 0.2H, O*H*-4″$_\beta$); 4.37 (d, J = 10.0 Hz, 0.8H, H-1$_\alpha$); 4.36 (m, 0.2H, H-1′$_\beta$); 4.27 (t, J = 5.5 Hz, 0.8H, O*H*-6″$_\alpha$); 4.13 (dd, J = 12.5, 5.0 Hz, 0.2H, H-6a $_\beta$); 4.05 (m, 1.6H, H-6$_\alpha$);

3.98 (td, J = 10.0, 3.0 Hz, 0.8H, H-5$_\alpha$); 3.93 (m, 0.2 H, H-5$_\beta$); 3.89 (d, J = 5.0 Hz, 0.2H, NH$_\beta$); 3.66 (dd, J = 9.5, 5.0 Hz, 0.2H, H-6a$''_\beta$); 3.58 (dd, J = 11.0, 2.0 Hz, 0.8H, H-6a$''_\alpha$); 3.04 (m, 1H, H-4$''$); 2.95 (d, J = 8.5 Hz, 0.8H, NH$_\alpha$) (m, 1H, H-5$''$); 3.45 (m, 1H, H-6$''$b); 3.41 (m, 0.2H, H-3$''_\beta$); 3.25 (m, 0.8H, H-3$''_\alpha$); 2.45 (m, 0.8H, H-2$''_\alpha$); 2.33 (td, J = 10.0, 5.0 Hz, 0.2H, H-2$''_\beta$); 2.05, 2.04, 2.03, 1.99, 1.98, 1.97, 1.96 (8 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.3, 169.6, 169.5, 169.2 (OCOCH$_3$); 95.6 (C-1$''_\beta$); 91.6 (C-1$''_\alpha$); 88.7 (C-1$_\beta$); 86.8 (C-1$_\alpha$); 76.6 (C-5$_\beta$); 74.3 (C-5$_\alpha$); 73.3 (C-3$_\beta$); 73.0 (C-3$_\alpha$, C-3$''_\alpha$, C-3$''_\beta$); 71.8 (C-5$_\alpha$, C-5$''_\beta$); 70.9 (C-4$''_\alpha$); 70.7 (C-4$''_\beta$); 69.1 (C-2$''_\alpha$, C-2$''_\beta$); 68.1 (C-4$_\alpha$); 67.6 (C-4$_\beta$); 67.3 (C-2$_\alpha$); 66.9 (C-2$_\beta$); 61.8 (C-6$_\alpha$, C-6$_\beta$); 61.3 (C-6$''_\alpha$, C-6$''_\beta$); 20.5 (2C), 20.4, 20.3 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 564 [M + Na]$^+$. HRMS: calcd for $C_{20}H_{31}NO_{14}SNa$ 564.1357, found 564.1353.

3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-α,*β*-D-glucopyranose (16a). Compound **16a** was obtained from compound **1** and amine **8** according to the general procedure 1. Purification by flash chromatography (5:2 acetone/petroleum spirit) afforded **16a** (27% yield) as a mixture of α and *β* anomers (α/*β* 35:65) as a light yellow gum. R_f = 0.16 (5:2 acetone/petroleum spirit). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.63 (d, J = 6.0 Hz, 0.6H, OH-1$'_\beta$); 6.27 (d, J = 4.5 Hz, 0.4H, OH-1$'_\alpha$); 5.30 (t, J = 9.5 Hz, 0.6H, H-3$_\beta$); 5.29 (t, J = 9.5 Hz, 0.4H, H-3$_\alpha$); 5.03 (t, J = 9.5 Hz, 0.4H, H-2$_\alpha$); 4.94 (m, 0.4H, H-1$_\alpha$); 4.92 (m, 1H, H-4$_\alpha$, H-4$_\beta$); 4.91 (t, J = 10.0 Hz, 0.6H, H-2$_\beta$); 4.71 (d, J = 10.0 Hz, 0.6H, H-1$_\beta$); 4.65 (d, J = 10.0 Hz, 0.4H, H-1$_\alpha$); 4.64 (d, J = 5.0 Hz, 0.6H, OH-2$'_\beta$); 4.48−4.46 (m, 1.2H, OH-6$'_\beta$, OH-4$'_\beta$); 4.38 (d, J = 5.5 Hz, 0.4H, OH-4$'_\alpha$); 4.35 (t, J = 6.0 Hz, 0.4H, OH-6$'_\alpha$); 4.31 (dd, J = 7.5, 6.5 Hz, 0.6H, H-1$'_\beta$); 4.15−4.11 (m, 2H, OH-2$'_\alpha$, H-6a$_\alpha$, H-6a$_\beta$, NH$_\beta$); 4.05−4.01 (m, 1.9H, H-6b$_\alpha$, H-6b$_\beta$); 3.98−3.92 (m, 1H, H-5$_\alpha$, H-5$_\beta$); 3.81 (d, J = 5.0 Hz, 0.4H, NH$_\alpha$); 3.65 (m, 0.6H, H-6a$'_\beta$); 3.58 (m, 1H, H-5$'_\beta$, H-6a$'_\alpha$); 3.43−3.38 (m, 3H, H-2$'_\alpha$, H-3$'_\beta$, H-5$'_\alpha$, H-6b$'_\alpha$, H-6b$'_\beta$); 3.21−3.16 (m, 1H, H-4$'_\alpha$, H-4$'_\beta$); 3.10 (m, 0.6H, H-2$'_\beta$); 2.81 (m, 0.4, H-3$'_\alpha$); 2.03, 2.02, 2.01, 1.98, 1.95 (6 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6, *β*-anomer): δ = 170.6, 170.1, 169.8, 169.7 (OCOCH$_3$); 98.0 (C-1$'$); 89.3 (C-1); 78.1 (C-5$'$); 74.8 (C-5); 73.8 (C-3); 71.8 (C-2$'$); 68.6, 68.3, 67.9 (C-2, C-4, C-4$'$); 64.8 (C-3$'$); 62.4 (C-6); 61.8 (C-6$'$); 21.1, 21.0, 20.8 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 564 [M + Na]$^+$. HRMS: calcd for $C_{20}H_{31}NO_{14}SNa$ 564.1367, found 564.1383.

Methyl 4-Deoxy-4-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-α-D-glucopyranoside (17a). Compound **17a** was prepared from compounds **1** and **9** according to the general procedure 1. Purification by flash chromatography (2:1 acetone/hexane) afforded the title compound as a light yellow gum (73% yield). R_f = 0.21 (2:1 acetone/hexane). $[\alpha]^{25}_D$ = +22 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.30 (t, J = 9.5 Hz, 1H, H-3); 4.99 (t, J = 9.5 Hz, 1H, H-2); 4.88 (t, J = 9.5 Hz, 1H, H-4); 4.69 (d, J = 6.5 Hz, 1H, OH-2$''$); 4.60 (d, J = 10.0 Hz, 1H, H-1); 4.56 (d, J = 6.0 Hz, 1H, OH-3$''$); 4.51 (d, J = 3.5 Hz, 1H, H-1$''$); 4.35 (t, J = 6.0 Hz, 1H, OH-6$''$); 4.16 (dd, J = 12.0, 5.0 Hz, 1H, H-6a); 4.02 (dd, J = 12.0, 2.0 Hz, 1H, H-6b); 3.96 (ddd, J = 10.0, 5.0, 2.0 Hz, 1H, H-5); 3.84 (d, J = 5.0 Hz, 1H, NH); 3.67 (m, 1H, H-6a$''$); 3.55 (m, 1H, H-3$''$); 3.51 (dd, J = 11.5, 5.5 Hz, 1H, H-6b$''$); 3.48 (m, 1H, H-5$''$); 3.24 (s, 3H, OCH$_3$); 3.20 (ddd, J = 10.0, 6.5, 3.5 Hz, 1H, H-2$''$); 2.54 (td, J = 10.0, 5.5 Hz, 1H, H-4$''$); 2.02, 2.01, 1.98, 1.95 (4 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.0, 169.5, 169.3, 169.2 (OCOCH$_3$); 99.6 (C-1$''$); 87.3 (C-1); 74.3 (C-5); 73.2 (C-3); 72.8 (C-2$''$); 71.4 (C-5$''$); 70.6 (C-3$''$); 68.1 (C-4); 67.6 (C-2); 62.1 (C-6); 62.0 (C-4$''$); 61.1 (C-6$''$); 54.2 (OCH$_3$); 20.7, 20.5, 20.3 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 555 [M + H]$^+$, 578 [M + Na]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{14}SNa$ 578.1514, found 578.1491.

Methyl 6-Deoxy-6-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-α-D-glucopyranoside (18a). Compound **18a** was obtained from compounds **1** and **10** according to the general procedure 1. Purification by flash chromatography (2:1 acetone/hexane) afforded **18a** as a light yellow gum (90% yield). R_f = 0.30 (2:1 acetone/hexane). LRMS (ESI$^+$): m/z = 556 [M + H]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{14}SNa$ 578.1514, found 578.1504. Compound **18a** was used as reagent for general procedure 3 without further purification.

***N*-(2,3,4,6-Tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosysulfonylamine (14b).** Compound **14b** was obtained from compound **14a** according to the general procedure 2. Purification by flash chromatography (1:2 EtOAc/hexane) afforded **14b** (65% yield) as a white solid. R_f = 0.39 (1:1 EtOAc/hexane). Mp = 90−93 °C. $[\alpha]^{25}_D$ = +4 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 9.14 (br s, 1H, NH); 5.42 (t, J = 9.0 Hz, 1H, H-3); 5.39 (t, J = 9.0 Hz, 1H, H-3$'$); 5.25 (t, J = 9.0 Hz, 1H, H-2$'$); 4.93−4.87 (m, 4H, H-1, H-2$'$, H-4, H-4$'$); 4.74 (br t, J = 9.0 Hz, 1H, H-1$'$); 4.23 (dd, J = 12.5, 3.5 Hz, 1H, H-6a); 4.18−4.10 (m, 3H, H-6b, H-6a$'$, H-6b$'$); 4.07 (m, 1H, H-5$'$); 4.03 (m, 1H, H-5); 2.04, 2.01, 2.00, 1.99, 1.98, 1.97, 1.93 (7 × s, 24H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.5, 170.0, 169.9, 169.8, 169.6, 169.5, 169.2, 169.1 (OCOCH$_3$); 87.1 (C-1$'$); 81.8 (C-1); 74.7 (C-5); 73.5 (C-2); 73.2, 72.5 (C-3, C-3$'$); 70.8 (C-2$'$); 72.5 (C-5$'$); 67.8, 67.5 (C-4, C-4$'$); 62.2 (C-6$'$); 61.7 (C-6); 21.1, 21.0, 20.9 (2C), 20.8 (2C). 20.7, 20.6 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 764 [M + Na]$^+$. HRMS: calcd for $C_{28}H_{39}NO_{20}SNa$ 764.1678, found 764.1653.

2-Deoxy-2-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-2-sulfonylamino-α,*β*-D-glucopyranose (15b). Compound **15b** was obtained from compound **15a** according to the general procedure 2. Purification by flash chromatography (1:1 acetone/toluene) afforded the title compound (71% yield) as a mixture of α and *β* anomers (α/*β* 85:15) as a white solid. R_f = 0.39 (2:1 acetone/toluene). Mp = 169−171 °C. ^{1}H NMR (500 MHz, DMSO-d_6, *β*-anomer): δ = 6.71 (d, J = 8.5 Hz, 1H, NH); 6.66 (d, J = 4.0 Hz, 1H, OH-1$'$); 5.38 (t, J = 9.5 Hz, 1H, H-3); 5.29 (t, J = 9.5 Hz, 1H, H-2); 5.06 (t, J = 4.0 Hz, 1H, H-1$'$); 5.02 (t, J = 9.5 Hz, 1H, H-4); 4.95 (d, J = 5.5 Hz, 1H, OH-3$'$ or OH-4$'$); 4.92 (d, J = 9.5 Hz, 1H, H-1); 4.63 (d, J = 5.0 Hz, 1H, OH-4$'$ or OH-3$'$); 4.34 (t, J = 6.0 Hz, 1H, OH-6$'$); 4.18 (dd, J = 12.0, 4.0 Hz, 1H, H-6a); 4.12 (ddd, J = 10.0, 5.5, 3.5, 10.0 Hz, 1H, H-5); 4.07 (dd, J = 12.0, 2.0 Hz, 1H, H-6b); 3.61 (dd, J = 11.5, 5.0 Hz, 1H, H-6a$'$); 3.57 (m, 1H, H-5$'$). 3.48 (m, H-4$'$ or H-3$'$); 3.46 (dd, J = 11.0, 5.5 Hz, 1H, H-6b$''$); 3.12 (m, 1H, H-3$'$ or H-4$'$); 2.04, 1.98, 1.97, 1.96 (8 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 169.5, 169.3, 169.1 (OCOCH$_3$); 91.7 (C-1$'$); 86.4 (C-1); 74.5 (C-5); 72.6 (C-3); 71.9 (C-5$'$); 70.8 (C-3$'$ or C-4$'$); 70.6 (C-4$'$ or C-3$'$); 67.6 (C-2); 67.4 (C-4); 61.3 (C-6); 61.1 (C-6$'$); 58.7 (C-2$'$); 20.5, 20.4, 20.3, 20.2 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 596 [M + Na]$^+$. LRMS (ESI$^-$): m/z = 572 [M - H]$^-$. HRMS: calcd for $C_{20}H_{31}NO_{16}SNa$ 596.1256, found 596.1245.

3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-3-sulfonylamino-α,*β*-D-glucopyranose (16b). Compound **16b** was obtained from compound **16a** according to the general procedure 2. Purification by flash chromatography (92:8 CH_2Cl_2/MeOH) afforded **16b** (79% yield) as a mixture of α and *β* anomers (α/*β* 50:50) as a colorless gum. R_f = 0.19 (92:8 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.65 (d, J = 7.5 Hz, 0.5H, NH$_\beta$); 7.53 (d, J = 7.0 Hz, 0.5H, NH$_\alpha$); 6.68 (d, J = 6.5 Hz, 0.5H, OH-1$_\beta$); 6.41 (d, J = 4.5 Hz, 0.5H, OH-1$_\alpha$); 5.25 (t, J = 9.5 Hz, 1H, H-3$_\alpha$, H-3$_\beta$); 5.24, 5.20 (2 × t, J = 9.5 Hz, 1H, H-2$_\alpha$, H-2$_\beta$); 4.96, 4.95 (2 × t, J = 9.0 Hz, 1H, H-4$_\alpha$, H-4$_\beta$); 4.95 (d, J = 9.5 Hz, 1H, H-1$_\alpha$, H-1$_\beta$); 4.93 (d, J = 4.5 Hz, 0.5H, H-1$'_\alpha$); 4.85 (d, J = 5.5 Hz, 1H, OH); 4.77(d, J = 7.0 Hz, 0.5H, OH); 4.56 (t, J = 6.0 Hz, 0.5H, OH-6$'$); 4.47 (t, J = 6.0 Hz, 0.5H, OH-6$'$); 4.30 (t, J = 6.5 Hz, 0.5H, H-1$'_\beta$); 4.23−4.20 (m, 1H, H-6a$_\alpha$, H-6a$_\beta$); 4.18 (d, J = 7.5 Hz, 0.5H, OH) 4.08, 4.05 (2 × dd, J = 10.0, 2.0 Hz, 1H, H-6b$_\alpha$, H-6b$_\beta$); 4.06−3.96 (m, 1H, H-5$_\alpha$, H-5$_\beta$);

3.68−3.65 (m, 0.5H, H-6a′); 3.60−3.57 (m, 1H, H-5, H-6a′); 3.50 (dd, J = 11.5, 5.0 Hz, 0.5H, H-6b′); 3.46 (dd, J = 11.5, 6.0 Hz, 0.5H, H-6b′); 3.28 (m, 0.5H, H-3′$_\alpha$); 3.23−3.18 (m, 1.5H, H-2′$_\omega$, H-4′$_\omega$, H-4′$_\beta$); 3.10−3.07 (m, 0.5H, H-5′); 3.01−2.98 (m, 1H, H-2′$_\beta$, H-3′$_\beta$); 2.02, 1.98, 1.96, 1.95, 1.94 (5 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.1, 169.5, 169.1, 168.6 (OCOCH$_3$); 97.5 (C-1′$_\beta$); 91.7 (C-1′$_\alpha$); 85.6, 85.3 (C-1$_\omega$, C-1$_\beta$); 77.6 (C-5′); 74.6 (C-5); 73.3 (C-2); 72.4 (C-2′); 69.0,68.9 (C-4′$_\omega$, C-4′$_\beta$); 67.7 (C-3); 67.6 (C-4); 62.5 (C-3′); 61.7, 61.6 (C-6$_\omega$, C-6$_\beta$); 61.0, 60.9 (C-6′$_\omega$ C-6′$_\beta$); 20.5 (2C), 20.3, 20.2 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 591 [M + NH$_4$]$^+$, 596 [M + Na]$^+$. HRMS: calcd for $C_{20}H_{31}NO_{16}SNa$ 596.1256, found 596.1255.

Methyl 4-Deoxy-4-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-4-sulfonylamino-α-D-glucopyranoside (17b). Compound **17b** was prepared from compound **17a** according to the general procedure 2. Purification by flash chromatography (2:1 acetone/hexane) afforded the title compound as a white solid (86% yield). R_f = 0.34 (2:1 acetone/hexane). Mp = 138−140 °C. $[\alpha]^{25}_D$ = +52 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.83 (d, J = 9.0 Hz, 1H, NH); 5.23 (t, J = 9.0 Hz, 1H, H-3); 5.17 (t, J = 9.5 Hz, 1H, H-2); 4.97 (t, J = 9.5 Hz, 1H, H-4); 4.96 (d, J = 10.0 Hz, 1H, H-1); 4.96 (br s, 2H, OH-2′, OH-3′); 4.54 (d, J = 3.5 Hz, 1H, H-1′); 4.45 (br t, J = 6.0 Hz, 1H, OH-6′); 4.23 (dd, J = 12.5, 4.0 Hz, 1H, H-6a); 4.06 (dd, J = 11.5, 1.5 Hz, 1H, H-6b); 3.98 (br dd, J = 10.0, 4.0 Hz, 1H, H-5); 3.67 (dd, J = 11.0, 6.0 Hz, 1H, H-6a′); 3.53 (td, J = 9.5, 4.5 Hz, 1H, H-3′); 3.45 (m, 1H, H-5′); 3.37 (dd, J = 12.0, 6.0 Hz, 1H, H-6b′); 3.26 (s, 3H, OCH_3); 3.21 (m, 1H, H-2′); 2.88 (m, 1H, H-4′); 2.03, 1.98, 1.95 (3 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.1, 169.5, 169.1, 168.6 (OCOCH$_3$); 99.4 (C-1′); 85.0 (C-1); 74.7 (C-5); 73.4 (C-3); 72.9 (C-2′); 71.3 (C-3′); 71.2 (C-5′); 67.6 (C-2); 67.5 (C-4); 61.5 (C-6); 61.0 (C-6′); 56.3 (C-4′); 54.4 (OCH$_3$); 20.5, 20.4, 20.2, 20.2 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 605 [M + NH$_4$]$^+$, 610 [M + Na]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{16}SNa$ 610.1412, found 610.1385.

Methyl 6-Deoxy-6-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-*β*-D-glucopyranosyl)-6-sulfonylamino-α-D-glucopyranoside (18b). Compound **18b** was obtained from compound **18a** according to the general procedure 2. Purification by flash chromatography (2:1 acetone/toluene) afforded **18a** (76% yield) as a light yellow gum. R_f = 0.44 (3:1 acetone/toluene). $[\alpha]^{25}_D$ = +21 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.43 (br s, 1H, NH); 5.33 (t, J = 9.5 Hz, 1H, H-3); 5.19 (t, J = 9.5 Hz, 1H, H-2); 5.08 (d, J = 5.5 Hz, 1H, OH-4′); 4.95 (d, J = 4.0 Hz, 1H, OH-3′); 4.91 (d, J = 2.0 Hz, 1H, OH-2′); 4.89 (t, J = 9.5 Hz, 1H, H-4); 4.82 (d, J = 10.0 Hz, 1H, H-1); 4.56 (d, J = 3.5 Hz, 1H, H-1′); 4.16 (dd, J = 12.0, 5.0 Hz, 1H, H-6a); 4.08 (m, 1H, H-5); 4.04 (dd, J = 12.0, 2.0 Hz, 1H, H-6b); 3.44 (br d, J = 13.5 Hz, 1H, H-6a′); 3.36 (m, 1H, H-3′); 3.34 (m, 1H, H-5′); 3.28 (s, 3H, OCH_3); 3.19 (m, 1H, H-2′); 3.03 (dd, J = 13.0, 7.5 Hz, 1H, H-6b′); 2.95 (td, J = 9.5, 5.5 Hz, 1H, H-4′); 1.98, 1.96, 1.93, 1.91 (4 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 171.0, 170.4, 170.1, 169.6 (OCOCH$_3$); 100.0 (C-1′); 87.0 (C-1); 75.1 (C-5); 73.5 (C-3′ or C-5′); 73.3 (C-3); 72.3 (C-2′); 72.0 (C-4′); 71.4 (C-3′ or C-5′); 68.2 (C-2); 68.1 (C-4); 62.2 (C-6); 55.1 (OCH$_3$); 45.5 (C-6′); 21.0, 20.9, 20.8, 20.7 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 588 [M + H]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{16}SNa$ 610.1412, found 610.1413.

***N*-(1-*S*-*β*-D-Glucopyranosyl)-α,*β*-D-glucopyranosylsulfonylamine (14c).** The title compound **14c** was obtained from compound **14b** according to the general procedure 3. Purification by flash chromatography (9:1 CH$_3$CN/H$_2$O) afforded **14c** as a mixture of α and β anomers (72% yield, α/β 70:30) as a clear oil. R_f = 0.15 (85:15 CH$_3$CN/H$_2$O). $[\alpha]^{25}_D$ = +12 (c = 1.0, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.53 (d, J = 6.5 Hz, 0.7H, NH_β); 6.17 (d, J = 4.5 Hz, 0.3H, NH_α); 5.12 (d, J = 5.0 Hz, 0.7H, OH_α); 5.08 (d, J = 5.0 Hz, 0.3H, OH_β); 5.05 (d, J = 4.5 Hz, 0.7H, OH_α); 5.03 (d, J = 6.0 Hz, 0.7H, OH_α); 4.98 (d, J = 4.5 Hz, 0.3H, OH_β); 4.90 (t, J = 5.0 Hz, 0.7H, H-1′$_\alpha$); 4.80 (d, J = 7.0 Hz, 0.7H, OH-2$_\alpha$); 4.78 (d, J = 4.5 Hz, 0.7H, OH_α); 4.72 (d, J = 5.5 Hz, 0.3H, OH_β); 4.62 (t, J = 6.0 Hz, 0.3H, OH-6$_\beta$); 4.58 (d, J = 4.5 Hz, 0.3H, OH_β); 4.49 (d, J = 5.5 Hz, 0.7H, OH_α); 4.47 (d, J = 5.5 Hz, 0.7H, OH_α); 4.44 (t, J = 6.0 Hz, 0.7H, OH-6$_\alpha$); 4.40 (d, J = 6.5 Hz, 0.7H, OH_β); 4.32 (t, J = 6.0 Hz, 0.3H, OH-6$_\beta$); 4.27 (dd, J = 7.5, 6.5 Hz, 0.3H, H-1′$_\beta$); 4.24 (d, J = 5.5 Hz, 0.3H, OH_β); 4.21 (d, J = 9.5 Hz, 0.3H, H-1$_\beta$); 4.05 (d, J = 9.5 Hz, 0.7H, H-1$_\alpha$); 3.70−3.66 (m, 1.3H, H-6$_\omega$, 2 × H-6$_\beta$); 3.58 (ddd, J = 11.5, 5.5, 2.5 Hz, 0.3H, H-6$_\beta$); 3.53 (dd, J = 13.0, 1.5 Hz, 0.7H, H-6$_\alpha$); 3.48−3.40 (m, 2.7H, H-2$_\omega$, H-2$_\beta$, 2 × H-6$_\omega$, H-6$_\beta$); 3.26−3.18 (m, 2.3 H), 3.10−3.02 (m, 4H) (H-2′$_\omega$, H-3$_\omega$, H-3$_\beta$, H-3′$_\omega$, H-3′$_\beta$, H-4$_\omega$, H-4$_\beta$, H-4′$_\omega$, H-4′$_\beta$, H-5$_\omega$, H-5$_\beta$, H-5′$_\omega$, H-5′$_\beta$); 2.89 (td, J = 9.0, 4.5 Hz, 0.3H, H-2′$_\beta$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 96.9 (C-1′$_\beta$); 92.2 (C-1′$_\alpha$); 90.5 (C-1$_\beta$); 84.6 (C-1$_\alpha$); 81.0 (C-5′$_\omega$, C-5′$_\beta$); 78.4, 76.8, 76.7, 73.1, 72.4, 70.6, 70.5, 69.8, 69.6, (C-2′$_\omega$, C-3$_\omega$, C-3$_\beta$, C-3′$_\omega$ C-3′$_\beta$, C-4$_\omega$, C-4$_\beta$, C-4′$_\omega$, C-4′$_\beta$); 77.3 (C-5$_\omega$, C-5$_\beta$); 74.8 (C-2′$_\beta$); 71.9 (C-2$_\beta$); 70.3 (C-2$_\alpha$); 61.2 (2C) (C-6$_\omega$, C-6′$_\alpha$); 61.0 (C-6$_\beta$, C-6′$_\beta$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 428 [M + Na]$^+$. HRMS: calcd for $C_{12}H_{23}NO_{12}SNa$ 428.0833, found 428.0832.

2-Deoxy-2-*N*-(1-*S*-*β*-D-glucopyranosyl)-2-sulfonylamino-α,*β*-D-glucopyranose (15c). The title compound **15c** was obtained from compound **15b** according to the general procedure 3. The lyophilized compound **15c** (87% yield, α/β 70:30) was obtained as a clear oil. R_f = 0.16 (95:5 CH$_3$CN/H$_2$O). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.89 (d, J = 9.0 Hz, 0.3H, NH_β); 6.73 (d, J = 5.5 Hz, 0.3H, OH-1$_\beta$); 6.61 (d, J = 8.5 Hz, 0.7H, NH_α); 6.58 (d, J = 4.5 Hz, 0.7H, OH-1$_\alpha$); 5.21 (d, J = 5.5 Hz, 0.7H), 5.11 (d, J = 5.0 Hz, 0.7H), 5.10 (d, J = 4.0 Hz, 0.3H), 5.07 (d, J = 5.5 Hz, 0.7H), 5.05 (d, J = 4.5 Hz, 0.3H), 5.04 (d, J = 6.5 Hz, 0.3H) (3 × OH_ω, 3 × OH_β); 4.98−4.96 (m, 1.7H, H-1′$_\alpha$, OH-6$_\alpha$, OH_β); 4.89 (d, J = 5.5 Hz, 0.7H), 4.86 (d, J = 6.0 Hz, 0.7H) (2 × OH_α); 4.52−4.48 (m, 0.6H, 2 × OH_β); 4.42−4.37 (m, 1.3H, H-1′$_\beta$, H-1$_\beta$, OH-6$_\alpha$); 4.30 (m, 0.3H, OH-6$_\beta$); 4.29 (d, J = 9.5 Hz, 0.7H, H-1$_\alpha$); 3.74 (m, 0.7H, H-6$_\alpha$); 3.68 (m, 0.3H, H-6$_\beta$); 3.60 (m, 1H, H-6$_{\alpha,\beta}$); 3.55 (m, 0.7H, H-5$_\alpha$); 3.51−3.42 (m, 3.6H, H-2$_{\alpha,\beta}$, H-5$_\omega$, 2 × H-5$_\beta$, H-6$_\omega$, 2 × H-6$_\beta$); 3.26−3.23 (m, 2.1H), 3.13−3.00 (m, 2.3H) (H-3$_{\alpha,\beta}$, H-3′$_{\alpha,\beta}$, H-4$_{\alpha,\beta}$, H-4′$_{\alpha,\beta}$, H-6$_\alpha$); 3.21 (t, J = 10.0 Hz, 0.3H, H-3′$_\beta$); 3.13 (m, 0.7H, H-2′$_\alpha$); 2.87 (q, J = 9.0 Hz, 0.3H, H-2′$_\beta$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 95.6 (C-1′$_\beta$); 91.9 (C-1′$_\alpha$); 90.5 (C-1$_\alpha$); 89.5 (C-1$_\beta$); 81.5, 80.7, 77.9, 77.2, 76.5, 74.5, 72.0, 70.9 (2C), 70.8, 70.1, 69.6 (C-2$_{\alpha,\beta}$, C-3$_{\alpha,\beta}$, C-3′$_{\alpha,\beta}$, C-4$_{\alpha,\beta}$, C-4′$_{\alpha,\beta}$, C-5$_{\alpha,\beta}$, C-5′$_{\alpha,\beta}$); 61.7 (C-2′$_\beta$); 61.2, 61.0 (C-6$_{\alpha,\beta}$, C-6′$_{\alpha,\beta}$); 58.7 (C-2′$_\alpha$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 428 [M + Na]$^+$. HRMS: calcd for $C_{12}H_{23}NO_{12}SNa$ 428.0833, found 428.0812.

3-Deoxy-3-*N*-(1-*S*-*β*-D-glucopyranosyl)-3-sulfonylamino-α,*β*-D-glucopyranose (16c). The title compound **16c** was obtained from compound **16b** according to the general procedure 3. The lyophilized compound was obtained as a colorless gum (84% yield) as a mixture of α and β anomers (α/β 40:60). R_f = 0.14 (85:15 CH$_3$CN/H$_2$O). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.04 (d, J = 7.0 Hz, 0.6H, NH_β); 6.99 (d, J = 7.5 Hz, 0.4H, NH_α); 6.66 (d, J = 6.0 Hz, 0.6H, OH-1$_\beta$); 6.41 (d, J = 4.0 Hz, 0.4H, OH-1$_\alpha$); 5.09 (br s, 2H), 5.03 (d, J = 4.0 Hz, 1H) (3 × OH_ω, 3 × OH_β); 4.94 (t, J = 3.5 Hz, 0.4H, H-1′$_\alpha$); 4.91 (d, J = 5.5 Hz, 0.6H, OH-2′$_\beta$); 4.75 (d, J = 6.5 Hz, 0.6H, OH_β); 4.70−4.67 (m, 1.4H, OH-6$_\beta$, 1 × OH_ω 1 × OH_β); 4.52 (t, J = 5.5 Hz, 0.6H, OH-6$_\beta$); 4.48 (d, J = 7.5 Hz, 0.4H, 1 × OH_α); 4.41 (m, 0.4H, 1 × OH_α); 4.40 (d, J = 9.5 Hz, 0.6H, H-1′$_\beta$); 4.39 (d, J = 9.5 Hz, 0.4H, H-1′$_\alpha$); 4.30 (br t, J = 6.0 Hz, 0.4H, H-1′$_\beta$); 3.72−3.69 (m, 1H, H-6$_\omega$, H-6$_\beta$); 6.65 (dd, J = 11.5, 3.0 Hz, 0.4H, H-6$_\alpha$); 3.57 (m, 0.6H, H-6$_\beta$); 3.46−3.38 (m, 3H, H-2$_\omega$, H-2$_\beta$, 2 × H-6$_\omega$, 2 × H-6$_\beta$); 3.22 (m, 0.4H, H-2′$_\alpha$); 3.21−3.03 (m, 5.4H, H-2′$_\omega$, H-3$_\omega$, H-3$_\beta$, H-4$_\omega$, H-4$_\beta$, H-4′$_\omega$, H-4′$_\beta$, H-5$_\omega$, H-5$_\beta$, H-5′$_\omega$, H-5′$_\beta$); 3.01 (m, 1H, H-3′$_\omega$, H-3′$_\beta$); 2.99−2.97 (m, 0.6H, H-2′$_\beta$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 97.4 (C-1′$_\beta$); 91.7 (C-1′$_\alpha$);

89.6 (C-1$_\beta$); 89.4 (C-1$_\alpha$); 81.1 (C-5′$_\alpha$); 81.0 (C-5′$_\beta$); 77.9, 77.8, 77.6 (C-3$_\omega$ C-3$_\beta$, C-5$_\omega$ C-5$_\beta$); 72.9 (C-2′$_\beta$); 72.4 (C-2′$_\alpha$); 70.9 (C-2$_\alpha$); 70.4 (C-2$_\beta$); 70.0 (C-4′$_\beta$); 69.9 (C-4′$_\alpha$); 69.1 (C-4$_\beta$); 68.9 (C-4$_\alpha$); 62.7 (C-3′$_\beta$); 61.2, 61.3 (C-6$_\omega$ C-6$_\beta$, C-6′$_\omega$ C-6′$_\beta$); 59.1 (C-3′$_\alpha$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 428 [M + Na]$^+$. HRMS: calcd for $C_{12}H_{23}NO_{12}SNa$ 428.0833, found 428.0817.

Methyl 4-Deoxy-4-*N*-(1-*S*-*β*-D-glucopyranosyl)-4-sulfonylamino-α-D-glucopyranoside (17c). The title compound **17c** was obtained from compound **17b** according to the general procedure 3. The lyophilized compound was obtained as a highly hygroscopic white solid (99% yield). R_f = 0.04 (8:2 CH_2Cl_2/MeOH). [α]$^{25}_D$ = +67 (c = 1.0, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.23 (d, J = 9.0 Hz, 1H, N*H*); 5.07 (br s, 1H, O*H*-3); 5.05 (d, J = 6.0 Hz, 1H, O*H*-2); 5.03 (br d, J = 3.5 Hz, 1H, O*H*-4); 4.85 (d, J = 5.0 Hz, 1H, O*H*-2′); 4.77 (d, J = 5.5 Hz, 1H, O*H*-3′); 4.69 (br t, J = 5.5 Hz, 1H, O*H*-6 or O*H*-6′); 4.54 (d, J = 3.5 Hz, 1H, H-1′); 4.44 (br t, J = 5.0 Hz, 1H, O*H*-6 or O*H*-6′); 4.33 (d, J = 10.0 Hz, 1H, H-1); 3.76−3.69 (m, 2H, H-6a, H-6a′); 3.56 (t d, J = 9.0, 5.5 Hz, 1H, H-3′); 3.43 (t, J = 9.0 Hz, 1H, H-2); 3.42−3.37 (m, 3H, H-5′, H-6b, H-6b′); 3.27 (s, 3H, OC*H*$_3$); 3.23−3.16 (m, 3H, H-2′, H-3, H-5′); 3.00 (br t, J = 8.0 Hz, 1H, H-4); 2.88 (q, J = 9.5 Hz, 1H, H-4′), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 99.3 (C-1′); 88.8 (C-1); 80.8 (C-2′); 78.0 (C-3); 72.7 (C-5); 72.0 (C-5′); 71.1 (C-3′); 70.6 (C-2); 70.2 (C-4); 61.5, 61.3 (C-6, C-6′); 56.7 (C-4′); 54.4 (OCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 437 [M + NH$_4$]$^+$, 442 [M + Na]$^+$. HRMS: calcd for $C_{13}H_{25}NO_{12}SNa$ 442.0990, found 442.1009.

Methyl 6-Deoxy-6-*N*-(1-*S*-*β*-D-glucopyranosyl)-6-sulfonylamino-α-D-glucopyranoside (18c). The title compound **18c** was obtained from compound **18b** according to the general procedure 3. The lyophilized compound was obtained as a highly hygroscopic white solid (87% yield). R_f = 0.15 (9:1 CH_3CN/H_2O). [α]$^{25}_D$ = +49 (c = 1.0, MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 6.78 (br s, 1H, N*H*); 5.11 (br s, 2H, O*H*-2, O*H*-2′); 5.04 (d, J = 4.5 Hz, 1H), 4.98 (d, J = 5.0 Hz, 1H) (O*H*-4, O*H*-4′); 4.77 (d, J = 3.5 Hz, 1H), 4.71 (d, J = 6.5 Hz, 1H) (O*H*-3, O*H*-3′); 4.52 (d, J = 3.5 Hz, 1H, H-1′); 4.47 (t, J = 6.0 Hz, 1H, O*H*-6); 4.20 (d, J = 9.5 Hz, 1H, H-1); 3.69 (dd, J = 11.5, 4.5 Hz, 1H, H-6a); 3.47 (dd, J = 11.5, 7.0 Hz, 1H, H-6b); 3.46 (t, J = 7.0 Hz, 1H, H-2); 3.43 (m, 1H, H-6a′); 3.40−3.35 (m, 2H, H-3, H-3′); 3.28 (s, 3H, OC*H*$_3$); 3.25−3.21 (m, 2H, H-5, H-5′); 3.19 (m, 1H, H-2′); 3.01 (td, J = 9.5, 4.5 Hz, 1H, H-4 or H-4′); 3.05 (m, 1H, H-6b′); 2.98 (td, J = 9.0, 4.0 Hz, 1H, H-4′ or H-4), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 99.7 (C-1′); 89.6 (C-1); 81.1, 77.3 (C-5, C-5′); 73.0 (C-3 or C-3′); 71.9 (C-2′); 71.6 (C-4 or C-4′); 71.1 (C-3′ or C-3); 70.6 (C-2); 69.4 (C-4′ or C-4); 60.8 (C-6); 54.5 (OCH$_3$); 44.7 (C-6′), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 437 [M + NH$_4$]$^+$, 442 [M + Na]$^+$. HRMS: calcd for $C_{13}H_{25}NO_{12}SNa$ 442.0990, found 442.0985.

2-Deoxy-2-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-*β*-D-lactosyl)-α,*β*-D-glucopyranose (19a). Compound **19a** was obtained from compound **2** and the glucosamine hydrochloride salt **7** according to the general procedure 1. Purification by flash chromatography (1:1 acetone/hexane) afforded **19a** as a mixture of α and β anomers (68% yield; α/β 70:30) as a light yellow solid. R_f = 0.22 (1:1 acetone/hexane). Mp = 111−113 °C. ^{1}H NMR (500 MHz, DMSO-d_6, β-anomer): δ = 6.28 (d, J = 4.5 Hz, 1H, O*H*-1); 5.25 (m, 1H, H-3); 5.23 (m, 1H, H-4′); 5.18 (dd, J = 10.0, 3.5 Hz, 1H, H-3′); 5.20 (d, J = 3.5 Hz, 1H, H-1″); 4.99 (t, J = 9.5 Hz, 1H, H-2); 4.85 (dd, J = 10.0, 8.0 Hz, 1H, H-2′); 4.77 (d, J = 4.5 Hz, 1H, O*H*-4″); 4.70 (d, J = 8.0 Hz, 1H, H-1′); 4.64 (d, J = 4.5 Hz, 1H, O*H*-3″); 4.34 (d, J = 9.5 Hz, 1H, H-1); 4.31 (br d, J = 12.0 Hz, 1H, H-6a′); 4.28 (t, J = 5.5 Hz, 1H, O*H*-6″); 4.22 (br t, J = 12.0 Hz, 1H, H-5′); 4.05−3.99 (m, 3H, H-6a, H-6b, H-6b′); 3.38−3.31 (m, 2H, H-4, H-5); 3.60 (dd, J = 11.0, 4.5 Hz, 1H, H-6a″); 5.44 (m, 1H, H-5″); 3.46 (dd, J = 11.0, 5.5 Hz, 1H, H-6b″); 3.26 (td, J = 10.0, 5.0 Hz, 1H, H-3″); 3.03 (td, J = 9.5, 4.5 Hz, 1H, H-4″); 2.97 (d, J = 8.0 Hz, 1H, N*H*); 2.44 (td, J = 9.0, 3.0 Hz, 1H, H-2″); 2.12, 2.11, 2.01, 2.00, 1.90 (5 × s, 21H, OCOC*H*$_3$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.6, 169.8 (2C), 169.5, 169.4, 169.3, 169.0 (OCOCH$_3$); 99.9 (C-1′); 91.5 (C-1″); 86.6 (C-1); 75.7, 75.5 (C-4, C-5); 73.1 (C-3); 72.7 (C-3″); 71.8 (C-5″); 70.9 (C-4″); 70.3 (C-3′); 69.5 (C-5′); 68.9 (C-2′); 68.6 (C-2″); 67.6 (C-2); 66.9 (C-4′); 62.2 (C-6′); 61.3 (C-6″); 60.6 (C-6); 20.7, 20.6 (2C), 20.5, 20.4, 20.3 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 852 [M + Na]$^+$. HRMS: calcd for $C_{32}H_{47}NO_{22}SNa$ 852.2203, found 852.2202.

Methyl 6-Deoxy-6-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-*β*-D-lactosyl)-α-D-glucopyranoside (20a). Compound **20a** was obtained from compound **2** and **10** according to the general procedure 1. Purification by flash chromatography (95:5 CH_2Cl_2/MeOH) afforded **20a** (80% purity, 84% yield) as a white solid. R_f = 0.25 (1:1 acetone/hexane). LRMS (ESI$^+$): m/z = 866 [M + Na]$^+$. HRMS: calcd for $C_{33}H_{49}NO_{22}SNa$ 866.2359, found 866.2399. Compound **20a** was used as reagent for general procedure 2 without further purification.

Methyl 6-Deoxy-6-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-*β*-D-maltosyl)-α-D-glucopyranoside (21a). Compound **21a** was obtained from compounds **3** and **10** according to the general procedure 1. Purification by flash chromatography (2:1 acetone/hexane) afforded **21a** (75% yield) as a white solid. R_f = 0.22 (1:1 acetone/hexane). Mp = 123 °C. [α]$^{25}_D$ = +54 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.38 (t, J = 9.5 Hz, 1H, H-3); 5.29 (d, J = 3.5 Hz, 1H, H-1′); 5.22 (t, J = 10.0 Hz, 1H, H-3′); 4.98 (t, J = 10.0 Hz, 1H, H-4′); 4.87 (d, J = 4.0 Hz, 1H, OH-4″); 4.86 (dd, J = 10.0, 3.5 Hz, 1H, H-2′); 4.83 (t, J = 9.5 Hz, 1H, H-2); 4.71 (d, J = 4.5 Hz, 1H, OH-3″); 4.67 (d, J = 8.5 Hz, 1H, OH-2″); 4.65 (d, J = 10.0 Hz, 1H, H-1); 4.50 (d, J = 3.5 Hz, 1H, H-1″); 4.41 (dd, J = 13.0, 3.0 Hz, 1H, H-6a); 4.16 (dd, J = 12.5, 4.5 Hz, 1H, H-6a′); 4.12 (dd, J = 12.0, 5.0 Hz, 1H, H-6b); 4.01 (dd, J = 12.5, 2.0 Hz, 1H, H-6b′); 3.97 (m, 1H, H-5′); 3.94 (m, 1H, H-5); 3.87 (t, J = 9.5 Hz, 1H, H-4); 3.46 (t, J = 6.0 Hz, 1H, N*H*); 3.35 (m, 2H, H-3″, H-5″); 3.28 (s, 3H, OC*H*$_3$); 3.18−3.16 (m, 2H, H-2″, H6a″); 2.95−2.89 (m, 2H, H-4″, H-6b″); 2.07, 2.02, 1.99, 1.98, 1.97, 1.95 (6 × s, 21H, OCOC*H*$_3$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 170.1, 170.0, 169.7 (2C), 169.6, 169.3 (OCOCH$_3$); 99.8 (C-1″); 95.6 (C-1′); 87.2 (C-1); 75.4 (C-3); 75.0 (C-5); 73.8 (C-4); 73.3 (C-3″); 72.0 (C-2″); 71.8 (C-4″); 71.2 (C-5″); 69.6 (C-2′); 69.0 (C-3′); 68.2 (C-2); 68.1 (C-5′); 67.9 (C-4′); 63.1 (C-6); 61.5 (C-6′); 55.5 (C-6″); 54.6 (OCH$_3$); 20.7, 20.6, 20.5 (2C), 20.4 (2C), 20.3 (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 844 [M + H]$^+$; 866 [M + Na]$^+$. HRMS: calcd for $C_{33}H_{49}NO_{22}SNa$ 866.2359, found 866.2332.

***N*-(2,2″,3,3″,4,6,6″-Hepta-*O*-acetyl-1-*S*-*β*-D-maltosyl)-2′,2″,3′,3″-,4″,6′6″-hepta-*O*-acetyl-*β*-D-maltosamine (22a).** Compound **22a** was obtained from compounds **3** and **11** according to the general procedure 1. Purification by flash chromatography (2:1 EtOAc/hexane) afforded **22a** (23% yield) as a white solid. R_f = 0.31 (2:1 EtOAc/hexane). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.36 (t, J = 9.0 Hz, 1H, H-3); 5.30 (d, J = 3.5 Hz, 2H, H-1″); 5.23 (td, J = 10.0, 2.0 Hz, 2H, H-3″); 5.21 (m, 1H, H-3′); 4.99 (td, J = 10.0, 3.5 Hz, 2H, H-4″); 4.92 (br d, J = 9.2 Hz, 1H, N*H*); 4.86 (dd, J = 10.5, 4.0 Hz, 2H, H-2″); 4.84 (t, J = 9.5 Hz, 1H, H-2); 4.72 (t, J = 9.0 Hz, 1H, H-2′); 4.65 (d, J = 10.0 Hz, 1H, H-1); 4.47 (dd, J = 12.5, 1.5 Hz, 1H, H-6a′); 4.41 (br d, J = 12.0 Hz, 1H, H-6a); 4.34 (t, J = 9.0 Hz, 1H, H-1′); 4.14 (br dd, J = 12.5, 4.0 Hz, 4H, H-6b, H-6b′, H-6a″); 4.03 (br d, J = 12.0 Hz, H-6b″); 3.98 (m, 2H, H-5″); 3.93 (m, 1H, H-5′); 3.83 (m, 3H, H-4, H-5, H-4′); 2.14, 2.10, 2.03, 2.01, 1.99, 1.98, 1.96, 1.94, 1.93 (10 × s, 42H, OCOC*H*$_3$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.7, 170.6, 170.4 (2C), 170.3 (2C), 170.1, 170.0, 169.9 (2C), 169.6 (3C); 169.5 (OCOCH$_3$); 95.9, 95.8 (C-1″); 91.2 (C-1′); 87.7 (C-1); 76.0 (C-3); 75.9 (C-3′); 75.4 (C-5′); 74.1, 73.9, 72.7 (C-4, C-5, C-4′); 71.6

(C-2′); 70.0, 69.9 (C-2″); 69.4 (2C) (C-3″); 68.5, 68.4 (C-5″); 68.4 (C-2); 68.2 (2C) (C-4″); 63.4 (C-6′); 63.3 (C-6); 61.9 (2C) (C-6″); 21.1 (2C), 21.0 (2C), 20.9 (5C); 20.8 (2C), 20.7 (3C) ($OCOCH_3$), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 1287 $[M + H]^+$; 1309 $[M + Na]^+$. HRMS: calcd for $C_{52}H_{71}NO_{34}SNa$ 1308.3470, found 1308.3427.

Methyl 6-Deoxy-6-*N*-([(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-[(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3-di-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-[(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3-di-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-α-D-glucopyranoside (23a). The title compound **23a** was prepared from thioacetate **4** and amine **10** according to the general procedure 1. Purification by flash chromatography (2:1 acetone/hexane) afforded **23a** (60% yield) as a white solid. R_f = 0.19 (1:1 acetone/hexane). ^1H NMR (500 MHz, DMSO-d_6): δ = 5.33 (t, J = 9.5 Hz, 1H); 5.30 (t, J = 9.5 Hz, 1H); 5.25 (t, J = 9.5 Hz, 1H); 5.18 (t, J = 10.0 Hz, 1H); 5.17 (t, J = 9.5 Hz, 1H); 5.13−5.07 (m, 3H); 5.00−4.71 (m, 14H); 4.68−4.61 (m, 3H); 4.55−4.48 (m, 3H); 4.30 (m, 1H); 4.14 (m, 1H, N*H*); 4.00 (m, 1H); 3.93−3.59 (m, 17H); 3.52−3.46 (m, 2H); 3.36−3.32 (m, 2H); 3.27 (s, 3H, OCH_3); 3.17−3.13 (m, 3H); 2.95−2.87 (m, 2H); 2.09, 2.08, 2.06, 2.05, 2.04, 2.01, 2.00, 1.99, 1.97, 1.96, 1.95, 1.92 (15 × s, 57H, $OCOCH_3$). LRMS (ESI^+): m/z = 2070 $[M + H]^+$; 2092 $[M + Na]^+$. HRMS: calcd for $C_{84}H_{117}NO_{56}SNa$ 2090.5951, found 2090.5989.

2-Deoxy-2-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-β-D-lactosyl)-2-sulfonylamino-α,β-D-glucopyranose (19b). Compound **19b** was obtained from compound **19a** according to the general procedure 2. Purification by flash chromatography (95:5 CH_2Cl_2/MeOH) afforded **19b** (53% yield, β-anomer) as a white solid. R_f = 0.32 (9:1 CH_2Cl_2/MeOH). Mp = 135−136 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 5.23 (br d, J = 3.5 Hz, 1H, H-4′); 5.20 (t, J = 9.0 Hz, 1H, H-3); 5.16 (dd, J = 10.5, 3.5 Hz, 1H, H-3′); 4.89 (d, J = 5.0 Hz, 1H, O*H*-3″); 4.85 (t, J = 10.0 Hz, 2H, H-2, H-2′); 4.76 (d, J = 8.0 Hz, 1H, H-1′); 4.73 (d, J = 3.5 Hz, 1H, O*H*-4″); 4.96 (d, J = 6.05 Hz, 1H, N*H*); 4.62 (d, J = 10.0 Hz, 1H, H-1); 4.51 (d, J = 3.5 Hz, 1H, H-1″); 4.34 (br d, J = 11.5 Hz, 1H, H-6a); 4.23 (br t, J = 7.0 Hz, 1H, H-5′); 4.03−3.99 (m, 3H, H6a′, H-6b, H-6b′); 3.82 (m, 1H, H-5); 3.74 (t, J = 9.5 Hz, 1H, H-4); 3.46 (t, J = 6.0 Hz, 1H, O*H*-6″); 3.38−3.33 (m, 2H, H-4″, H-5″); 3.21−3.15 (m, 3H, H-2″, H-6a″, O*H*-1″), 3.962.91(m, 2H, H-3″, H-6b″); 2.11, 2.08, 2.01, 2.00, 1.99, 1.98, 1. (7 × s, 21H, $OCOCH_3$), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 169.8, 169.6, 169.5, 169.4, 169.3, 169.0 ($OCOCH_3$); 99.9 (C-1′); 99.7 (C-1″); 87.4 (C-1); 76.1 (C-4); 75.4 (C-5); 73.4 (C-3); 73.2 (C-5″); 71.9 (C-2″); 71.7 (C-3″); 71.1 (C-4″); 70.3 (C-3′); 69.7 (C-5′); 68.9, 67.8 (C-2, C-2′); 67.1 (C-4′); 62.4 (C-6); 60.8 (C-6′); 55.3 (C-6″); 20.6, 20.5, 20.4 (2C), 20.3 (2C), 20.2 ($OCOCH_3$), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 879 $[M + NH_4]^+$, 884 $[M + Na]^+$. HRMS: calcd for $C_{32}H_{47}NO_{24}SNa$ 884.2101, found 884.2113.

Methyl 6-Deoxy-6-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-β-D-lactosyl)-6-sulfonylamino-α-D-glucopyranoside (20b). Compound **20b** was obtained from compound **20a** according to the general procedure 2. Purification by flash chromatography (3:2 acetone/hexane) afforded **20b** (72% yield) as a white solid. R_f = 0.16 (3:2 acetone/hexane). Mp = 114−115 °C. $[\alpha]^{25}_D$ = +15 (c = 1.0, chloroform). ^1H NMR (500 MHz, DMSO-d_6): δ = 7.45 (br s, 1H, N*H*); 5.29 (t, J = 9.5 Hz, 1H, H-3); 5.24 (d, J = 3.0 Hz, 1H, H-4′); 5.16 (dd, J = 10.5, 4.5 Hz, 1H, H-3′); 5.15 (t, J = 9.5 Hz, 1H, H-2); 4.97 (d, J = 5.5 Hz, 1H, O*H*-4″); 4.84 (dd, J = 10.0, 8.0 Hz, 1H, H-2′); 4.81 (d, J = 10.0 Hz, 1H, H-1); 4.81 (br s, 1H, O*H*-3″); 4.78 (d, J = 9.0 Hz, H-1′); 4.73 (d, J = 6.5 Hz, 1H, O*H*-2″); 4.55 (d, J = 3.5 Hz, 1H, H-1″); 4.32 (br d, J = 11.5 Hz, 1H, H-6a); 4.22 (t, J = 6.5 Hz, 1H, H-5′); 4.07 (dd, J = 11.5, 7.0 Hz, 1H, H-6b); 4.02−3.98 (m, 3H, H-5, H-6a′, H-6b′); 3.81 (t, J = 9.5 Hz, 1H, H-4); 3.47 (dd, J = 12.0, 7.0 Hz, 1H, H-6a″); 3.88−3.35 (m, 2H, H-3″, H-5″); 3.30 (s, 3H, OCH_3); 3.19 (m, 1H, H-2″); 3.03 (m, 1H, H-6b″); 2.91 (td, J = 9.5, 5.5 Hz, 1H, H-4″); 2.10, 2.08, 2.02, 2.01, 1.98, 1.94, 1.90 (7 × s, 21H, $OCOCH_3$), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 169.9, 169.8, 169.4, 169.3, 169.1, 168.7 ($OCOCH_3$); 99.9 (C-1′); 99.6 (C-1″); 86.5 (C-1); 76.0 (C-4); 75.5 (C-5); 73.1, 73.0 (C-3, C-3″); 71.9 (C-2″); 71.8 (C-4″); 71.2 (C-5″); 70.3 (C-3′); 69.7 (C-5′); 68.9 (C-2′); 67.9 (C-2); 67.1 (C-4′); 62.4 (C-6); 60.8 (C-6′); 54.5 (OCH_3); 45.3 (C-6″); 20.6, 20.5, 20.4 (2C), 20.3 (2C), 20.2 ($OCOCH_3$), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 898 $[M + Na]^+$. HRMS: calcd for $C_{33}H_{49}NO_{24}SNa$ 898.2257, found 898.2292.

Methyl 6-Deoxy-6-*N*-(2,2′,3,3′,4′,6,6′-hepta-*O*-acetyl-1-*S*-β-D-maltosyl)-6-sulfonylamino-α-D-glucopyranoside (21b). Compound **21b** was obtained from compound **21a** according to the general procedure 2. Purification by flash chromatography (3:1 acetone/hexane) afforded **21b** (87% yield) as a white solid. R_f = 0.30 (3:1 acetone/hexane). Mp = 121 °C. $[\alpha]^{25}_D$ = +71 (c = 1.0, chloroform). ^1H NMR (500 MHz, DMSO-d_6): δ = 7.47 (br s, 1H, N*H*); 5.44 (t, J = 9.0 Hz, 1H, H-3); 5.29 (d, J = 3.5 Hz, 1H, H-1′); 5.22 (t, J = 10.0 Hz, 1H, H-3′); 5.12 (t, J = 9.5 Hz, 1H, H-2); 4.97 (t, J = 10.0 Hz, 1H, H-4′); 4.95 (d, J = 6.0 Hz, 1H, O*H*-4″); 4.88 (dd, J = 10.5, 4.0 Hz, 1H, H-2′); 4.85 (d, J = 9.5 Hz, 1H, H-1); 4.79 (d, J = 5.0 Hz, 1H, O*H*-3″); 4.72 (d, J = 6.5 Hz, 1H, O*H*-2″); 4.55 (d, J = 3.5 Hz, 1H, H-1″); 4.41 (dd, J = 12.0, 2.0 Hz, 1H, H-6a); 4.18−4.14 (m, 2H, H-6a′, H-6b); 4.11 (m, 1H, H-5); 4.01 (dd, J = 12.5, 2.5 Hz, 1H, H-6b′); 3.98 (m, 1H, H-5′); 3.93 (t, J = 9.0 Hz, 1H, H-4); 3.46 (dd, J = 13.0, 4.0 Hz, 1H, H-6a″); 3.38−3.33 (m, 2H, H-3″, H-5″); 3.30 (s, 3H, OCH_3); 3.19 (ddd, J = 10.0, 7.0, 4.0 Hz, 1H, H-2″); 3.03 (m, 1H, H6b″); 2.92 (dt, J = 9.0, 6.0 Hz, 1H, H-4″); 2.07, 2.02, 1.99, 1.98, 1.95, 1.94 (6 × s, 21H, $OCOCH_3$), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.1, 170.0, 169.8, 169.6, 169.5, 169.1, 168.8 ($OCOCH_3$); 99.6 (C-1″); 95.7 (C-1′); 86.5 (C-1); 75.0 (C-5); 74.7 (C-3); 73.8 (C-4); 73.1 (C-3″); 71.9 (C-2″); 71.8 (C-4″); 71.2 (C-5″); 69.4 (C-2′); 68.9 (C-3′); 68.3 (C-2); 68.1 (C-5′); 67.8 (C-4′); 63.0 (C-6); 61.4 (C-6′); 54.5 (OCH_3); 45.2 (C-6″); 20.6, 20.5, 20.4 (2C), 20.3 (2C), 20.2 ($OCOCH_3$), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 898 $[M + Na]^+$; LRMS (ESI^-): m/z = 874 $[M - H]^-$. HRMS: calcd for $C_{33}H_{49}NO_{24}SNa$ 898.2257, found 898.2270.

***N*-(2,2″,3,3″,4,6,6″-Hepta-*O*-acetyl-1-*S*-β-D-maltosyl)-2′,2″,3′-,3″,4″,6′6″-hepta-*O*-acetyl-β-D-maltosylsulfonylamine (22b).** The title compound **22b** was prepared from sulfenamide **22a** according to the general procedure 2. Purification by flash chromatography (3:2 EtOAc/petroluem spirit) afforded **22b** (53% yield) as a white solid. R_f = 0.30 (3:2 EtOAc/hexane). Mp =117−119 °C. $[\alpha]^{25}_D$ = +77 (c = 1.0, chloroform). ^1H NMR (500 MHz, DMSO-d_6): δ = 9.04 (br s, 1H, N*H*); 5.43 (t, J = 9.0 Hz, 1H, H-3); 5.33 (t, J = 9.5 Hz, 1H, H-2); 5.32 (d, J = 3.5 Hz, 1H, H-1″); 5.26 (m, 1H, H-3′); 5.25 (br s, 1H, H-1″); 5.23 (br t, J = 10.5 Hz, 2H, 2 × H3″); 4.99, 4.98 (2 × t, J = 9.5 Hz, 2H, 2 × H4″); 4.88 (d, J = 10.5 Hz, 1H, H-1); 4.87, 4.86 (2 × t, J = 10.0 Hz, 2H, 2 × H2″); 4.75 (t, J = 9.5 Hz, 1H, H-2′); 4.66 (d, J = 9.0 Hz, 1H, H-1′); 4.56 (br d, J = 11.5 Hz, 1H, H-6a); 4.40 (br d, J = 12.0 Hz, 1H, H-6a′); 4.19 (dd, J = 13.5, 2.5 Hz, 1H, H-6b); 4.16 (dd, J = 11.5, 2.5 Hz, 1H, H-6b′); 4.15−4.12 (m, 3H), 4.03−3.93 (m, 5H) (H-5, H-5′, 2 × H5″, 4 × H6″); 3.89 (t, J = 9.0 Hz, 1H), 3.85 (t, J = 9.5 Hz, 1H) (H-4, H-4′); 2.09, 2.08, 2.02, 2.01, 1.99, 1.98, 1.96, 1.95, 1.94, 1.93 (11 × s, 42H, $OCOCH_3$), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 170.0, 169.9 (2C), 169.8 (2C), 169.7, 169.5 (2C), 169.4, 169.2, 169.1, 169.1, 168.9 ($OCOCH_3$); 95.7, 95.2 (C1″); 86.2 (C-1); 81.0 (C-1′); 75.1 (C-3′); 74.8 (C-3); 74.3, 74.2 (C-5, C-5′), 72.7 (2C) (C-5″); 70.8 (C-2′); 69.4 (2C) (C-2″); 68.9 (2C) (C-3″); 68.4 (C-4); 67.8 (C-4′); 67.8 (2C) (C-4″); 67.6 (C-2); 62.8 (C-6′); 62.2 (C-6); 61.5, 61.2 (C-6″); 20.6 (2C), 20.5, 20.4 (4C), 20.3 (5C), 20.2

(2C) ($OCOCH_3$), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 1340 $[M + Na]^+$. HRMS: calcd for $C_{52}H_{71}NO_{36}SNa$ 1340.3369, found 1340.3367.

Methyl 6-Deoxy-6-*N*-([(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-[(2,3,-4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3-di-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-[(2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl)-(1→6)]-(2,3-di-*O*-acetyl-β-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-6-sulfonylamino-α-D-glucopyranoside (23b). The title compound **23b** was prepared from sulfenamide **23a** according to the general procedure 2. Purification by flash chromatography (5:2 acetone/hexane) afforded **23b** (59% yield) as a white solid. R_f = 0.50 (5:2 acetone/toluene). Mp = 133−135 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 7.46 (t, *J* = 5.5 Hz, 1H, N*H*); 5.36 (t, *J* = 9.5 Hz, 1H); 5.30 (t, *J* = 9.5 Hz, 1H); 5.27 (t, *J* = 9.5 Hz, 1H); 5.25 (t, *J* = 9.5 Hz, 1H); 5.17 (t, *J* = 10.0 Hz, 1H); 5.11 (t, *J* = 9.0 Hz, 1H); 5.10 (t, *J* = 9.0 Hz, 1H); 5.08−5.05 (m, 2H); 5.00−4.72 (m, 16H); 4.64 (t, *J* = 9.0 Hz, 1H); 4.55−4.52 (m, 2H); 4.49 (t, *J* = 8.5 Hz, 1H); 4.30 (d, *J* = 11.5 Hz, 1H); 4.08 (m, 1H); 3.96 (d, *J* = 9.0 Hz, 1H); 3.93−3.87 (m, 2H); 3.85−3.61 (m, 17H); 3.51−3.43 (m, 2H); 3.38−3.34 (m, 1H); 3.29 (s, 3H, OCH_3); 3.17 (m, 1H); 3.01 (ddd, *J* = 13.0, 9.0, 3.5 Hz, 1H); 2.89 (br t, *J* = 9.0 Hz, 1H); 2.06, 2.05, 2.04, 2.01, 2.00, 1.99, 1.97, 1.96, 1.95, 1.92 (12 × s, 57H, $OCOCH_3$). LRMS (ESI^+): m/z = 2124 $[M + Na]^+$.

2-Deoxy-2-*N*-(1-*S*-β-D-lactosyl)-2-sulfonylamino-α,β-D-glucopyranose (19c). The title compound **19c** was obtained from compound **19b** according to the general procedure 3 as a mixture of α- and β-anomers (94% yield; α/β 80:20) as a white solid. R_f = 0.16 (8:2 CH_3CN/H_2O). Mp = 171 °C dec. ^1H NMR (500 MHz, DMSO-d_6, α-anomer): δ = 6.58 (d, *J* = 4.0 Hz, 1H, O*H*-1″); 6.55 (br s, 1H, N*H*); 5.39 (d, *J* = 5.0 Hz, 1H), 5.07 (br s, 1H), 4.99 (br s, 1H) (3 × O*H*); 4.99 (d, *J* = 3.5 Hz, 1H, H-1″); 4.93 (m, 1H), 4.90 (d, *J* = 5.5 Hz, 1H), 4.83 (br s, 1H), 4.76 (m, 1H), 4.67 (t, *J* = 4.0 Hz, 1H), 4.50 (d, *J* = 3.5 Hz, 1H), 4.41 (d, *J* = 5.5 Hz, 1H) (7 × O*H*); 4.38 (d, *J* = 9.0 Hz, 1H, H-1); 4.20 (d, *J* = 7.0 Hz, 1H, H-1′); 3.85 (dd, *J* = 11.5, 5.0 Hz, 1H, H-6a); 3.62−3.50 (m, 7H), 3.47−3.43 (m, 5H), 3.33−3.29 (m, 3H), 3.10 (m, 1H) (H-2, H-2″, H-3, H-3′, H-3″, H-4, H-4′, H-4″, H-5, H-5′, H-5″, H-6b, H-6a′, H-6b′, H-6a″, H-6b″); 3.12 (m, 1H, H-2″), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 103.7 (C-1′); 91.9 (C-1″); 90.0 (C-1); 79.8, 79.4, 75.6, 75.5, 73.3, 72.0, 70.9 (2C), 70.7, 70.6, 68.2 (C-2, C-2″, C-3, C-3′, C-3″, C-4, C-4′, C-4″, C-5, C-5′, C-5″); 61.1, 60.5 (2C) (C-6, C-6′, C-6″); 58.7 (C-2′), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 590 $[M + Na]^+$; LRMS (ESI^-): m/z = 566 $[M - H]^-$. HRMS: calcd for $C_{18}H_{33}NO_{17}SNa$ 590.1361, found 590.1340.

Methyl 6-Deoxy-6-*N*-(1-*S*-β-D-lactosyl)-6-sulfonylamino-α-D-glucopyranoside (20c). The title compound **20c** was obtained from compound **20b** as a light orange gum according to the general procedure 3 (98% yield). R_f = 0.18 (8:2 CH_3CN/H_2O). $[\alpha]^{25}_D$ = +62 (*c* = 1.0, methanol). ^1H NMR (500 MHz, DMSO-d_6, α-anomer): δ = 6.79 (dd, *J* = 6.5, 5.5 Hz, 1H, N*H*); 5.31 (d, *J* = 6.0 Hz, 1H, O*H*-2); 5.07 (d, *J* = 4.0 Hz, 1H, O*H*-2′); 4.98 (d, *J* = 5.5 Hz, 1H, O*H*-4″); 4.78 (m, 2H), 4.75 (d, *J* = 4.0 Hz, 1H) (O*H*-3, O*H*-3′, O*H*-3″); 4.72 (d, *J* = 6.5 Hz, 1H, O*H*-2″); 4.64 (t, *J* = 5.0 Hz, 1H, O*H*-6′); 4.53 (t, *J* = 6.0 Hz, 1H, O*H*-6); 4.53 (d, *J* = 3.5 Hz, 1H, H-1″); 4.49 (d, *J* = 5.0 Hz, 1H, O*H*-4′); 4.29 (d, *J* = 9.0 Hz, 1H, H-1); 4.21 (d, *J* = 7.5 Hz, 1H, H-1′); 3.77 (ddd, *J* = 12.5, 6.0, 2.5 Hz, 1H, H-6a); 3.64 (br dd, *J* = 11.5, 5.0 Hz, 1H, H-6b); 3.62 (m, 1H, H-4′); 3.53 (m, 1H, H-2); 3.52−3.49 (m, 2H, H-6a′, H-6b′); 3.47−3.41 (m, 4H, H-3, H-3′, H-5, H-6a″); 3.39−3.31 (m, 5H, H-2′, H-3″, H-4, H-5′, H-5″); 3.30 (s, 3H, OCH_3); 3.20 (ddd, *J* = 10.0, 6.0, 3.5 Hz, 1H, H-2″); 3.05 (ddd, *J* = 13.0, 7.5, 5.5 Hz, 1H, H-6b″); 2.98 (td, *J* = 9.0, 5.5 Hz, 1H, H-2″), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 103.7 (C-1″); 99.7 (C-1″); 89.1 (C-1); 79.6, 79.0 (C-5, C-5′); 75.6, 75.5 (C-3, C-3′); 73.2, 73.1 (C-3″, C-4); 71.9 (C-2″); 71.5 (C-4″); 71.1 (C-5″); 70.5 (2C) (C-2, C-2′); 68.2 (C-4′); 60.4 (C-6′); 60.2 (C-6); 54.6 (OCH_3); 44.7 (C-6″) assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 583 $[M + H]^+$. LRMS (ESI^-): m/z = 580 $[M - H]^-$, 617 $[M + Cl]^-$. HRMS: calcd for $C_{19}H_{35}NO_{17}SNa$ 604.1518, found 604.1515.

Methyl 6-Deoxy-6-*N*-(1-*S*-β-D-maltosyl)-6-sulfonylamino-α-D-glucopyranoside (21c). The title compound **21c** was obtained from compound **21b** according to the general procedure 3 as a white solid (98% yield). R_f = 0.34 (75:25 CH_3CN/H_2O). $[\alpha]^{25}_D$ = +94 (*c* = 1.0, methanol). Mp = 159 °C. ^1H NMR (500 MHz, DMSO-d_6): δ = 6.84 (t, *J* = 6.0 Hz, 1H, N*H*); 5.64 (d, *J* = 2.5 Hz, 1H, O*H*-4′); 5.40 (d, *J* = 6.0 Hz, 1H, O*H*-2′); 5.24 (d, *J* = 5.5 Hz, 1H, O*H*-2); 5.03 (d, *J* = 3.5 Hz, 1H, H-1′); 4.99 (d, *J* = 6.0 Hz, 1H, O*H*-4″); 4.90 (d, *J* = 5.5 Hz, 1H, O*H*-3); 4.87 (d, *J* = 4.5 Hz, 1H); 4.79 (d, *J* = 4.5 Hz, 1H) (O*H*-3′, O*H*-3″); 4.74 (d, *J* = 6.5 Hz, 1H, O*H*-2″); 4.54 (t, *J* = 5.5 Hz, 1H, O*H*-6′); 4.53 (d, *J* = 3.5 Hz, 1H, H-1″); 4.49 (t, *J* = 6.0 Hz, 1H, O*H*-6); 4.27 (d, *J* = 9.0 Hz, 1H, H-1); 3.73 (dd, *J* = 12.0, 6.0 Hz, 1H, H-6a); 3.62 (dd, *J* = 5.5 Hz, 1H, O*H*-3); 3.62 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6a′); 3.59 (m, 1H, H-6b); 3.52 (td, *J* = 7.0, 2.0 Hz, 1H, H-4′); 3.50 (td, *J* = 10.0, 5.5 Hz, 1H, H-2); 3.47−3.42 (m, 3H, H-4, H-6a″, H-6b′); 3.39−3.34 (m, 5H, H-3′, H-3″, H-5, H-5′, H-5″); 3.30 (s, 3H, OCH_3); 3.23 (m, 1H, H-2′), 3.19 (m, 1H, H-2″); 3.06 (m, 1H, H-6b″); 3.03 (m, 1H, H-3); 2.98 (td, *J* = 9.0, 5.5 Hz, 1H, H-4″), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 100.8 (C-1′); 99.7 (C-1″); 89.4 (C-1); 79.3, 78.8 (C-5, C-5′); 76.9 (C-4′); 73.6 (C-4); 73.3, 73.1 (C-3′, C-3″); 72.5 (C-2′); 71.9 (C-2″); 71.6 (C-4″); 71.2 (C-5″); 70.3 (C-2); 70.0 (C-3); 60.9 (C-6′); 60.4 (C-6); 54.7 (OCH_3); 44.7 (C-6″), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 599 $[M + NH_4]^+$, 604 $[M + Na]^+$. HRMS: calcd for $C_{19}H_{35}NO_{17}SNa$ 604.1518, found 604.1495.

***N*-(1-*S*-β-D-Maltosyl)-β-D-maltosylsulfonylamine (22c).** The title compound **22c** was obtained from compound **22b** according to the general procedure 3 as a highly hygroscopic white solid (99% yield). R_f = 0.35 (7:3 CH_3CN/H_2O). $[\alpha]^{25}_D$ = +131 (*c* = 1.0, methanol). ^1H NMR (500 MHz, DMSO-d_6): δ = 5.74 (br s, 1H), 5.67 (br s, 1H), 5.58 (br s, 1H), 5.45 (br s, 2H), 5.38 (br s, 1H) (6 × O*H*); 5.02 (m, 3H, 2 × H-1″, N*H*); 4.91 (br s, 3H, 3 × O*H*); 4.68 (br s), 4.52 (br s, 4H) (5 × O*H*); 4.27 (d, *J* = 7.5 Hz, 1H), 4.26 (d, *J* = 9.0 Hz, 1H) (H-1, H-1′); 3.82 (t, *J* = 8.0 Hz, 1H), 3.76−3.68 (m, 3H), 3.62−3.54 (m, 5H), 3.51 (d, *J* = 7.5 Hz, 1H), 3.48−3.42 (m, 6H), 3.29 (m, 1H), 3.23−3.21 (m, 4H), 3.13 (t, *J* = 7.5 Hz, 1H), 3.06 (br t, *J* = 7.5 Hz, 2H), assignments were confirmed by $^1H-^1H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 100.8 (2C) (2 × C-1″); 100.1 (C-1′); 90.3 (C-1); 79.3, 79.2, 78.9, 77.1, 77.0, 76.6, 73.6, 73.5, 73.3 (2C), 72.5 (3C), 70.2, 69.9 (2C); 60.8 (3C), 60.5 (C-6, C-6′, 2 × C-6″), assignments were confirmed by $^1H-^{13}C$ HSQC. LRMS (ESI^+): m/z = 752 $[M + Na]^+$. HRMS: calcd for $C_{24}H_{43}NO_{22}SNa$ 752.1890, found 752.1884.

Methyl 3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-α,β-D-allopyranoside (24a). Compound **24a** was obtained from compound **1** and amine **12** according to the general procedure 1. Purification by flash chromatography (1:1 acetone/petroleum spirit) afforded **24a** (39% yield) as a light yellow gum. Compound **24a** was used as reagent for general procedure 2 without further purification. R_f = 0.45 (2:1 acetone/hexane). LRMS (ESI^+): m/z = 578 $[M + Na]^+$. HRMS: calcd for $C_{21}H_{33}NO_{14}SNa$ 578.1514, found 578.1534

Methyl 3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-3-sulfonylamino-α,β-D-allopyranoside (24b). Compound **24b** was obtained from compound **24a** according to the general procedure 2. Purification by flash chromatography (1:1 acetone/petroleum spirit) afforded **24a** as a mixture of α- and β-anomers (68% yield; α/β 20:80) as a colorless gum. R_f = 0.26 (1:1 acetone/hexane). ^1H NMR (500 MHz, DMSO-d_6, β-anomer): δ = 7.21 (br s, 1H, N*H*); 5.33 (t, *J* = 9.5 Hz, 1H, H-3); 5.26 (t, *J* = 9.5 Hz, 1H, H-5); 5.19 (d, *J* = 6.0 Hz, 1H, O*H*-2′); 4.96 (t, *J* = 9.5 Hz, 1H, H-4); 4.94 (d, *J* = 10.0 Hz, 1H, H-1); 4.85 (d, *J* = 6.5 Hz, 1H, O*H*-4′); 4.57 (t, *J* = 6.0 Hz, 1H, O*H*-6′); 4.50 (d, *J* = 6.0 Hz, 1H, H-1′); 4.22 (dd, *J* = 12.5, 5.0 Hz, 1H, H-6a); 4.03−3.99 (m, 2H, H-5, H-6b); 3.72 (br s,

1H, H-3′); 3.67−3.57 (m, 2H, H-5′, H-6a′); 3.56 (m, 1H, H-4′); 3.46 (br t, J = 6.0 Hz, 1H, H-2′); 3.41 (m, 1H, H-6b′); 3.34 (s, 3H, OCH_3); 2.01, 1.98, 1.96, 1.95 (4 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.0, 169.5, 169.1, 168.9 (OCOCH$_3$); 101.4 (C-1′); 86.0 (C-1); 76.7 (C-5′); 74.7 (C-5); 73.0 (C-3); 69.3 (C-2′); 67.7 (C-2); 67.5 (C-4); 66.6 (C-4′); 61.4 (C-6); 61.3 (C-6′); 55.5 (OCH_3); 54.6 (C-3′); 20.5, 20.3 (2C), 20.2 (OCOCH_3), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 610 [M + Na]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{16}SNa$ 610.1412, found 610.1386.

Methyl 6-Deoxy-6-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-α-D-mannopyranosyl)-α-D-glucopyranoside (25a). Compound **25a** was obtained from compounds **5** and **10** according to the general procedure 1. Purification by flash chromatography (9:1 CH_2Cl_2/MeOH) afforded **25a** (76% yield) as a light yellow gum. Compound **25a** was used as reagent for general procedure 2 without further purification. R_f = 0.45 (9:1 CH_2Cl_2/MeOH). LRMS (ESI$^+$): m/z = 578 [M + Na]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{14}SNa$ 578.1514, found 578.1497.

Methyl 6-Deoxy-6-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-α-D-mannopyranosyl)-6-sulfonylamino-α-D-glucopyranoside (25b). Compound **25b** was obtained from compound **25a** according to the general procedure 2. Purification by flash chromatography (9:1 CH_2Cl_2/MeOH) afforded **25b** (80% yield) as a light yellow gum. R_f = 0.38 (9:1 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.89 (t, J = 6.0 Hz, 1H, NH); 5.71 (dd, J = 4.0, 1.5 Hz, 1H, H-2); 5.45 (dd, J = 10.0, 4.0 Hz, 1H, H-3); 5.21 (t, J = 10.0 Hz, 1H, H-4); 5.10 (d, J = 1.0 Hz, 1H, H-1); 4.52 (d, J = 3.5 Hz, 1H, H-1′); 4.51 (m, 1H, H-5); 4.16 (dd, J = 12.5, 4.0 Hz, 1H, H-6a); 4.12 (dd, J = 12.5, 2.5 Hz, 1H, H-6b); 3.47 (m, 1H, H-6a′); 3.41−3.36 (m, 2H, H-3′, H-5′); 3.30 (s, 3H, OCH_3); 3.20 (dd, J = 9.5, 3.5 Hz, 1H, H-2′); 3.04 (m, 1H, H-6b′); 2.95 (t, J = 9.5 Hz, 1H, H-4′); 2.13, 2.03, 2.02, 1.94 (4 × s, 12H, OCOCH_3), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.9, 169.4, 169.3, 169.2 (OCOCH$_3$); 99.8 (C-1′); 87.1 (C-1); 73.0 (C-5′); 72.1 (C-5); 71.8 (C-2′); 71.5 (C-4′); 71.2 (C-3′); 68.2 (C-3); 65.9 (C-2); 64.4 (C-4); 61.7 (C-6); 54.6 (OCH_3); 44.3 (C-6′); 20.5, 20.4, 20.3 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 610 [M + Na]$^+$. HRMS: calcd for $C_{21}H_{33}NO_{16}SNa$ 610.1412, found 610.1401.

3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (26a). Compound **26a** was obtained from compounds **1** and **13** according to the general procedure 1. Purification by flash chromatography (1:3 EtOAc/petroleum spirit) afforded the title compound **26a** as a light off-white solid (73% yield). R_f = 0.17 (1:2 EtOAc/petroleum spirit). Mp = 109 °C. $[\alpha]^{25}_D$ = −5 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.79 (d, J = 3.5 Hz, 1H, H-1″); 5.51 (t, J = 9.5 Hz, 1H, H-2); 5.38 (t, J = 9.5 Hz, 1H, H-3); 4.95 (t, J = 10.0 Hz, 1H, H-4); 4.77 (t, J = 4.5 Hz, 1H, H-2″); 4.46 (d, J = 10.0 Hz, 1H, H-1); 4.27 (m, 1H, H-5″); 4.25 (m, 1H, H-6a); 4.04−4.01 (m, 2H, H-5, H-6b); 3.94 (t, J = 7.5 Hz, 1H, H-6a″); 3.82 (t, J = 7.5 Hz, 1H, H-6b″); 3.74 (dd, J = 10.0, 2.0 Hz, 1H, H-4″); 3.59 (d, J = 10.0 Hz, 1H, NH); 3.19 (td, J = 10.0, 50.0 Hz, 1H, H-3″); 2.04, 2.02, 1.97 (3 × s, 12H, OCOCH_3); 1.48, 1.39, 1.34, 1.27 (4 × s, 12H, C(CH_3)$_2$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 170.2, 169.9, 169.5, 169.1 (OCOCH$_3$); 111.1, 108.6 (C(CH$_3$)$_2$); 104.0 (C-1″); 86.1 (C-1); 78.8 (C-2″); 76.6 (C-4″); 74.9 (C-5″); 74.3 (C-5); 73.0 (C-3); 67.6 (C-4); 67.4 (C-2); 66.8 (C-3″); 63.8 (C-6″); 61.7 (C-6); 26.8, 26.6, 26.3, 25.3 (C(CH$_3$)$_2$); 20.5, 20.4, 20.3 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 644 [M + Na]$^+$. HRMS: calcd for $C_{26}H_{39}NO_{14}SNa$ 644.1983, found 644.1953.

3-Deoxy-3-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*-β-D-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-3-sulfonylamino-α-D-allofuranose (26b). Compound **26b** was obtained from compound **26a** according to the general procedure 2. Purification by flash chromatography (1:2 EtOAc/petroleum spirit) afforded the title compound **26b** as a light off-white solid (83% yield). R_f = 0.33 (1:1 EtOAc/petroleum spirit). Mp = 174 °C. $[\alpha]^{25}_D$ = +23 (c = 1.0, chloroform). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.40 (d, J = 9.5 Hz, 1H, NH); 5.80 (d, J = 3.5 Hz, 1H, H-1′); 5.43 (m, 1H, H-3); 5.41 (m, 1H, H-2); 5.00 (t, J = 9.5 Hz, 1H, H-4); 4.96 (d, J = 9.0 Hz, 1H, H-1); 4.66 (t, J = 4.0 Hz, 1H, H-2′); 4.33 (dd, J = 12.5, 4.0 Hz, 1H, H-6a); 4.26 (td, J = 7.0, 2.5 Hz, 1H, H-5′); 4.15 (br td, J = 10.0, 3.0 Hz, 1H, H-5); 4.03 (m, 1H, H-6b); 4.02 (m, 1H, H-4′); 3.92 (t, J = 7.5 Hz, 1H, H-6a′); 3.85 (t, J = 7.5 Hz, 1H, H-6b′); 3.62 (td, J = 9.5, 5.0 Hz, 1H, H-3′); 2.02, 1.98, 1.97, 1.96 (4 × s, 12H, OCOCH_3); 1.49, 1.35, 1.33, 1.27 (4 × s, 12H, C(CH_3)$_2$), assignments were confirmed by ^{1}H−^{1}H gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6): δ = 169.9, 169.5, 169.3, 169.0 (OCOCH$_3$); 111.5, 108.6 (C(CH$_3$)$_2$); 103.8 (C-1′); 85.9 (C-1); 78.6 (C-2′); 76.5 (C-4′); 74.5 (2C) (C-5, C-5′); 72.7 (C-3); 67.6 (C-2); 67.2 (C-4); 63.6 (C-6′); 61.1 (C-6); 55.9 (C-3′); 26.6, 26.5, 26.1, 25.2 (C(CH$_3$)$_2$); 20.5, 20.4, 20.2 (2C) (OCOCH$_3$), assignments were confirmed by ^{1}H−^{13}C HSQC. LRMS (ESI$^+$): m/z = 671 [M + NH$_4$]$^+$, 676 [M + Na]$^+$. HRMS: calcd for $C_{26}H_{39}NO_{16}SNa$ 676.1882, found 676.1871.

3-Deoxy-3-*N*-(1-*S*-β-D-glucopyranosyl)-1,2:5,6-di-*O*-isopropylidene-3-sulfonylamino-α-D-allofuranose (26c). The title compound **26c** was obtained from compound **26b** according to the general procedure 3. The lyophilized compound was obtained as a colorless gum (95% yield). R_f = 0.79 (8:2 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.27 (s, 2H, NH); 5.70 (d, J = 3.5 Hz, 1H, H-1′); 5.16 (d, J = 3.5 Hz, 1H, OH-3); 5.04 (d, J = 5.0 Hz, 1H, OH-4); 4.93 (br s, 1H, OH-2); 4.67 (t, J = 3.5 Hz, 1H, H-2′); 4.38 (t, J = 6.0 Hz, 1H, OH-6); 4.29 (td, J = 7.0, 1.5 Hz, 1H, H-5′); 4.23 (d, J = 8.5 Hz, 1H, H-1); 3.96 (dd, J = 10.0, 1.5 Hz, 1H, H-4′); 3.91 (t, J = 7.5 Hz, 1H, H-6a′); 3.85 (t, J = 7.5 Hz, 1H, H-6b′); 3.68 (dd, J = 10.5, 6.5 Hz, 1H, H-6a); 3.58 (m, 1H, H-3′); 3.53−3.49 (m, 2H, H-2, H-6b); 3.26−3.24 (m, 2H, H-3, H-5); 3.15 (m, 1H, H-4); 1.45, 1.34, 1.27, 1.23 (4 × s, 12H, C(CH_3)$_2$), assignments were confirmed by ^{1}H−^{1}H gCOSY. LRMS (ESI$^+$): m/z = 503 [M + NH$_4$]$^+$, 508 [M + Na]$^+$.

3-Deoxy-3-*N*-(1-*S*-β-D-glucopyranosyl)-1,2-*O*-isopropylidene-3-sulfonylamino-α-D-allofuranose (26d). A suspension of compound **26c** (35 mg, 72.1 μmol) in water (2 mL) was stirred gently overnight in presence of Amberlite IR-120H$^+$ resin (350 mg). The reaction mixture was filtered to remove the resin, and the filtrate was evaporated to dryness in presence of silica. Purification by solid addition flash chromatography (8:2 CH_2Cl_2/MeOH) afforded the title compound **26d** as a colorless gum (20 mg, 44.9 μmol, 63% yield). R_f = 0.13 (8:2 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 7.05 (br s, 1H, NH); 5.65 (d, J = 3.5 Hz, 1H, H-1′); 5.13 (d, J = 4.5 Hz, 1H, OH-3); 5.03 (d, J = 5.0 Hz, 1H, OH-4); 4.87 (br s, 1H, OH-2); 4.83 (br s, 1H, OH-6); 4.66 (4, J = 4.0 Hz, 1H, H-2′); 4.48 (br s, 1H, OH-5′); 4.45 (br t, J = 5.5 Hz, 1H, OH-6′); 4.21 (d, J = 9.5 Hz, 1H, H-1); 3.92 (dd, J = 9.5, 4.0 Hz, 1H, H-3′); 3.88 (dd, J = 10.0, 2.0 Hz, 1H, H-4′); 3.75 (br t, J = 6.5 Hz, 1H, H-6a); 3.69 (ddd, J = 12.0, 6.5, 1.5 Hz, 1H, H-5′); 3.56 (d, J = 9.5 Hz, 1H, H-2); 3.52 (dd, J = 13.0, 5.5 Hz, 1H, H-6b); 3.49 (dd, J = 11.0, 5.0 Hz, 1H, H-6b′); 3.42 (dd, J = 10.5, 7.5 Hz, 1H, H-6b′); 3.26 (td, J = 9.5, 4.0 Hz, 1H, H-3); 3.24 (m, 1H, H-5); 3.15 (td, J = 9.5, 4.5 Hz, 1H, H-4); 1.45, 1.26 (2 × s, 6H, C(CH_3)$_2$), assignments were confirmed by ^{1}H−^{1}H gCOSY. LRMS (ESI$^+$): m/z = 468 [M + Na]$^+$.

3-Deoxy-3-*N*-(1-*S*-β-D-glucopyranosyl)-3-sulfonylamino-α,β-D-allopyranose (26e). Compound **26d** (20 mg, 44.9 μmol) was solubilized in 50% aqueous trifluoroacetic acid (3 mL) and stirred at rt for 24 h. The mixture was evaporated to dryness in the presence of silica. Purification by flash chromatography (85:15 CH_3CN/H_2O) afforded the title compound **26e** as a mixture of α- and β-anomers (13 mg, 32.1 μmol, 72% yield; α/β 70:30) as a light yellow gum. R_f = 0.39 (8:2 CH_3CN/H_2O). ^{1}H NMR (500 MHz, DMSO-d_6, α-anomer): δ = 6.60 (d, J = 9.5 Hz, 1H, NH); 4.96 (br s, 1H, H-1′); 4.28 (d, J = 9.5 Hz, 1H, H-1); 4.01 (td, J = 8.0, 5.0 Hz, 1H, H-3′); 3.81 (m, 1H, H-2′), 3.78−3.19 (m, 7H, H-4′, H-5, H-5′, H-6a, H-6a′, H-6b, H-6b′); 3.50 (m, H-2); 3.28 (t, J = 9.0 Hz, 1H, H-3); 3.01 (t, J = 9.0

Hz, 1H, H-4), assignments were confirmed by $^{1}H-^{1}H$ gCOSY. ^{13}C NMR (125 MHz, DMSO-d_6, α-anomer): δ = 101.2 (C-1′); 86.7 (C-1); 81.3, 81.2 (C-5, C-5′); 77.2 (C-3); 74.3 (C-2′); 72.2 (C-4′); 70.3 (C-2); 69.8 (C-4); 62.0, 61.2 (C-6, C-6′); 54.0 (C-3′), assignments were confirmed by $^{1}H-^{13}C$ HSQC. LRMS (ESI^{+}): m/z = 428 $[M + Na]^{+}$. HRMS: calcd for $C_{12}H_{23}NO_{12}SNa$ 428.0833, found 428.0847.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of compounds **14a**−**17a**, **19a**, **21a**−**23a**, **26a**, **14b**−**26b**, **14c**−**22c**, and **26c**−**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: s.poulsen@griffith.edu.au.

■ ACKNOWLEDGMENT

The Australian Research Council is gratefully acknowledged for financial support (Grant Nos. DP0877554 and LE0237908 to S.-A.P.).

■ REFERENCES

(1) Ernst, B.; Magnani, J. *Nat. Rev. Drug Discov.* **2009**, *8*, 661.
(2) Boltje, T. J.; Buskas, T.; Boons, G.-J. *Nature Chem.* **2009**, *1*, 611.
(3) Williams, N. R.; Davison, B. E.; Ferrier, R. J.; Furneaux, R. H. *Carbohydr. Chem.* **1985**, *17*, 15.
(4) Paterson, D. E.; Griffin, F. K.; Alcaraz, M.-L.; Taylor, R. J. K. *Eur. J. Org. Chem.* **2002**, *7*, 1323.
(5) Turnbull, W. B.; Fascione, M. A.; Stalford, S. A. *Sci. Synth.* **2007**, *29*, 923.
(6) Morais, G. R.; Humphrey, A. J.; Falconer, R. A. *Tetrahedron* **2008**, *64*, 7426.
(7) Tony, K. A.; Denton, R. W.; Dilhas, A.; Jimenez-Barbero, J.; Mootoo, D. R. *Org. Lett.* **2007**, *9*, 1441.
(8) Linek, K.; Alfoldi, J.; Defaye, J. *Carbohydr. Res.* **1993**, *247*, 329.
(9) Jarreton, O.; Skrydstrup, T.; Espinosa, J.-F.; Jimenez-Barbero, J.; Beau, J.-M. *Chem.—Eur. J.* **1999**, *5*, 430.
(10) Micheel, F.; Heinemann, K. H.; Schwieger, K. H.; Frowein, A. *Tetrahedron Lett.* **1965**, *42*, 3769.
(11) Wong, C.-H.; Moris-Varas, F.; Hung, S.-C.; Marron, T. G.; Lin, C.-C.; Gong, K. W.; Weitz-Schmidt, G. *J. Am. Chem. Soc.* **1997**, *119*, 8152.
(12) Postema, M. H. D.; Piper, J. L.; Liu, L.; Shen, J.; Faust, M.; Andreana, P. *J. Org. Chem.* **2003**, *68*, 4748.
(13) Waldscheck, B.; Streiff, M.; Notz, W.; Kinzy, W.; Schmidt, R. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 4007.
(14) Freudenberg, K.; Oertzen, K. *Liebigs Ann. Chem.* **1951**, *574*, 37.
(15) Kawai, Y.; Ando, H.; Ozeki, H.; Koketsu, M.; Ishihara, H. *Org. Lett.* **2005**, *7*, 4653.
(16) Zeitouni, J.; Norsikian, S.; Merlet, D.; Lubineau, A. *Adv. Synth. Catal.* **2006**, *348*, 1662.
(17) Renaudet, O.; Dumy, P. *Tetrahedron Lett.* **2002**, *58*, 2127.
(18) Chakka, N.; Johnston, B. D.; Pinto, B. M. *Can. J. Chem.* **2005**, *83*, 929.
(19) Miquel, N.; Doisneau, G.; Beau, J.-M. *Angew. Chem., Int. Ed.* **2000**, *39*, 4111.
(20) Peri, F.; Deutman, A.; La Ferla, B.; Nicotra, F. *Chem. Commun.* **2002**, 1504.
(21) Fiore, M.; Marra, A.; Dondoni, A. *J. Org. Chem.* **2009**, *74*, 4422.
(22) Czernecki, S.; Randriamandimby, D. *J. Carbohydr. Chem.* **1996**, *15*, 183.
(23) Maijs, L.; Fisers, G.; Tsereteli, I. Y. *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* **1969**, *4*, 496.
(24) Lopez, M.; Drillaud, N.; Bornaghi, L. F.; Poulsen, S.-A. *J. Org. Chem.* **2009**, *74*, 2811.
(25) Lopez, M.; Bornaghi, L. F.; Innocenti, A.; Vullo, D.; Charman, S. A.; Supuran, C. T.; Poulsen, S.-A. *J. Med. Chem.* **2010**, *53*, 2913.
(26) Pfrengle, F.; Reissig, H.-U. *Chem. Soc. Rev.* **2010**, *39*, 549.
(27) Ibatullin, F. M.; Shabalin, K. A.; Jänis, J. V.; Shavvac, A. G. *Tetrahedron Lett.* **2003**, *44*, 7961.
(28) Zemplén, G. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 1254.
(29) Bell, R. H.; Horton, D. *Carbohydr. Res.* **1969**, *9*, 187.
(30) Linek, K.; Alföldi, J.; Defaye, J. *Carbohydr. Res.* **1987**, 195.
(31) Moitessier, N.; Chapleur, Y. *Tetrahedron Lett.* **2003**, *44*, 1731.
(32) Smith, D. A.; Jones, R. M. *Curr. Opin. Drug Disc. Dev.* **2008**, 72.
(33) Perrin, C. L.; Armstrong, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 6825.
(34) Guo, J.; Frost, J. W. *J. Am. Chem. Soc.* **2002**, *124*, 10642.
(35) Reist, E. J.; Spencer, R. R.; Calkins, D. F.; Baker, B. R.; Goodman, L. *J. Org. Chem.* **1965**, *30*, 2312.
(36) Ramirez, J.; Yu, L.; Li, J.; Braunschweiger, P. G.; Wang, P. G. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2575.
(37) Christiansen-Brams, I.; Meldal, M.; Bock, K. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1461.
(38) Baer, H. H.; Gan, Y. *Carbohydr. Res.* **1991**, *210*, 233.
(39) Tronchet, J. M. J.; Poncet, J. *Carbohydr. Res.* **1975**, *42*, 347.