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## Radical Mediated Diastereoselective Synthesis of Benzothiazole Sulfonyl Ethyl C-Glycosides<sup>#</sup>

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### ABSTRACT

Diastereoselective synthesis of a variety of benzothiazole sulfonyl ethyl C-glycosides has been developed by a radical mediated approach on the reaction of glycosyl bromides and benzothiazolyl vinyl sulfone in the presence of *n*-Bu<sub>3</sub>SnH and AIBN in good yields.

*Key Words:* C-glycosides; Radical reaction; Benzothiazolyl vinyl sulfone; Glycosyl halides.

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## INTRODUCTION

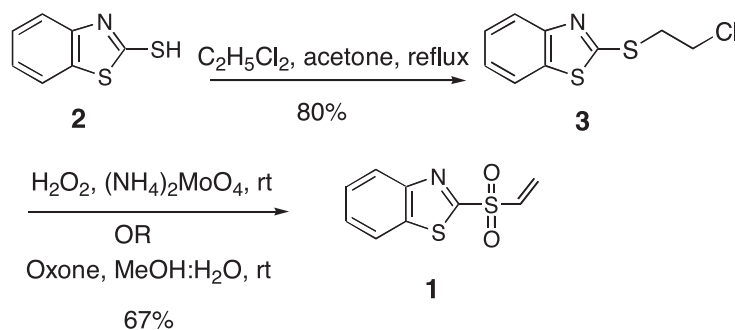
The plethora of methods developed for the synthesis of C-glycosides and C-saccharides bears testimony to the growing importance of glycosyl mimics. This class of compounds has varied biological activity such as anti-tumor, anti-bacterial or anti-viral activity<sup>[1,2]</sup> and plays effective roles as modulators and inhibitors,<sup>[3]</sup> which is attributed to their higher hydrolytic tolerance as compared to natural counterparts. The importance of C-glycoside sulfones (sulfones are non-ionic and increase membrane permeability), like anomeric sugar phosphates,<sup>[4]</sup> as glycosyl transferase inhibitors, has given impetus to the synthesis of sulfonyl methyl C-glycosides.<sup>[5]</sup> Our continued interest in glycosyl mimics has resulted in newer methodologies for synthesis of C-alkyl glycosides,<sup>[6]</sup> C-vinyl glycosides,<sup>[7]</sup> C-C disaccharides,<sup>[8]</sup> C-linked spiro saccharides<sup>[9]</sup> and pseudo saccharide precursors.<sup>[10]</sup> Herein, we report a radical mediated protocol for the synthesis of benzothiazole sulfonyl ethyl-C-glycosides from glycosyl bromides.

In earlier reports, C-glycoside sulfones were prepared by a Wittig approach<sup>[11]</sup> or by a radical addition of thioacetic acid<sup>[5]</sup> to perbenzylated exocyclic glycal and the oxidation of the thus formed C-glycoside sulfide to sulfone. Even though glycosyl radicals have been generated and reacted with a variety of Michael acceptors<sup>[12–14]</sup> use of vinyl sulfones for such a reaction resulting in C-glycoside sulfones is yet to be realised. Hence, in the present study, benzothiazolyl vinyl sulfone<sup>[15]</sup> (**1**) was prepared and used as a radical acceptor for the synthesis of C-glycoside sulfones.

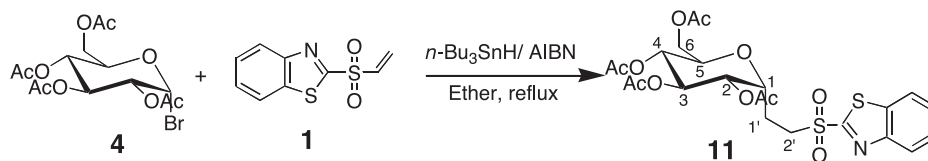
## RESULTS AND DISCUSSION

The requisite Michael acceptor, benzothiazolyl vinyl sulfone (**1**), was prepared from mercaptobenzothiazole **2** in 3 steps (Scheme 1). Accordingly, reaction of ethylene dichloride with mercaptobenzothiazole in acetone at reflux gave the corresponding sulfide **3** (80%), which on reaction with either ammonium molybdate in the presence of hydrogen peroxide [(NH<sub>4</sub>)<sub>2</sub>MoO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>] at room temperature or oxone in MeOH:H<sub>2</sub>O (1: 1.25) resulted in the formation of **1** (67%).

The vinyl sulfone (**1**) was utilized as a Michael acceptor for the first time in the reductive radical reaction of glycosyl bromides to give the C-glycoside sulfones.



Scheme 1.



Scheme 2.

Accordingly, a mixture of acetobromo glucose (**4**) and vinyl sulfone (**1**) in ether was treated with  $n\text{-Bu}_3\text{SnH}$  in the presence of AIBN at reflux to afford the C-glycoside (**11**) in 66% yield (Scheme 2), which was thoroughly characterised from spectral data. In the  $^1\text{H}$  NMR of **11**, H-2 resonated at  $\delta$  5.1 as a double doublet with coupling constants of 5.6 Hz ( $J_{1,2}$ ) and 9.0 Hz ( $J_{2,3}$ ) corroborative of the assigned structure.

The validity of the present methodology was demonstrated by the conversion of a variety of sugar substrates such as aldohexoses **4–7**, uronate **8**, aldopentose **9** and disaccharide **10** containing different protecting groups such as acetate, benzoate and ester, into the corresponding C-glycoside sulfones, **11–14**, **15**, **16** and **17**, respectively, in 60–73% yields (Table 1). Similarly, the C-glycosides **12–17** were characterized as  $\alpha$ -C-glycoside sulphones by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and positive values of rotation. The assigned structures **13** and **14** were further supported by NOESY spectra (Figure 1). For instance, **13** showed NOESY cross peaks between H1-H2, H1-H1'a, H2-H2'a, and between H3-H4, H3-H5 and H4-H6b, indicating that they are on the same side of the sugar ring, respectively. It was also observed that there was no NOE between H1-H5 and H1-H3 confirming the compound to be an  $\alpha$  anomer. Likewise **14** exhibited NOESY cross peaks between H1-H1'a, H1-H6a, H2-H2'b and H3-H5. No NOE was observed between H1 and H5 or H1 and H2, which unequivocally confirms the assigned structures. The stereoselective C-glycosidation, with a preference for the formation of  $\alpha$ -anomers is in concurrence with the literature.<sup>[16]</sup>

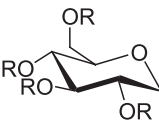
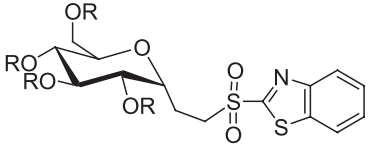
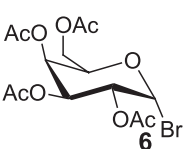
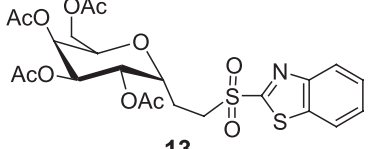
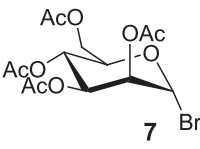
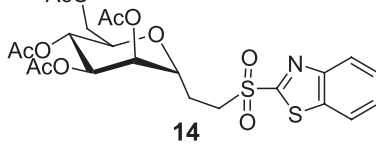
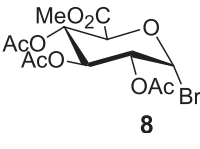
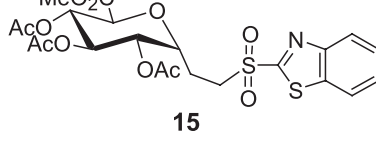
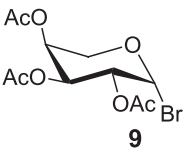
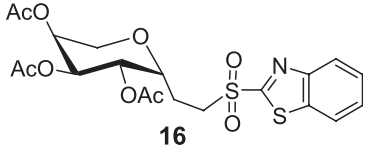
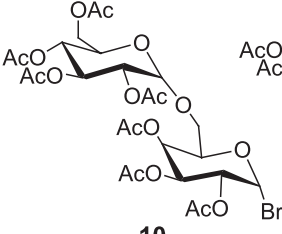
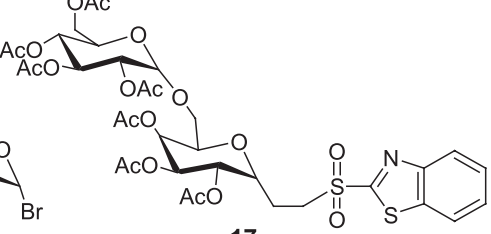
In conclusion, a protocol for the conversion of glycosyl radicals into C- $\alpha$ -glycoside sulfones using benzothiazolyl vinyl sulfone as Michael acceptor is achieved and the resulting C-glycosyl sulfones would find use in glycochemistry. The advantage of using **1**, for C-glycoside sulfone synthesis is evident since thiazoles, benzothiazoles and thiazolesulfones are important chromophores in several bioactive compounds and therapeutics, biological evaluation of these C-glycosides<sup>[17]</sup> would be an attractive proposition.

## EXPERIMENTAL

**General methods.** Solvents were dried over standard drying agents and freshly dried prior to use.  $^1\text{H}$  NMR (200 MHz, 400 MHz, 500 MHz) and  $^{13}\text{C}$  NMR (50 MHz, 100 MHz, 125 MHz) spectra were recorded in deuteriochloroform solution with tetramethylsilane as an internal reference on Varian Gemini-200 MHz, Unity-400 MHz and INOVA-500 MHz spectrometers and J values are given in Hz. 2D experiments like NOESY were carried out with 2X192 transitions. The NOESY experiments were



**Table 1.** Synthesis of C-glycosyl sulphones.

Starting material	Product	Time(h)	Yield(%)
 <b>4</b> R = Ac <b>5</b> R = Bz	 <b>11</b> R = Ac <b>12</b> R = Bz	12 15	66 71
 <b>6</b>	 <b>13</b>	11	73
 <b>7</b>	 <b>14</b>	21	70
 <b>8</b>	 <b>15</b>	22	63
 <b>9</b>	 <b>16</b>	22	60
 <b>10</b>	 <b>17</b>	23	68

performed with mixing time of 0.4 seconds. Optical rotations were measured with a JASCO DIP-370 instrument and  $[\alpha]_D$  values are in units of  $10^{-1} \text{ deg cm}^2 \text{ g}^{-1}$  at  $25^\circ\text{C}$ . Organic solutions were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated below  $40^\circ\text{C}$  under vacuum. HRMS were recorded on V G Autospec Mass Spectrometer at 5 or 7 K resolution using perfluoro kerosene as an internal reference.

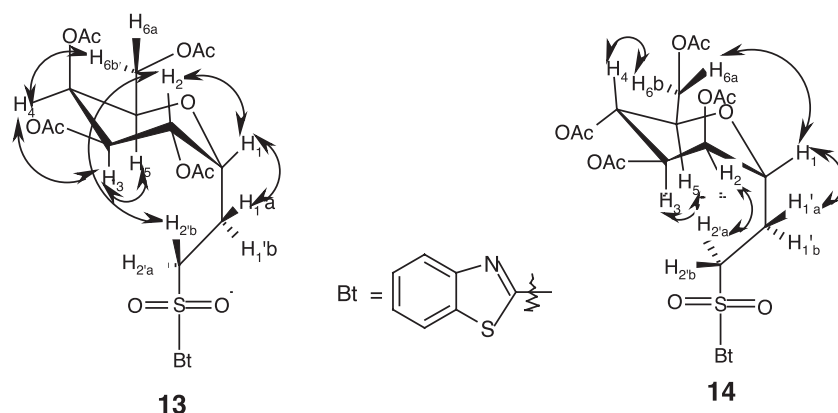


Figure 1. NOEs of compounds **13** and **14**.

**2-(2-Chloroethylsulfonyl)benzo[d][1,3]thiazole 3:** To a solution of mercapto-benzothiazole (**2**, 10 g, 59.8 mmol) in acetone (100 mL),  $K_2CO_3$  (16.5 g, 119.7 mmol) and ethylene dichloride (37 mL, 37.3 mmol) were added and the contents stirred at reflux for 12 h. The solvent was evaporated and the residue extracted with ethyl acetate, washed with brine (50 mL), dried ( $Na_2SO_4$ ), concentrated and purified by column chromatography (silica gel, EtOAc: hexane, 0.05:1) to afford monoalkylated product **3** in 66% (9.0 g) yield as syrup.  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  7.86 (d, 1H, J 9.5 Hz, Ar-H), 7.7 (d, 1H, J 9.5 Hz, Ar-H), 7.40–7.20 (m, 2H, Ar-H), 3.90 (dd, 2H, J 9.5, 16.6 Hz, H-1), 3.65 (dd, 2H, J 9.5, 16.6 Hz, H-2).

Anal. Calcd for  $C_9H_8ClNS_2$ : C 47.05, H 3.51, N 6.10, S 27.91; Found: C 47.03, H 3.53, N 6.08, S 27.89.

**2-Vinylsulfonylbenzo[d][1,3]thiazole 1: Method A:** The alkylated product **3** (9.0 g, 34.4 mmol) in ethanol (90 mL) was treated with  $(NH_4)_2MoO_4$  (12 g, 9.8 mmol) and  $H_2O_2$  (40 mL, 30% solution) at  $0^\circ C$  and the stirred solution allowed to attain room temperature. The reaction mixture was concentrated under reduced pressure and the residue extracted with  $CH_2Cl_2$  ( $2 \times 100$  mL) to afford crude product which was purified by chromatography (silica gel, EtOAc: hexane, 1:9) to afford **1** in 66% yield (7.6 g) as a thick syrup.  $^1H$  NMR (200 MHz,  $CDCl_3$ ):  $\delta$  8.20 (d, 1H, J 8.0 Hz, Ar-H), 8.00 (d, 1H, J 8.00 Hz, Ar-H), 7.82–7.54 (m, 2H, Ar-H), 7.00 (dd, 1H, J 12.0, 8.2 Hz, H-1a), 6.70 (d, 1H, J 16 Hz, H-1b), 6.38 (d, 1H, J 8 Hz, H-2).

Anal. Calcd for  $C_9H_7NO_2S_2$ : C 47.98, H 3.13, N 6.22, S 28.47; Found: C 47.95, H 3.11, N 6.21, S 28.46.

**Method B:** Oxone (39.3 g, 34.54 mmol) was added to a solution of **3** (4.9 g, 18.72 mmol) in methanol:water (176 mL, 1:1.25), and the reaction mixture stirred at room temperature overnight. The solvent was removed under reduced pressure, the residue was dissolved in water (50 mL), extracted with  $CHCl_3$  ( $2 \times 50$  mL), washed with brine ( $1 \times 25$  mL), dried ( $Na_2SO_4$ ) and the organic solution concentrated



to give crude product which was purified by column chromatography (silica gel, EtOAc: hexane, 1:9) to afford **1** in 67.5% yield (4.9 g) as a thick syrup.

**2'-(Benzothiazolyl sulfonyl)-1'-(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl)-ethane **11**.** A mixture of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromide<sup>[18]</sup> (**4**, 0.2 g, 0.48 mmol), **1** (1.6 g, 6.2 mmol), Bu<sub>3</sub>SnH (0.268 mL, 0.9 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 15 h. The solvent was evaporated under reduced pressure and the residue purified by column chromatography (silica gel, EtOAc: hexane, 2:3) to afford **11** in 66% yield (0.14 g) as colourless syrup.  $[\alpha]_D + 10.8$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.22 (d, 1H, *J* 7.6 Hz, Ar-H), 8.05 (d, 1H, *J* 7.6 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.26 (t, 1H, *J* 9.0 Hz, H-3), 5.10 (dd, 1H, *J* 9.0, 5.6 Hz, H-2), 4.94 (t, 1H, *J* 8.8 Hz, H-4), 4.30–4.20 (m, 3H, H-1, H-6), 4.12 (m, 1H, H-5), 3.80 (m, 1H, H-2'a), 3.70 (m, 1H, H-2'b), 2.43–2.20 (m, 2H, H-1'), 2.08, 2.03, 2.02, 2.01 (4s, 12H, OAc); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  171.6, 170.3, 170.0, 169.9, 128.1(2C), 127.7(2C), 125.3, 122.3, 117.5, 101.3, 75.8, 71.50, 69.80, 68.0, 66.7, 50.5, 29.0, 20.0(4C); FAB-MS (*m/z*): 558 (*M*<sup>+</sup> + 1); FAB-HRMS (*M*<sup>+</sup> + 1): calculated for C<sub>23</sub>H<sub>28</sub>NO<sub>11</sub>S<sub>2</sub>: 558.110380; Found: 558.114059.

**2'-(Benzothiazolyl sulfonyl)-1'-(2,3,4,6-tetra-*O*-benzoyl- $\alpha$ -D-glucopyranosyl)-ethane **12**.** 2,3,4,6-Tetra-*O*-benzoyl-D-glucopyranosyl bromide<sup>[18]</sup> (**5**, 0.1 g, 0.15 mmol), **1** (0.33 g, 1.27 mmol), Bu<sub>3</sub>SnH (0.05 mL, 0.17 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 15 h. Workup and purification by column chromatography (silica gel, EtOAc: hexane, 3:7) as reported for compound **11** afforded **12** in 71% yield (0.09 g) as a thick syrup.  $[\alpha]_D + 29.2$  (*c* 0.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.0 (m, 10H, Ar-H), 7.4 (m, 14H, Ar-H), 5.75 (t, 1H, *J* 9.3 Hz, H-3), 5.5 (dd, 1H, *J* 6.9, 2.3 Hz, H-2), 5.3 (dd, 1H, *J* 4.6, 2.3 Hz, H-4), 4.65 (m, 3H, H-1, H-5, H-6a), 4.40 (m, 1H, H-6b), 4.3 (m, 1H, H-2a), 3.85 (m, 1H, H-2'b), 2.45–2.03 (m, 2H, H-1'); FAB-MS (*m/z*): 558 (*M*<sup>+</sup> + 1).

Anal. Calcd for C<sub>47</sub>H<sub>43</sub>NO<sub>11</sub>S<sub>2</sub>: C 65.49, H 5.03, N 1.62, S 7.44; Found: C 65.3, H 5.06, N 1.60, S 7.41.

**2'-(Benzothiazolyl sulfonyl)-1'-(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-galactopyranosyl)-ethane **13**.** 2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl bromide<sup>[19]</sup> (**6**, 0.1 g, 0.15 mmol), **1** (0.81 g, 3.14 mmol), Bu<sub>3</sub>SnH (0.13 mL, 0.46 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 11 h. Workup and purification by column chromatography (silica gel, EtOAc: hexane, 2:3) as reported for **11** afforded **13** in 73% yield (0.16 g) as a thick syrup.  $[\alpha]_D + 12.25$  (*c* 0.8, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d, 1H, *J* 8.15 Hz, Ar-H), 8.05 (d, 1H, *J* 8.15 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.40 (br.t, 1H, *J* 5.73 Hz, H-4), 5.25 (dd, 1H, *J* 4.83, 8.76 Hz, H-3), 5.17 (dd, 1H, *J* 3.32, 8.76 Hz, H-2), 4.30 (m, 2H, H-5, 6a), 4.09 (dd, 1H, *J* 4.50, 11.14 Hz, H-6b), 4.04 (dt, 1H, *J* 3.02, 7.55 Hz, H-1), 3.72–3.68 (m, 1H, H-2'b), 3.57–3.50 (m, 1H, H-2'a), 2.36–2.28 (m, 2H, H-1'), 2.11, 2.06, 2.03, 2.01 (4s, 12H, OAc); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  170.35(2C), 170.0(2C), 128.1, 127.7, 125.3, 122.3, 101.3, 75.8, 70.9, 70.8, 69.5, 69.3, 69.1(2C), 66.7, 60.8, 50.6, 20.5(4C); FAB-MS (*m/z*): 558 (*M*<sup>+</sup> + 1).

Anal. Calcd for C<sub>23</sub>H<sub>27</sub>NO<sub>11</sub>S<sub>2</sub>: C 49.54, H 4.88, N 2.51, S 11.50; Found: C 49.49, H 4.78, N 2.52, S 11.40.



**2'-(Benzothiazolyl sulfonyl)-1'-(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-mannopyranosyl)-ethane 14.** 2,3,4,6-Tetra-*O*-acetyl-D-mannopyranosyl bromide<sup>[18]</sup> (**7**, 0.10 g, 0.39 mmol), **1** (0.81 g, 3.13 mmol), Bu<sub>3</sub>SnH (0.13 mL, 0.39 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 15 h. Workup and purification of the residue by column chromatography (silica gel, EtOAc: hexane, 2:3) as reported for **11** afforded **14** in 70% yield (0.15 g) as a syrup.  $[\alpha]_D + 18.25$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  8.20 (d, 1H, *J* 8.28 Hz, Ar-H), 8.04 (d, 1H, *J* 8.28 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.24 (dd, 1H, *J* 2.7, 5.7 Hz, H-4), 5.06 (dd, 1H, *J* 4.0, 7.2 Hz, H-3), 5.0 (dd, 1H, *J* 2.3, 4.7 Hz, H-2), 4.51 (dd, 1H, *J* 7.8, 11.8 Hz, H-1), 4.11 (dt, 1H, H-6b), 4.0 (m, 1H, H-7), 3.80 (m, 1H, H-6a), 3.75 (m, 1H, H-2'b), 3.45 (m, 1H, H-2'a), 2.40–2.20 (m, 2H, H-1'), 2.20, 2.12, 2.09, 2.05 (4s, 12H, OAc); <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  172.0, 170.8(2C), 169.0, 128.5, 128.1, 127.9, 127.7, 125.6, 125.4, 122.3, 105, 71.64, 68.6, 68.1, 64.0, 62.7, 54.4, 20.9, 20.6(4C), FAB-MS (*m/z*): 558 (*M*<sup>+</sup> + 1).

Anal. Calcd for C<sub>23</sub>H<sub>27</sub>NO<sub>11</sub>S<sub>2</sub>: C 49.54, H 4.88, N 2.51, S 11.50; Found: C 49.51, H 4.82, N 2.52, S 11.48.

**2'-(Benzothiazolyl sulfonyl)-1'-[methyl (2,3,4-tri-*O*-acetyl- $\alpha$ -D-glucopyranosyl)uronate]ethane 15.** Methyl (2,3,4-tri-*O*-acetyl-D-glucopyranosyl bromide)uronate<sup>[20]</sup> (**8**, 0.10 g, 0.25 mmol), **1** (0.52 g, 2.0 mmol), Bu<sub>3</sub>SnH (0.08 mL, 0.29 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 22 h. Workup and purification of the residue by column chromatography (silica gel, EtOAc: hexane, 2:3) as reported for **11** afforded **15** in 63% yield (0.08 g) as a syrup.  $[\alpha]_D + 16.40$  (*c* 0.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (d, 1H, *J* 8.16 Hz, Ar-H), 8.05 (d, 1H, *J* 8.16 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.25 (br.s, 1H, H-5), 5.10 (t, 1H, *J* 7.3 Hz, H-3), 4.70 (br.t, 1H, *J* 6.6 Hz, H-2), 4.52 (br.s, 1H, H-4), 4.50 (br.d, 1H, *J* 9.5 Hz, H-1), 3.80 (s, 3H, OCH<sub>3</sub>), 3.70 (m, 2H, H-2'), 2.35–2.20 (m, 2H, H-1'), 2.15 (br.s, 6H, OAc), 2.0 (s, 3H, OAc); FAB-MS (*m/z*): 544 (*M*<sup>+</sup> + 1).

Anal. Calcd for C<sub>22</sub>H<sub>26</sub>NO<sub>11</sub>S<sub>2</sub>: C 48.61, H 4.64, N 2.58, S 11.80; Found: C 48.53, H 4.86, N 2.60, S 11.76.

**2'-(Benzothiazolyl sulfonyl)-1'-(2,3,4-tri-*O*-acetyl- $\alpha$ -D-arabinopyranosyl)ethane 16.** 2,3,4-Tri-*O*-acetyl-D-arabinopyranosyl bromide<sup>[18]</sup> (**9**, 0.1 g, 0.34 mmol), **1** (0.70 g, 2.7 mmol), Bu<sub>3</sub>SnH (0.12 mL, 0.41 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 11 h. Workup and purification of the residue by column chromatography (silica gel, EtOAc: hexane, 3:7) as reported for **11** afforded **16** in 60% yield (0.11 g) as a thick syrup.  $[\alpha]_D + 20.40$  (*c* 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  8.25 (dd, 1H, *J* 8.05, 2.3 Hz, Ar-H), 8.05 (dd, 1H, *J* 8.05, 2.3 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.30 (t, 1H, *J* 4.3 Hz, H-4), 5.25 (dd, 1H, *J* 4.3, 7.8 Hz, H-3), 4.90 (dd, 1H, *J* 3.56, 7.8 Hz, H-2), 4.20 (d, 1H, *J* 4.65 Hz, H-5a), 3.90 (dt, 1H, *J* 3.0, 7.6 Hz, H-1), 3.80 (dd, 1H, *J* 4.65, 2.3 Hz, H-5b), 3.70–3.40 (m, 2H, H-2'), 2.35–2.21 (m, 2H, H-1'), 2.20, 2.15, 2.05 (3s, 9H, OAc); FAB-MS (*m/z*): 486 (*M*<sup>+</sup> + 1).

Anal. Calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>9</sub>S<sub>2</sub>: C 49.48, H 4.77, N 2.88, S 13.21; Found: C 49.42, H 4.76, N 2.86, S 13.24.

**2'-(Benzothiazolyl sulfonyl)-1'-[2,3,4-tri-*O*-acetyl-6-*O*-(2'',3'',4'',6''-tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl)- $\alpha$ -D-galactopyranosyl]ethane 17.** 2, 3, 4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-glucopyranosyl)- $\alpha$ -D-galactopyranosyl bromide<sup>[21]</sup> (**10**,





0.10 g, 0.29 mmol), **1** (0.60 g, 2.33 mmol), Bu<sub>3</sub>SnH (0.10 mL, 0.34 mmol) and AIBN (cat.) in dry Et<sub>2</sub>O (10 mL) was stirred at reflux for 22 h. Workup and purification of the residue by column chromatography (silica gel, EtOAc: hexane, 2:3) as reported for **11** afforded **17** in 68% yield (0.108 g) as a syrup.  $[\alpha]_D^{25} + 15.6$  (c 1.0, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.20 (d, 1H, J 7.6 Hz, Ar-H), 8.05 (d, 1H, J 7.6 Hz, Ar-H), 7.65 (m, 2H, Ar-H), 5.36 (d, 1H, J 3.2 Hz, H-3''), 5.32 (t, 1H, J 7.2 Hz, H-3), 5.12 (t, 1H, J 9.0 Hz, H-4), 4.90 (dd, 1H, J 7.2, 3.5 Hz, H-2), 4.80 (m, 1H, H-2''), 4.52 (d, 1H, J 7.8 Hz, H-1''), 4.34 (dd, 1H, J 2.95, 11.8 Hz, H-6a), 4.20 (m, 2H, H-6b, H-1), 4.10 (dd, 2H, J 2.68 Hz, H-6''), 3.90 (t, 1H, J 6.45 Hz, H-2'a), 3.80 (m, 1H, H-4''), 3.70 (m, 2H, H-5, H-5''), 3.64 (t, 1H, J 7.2 Hz, H-2'b), 2.52–2.43 (m, 2H, H-1'), 2.15, 2.13, 2.10, 2.05 (7s, 21H, OAc); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.2, 169.9, 169.7, 169.2, 128.1(2C), 127.8, 125.4, 122.3, 101.4, 96.1(2C), 75.9, 71.7(2C), 70.9(2C), 70.8(2C), 69.5, 69.3, 69.1(2C), 66.7, 61.9, 60.8, 50.6, 29.6, 20.5(7C); FAB-MS (*m/z*): 868 (M<sup>+</sup> + 23).

Anal. Calcd for C<sub>47</sub>H<sub>43</sub>NO<sub>11</sub>S<sub>2</sub>: C 49.70, H 5.12 N 1.66 S 7.58; Found: C 49.69, H 5.16, N 1.64, S 7.54.

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