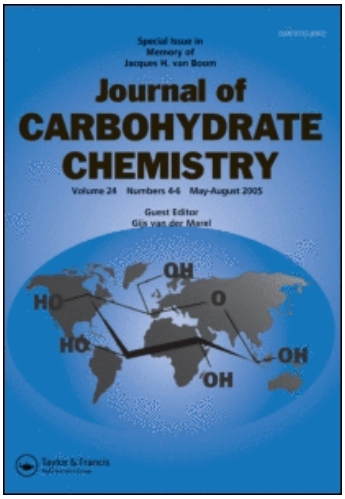


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Radical Mediated Diastereoselective Synthesis of Benzothiazole Sulfonyl Ethyl C-Glycosides

Palakodety Radha Krishna[a]; B. Lavanya[a]; Y. Jyothi[a]; G. V. M. Sharma[a]
[a] 206/B, Discovery Laboratory, Organic Chemistry Division III, Indian Institute of Chemical Technology, Hyderabad, India

Online publication date: 30 September 2003

To cite this Article Krishna, Palakodety Radha , Lavanya, B. , Jyothi, Y. and Sharma, G. V. M.(2003) 'Radical Mediated Diastereoselective Synthesis of Benzothiazole Sulfonyl Ethyl C-Glycosides', Journal of Carbohydrate Chemistry, 22: 6, 423 — 431
To link to this Article: DOI: 10.1081/CAR-120025328
URL: http://dx.doi.org/10.1081/CAR-120025328

JOURNAL OF CARBOHYDRATE CHEMISTRY
Vol. 22, No. 6, pp. 423–431, 2003

Radical Mediated Diastereoselective Synthesis of Benzothiazole Sulfonyl Ethyl C-Glycosides[#]

Palakodety Radha Krishna,[*] B. Lavanya, Y. Jyothi, and G. V. M. Sharma

Discovery Laboratory, Organic Chemistry Division III,
Indian Institute of Chemical Technology,
Hyderabad, India

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_3SnH and AIBN in good yields.

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

[#]IICT Communication No. 4169

[*]Correspondence: Palakodety Radha Krishna, 206/B, Discovery Laboratory, Organic Chemistry Division III, Indian Institute of Chemical Technology, Hyderabad 500 007, India; E-mail: prkgenius@iict.ap.nic.in.

DOI: 10.1081/CAR-120025328
0732-8303 (Print); 1532-2327 (Online)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

INTRODUCTION

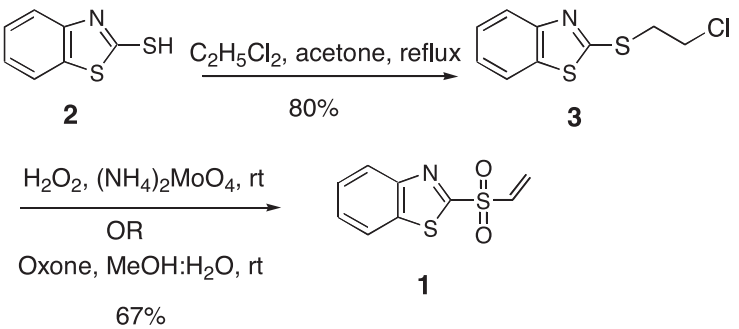
The plethora of methods developed for the synthesis of C-glycosides and C-saccharides bears testimony to the growing importance of glycosyl mimics. This class of compounds has varied biological activity such as anti-tumor, anti-bacterial or anti-viral activity[1,2] and plays effective roles as modulators and inhibitors,[3] 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,[4] as glycosyl transferase inhibitors, has given impetus to the synthesis of sulfonyl methyl C-glycosides.[5] Our continued interest in glycosyl mimics has resulted in newer methodologies for synthesis of C-alkyl glycosides,[6] C-vinyl glycosides,[7] C-C disaccharides,[8] C-linked spiro saccharides[9] and pseudo saccharide precursors.[10] 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[11] or by a radical addition of thioacetic acid[5] 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[12–14] 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[15] (**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 [$(NH_4)_2MoO_4/H_2O_2$] at room temperature or oxone in MeOH: H_2O (1: 1.25) resulted in the formation of **1** (67%).

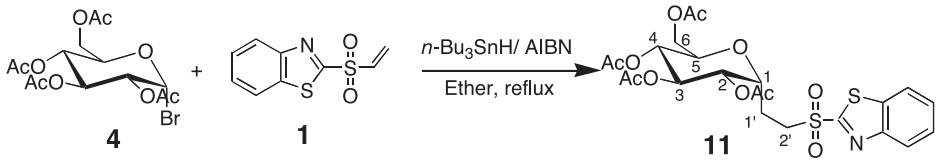
The vinyl sulfone (**1**) was utilized as a Michael acceptor for the first time in the reductive radical reaction of glycosyl bromides to give the C-glycoside sulfones.



2 3 1

Scheme 1.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016



Scheme 2.

Accordingly, a mixture of acetobromo glucose (**4**) and vinyl sulfone (**1**) in ether was treated with *n*-Bu_3SnH 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 ^1H NMR of **11**, H-2 resonated at δ 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.

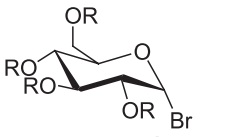
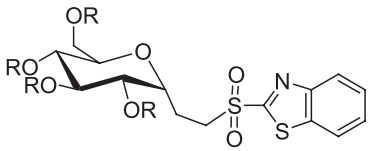
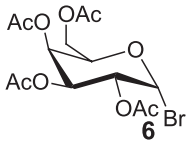
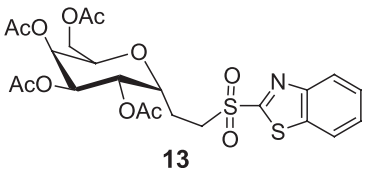
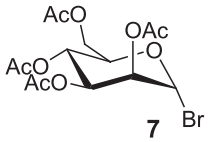
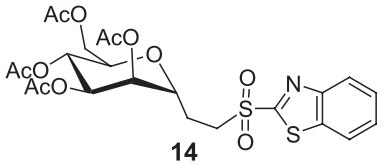
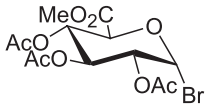
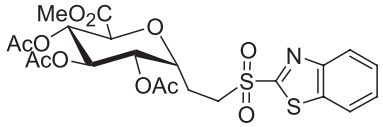
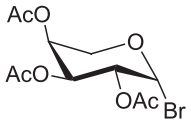
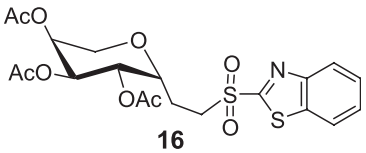
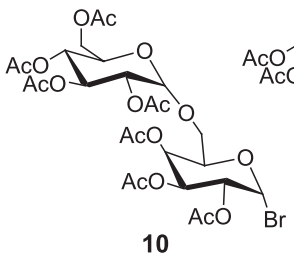
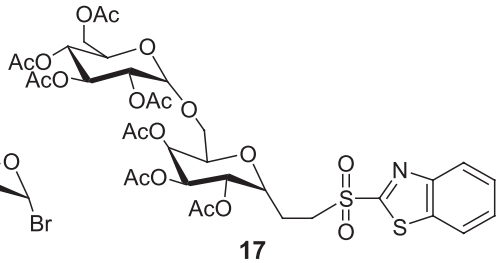
The validity of the present methodology was demonstrated by the conversion of a variety of sugar substrates such as aldohexoses **4–7**, uronate **8**, aldopentose **9** and disaccharide **10** containing different protecting groups such as acetate, benzoate and ester, into the corresponding C-glycoside sulfones, **11–14**, **15, 16** and **17**, respectively, in 60–73% yields (Table 1). Similarly, the C-glycosides **12–17** were characterized as α-C-glycoside sulphones by ^1H NMR, ^{13}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 α 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 α-anomers is in concurrence with the literature.[16]

In conclusion, a protocol for the conversion of glycosyl radicals into C-α-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[17] would be an attractive proposition.

EXPERIMENTAL

General methods. Solvents were dried over standard drying agents and freshly dried prior to use. ^1H NMR (200 MHz, 400 MHz, 500 MHz) and ^{13}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(%)
 **4** R = Ac **5** R = Bz	 **11** R = Ac **12** R = Bz	12 15	66 71
 **6**	 **13**	11	73
 **7**	 **14**	21	70
 **8**	 **15**	22	63
 **9**	 **16**	22	60
 **10**	 **17**	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} deg cm^2 g^{-1} at 25°C. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°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.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

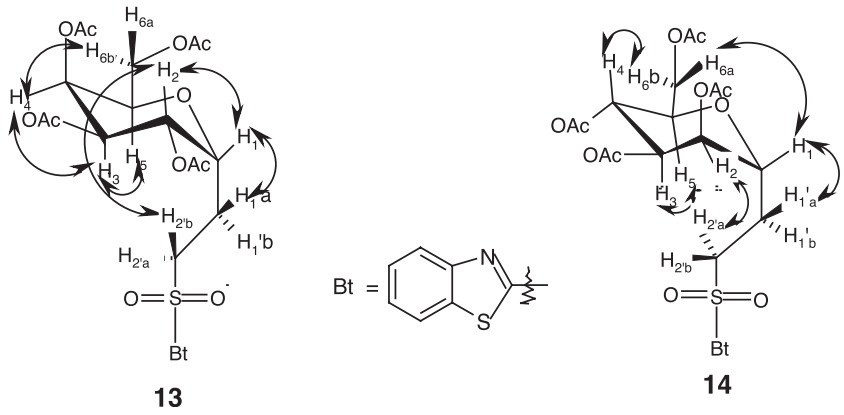


Figure 1. NOEs of compounds **13** and **14**.

2-(2-Chloroethylsulfonyl)benzo[d][1,3]thiazole 3: To a solution of mercaptobenzothiazole (**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. ^{1}H NMR (200 MHz, $CDCl_3$): δ 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_8 $ClNS_2$: 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-Vinylsufonylbenzo[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°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 × 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. ^{1}H NMR (200 MHz, $CDCl_3$): δ 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_7 NO_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 × 50 mL), washed with brine (1 × 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-α-D-glucopyranosyl)-ethane 11. A mixture of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranosyl bromide[18] (**4**, 0.2 g, 0.48 mmol), **1** (1.6 g, 6.2 mmol), Bu_3SnH (0.268 mL, 0.9 mmol) and AIBN (cat.) in dry Et_2O (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, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 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); ^{13}C NMR (50 MHz, $CDCl_3$): δ 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^++ 1); FAB-HRMS (M^++ 1): calculated for $C_{23}H_{28}NO_{11}S_2$. 558.110380; Found: 558.114059.

2′-(Benzothiazolyl sulfonyl)-1′-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-ethane 12. 2,3,4,6-Tetra-*O*-benzoyl-D-glucopyranosyl bromide[18] (**5**, 0.1 g, 0.15 mmol), **1** (0.33 g, 1.27 mmol), Bu_3SnH (0.05 mL, 0.17 mmol) and AIBN (cat.) in dry Et_2O (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, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 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^++ 1).

Anal. Calcd for $C_{47}H_{43}NO_{11}S_2$: 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-α-D-galactopyranosyl)-ethane 13. 2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl bromide[19] (**6**, 0.1 g, 0.15 mmol), **1** (0.81 g, 3.14 mmol), Bu_3SnH (0.13 mL, 0.46 mmol) and AIBN (cat.) in dry Et_2O (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, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (50 MHz, $CDCl_3$): δ 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^++ 1).

Anal. Calcd for $C_{23}H_{27}NO_{11}S_2$: 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-α-D-mannopyranosyl)-ethane 14. 2,3,4,6-Tetra-*O*-acetyl-D-mannopyranosyl bromide[18] (**7**, 0.10 g, 0.39 mmol), **1** (0.81 g, 3.13 mmol), Bu_3SnH (0.13 mL, 0.39 mmol) and AIBN (cat.) in dry Et_2O (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, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 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); ^{13}C NMR (50 MHz, $CDCl_3$): δ 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^++ 1).

Anal. Calcd for $C_{23}H_{27}NO_{11}S_2$: 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-α-D-glucopyranosyl) uronate)]ethane 15. Methyl (2,3,4-tri-*O*-acetyl-D-glucopyranosyl bromide)uronate[20] (**8**, 0.10 g, 0.25 mmol), **1** (0.52 g, 2.0 mmol), Bu_3SnH (0.08 mL, 0.29 mmol) and AIBN (cat.) in dry Et_2O (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, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 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 9.5Hz, H-1), 3.80 (s, 3H, OCH_3), 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^+ + 1).

Anal. Calcd for $C_{22}H_{26}NO_{11}S_2$: 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-α-D-arabinopyranosyl)ethane 16. 2,3,4-Tri-*O*-acetyl-D-arabinopyranosyl bromide[18] (**9**, 0.1 g, 0.34 mmol), **1** (0.70 g, 2.7 mmol), Bu_3SnH (0.12 mL, 0.41 mmol) and AIBN (cat.) in dry Et_2O (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 (0.11g) as a thick syrup. $[\alpha]_D$ + 20.40 (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 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^++ 1).

Anal. Calcd for $C_{20}H_{23}NO_9S_2$: 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-α-D-glucopyranosyl)-α-D-galactopyranosyl]ethane 17. 2, 3, 4-Tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-galactopyranosyl bromide[21] (**10**,

0.10 g, 0.29 mmol), **1** (0.60 g, 2.33 mmol), Bu_3SnH (0.10 mL, 0.34 mmol) and AIBN (cat.) in dry Et_2O (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. $[\alpha]_D$ + 15.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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^+ + 23).

Anal. Calcd for $C_{47}H_{43}NO_{11}S_2$: C 49.70, H 5.12 N 1.66 S 7.58; Found: C 49.69, H5.16, N 1.64, S 7.54.

ACKNOWLEDGMENTS

Two of the authors, B. Lavanya and Y. Jyothi, are thankful to CSIR, New Delhi, India for the financial support.

REFERENCES

1. Postema, M.H.D. *C-glycoside Synthesis*; CRC Press: London, 1995.
2. Levy, D.E.; Tang, C. *The Chemistry of C-glycosides*; Pergamon Press: Oxford, 1995.
3. Czernicki, S. New aspects of glycosylation reactions. In *Carbohydrates –Synthetic Methods and Applications in Medicinal Chemistry*; Ogura, H., Hasegawa, A., Suami, T., Eds.; VCH Publications: New York, 1991; 28 and references cited therein.
4. Unker, H.-D.; Fessner, W.-D. Diastereoselective syntheses of C-glycosylphosphates via free radical glycosylation. Tetrahedron Lett. **1998**, *39*, 269–272.
5. Gervay, J.; Flaherty, T.M.; Holmes, D. Studies on the synthesis of C-glycoside sulfones as potential glycosyl transferase inhibitors. Tetrahedron **1997**, *53*, 16355–16364.
6. Sharma, G.V.M.; Chander, A.S.; Krishnudu, K.; Radha Krishna, P. A simple and efficient $PdCl_2$ mediated conversion of α, γ-olefinic alcohols into C-glycosides. Tetrahedron Lett. **1997**, *38*, 9051–9054.
7. Sharma, G.V.M.; Chander, A.S.; Krishnudu, K.; Radha Krishna, P. $Pd(OAc)_2$ mediated oxidative cyclisation of γ, δ-olefinic alcohols: a new route to C-vinyl furanosides. Tetrahedron Lett. **1998**, *39*, 6957–6960.
8. Sharma, G.V.M.; Hymavathi, L.; Radha Krishna, P. Carbon-carbon linked disaccharides by *de novo* construction from furanyl sugar templates. Tetrahedron Lett. **1997**, *38*, 6929–6932.
9. Sharma, G.V.M.; Reddy, V.G.; Radha Krishna, P. Synthesis of spiro carbon linked

disaccharides: *de novo* synthesis from furan by chirality transfer from sugar derived templates. Tetrahedron Lett. **1999**, *40*, 1783–1786.
10. Sharma, G.V.M.; Chander, A.S.; Radha Krishna, P.; Krishnudu, K.; Ramana Rao, M.H.V.; Kunwar, A.C. 'Off template site' [3 + 3] annulation reaction on sugar derived enal: stereoselective synthesis of C-C-linked pseudo-saccharide precursors. Tetrahedron: Asymmetry **2000**, *11*, 2643–2646.
11. Davidson, A.H.; Hughes, L.R.; Qureshi, S.S.; Wright, B. Wittig reactions on unprotected aldoses: formation of optically active tetrahydrofurans and tetrahydropyrans. Tetrahedron Lett. **1988**, *29*, 693–696.
12. Spencer, R.P.; Schwartz, J. Titanium (III)-promoted stereoselective synthesis of simple C-glycosides. J. Org. Chem. **1997**, *62*, 4204–4205.
13. Giese, B.; Dupuris, J.; Liesing, M.; Nix, M.; Lindner, H.J. Synthesis of C-pento, -hexo and -hepto pyranosyl compounds via radical C—C bond formation reactions. Carbohydr. Res. **1987**, *171*, 329–335.
14. Giese, B.; Kopping, B.; Gobel, T.; Dickhaut, J.; Thoma, G.; Kulicke, K.J.; Trach, F. Radical cyclization reactions. In *Organic Reactions*; Paquette, L.A., et al, Eds.; John Wiley & Sons Inc.: New York, 1996; 48, 301–856.
15. Prilezhaeva, N.; Shmonia, L.I. Synthesis based on 2-benzothiazololyl vinyl sufide. Zh. Org. Khim. **1966**, *2* (10), 1883–1891.
16. Togo, H.; He, W.; Waki, Y.; Yokoyama, M. C-glycosidation technology with free radical reactions. Synlett **1998**, 700–717.
17. Jerome, K. 6-Ethoxybenzothiazole-2-sulfonamide, US patent, 1959, 2,868,800. In *The Merck Index*; Merck & Co Inc.: NJ, 1996; 12, 641.
18. Vogel, A.I. *Textbook of Practical Organic Chemistry*; Longman Group Ltd.: UK, 1989; 647–648.
19. Bochkov, A.F.; Zaikov, G.E. *Chemistry of the O-glycosidic Bond: Formation and Cleavage*; Pergamon Press: Oxford, UK, 1979; 61.
20. Chernyak, A.Y.; Sharma, G.V.M.; Kononov, L.O.; Radha Krishna, P.; Rama Rao, A.V.; Kochetkov, N.K. Synthesis of glycuronamides of amino acids, constituents of microbial polysaccharides and their conversion into neoglycoconjugates of copolymer type. Glycoconj. J. **1991**, *8*, 82–89.
21. Sharma, G.V.M.; Radha Krishna, P. A practical synthesis of 2-azidoethyl α-glycosides useful spacer-arm glycosides for the synthesis of neoglycoconjugates. Carbohydr. Res. **1993**, *243*, 393–397.

Received October 16, 2002
Accepted May 30, 2003