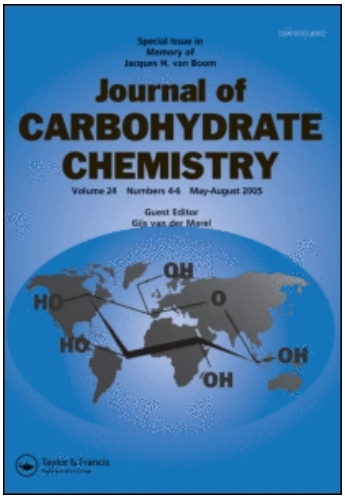

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AN EFFICIENT METHOD FOR THE SYNTHESIS OF A 1,6-ANHYDRO-α-D-GALACTOFURANOSE DERIVATIVE AND ITS APPLICATION IN THE SYNTHESIS OF OLIGOSACCHARIDES

Sujit Kumar Sarkar, Ambar Kumar Choudhury,
Balaram Mukhopadhyay and Nirmolendu Roy*

Department of Biological Chemistry
Indian Association for the Cultivation of Science,
Calcutta 700 032, India
Fax: +91 33 4732805. E-mail: bcnr@mahendra.iacs.res.in

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ABSTRACT

Synthesis of 1,6-anhydro-2,3,5-tri-*O*-benzoyl-β-D-galactofuranose (**3**) has been achieved in good yield by stannic chloride catalysed ring closure of methyl 2,3,4-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranoside (**1**). The anhydro compound **3** was converted to the furanoside donors **6** and **7** with an easily removable *O*-6 acetyl group. The donors **6** and **7** were utilised for the synthesis of a di- and a trisaccharide containing β-D-galactofuranosides.

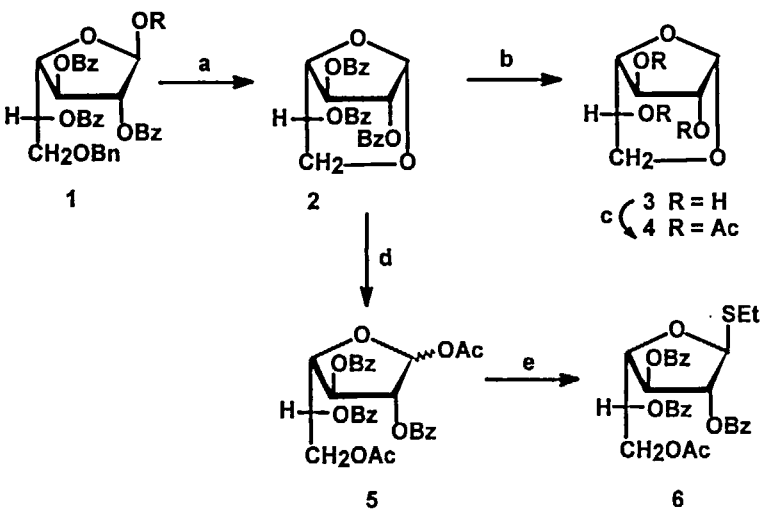
INTRODUCTION

1,6-Anhydro-α-D-galactofuranose was obtained previously by pyrolysis[1] or acid treatment[2] of D-galactose in less than 5% yields, respectively. The compound was also reported[3] recently as its 2,3-di-*O*-benzyl derivative together with 1,6-anhydro-2,3-di-*O*-benzyl-α-D-galactopyranose in a 1:1 ratio when methyl 2,3-di-*O*-benzyl-α-D-galactopyranoside was treated with camphorsulfonic acid in toluene. Considering

the utility of anhydrosugars in synthetic carbohydrate chemistry, we report here an efficient synthesis of a 1,6-anhydro-D-galactofuranose derivative from methyl 2,3,5-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranoside and its conversion to a useful thioglycoside donor.

RESULTS AND DISCUSSION

Methyl 2,3,5-tri-*O*-benzoyl-6-*O*-benzyl-β-D-galactofuranoside (1)[4] was prepared from 1,2:3,4-di-*O*-isopropylidene-D-galactose[5] by benzylation, followed by methanolysis and benzoylation of the product in an overall yield of 47% . Treatment of 1 with stannic chloride in dichloromethane, resulted in the formation of 1,6-anhydro-2,3,5-tri-*O*-benzoyl-α-D-galactofuranose (2) as the exclusive product (Scheme 1). The facile formation of the 1,6-anhydro compound (2) was probably due to the lability of the 6-*O*-benzyl group of 1 and 2 in the presence of a strong Lewis acid, and also because of the high stability of the product formed. Compound 2 was characterized by removal of its benzoyl groups with sodium methoxide[6] followed by acetylation[7] of the resulting product



Scheme 1

Reagents: a) CH_2Cl_2, $SnCl_4$, 0 °C, 2 h, 79%; b) 0.1 M NaOMe, MeOH; c) Ac_2O, Pyr, rt, 4 h; d) Ac_2O:H_2SO_4 (2.5:0.1, v/v), 0 °C, 1.5 h, 80%; e) EtSH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0 °C, 2 h, 79%.

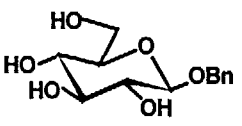
(3) to afford the acetate **4**, which has three signals for OCOC*H*$_3$ in its ^{1}H NMR spectrum. Compounds **2**, **3** and **4** have similar ^{1}H NMR spectral patterns with signals for H-1 at δ 5.83, 5.18 and 5.45, respectively. ^{13}C NMR spectra showed the anomeric carbons of **2** and **3** at δ 95.54 and 98.24, respectively together with five additional ring carbons.

The 1,6-anhydro ring of **2** was opened by treatment with acetic anhydride-sulfuric acid to afford the acetate **5** as an inseparable mixture of 2,3,5-tri-*O*-benzoyl-6-acetyl-β-D-galactofuranosylacetate and its α-anomer (ca. 9:1) as revealed in their ^{1}H NMR spectra. The acetate **5** was allowed to react with ethanethiol[8] in the presence of boron trifluoride etherate to give the thioglycoside **6** in 73% yield. Compound **6** showed characteristic ^{1}H NMR signals at δ 5.41 (H-1) and 5.85 (H-5), and ^{13}C NMR signals at δ 15.4 (SCH$_2$*C*H$_3$), 21.1 (OCO*C*H$_3$), 25.7 (S*C*H$_2$CH$_3$), 88.6 (C-1), 165.8, 165.9, 166.1 (3 O*C*OC$_6$H$_5$), and 171.0 (O*C*OCH$_3$).

It was of interest to synthesize oligosaccharides containing β-D-galactofuranosyl moieties in which the 6-position could be selectively manipulated. Compounds **5** and **6** were tested as donors for the construction of glycofuranosidic linkages. The model acceptor chosen for this purpose was benzyl 2,3-di-*O*-benzoyl-β-D-galactopyranoside (**10**), which was prepared from benzyl β-D-galactopyranoside (**7**)[9] in three steps. Treatment of **7** with α,α-dimethoxybenzaldehide[10] gave the 4,6-benzylidene derivative (**8**) which was benzoylated[4] to afford the dibenzoate **9**. Removal of the benzylidene[10] group from **9** gave **10**.

The acetate **5** was allowed to react with **10** in the presence of trimethylsilyl triflate[11] (TMS-OTf) at 30 °C to afford benzyl 6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3-di-*O*-benzyl-β-D-glucopyranoside (**11**) in 60% yield. Compound **11** has ^{1}H NMR signals at δ 4.67 (H-1, d, J=7.8 Hz), 5.35 (H-1', bs), and 5.81 (H-5', m) and ^{13}C NMR signals at δ 21.11(OCO*C*H$_3$), 99.77 (C-1) and 106.76 (C-1'). The characteristic signal[4,12] at ~δ 107 in the ^{13}C NMR spectrum, confirmed the β-D-galactofuranosidic configuration of the glycosidic linkage in **11**. The presence of a free 4-OH group in **11** was also confirmed by its acetylation.[7] When the ^{1}H NMR spectrum of the derived acetate **12** was compared with that of **11**, it was apparent that the signal from H-4 had moved from 4.12 ppm to 5.54 ppm. The identical disaccharide derivative (**11**) was also obtained in 81% yield when the acceptor **10** was allowed to react with the thioglycoside **6** in the presence of *N*-iodosuccinimide-triflic acid (NIS-TfOH)[13] at –15 °C.

Compound **11** was again allowed to react with **6** in the presence of NIS-TfOH at 0 °C and the trisaccharide derivative **13** was obtained in 75% yield. This yield was significant considering the steric and electronic hindrance at the 4-position of the disaccharide **11.** Compound **13** has ^{1}H NMR signals at δ 1.79, 1.91 (2 OCOC*H*$_3$), 4.71 (H-1, d, J=7.8), 5.14 (H-1", bs), 5.30 (H-1', bs) and ^{13}C NMR signals at δ 21.02, 21.10 (2 OCO*C*H$_3$), 99.94 (C-1), 105.33 (C-1") and 107.01 (C-1') characteristic of the two β-D-galactofuranosyl linkages and a benzyl β-glucoside. Removal of acyl groups from **13** afforded the trisaccharide **14** as its benzyl glycoside. The ^{13}C NMR spectrum of **14** showed anomeric carbon signals at δ 101.68 (C-1), 108.11 and 108.24 (C-1' and C-1").



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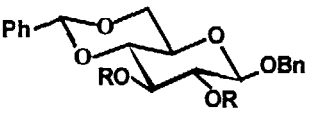
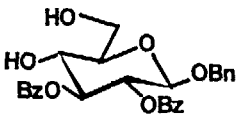


8 R=H
9 R=Bz



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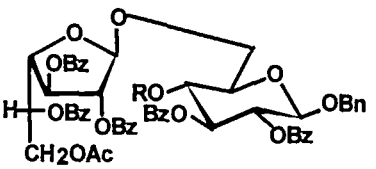
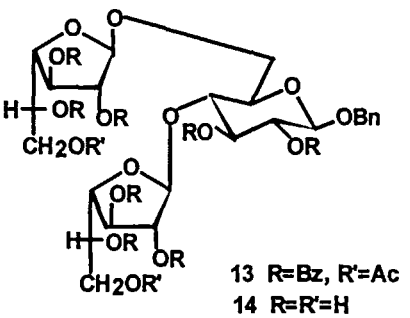


11 R=H
12 R=Ac



13 R=Bz, R'=Ac
14 R=R'=H

EXPERIMENTAL

General Methods. All reactions were monitored by TLC on Silica gel G (E. Merck). Column chromatography was performed on 100-200 mesh silica gel (SRL, India). All solvents were distilled and/or dried before use and all evaporations were conducted below 40 °C under reduced pressure unless stated otherwise. Optical rotations were measured with a Perkin-Elmer model 241 MC polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer using $CDCl_3$ as solvent (internal standard Me_4Si) unless otherwise stated. Melting points were determined on a paraffin oil bath and are uncorrected.

1,6-Anhydro-2,3,5-tri-*O*-benzoyl-α-D-galactofuranose (2). To a solution of **1**[4] (190 mg, 0.32 mmol) in CH_2Cl_2 (3 mL) at 25 °C under nitrogen atmosphere, $SnCl_4$ (45 μL, 0.38 mmol) was added with vigorous stirring. The reaction was allowed to proceed for 3 h with continued stirring. The mixture was then diluted with CH_2Cl_2 and stirred with cold aq $NaHCO_3$ (1 mL). After 30 min, the organic layer was washed with water, dried (Na_2SO_4), filtered and concentrated to a syrup. The residue was purified by column chromatography with 8:1 toluene-EtOAc to give **2** which crystallised from ethanol (120 mg, 79 %): mp 142 °C; $[\alpha]_D^{25}$ + 134.5° (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 3.94 (t, 1H, J = 11.1 Hz, H-6_a), 4.32 (m, 1H, H-6_e), 4.64 (d, 1H, J=4.5 Hz, H-4), 5.34 (m, 1H, H-5), 5.51 (dd, 1 H, $J_{1,2}$ = 4.5 Hz, $J_{2,3}$ = 2.1 Hz, H-2), 5.73 (d, 1 H, $J_{1,2}$ = 4.5 Hz, H-1), 5.86 (d, 1H, J = 2.4 Hz, H-3), 7.43-8.18 (m, 15H, aromatic protons); ^{13}C NMR δ 61.40 (C-6), 62.60, 74.53, 77.63 (C-2), 78.28 (C-4), 95.54 (C-1), 126.97-132.16 (aromatic carbons), and 164.37-164.83 (3 OCOPh).

Anal. Calcd for $C_{27}H_{22}O_8$: C, 68.34; H, 4.67. Found: C, 68.20; H, 4.51.

1,6-Anhydro-α-D-galactofuranose (3).[2] Compound **2** (200 mg, 0.21 mmol) was de-*O*-benzoylated[6] with 0.1 M NaOMe to give **3** (65 mg, 96%); mp 178-180 °C; $[\alpha]_D^{25}$ +54° (*c* 1.4, water). Lit[2] mp 181-182 °C, $[\alpha]_D^{25}$ +55°. ^{1}H NMR (D_2O) δ 3.42 (m, 1 H, H-6_e), 3.90 (m, 2 H, H-4, H-6_a), 4.05 (m, 1 H, H-5), 4.09-4.13 (m, 2 H, H-3, H-2), 5.18 (d, 1H, $J_{1,2}$ = 4.5 Hz, H-1); ^{13}C NMR (D_2O) δ 62.09 (C-6), 64.99, 74.93, 80.34 (C-2), 84.87 (C-4), and 98.24 (C-1).

1,6-Anhydro-2,3,5-tri-*O*-acetyl-α-D-galactofuranose (4).[1] To a solution of **3** (50 mg, 0.30 mmol) in pyridine (0.5 mL), was added Ac_2O (0.5 mL) and the solution was allowed to stand at 30 °C for 3 h when TLC (3:1 toluene-EtOAc) showed completion of the reaction. The mixture was concentrated to a syrup and chromatographed with the same solvent to afford **4** (84 mg, 95%); mp 77-79 °C (ethanol); $[\alpha]_D$ +144° (*c* 0.5, ethanol); Lit[1] mp 79-80 °C (ethanol), $[\alpha]_D$ +144.9°. ^{1}H NMR δ 2.03, 2.05 and 2.10 (3 s, 9 H, 3 OCOC*H*$_3$), 3.66 (t, 1H, H-6_a), 4.02 (m, 1H, H-6_e), 4.35 (dd, 1H, H-4), 4.97 (m, 1H, H-5), 5.04 (dd, 1 H, $J_{1,2}$ = 4.5 Hz, $J_{2,3}$ = 2.1 Hz, H-2), 5.24 (d, 1H, J = 2.4 Hz, H-3), 5.45 (d, 1H, $J_{1,2}$ = 4.5 Hz,H-1).

Anal. Calcd for $C_{12}H_{16}O_8$: C, 50.00; H, 5.59. Found: C, 50.36; H, 4.75.

6-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-α,β-D-galactofuranosyl Acetate (5). A solution of **2** (250 mg, 0.4 mmol) in Ac_2O (0.10 mL) was cooled to 0 °C and H_2SO_4 (40 μL) was

added with stirring. After 1.5 h, the solution was diluted with CH_2Cl_2 (20 mL) and then washed with water, saturated $NaHCO_3$ and water in succession, then dried (Na_2SO_4), filtered and concentrated to a syrup. Column chromatography with 8:1 toluene-EtOAc gave **5** (230 mg, 75.7%): $[\alpha]_D^{25}$ – 56.3° (*c* 0.5, $CHCl_3$). The ^1H NMR spectrum of the product showed the presence of β and α anomers in the ratio 9:1. The anomers could not be separated. ^1H NMR (β-anomer) δ 2.20 and 2.01 (2 s, 6 H, 2 OCOC*H*$_3$), 6.49 (bs, 1H, H-1), 8.07-7.19 (m, 15H, aromatic protons); ^1H NMR (α-anomer) δ 1.99, 2.08 (2 s, 6 H, 2 OCOC*H*$_3$), 6.64 (d, 1H, J=4.8 Hz, H-1); ^{13}C NMR ($CDCl_3$) for the β-anomer δ 171.06, 169.6 (2*C*OCH$_3$), 166.1, 165.9, 165.7 (3*C*OPh), 134.1-125.7 (aromatic carbons), 99.7 (C-1), 83.9 (C-4), 81.7 (C-2), 76.6, 70.5, 63.3 (C-6), 21.5 and 21.1 (2 OCO*C*H$_3$).

Anal. Calcd for $C_{31}H_{28}O_{11}$: C, 64.58; H, 4.89. Found: C, 64.32, H, 5.10

Ethyl 6-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-1-thio-β-D-galactofuranoside (6). To a solution of **5** (288 mg, 0.5 mmol) in CH_2Cl_2 (8 mL) cooled to 0 °C EtSH (90 μL, 1.2 mmol) and $BF_3{\cdot}OEt_2$ (0.23 mL, 1.8 mmol) were added and the solution was stirred for 2 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), then washed with water, saturated $NaHCO_3$ and water in succession. The organic layer was dried (Na_2SO_4), filtered, then concentrated to a syrup. Column chromatography with 8:1 toluene-EtOAc gave **7** (225 mg, 78%); $[\alpha]_D^{25}$ – 45° (*c* 1.5, $CHCl_3$); ^1H NMR δ 1.27 (t, 3H, J=7.2 Hz, SCH$_2$C*H*$_3$), 1.92 (s, 3H, OCOC*H*$_3$), 2.67 (m, 2H, SC*H*$_2$CH$_3$), 4.42 (m, 2H, H-6), 4.67 (dd, 1H, $J_{3,4}$ 4.5 Hz, $J_{4,5}$ 3.8 Hz, H-4), 5.41 (bs, 1H, H-1), 5.52 (d, 1H, J =4.5 Hz, H-3), 5.57 (bs, 1H, H-2), 5.85 (m, 1H, H-5). ^{13}C NMR δ 15.4 (SCH$_2$*C*H$_3$), 21.1 (OCO*C*H$_3$), 25.7 (S*C*H$_2$CH$_3$), 63.2 (C-6), 70.6, 78.2,81.4 (C-2), 83.3 (C-4), 88.6 (C-1), 165.8, 165.9, 166.1 (3 O*C*OC$_6$H$_5$ and 171.0 (O*C*OCH$_3$).

Anal. Calcd for $C_{31}H_{30}O_9S$: C, 64.35, H, 5.23. Found : C, 64.19; H, 5.42.

Benzyl 4,6-*O*-Benzylidene-β-D-glucopyranoside (8). To a solution of benzyl β-D-glucopyranoside[9] (7) (800 mg, 2.96 mmol) in acetonitrile (15 mL), α,α-dimethoxytoluene (370 μL, 3.55 mmol), *p*-TsOH (25 mg) were added and the mixture was stirred at 30 °C for 16 h. The reaction was quenched with Et_3N and the mixture was concentrated to a syrup. Column chromatography with 3:1 toluene-EtOAc gave **8** (900 mg, 84.9%); $[\alpha]_D$ - 60.5° (*c* 1.2, $CHCl_3$); ^1H NMR δ 3.43 (m, 1H, H-5), 3.78 (m, 2H, H-6), 3.77 (m, 2H, H-2, H-3), 4.34 (dd, 1H, H-4, $J_{3,4}$= 4.8 Hz, $J_{4,5}$= 10.4 Hz), 4.47 (d, 1H,

H-1, J= 7.7 Hz), 4.61, 4.91 (2d, 2H, J= 11.6 Hz, PhCH_2), 5.51 (s, 1H, PhC*H*), 7.24-7.49 (m, 10H, aromatic protons).

Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C,66.81; H, 6.42.

Benzyl 4,6-*O*-Benzylidene-2,3-di-*O*-benzoyl-β-D-glucopyranoside (9). To a solution of **8** (750 mg, 2.09 mmol) in pyridine (5 mL), was added benzoyl chloride (970 μL, 8.4 mmol) at 0 °C and the solution was stirred at room temperature for 3 h. The reaction mixture was concentrated, diluted with CH_2Cl_2 and filtered. The filtrate was washed successively with water, saturated $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated to a syrup. Column chromatography with 10:1 toluene-EtOAc gave pure **8** (1.02 g, 86%); $[\alpha]_D$ -12.2° (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 3.78 (m, 1H, H-5), 4.01 (m, 2H, H-6), 4.54 (dd, 1H, H-4, $J_{3,4}$= 4.8 Hz, $J_{4,5}$= 10.4 Hz), 4.91 (d, 1H, H-1, J= 7.8 Hz), 4.75, 4.99 (2d, 2H, J= 12.5 Hz, PhCH_2), 5.63 (t, 1H, H-3, J= 9.7 Hz), 5.63 (s, 1H, PhC*H*), 5.81 (t, 1H, H-2, J= 9.5 Hz), 7.26-8.29 (m, 20H, aromatic protons).

Anal. Calcd for $C_{34}H_{30}O_8$: C, 72.07; H, 5.34. Found: C, 71.80; H, 5.49

Benzyl 2,3-Di-*O*-benzoyl-β-D-glucopyranoside (10). A solution of **9** (500 mg, 0.9 mmol) in 80% acetic acid was heated at 80 °C with stirring for 2 h. The solution was concentrated to a thick glass. Column chromatography with 3:1 toluene-EtOAc gave **9** (340 mg, 80.6%); $[\alpha]_D$ +58.9° (*c* 1.1, $CHCl_3$); ^{1}H NMR δ 1.71 (OH), 3.48 (m, 1H, H-5), 3.90 (m, 3H, H-4, H-6), 4.63, 4.81 (2d, 2H, J=12.6 Hz, C$H_2C_6H_5$), 4.69 (d, 1H, J=7.8 Hz, H-1), 5.28 (t, 1H, J=9.4 Hz, H-3), 5.42 (dd, 1H, $J_{1,2}$=7.6 Hz, $J_{2,3}$=9.6 Hz, H-2), 7.12-7.90 (m, 10H, aromatic protons).

Anal. Calcd for $C_{27}H_{26}O_8$: C, 67.77, H, 5.48. Found: C, 67.58, H, 5.75.

Benzyl 6-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)-2,3-di-*O*-benzoyl-β-D-glucopyranoside (11). A mixture of **5** (150 mg, 0.26 mmol), **10** (149 mg, 0.31 mmol) and 4Å molecular sieves (500 mg) in CH_2Cl_2 (10 mL) was stirred for 1h under N_2 atmosphere at 0 °C. TMS-OTf (55 μL, 0.28 mmol) was then added and the mixture was stirred at 25 °C. After 1.5 h, the reaction was quenched with Et_3N, the mixture was diluted with CH_2Cl_2 (20 mL) and filtered. The filtrate was washed successively with aq N HCl, saturated $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated to a glassy product. Column chromatography with 10:1 toluene-EtOAc gave **11** (130 mg, 50.4%): $[\alpha]_D$ +5.7°(*c* 0.7, $CHCl_3$); ^{1}H NMR δ 1.61 (OH), 1.94 (s, 3H, OCOCH_3), 3.65 (m, 1H, H-5), 3.91 (m, 2H, H-6), 4.12 (m, 1H, H-4),

4.47 (m, 2H, H-6'), 4.62, 4.80 (2d, 2H, $CH_2C_6H_5$), 4.65 (m, 1H, H-4'), 4.67 (d, 1H, J=7.8, H-1), 5.33 (m, 1H, H-3), 5.35 (bs, 1H, H-1'), 5.41 (bs, 1H, H-2'), 5.43 (m, 1H, H-2), 5.55 (m, 1H, H-3'), 5.80 (m, 1H, H-5'), 7.08-8.03 (m, 30H, aromatic protons); ^{13}C NMR δ 30.1 ($OCOCH_3$), 63.3 (C-6), 67.1 (C-6'), 70.3, 70.6, 70.8, 71.9, 75.7, 77.4, 81.6, 82.7, 99.8 (C-1), 106.8 (C-1'), 128.1-137.2 (aromatic carbons), 165.6, 166.1, 166.1, 166.1, 167.7 (5 $OCOC_6H_5$), 171.1 ($OCOCH_3$).

Anal. Calcd for $C_{56}H_{50}O_{17}$: C, 67.50; H, 5.07. Found: C, 67.25; H, 5.29.

Compound **11** (15 mg) was acetylated as described for the preparation of **4** and the product was purified by column chromatography with 10:1 toluene-EtOAc to give **12** (12 mg, 77%); $[\alpha]_D$ +8.5° (*c* 0.6, $CHCl_3$); ^{1}H NMR δ 1.88, 1.94 (2s, 6H, 2 $OCOCH_3$), 3.64 (m, 1H, H-5), 3.80 (m, 2H, H-6), 4.47 (m, 2H, H-6'), 4.58 (m, 1H, H-4'), 4.59, 4.77 (2d, 2H, J=12.6 Hz, $OCH_2C_6H_5$), 4.61 (d, 1H, J=7.3 Hz, H-1), 5.23 (m, 1H, H-3), 5.37 (bs, 1H, H-1'), 5.41 (m, 1H, H-2), 5.44 (bs, 1H, H-2'), 5.54 (m, 2H, H-4, H-3'), 5.83 (m, 1H, H-5'), 7.05-8.02 (m, 30H, aromatic protons).

In a separate experiment, a mixture of **6** (50 mg, 0.09 mmol), **10** (45.4 mg, 0.10 mmol), and 4Å molecular sieves (300 mg) in $(CH_2Cl)_2$ (5 mL) was stirred at –15 °C under N_2. After 1 h, NIS (22 mg, 0.10 mmol) and TfOH (1μL, 0.01 mmol) were added and stirring was continued for 30 min at –15 °C. The reaction was quenched with NEt_3 (5 μL), the mixture was diluted with CH_2Cl_2 (10 mL) and filtered. The filtrate was washed successively with 5% $Na_2S_2O_3$, 1M HCl, saturated $NaHCO_3$ and water. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography with 10:1 toluene-EtOAc gave **11** (69.7 mg, 81%) which had identical specific rotation, ^{1}H and ^{13}C NMR data as detailed above.

Benzyl 6-*O*-Acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→4)-[6-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-galactofuranosyl-(1→6)]-2,3-di-*O*-benzoyl-β-D-glucopyranoside (13). A mixture of the thioglycoside **6** (87 mg, 0.15 mmol), the disaccharide **11** (100 mg, 0.10 mmol), and 4Å molecular sieves (300 mg) in $(CH_2Cl)_2$ (6 mL) was stirred under N_2 at 0 °C. After 2 h, NIS (26 mg, 0.12 mmol) and TfOH (1.1 μL, 0.012 mmol) were added and the mixture was stirred vigorously at 0 °C for 30 min. The reaction was stopped and worked up in the manner as described for **11** to afford pure **13** (114 mg, 75%): $[\alpha]_D$ + 0.79° (*c* 1, $CHCl_3$); ^{1}H NMR δ 1.79, 1.91 (2s, 6H, $OCOCH_3$), 3.69 (m, 1H, H-5), 3.75, 3.97 (2 dd, 2H, H-6), 4.08 (m, 1H, H-4), 4.16 (m, 2H, H-6"),

4.30 (m, 1H, H-4"), 4.48 (m, 2H, H-6'), 4.62, 4.78 (2d, 2H, $CH_2C_6H_5$), 4.64 (m, 1H, H-4'), 4.71 (d, 1H, J=7.8 Hz, H-1), 5.14 (bs, 1H, H-1"), 5.30 (bs, 1H, H-1'), 5.30 (s, 1H, H-2'), 5.41 (dd, 1H, $J_{2,3}$= Hz, $J_{3,4}$= Hz, H-3), 5.50 (d, 1H, J=4.2 Hz, H-3"), 5.54 (s, 1H, H-2'), 5.60 (d, 1H, J=4.5 Hz, H-3'), 5.66 (m, 1H, H-2), 5.79-5.84 (m, 2H, H-5', H-5"), 6.90-8.00 (m, 45H, aromatic protons); ^{13}C NMR δ 21.02, 21.10 (2 $COCH_3$), 63.04 (C-6), 63.50, 64.27 (C-6', C-6"), 70.26,70.70, 70.73, 72.65, 73.84, 74.76, 74.84, 77.04, 77.54, 77.63, 81.85, 82.44, 82.54, 83.00, 99.94 (C-1), 105.33 (C-1"), 107.01(C-1'), 128.09-137.29 (aromatic carbons), 165.51, 165.58, 165.84, 166.04, 166.07, 166.16, 166.19, 166.47 (8 $OCOC_6H_5$), 170.66, 171.08 (2 $OCOCH_3$).

Anal. Calcd for $C_{85}H_{74}O_{26}$: C, 67.54; H, 4.93. Found: C, 67.78; H, 5.01.

Benzyl β-D-Galactofuranosyl-(1→4)-[β-D-galactofuranosyl-(1→6)]-β-D-glucopyranoside (14). To a solution **13** (60 mg, 0.04 mmol) in dry MeOH (4 mL), 0.25 M NaOMe in MeOH (1 mL) was added and the mixture was stirred at 25 °C for 4 h. The solution was neutralized with Dowex 50W (H^+) resin, filtered, and the filtrate was concentrated to dryness. The product was purified by column chromatography with 3:1:0.1 CH_2Cl_2-EtOH- H_2O to pure **14** (21 mg, 89%): $[\alpha]_D$ - 80° (*c* 0.4, H_2O); ^{1}H NMR δ 4.43 (d, 1H, J=7.9 Hz, H-1), 4.95 (bs, 1H, H-1"), 5.16 (bs, 1H, H-1'); ^{13}C NMR δ 63.14 (C-6', C-6"), 66.29 (C-6), 70.78, 71.13, 72.00, 73.45, 73.97, 74.58, 76.33, 77.19, 77.39, 81.34, 81.39 (C-2', C-2"), 82.94, 83.32 (C-4', C-4"), 101.68 (C-1), 108.11, 108.24 (C-1', C-1"), 128.82-136.90 (aromatic carbons).

Anal. Calcd for $C_{25}H_{38}O_{16}$: C, 50.50, H, 6.44. Found: C, 50.23, H, 6,72.

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