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→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 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. 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. 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. 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. 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. 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.
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\(^2\)\(^-\)\(^25\), 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 \([(\text{sugar})_n\text{-SO}_2\text{-NH-}(\text{sugar})_n, n \geq 1]\). We first explored the synthesis of \((1\leftrightarrow1), (1\rightarrow2), (1\rightarrow3), (1\rightarrow4)\) and \((1\rightarrow6)\) sulfonamide-bridged disaccharides, Figure 2.

![Figure 2. Target sulfonamide-bridged disaccharides. (\(\overset{\circ}{\text{O}}\) represents the pyranosyl moiety).](image-url)
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.\textsuperscript{26,27} Specifically, we examined the reaction of 1-S-acetyl-2,3,4,6-tetra-O-acetyl-1-thio-\(\beta\)-D-glucopyranose (1) with each of per-\(O\)-acylated 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 conditions\textsuperscript{30} 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 \((1\rightarrow 1), (1\rightarrow 2), (1\rightarrow 3), (1\rightarrow 4)\) and \((1\rightarrow 6)\) 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 \(\alpha-, \beta-,\) equatorial or axial, had implications to the generality of
this method. 1-S-Acetyl-2,3,4,6-tetra-O-acetyl-1-thio-\(\alpha\)-\(\alpha\)-mannopyranose (5) and methyl 3-amino alloside (12) allowed the effect of an \(\alpha\)-anomer of the thioacetate and an axial amine to be assessed, respectively. There were no notable differences in reaction behaviour of 5 (\(\alpha\)-anomer) and 1 (\(\beta\)-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.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product$^a$</th>
<th>Yield$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 and 7</td>
<td><img src="image1.png" alt="Image" /></td>
<td>19a (68%)</td>
</tr>
<tr>
<td>2</td>
<td>2 and 10</td>
<td><img src="image2.png" alt="Image" /></td>
<td>19b (53%), 19c (94%)</td>
</tr>
<tr>
<td>3</td>
<td>3 and 10</td>
<td><img src="image3.png" alt="Image" /></td>
<td>20a (84%)</td>
</tr>
<tr>
<td>4</td>
<td>3 and 11</td>
<td><img src="image4.png" alt="Image" /></td>
<td>20b (72%), 20c (98%)</td>
</tr>
<tr>
<td>5</td>
<td>4 and 10</td>
<td><img src="image5.png" alt="Image" /></td>
<td>21a (75%)</td>
</tr>
<tr>
<td>6</td>
<td>1 and 12</td>
<td><img src="image6.png" alt="Image" /></td>
<td>21b (87%), 21c (98%)</td>
</tr>
<tr>
<td>7</td>
<td>5 and 10</td>
<td><img src="image7.png" alt="Image" /></td>
<td>22a (23%), 22b (53%), 22c (99%)</td>
</tr>
<tr>
<td>8</td>
<td>4 and 11</td>
<td><img src="image8.png" alt="Image" /></td>
<td>23a (60%), 23b (59%)</td>
</tr>
<tr>
<td>9</td>
<td>3 and 12</td>
<td><img src="image9.png" alt="Image" /></td>
<td>24a (39%), 24b (68%)</td>
</tr>
<tr>
<td>10</td>
<td>5 and 11</td>
<td><img src="image10.png" alt="Image" /></td>
<td>25a (76%), 25b (80%)</td>
</tr>
</tbody>
</table>
a: $X = S, \, R = \text{Ac}; \, b: X = \text{SO}_2, \, R = \text{Ac}; \, c: X = \text{SO}_2, \, R = \text{H}.$

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 disulfide\textsuperscript{29} and (ii) a diglycosylamine (possible only from amino sugars 6 and 11).\textsuperscript{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.\textsuperscript{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-\alpha-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 glycoso 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, 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 (\(\lambda = 254\) nm) and charring with orcinol stain (1 g of orcinol monohydrate in a mixture of EtOH:H\(_2\)O:H\(_2\)SO\(_4\) 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 (\(\delta = 2.50\) ppm) and carbon (\(\delta = 39.5\) ppm) signals, respectively. Chemical shifts for \(^1\)H NMR acquired in CDCl\(_3\) 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.

![Diagram of sugar structures](image)

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.**

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. Rf = 0.24 (1:1 EtOAc/hexane). m.p. = 125-127 °C. [α]_{D}^{25} = + 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, 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 (dd, $J = 10.0$ 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, OCOCH$_3$), 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 (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 $^1$H-$^{13}$C 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). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ = 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-3a); 5.28 (t, $J = 9.0$ Hz, 0.2H, H-3p); 5.21 (br t, $J = 4.0$ Hz, 0.8H, H-1”α); 5.06 (t, $J = 9.5$ Hz, 0.8H, H-2a); 4.98 (t, $J = 9.5$ Hz, 0.8H, H-4a); 4.93 (t, $J = 10.0$ Hz, 0.2H, H-2p); 4.90 (t, $J = 9.0$ Hz, 0.2H, H-4p); 4.74 (d, $J = 5.5$ Hz, 0.8H, OH-4”α); 4.69 (d, $J = 10.5$ Hz, 0.2H, H-1p); 4.64 (d, $J = 5.0$ Hz, 0.8H, OH-3”a); 4.46 (d, $J = 4.5$ Hz, 0.2H, OH-3”p); 4.44 (d, $J = 6.5$ Hz, 0.2H, OH-4”p); 4.37 (d, $J = 10.0$ Hz, 0.8H, H-1a); 4.36 (m, 0.2H, H-1’β); 4.27 (t, $J = 5.5$ Hz, 0.8H, OH-6”a); 4.13 (dd, $J = 12.5$, 5.0 Hz, 0.2H, H-6aβ); 4.05 (m, 1.6H, H-6a); 3.98 (td, $J = 10.0$, 3.0 Hz, 0.8H, H-5a); 3.93 (m, 0.2 H, H-5p); 3.89 (d, $J = 5.0$ Hz, 0.2H, NHp); 3.66 (dd, $J = 9.5$, 5.0 Hz, 0.2H, H-6a’β); 3.58 (dd, $J = 11.0$, 2.0 Hz, 0.8H, H-6a”a); 3.04 (m, 1H, H-4”’); 2.95 (d, $J = 8.5$ Hz, 0.8H, NHa) (m, 1H, H-5”); 3.45 (m, 1H, H-6”b); 3.41 (m, 0.2H, H-3”p); 3.25 (m, 0.8H, H-3”a); 2.45 (m, 0.8H, H-2”a); 2.33 (td, $J = 10.0$, 5.0 Hz, 0.2H, H-2”p); 2.05, 2.04, 2.03, 1.99, 1.98, 1.97, 1.96 (8 × s, 12H, OCOCH₃), assignments were confirmed by $^1$H-$^1$H gCOSY. $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta$ = 170.3, 169.6, 169.5, 169.2 (OCOCH₃); 95.6 (C-1”p); 91.6 (C-1”a); 88.7 (C-1β); 86.8 (C-1α); 76.6 (C-5p); 74.3 (C-5a); 73.3 (C-3β); 73.0 (C-3α, C-3”a, 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 (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. Rᵢ = 0.16 (5:2 acetone/petroleum spirit). ¹H NMR (500 MHz, DMSO-ｄ₆): 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\'\gamma); 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, NH₂); 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, NH₂); 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\'\beta, 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, OCOCH₃), assignments were confirmed by ¹H-¹³C gCOSY. ¹³C NMR (125 MHz, DMSO-ｄ₆, 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 C\(_{20}\)H\(_{31}\)NO\(_4\)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). \([\alpha]^{25}\) = + 22 (c = 1.0, chloroform). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 5.30\) (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, 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-\(d_6\)): \(\delta = 170.0, 169.5, 169.3, 169.2\) (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\(_4\)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.

\[ \text{N-(2,3,4,6-Tetra-O-acetyl-1-S-\(\beta\)-d-glucopyranosyl)-2,3,4,6-tetra-O-acetyl-\(\beta\)-d-glucopyranosylsulfonylamine (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). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) = 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, OCOCH₃), assignments were confirmed by \(^1\)H-\(^1\)H gCOSY. \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) = 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 \(^1\)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.

\[ \text{2-Deoxy-2-N-(2,3,4,6-tetra-O-acetyl-1-S-\(\beta\)-d-glucopyranosyl)-2-sulfonylamino-\(\alpha,\beta\)-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 \(\alpha\) and \(\beta\) anomers (\(\alpha/\beta\) 85:15) as a white solid. R_f = 0.39 (2:1
acetone/toluene). m.p. = 169-171 °C. \(^1\)H NMR (500 MHz, DMSO-\(d_6\), \(\beta\)-anomer): \(\delta = 6.71\) (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, \(J = 9.5\) Hz, 1H, H-2'); 4.20, 1.98, 1.97, 1.96 (8 × s, 12H, OCOC\(\text{H}_3\)), assignments were confirmed by \(^1\)H-\(^1\)H gCOSY. \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta = 170.2, 169.5, 169.3, 169.1\) (O\(\text{C}\)O\(\text{CH}_3\)); 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 (OCOC\(\text{H}_3\)), 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\(_{16}\)Na 596.1256, Found 596.1245.

3-Deoxy-3-N-(2,3,4,6-tetra-O-acetyl-1-\(\beta\)-D-glucopyranosyl)-3-sulfonlamino-\(\alpha\),\(\beta\)-D-glucopyranose (16b). Compound 16b was obtained from compound 16a according to the general procedure 2. Purification by flash chromatography (92:8 CH\(_2\)Cl\(_2\)/MeOH) afforded 16b (79% yield) as a mixture of \(\alpha\) and \(\beta\) anomers (\(\alpha/\beta\) 50:50) as a colorless gum. \(R_f = 0.19\) (92:8 CH\(_2\)Cl\(_2\)/MeOH). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta = 7.65\) (d, \(J = 7.5\) Hz, 0.5H, NH\(\alpha\)); 7.53 (d, \(J = 7.0\) Hz, 0.5H, NH\(\beta\)); 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,
O\textsubscript{H-6}'); 4.30 (t, \(J = 6.5\) Hz, 0.5H, H-1'\textsubscript{β}); 4.23-4.20 (m, 1H, H-6a\textsubscript{α}, H-6a\textsubscript{β}); 4.18 (d, \(J = 7.5\) Hz, 0.5H, O\textsubscript{H}) 4.08, 4.05 (2 × dd, \(J = 10.0, 2.0\) Hz, 1H, H-6b\textsubscript{α}, H-6b\textsubscript{β}); 4.06-3.96 (m, 1H, H-5\textsubscript{α}, H-5\textsubscript{β}); 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'\textsubscript{α}); 3.23-3.18 (m, 1.5H, H-2'\textsubscript{α}, H-2'\textsubscript{β}, H-3'\textsubscript{β}); 3.10-3.07 (m, 0.5H, H-5'); 3.01-2.98 (m, 1H, H-2'\textsubscript{β}, H-3'\textsubscript{β}); 2.02, 1.98, 1.96, 1.95, 1.94 (5 × s, 12H, OCO\textsubscript{CH\textsubscript{3}}), assignments were confirmed by \textsuperscript{1}H-\textsuperscript{1}H gCOSY. \textsuperscript{13}C NMR (125 MHz, DMSO-\textsubscript{d}\textsubscript{6}): \(δ = 170.1, 169.5, 169.1, 168.6\) (OCO\textsubscript{CH\textsubscript{3}}); 97.5 (C-1'\textsubscript{β}); 91.7 (C-1'\textsubscript{α}); 85.6, 85.3 (C-1\textsubscript{α}, C-1\textsubscript{β}); 77.6 (C-5'); 74.6 (C-5); 73.3 (C-2); 72.4 (C-2'); 69.0, 68.9 (C-4'\textsubscript{α}, C-4'\textsubscript{β}); 67.7 (C-3); 67.6 (C-4); 62.5 (C-3'); 61.7, 61.6 (C-6\textsubscript{α}, C-6\textsubscript{β}); 61.0, 60.9 (C-6'\textsubscript{α}, C-6'\textsubscript{β}); 20.5 (2C), 20.3, 20.2 (OCO\textsubscript{CH\textsubscript{3}}), assignments were confirmed by \textsuperscript{1}H-\textsuperscript{13}C HSQC. LRMS (ESI\textsuperscript{+}): \(m/z = 591\) [M + NH\textsubscript{4}]\textsuperscript{+}, 596 [M + Na]\textsuperscript{+}. HRMS: Calcd for C\textsubscript{20}H\textsubscript{31}NO\textsubscript{16}SNa 596.1256, Found 596.1255.

**Methyl 4-deoxy-4-N-(2,3,4,6-tetra-O-acetyl-1-\textbeta-D-glucopyranosyl)-4-sulfonylamino-\alpha-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. [α]\textsuperscript{25}\textsubscript{D} = + 52 (c = 1.0, chloroform). \textsuperscript{1}H NMR (500 MHz, DMSO-\textsubscript{d}\textsubscript{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\textsubscript{3}); 3.21 (m, 1H, H-2'); 2.88 (m, 1H, H-4'); 2.03, 1.98, 1.95 (3 × s, 12H, OCO\textsubscript{CH\textsubscript{3}}), assignments were
confirmed by $^1$H-$^1$H gCOSY. $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta = 170.1$, 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-$\beta$-D-glucopyranosyl)-6-sulfonylamino-$\alpha$-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). $[\alpha]_{D}^{25} = +21$ ($c = 1.0$, chloroform). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta = 7.43$ (br s, 1H, N$H$); 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 $\times$ s, 12H, OCOCH$_3$), assignments were confirmed by $^1$H-$^1$H gCOSY. $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta = 171.0$, 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 CH₃CN/H₂O) afforded 14c as a mixture of α and β anomers (72% yield, α/β 70:30) as a clear oil. Rᵣ= 0.15 (85:15 CH₃CN/H₂O). [α]²⁵D = +12 (c = 1.0, MeOH). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.53 (d, J = 6.5 Hz, 0.7H, NH₃); 6.17 (d, J = 4.5 Hz, 0.3H, NH₆); 5.12 (d, J = 5.0 Hz, 0.7H, OHA); 5.08 (d, J = 5.0 Hz, 0.3H, OHB); 5.05 (d, J = 4.5 Hz, 0.7H, OHA); 5.03 (d, J = 6.0 Hz, 0.7H, OHA); 4.98 (d, J = 4.5 Hz, 0.3H, OHB); 4.90 (t, J = 5.0 Hz, 0.7H, H-1 '); 4.80 (d, J = 7.0 Hz, 0.7H, OH-2 α); 4.78 (d, J = 4.5 Hz, 0.7H, OHA); 4.72 (d, J = 5.5 Hz, 0.3H, OHB); 4.62 (t, J = 6.0 Hz, 0.3H, OH-6 δ); 4.58 (d, J = 4.5 Hz, 0.3H, OHB); 4.49 (d, J = 5.5 Hz, 0.7H, OHA); 4.47 (d, J = 5.5 Hz, 0.7H, OHA); 4.44 (t, J = 6.0 Hz, 0.7H, OH-6 α); 4.40 (d, J = 6.5 Hz, 0.7H, OHB); 4.32 (t, J = 6.0 Hz, 0.3H, OH-6 δ); 4.27 (dd, J = 7.5, 6.5 Hz, 0.3H, H-1' β); 4.24 (d, J = 5.5 Hz, 0.3H, OHB); 4.21 (d, J = 9.5 Hz, 0.3H, H-1 β); 4.05 (d, J = 9.5 Hz, 0.7H, H-1 α); 3.70-3.66 (m, 1.3H, H-6 α, 2 × H-6 β); 3.58 (ddd, J = 11.5, 5.5, 2.5 Hz, 0.3H, H-6 δ); 3.53 (dd, J = 13.0, 1.5 Hz, 0.7H, H-6 α); 3.48-3.40 (m, 2.7H, H-2 α, H-2 β, 2 × H-6 α, H-6 δ); 3.26-3.18 (m, 2.3 H), 3.10-3.02 (m, 4H) (H-2' α, H-3 α, H-3 β, H-3' α, H-3' δ, H-4 α, H-4 δ, H-4' α, H-4' δ, H-5 α, H-5 δ, H-5' α, H-5' δ); 2.89 (td, J = 9.0, 4.5 Hz, 0.3H, H-2' δ), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-d₆): δ = 96.9 (C-1' β); 92.2 (C-1' α); 90.5 (C-1 β); 84.6 (C-1 α); 81.0 (C-5' α, C-5' β); 78.4, 76.8, 76.7, 73.1, 72.4, 70.6, 70.5, 69.8, 69.6, (C-2' α, C-3 α, C-3 δ, C-3' α, C-3' δ, C-4 α, C-4 δ, C-4' α, C-4' δ); 77.3 (C-5 α, C-5 δ); 74.8 (C-2' β); 71.9 (C-2 δ); 70.3 (C-2 α); 61.2 (2C) (C-6 α, C-6' α); 61.0 (C-6 δ, C-6' δ), assignments were confirmed by ¹H-¹³C HSQ. 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. Rf = 0.16 (95:5 CH3CN/H2O). 1H NMR (500 MHz, DMSO-d6): δ = 6.89 (d, J = 9.0 Hz, 0.3H, NHβ); 6.73 (d, J = 5.5 Hz, 0.3H, OH-1β); 6.61 (d, J = 8.5 Hz, 0.7H, NHα); 6.58 (d, J = 4.5 Hz, 0.7H, OH-1α); 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 × OHα, 3 × OHβ); 4.98-4.96 (m, 1.7H, H-1′α, OH-6α, OHβ); 4.89 (d, J = 5.5 Hz, 0.7H), 4.86 (d, J = 6.0 Hz, 0.7H) (2 × OHα); 4.52-4.48 (m, 0.6H, 2 × OHβ); 4.42-4.37 (m, 1.3H, H-1′β, H-1β, OH-6α); 4.30 (m, 0.3H, OH-6β); 4.29 (d, J = 9.5 Hz, 0.7H, H-1α); 3.74 (m, 0.7H, H-6α); 3.68 (m, 0.3H, H-6β); 3.60 (m, 1H, H-6αβ); 3.55 (m, 0.7H, H-5α); 3.51-3.42 (m, 3.6H, H-2αβ, H-5α, 2 × H-5β, H-6α, 2 × H-6β); 3.26-3.23 (m, 2.1H), 3.13-3.00 (m, 2.3H) (H-3αβ, H-3′αβ, H-4αβ, H-4′αβ, H-6α); 3.21 (t, J = 10.0 Hz, 0.3H, H-3′β); 3.13 (m, 0.7H, H-2′α); 2.87 (q, J = 9.0 Hz, 0.3H, H-2′β), assignments were confirmed by 1H-1H gCOSY. 13C NMR (125 MHz, DMSO-d6): δ = 95.6 (C-1′β); 91.9 (C-1′α); 90.5 (C-1α); 89.5 (C-1β); 81.5, 80.7, 77.9, 77.2, 76.5, 74.5, 72.0, 70.9 (2C), 70.8, 70.1, 69.6 (C-2αβ, C-3αβ, C-3′αβ, C-4αβ, C-4′αβ, C-5αβ, C-5′αβ); 61.7 (C-2′β); 61.2, 61.0 (C-6αβ, C-6′αβ); 58.7 (C-2′α), assignments were confirmed by 1H-13C HSQC. LRMS (ESI+): m/z = 428 [M + Na]⁺. HRMS: Calcd for C12H23NO12SNa 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). Rf = 0.14 (85:15 CH3CN/H2O). 1H NMR (500 MHz, DMSO-d6): δ = 7.04 (d, J
= 7.0 Hz, 0.6H, NH$_\beta$); 6.99 (d, J = 7.5 Hz, 0.4H, NH$_\alpha$); 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$_\alpha$, 3 × 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$_\beta$); 4.70-4.67 (m, 1.4H, OH-6$_\beta$, 1 × OH$_\alpha$, 1 × OH$_\beta$); 4.52 (t, J = 5.5 Hz, 0.6H, OH-6$_\beta$); 4.48 (d, J = 7.5 Hz, 0.4H, 1 × OH$_\alpha$); 4.41 (m, 0.4H, 1 × 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 × H-6$_\alpha$, 2 × H-6$_\beta$); 3.22 (m, 0.4H, H-2’$_\alpha$); 3.21-3.03 (m, 5.4H, 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 $^1$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$_\alpha$, 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$_\alpha$); 68.9 (C-4$_\beta$); 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 $^1$H-$^{13}$C HSQC. LRMS (ESI$^+$): m/z = 428 [M + Na]$^+$. HRMS: Calcd for C$_{12}$H$_{23}$NO$_7$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$_2$Cl$_2$/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, 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-6a, H-6a’); 3.56 (t d, J = 9.0, 5.5 Hz, 1H, H-
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). Rf = 0.15 (9:1 CH3CN/H2O). [α]25D = + 49 (c = 1.0, MeOH). 1H NMR (500 MHz, DMSO-d6): δ = 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-d6): 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 (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.

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. Rf = 0.22 (1:1 acetone/hexane). m.p. = 111-113 °C. 1H NMR (500 MHz, DMSO-d6, 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, 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, H-2’); 4.22 (br t, J = 12.0 Hz, 1H, H-5’); 4.05-3.99 (m, 3H, H-6a, H-6b, H-6b’); 3.88-3.31 (m, 2H, H-5, C-6a); 3.10 (m, 1H, H-5’); 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, OCOCH3), assignments were confirmed by 1H-1H gCOSY. 13C NMR (125 MHz, DMSO-d6): 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-13C HSQC. LRMS (ESI+): m/z = 852 [M + Na]+. HRMS: Caled 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. [α]_25 D = + 54 (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-d₆): 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 × s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-d₆): 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.

\( N-(2,2',3,3',4,6,6''\text{-hepta-O-acetyl-1-S-\(\beta\)-d-maltosyl})-2',2'',3',3'',4'',6''\text{-hepta-O-acetyl-\(\beta\)-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. Rₚ = 0.31 (2:1 EtOAc/hexane). ^1H NMR (500 MHz, DMSO-d₆): 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-d₆): 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→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, OCOC\(_3\)H\(_3\)). 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\(_2\)Cl\(_2\)/MeOH) afforded 19b (53% yield, β-anomer) as a white solid. \( R_f = 0.19 \) (9:1 CH\(_2\)Cl\(_2\)/MeOH). m.p. = 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, 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 x s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-d₆): 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 C₃₂H₄₇NO₂₄SNa 884.2101, Found 884.2113.

Methyl 6-deoxy-6-N-(2’,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. [α]²⁵_D = + 15 (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-d₆): 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 x s, 21H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz,
DMSO-\textit{d}_6): \delta = 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 \textsuperscript{1}H-\textsuperscript{13}C HSQC. LRMS (ESI\textsuperscript{+}): \textit{m/z} = 898 [M + Na]\textsuperscript{+}. 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-\beta-d-maltosyl)-6-sulfonylamino-\alpha-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\textsubscript{f} = 0.30 (3:1 acetone/hexane). m.p. = 121°C. [\alpha]^{25}_{D} = +71 (c = 1.0, chloroform). \textsuperscript{1}H NMR (500 MHz, DMSO-\textit{d}_6): \delta = 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, O\textit{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\textit{H}-3’’); 4.72 (d, J = 6.5 Hz, 1H, O\textit{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 \times s, 21H, OCOCH_3), assignments were confirmed by \textsuperscript{1}H-\textsuperscript{1}H gCOSY. \textsuperscript{13}C NMR (125 MHz, DMSO-\textit{d}_6): \delta = 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 (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 C₁₃H₄₀NO₂₄SNa 898.2257, Found 898.2270.

N-(2,2″,3,3″,4,6,6″-Hepta-O-acetyl-1-β-D-maltosyl)-2',2″,3',3″,4″,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/petroleum spirit) afforded 22b (53% yield) as a white solid. Rf = 0.30 (3:2 EtOAc/hexane). m.p. = 117-119 °C. [α]²⁵D = + 77 (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-d₆): 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 × 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-d₆): 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→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. Rf = 0.50 (5:2 acetone/toluene). m.p. = 133-135 °C. 1H NMR (500 MHz, DMSO-d6): 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); 5.17 (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, OC(CH3)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, OCOCH3). 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. Rf = 0.16 (8:2 CH3CN/H2O). m.p. = 171 °C (decomposition). 1H NMR (500 MHz, DMSO-d6, 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 × 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 × 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. 13C NMR (125 MHz, DMSO-d6): δ = 103.7 (C-1’); 91.9 (C-1”); 90.0 (C-1); 79.8, 79.4, 75.6, 75.5, 75.4, 75.3, 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-13C 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). [α]_{25}^D = +62 (c = 1.0, methanol). 1H NMR (500 MHz, DMSO-d6, α-anomer): δ = 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, 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
**Methyl 6-deoxy-6-N-(1-S-β-D-maltosyl)-6-sulfonlamino-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). Rf = 0.34 (75:25 CH3CN/H2O). [α]25D = + 94 (c = 1.0, methanol). m.p. = 159 °C.

1H NMR (500 MHz, DMSO-d6): 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 = 5.5 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’); 4.53 (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, OCH3); 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. 13C NMR (125 MHz, DMSO-d6): 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 (OCH3); 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$_{10}$H$_{15}$NO$_7$SNa 604.1518, Found 604.1495.

$N$-(1-$S$-$\beta$-$d$-Maltosyl)-$\beta$-$d$-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$_3$CN/H$_2$O). $\alpha$$^\circ$25 = + 131 (c = 1.0, methanol). $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta = 5.74$ (br s, 1H), 5.67 (br s, 1H), 5.58 (br s, 1H), 5.45 (br s, 2H), 5.38 (br s, 1H) (6 $\times$ OH); 5.02 (m, 3H, 2 $\times$ H-1”, NH); 4.91 (br s, 3H, 3 $\times$ OH); 4.68 (br s), 4.52 (br s, 4H) (5 $\times$ 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 $^1$H-$^1$H gCOSY. $^{13}$C NMR (125 MHz, DMSO-$d_6$): $\delta = 100.8$ (2C) (2 $\times$ 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 $\times$ C-6”), assignments were confirmed by $^1$H-$^{13}$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-$S$-$\beta$-$d$-glucopyranosyl)-$\alpha$,$\beta$-$d$-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. Rf = 0.26 (1:1 acetone/hexane). 1H NMR (500 MHz, DMSO-d6, 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, OCH3); 2.01, 1.98, 1.96, 1.95 (4 × s, 12H, OCOCH3), assignments were confirmed by 1H-1H gCOSY. 13C NMR (125 MHz, DMSO-d6): δ = 170.0, 169.5, 169.1, 168.9 (OCOCH3); 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 (OCH3); 54.6 (C-3'); 20.5, 20.3 (2C), 20.2 (OCOCH3), assignments were confirmed by 1H-13C 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. Rf = 0.45 (9:1 CH2Cl2/MeOH). LRMS (ESI+): m/z = 578 [M + Na]+. HRMS: Calcd for C21H33NO16SNa 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. Rᶠ = 0.38 (9:1 CH₂Cl₂/MeOH). ¹H NMR (500 MHz, DMSO-d₆): 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 × s, 12H, OCOCH₃), assignments were confirmed by ¹H-¹H gCOSY. ¹³C NMR (125 MHz, DMSO-d₆): δ = 169.9, 169.4, 169.3, 169.2 (OOCCH₃); 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). Rᶠ = 0.17 (1:2 EtOAc/petroleum spirit). m.p. = 109 °C. [α]²⁵D = -5 (c = 1.0, chloroform). ¹H NMR (500 MHz, DMSO-d₆): 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). m.p. = 174 °C. [α]$^{25}$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) (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). Rf = 0.79 (8:2 CH₂Cl₂/MeOH). ¹H NMR (500 MHz, DMSO-d₆): δ = 7.27 (s, 2H, NH); 5.70 (d, J = 3.5 Hz, 1H, H-1'); 5.16 (d, J = 3.5 Hz, 1H, O-H-3); 5.04 (d, J = 5.0 Hz, 1H, O-H-4); 4.93 (br s, 1H, O-H-2); 4.67 (t, J = 3.5 Hz, 1H, H-1'); 4.38 (t, J = 6.0 Hz, 1H, O-H-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). Rf = 0.13 (8:2 CH₂Cl₂/MeOH). ¹H NMR (500 MHz, DMSO-d₆): 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, O-H-3); 5.03 (d, J = 5.0 Hz, 1H, O-H-4); 4.87 (br s, 1H, O-H-2); 4.83 (br s, 1H, O-H-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 (m, 1H, H-5); 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 24h. The mixture was evaporated to dryness in the presence of silica. Purification by flash chromatography (85:15 CH$_3$CN/H$_2$O) 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$_3$CN/H$_2$O). $^1$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: Caled for C$_{12}$H$_{23}$NO$_{12}$SNa 428.0833, Found 428.0847.

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Supporting Information Available

$^1$H and $^{13}$C 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.

References

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