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REDUCTION OF 2-ARYLTHIO-β-*C*-D-GLUCOPYRANOSIDES WITH DIFFERENT FUNCTIONAL GROUPS IN THE LATERAL CHAIN

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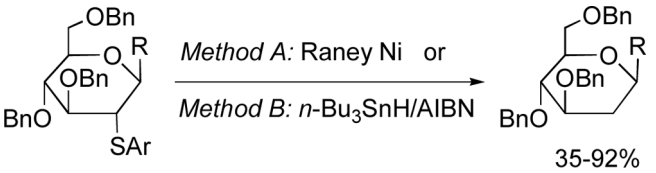
GRAPHICAL ABSTRACT



R = alkyl chain with an additional functional group

Abstract *2-Arylthio-β-C-D-glucopyranosides with a carbonyl or methoxy group in the lateral chain (***1** *and* **2***) can be converted to the corresponding 2-deoxy-β-C-D-glucopyranosides (***1a** *and* **2a***) using Raney Ni. Reduction of 2-arylthio-β-C-D-glucopyranosides bearing an ester, methoxy, C≡N, or C=C moiety in the side chain (***3**–**6***) using* n-*Bu_3SnH in the presence of azobisisobutyronitrile (AIBN) provided the corresponding 2-deoxy-β-C-D-glucopyranosides (***3a**–**6a***) without reducing additional functional groups. The application of* n-*Bu_3SnH and AIBN in reaction with 2-arylthio-β-C-D-glucopyranoside (***7***) containing a Me_3Si group bonded to the carbonyl fragment (***7***) resulted in the reduction of both the 2-ArS and C=O groups.*

Keywords 2-Arylthio-β-*C*-D-glucopyranosides; 2-deoxy-β-*C*-D-glucopyranosides; β-*C*-D-glucopyranosides; Raney Ni; tributyltin hydride

INTRODUCTION

Stereoselective synthesis of *C*-β-D-glycosides, including their 2-deoxy derivatives, is of great interest because compounds of this class are found in nature and some of them exhibit physiological activity of various types.[1] *C*-Glycosides can also serve as nonhydrolizable enzyme inhibitors,[2] stable carbohydrate mimetics for the

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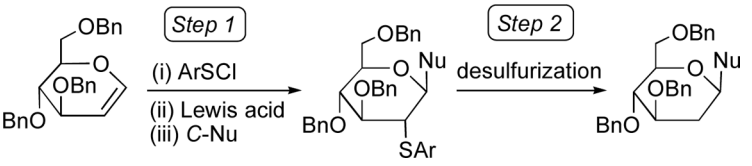


Scheme 1. Two-step synthesis of 2-deoxy-β-*C*-D-glucopyranosides from D-glucals.

study of carbohydrate recognition in biological systems,[3] and chiral precursors for the synthesis of other important compounds.[4]

Previously, we have reported a general method for preparation of 2-arylthio-*C*-β-D-glucopyranosides from tri-*O*-benzyl-D-glucal.[5] In the proposed one-pot protocol, (i) tri-*O*-benzyl-D-glucal reacts with ArSCl, (ii) using a Lewis acid, the formed ArSCl adducts of the glucal are converted to the corresponding episulfonium ions, and (iii) the *S*-stabilized three-membered intermediates react with *C*-nucleophiles [e.g., vinyl ethers, trimethyl cyanide (TMSCN), allyltrimethylsilane, trimethylsilyl enol ethers, and trimethylsilyl ketene acetals] to yield 2-arylthio-*C*-β-glucopyranosides with high stereoselectivity (β-gluco/α-manno up to 95:5, Scheme 1, step 1). Here we report two general procedures for the removal of the arylthio group from 2-arylthio-*C*-β-glucosides (**1**–**7**) having various functional groups in the lateral chain (Scheme 1, step 2).

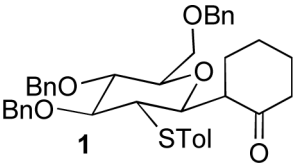
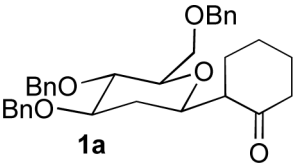
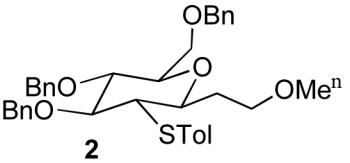
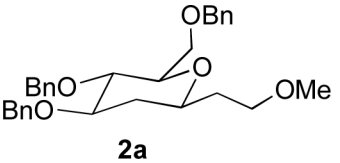
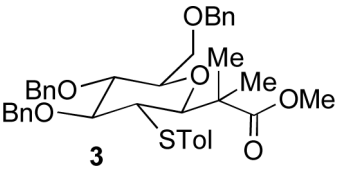
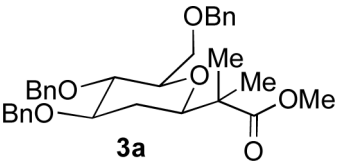
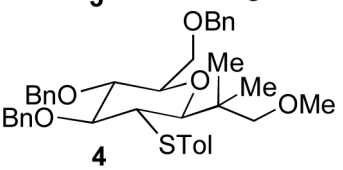
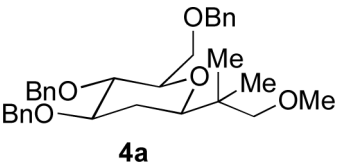
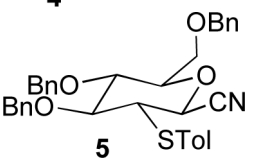
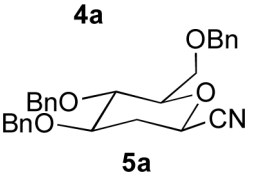
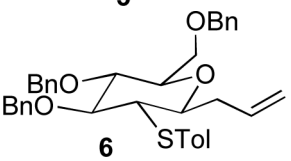
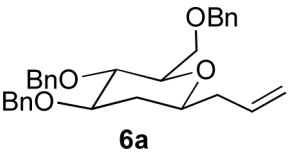
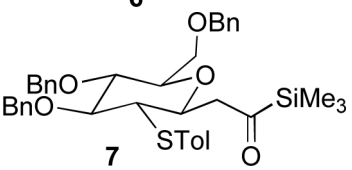
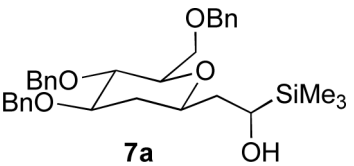
RESULTS

2-Arylthio-*C*-β-glycosides **1**–**7** (Table 1) were synthesized by the previously described method from tri-*O*-benzyl-D-glucal, ArSCl, and one of the following *C*-nucleophiles: 1-(trimethylsiloxy)cyclohexene,[6] methyl vinyl ether,[7] 1-methoxy-2-methyl-1-(trimethylsiloxy)propene,[6] 1-methoxy-2-methylpropene,[7] trimethylsilyl cyanide,[6] allyltrimethylsilane,[6] and 1-(trimethylsilyl)-1-(trimethylsiloxy)ethylene.[7] To obtain the desired 2-deoxy-β-*C*-glycosides, the 2-*p*-TolS group in compounds **1**–**7** had to be removed. In this study, two distinct methods were used.

Raney Ni is one of the most common reducing agents for ArS-substituted compounds.[8] In particular, this method was successfully used for desulfurization of *S*-containing *O*-glycosides.[9,10] In our study, reduction of the 2-*p*-TolS-substituted *C*-glycoside **1** by Raney Ni at room temperature yielded 2-deoxy-β-*C*-D-glucopyranoside **1a** (Table 1). As expected, the ketone C=O moiety in the lateral chain remained intact.[11] A similar result was obtained for compound **2**. However, we found that many factors—reactivity of Raney Ni, reaction time, temperature, and concentration of *C*-glucosides—have effects on the reproduction of the results. For example, higher temperature and longer reaction time led to the partial removal of benzyl groups. This prompted us to test *n*-Bu_3SnH for reduction of 2-ArS-substituted *C*-glycosides.

We found that the desulfurization of *C*-glycosides **3**–**6** by Bu_3SnH readily occurred in toluene at 105 °C. The reactions required the use of azobisisobutyronitrile (AIBN) as a radical initiator. Regardless the functional group—an ester, methoxy, C≡N, or C=C group—present in the lateral chain of glucosides **3**–**6**, only the

Table 1. Reduction of 2-*p*-tolylthio-β-*C*-glucopyranosides

Entry	2-*p*-TolS-β-*C*-glucopyranoside	Reducing agent	Product	Yield (%)
1	 **1**	Raney Ni	 **1a**	51
2	 **2**	Raney Ni	 **2a**	84
3	 **3**	*n*-Bu_3SnH	 **3a**	92
4	 **4**	*n*-Bu_3SnH	 **4a**	85
5	 **5**	*n*-Bu_3SnH	 **5a**	91
6	 **6**	*n*-Bu_3SnH	 **6a**	90
7	 **7**	*n*-Bu_3SnH	 **7a**	35

ArS group was removed, providing the corresponding 2-deoxy derivatives in good yield (Table 1). As expected,[12] the use of Bu_3SnH/AIBN in the reaction of *C*-glycoside **7** with the lateral chain containing a Me_3Si group bonded to the carbonyl moiety and provided 2-deoxy compound **7a** with a hydroxyl group.

The elemental composition of 2-deoxy-β-*C*-glycosides **1a**–**7a** was confirmed by high-resolution mass spectrographic (HRMS) data. The structures of synthesized

compounds were determined using ^{1}H, ^{13}C, correlation spectroscopy (COSY), and distortion less enhancement by polarization transfer (DEPT) NMR spectra.

In summary, we described the desulfurization step of the two-pot protocol for the stereoselective synthesis of β-*C*-D-glucopyranosides with additional functional groups in the lateral chain from commercially available tri-*O*-benzyl-D-glucal.

EXPERIMENTAL

Instrumentation and Materials

^{1}H and ^{13}C NMR spectra (300 MHz and 75 MHz, respectively) were recorded on a 300-MHz Varian NMR spectrometer using $CDCl_3$ as a solvent and Me_4Si as a standard unless stated otherwise. Coupling constants, *J*, are given in hertz. Infrared (IR) spectra were recorded on an ATI Mattson Genesis Series Fourier transform (FT)-IR instrument. Optical rotations were measured on a Rudolph Autopol III automatic polarimeter. HRMS were recorded at the University of California, Riverside, using VG-ZAB (FAB) or VG-7070 (CI/NH_3) mass spectrometers.

All reactions were carried out in dry nitrogen using oven-dried or flame-dried glassware and freshly distilled and dried solvents. Preparative thin-layer chromatography (TLC) was carried out by using glass plates, 200 × 250 mm, with an unfixed layer of Sigma-Aldrich or Natland silica gel 60 (230–400 mesh). The purity of the synthesized compounds was confirmed by analytical TLC, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra.

General Procedure for the Synthesis of 2-Arylthio-β-*C*-D-glucopyranosides 1–6[6,7]

A solution of 0.25 mmol of *p*-TolSCl in 0.3 mL of CH_2Cl_2 was added dropwise to a solution of 0.25 mmol of tri-*O*-benzyl-D-glucal in 10 mL of CH_2Cl_2 at room temperature. The color of the reaction mixture changed from yellow to colorless. After 10 min, the mixture was cooled to −78 °C, and a solution of 0.3 mmol of $SnCl_4$ in 0.3 mL CH_2Cl_2 was added, followed by 0.3 mmol of the corresponding *C*-Nu. The mixture was stirred for 1 h at −78 °C, quenched with a saturated solution of $NaHCO_3$ (in the case of compound **2**, the reaction mixture was first treated with a solution of *n*-Bu_4NBH_4 in CH_2Cl_2), extracted with ether, and dried over Na_2SO_4. Preparative TLC (diethyl ether–hexane, 1:4) of the crude material after solvent removal in vacuum afforded a pure *C*-glycoside.

Reduction method A. A solution of 0.100 mmol of 2-arylthio-*C*-β-D-glucopyranoside in 2 mL abs. THF was treated with a freshly made[13] W-2 Raney nickel (0.630 g). The reaction mixture was stirred at room temperature for 4–10 h, and its composition was monitored by TLC every hour. The nickel was removed by filtration. After solvent removal in vacuum, preparative TLC (diethyl ether–hexane, 1:4) of the crude product provided a pure *C*-glycoside.

Reduction method B. To a solution of 0.100 mmol of 2-arylthio-β-*C*-D-glucopyranoside in 1 mL of abs. toluene, 0.120 mmol Bu_3SnH and 10 mg AIBN were added. The reaction mixture was stirred at 105 °C for 12 h; 10 mg AIBN were

added every 4 h. After cooling the mixture to rt, the solvent was removed in vacuum. Preparative TLC (diethyl ether–hexane, 1:4) of the crude product afforded a pure *C*-glycoside.

3,4,6-(Tri-*O*-benzyl)-2-deoxy-1-(1′-oxocyclohexanyl)-β-D-glucopyranoside (1a)

The compound was synthesized from **1** (0.100 mmol, 63.7 mg) by method A in a yield of 51% (26.2 mg). R_f 0.38 (diethyl ether–hexane, 1:1); $[\alpha]_D^{20} + 8.35$ (c 0.470, $CHCl_3$); IR (film): 1706 cm^{-1} (C=O); ^1H NMR (500 MHz, δ, ppm): 1.26 [q, $J_{2a,2b} \approx J_{1.2a} \approx J_{3,2a} \approx 11.5$, 1H, H(2a)], 1.48–1.75, 1.90, 2.05, 2.28–2.48 (m, 9H, 9H of cyclohexanone), 2.44 [m, 1H, H(2b)], 3.36 [dt, $J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 3.0$, 1H, (5)], 3.50 [t, $J_{3,4} = J_{4,5} = 9.5$, 1H, H(4)], 3.61 [ddd, $J_{1,2b} = 11.0$, $J_{1,1'} = 7.5$, $J_{1,2a} = 1.5$, 1H, H(1)], 3.70 [m, 2H, H(6ab)], 3.73 [m, 1H, H(3)], 4.54 and 4.61 (two d, $J_{AB} = 12.5$, 2H, CH_2Ph), 4.55 and 4.91 (two d, $J_{AB} = 10.5$, 2H, CH_2Ph), 4.60 and 4.70 (two d, $J_{AB} = 11.5$, 2H, CH_2Ph), 7.30 (m, 15H, H arom); ^{13}C NMR (δ, ppm): 24.65 (CH_2), 28.19 (CH_2), 30.29 (CH_2), 35.45 (CH_2), 42.81 ($\underline{C}H_2CO$), 55.46 ($\underline{C}HCO$), 69.45, 71.29, 73.33 and 73.70 (4 groups OCH_2), 74.90, 78.36, 79.00 and 81.07 (4 groups OCH), 127.47, 127.51, 127.68, 127.93, 128.27, 128.34, 138.43 and 138.58 (C arom). 211.66 (C=O). HRMR calcd for $C_{33}H_{38}O_5$ (M^+) m/e 514.2720; found m/e 514.2735.

1-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-2-methoxyethane (2a)

The compound was synthesized from **2** (0.100 mmol, 59.9 mg) by method A in a yield of 84% (40.0 mg). R_f 0.30 (diethyl ether–hexane, 1:1); $[\alpha]_D^{22} + 12.1$ (c 0.240, $CHCl_3$); ^1H NMR (500 MHz, δ, ppm): 1.45 [q, $J_{2a,2b} \approx J_{1.2a} \approx J_{3,2a} \approx 11.0$, 1H, H(2a)], 1.76 [m, 1H, H(1a')], 1.90 [m, 1H, H(1b')], 2.17 [br, dd, $J_{2a,2b} = 11.0$, $J_{2b,3} = 5.0$, 1H, H(2b)], 3.35 (s, 3H, OCH_3), 3.52 [m, 4H, H(1), H(3), H(7ab)], 3.66 [dd, $J_{4,5} = 6.4$, $J_{3,4} = 8.4$, 1H, H(4)], 3.72 [m, 2H, H(6ab)], 4.57 and 4.92 (two d, $J_{AB} = 10.7$, 2H, CH_2Ph), 4.58 and 4.65 (two d, $J_{AB} = 12.2$, 2H, CH_2Ph), 4.66 and 4.72 (two d, $J_{AB} = 11.6$, 2H, CH_2Ph), 7.30 (m, 15 H, H arom); ^{13}C NMR (δ, ppm): 35.67 and 37.06 (2 groups CH_2), 58.63 (OCH_3), 60.29, 69.53, 71.39, 72.61 and 73.58 (5 groups OCH_2), 74.95, 78.56, 78.89 and 81.12 (4 groups OCH), 127.48, 127.55, 127.63, 127.56, 127.96, 128.29 and 128.37 (C arom). HRMS calcd. for $C_{30}H_{36}O_5$ (M^+) m/e 476.2563; found m/e 476.2631.

Methyl 2-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-2-methylpropionate (3a)

The compound was obtained from glycoside **3** (0.100 mmol, 64.1 mg) by method B in 92% yield (47.7 mg). R_f 0.34 (diethyl ether–hexane, 1:2); $[\alpha]_D^{22} + 10.9$ (c 0.880, $CHCl_3$); IR ($CHCl_3$ soln.): 1727 cm^{-1} (C=O); ^1H NMR (δ, ppm): 1.18 and 1.26 [two s, 6H, $C(CH_3)_2$], 1.48 [q, $J_{1,2a} = J_{2a,3} = 11.2$, $J_{2a,2b} = 12.3$, 1H, H(2a)], 2.40 [dd, $J_{2a,2b} = 12.3$, $J_{2b,3} = 4.9$, 1H, H(2b)], 3.43 [ddd, $J_{4,5} = 9.3$, $J_{5,6a} = 2.9$, $J_{5,6b} = 5.6$, 1H, H(5)], 3.51 [t, $J_{3,4} = J_{4,5} = 9.3$, 1H, H(4)], 3.62 [d,

$J_{1,2a} = 11.2$, 1H, H(1)], 3.68 (s, 3H, OCH_3), 3.75 [m, 3H, H(6ab), H(3)], 4.57 and 4.63 (two d, $J_{AB} = 12.3$, 2H, CH_2Ph), 4.65 and 4.92 (two d, $J_{AB} = 10.8$, 2H, CH_2Ph), 4.68 and 4.72 (two d, $J_{AB} = 11.5$, 2H, CH_2Ph), 7.31 (m, 15H, H arom); ^{13}C NMR (δ, ppm): 21.00 and 21.30 [$C(\underline{C}H_3)_2$], 31.42 (CH_2), 46.41 [$\underline{C}(CH_3)_2$], 52.11 (OCH_3), 69.56, 71.86, 73.39 and 75.20 (4 groups OCH_2), 78.88, 79.72, 79.79 and 81.52 (4 groups OCH), 127.54, 127.68, 127.74, 127.82, 128.19, 128.46, 128.53, 128.59, 138.74 and 138.92 (C arom). 177.05 (C=O). HRMS calcd. for $C_{32}H_{38}O_6(M^+)$ m/e 518.2669; found for $(M+1)^+$ m/e 519.2751.

1-Methoxy-2-methyl-2-(3,4,6-tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)propane (4a)

The compound was obtained from glycoside **4** (0.100 mmol, 62.7 mg) by method B in 85% yield (42.9 mg). R_f 0.45 (diethyl ether–hexane, 1:2); $[\alpha]_D^{20} + 8.4$ (c 0.50, $CHCl_3$); ^1H NMR (δ, ppm): 0.90 and 0.94 [two s, 6H, $C(CH_3)_2$], 1.45 [q, $J_{1,2a} = 11.7$, $J_{2a,2b} = 12.1$, $J_{2a,3} = 13.4$, 1H, H(2a)], 2.07 [ddd, $J_{2a,2b} = 12.1$, $J_{2b,3} = 5.0$, $J_{1,2b} = 1.4$, 1H, H(2b)], 3.14 and 3.26 (two d, $J_{7a,7b} = 8.9$, 2H, $C\underline{H}_2OCH_3$), 3.25 [dd, $J_{1,2b} = 1.4$, $J_{1,2a} = 11.7$, H(1)], 3.30 (s, 3H, OCH_3), 3.36 [dt, $J_{4,5} = 9.5$, $J_{5,6a} = J_{5,6b} = 6.4$, 1H, H(5)], 3.45 [t, $J_{3,4} = J_{4,5} = 9.5$, 1H, H(4)], 3.65 [ddd, $J_{3,2a} = 13.4$, $J_{3,4} = 9.5$, $J_{3,2b} = 5.0$, 1H, H(3)], 3.75 [m, 2H, H(6a,b)], 4.57 and 4.72 (two d, $J_{AB} = 11.6$, 2H, CH_2Ph), 4.58 and 4.65 (two d, $J_{AB} = 12.2$, 2H, CH_2Ph), 4.63 and 4.91 (two d, $J_{AB} = 10.9$, 2H, CH_2Ph), 7.30 (m, 15H, H arom); ^{13}C NMR (δ, ppm): 20.70 and 21.67 [$C(\underline{C}H_3)_2$], 31.24 (CH_2), 38.38 [$\underline{C}(CH_3)_2$], 59.55 (OCH_3), 70.99, 71.82, 73.46, 75.14 and 79.47 (5 groups OCH_2), 79.07, 79.20, 79.83 and 82.04 (4 groups OCH), 127.56, 127.68, 127.77, 127.86, 128.21, 128.48, 128.54, 128.69, 138.90, 138.95 and 139.06 (C arom). HRMS: calcd. for $C_{32}H_{40}O_5$ (M^+) m/e 504.2877; found for $(M+1)^+$ m/e 505.2957.

3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)carbonitrile (5a)

The compound was obtained from **5** (0.100 mmol, 56.6 mg) by method B in 91% yield (40.4 mg). R_f 0.81 (diethyl ether–hexane, 1:2); $[\alpha]_D^{20} + 15.7$ (c 0.470, $CHCl_3$); ^1H NMR (δ, ppm): 1.99 [q, $J_{1,2a} = 12.3$, $J_{2a,2b} = 12.6$, $J_{2a,3} = 13.3$, 1H, H(2a)], 2.43 [ddd, $J_{2a,2b} = 12.6$, $J_{2b,3} = 4.0$, $J_{1,2b} = 2.2$, 1H, H(2b)], 3.40 [m, 1H, H(5)], 3.57 [t, $J_{3,4} = J_{4,5} = 8.8$, 1H, H(4)], 3.63 [m, $J_{3,2a} = 13.3$, $J_{3,2b} = 4.0$, $J_{3,4} = 8.8$, 1H, H(3)], 3.72 [m, 2H, H(6ab)], 4.21 [dd, $J_{1,2a} = 12.3$, $J_{1,2b} = 2.2$, 1H, H(1)], 4.56 and 4.63 (two d, $J_{AB} = 12.2$, 2H, CH_2Ph), 4.57 and 4.89 (two d, $J_{AB} = 10.8$, 2H, CH_2Ph), 4.64 and 4.71 (two d, $J_{AB} = 11.7$, 2H, CH_2Ph), 7.30 (m, 15H, H arom); ^{13}C NMR (δ, ppm): 35.31 (CH_2), 63.88 ($\underline{C}HCN$), 68.83, 72.14, 73.84 and 75.51 (4 groups OCH_2), 77.22, 79.41 and 80.24 (3 groups OCH), 117.15 (CN), 127.95, 128.00, 128.09, 128.13, 128.19, 128.23, 128.67, 128.78, 137.99, 138.06, and 138.17 (C arom). HRMS calcd. for $C_{28}H_{29}NO_4$ (M^+) m/e 443.2098; found $(M+1)^+$ m/e 444.2164.

3-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-1-propene (6a)

The compound was obtained from **6** (0.100 mg, 58.1 mg) by method B in 90% yield (41.3 mg). R_f 0.43 (diethyl ether–hexane, 1:2); $[\alpha]_D^{20} + 2.73$ (c 0.440, $CHCl_3$); ^1H

NMR (δ, ppm): 1.40 [q, $J_{2a,2b} \approx J_{2a,1} \approx J_{2a,3} \approx 11.7$, 1H, H(2a)], 2.16 [br. dd, $J_{2a,2b} = 11.7$, $J_{2b,3} = 4.9$, 1H, H(2b)], 2.26 [m, 1H, H(7a)], 2.45 [m, 1H, H(7b)], 3.40 [m, 2H, H(1), H(3)], 3.48 [t, $J_{3,4} = J_{4,5} = 9.4$, H(4)], 3.65 [m, $J_{4,5} = 9.4$, $J_{5,6a} = 11.5$, $J_{5,6b} = 3.5$, 1H, H(5)], 3.73 [m, $J_{5,6a} = 11.5$, $J_{5,6b} = 3.5$, 2H, H(6ab)], 4.56 and 4.62 (two d, $J_{AB} = 12.2$, 2H, CH_2Ph), 4.58 and 4.67 (two d, $J_{AB} = 12.2$, 2H, CH_2Ph), 4.62 and 4.71 (two d, $J_{AB} = 11.7$, 2H, CH_2Ph), 5.10 [m, 2H, H(9), H(10)], 5.82 [m, 1H, H(8)]. ^{13}C NMR (δ, ppm): 36.48 (CH_2), 40.27 ($\underline{C}H_2$-CH=CH_2), 69.74, 71.56, 73.62, and 75.28 (4 groups OCH_2), 75.19, 78.80, 79.26, and 81.35 (4 groups OCH), 117.36 ($H_2\underline{C}$=CH), 134.71 (H$\underline{C}$=CH_2), 127.70, 127.77, 127.82, 127.93, 128.01, 128.10, 128.16, 128.52, 128.59, 138.63, 138.72 and 138.85 (C arom). HRMS calcd. for $C_{30}H_{34}O_4$ (M^+) m/e 458.2458; found for $(M+1)^+$ m/e 459.2526.

2-(3,4,6-Tri-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-1-(Trimethylsilyl)ethanol (7a)

The compound was obtained from **7** (0.100 mmol, 65.5 mg) using method B in 35% yield (18.7 mg). ^{1}H NMR (δ, ppm): 0.27 (s, 9H, $SiMe_3$), 1.45–1.6 [m, 2H, H(2a′), H(2a)], 1.83 [m, 1H, H(2b′)], 2.17 [ddd, $J_{2a,2b} = 12.5$, $J_{2b,3} = 5.0$, $J_{1,2b} = 1.6$, 1H, H(2b)], 3.45–3.72 [m, 7H, H(1), H(3), H(4), H(5), H(6ab), H(1′)], 4.63 and 4.71 (two d, $J_{AB} = 11.7$, CH_2Ph), 4.55 and 4.90 (two d, $J_{AB} = 10.8$, CH_2Ph), 4.52 and 4.57 (two d, $J_{AB} = 12.7$, CH_2Ph), 7.30 (m, 15H, H arom); ^{13}C NMR (δ, ppm): −3.91 ($SiMe_3$), 29.96 (CH_3), 37.58 (CH_2), 66.56 (COH), 69.89, 71.70, 73.76 and 75.34 (4 groups OCH_2), 78.64, 79.05, 80.26 and 80.93 (4 groups OCH), 127.85, 127.89, 128.14, 128.29, 128.61, 128.68, 138.35, 138.59 and 138.77 (C arom). HRMS calcd. for $C_{32}H_{43}SiO_5$ $(M+1)$ m/e 535.2881; found $(M+1)^+$ m/e 535.2904.

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