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Convenient preparation of thioglycomimetics: *S*-glycosyl sulfenamides, sulfinamides and sulphonamides†

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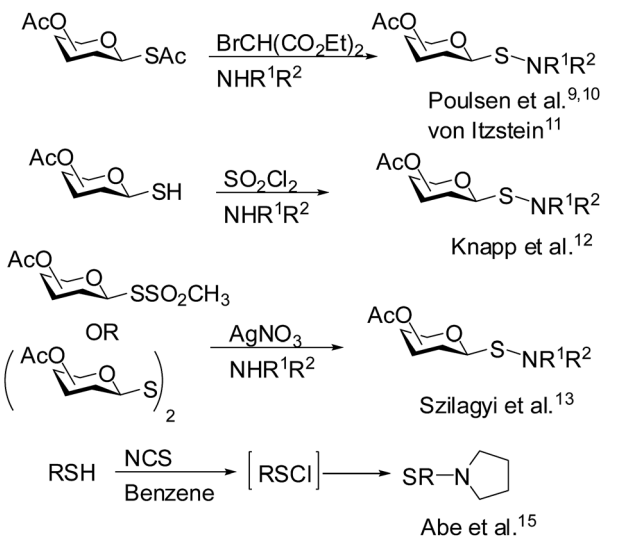
A series of *S*-glycosyl sulfenamide derivatives has been prepared in good yield from glycosyl thiols using *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) as activator under significantly fast reaction conditions avoiding the use of hazardous reagents. Controlled and complete oxidation of the sulfenamide derivatives under mild reaction conditions led to the formation of the corresponding sulfinamides and sulfonamides in excellent yield.

Introduction

1-Thiosugar derivatives are useful intermediates for the preparation of a variety of glycomimetics and pharmaceutically important compounds.[1,2] Because of the extra stability of the anomeric carbon–sulfur bond they are resistant towards enzymatic hydrolysis and thereby considered as useful intermediates in the design of novel enzyme inhibitors.[3,4] Over the years, a plethora of reports have appeared in the literature for the construction of glycomimetics and neoglycoconjugates in which 1-thiosugars have been used extensively.[5–7] Among several glycomimetics developed so far, glycosyl sulphonamides, sulfinamides and sulfenamides are noteworthy. Although sulphonamide functionality can be found in several compounds having therapeutic potential, most of them are aromatic in nature.[8] Till date, only a few reports are available on the preparation of *S*-glycosyl sulphonamides. Poulsen *et al.*,[9,10] and von Itzstein *et al.*[11] prepared *S*-glycosyl sulfenamide derivative by the treatment of glycosylthioacetate with diethyl bromomalonate in the presence of an amine. In another report, Knapp *et al.*[12] described the preparation of *S*-glycosyl sulfenamide from glycosyl thiol *via* the formation of glycosyl sulfenyl chloride generated *in situ* by the treatment with sulfuryl chloride followed by addition of an appropriate amine. In addition, *S*-glycosyl sulfenamide derivatives have also been prepared by the treatment of diglycosyl disulfide with amine in the presence of silver salts.[13] Earlier, Kahne *et al.* demonstrated the formation of glycosyl sulfenate intermediates during the glycosylation reaction using glycosyl sulfoxides.[14] In an ongoing program towards the preparation of glycomimetics, we were in need to prepare *S*-glycosyl sulfenamide derivatives and their oxidized products starting from glycosyl thiols. Following earlier reported reaction conditions, treatment of glycosyl thiols with diethyl bromomalonate or sulfuryl chloride followed by reaction with amine did not furnish satisfactory yield of glycosyl sulfenamide instead diglycosylated disulfide derivative was obtained as predominant product. Therefore, it is pertinent to develop novel reaction condition to overcome these shortcomings. In searching for a better alternative, we envisioned that treatment of glycosyl thiol with a halonium ion (X^+) generating agent such as *N*-bromosuccinimide (NBS) or *N*-chlorosuccinimide (NCS) or *N*-iodosuccinimide (NIS) or carbon tetrabromide (CBr_4) *etc.* could lead to the *in situ* formation of glycosyl sulfenyl halide intermediate, which on treatment with appropriate amine could furnish glycosyl sulfenamide derivative and further oxidation of the product could provide glycosyl sulfinamide and sulphonamide derivatives. Reaction of simple alkyl and aryl thiols with *N*-



Scheme 1 Previously reported reaction methodologies for the preparation of *S*-glycosyl sulfenamide derivatives.

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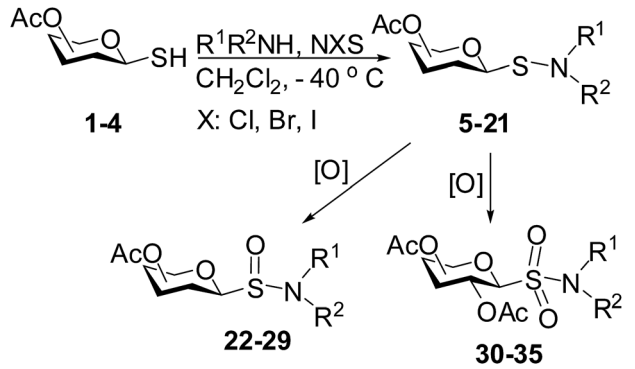
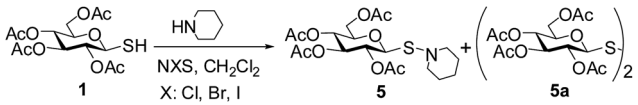
† Electronic supplementary information (ESI) available: Copies of NMR spectra of compounds **4–31**. See DOI: 10.1039/c7ra05339h



Scheme 2 Preparation of glycosyl sulfenamide derivatives using *N*-halosuccinimides in the presence of an amine and their oxidized products.

Table 1 Halonium ion (X^+) mediated preparation of glucosyl piperidinyl sulfenamide derivative from compound **1** in the presence of piperidine in a variety of solvents



Sl. no.	Thiol	Activator	Solvent	Temp (°C)	Time (min)	**5** (%)	**5a** (%)
1	**1**	NBS	CH_2Cl_2	25	>2	0	92
2	**1**	NBS	CH_2Cl_2	−40	2	75	20
3	**1**	NBS	CH_2Cl_2	−60	5	75	20
4	**1**	NCS	CH_2Cl_2	25	2	0	94
5	**1**	NCS	CH_2Cl_2	−40	2	75	20
6	**1**	NIS	CH_2Cl_2	−40	2	30	60
7	**1**	NIS	CH_2Cl_2	−60	2	40	50
8	**1**	CBr_4	CH_2Cl_2	−40	2	0	95
9	**1**	NCS	$(CH_2Cl)_2$	−40	2	74	15
10	**1**	NCS	$CHCl_3$	−40	2	72	20
11	**1**	NCS	THF	−40	30	40	50
12	**1**	NCS	DMF	−40	15	15	70
13	**1**	NCS	CH_3CN	−40	20	20	60
14	**1**	NCS	Toluene	−40	120	25	30

halosuccinimide was reported earlier by Abe *et al.*[15] for the preparation of *N*-alkyl or *N*-arylthio succinimides derivatives *via in situ* generation of sulfenyl chloride (Scheme 1). We report herein our findings on the treatment of glycosyl thiols with halonium ion followed by reaction with different amines to furnish glycosyl sulfenamides and their oxidized products (Scheme 2).

Results and discussion

In a set of initial experiments, it was decided to screen a set of halonium ion source, such as NIS, NBS and NCS for the generation of stable glycosyl sulfenium halide intermediate for its reaction with appropriate amines. In order to do so, compound **1** was treated with a varied quantity of *N*-halosuccinimide in CH_2Cl_2 at low temperature and room temperature. After a series of experimentation it was observed that treatment of compound **1** with NBS (1 equiv.) or NCS (1 equiv.) in CH_2Cl_2 at −40 °C in the presence of piperidine resulted in the formation of expected glycosyl sulfenamide derivative (**5**) in 60% yield together with diglucosyldisulfide (**5a**) in 25% yield within 2 min. Changing the reaction condition by the variation of temperature, time and quantity of reagents did not reflect any further improvement in the yield of the product. Satisfactory yields of the corresponding glycosyl sulfenamide derivatives were also obtained using primary amines and aromatic amines under similar reaction conditions. In contrast, treatment of compound **1** with NIS (1 equiv.) in the presence of secondary amines furnished poor yield of the corresponding sulfenamide derivatives and use of primary amines or aromatic amines led to the formation of disulfide derivative only. In another experiment, treatment of compound **1** with a combination of carbon tetrabromide (CBr_4) (1 equiv.) and triethylamine (Et_3N) in the presence of piperidine in CH_2Cl_2 at room temperature instantly led to the exclusive formation of disulfide derivative instead of expected sulfenamide derivative. There was no improvement in the formation of required product by carrying out the reaction at low temperature (−10 to −30 °C). A number of commonly used solvents such as CH_2Cl_2, $CHCl_3$, THF, DMF, toluene, CH_3CN *etc.* were screened and CH_2Cl_2 was found as the best solvent to furnish highest yield of the products. Detailed observation on the optimization of the reaction conditions is presented in Table 1. A comparative study has been carried out for the formation of glycosyl sulfenamide from glycosyl thiols using the present reaction condition together with earlier reported conditions, which is presented in Table 2. It is noteworthy to mention that the present reaction condition has several advantages such as, significantly fast, simple reaction condition, good yielding, involves non-hazardous reagents

Table 2 Comparative studies for the preparation of glycosyl sulfenamide **4** using different activators in CH_2Cl_2

Sl. no.	Thiol	Activator	Solvent	Temp (°C)	Time[a] (min)	Time[b] (h)	**5** (%)
1	**1**	SO_2Cl_2	CH_2Cl_2	−40	30[a]	2	55
2	**1**	$BrCH(CO_2Et)_2$	CH_2Cl_2	20	20[a]	12	65
3	**1**	NBS	CH_2Cl_2	−40	2	—	75
4	**1**	NCS	CH_2Cl_2	−40	2	—	75
5	**1**	$AgNO_3$	CH_3CN	20	—	24	35

[a] Time required for the formation of sulfenyl chloride. [b] Time allowed at room temperature after the formation of sulfenyl chloride.

Table 3 Preparation of glycosyl sulfenamide derivatives using NBS or NCS in CH_2Cl_2 at −40 °C[a]

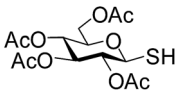
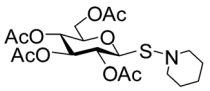
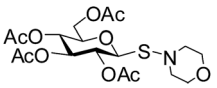
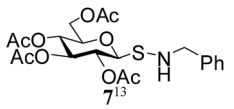
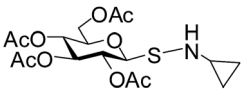
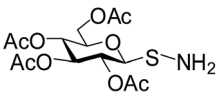
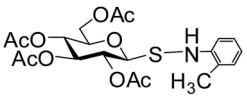
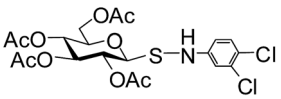
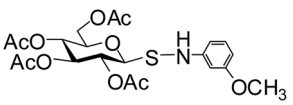
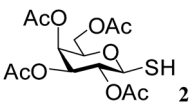
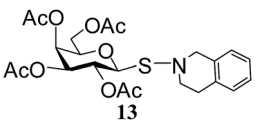
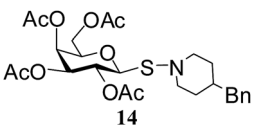
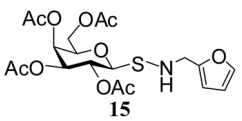
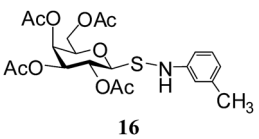
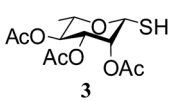
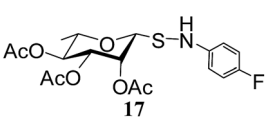
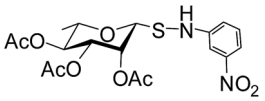
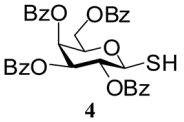
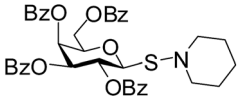
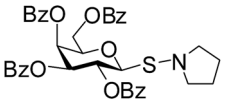
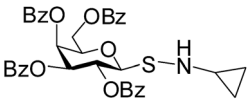
Sl. no.	Thiol	Sulfenamide	Time (min)	Yield (%)
1	 **1**	 **5**[13]	2	75
2	**1**	 **6**	2	70
3	**1**	 **7**[13]	2	68
4	**1**	 **8**	2	66
5	**1**	 **9**[a]	5	60
6	**1**	 **10**	5	68
7	**1**	 **11**	5	66
8	**1**	 **12**	5	68
9	 **2**	 **13**	2	68
10	**2**	 **14**	2	74
11	**2**	 **15**	2	67
12	**2**	 **16**	5	66
13	 **3**	 **17**	5	65

Table 3 (*Contd.*)

Sl. no.	Thiol	Sulfenamide	Time (min)	Yield (%)
14	**3**	 **18**	5	65
15	 **4**	 **19**	5	82
16	**4**	 **20**	5	85
17	**4**	 **21**	5	72

[a] NH_4OH used as amine.

without requirement of any special reaction condition. Following the optimized reaction condition a series of *S*-glycosyl sulfenamide derivatives (**5–21**) have been synthesized in good yield (Table 3). The reaction condition is significantly fast and better yield of the sulfenamide derivatives were obtained using aliphatic amines in comparison to the aromatic amines. The reaction condition is compatible to the various functional groups used for the functionalization of carbohydrates. In every case minor quantities of diglycosyl disulfide was obtained as by product. All synthesized products were characterized with their NMR and mass spectral analysis.

After preparing a series of glycosyl sulfenamide derivatives it was sought to achieve glycosyl sulfinamide and sulphonamide derivatives applying suitable oxidizing conditions. Following the earlier findings reported by Knapp *et al.*,[12] controlled treatment of compound **5** with 1.0 equiv. of 3-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 at −20 °C furnished corresponding sulfinamide **22** in 72% yield without formation of overoxidized product (*e.g.* sulphonamide). Applying similar reaction conditions, a series of glycosyl sulfinamide derivatives (**22–29**) have been synthesized (Table 4). It is noteworthy that glycosylsulfoxides were obtained as a mixture of regioisomers, which were inseparable by column chromatography. The ratio of the isomers was calculated from the integration values in the ^1H NMR spectra of compounds.

Having achieved the successful transformation of glycosyl sulfenamides into sulfinamides, we turned our attention towards the preparation of glycosyl sulphonamide derivatives. For this purpose, we have applied a rapid, neutral oxidation condition using a combination of $KMnO_4$ and $CuSO_4 \cdot 5H_2O$, which have been used earlier[13] for the oxidation of sulphides into sulfone derivatives in our laboratory. A series of glycosyl sulfenamide derivatives have been treated with a mixture of $KMnO_4/CuSO_4 \cdot 5H_2O$ (1.5 : 1) in $CH_3CN–H_2O$ (5 : 1) at room temperature to furnish excellent yield of corresponding sulphonamide derivatives (**30–35**) in short period of time (Table 5).

Conclusions

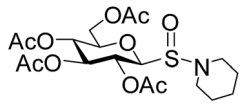
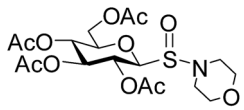
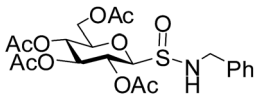
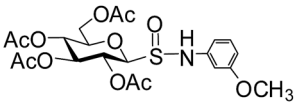
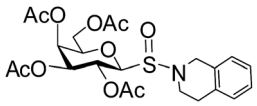
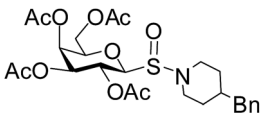
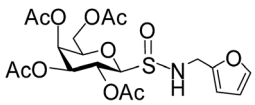
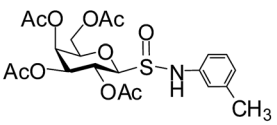
In summary, a series of glycosyl sulfenamides, sulfinamides and sulfonamides have been synthesized from glycosyl thiols under mild reaction conditions using easily accessible reagents. These compounds could be useful as precursors for the development of pharmaceutically important glycomimetics. Noteworthy to mention that the formation of sulfenamide derivatives is significantly fast and should be considered as better alternative for the preparation of a wide range of glycosyl sulfenamides, sulfinamides and sulphonamides because of their operational simplicity, use of mild reaction conditions avoiding hazardous reagents, selectivity for the product formation, reasonably high yield, easy to scale up.

Experimental

General methods

All reactions were monitored by thin layer chromatography over silica gel coated TLC plates. The spots on TLC were visualized by warming ceric sulphate (2% $Ce(SO_4)_2$ in 2 N H_2SO_4) sprayed plates on a hot plate. Silica gel 230–400 mesh was used for column chromatography. ^1H and ^{13}C NMR, 2D COSY, HSQC spectra were recorded on Bruker Avance 500 MHz spectrometer using $CDCl_3$ as solvent and TMS as internal reference unless stated otherwise. Chemical shift values are expressed in δ ppm.

Table 4 Preparation of glycosyl sulfinamides from the corresponding sulfenamides using *m*CPBA at −20 °C[a]

Sl. no.	Compound	Sulfinamides	Isomeric ratio	Yield (%)
1	**5**	 **22**	3	78
2	**6**	 **23**	3	75
3	**7**	 **24**	3	75
4	**12**	 **25**	3	76
5	**13**	 **26**	3	75
6	**14**	 **27**	3	76
7	**15**	 **28**	3	74
8	**16**	 **29**	3	76

[a] All reactions took 3 h for completion.

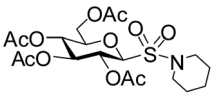
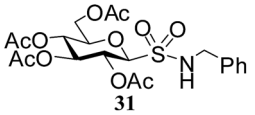
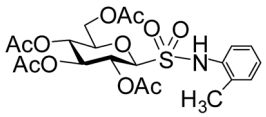
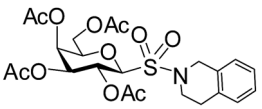
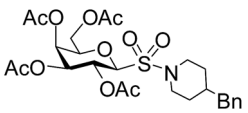
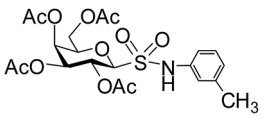
ESI-MS were recorded on a Micromass mass spectrometer. Elementary analysis was carried out on Carlo Erba analyzer.

Typical experimental condition for the preparation of glycosyl sulfenamide (5–21)

A solution of per-*O*-acetylated glycosyl thiol (1 mmol) and amine (1 mmol) in anhydrous CH_2Cl_2 (10 mL) was cooled to −40 °C. To the cooled reaction mixture was added a solution of NBS or NCS (1 mmol) in CH_2Cl_2 (5 mL) drop wise and the reaction stirred for appropriate time (Table 2). The reaction takes place instantaneously. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and successively washed with 5% $Na_2S_2O_3$ (50 mL) and H_2O (50 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc (2 : 1) to give pure compound **5–21** (Table 2). All products were characterized using their spectral analysis. Analytical data of synthesized compounds those are not reported earlier:

***N*-Morpholinyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (6).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.19 (m, 2H, H-2, H-3), 5.04 (t, J = 8.5 Hz, 1H, H-4), 4.55 (d, J = 9.5 Hz, 1H, H-1), 4.20 (dd, J = 12.0, 4.5 Hz, 1H, H-6_a), 4.11 (dd, J = 12.0, 1.2 Hz, 1H, H-6_b), 3.72–3.60 (m, 5H, H-5, 2 OCH_2), 3.06–2.92 (m, 4H, 2 NCH_2), 2.06, 2.03, 2.02, 2.01 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 168.8, 168.7 (4C, 4 CH_3CO), 85.5 (C-1), 75.7 (C-5), 74.1 (C-3), 68.0 (C-4), 67.5 (C-2), 67.3 (OCH_2), 61.9 (C-6), 57.4 (NCH_2), 20.5, 20.4 (2C), 20.3 (4 CH_3CO); ESI-MS: 472.1

Table 5 Preparation of glycosyl sulfonamides from the corresponding sulfenamides using $KMnO_4/CuSO_4 \cdot 5H_2O$ at room temperature

Sl. no.	Compound	Sulfonamides	Time (min)	Yield (%)
1	**5**	 **30**	30	90
2	**7**	 **31**	30	85
3	**10**	 **32**	45	84
4	**13**	 **33**	45	90
5	**14**	 **34**	30	90
6	**16**	 **35**	45	86

$[M + Na]^+$; anal. calcd for $C_{18}H_{27}NO_{10}S$ (449.47): C, 48.10; H, 6.05; found: C, 47.95; H, 6.25.

***N*-Cyclopropyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (8).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.27 (t, J = 9.5 Hz, 1H, H-2), 5.15 (t, J = 10 Hz, 1H, H-3), 5.06 (t, J = 9.5 Hz, 1H, H-4), 4.24 (dd, J = 12.0, 4.0 Hz, 1H, H-6_a), 4.20–4.13 (m, 1H, H-6_b, H-1), 3.74–3.68 (m, 1H, H-5), 3.31 (br s, 1H, N*H*), 2.63–2.59 (m, 1H, NC*H*), 2.06, 2.05, 2.02, 2.00 (4 s, 12H, 4 COCH_3), 0.58–0.51 (m, 4H, 2 CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 169.7, 169.6, 169.1 (4C, 4 CH_3CO), 87.4 (C-1), 75.7 (C-5), 73.7 (C-3), 68.1 (C-4), 67.4 (C-2), 61.7 (C-6), 33.5 (*C*H), 20.6, 20.5 (2C), 20.4 (4 *C*H_3CO), 8.8 (*C*H_2), 8.4 (*C*H_2); ESI-MS: 442.1 $[M + Na]^+$; anal. calcd for $C_{17}H_{25}NO_9S$ (419.45): C, 48.68; H, 6.01; found: C, 48.50; H, 6.20.

1-*S*-(2,3,4,6-Tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.30 (t, J = 9.5 Hz, 1H, H-2), 5.19 (t, J = 9.5 Hz, 1H, H-3), 5.03 (t, J = 9.5 Hz, 1H, H-4), 4.30 (dd, J = 12.5, 5.0 Hz, 1H, H-6_a), 4.24 (d, J = 11 Hz, 1H, H 6_b), 4.0 (d, J = 9.5 Hz, 1H, H-1), 3.80–3.75 (m, 1H, H-5), 2.53 (br s, 2H, NH_2), 2.10, 2.07, 2.02, 2.01 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.2, 169.8, 169.6, 169.1 (4C, 4 CH_3CO), 86.4 (C-1), 75.9 (C-5), 73.4 (C-3), 68.1 (C-4), 66.5 (C-2), 61.9 (C-6), 20.5, 20.4 (2C), 20.3 (4 *C*H_3CO); ESI-MS: 402.1 $[M + Na]^+$; anal. calcd for $C_{14}H_{21}NO_9S$ (379.38): C, 44.32; H, 5.58; found: C, 44.15; H, 5.74.

***N*-(2-Methylphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (10).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–6.72 (m, 4H, Ar-H), 5.26 (t, J = 9.5 Hz, 1H, H-2), 5.12 (t, J = 9.5 Hz, 1H, H-3), 5.05 (s, 1H, N*H*), 4.95 (t, J = 9.5 Hz, 1H, H-4), 4.27–4.24 (m, 1H, H-6_a), 4.21 (d, J = 9.5 Hz, 1H, H-1), 4.05 (dd, J = 12.5, 4.0 Hz, 1H, H-6_b), 3.67–3.60 (m, 1H, H-5), 2.25 (s, 3H, CH_3), 2.14, 2.00, 1.99, 1.91 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.9, 169.6, 168.9 (4C, 4 *C*OCH_3), 144.7–113.6 (Ar-C), 87.9 (C-1), 75.9 (C-5), 73.5 (C-3), 68.0 (C-4), 67.6 (C-2), 61.4 (C-6), 20.8, 20.6, 20.4, 20.3 (4 *C*H_3CO), 17.2 (CH_3); ESI-MS: 492.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_9S$ (469.51): C, 53.72; H, 5.80; found: C, 53.56; H, 6.00.

***N*-(3,4-Dichlorophenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (11).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28–6.87 (m, 3H, Ar-H), 5.27 (t, J = 9.5 Hz, 1H, H-2), 5.15 (br s, 1H, N*H*), 5.1 (t, J = 9.5 Hz, 1H, H-3), 4.92 (t, J = 9.5 Hz, 1H, H-4), 4.19–4.16 (m, 1H, H-6_a), 4.15 (d, J = 9.5 Hz, 1H, H-1), 4.08 (dd, J = 12.5, 4.0 Hz, 1H, H-6_b), 3.68–3.64 (m, 1H, H-5), 2.13, 2.00, 1.99, 1.92 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 170, 169.6, 168.8 (4 *C*OCH_3), 146.9–114.2 (Ar-C), 87.9 (C-1), 75.7 (C-5), 73.2 (C-3), 67.7 (C-4), 67.4 (C-2), 61.3 (C-6), 20.6, 20.4, 20.3, 20.2 (4 *C*H_3CO); ESI-MS: 546.0 $[M + Na]^+$; anal. calcd for $C_{20}H_{23}Cl_2NO_9S$ (524.37): C, 45.81; H, 4.42; found: C, 45.66; H, 4.58.

***N*-(3-Methoxyphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfenamide (12).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–6.36 (m, 4H, Ar-H), 5.28 (t, J = 9.5 Hz, 1H, H-2), 5.16–5.10 (m, 2H, N*H*, H-3), 4.95 (t, J = 9.5 Hz, 1H, H-4), 4.24 (d, J = 10.0 Hz, 1H, H-1), 4.19 (dd, J = 12.0, 1.5 Hz, 1H, H-6$_a$), 4.14–4.05 (m, 1H, H-6$_b$), 3.75 (s, 3H, OCH_3), 3.68–3.65 (m, 1H, H-5), 2.12, 2.01, 1.99, 1.92 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.7, 169.6, 169.0 (4 *C*OCH$_3$), 160.3–107.9 (Ar-C), 87.9 (C-1), 75.6 (C-5), 73.5 (C-3), 67.9 (C-4), 67.6 (C-2), 61.5 (C-6), 54.6 (O*C*H$_3$), 20.6, 20.5 (2C), 20.4 (4 *C*H$_3$CO); ESI-MS: 508.1 [M + Na]$^+$; anal. calcd for $C_{21}H_{27}NO_{10}S$ (485.50): C, 51.95; H, 5.61; found: C, 51.80; H, 6.80.

***N*-(3,4-Dihydroisoquinolinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl sulfenamide (13).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–6.95 (m, 4H, Ar-H), 5.37 (d, J = 3.0 Hz, 1H, H-4), 5.32 (t, J = 10.0 Hz, 1H, H-2), 5.06 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 4.68 (d, J = 10.0 Hz, 1H, H-1), 4.23 (s, 2H, NCH_2), 4.16 (dd, J = 11.5, 6.5 Hz, 1H, H-6$_a$), 4.09 (dd, J = 11.5, 6.5 Hz, 1H, H-6$_b$), 3.38–3.26 (m, 2H, NCH_2), 3.06–2.90 (m, 2H, CH_2), 2.09, 2.02, 2.01, 1.97 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 169.0 (4 *C*OCH$_3$), 134.9–125.6 (Ar-C), 86.9 (C-1), 74.0 (C-5), 72.0 (C-4), 67.0 (C-3), 65.0 (C-2), 61.4 (C-6), 58.8 (N*C*H$_2$), 55.2 (N*C*H$_2$), 30.0 (*C*H$_2$), 20.6, 20.5 (2C), 20.4 (4 *C*H$_3$CO); ESI-MS: 518.1 [M + Na]$^+$; anal. calcd for $C_{23}H_{29}NO_9S$ (495.54): C, 55.75; H, 5.90; found: C, 55.60; H, 5.72.

***N*-(4-Benzylpiperidinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosylsulfenamide (14).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.08 (m, 5H, Ar-H), 5.39 (d, J = 3.0 Hz, 1H, H-4), 5.26 (t, J = 10.0 Hz, 1H, H-2), 5.06 (dd, J = 9.5, 3.5, Hz, 1H, H-3), 4.67 (d, J = 10.0 Hz, 1H, H-1), 4.14–4.06 (m, 2H, H-6$_{ab}$), 3.96–3.89 (m, 1H, H-5), 3.24–3.03 (m, 2H, NCH_2), 2.88–2.74 (m, 2H, NCH_2), 2.5 (d, J = 6.5 Hz, 2H, PhCH_2), 2.15, 2.05, 2.01, 1.98 (4 s, 12H, 4 COCH_3), 1.60 (m, 2H, CH_2), 1.40 (br s, 1H, C*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7 (2C), 169.0 (4 *C*OCH$_3$), 140–125.7 (Ar-C), 85.9 (C-1), 73.9 (C-5), 72.0 (C-4), 67.2 (C-3), 65.1 (C-2), 61.3 (C-6), 58.6 (N*C*H$_2$), 57.2 (N*C*H$_2$), 42.9 (Ph*C*H$_2$), 36.8 (*C*H), 33.3 (*C*H$_2$), 33.0 (*C*H$_2$), 20.6, 20.5 (2C), 20.4 (4 *C*H$_3$CO); ESI-MS: 560.2 [M + Na]$^+$; anal. calcd for $C_{26}H_{35}NO_9S$ (537.62): C, 58.09; H, 6.56; found: C, 57.93; H, 6.75.

***N*-(2-Furanylmethyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galacto pyranosyl sulfenamide (15).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–6.22 (m, 3H, Ar-H), 5.42 (d, J = 2.5 Hz, 1H, H-4), 5.38 (t, J = 10.0 Hz, 1H, H-2), 5.12 (dd, J = 10.0, 3.0 Hz, 1H, H-3), 4.26 (dd, J = 14.5, 2.5 Hz, 1H, H-6$_a$), 4.18–4.05 (m, 2H, H-1, H-6$_b$), 3.92–3.88 (m, 1H, H-5), 3.18 (s, 1H, N*H*), 2.16, 2.07, 2.05, 1.87 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.9, 169.8, 169.7 (4 *C*OCH$_3$), 153–107.2 (Ar-C), 88.6 (C-1), 74.3 (C-5), 71.7 (C-4), 67.1 (C-3), 64.7 (C-2), 61.3 (C-6), 50.2 (N*C*H$_2$), 20.6, 20.5 (2C), 20.4 (4 CH$_3$CO); ESI-MS: 482.1 [M + Na]$^+$; anal. calcd for $C_{19}H_{25}NO_{10}S$ (459.47): C, 49.67; H, 5.48; found: C, 49.50; H, 5.65.

***N*-(3-Methylphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galacto pyranosylsulfenamide (16).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07–6.64 (m, 4H, Ar-H), 5.31 (br s, 1H, N*H*), 5.29 (t, J = 10.0 Hz, 1H, H-2), 5.17 (d, J = 5.5 Hz, 1H, H-4), 5.09 (d, J = 10.0 Hz, 1H, H-3), 4.29 (d, J = 10.0 Hz, 1H, H-1), 4.12–4.10 (m, 1H, H-6$_a$), 4.05–4.03 (m, 1H, H-6$_b$), 3.88 (m, 1H, H-5), 2.29 (s, 3H, CH_3), 2.17, 2.07, 2.02, 1.95 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 170, 169.9, 169.7 (4 *C*OCH$_3$), 147.0–112.6 (Ar-C), 88.6 (C-1), 73.9 (C-5), 71.5 (C-4), 66.8 (C-3), 64.9 (C-2), 61.2 (C-6), 21.4 (*C*H$_3$), 20.8, 20.5 (2C), 20.3 (4 CO*C*H$_3$); ESI-MS: 492.1 [M + Na]$^+$; anal. calcd for $C_{21}H_{27}NO_9S$ (469.51): C, 53.72; H, 5.80; found: C, 53.56; H, 6.00.

***N*-(4-Fluorophenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-L-rhamnopyranosylsulfenamide (17).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81–6.54 (m, 4H, Ar-H), 5.37 (dd, J = 1.3 Hz, 1H, H-2), 5.03 (t, J = 8.5 Hz, 1H, H-4), 4.94 (dd, J = 10.5, 3.5 Hz, 1H, H-3), 4.60 (d, J = 1.2 Hz, 1H, H-1), 3.60–3.55 (m, 1H, H-5), 3.44 (s, 1H, N*H*), 2.17, 2.02, 1.95 (3 s, 9H, 3 COCH_3), 1.29 (d, J = 6.5 Hz, 3H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 169.4 (2C) (3*C*OCH$_3$), 142.2–115.5 (Ar-C), 84.8 (C-1), 72.9 (C-3), 70.9 (C-5), 69.9 (C-4), 69.6 (C-2), 20.7, 20.5 (2C) (3 *C*OCH$_3$), 17.4 (C*C*H$_3$); ESI-MS: 438.1 [M + Na]$^+$; anal. calcd for $C_{18}H_{22}FNO_7S$ (415.43): C, 52.04; H, 5.34; found: C, 51.87; H, 5.53.

***N*-(3-Nitrophenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-L-rhamnopyranosylsulfenamide (18).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56–6.90 (m, 4H, Ar-H), 5.41 (dd, J = 3.5, 1.5 Hz, 1H, H-2), 5.07 (t, J = 10.0 Hz, 1H, H-4), 4.97 (dd, J = 10.0, 3.0 Hz, 1H, H-3), 4.64 (br s, 1H, H-1), 3.97 (br s, 1H, N*H*), 3.63–3.60 (m, 1H, H-5), 2.21, 2.05, 1.98 (3 s, 9H, 3 COCH_3), 1.33 (d, J = 6.5 Hz, 3H, CCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 169.4 (2C) (3 *C*OCH$_3$), 129.8–119.0 (Ar-C), 84.8 (C-1), 72.9 (C-3), 70.9 (C-5), 69.9 (C-4), 69.6 (C-2), 20.7, 20.5 (2C) (3 CH$_3$CO), 17.4 (C*C*H$_3$); ESI-MS: 465.1 [M + Na]$^+$; anal. calcd for $C_{18}H_{22}N_2O_9S$ (442.44): C, 48.86; H, 5.01; found: C, 48.70; H, 5.20.

***N*-Piperidinyl-1-*S*-(2,3,4,6-tetra-*O*-benzoyl)-β-D-galactopyranosyl sulfenamide (19).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12–7.23 (m, 20H, Ar-H), 6.10 (d, J = 3.0 Hz, 1H, H-4), 5.90 (t, J = 10.0 Hz, 1H, H-2), 5.16 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 5.02 (d, J = 10.0 Hz, 1H, H-1), 4.62–4.60 (m, 1H, H-5), 4.41–4.37 (m, 2H, H-6$_{ab}$), 3.07–3.04 (m, 2H, NCH_2), 2.94–2.92 (m, 2H, NCH_2), 1.58–1.50 (m, 4H, CH_2), 1.38–1.36 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (2C), 165.1 (2C) (4 Ph*C*O), 133.5–128.2 (Ar-C), 86.2 (C-1), 74.8 (C-3), 73.2 (C-4), 68.5 (C-2), 66.0 (C-5), 62.5 (C-6), 59.0 (2C, N*C*H$_2$), 27.0 (2C, *C*H$_2$); ESI-MS: 718.2 [M + Na]$^+$; anal. calcd for $C_{39}H_{37}NO_9S$ (695.21): C, 67.32; H, 5.36; found: C, 67.20; H, 5.50.

***N*-Pyrrolidinyl-1-*S*-(2,3,4,6-tetra-*O*-benzoyl)-β-D-galactopyranosyl sulfenamide (20).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–7.23 (m, 20H, Ar-H), 6.01 (d, 2.5 Hz, 1H, H-4), 5.99 (t, J = 10.0 Hz, 1H, H-2), 5.63 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 4.89 (d, J = 10.0 Hz, 1H, H-1), 4.68–4.62 (m, 1H, H-5), 4.39–4.35 (m, 2H, H-6$_{ab}$), 3.13–3.10 (m, 4H, NCH_2), 1.82–1.78 (m, 4H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 165.5, 165.3, 165.2 (4 Ph*C*O), 133.5–128.2 (Ar-C), 87.7 (C-1), 74.8 (C-3), 73.3 (C-4), 68.4 (C-2), 66.0 (C-5), 62.4 (C-6), 57.0 (2C, N*C*H$_2$), 25.6 (2C, *C*H$_2$); ESI-MS: 704.2 [M + Na]$^+$; anal. calcd for $C_{38}H_{35}NO_9S$ (681.20): C, 66.95; H, 5.17; found: C, 66.80; H, 5.30.

***N*-Cyclopropyl-1-*S*-(2,3,4,6-tetra-*O*-benzoyl)-β-D-galactopyranosyl sulfenamide (21).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07–7.23 (m, 20H, Ar-H), 6.04 (d, J = 3.0 Hz, 1H, H-4), 5.98 (t, J = 10.0 Hz, 1H, H-2), 5.75 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 4.70–4.65 (m, 1H, H-5), 4.50 (d, J = 10.0 Hz, 1H, H-1), 4.40–4.30 (m, 2H, H-6$_{ab}$), 3.50 (br s, 1H, N*H*), 2.88–2.82 (m, 1H, NC*H*), 1.51–1.49 (m, 4H,

CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.4 (2C), 165.2 (2C) (4 Ph*C*O), 133.5–128.2 (Ar-C), 88.4 (C-1), 75.0 (C-3), 72.6 (C-4), 68.4 (C-2), 66.0 (C-5), 62.1 (C-6), 33.6 (N*C*H), 9.0, 8.7 (2C, *C*H_2); ESI-MS: 690.1 $[M + Na]^+$; anal. calcd for $C_{37}H_{33}NO_9S$ (667.18): C, 66.55; H, 4.98; found: C, 66.40; H, 5.20.

Typical experimental condition for the preparation of glycosyl sulfinamide (22–29)

A solution of glycosyl sulfenamide (1.0 mmol) in CH_2Cl_2 (15 mL) was cooled to −20 °C. To the cooled reaction mixture was added *m*CPBA (1.0 mmol) and it was allowed to stir at same temperature for 3 h. The reaction was quenched by addition of satd. Na_2SO_3 (15 mL) and extracted with CH_2Cl_2 (50 mL). The organic layer was successively washed with satd. $NaHCO_3$ (50 mL), H_2O (50 mL), dried (Na_2SO_4) and concentrated. The crude product was purified over SiO_2 using hexane–EtOAc (1 : 2) to give pure sulfinamide derivatives (**22–29**) as a mixture of regioisomers (Table 3). Analytical data of synthesized compounds those are not reported earlier:

***N*-Piperidinyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfinamide (22) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.33 (t, J = 9.0 Hz, 1H, H-3), 5.25 (t, J = 9.5 Hz, 1H, H-2), 5.05 (t, J = 8.5 Hz, 1H, H-4), 4.25–4.19 (m, 2H, H-6_{ab}), 4.11 (d, J = 10.0 Hz, 1H, H-1), 3.71–3.69 (m, 1H, H-5), 3.22–3.17 (m, 4H, 2 OCH_2), 2.06, 2.03, 2.02, 2.01 (4 s, 12H, 4 COCH_3), 1.70–1.54 (m, 6H, 3 CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 168.8, 168.7 (4C, 4 CH_3CO), 90.1 (C-1), 76.4 (C-5), 73.5 (C-3), 68.3 (C-4), 67.7 (C-2), 61.9 (C-6), 48.4 (NCH_2), 26.2 (2C), 24.3 (3 *C*H_2), 20.5, 20.4 (2C), 20.3 (4 *C*H_3CO); ESI-MS: 486.1 $[M + Na]^+$; anal. calcd for $C_{19}H_{29}NO_{10}S$ (463.50): C, 49.23; H, 6.31; found: C, 49.10; H, 6.47.

***N*-Morpholinyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfinamide (23) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.32 (t, J = 9.0 Hz, 1H, H-3), 5.24 (t, J = 9.5 Hz, 1H, H-2), 5.01 (t, J = 8.5 Hz, 1H, H-4), 4.25–4.19 (m, 1H, H-6_a), 4.17–4.12 (m, 2H, H-1, H-6_b), 3.75–3.69 (m, 5H, H-5, 2 OCH_2), 3.03–3.20 (m, 4H, 2 NCH_2), 2.06, 2.03, 2.02, 2.01 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.7, 168.8, 168.7 (4C, 4 CH_3CO), 90.5 (C-1), 77.2 (C-5), 73.2 (C-3), 68.0 (C-4), 67.8 (C-2), 67.0 (OCH_2), 61.9 (C-6), 47.4 (NCH_2), 20.5, 20.4 (2C), 20.3 (4 *C*H_3CO); ESI-MS: 488.1 $[M + Na]^+$; anal. calcd for $C_{18}H_{27}NO_{11}S$ (465.47): C, 46.45; H, 5.85; found: C, 46.30; H, 6.00.

***N*-Benzyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfinamide (24) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.25 (m, 5H, Ar-H), 5.22–5.17 (m, 2H, H-2, H-3), 5.07 (t, J = 9.5 Hz, 1H, H-4), 4.68–4.66 (m, 1H, N*H*), 4.35–4.15 (m, 5H, H-1, H-6_{ab}, NCH_2), 4.17–4.15 (m, 1H, H-5), 2.10, 2.07, 2.02, 2.01 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7 (2C), 169.0 (4 *C*OCH$_3$), 138.6–124.1 (Ar-C), 91.7 (C-1), 76.9 (C-5), 73.7 (C-3), 68.4 (C-4), 67.4 (C-2), 61.1 (C-6), 48.2 (*C*NH), 20.6, 20.5 (2C), 20.4 (4 *C*H_3CO); ESI-MS: 508.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_{10}S$ (485.50): C, 51.95; H, 5.61; found: C, 51.80; H, 5.75.

***N*-(3-Methoxyphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfinamide (25): (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03–6.36 (m, 4H, Ar-H), 5.43 (t, J = 9.5 Hz, 1H, H-2), 5.21–5.06 (m, 3H, N*H*, H-3, H-4), 4.41 (d, J = 10.0 Hz, 1H, H-1), 4.29–4.06 (m, 2H, H-6_{ab}), 3.80 (s, 3H, OCH_3), 3.72–3.68 (m, 1H, H-5), 2.12, 2.01, 1.99, 1.92 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.7, 169.6, 169.0 (4 *C*OCH$_3$), 160.3–107.9 (Ar-C), 89.0 (C-1), 69.9 (C-5), 69.8 (C-3), 69.2 (C-4), 67.8 (C-2), 61.3 (C-6), 55.2 (OCH_3), 20.6, 20.5 (2C), 20.4 (4 *C*H_3CO); ESI-MS: 524.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_{11}S$ (501.13): C, 50.29; H, 5.43; found: C, 50.12; H, 5.58.

***N*-(3,4-Dihydroisoquinolinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl sulfinamide (26) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–6.95 (m, 4H, Ar-H), 5.51 (t, J = 10.0 Hz, 1H, H-2), 5.36 (d, J = 3.0 Hz, 1H, H-4), 5.06 (dd, J = 10.0, 3.5 Hz, 1H, H-3), 4.48–4.40 (s, 2H, NCH_2), 4.20 (d, J = 10.0 Hz, 1H, H-1), 4.16–4.00 (m, 2H, H-6_{ab}), 3.38–3.26 (m, 2H, NCH_2), 3.85–3.79 (m, 1H, H-5), 3.55–3.50 (m, 2H, CH_2), 2.09, 2.02, 2.01, 1.97 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 169.0 (4 *C*OCH$_3$), 138.9–114.0 (Ar-C), 90.9 (C-1), 75.2 (C-5), 71.4 (C-4), 66.8 (C-3), 65.5 (C-2), 61.4 (C-6), 46.8 (NCH_2), 44.6 (NCH_2), 33.8 (*C*H_2), 20.6, 20.5 (2C), 20.4 (4 *C*H_3CO); ESI-MS: 534.1 $[M + Na]^+$; anal. calcd for $C_{23}H_{29}NO_{10}S$ (511.54): C, 54.00; H, 5.71; found: C, 53.82; H, 5.85.

***N*-(4-Benzylpiperidinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl sulfinamide (27) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.08 (m, 5H, Ar-H), 5.52 (t, J = 10.0 Hz, 1H, H-2), 5.42 (d, J = 3.0 Hz, 1H, H-4), 5.06 (dd, J = 9.5, 3.5, Hz, 1H, H-3), 4.10 (d, J = 10.0 Hz, 1H, H-1), 4.09–4.03 (m, 2H, H-6_{ab}), 3.96–3.89 (m, 1H, H-5), 3.62–3.48 (m, 2H, NCH_2), 2.88–2.75 (m, 2H, NCH_2), 2.54 (d, J = 6.5 Hz, 2H, PhCH_2), 2.15, 2.05, 2.01, 1.98 (4 s, 12H, 4 COCH_3), 1.80–1.60 (m, 2H, C*H*, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7 (2C), 169.0 (4 *C*OCH$_3$), 139.6–125.7 (Ar-C), 90.6 (C-1), 75.1 (C-5), 71.4 (C-4), 65.3 (C-3), 65.2 (C-2), 61.2 (C-6), 47.2 (NCH_2), 43.0 (NCH_2), 36.3 (*C*H), 32.5 (PhCH_2), 32.3 (*C*H_2), 29.8 (*C*H_2), 20.6, 20.5 (2C), 20.4 (4 *C*H_3CO); ESI-MS: 576.2 $[M + Na]^+$; anal. calcd for $C_{26}H_{35}NO_{10}S$ (553.62): C, 56.41; H, 6.37; found: C, 56.30; H, 6.55.

***N*-(2-Furanylmethyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galacto pyranosyl sulfinamide (28) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–6.27 (m, 3H, Ar-H), 5.48 (d, J = 2.5 Hz, 1H, H-4), 5.36 (t, J = 10.0 Hz, 1H, H-2), 5.06 (dd, J = 10.0, 3.0 Hz, 1H, H-3), 4.77–4.70 (m, 1H, NH), 4.40–4.26 (m, 3H, H-1, CH2), 4.24–4.16 (m, 2H, H-6ab), 4.06–4.02 (m, 1H, H-5), 2.16, 2.07, 2.05, 1.87 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 169.9, 169.8, 169.7 (4 *C*OCH$_3$), 153–107.2 (Ar-C), 89.6 (C-1), 75.3 (C-5), 71.6 (C-4), 66.7 (C-3), 65.7 (C-2), 60.5 (C-6), 40.5 (NCH_2), 20.6, 20.5 (2C), 20.4 (4 CH_3CO); ESI-MS: 498.1 $[M + Na]^+$; anal. calcd for $C_{19}H_{25}NO_{11}S$ (475.47): C, 48.00; H, 5.30; found: C, 47.86; H, 5.45.

***N*-(3-Methylphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galacto pyranosyl sulfinamide (29) (major isomer).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07–6.64 (m, 4H, Ar-H), 5.58 (t, J = 10.0 Hz, 1H, H-2), 5.46 (br s, 2H, H-4, N*H*), 5.21 (dd, J = 9.5, 3.0 Hz, 1H, H-3), 4.40 (d, J = 10.0 Hz, 1H, H-1), 4.38–4.18 (m, 2H, H-6_{ab}), 4.15–4.10 (m, 3H, H-5), 2.34 (s, 3H, CH_3), 2.17, 2.07, 2.02, 1.95 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.1, 170, 169.9, 169.7 (4 *C*OCH$_3$), 140.0–116.6 (Ar-C), 89.6 (C-1), 76.9 (C-5), 71.5 (C-4), 67.8 (C-3), 65.3 (C-2), 61.4 (C-6), 22.4 (*C*H_3), 20.8, 20.5 (2C), 20.3

(4 COCH_3); ESI-MS: 508.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_{10}S$ (485.50): C, 51.95; H, 5.61; found: C, 51.80; H, 5.75.

Typical experimental condition for the preparation of glycosyl sulfonamide (30–35)

To a solution of glycosyl sulfenamide (1.0 mmol) in CH_3CN–H_2O (15 mL; 5 : 1 v/v) was added a mixture of solid $KMnO_4$/$CuSO_4 \cdot 5H_2O$ (500 mg; 1.5 : 1 molar ratio) and it was allowed to stir at room temperature for appropriate time (Table 4). After completion of the reaction (TLC; hexane : EtOAc 1 : 1), the reaction mixture concentrated under reduced pressure and the crude mass was extracted with CH_2Cl_2 (50 mL). The organic layer was washed with water (50 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified over SiO_2 using hexane–EtOAc (3 : 1) to give pure sulfonamide derivatives (**30–35**) (Table 4). Analytical data of synthesized compounds those are not reported earlier:

***N*-Piperidinyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfonamide (30).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.34 (t, J = 9.5 Hz, 1H, H-2), 5.24 (t, J = 9.5 Hz, 1H, H-3), 5.09 (t, J = 9.5 Hz, 1H, H-4), 4.50 (d, J = 10.0 Hz, 1H, H-1), 4.26 (dd, J = 12.5, 5.0 Hz, 1H, H-6_a), 4.20 (dd, J = 12.5, 6.5 Hz, 1H, H-6_b), 3.80–3.77 (m, 1H, H-5), 3.40–3.30 (br s, 4H, 4 NC*H*), 2.08, 2.05, 2.04, 2.01 (4 s, 12H, 4 COCH_3), 1.70–1.55 (m, 6H, 6 C*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7 (2C), 169 (4 *C*OCH$_3$), 87.9 (C-1), 76.1 (C-5), 73.3 (C-3), 67.5 (C-4), 67.4 (C-2), 61.5 (C-6), 47.5 (NCH_2), 25.9 (CH_2), 23.8 (CH_2), 20.5, 20.4 (2C), 20.3 (4 CH_3CO); ESI-MS: 502.1 $[M + Na]^+$; anal. calcd for $C_{19}H_{29}NO_{11}S$ (479.50): C, 47.59; H, 6.10; found: C, 47.42; H, 6.25.

***N*-Benzyl-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfonamide (31).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57–7.22 (m, 6H, Ar-H, N*H*), 5.22 (*t*, J = 10.0 Hz, 1H, H-2), 5.15–5.10 (m, 1H, H-3), 4.99 (t, J = 9.5 Hz, 1H, H-4), 4.45 (dd, J = 12.5, 6.0 Hz, 1H, H-6_a), 4.36 (dd, J = 11.0, 5.5 Hz, 1H, H-6_b), 4.29–4.20 (m, 2H, NCH_2), 4.11 (d, J = 12.5 Hz, 1H, H-1), 3.67–3.62 (m, 1H, H-5), 2.10, 2.07, 2.02, 2.01 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7 (2C), 169.0 (4 *C*OCH$_3$), 140.6–124.1 (Ar-C), 87.7 (C-1), 76.2 (C-5), 72.7 (C-3), 67.7 (C-4), 67.4 (C-2), 61.0 (C-6), 53.0 (*C*NH), 20.6, 20.5 (2C), 20.4 (4 CH_3CO); ESI-MS: 524.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_{11}S$ (501.50): C, 50.29; H, 5.43; found: C, 50.15; H, 5.60.

***N*-(2-Methylphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranosyl sulfonamide (32).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.11 (m, 4H, Ar-H), 5.44 (t, J = 10.0 Hz, 1H, H-2), 5.29 (br s, 1H, N*H*), 5.26 (t, J = 9.5 Hz, 1H, H-3), 5.10 (t, J = 9.5 Hz, 1H, H-4), 4.46 (d, J = 10.0 Hz, 1H, H-1), 4.23 (dd, J = 9.0, 3.5 Hz, 1H, H-6_a), 4.12–4.06 (m, 1H, H-6_b), 3.82–3.79 (m, 1H, H-5), 2.39 (s, 3H, CH_3), 2.07, 2.05, 2.02, 1.97 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 169.7, 169.5, 168.8 (4 *C*OCH$_3$), 134.1–119 (6C, Ar-C), 86.1 (C-1), 76.3 (C-5), 72.8 (C-3), 67.5 (C-4), 67.3 (C-2), 60.0 (C-6), 20.8 (CH_3), 20.8, 20.4 (2C), 20.3 (4 CH_3CO); ESI-MS: 524.1 $[M + Na]^+$; anal. calcd. for $C_{21}H_{27}NO_{11}S$ (501.50): C, 50.29; H, 5.43; found: C, 50.15; H, 5.62.

***N*-(3,4-Dihydroisoquinolinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl sulfonamide (33).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.07 (m, 4H, Ar-H), 5.50 (t, J = 10.0 Hz, 1H, H-2), 5.34 (d, J = 3.0 Hz, 1H, H-4), 5.03 (dd, J = 10.0, 3.0 Hz, 1H, H-3), 4.66–4.54 (m, 2H, H-6_{ab}), 4.52 (d, J = 10.0 Hz, 1H, H-1), 3.96–3.94 (m, 3H, NCH_2, H-5), 3.76–3.66 (m, 2H, NCH_2), 2.99–2.97 (m, 2H, CH_2), 2.07, 2.00, 1.97, 1.96 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 169.5 (2C), 169 (4 *C*OCH$_3$), 133.1–125.9 (Ar-C), 88.8 (C-1), 74.7 (C-5), 71.2 (C-4), 66.5 (C-3), 64.4 (C-2), 60.6 (C-6), 47.9 (NCH_2), 44.1 (NCH_2), 29.2 (CH_2), 20.6, 20.3 (2C), 20.2 (4 CH_3CO); ESI-MS: 550.1 $[M + Na]^+$; anal. calcd for $C_{23}H_{29}NO_{11}S$ (527.54): C, 52.36; H, 5.54; found: C, 52.20; H, 5.67.

***N*-(4-Benzylpiperidinyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galactopyranosyl sulfonamide (34).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27–7.08 (m, 5H, Ar-H), 5.50 (t, J = 10.0 Hz, 1H, H-2), 5.41 (br s, 1H, H-4), 5.05 (d, J = 10.0 Hz, 1H, H-3), 4.47 (d, J = 10.0 Hz, 1H, H-1), 4.19–4.10 (m, 2H, H-6_{ab}), 4.02–3.99 (m, 1H, H-5), 3.91–3.82 (m, 2H, NCH_2), 2.92–2.80 (m, 2H, NCH_2), 2.56 (d, J = 7.0 Hz, 2H, PhCH_2), 2.19, 2.06, 2.04, 1.99 (4 s, 12H, 4 COCH_3), 1.78–1.70 (m, 2H, CH_2), 1.67–1.63 (m, 1H, C*H*); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 169.5, 168.9 (2C) (4 *C*OCH$_3$), 139.1–123.8 (Ar-C), 88.6 (C-1), 74.6 (C-5), 71.2 (C-4), 66.7 (C-3), 64.3 (C-2), 60.9 (C-6), 47.4 (*C*NH), 46.5 (*C*NH), 42.7 (Ph*C*H$_2$), 37.7 (*C*H), 32.1 (CH_2), 32.0 (CH_2), 20.6, 20.5, 20.4, 20.3 (4 CH_3CO); MALDI-MS: 592.1 $[M + Na]^+$; anal. calcd for $C_{26}H_{35}NO_{11}S$ (569.62): C, 54.82; H, 6.19; found: C, 54.70; H, 6.35.

***N*-(3-Methylphenyl)-1-*S*-(2,3,4,6-tetra-*O*-acetyl)-β-D-galacto pyranosyl sulfonamide (35).** ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–6.99 (m, 4H, Ar-H), 5.59 (t, J = 10.0 Hz, 1H, H-2), 5.31 (s, 1H, N*H*), 5.29 (d, J = 1.2 Hz, 1H, H-4), 5.05 (dd, J = 10.0, 3.0 Hz, 1H, H-3), 4.41 (d, J = 10.0 Hz, 1H, H-1), 4.15–4.10 (m, 2H, H-6_{ab}), 3.99–3.95 (m, 1H, H-5), 2.36 (s, 3H, CH_3), 2.12, 2.05, 2.00, 1.97 (4 s, 12H, 4 COCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.6, 169.5 (2C), 169.4 (4 *C*OCH$_3$), 139.0–119.1 (Ar-C), 86.7 (C-1), 74.9 (C-5), 70.9 (C-4), 66.6 (C-3), 64.5 (C-2), 61.1 (C-6), 50.2 (N*C*H), 21.3 (CH_3), 20.7, 20.5, 20.4, 20.3 (4 CH_3CO); ESI-MS: 524.1 $[M + Na]^+$; anal. calcd for $C_{21}H_{27}NO_{11}S$ (501.50): C, 50.29; H, 5.43; found: C, 50.16; H, 5.61.

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