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Application of HOF·CH_3CN to the synthesis of glycosyl sulfones

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ABSTRACT

A fast, complete and clean conversion of thioglycosides into glycosyl sulfones under mild acidic conditions is described, using the HOF·CH_3CN complex at room temperature. This methodology affords glycosyl sulfones in high yields and in excellent purity.

1. Introduction

Due to stronger chemical and enzymatic stabilities than their *O*-glycosyl counterparts, glycosides bearing a sulfur atom at the anomeric carbon have been extensively studied either as glycosyl mimics or as synthetic intermediates. The highly oxidised form present in glycosyl sulfones is a non-ionic, achiral isosteric analogue of the phosphate diester[1] and as such is of particular interest as a tool for probing biological systems. Sulfones have also been shown to increase membrane permeability (as less polar mimics of phosphate diesters)[2] and have been studied as glycosyltransferase inhibitors[3] and potential anti-tumour agents.[4] They have long been used as key intermediates in organic synthesis, being employed as glycosyl donors in the synthesis of glycosides when treated with an alcohol and activated with magnesium bromide etherate[5] or with samarium(III) triflate.[6] The utilisation of glycosyl sulfones in the synthesis of C-glycosides is well documented, via the coupling of the lithiated anion[7] with carbonyl groups or via the Ramberg–Bäcklund rearrangement.[8–13] Excellent stereocontrol at the anomeric position has been achieved using samarium-mediated reductive coupling.[14–17] Glycals have also been synthesised from glycosyl sulfones.[18–21] Recently, chromium(II) complexes have been used to react with glycosyl sulfones producing glycals and/or C-glycosides.[22]

Due to their importance as synthetic tools, the synthesis of glycosyl sulfones via the oxidation of thioglycosides has received much attention. Oxidants such as $RuCl_3/NaIO_4$,[19] dimethyldioxirane (DMD),[3] oxone,[11,20] monoperoxyphthalic acid (MMPA),[8,9] magnesium bis(monoperoxyphthalate) (MMPP),[23] OsO_4/tertiary amine *N*-oxides[24] and $KMnO_4$/acetic acid[25] have all been employed for this purpose. Recent success in the use of $KMnO_4/CuSO_4 \cdot 5H_2O$[26] for the oxidation of thioglycosides bearing labile acidic groups has been reported. Probably, the most frequently used reagent is *m*-chloroperoxybenzoic acid (*m*-CPBA).[4,6,10,12,21] However, the low solubility of *m*-CPBA in dichloromethane, the frequent requirement for strict control of temperature and the difficulty in removing the by-product (*m*-chlorobenzoic acid) are drawbacks to its use. In addition, commercially available *m*-CPBA lacks purity. The use of peroxy-acids[27] also has the inconvenience of lengthy reaction times. There is clearly still a need for the development of more efficient methodologies in the preparation of glycosyl sulfones.

Around 20 years ago, with the pioneering work of Rozen, a new oxidising agent was developed.[28] The HOF·CH_3CN complex was prepared by bubbling elemental fluorine through aqueous acetonitrile and proved to be a strong oxygen transfer agent. It has since been applied to the oxidation of alcohols to ketones,[29] amines[30,31] and azides[32,33] to nitro derivatives, amino acids to the corresponding α-nitro acids,[34] tertiary amines to *N*-oxides and *N*,*N*-dioxides[35,36] and olefins to epoxides.[28,37] Oxidations promoted on the sulfur atom by HOF·CH_3CN have also been explored. Sulfides bearing electron-donating or electron-withdrawing groups, aliphatic sulfides, thiophenes and episulfides were rapidly oxidised to the corresponding sulfones in excellent yields.[38–42] It was shown that the HOF·CH_3CN complex is more reactive towards sulfides than sulfoxides, and that its oxidising power is due to the strong electrophilic character of the oxygen. Sulfoxides could be isolated, but only at very low temperatures.[41] Thiols and disulfides have been more recently oxidised to sulfonic and sulfinic acids using the same oxidising agent.[43]

Our interest in the synthesis of a series of glycosyl sulfones for comparative metabolic studies in biological systems necessitated a method in which a large number of target molecules could be

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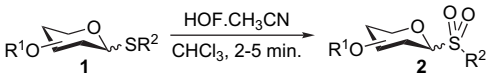
prepared in a rapid and facile manner. In addition, we wished to avoid procedures involving heavy metals, to minimise the risk of residual contamination. We proceeded to explore the application of HOF·CH_3CN to the oxidation of structurally versatile thioglycosides to their corresponding sulfones.

2. Results and discussion

A series of α- and β-thioglycosides were initially prepared. Structurally diverse aglycone moieties were selected in order to study the compatibility of different functional groups with the oxidative conditions. Synthesis of thioglycosides **1a**–**1o** (Table 1) was carried out according to published procedures.

Methods used include (i) base promoted nucleophilic attack by the thiol of the thiosugar to the halide,[44] (ii) base promoted nucleophilic attack to a suitably protected bromosugar under phase-transfer catalysis[45] and (iii) Lewis acid-catalysed coupling of per-*O*-acetylated sugars to thiols proved successful in yielding a number of the thioglycosides.[46]

As a general procedure, a solution of thioglycoside was subsequently treated with HOF·CH_3CN (4 equiv) in chloroform at room temperature (Scheme 1). HOF·CH_3CN concentrations were typically in the range 0.1–0.2 mM using the commercially available F_2/N_2 mixture as compared to 0.4–0.6 mM reported by Rozen.[36] Reactions were quenched after 2 min. In most cases, with the exception of **1e** and **1n**, only one product was detected by TLC. Complete oxidation of the thioglycosides occurred, with no sulfoxide detected. Simple extraction produced glycosyl sulfones in excellent purity, as confirmed by proton NMR spectroscopy. Further purification by column chromatography was not required for the majority of reactions, except for the purification of **2e** and **2n**.



Scheme 1.

Oxidation of thioglycosides **1e** and **1n** afforded two products, the second being most likely due to partial oxidation of the ring nitrogen and/or sulfur atom. In both instances, easy purification of the major oxidation product was achieved with column chromatography.

Thioglycoside **1f**, containing an olefin in addition to the thioether, was included to investigate reactivity. The fully oxidised sulfone and epoxide-containing compound **2f** was the only product. Despite previous reports indicating stereospecific epoxidation of olefins with HOF·CH_3CN,[28] **2f** was obtained as a mixture of diastereoisomers in a 1:0.7 ratio, as determined by NMR analysis.

Interestingly, HOF·CH_3CN hydroxylation of sp^3 C–H centres has been reported in the absence of alkenes or other readily oxidisable species.[47] However, thioglycosides bearing aliphatic (**1i**, **1j** and **1k**) and alicyclic (**1c**) moieties produced only the respective sulfones. In the case of benzylic thioglycosides **1a**, **1g** and **1h**, no benzylic oxidation was detected, with glycosyl sulfones **2a**, **2g** and **2h** being isolated.

The low isolated yields observed for thioglycosides **2d** and **2l** were most likely due to the solubility of these products in the aqueous medium. No oxidation of the hydroxyl or nitrile function was detected. Finally, oxidation of the sterically hindered thiodisaccharide **1o** afforded glycosyl sulfone **2o** in the same straightforward manner and in excellent yield.

3. Conclusion

In summary, we have successfully demonstrated the application of HOF·CH_3CN to the synthesis of glycosyl sulfones in excellent yield and purity. The lower concentrations of HOF·CH_3CN (as compared to literature methods) obtained using the commercially available mixture of 5% F_2 in nitrogen proved sufficient to produce rapid oxidation in high yield. Use of this mixture rather than neat F_2 also reduced the production of unwanted HF as a side reaction. Oxidation of alcohols, other heteroatoms and aromatic rings was not observed, although simultaneous oxidation of an alkene could not be avoided. A key advantage of this method is the clean nature of the oxidation, largely eliminating the need for flash column chromatography.

4. Experimental

4.1. General methods

Optical rotations were measured using a PerkinElmer 341 polarimeter. Infra red spectra were recorded using a PerkinElmer FT-IR Spectrometer PARAGON 1000. Melting points were measured with a Sanyo Gallenkamp variable heater and are reported uncorrected. NMR spectra were generated on a JEOL ECA-600 spectrometer. Chemical shifts are reported in parts per million downfield relative to tetramethylsilane (solvent $CDCl_3$). Low resolution mass spectra (LRMS) were generated using a Micromass Quattro Ultima. Analytical thin-layer chromatography (TLC) was performed on plates of precoated silica plates 60 F_{254} (Merck). Visualisation of the plates was carried out using UV light (254 nm) and/or a solution of 10% H_2SO_4 in EtOH followed by heating. Flash column chromatography was carried out on silica gel (Merck). All solvents were of reagent grade. The alkyl halides, alkyl mercaptans and 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose were obtained commercially from Sigma–Aldrich. 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-galactopyranose and 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranose were prepared from the respective non-protected reducing sugars in a three step procedure: (1) per-O-acetylation of hydroxyl groups (Ac_2O, pyridine), (2) bromination at the anomeric carbon using HBr–AcOH and (3) reaction of the aceto-bromosugar with thiourea, followed by basic hydrolysis.[56] 6-Deoxy-2,3,4-tri-*O*-acetyl-α/β-L-mannopyranose was prepared according to the literature method.[56] The 5% F_2 in N_2 cylinder was purchased from BOC gases (UK).

4.2. General procedure for the synthesis of thioglycosides

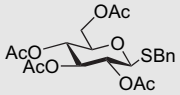
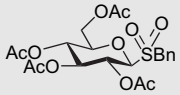
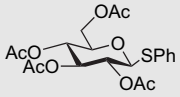
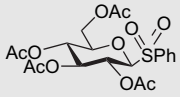
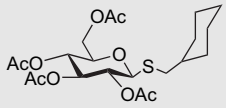
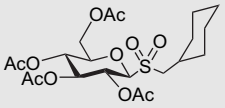
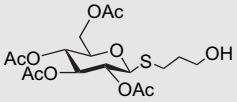
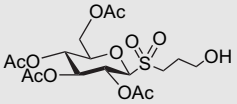
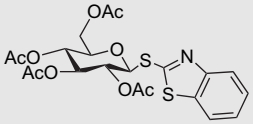
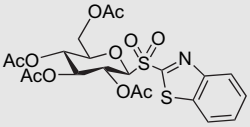
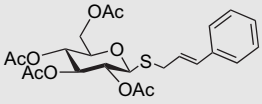
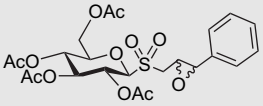
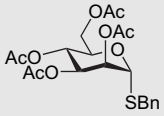
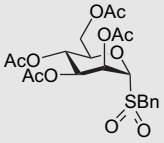
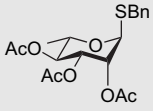
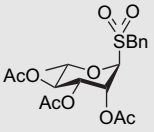
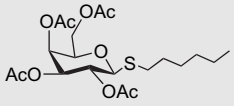
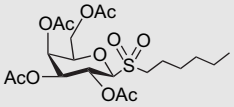
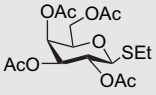
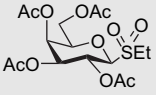
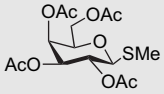
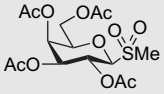
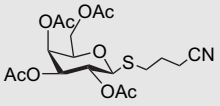
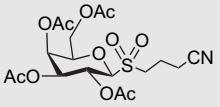
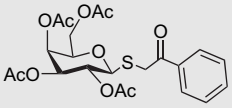
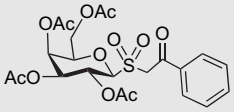
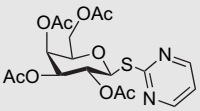
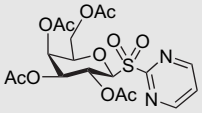
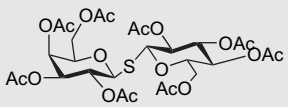
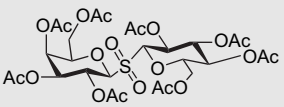
Procedure A. A solution of thiosugar (1 mmol), Et_2NH (1 mmol) and alkyl halide (1.5 mmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature for 2–6 h (end point determined by TLC). Thereafter, the reaction mixture was diluted with CH_2Cl_2 (25 mL) and extracted with satd aq NH_4Cl (25 mL). The organic phase was dried over $MgSO_4$, filtered and evaporated. Column chromatography on silica gel (petroleum ether bp 60–80 °C–EtOAc 1:1 v/v) of the crude material afforded the respective thioglycoside.

Procedure B. $BF_3·Et_2O$ (6 mmol) and RSH (2 mmol) were added to a solution of per-*O*-acetylated sugar (1 mmol) in anhydrous CH_2Cl_2 (2.5 mL) under an inert atmosphere. After 18 h, the reaction mixture was diluted with CH_2Cl_2 (50 mL) and extracted with satd aq $NaHCO_3$ (50 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent evaporated. Column chromatography on silica gel gave the desired thioglycoside.

*4.2.1. (Cyclohexylmethyl)-2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranoside (**1c**)*

Prepared according to procedure A; oil, $[\alpha]_D^{20}$ −41±1.0 (*c* 0.57, $CHCl_3$); R_f=0.45 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 0.90 (2H, m), 1.09–1.22 (3H, m), 1.44 (1H, m), 1.60–1.80 (5H, m), 1.97, 1.99, 2.02, 2.05 (4s, 12H, 4OAc), 2.49 (dd, 1H, SC*H*H, *J* 7.2, 12.3 Hz), 2.55 (dd, 1H, SCH*H*, *J* 6.6, 12.3 Hz), 3.67 (m, 1H, H-5), 4.10 (dd, 1H,

Table 1
Oxidation of thioglycosides to glycosyl sulfones using $HOF{\cdot}CH_3CN$

Entry	Thioglycoside (**1**)		Glycosyl sulfone (**2**)		Yield (%)
1		**1a**[46]		**2a**[11]	75
2		**1b**[48]		**2b**[49]	87
3		**1c**		**2c**	81
4		**1d**[50]		**2d**	68
5		**1e**[51]		**2e**	73[a]
6		**1f**[52]		**2f**	89
7		**1g**[53]		**2g**	92
8		**1h**		**2h**	95
9		**1i**[54]		**2i**	76
10		**1j**[54]		**2j**	81
11		**1k**[54]		**2k**	95
12		**1l**		**2l**	62
13		**1m**		**2m**	81
14		**1n**[55]		**2n**	73[a]
15		**1o**[45]		**2o**	95

[a] Purified by extraction followed by column chromatography on silica gel.

H-6a, $J_{5,6a}$ 1.8 Hz, $J_{6a,6b}$ 12.6 Hz), 4.20 (dd, 1H, H-6b, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.6 Hz), 4.43 (d, 1H, H-1, $J_{1,2}$ 9.6 Hz), 4.00 (dd, 1H, H-4, $J_{3,4}$ 9.6 Hz, $J_{4,5}$ 9.6 Hz), 5.05 (dd, 1H, H-2, $J_{1,2}$ 9.6 Hz, $J_{2,3}$ 9.6 Hz), 5.18 (dd, 1H, H-3, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 9.6 Hz); δ_C (150 MHz, $CDCl_3$) 20.67, 20.70, 20.79, 20.82, 26.03, 26.07, 26.33, 32.55, 32.84, 37.29, 38.01, 62.25, 68.38, 70.01, 73.97, 75.89, 83.93, 169.45, 169.49, 170.29, 170.72; MS (ESI) *m/z*: 478.2 $[M+NH_4]^+$; HRMS (ESI, $M+NH_4$) calcd for $C_{21}H_{36}NO_9S$ 478.2105, found 478.2103.

4.2.2. (Benzyl)-6-deoxy-2,3,4-tri-O-acetyl-1-thio-α-L-rhamnopyranose (**1h**)

Prepared according to procedure B; $[\alpha]_D^{20}$ −165±0.5 (*c* 1.39, $CHCl_3$); R_f=0.29 (EtOAc–petroleum ether 1:3); ν_{max} (film) 3015, 2916, 1750, 1341, 1237, 1183, 923 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.16 (d, 3H, ^3J 6.3 Hz), 1.95, 2.04, 2.10 (3s, 9H, 3OAc), 3.72 (d, 1H, SCH_2, ^2J 13.7 Hz), 3.78 (d, 1H, SCH_2, ^2J 13.7 Hz), 4.17–4.19 (m, 1H, H-5), 5.01 (d, 1H, H-1, $J_{1,2}$ 1.3 Hz), 5.06 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz), 5.21 (dd, 1H, H-3, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.9 Hz), 5.28 (dd, 1H, H-2, $J_{1,2}$ 1.3 Hz, $J_{2,3}$ 3.4 Hz), 7.23–7.26 (m, 1H), 7.29–7.30 (m, 4H); δ_C (150 MHz, $CDCl_3$) 17.41, 20.76, 20.91, 21.02, 34.98, 67.11, 69.74, 71.06, 71.33, 81.32, 127.40, 128.71 (2C), 129.04 (2C), 137.24, 169.97, 170.02, 170.09; MS (ESI) *m/z*: 419 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{19}H_{28}NO_7S$ 414.1581, found 414.1582.

4.2.3. (3′-Cyanopropyl) 2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (**1l**)

Prepared according to procedure A; $[\alpha]_D^{20}$ −2.6±0.5 (*c* 1.87, $CHCl_3$); R_f=0.65 (CH_2Cl_2–MeOH 95:5); δ_H (600 MHz, $CDCl_3$) 1.94, 2.01, 2.03, 2.12 (4s, 12H, 4OAc), 2.49 (t, 2H, *J* 6.9 Hz), 2.70–2.75 (m, 2H), 2.85–2.90 (m, 2H), 3.91 (dd, 1H, H-5, $J_{5,6a}$ 6.1 Hz, $J_{5,6b}$ 6.9 Hz), 4.05–4.11 (m, 2H, H-6a and H-6b), 4.43 (d, 1H, H-1, $J_{1,2}$ 9.6 Hz), 5.00 (dd, 1H, H-3, $J_{3,4}$ 2.7 Hz, $J_{3,2}$ 9.6 Hz), 5.19 (dd, 1H, H-2, $J_{2,3}$ 9.6 Hz, $J_{2,1}$ 9.6 Hz), 5.39 (d, 1H, H-4, $J_{4,3}$ 2.7 Hz); δ_C (150 MHz, $CDCl_3$) 15.77, 20.51, 20.63 (2C), 20.74, 25.78, 28.86, 61.46, 66.82, 67.14, 71.62, 74.57, 84.08, 119.04, 169.56, 169.95, 170.11, 170.32; MS (ESI) *m/z*: 454 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{18}H_{29}N_2O_9S$ 449.1588, found 449.1585.

4.2.4. (2′-Oxo-2′-phenylethyl)-2,3,4,6-tetra-O-acetyl-1-thio-β-D-galactopyranoside (**1m**)

Prepared according to procedure A; $[\alpha]_D^{20}$ −32±0.5 (*c* 0.88, $CHCl_3$); R_f=0.34 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 1.91, 1.95, 2.01, 2.13 (4s, 12H, 4OAc), 3.91 (t, 1H, H-5, $J_{5,6}$ 6.9 Hz), 4.00 (d, 1H, ^2J 14.4 Hz), 4.05 (d, 2H, 2H-6, $J_{6,5}$ 6.9 Hz), 4.07 (d, 1H, ^2J 14.4 Hz), 4.58 (d, 1H, H-1, $J_{1,2}$ 10.3 Hz), 5.02 (dd, 1H, H-3, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 10.3 Hz), 5.22 (dd, 1H, H-2, $J_{1,2}$ 10.3 Hz, $J_{2,3}$ 10.3 Hz), 5.40 (d, 1H, H-4, $J_{4,3}$ 3.4 Hz), 7.47 (dd, 2H, ^3J 8.2, 7.5 Hz), 7.58 (dt, 1H, ^3J 7.5 Hz, ^4J 1.3 Hz), 7.94 (dd, 2H, ^3J 8.2 Hz, ^4J 1.3 Hz); δ_C (150 MHz, $CDCl_3$) 20.54, 20.57, 20.65 (2C), 35.35, 61.22, 66.99, 67.14, 71.66, 74.78, 82.85, 128.63, 128.73, 133.57, 135.19, 169.73, 169.94, 170.16, 170.35, 194.35; MS (ESI) *m/z*: 505 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{22}H_{30}NO_{10}S$ 500.1585, found 500.1578.

4.3. General procedure for the generation of HOF·CH$_3$CN

A mixture of 5% fluorine in nitrogen was passed through an aqueous acetonitrile solution (CH_3CN–H_2O 10:1 v/v) at −15 °C. A soda lime trap was connected to the three-necked round-bottom flask reactor in order to consume any unreacted fluorine. As a secondary precaution, any fluorine gas escaping from this trap was reacted with an aqueous solution of NaF in a second trap, which neutralised the in situ formed HF (as a result of the reaction of F_2 with H_2O). Regular glassware was used without problem in these experiments. The formation of HOF·CH_3CN was monitored by reacting aliquots of the solution with an acidic aqueous solution of KI. Titration of the liberated iodine indicated concentrations between 0.1 and 0.2 mol/L of the oxidising agent. The reagent was used within 1 h of preparation.

4.4. General procedure for the oxidation reaction

Thioglycoside (1 mmol) was dissolved in $CHCl_3$ (5 mL). A solution of HOF·CH_3CN (4 mmol) was then added at room temperature. After 2 min, the reaction mixture was quenched with satd aq $NaHCO_3$ (30 mL) and was extracted with $CHCl_3$ (30 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent concentrated under vacuum to give the respective sulfone in high purity.

4.4.1. Cyclohexylmethyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-glucopyranoside (**2c**)

Colourless solid, mp: 179–182 °C; $[\alpha]_D^{20}$ −21±1 (*c* 0.79, $CHCl_3$); R_f=0.48 (EtOAc–petroleum ether 1:1); ν_{max} (KBr) 3480, 2933, 2855, 1748, 1225, 1035 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.08–1.16 (m, 3H), 1.27–131 (m, 2H), 1.63–1.65 (m, 1H), 1.69–1.71 (m, 2H), 1.85–1.87 (m, 1H), 1.94–1.96 (m, 1H), 2.01, 2.02, 2.04, 2.07 (4s, 12H, 4OAc), 2.07–2.09 (m, 1H), 2.96–2.97 (m, 2H), 3.79–3.81 (m, 1H, H-5), 4.18 (d, 1H, H-6a, $J_{6a,6b}$ 12.5 Hz), 4.25 (dd, 1H, H-6b, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.5 Hz), 4.34 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.10 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz), 5.29 (dd, 1H, H-3, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 9.9 Hz), 5.45 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 20.61, 20.63, 20.72, 20.77, 25.72, 25.77, 25.87, 31.59, 33.21, 33.36, 55.06, 61.55, 66.54, 67.53, 73.19, 76.80, 88.36, 169.34, 169.44, 170.15, 170.52; MS (ESI) *m/z*: 515 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{21}H_{36}NO_{11}S$ 510.2004, found 510.2005.

4.4.2. (3′-Hydroxypropyl) 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-glucopyranoside (**2d**)

Colourless solid, mp: 192–194 °C; $[\alpha]_D^{20}$ −16±2 (*c* 0.20, $CHCl_3$); R_f=0.53 (EtOAc); δ_H (600 MHz, $CDCl_3$) 2.02, 2.03, 2.05, 2.08 (4s, 12H, 4OAc), 2.08–2.11 (m, 2H), 3.27 (t, 2H, ^3J 7.3 Hz), 3.78 (t, 2H, ^3J 4.9 Hz), 3.80–3.83 (m, 1H, H-5), 4.22 (dd, 1H, H-6a, $J_{5,6a}$ 2.5 Hz, $J_{6a,6b}$ 12.5 Hz), 4.26 (dd, 1H, H-6b, $J_{5,6b}$ 4.8 Hz, $J_{6a,6b}$ 12.5 Hz), 4.44 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.11 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz), 5.30 (dd, 1H, H-3, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 9.9 Hz), 5.48 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 20.61, 20.63, 20.71, 20.79, 24.17, 46.27, 60.56, 61.41, 66.57, 67.48, 73.14, 88.12, 169.31, 169.53, 170.15, 170.70; MS (ESI) *m/z*: 477 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{17}H_{30}NO_{12}S$ 472.1483, found 472.1481.

4.4.3. Benzothiazolyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-glucopyranoside (**2e**)

Colourless solid, mp: 202–205 °C; $[\alpha]_D^{20}$ −38±1.5 (*c* 1.21, $CHCl_3$); R_f=0.35 (EtOAc–petroleum ether 1:1); ν_{max} (KBr) 3476, 2948, 1746, 1241, 1219, 1113, 1037 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.55, 1.98, 2.01, 2.09 (4s, 12H, 4OAc), 3.70–3.73 (m, 1H, H-5), 3.95 (dd, 1H, H-6a, $J_{5,6a}$ 2.4 Hz, $J_{6a,6b}$ 12.5 Hz), 4.01 (dd, 1H, H-6b, $J_{5,6b}$ 5.6 Hz, $J_{6a,6b}$ 12.5 Hz), 4.99–5.03 (m, 2H, H-1 and H-4), 5.31 (dd, 1H, H-3, $J_{2,3}$ 9.5 Hz, $J_{3,4}$ 9.5 Hz), 5.70 (dd, 1H, H-2, $J_{1,2}$ 9.5 Hz, $J_{2,3}$ 9.5 Hz), 7.60–7.65 (m, 2H), 8.02 (d, 1H, ^3J 8.0 Hz), 8.26 (d, 1H, ^3J 8.2 Hz); δ_C (150 MHz, $CDCl_3$) 20.01, 20.56, 20.64, 20.69, 61.43, 66.46, 67.45, 73.30, 76.60, 88.57, 122.35, 125.97, 127.85, 128.47, 137.66, 152.67, 162.80, 169.09, 169.23, 170.17 (2C); MS (ESI) *m/z*: 552.0 [M+Na]; HRMS (ESI, $M+NH_4$) calcd for $C_{21}H_{27}N_2O_{11}S_2$ 547.1051, found 547.1050.

4.4.4. (1′-Phenyl-1′,2′-epoxypropane) 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-glucopyranoside (**2f**)

Major diastereoisomer: R_f=0.31 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 2.01, 2.02, 2.05, 2.07 (4s, 12H, 4OAc), 3.38 (dd, 1H, ^3J 2.6 Hz, ^2J 14.5 Hz), 3.41–3.43 (m, 1H), 3.52 (dd, 1H, *J* 5.7, 8.7 Hz), 3.79 (d, 1H, ^3J 1.7 Hz), 3.83–3.85 (m, 1H, H-5), 4.17 (dd, 1H, H-6a, $J_{5,6a}$ 5.1 Hz, $J_{6a,6b}$ 12.5 Hz), 4.24 (dd, 1H, H-6b, $J_{5,6b}$ 2.2 Hz, $J_{6a,6b}$ 12.5 Hz), 4.69 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 4.14 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz,

$J_{4,5}$ 9.9 Hz), 5.34 (dd, 1H, H-3, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 9.9 Hz), 5.58 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz), 7.33–7.36 (m, 5H); δ_C (150 MHz, $CDCl_3$) 20.63 (2C), 20.65, 20.70, 53.01, 55.06, 58.53, 61.30, 65.58, 65.99. 67.50, 73.43, 87.62, 125.78 (2C), 128.83 (2C), 129.11, 169.27, 169.28, 169.34, 170.20.

Minor diastereoisomer: R_f=0.31 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 2.01, 2.01, 2.03, 2.05 (4s, 12H, 4OAc), 3.43–3.47 (m, 2H), 3.53 (dd, 1H, ^3J 3.1 Hz, ^2J 14.4 Hz), 3.85–3.87 (m, 1H, H-5), 3.90 (d, 1H, ^3J 1.7 Hz), 4.16 (dd, 1H, H-6a, $J_{5,6a}$ 4.8 Hz, $J_{6a,6b}$ 12.7 Hz), 4.25 (dd, 1H, H-6b, $J_{5,6b}$ 2.2 Hz, $J_{6a,6b}$ 12.7 Hz), 4.52 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.11 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz), 5.29 (dd, 1H, H-3, $J_{2,3}$ 9.9 Hz, $J_{3,4}$ 9.9 Hz), 5.61 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz), 7.25–7.28 (m, 5H); δ_C (150 MHz, $CDCl_3$) 20.61, 20.68, 20.72, 20.83, 53.30, 54.50, 58.09, 61.49, 65.62, 66.31, 67.38, 73.17, 88.53, 125.78 (2C), 128.85 (2C), 129.01, 168.43, 169.23, 170.59, 171.67; MS (ESI) *m*/*z*: 567.2 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{23}H_{32}NO_{12}S$ 546.1640, found 546.1637.

4.4.5. Benzyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-α-D-mannopyranoside (**2g**)

Colourless solid, mp: 174–176 °C; $[\alpha]_D^{20}$ +83.5±1 (*c* 0.46, $CHCl_3$); R_f=0.36 (EtOAc–petroleum ether 1:1); ν_{max} (KBr) 3062, 3025, 2960, 1758, 1312, 1246, 1167, 1112, 978, 540 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.97, 2.05, 2.09, 2.12 (4s, 12H, 4OAc), 4.13 (dd, 1H, H-6a, $J_{5,6a}$ 1.5 Hz, $J_{6a,6b}$ 12.5 Hz), 4.24 (d, 1H, ^2J 14.4 Hz), 4.27 (dd, 1H, H-6b, $J_{5,6b}$ 6.0 Hz, $J_{6a,6b}$ 12.5 Hz), 4.51 (d, 1H, ^2J 14.4 Hz), 4.66 (d, 1H, H-1, $J_{1,2}$ 1.7 Hz), 4.70–4.72 (m, 1H, H-5), 5.27 (dd, 1H, H-4, $J_{3,4}$ 9.9 Hz, $J_{4,5}$ 9.9 Hz), 5.57 (dd, 1H, H-3, $J_{2,3}$ 3.7 Hz, $J_{3,4}$ 9.9 Hz), 5.88 (dd, 1H, H-2, $J_{1,2}$ 1.7 Hz, $J_{2,3}$ 3.7 Hz), 7.40–7.41 (m, 5H); δ_C (150 MHz, $CDCl_3$) 20.58, 20.74, 20.75, 20.86, 57.13, 62.63, 64.55, 65.33, 68.93, 73.45, 86.13, 126.92, 129.31 (2C), 129.45, 130.92 (2C), 169.20, 169.32, 169.75, 170.49; MS (ESI) *m*/*z*: 509 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{21}H_{30}NO_{11}S$ 504.1534, found 504.1525.

4.4.6. (Benzyl)-6-deoxy-2,3,4-tri-O-acetyl-1-sulfonyl-α-L-rhamnopyranose (**2h**)

Colourless solid, mp: 72–73 °C; $[\alpha]_D^{20}$ −82±0.5 (*c* 0.75, $CHCl_3$); R_f=0.71 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 1.27 (d, 3H, ^3J 6.1 Hz), 1.97, 2.05, 2.08 (3s, 9H, 3OAc), 4.22 (d, 1H, ^2J 14.4 Hz), 4.48 (d, 1H, ^2J 14.4 Hz), 4.53–4.58 (m, 1H, H-5), 4.62 (d, 1H, H-1, $J_{1,2}$ 1.6 Hz), 5.07 (dd, 1H, H-4, $J_{3,4}$ 9.4 Hz, $J_{4,5}$ 9.4 Hz), 5.52 (dd, 1H, H-3, $J_{2,3}$ 3.6 Hz, $J_{3,4}$ 9.4 Hz), 5.87 (dd, 1H, H-2, $J_{1,2}$ 1.6 Hz, $J_{2,3}$ 3.6 Hz), 7.39–7.40 (m, 5H); δ_C (150 MHz, $CDCl_3$) 18.12, 20.63, 20.76, 20.85, 57.24, 64.91, 68.97, 70.08, 71.74, 86.46, 127.10, 128.23 (2C), 129.34, 130.92 (2C), 169.30, 169.41, 170.01; MS (ESI) *m*/*z*: 446.2 [M+NH_4]; HRMS (ESI, M+NH_4) calcd for $C_{19}H_{28}NO_9S$ 446.1479, found 446.1471.

4.4.7. Hexanyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2i**)

Oil, $[\alpha]_D^{20}$ −3.0±0.5 (*c* 0.47, $CHCl_3$); R_f=0.46 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 0.88 (t, 3H, ^3J 6.9 Hz), 1.31–1.32 (m, 4H), 1.41–1.45 (m, 2H), 1.82–1.85 (m, 2H), 1.99, 2.04, 2.06, 2.17 (4s, 12H, 4OAc), 3.09–3.11 (m, 2H), 4.04 (dd, 1H, H-5, $J_{5,6a}$ 6.1 Hz, $J_{5,6b}$ 6.8 Hz), 4.13 (dd, 1H, H-6a, $J_{5,6a}$ 6.1 Hz, $J_{6a,6b}$ 11.5 Hz), 4.17 (dd, 1H, H-6b, $J_{5,6b}$ 6.8 Hz, $J_{6a,6b}$ 11.5 Hz), 4.38 (d, 1H, H-1, $J_{1,2}$ 9.8 Hz), 5.12 (dd, 1H, H-3, $J_{3,4}$ 2.8 Hz, $J_{2,3}$ 9.9 Hz), 5.45 (d, 1H, H-4, $J_{3,4}$ 2.8 Hz), 5.66 (dd, 1H, H-2, $J_{1,2}$ 9.8 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 14.03, 20.62, 20.70, 20.74, 20.80, 20.84, 22.39, 28.35, 31.30, 49.17, 61.20, 63.52, 66.75, 71.33, 75.59, 88.47, 170.05 (2C), 170.07, 170.35; MS (ESI) *m*/*z*: 503 [M+Na]; HRMS (ESI, M+Na) calcd for $C_{20}H_{32}O_{11}NaS$ 503.1558, found 503.1563.

4.4.8. Ethyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2j**)

Oil, $[\alpha]_D^{20}$ +7±0.5 (*c* 0.57, $CHCl_3$); R_f=0.24 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 1.39 (t, 3H, *J* 7.4 Hz), 1.99, 2.04, 2.06, 2.16 (4s, 12H, 4OAc), 3.14 (q, 2H, *J* 7.4 Hz), 4.04 (dd, 1H, H-5, $J_{5,6a}$ 6.0 Hz, $J_{5,6b}$ 6.8 Hz), 4.11 (dd, 1H, H-6a, $J_{5,6a}$ 6.0 Hz, $J_{6a,6b}$ 11.5 Hz), 4.18 (dd, 1H, H-6b, $J_{5,6b}$ 6.8 Hz, $J_{6a,6b}$ 11.5 Hz), 4.41 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.12 (dd, 1H, H-3, $J_{3,4}$ 3.2 Hz, $J_{2,3}$ 9.9 Hz), 5.45 (dd, 1H, H-4, $J_{4,5}$ 1.0 Hz, $J_{3,4}$ 3.2 Hz), 5.66 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 5.48, 20.62, 20.71, 20.72, 20.84, 43.84, 61.19, 63.54, 66.76, 71.33, 75.62, 88.25, 169.55, 170.04, 170.06, 170.36; MS (ESI) *m*/*z*: 447.1 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{16}H_{28}NO_{11}S$ 442.1378, found 442.1381.

4.4.9. Methyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2k**)

Oil, $[\alpha]_D^{20}$ +14±0.5 (*c* 0.63, $CHCl_3$); R_f=0.30 (EtOAc–petroleum ether 1:1); δ_H (600 MHz, $CDCl_3$) 1.99, 2.04, 2.07, 2.17 (4s, 12H, 4OAc), 2.06 (s, 3H, CH_3), 4.08 (dd, 1H, H-5, $J_{5,6a}$ 6.1 Hz, $J_{5,6b}$ 6.5 Hz), 4.13 (dd, 1H, H-6a, $J_{5,6a}$ 6.1 Hz, $J_{6a,6b}$ 11.5 Hz), 4.20 (dd, 1H, H-6b, $J_{5,6b}$ 6.5 Hz, $J_{6a,6b}$ 11.5 Hz), 4.31 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.12 (dd, 1H, H-3, $J_{3,4}$ 2.9 Hz, $J_{2,3}$ 9.9 Hz), 5.45 (d, 1H, H-4, $J_{3,4}$ 2.9 Hz), 5.59 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 20.60, 20.72 (2C), 20.83, 36.30, 61.06, 63.79, 66.78, 71.19, 75.62, 88.97, 169.80, 169.99, 170.02, 170.39; MS (ESI) *m*/*z*: 433.2 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{15}H_{26}NO_{11}S$ 428.1221, found 428.1218.

4.4.10. (3′-Cyanopropyl) 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2l**)

Oil, $[\alpha]_D^{20}$ +3±1 (*c* 0.90, $CHCl_3$); R_f=0.13 (EtOAc–petroleum ether 1:1); ν_{max} (film) 3018, 2946, 2880, 2268, 1627, 1397, 1452, 1306, 1125, 1098 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.99, 2.05, 2.06, 2.18 (4s, 12H, 4OAc), 2.23–2.37 (m, 2H, CH_2), 2.57–2.66 (m, 2H, $S(O_2)CH_2$), 3.29 (t, 2H, CH_2CN, ^3J 7.2 Hz), 4.07 (dd, 1H, H-5, $J_{5,6a}$ 6.0 Hz, $J_{5,6b}$ 6.7 Hz), 4.13 (dd, 1H, H-6a, $J_{5,6a}$ 6.0 Hz, $J_{6a,6b}$ 11.7 Hz), 4.21 (dd, 1H, H-6b, $J_{5,6b}$ 6.7 Hz, $J_{6a,6b}$ 11.7 Hz), 4.41 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.12 (dd, 1H, H-3, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 9.9 Hz), 5.46 (d, 1H, H-4, $J_{3,4}$ 3.4 Hz), 5.63 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 16.51, 17.83, 20.60, 20.74 (2C), 20.80, 47.33, 61.18, 63.50, 66.73, 71.13, 75.89, 89.18, 118.16, 169.62, 169.98, 170.06, 170.40; MS (ESI) *m*/*z*: 486 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{18}H_{29}N_2O_{11}S$ 481.1487, found 481.1486.

4.4.11. (2′-Oxo-2′-phenylethyl)-2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2m**)

Oil, $[\alpha]_D^{20}$ −6.0±0.5 (*c* 0.6, $CHCl_3$); R_f=0.42 (EtOAc–petroleum ether 2:1); δ_H (600 MHz, $CDCl_3$) 1.77, 1.99, 2.05, 2.17 (4s, 12H, 4OAc), 4.02–4.16 (m, 3H, H-5, H-6a and H-6b), 4.68 (d, 1H, ^2J 15.4 Hz), 4.83 (d, 1H, ^2J 15.4 Hz), 4.94 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.15 (dd, 1H, H-3, $J_{3,4}$ 3.3 Hz, $J_{2,3}$ 9.9 Hz), 5.45 (d, 1H, H-4, $J_{3,4}$ 3.3 Hz), 5.82 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz), 7.52 (t, 2H, ^3J 7.5 Hz), 7.56 (t, 1H, ^3J 7.5 Hz), 7.94 (d, 2H, ^3J 7.5 Hz); δ_C (150 MHz, $CDCl_3$) 20.37, 20.63, 20.74, 20.79, 56.82, 61.49, 63.04, 66.96, 71.46, 76.08, 88.17, 128.92 (2C), 129.20 (2C), 134.88, 135.52, 169.19, 170.05, 170.23, 170.33, 188.45; MS (ESI) *m*/*z*: 537 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{22}H_{30}NO_{12}S$ 532.1483, found 532.1483.

4.4.12. Pyrimidinyl 2,3,4,6-tetra-O-acetyl-1-sulfonyl-β-D-galactopyranoside (**2n**)

Oil, $[\alpha]_D^{20}$ −19±0.5 (*c* 0.7, $CHCl_3$); R_f=0.12 (EtOAc–petroleum ether 2:1); ν_{max} (film) 3019, 2916, 2848, 1700, 1390, 1255 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.89, 2.00, 2.08, 2.13 (4s, 12H, 4OAc), 3.84 (dd, 1H, H-6a, $J_{5,6a}$ 6.3 Hz, $J_{6a,6b}$ 11.4 Hz), 3.90 (dd, 1H, H-5, $J_{5,6b}$ 4.9 Hz, $J_{5,6a}$ 6.3 Hz), 3.93 (dd, 1H, H-6b, $J_{5,6b}$ 4.9 Hz, $J_{6a,6b}$ 11.4 Hz), 5.14 (dd, 1H, H-3, $J_{3,4}$ 3.4 Hz, $J_{2,3}$ 9.9 Hz), 5.23 (d, 1H, H-1, $J_{1,2}$ 9.9 Hz), 5.40 (d, 1H, H-4, $J_{3,4}$ 3.4 Hz), 6.00 (dd, 1H, H-2, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz), 7.59 (t, 1H, ^3J 4.8 Hz), 8.98 (d, 2H, ^3J 4.8 Hz); δ_C (150 MHz, $CDCl_3$) 20.58, 20.65, 20.71, 20.82, 60.91, 63.50, 66.61, 71.58, 75.30, 86.94, 124.00, 158.71 (2C), 164.28, 169.05, 170.05, 170.17 (2C); MS (ESI) *m*/*z*: 497.0 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{18}H_{26}N_3O_{11}S$ 492.1283, found 492.1284.

*4.4.13. β-D-Galactopyranoside (2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl) 1-sulfonyl-tetraacetate (**2o**)*

Colourless solid, mp: 113–117 °C; $[\alpha]_D^{20}$ −7±1 (*c* 0.24, $CHCl_3$); R_f=0.34 (EtOAc–petroleum ether 2:1); ν_{max} (KBr) 3487, 2915, 1755, 1371, 1235, 1102, 592 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 1.98, 2.01, 2.03, 2.04, 2.05, 2.05, 2.09, 2.17 (8s, 24H, 8OAc), 3.73–3.75 (m, 1H, H-5_{glu}), 3.99 (dd, 1H, H-5gal, $J_{5,6a}$ 5.4 Hz, $J_{5,6b}$ 5.5 Hz), 4.09–4.17 (m, 3H, H-$6a_{glu}$, H-$6a_{gal}$ and H-$6b_{gal}$), 4.32 (dd, 1H, H-$6b_{glu}$, $J_{5,6b}$ 2.2 Hz, $J_{6a,6b}$ 12.7 Hz), 4.82 (d, 1H, H-1_{gal}, $J_{1,2}$ 9.9 Hz), 4.83 (d, 1H, H-1_{glu}, $J_{1,2}$ 9.9 Hz), 5.06 (dd, 1H, H-4_{glu}, $J_{3,4}$ 9.3 Hz, $J_{4,5}$ 9.9 Hz), 5.14 (dd, 1H, H-3_{gal}, $J_{3,4}$ 3.3 Hz, $J_{2,3}$ 9.9 Hz), 5.31 (dd, 1H, H-3_{glu}, $J_{2,3}$ 9.3 Hz, $J_{3,4}$ 9.3 Hz), 5.46 (d, 1H, H-4_{gal}, $J_{3,4}$ 3.3 Hz), 5.55 (dd, 1H, H-2_{glu}, $J_{2,3}$ 9.3 Hz, $J_{1,2}$ 9.9 Hz), 5.74 (dd, 1H, H-2_{gal}, $J_{1,2}$ 9.9 Hz, $J_{2,3}$ 9.9 Hz); δ_C (150 MHz, $CDCl_3$) 20.62 (3C), 20.64, 20.73, 20.75 (2C), 20.82, 61.56, 61.87, 62.00, 65.04, 66.93, 67.61, 71.31, 73.28, 75.93, 84.82, 85.41, 168.96, 169.03, 169.27, 170.05, 170.17, 170.21 (2C), 170.54; MS (ESI) *m*/*z*: 749.3 [M+Na]; HRMS (ESI, M+NH_4) calcd for $C_{28}H_{42}NO_{20}S$ 744.2015, found 744.2014.

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