Synthesis of sulfonamide-bridged glycomimetics

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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 ($1\leftrightarrow 1$) and head-to-tail ($1\rightarrow 2$), ($1\rightarrow 3$), ($1\rightarrow 4$) and ($1\rightarrow 6$) sulfonamide-bridged glycomimetics. The synthesis proceeds with retention of configuration at the anomeric centre, 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 towards 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 ($1\leftrightarrow 1$) or head-to-tail ($1\rightarrow 2$), ($1\rightarrow 3$), ($1\rightarrow 4$) and ($1\rightarrow 6$) 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

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. (↗ represents the pyranosyl moiety).

Results and Discussion

Given there is no prior general methodology that provides a common synthetic route to glycomimetics linked via the anomeric centre 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 towards 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 [(sugar)_n-SO₂-NH-(sugar)_n, n ≥ 1]. We first explored the synthesis of (1↔1), (1→2), (1→3), (1→4) and (1→6) sulfonamide-bridged disaccharides, Figure 2.

Figure 2. Target sulfonamide-bridged disaccharides. (↗ represents the pyranosyl moiety).

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 each of per-*O*-acetylated glucosylamine **6**, 2-glucosamine (**7**), 3-amino-glucose (**8**), methyl 4-amino-glucoside (**9**) and methyl 6-amino-glucoside (**10**), Scheme 1. The reaction of thioacetate **1** with amines **6-10** in the presence of diethylbromomalonate 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 standard Zemplén conditions³⁰ 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.

SCHEME 1. Synthesis of (1↔1), (1→2), (1→3), (1→4) and (1→6) sulfonamide-bridged disaccharides.

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. 1-*S*-Acetyl-2,3,4,6-tetra-*O*-acetyl-1-thio- α -D-mannopyranose (**5**) and methyl 3-amino alloside (**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 behaviour of **5** (α -anomer) and **1** (β -anomer) or **12** (axial amine) compared to **8** (equatorial amine), Table 1, entries **6** and **7**.

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 a: X = S, R = Ac; b: X=SO₂, R = Ac; c: X=SO₂, R = H.

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 disulfide²⁹ 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) analog **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.

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 towards 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 glucose 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 ($1\leftrightarrow 1$) and head-to-tail ($1\rightarrow 2$), ($1\rightarrow 3$), ($1\rightarrow 4$) and ($1\rightarrow 6$) 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 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 4 silica plates with visualization of product bands by UV fluorescence ($\lambda = 254$ nm) and charring with orcinol stain (1 g of orcinol monohydrate in a mixture of EtOH:H₂O:H₂SO₄ 72.5:22.5:5). Silica gel flash chromatography was performed using silica gel 60 Å (230-400 mesh). NMR (¹H, ¹³C {¹H}, gCOSY and HSQC) spectra were recorded on a 500 MHz spectrometer at 30 °C. Chemical shifts for ¹H and ¹³C NMR acquired in DMSO-*d*₆ are reported in ppm relative to residual solvent proton ($\delta = 2.50$ ppm) and carbon ($\delta = 39.5$ ppm) signals, respectively. Chemical shifts for ¹H NMR acquired in CDCl₃ are reported in ppm relative to residual solvent proton ($\delta = 7.26$ 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 wave length and a 100 mm cell and reported as an average of ten measurements.

General procedure 1 – Synthesis of glycomimetic sulfenamides. The thioacetate derivative (1.0 equiv.) was solubilized in anhydrous methanol under a nitrogen atmosphere. Diethylbromomalonate (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 diisopropyl ethylamine (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 CH₂Cl₂ and washed with brine. After back extraction of each aqueous phase with CH₂Cl₂ the organic fractions were combined, dried over MgSO₄, 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 CH₂Cl₂. *m*-CPBA (7.0 equiv.) as a solution in CH₂Cl₂ 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 CH₂Cl₂ and quenched with saturated NaHCO₃. The resulting mixture was filtered through celite. After extraction with CH₂Cl₂, the organic layer was washed with saturated NaHCO₃ and brine. The aqueous phases were back extracted with CH₂Cl₂. The organic fractions were combined, dried over MgSO₄, filtered and concentrated. For the remaining sulfonamide compounds no aqueous wash was performed due to 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 allowed to warm to rt and left to stir until full deprotection was evidenced by TLC (30 min - overnight). The reaction mixture was neutralized with Amberlite IR-120 [H⁺], 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). m.p. = 125-127 °C. $[\alpha]_D^{25} = +5$ (c = 1.0, chloroform). ¹H 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, NH); 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 $\times$ s, 24H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.1, 170.0,

169.5, 169.2 (2C), 169.0, 168.9 (OCOCH₃); 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) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): $m/z = 732$ [M + Na]⁺. HRMS: Calcd for C₂₈H₃₉NO₁₈SNa 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). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 6.48 (d, $J = 6.5$ Hz, 0.2H, OH-1''_β); 6.45 (d, $J = 4.5$ Hz, 0.8H, OH-1''_α); 5.37 (t, $J = 9.5$ Hz, 0.8H, H-3_α); 5.28 (t, $J = 9.0$ Hz, 0.2H, H-3_β); 5.21 (br t, $J = 4.0$ Hz, 0.8H, H-1''_α); 5.06 (t, $J = 9.5$ Hz, 0.8H, H-2_α); 4.98 (t, $J = 9.5$ Hz, 0.8H, H-4_α); 4.93 (t, $J = 10.0$ Hz, 0.2H, H-2_β); 4.90 (t, $J = 9.0$ Hz, 0.2H, H-4_β); 4.74 (d, $J = 5.5$ Hz, 0.8H, OH-4''_α); 4.69 (d, $J = 10.5$ Hz, 0.2H, H-1_β); 4.64 (d, $J = 5.0$ Hz, 0.8H, OH-3''_α); 4.46 (d, $J = 4.5$ Hz, 0.2H, OH-3''_β); 4.44 (d, $J = 6.5$ Hz, 0.2H, OH-4''_β); 4.37 (d, $J = 10.0$ Hz, 0.8H, H-1_α); 4.36 (m, 0.2H, H-1'_β); 4.27 (t, $J = 5.5$ Hz, 0.8H, OH-6''_α); 4.13 (dd, $J = 12.5, 5.0$ Hz, 0.2H, H-6_α); 4.05 (m, 1.6H, H-6_α); 3.98 (td, $J = 10.0, 3.0$ Hz, 0.8H, H-5_α); 3.93 (m, 0.2 H, H-5_β); 3.89 (d, $J = 5.0$ Hz, 0.2H, NH_β); 3.66 (dd, $J = 9.5, 5.0$ Hz, 0.2H, H-6_α''); 3.58 (dd, $J = 11.0, 2.0$ Hz, 0.8H, H-6_α''); 3.04 (m, 1H, H-4''); 2.95 (d, $J = 8.5$ Hz, 0.8H, NH_α) (m, 1H, H-5''); 3.45 (m, 1H, H-6''_b); 3.41 (m, 0.2H, H-3''_β); 3.25 (m, 0.8H, H-3''_α); 2.45 (m, 0.8H, H-2''_α); 2.33 (td, $J = 10.0, 5.0$ Hz, 0.2H, H-2''_β); 2.05, 2.04, 2.03, 1.99, 1.98, 1.97, 1.96 (8 × s, 12H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.3, 169.6, 169.5, 169.2 (OCOCH₃); 95.6 (C-1''_β); 91.6 (C-1''_α); 88.7 (C-1_β); 86.8 (C-1_α); 76.6 (C-5_β); 74.3 (C-5_α); 73.3 (C-3_β); 73.0 (C-3_α, C-3''_α, C-

3''_β); 71.8 (C-5_α, C-5''_β); 70.9 (C-4''_α); 70.7 (C-4''_β); 69.1 (C-2''_α, C-2''_β); 68.1 (C-4_α); 67.6 (C-4_β); 67.3 (C-2_α); 66.9 (C-2_β); 61.8 (C-6_α, C-6_β); 61.3 (C-6''_α, C-6''_β); 20.5 (2C), 20.4, 20.3 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): *m/z* = 564 [M + Na]⁺. HRMS: Calcd for C₂₀H₃₁NO₁₄SNa 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). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 6.63 (d, *J* = 6.0 Hz, 0.6H, *OH*-1'_β); 6.27 (d, *J* = 4.5 Hz, 0.4H, *OH*-1'_α); 5.30 (t, *J* = 9.5 Hz, 0.6H, H-3_β); 5.29 (t, *J* = 9.5 Hz, 0.4H, H-3_α); 5.03 (t, *J* = 9.5 Hz, 0.4H, H-2_α); 4.94 (m, 0.4H, H-1_α); 4.92 (m, 1H, H-4_α, H-4_β); 4.91 (t, *J* = 10.0 Hz, 0.6H, H-2_β); 4.71 (d, *J* = 10.0 Hz, 0.6H, H-1_β); 4.65 (d, *J* = 10.0 Hz, 0.4H, H-1_α); 4.64 (d, *J* = 5.0 Hz, 0.6H, *OH*-2'_β); 4.48-4.46 (m, 1.2H, *OH*-6'_β, *OH*-4'_β); 4.38 (d, *J* = 5.5 Hz, 0.4H, *OH*-4'_α); 4.35 (t, *J* = 6.0 Hz, 0.4H, *OH*-6'_α); 4.31 (dd, *J* = 7.5, 6.5 Hz, 0.6H, H-1'_β); 4.15-4.11 (m, 2H, *OH*-2'_α, H-6a_α, H-6a_β, NH_β); 4.05-4.01 (m, 1.9H, H-6b_α, H-6b_β); 3.98-3.92 (m, 1H, H-5_α, H-5_β); 3.81 (d, *J* = 5.0 Hz, 0.4H, NH_α); 3.65 (m, 0.6H, H-6a'_β); 3.58 (m, 1H, H-5'_β, H-6a'_α); 3.43-3.38 (m, 3H, H-2'_α, H-3'_β, H-5'_α, H-6b'_α, H-6b'_β); 3.21-3.16 (m, 1H, H-4'_α, H-4'_β); 3.10 (m, 0.6H, H-2'_β); 2.81 (m, 0.4, H-3'_α); 2.03, 2.02, 2.01, 1.98, 1.95 (6 × s, 12H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆, β-anomer): δ = 170.6, 170.1, 169.8, 169.7 (OCOCH₃); 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) (OCOCH₃), assignments were confirmed by ¹H-¹³C

HSQC. LRMS (ESI⁺): m/z = 564 [M + Na]⁺. HRMS: Calcd for C₂₀H₃₁NO₁₄SNa 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). ¹H 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, OCH₃); 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, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.0, 169.5, 169.3, 169.2 (OCOCH₃); 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 (OCH₃); 20.7, 20.5, 20.3 (2C) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 555 [M + H]⁺, 578 [M + Na]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₄SNa 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 C₂₁H₃₃NO₁₄SNa 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-**

glucopyranosylsulfonamide (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). m.p. = 90-93 °C. $[\alpha]_D^{25}$ = + 4 (c = 1.0, chloroform). ¹H 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 $\times$ s, 24H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.5, 170.0, 169.9, 169.8, 169.6, 169.5, 169.2, 169.1 (OCOCH₃); 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 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 764 [M + Na]⁺. HRMS: Calcd for C₂₈H₃₉NO₂₀SNa 764.1678, Found 764.1653.

2-Deoxy-2-*N*-(2,3,4,6-tetra-*O*-acetyl-1-*S*- β -D-glucopyranosyl)-2-sulfonamino- 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). m.p. = 169-171 °C. ^1H 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 $\times$ s, 12H, OCOCH₃), assignments were confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, DMSO- d_6): δ = 170.2, 169.5, 169.3, 169.1 (OCOCH₃); 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 (OCOCH₃), assignments were confirmed by ^1H - ^{13}C HSQC. LRMS (ESI⁺): m/z = 596 [M + Na]⁺; LRMS (ESI⁻): m/z = 572 [M - H]⁻. HRMS: Calcd for C₂₀H₃₁NO₁₆SNa 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 CH₂Cl₂/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 CH₂Cl₂/MeOH). ^1H 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 $\times$ t, J = 9.5 Hz, 1H, H-2 $_{\alpha}$, H-2 $_{\beta}$); 4.96, 4.95 (2 $\times$ 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 $\times$ 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' $_{\alpha}$, H-4' $_{\alpha}$, 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 $\times$ s, 12H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): $\delta = 170.1, 169.5, 169.1, 168.6$ (OCOCH₃); 97.5 (C-1' $_{\beta}$); 91.7 (C-1' $_{\alpha}$); 85.6, 85.3 (C-1 $_{\alpha}$, 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' $_{\alpha}$, C-4' $_{\beta}$); 67.7 (C-3); 67.6 (C-4); 62.5 (C-3'); 61.7, 61.6 (C-6 $_{\alpha}$, C-6 $_{\beta}$); 61.0, 60.9 (C-6' $_{\alpha}$, C-6' $_{\beta}$); 20.5 (2C), 20.3, 20.2 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): $m/z = 591$ [M + NH₄]⁺, 596 [M + Na]⁺. HRMS: Calcd for C₂₀H₃₁NO₁₆SNa 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). m.p. = 138-140 °C. $[\alpha]^{25}_D = +52$ ($c = 1.0$, chloroform). ¹H NMR (500 MHz, DMSO-*d*₆): $\delta = 7.83$ (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, OCH₃); 3.21 (m, 1H, H-2'); 2.88 (m, 1H, H-4'); 2.03, 1.98, 1.95 (3 $\times$ s, 12H, OCOCH₃), assignments were

confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, DMSO- d_6): δ = 170.1, 169.5, 169.1, 168.6 (OCOCH₃); 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 (OCH₃); 20.5, 20.4, 20.2, 20.2 (OCOCH₃), assignments were confirmed by ^1H - ^{13}C HSQC. LRMS (ESI⁺): m/z = 605 [M + NH₄]⁺, 610 [M + Na]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₆SNa 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). ^1H 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, OCH₃); 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 $\times$ s, 12H, OCOCH₃), assignments were confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, DMSO- d_6): δ = 171.0, 170.4, 170.1, 169.6 (OCOCH₃); 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 (OCH₃); 45.5 (C-6'); 21.0, 20.9, 20.8, 20.7 (OCOCH₃), assignments were confirmed by ^1H - ^{13}C HSQC. LRMS (ESI⁺): m/z = 588 [M + H]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₆SNa 610.1412, Found 610.1413.

***N*-(1-*S*- β -D-Glucopyranosyl)- α,β -D-glucopyranosylsulfonamide (14c).** The title compound **14c** was obtained from compound **14b** according to the general procedure 3. Purification by flash chromatography (9:1 CH₃CN/H₂O) 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 CH₃CN/H₂O). $[\alpha]^{25}_D$ = + 12 (c = 1.0, MeOH). ¹H 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 $_\alpha$, 2 $\times$ 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 $_\alpha$, H-2 $_\beta$, 2 $\times$ H-6 $_\alpha$, H-6 $_\beta$); 3.26-3.18 (m, 2.3 H), 3.10-3.02 (m, 4H) (H-2' $_\alpha$, H-3 $_\alpha$, H-3 $_\beta$, H-3' $_\alpha$, H-3' $_\beta$, H-4 $_\alpha$, H-4 $_\beta$, H-4' $_\alpha$, H-4' $_\beta$, H-5 $_\alpha$, H-5 $_\beta$, H-5' $_\alpha$, H-5' $_\beta$); 2.89 (td, J = 9.0, 4.5 Hz, 0.3H, H-2' $_\beta$), assignments were confirmed by ¹H-¹H gCOSY. ¹³C 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' $_\alpha$, C-5' $_\beta$); 78.4, 76.8, 76.7, 73.1, 72.4, 70.6, 70.5, 69.8, 69.6, (C-2' $_\alpha$, C-3 $_\alpha$, C-3 $_\beta$, C-3' $_\alpha$, C-3' $_\beta$, C-4 $_\alpha$, C-4 $_\beta$, C-4' $_\alpha$, C-4' $_\beta$); 77.3 (C-5 $_\alpha$, C-5 $_\beta$); 74.8 (C-2' $_\beta$); 71.9 (C-2 $_\beta$); 70.3 (C-2 $_\alpha$); 61.2 (2C) (C-6 $_\alpha$, C-6' $_\alpha$); 61.0 (C-6 $_\beta$, C-6' $_\beta$), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 428 [M + Na]⁺. HRMS: Calcd for C₁₂H₂₃NO₁₂SNa 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 CH₃CN/H₂O). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 6.89 (d, J = 9.0 Hz, 0.3H, NH $_{\beta}$); 6.73 (d, J = 5.5 Hz, 0.3H, OH-1 $_{\beta}$); 6.61 (d, J = 8.5 Hz, 0.7H, NH $_{\alpha}$); 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 $\times$ OH $_{\alpha}$, 3 $\times$ OH $_{\beta}$); 4.98-4.96 (m, 1.7H, H-1' $_{\alpha}$, OH-6 $_{\alpha}$, OH $_{\beta}$); 4.89 (d, J = 5.5 Hz, 0.7H), 4.86 (d, J = 6.0 Hz, 0.7H) (2 $\times$ OH $_{\alpha}$); 4.52-4.48 (m, 0.6H, 2 $\times$ OH $_{\beta}$); 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 $_{\alpha}$, 2 $\times$ H-5 $_{\beta}$, H-6 $_{\alpha}$, 2 $\times$ 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 ¹H-¹H gCOSY. ¹³C 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 ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 428 [M + Na]⁺. HRMS: Calcd for C₁₂H₂₃NO₁₂SN_a 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 CH₃CN/H₂O). ¹H 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) ($3 \times OH_{\alpha}$, $3 \times OH_{\beta}$); 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, $OH-6_{\beta}$, $1 \times OH_{\alpha}$, $1 \times OH_{\beta}$); 4.52 (t, $J = 5.5$ Hz, 0.6H, $OH-6_{\beta}$); 4.48 (d, $J = 7.5$ Hz, 0.4H, $1 \times OH_{\alpha}$); 4.41 (m, 0.4H, $1 \times OH_{\alpha}$); 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, $H-6_{\alpha}$, $H-6_{\beta}$); 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, $H-2_{\alpha}$, $H-2_{\beta}$, $2 \times H-6_{\alpha}$, $2 \times H-6_{\beta}$); 3.22 (m, 0.4H, $H-2'_{\alpha}$); 3.21-3.03 (m, 5.4H, $H-2'_{\alpha}$, $H-3_{\alpha}$, $H-3_{\beta}$, $H-4_{\alpha}$, $H-4_{\beta}$, $H-4'_{\alpha}$, $H-4'_{\beta}$, $H-5_{\alpha}$, $H-5_{\beta}$, $H-5'_{\alpha}$, $H-5'_{\beta}$); 3.01 (m, 1H, $H-3'_{\alpha}$, $H-3'_{\beta}$); 2.99-2.97 (m, 0.6H, $H-2'_{\beta}$), assignments were confirmed by 1H - 1H gCOSY. ^{13}C NMR (125 MHz, DMSO- d_6): $\delta = 97.4$ ($C-1'_{\beta}$); 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 ($C-3_{\alpha}$, $C-3_{\beta}$, $C-5_{\alpha}$, $C-5_{\beta}$); 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 ($C-6_{\alpha}$, $C-6_{\beta}$, $C-6'_{\alpha}$, $C-6'_{\beta}$); 59.1 ($C-3'_{\alpha}$), assignments were confirmed by 1H - ^{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). $[\alpha]^{25}_D = +67$ ($c = 1.0$, MeOH). 1H NMR (500 MHz, DMSO- d_6): $\delta = 7.23$ (d, $J = 9.0$ Hz, 1H, NH); 5.07 (br s, 1H, $OH-3$); 5.05 (d, $J = 6.0$ Hz, 1H, $OH-2$); 5.03 (br d, $J = 3.5$ Hz, 1H, $OH-4$); 4.85 (d, $J = 5.0$ Hz, 1H, $OH-2'$); 4.77 (d, $J = 5.5$ Hz, 1H, $OH-3'$); 4.69 (br t, $J = 5.5$ Hz, 1H, $OH-6$ or $OH-6'$); 4.54 (d, $J = 3.5$ Hz, 1H, $H-1'$); 4.44 (br t, $J = 5.0$ Hz, 1H, $OH-6$ or $OH-6'$); 4.33 (d, $J = 10.0$ Hz, 1H, $H-1$); 3.76-3.69 (m, 2H, $H-6_{\alpha}$, $H-6_{\alpha}'$); 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, OCH₃); 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 ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): $\delta = 99.3$ (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 (OCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): $m/z = 437$ [M + NH₄]⁺, 442 [M + Na]⁺. HRMS: Calcd for C₁₃H₂₅NO₁₂SNa 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 CH₃CN/H₂O). $[\alpha]_D^{25} = +49$ ($c = 1.0$, MeOH). ¹H NMR (500 MHz, DMSO-*d*₆): $\delta = 6.78$ (br s, 1H, NH); 5.11 (br s, 2H, OH-2, OH-2'); 5.04 (d, $J = 4.5$ Hz, 1H), 4.98 (d, $J = 5.0$ Hz, 1H) (OH-4, OH-4'); 4.77 (d, $J = 3.5$ Hz, 1H), 4.71 (d, $J = 6.5$ Hz, 1H) (OH-3, OH-3'); 4.52 (d, $J = 3.5$ Hz, 1H, H-1'); 4.47 (t, $J = 6.0$ Hz, 1H, OH-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, OCH₃); 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 ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): $\delta = 99.7$ (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 (OCH₃); 44.7 (C-6'), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): $m/z = 437$ [M + NH₄]⁺, 442 [M + Na]⁺. HRMS: Calcd for C₁₃H₂₅NO₁₂SNa 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). m.p. = 111-113 °C. ^1H NMR (500 MHz, DMSO- d_6 , β -anomer): δ = 6.28 (d, J = 4.5 Hz, 1H, OH-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, OH-4''); 4.70 (d, J = 8.0 Hz, 1H, H-1'); 4.64 (d, J = 4.5 Hz, 1H, OH-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, OH-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, NH); 2.44 (td, J = 9.0, 3.0 Hz, 1H, H-2''); 2.12, 2.11, 2.01, 2.00, 1.90 (5 $\times$ s, 21H, OCOCH₃), assignments were confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, DMSO- d_6): δ = 170.6, 169.8 (2C), 169.5, 169.4, 169.3, 169.0 (OCOCH₃); 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) (OCOCH₃), assignments were confirmed by ^1H - ^{13}C HSQC. LRMS (ESI⁺): m/z = 852 [M + Na]⁺. HRMS: Calcd for C₃₂H₄₇NO₂₂SNa 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 CH₂Cl₂/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 C₃₃H₄₉NO₂₂SNa 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 compound **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). m.p. = 123 °C. $[\alpha]_D^{25}$ = + 54 (c = 1.0, chloroform). ¹H 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, NH); 3.35 (m, 2H, H-3'', H-5''); 3.28 (s, 3H, OCH₃); 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 $\times$ s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.2, 170.1, 170.0, 169.7 (2C), 169.6, 169.3 (OCOCH₃); 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 (OCH₃); 20.7, 20.6, 20.5 (2C), 20.4 (2C), 20.3 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC.

LRMS (ESI⁺): m/z = 844 [M + H]⁺; 866 [M + Na]⁺. HRMS: Calcd for C₃₃H₄₉NO₂₂SNa 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 compound **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). ¹H 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, *NH*); 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, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C 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 (OCOCH₃); 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) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 1287 [M + H]⁺; 1309 [M + Na]⁺. HRMS: Calcd for C₅₂H₇₁NO₃₄SNa 1308.3470, Found 1308.3427.

Methyl 6-deoxy-6-*N*-([(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3,4-tri-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-[(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3-di-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-[(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3-di-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 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, *NH*); 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 $\times$ s, 57H, OCOCH_3). LRMS (ESI $^+$): m/z = 2070 [$\text{M} + \text{H}$] $^+$; 2092 [$\text{M} + \text{Na}$] $^+$. HRMS: Calcd for $\text{C}_{84}\text{H}_{117}\text{NO}_{56}\text{SNa}$ 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 $\text{CH}_2\text{Cl}_2/\text{MeOH}$) afforded **19b** (53% yield, β -anomer) as a white solid. R_f = 0.32 (9:1 $\text{CH}_2\text{Cl}_2/\text{MeOH}$). m.p. = 135-136 $^\circ\text{C}$. ^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, OH-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, OH-4''); 4.96 (d, J = 6.05 Hz, 1H, *NH*); 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, OH-6''); 3.38-3.33 (m, 2H, H-4'', H-5''); 3.21-3.15 (m, 3H, H-2'', H-6a'', OH-1''), 3.962.91(m, 2H, H-3'', H-6b''); 2.11, 2.08, 2.01, 2.00, 1.99, 1.98, 1. (7 $\times$ s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.2, 169.8, 169.6, 169.5, 169.4, 169.3, 169.0 (OCOCH₃); 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 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 879 [M + NH₄]⁺, 884 [M + Na]⁺. HRMS: Calcd for C₃₂H₄₇NO₂₄SN_a 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). m.p. = 114-115 °C. $[\alpha]^{25}_D = + 15$ (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.45 (br s, 1H, NH); 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, OH-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, OH-3''); 4.78 (d, $J = 9.0$ Hz, H-1'); 4.73 (d, $J = 6.5$ Hz, 1H, OH-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, OCH₃); 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 $\times$ s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz,

DMSO-*d*₆): δ = 170.2, 169.9, 169.8, 169.4, 169.3, 169.1, 168.7 (OCOCH₃); 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 (OCH₃); 45.3 (C-6''); 20.6, 20.5, 20.4 (2C), 20.3 (2C), 20.2 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 898 [M + Na]⁺. HRMS: Calcd for C₃₃H₄₉NO₂₄SNa 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). m.p. = 121°C. $[\alpha]_D^{25}$ = + 71 (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 7.47 (br s, 1H, NH); 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, OH-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, OH-3''); 4.72 (d, J = 6.5 Hz, 1H, OH-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, OCH₃); 3.19 (ddd, J = 10.0, 7.0, 4.0 Hz, 1H, H-2''); 3.03 (m, 1H, H-6b''); 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 $\times$ s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 170.1, 170.0, 169.8, 169.6, 169.5, 169.1, 168.8 (OCOCH₃); 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 (OCH₃); 45.2 (C-6''); 20.6, 20.5, 20.4 (2C), 20.3 (2C), 20.2 (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): *m/z* = 898 [M + Na]⁺; LRMS (ESI⁻): *m/z* = 874 [M - H]⁻. HRMS: Calcd for C₃₃H₄₉NO₂₄SNa 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-maltosylsulfonamide (22b).** The title compound **22b** was prepared from sulfenamide **22a** according to the general procedure 2. Purification by flash chromatography (3:2 EtOAc/petroleum spirit) afforded **22b** (53% yield) as a white solid. *R_f* = 0.30 (3:2 EtOAc/hexane). m.p. = 117-119 °C. [α]_D²⁵ = + 77 (*c* = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.04 (br s, 1H, NH); 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, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C 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 (OCOCH₃); 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) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): *m/z* = 1340 [M + Na]⁺. HRMS: Calcd for C₅₂H₇₁NO₃₆SNa 1340.3369, Found 1340.3367.

Methyl 6-deoxy-6-*N*-([(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3,4-tri-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-[(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3-di-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 4)-[(2,3,4-tri-*O*-acetyl- α -D-xylopyranosyl)-(1 $\rightarrow$ 6)]-(2,3-di-*O*-acetyl- β -D-glucopyranosyl)-(1 $\rightarrow$ 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). m.p. = 133-135 °C. ^1H NMR (500 MHz, DMSO- d_6): δ = 7.46 (t, J = 5.5 Hz, 1H, NH); 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 $\times$ s, 57H, OCOCH_3). LRMS (ESI $^+$): m/z = 2124 [$\text{M} + \text{Na}$] $^+$.

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 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$). m.p. = 171 °C (decomposition). ^1H NMR (500 MHz, DMSO- d_6 , α -anomer): δ = 6.58 (d, J = 4.0 Hz, 1H, OH-1''); 6.55 (br s, 1H, NH); 5.39 (d, J = 5.0 Hz, 1H), 5.07 (br s, 1H), 4.99 (br s, 1H) (3 $\times$ OH); 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) ($7 \times OH$); 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): $\delta = 103.7$ (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 C₁₈H₃₃NO₁₇SNa 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 CH₃CN/H₂O). $[\alpha]_D^{25} = +62$ ($c = 1.0$, methanol). 1H NMR (500 MHz, DMSO- d_6 , α -anomer): $\delta = 6.79$ (dd, $J = 6.5, 5.5$ Hz, 1H, *NH*); 5.31 (d, $J = 6.0$ Hz, 1H, *OH*-2); 5.07 (d, $J = 4.0$ Hz, 1H, *OH*-2'); 4.98 (d, $J = 5.5$ Hz, 1H, *OH*-4''); 4.78 (m, 2H), 4.75 (d, $J = 4.0$ Hz, 1H) (*OH*-3, *OH*-3', *OH*-3''); 4.72 (d, $J = 6.5$ Hz, 1H, *OH*-2''); 4.64 (t, $J = 5.0$ Hz, 1H, *OH*-6'); 4.53 (t, $J = 6.0$ Hz, 1H, *OH*-6); 4.53 (d, $J = 3.5$ Hz, 1H, H-1''); 4.49 (d, $J = 5.0$ Hz, 1H, *OH*-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, OCH₃); 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, $\text{DMSO-}d_6$): 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 $[\text{M} + \text{H}]^+$; LRMS (ESI^-): m/z = 580 $[\text{M} - \text{H}]^-$, 617 $[\text{M} + \text{Cl}]^-$. HRMS: Calcd for $\text{C}_{19}\text{H}_{35}\text{NO}_{17}\text{SNa}$ 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 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$). $[\alpha]_D^{25} = +94$ (c = 1.0, methanol). m.p. = 159 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ = 6.84 (t, J = 6.0 Hz, 1H, NH); 5.64 (d, J = 2.5 Hz, 1H, OH-4'); 5.40 (d, J = 6.0 Hz, 1H, OH-2'); 5.24 (d, J = 5.5 Hz, 1H, OH-2); 5.03 (d, J = 3.5 Hz, 1H, H-1'); 4.99 (d, J = 6.0 Hz, 1H, OH-4''); 4.90 (d, J = 5.5 Hz, 1H, OH-3); 4.87 (d, J = 4.5 Hz, 1H); 4.79 (d, J = 4.5 Hz, 1H) (OH-3', OH-3''); 4.74 (d, J = 6.5 Hz, 1H, OH-2''); 4.54 (t, J = 5.5 Hz, 1H, OH-6'); 4.53 (d, J = 3.5 Hz, 1H, H-1''); 4.49 (t, J = 6.0 Hz, 1H, OH-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, OH-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, $\text{DMSO-}d_6$): 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 + NH₄]⁺, 604 [M + Na]⁺. HRMS: Calcd for C₁₉H₃₅NO₁₇SNa 604.1518, Found 604.1495.

***N*-(1-*S*-β-*D*-Maltosyl)-β-*D*-maltosylsulfonamide (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 CH₃CN/H₂O). $[\alpha]^{25}_{\text{D}}$ = + 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 × OH); 5.02 (m, 3H, 2 × H-1'', NH); 4.91 (br s, 3H, 3 × OH); 4.68 (br s), 4.52 (br s, 4H) (5 × OH); 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 C₂₄H₄₃NO₂₂SNa 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 C₂₁H₃₃NO₁₄SNa 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, *NH*); 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, *OH*-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, *OH*-4'); 4.57 (t, J = 6.0 Hz, 1H, *OH*-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 $\times$ s, 12H, *OCOCH*₃), assignments were confirmed by ^1H - ^1H 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 ^1H - ^{13}C HSQC. LRMS (ESI⁺): m/z = 610 [*M* + Na]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₆SNa 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 CH₂Cl₂/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 CH₂Cl₂/MeOH). LRMS (ESI⁺): m/z = 578 [*M* + Na]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₄SNa 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 CH₂Cl₂/MeOH) afforded **25b** (80% yield) as a light yellow gum. R_f = 0.38 (9:1 CH₂Cl₂/MeOH). ¹H 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, OCH₃); 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 $\times$ s, 12H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 169.9, 169.4, 169.3, 169.2 (OCOCH₃); 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 (OCH₃); 44.3 (C-6'); 20.5, 20.4, 20.3 (2C) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): m/z = 610 [M + Na]⁺. HRMS: Calcd for C₂₁H₃₃NO₁₆SNa 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). m.p. = 109 °C. $[\alpha]_D^{25}$ = - 5 (c = 1.0, chloroform). ¹H 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 ($3 \times s$, 12H, OCOCH_3); 1.48, 1.39, 1.34, 1.27 ($4 \times s$, 12H, $\text{C}(\text{CH}_3)_2$), assignments were confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): $\delta = 170.2, 169.9, 169.5, 169.1$ (OCOCH_3); 111.1, 108.6 ($\text{C}(\text{CH}_3)_2$); 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 ($\text{C}(\text{CH}_3)_2$); 20.5, 20.4, 20.3 (2C) (OCOCH_3), assignments were confirmed by ^1H - ^{13}C HSQC. LRMS (ESI⁺): $m/z = 644$ [$\text{M} + \text{Na}$]⁺. HRMS: Calcd for $\text{C}_{26}\text{H}_{39}\text{NO}_{14}\text{SNa}$ 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). m.p. = 174 °C. $[\alpha]_D^{25} = +23$ ($c = 1.0$, chloroform). ^1H NMR (500 MHz, $\text{DMSO}-d_6$): $\delta = 7.40$ (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 ($4 \times s$, 12H, OCOCH_3); 1.49, 1.35, 1.33, 1.27 ($4 \times s$, 12H, $\text{C}(\text{CH}_3)_2$), assignments were confirmed by ^1H - ^1H gCOSY. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): $\delta = 169.9, 169.5, 169.3, 169.0$ (OCOCH_3); 111.5, 108.6 ($\text{C}(\text{CH}_3)_2$); 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 ($\text{C}(\text{CH}_3)_2$);

20.5, 20.4, 20.2 (2C) (OCOCH₃), assignments were confirmed by ¹H-¹³C HSQC. LRMS (ESI⁺): *m/z* = 671 [M + NH₄]⁺, 676 [M + Na]⁺. HRMS: Calcd for C₂₆H₃₉NO₁₆SNa 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 CH₂Cl₂/MeOH). ¹H 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(CH₃)₂), assignments were confirmed by ¹H-¹H gCOSY. LRMS (ESI⁺): *m/z* = 503 [M + NH₄]⁺, 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, the filtrate was evaporated to dryness in presence of silica. Purification by solid addition flash chromatography (8:2 CH₂Cl₂/MeOH) afforded the title compound **26d** as a colorless gum (20 mg, 44.9 μmol, 63% yield). *R_f* = 0.13 (8:2 CH₂Cl₂/MeOH). ¹H 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 ($2 \times$ s, 6H, C(CH₃)₂), assignments were confirmed by ¹H-¹H 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 μ mol) was solubilized in 50% aqueous trifluoroacetic acid (3 mL) and stirred at rt for 24h. The mixture was evaporated to dryness in the presence of silica. Purification by flash chromatography (85:15 CH₃CN/H₂O) afforded the title compound **26e** as a mixture of α - and β -anomers (13 mg, 32.1 μ mol, 72% yield; α/β 70:30) as a light yellow gum. $R_f = 0.39$ (8:2 CH₃CN/H₂O). ¹H NMR (500 MHz, DMSO-*d*₆, α -anomer): $\delta = 6.60$ (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 ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-*d*₆, α -anomer): $\delta = 101.2$ (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 ¹H-¹³C HSQC. LRMS (ESI⁺): $m/z = 428$ [M + Na]⁺. HRMS: Calcd for C₁₂H₂₃NO₁₂SNa 428.0833, Found 428.0847.

Acknowledgment

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

Supporting Information Available

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

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