A One-Pot Synthesis of β-*C*-Glucopyranosides from *exo*-Glucal, *p*-Tolylsulfenyl Chloride, an α-Methoxyalkene and an External Nucleophile

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Supporting Information

Instruments and materials

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer (500 MHz for ^{1}H and 125 MHz for ^{13}C). Chemical shifts are given in ppm and relative to $CDCl_3$. Coupling constants, *J*, are provided in Hz. Mass spectrometric data were obtained on a VG-ZAB-2SE instrument with FAB ionization. IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrometer. Optical Rotation data were measured on an Autopol III automatic polarimeter. Preparative TLC were carried out by using glass plates, 200 x 250 mm, with an unfixed layer of Aldrich silica gel, 230-400 mesh. Analytical TLC was performed on Whatman precoated plates of silica gel 60 F_{254}. All reactions were carried out under an atmosphere of dry nitrogen using oven-dried or flame-dried glassware and freshly distilled and dried solvents.

p-Tolylsulfenyl chloride was obtained from 4-methylbenzenethiol using SO_2Cl_2.[1] 1-Methoxy-2-methylpropene was prepared by pyrolysis of the corresponding acetal using *p*-toluenesulfonic acid as a catalyst. Other chemicals were purchased from Aldrich Chemical Co.

General procedure for synthesis of glycosides ***10a-15a***

A 50 mL three neck round bottom flask was charged under dry N_2 with 20 mL of dry CH_2Cl_2 and 0.28 mL (0.50 mmol) of a 1.8*M* solution of *p*-TolSCl in CH_2Cl_2. The solution was cooled to —78°C and 0.5 mL (0.5 mmol) of a 1.0*M* solution of 1-methoxy-2-methylpropene in CH_2Cl_2 was slowly added dropwise (the red-orange color of *p*-TolSCl disappeared and the mixture became colorless). Then 0.60 mL (0.60 mmol) of a 1.0*M* solution of $SnCl_4$ in CH_2Cl_2 was introduced followed by 0.8 mL (0.4 mmol) of a 0.5*M* solution of *exo*-glucal in CH_2Cl_2. The mixture was stirred for 3 hours at —78°C. To obtain glycoside **6**, the reaction mixture was poured into an ice cold saturated aqueous solution of $NaHCO_3$. To form glycoside **7**, a cold (-78 °C) suspension of 1.2 g of K_2CO_3 in 4 mL of dry MeOH was added to the reaction complex and was stirred at -78 °C for 1 h. Glycoside **8** was synthesized by adding 4.0 mL (4.0 mmol) of a cold (-78 °C) 1.0*M* solution of $NaCNBH_3$ in THF to the reaction complex; the mixture was stirred at —78°C for 1 h. To prepare glycoside **9**, 4.0 mL (4.0 mmol) of a 1.0*M* solution of $NaCNBH_3$ in THF was added to the reaction complex; the mixture was stirred at 0 °C for 1 h. The resulting mixture was extracted with ether (3 × 20 mL) and dried over Na_2SO_4. After solvent removal, the crude product was purified using gradient elution column chromatography (hexane to 6:1 hexane-ethyl acetate) and/or preparative TLC (10:1 hexane-ethyl acetate).

*(2*S*)-Methoxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-1-hydroxy-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**10a**)

Colorless oil; R_f 0.26 (1:6 hexane-ethyl acetate); $[\alpha]^{21}_{D}$ −11.6° (*c* 0.90, $CHCl_3$); IR (neat, ν, cm^{-1}): 3449 br (OH); ^{1}H NMR ($CDCl_3$, δ): 1.01 and 1.12 (two s, 6H, $C(CH_3)_2$), 1.65 (dd, $J_{1a',2'}$ = 2.8, $J_{1a',1b'}$ = 14.3, 1H, H(1a′)), 2.07 (dd, $J_{1b',2'}$ = 11.5, $J_{1a',1b'}$ = 14.3, 1H, H(1b′)), 1.55 (s, 1H, OH), 2.29 (s, 3H, CH_3), 3.28 (d, $J_{2,3}$ = 9.5, 1H, H(2)), 3.42 (s, 3H, OCH_3), 3.64 (br t, $J_{3,4} = J_{4,5}$ = 9.5, 1H, H(4)), 3.67 (dd, $J_{5,6a}$ = 1.8, $J_{6a,6b}$ = 10.5, 1H, H(6a)), 3.73 (dd, $J_{5,6b}$ = 6.4, $J_{6a,6b}$ = 10.5, 1H, H(6b)), 3.75 (m, 1H, H(2′)), 4.11 (ddd, $J_{4,5}$ = 9.5, $J_{5,6a}$ = 1.8, $J_{5,6b}$ = 6.4, 1H, H(5)), 4.13 (t, $J_{3,4} = J_{2,3}$ = 9.5, 1H, H(3)), 4.50 and 4.57 (two d, J_{AB} = 12.2, 2H, C*H₂*Ph), 4.62 and 4.69 (two d, J_{AB} = 11.7, 2H, CH_2Ph), 4.90 and 4.91 (two d, J_{AB} = 10.7, 2H, CH_2Ph), 4.94 and 4.96 (two d, J_{AB} = 10.8, 2H, CH_2Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 21.2, 24.4, and 25.8 (3 CH_3), 36.3 (CH_2), 52.8 (*C*$(CH_3)_2$), 61.1 (OCH_3), 69.4, 73.3, 74.8, 75.3, and 75.7 (5 OCH_2 groups), 70.7, 78.9, 83.4, 83.5, and 85.1 (5 CHOR groups), 98.2 (*C*(OH)O), 127.5, 127.6, 127.7, 127.9, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 129.1, 129.3, 129.5, and 137.6 (CH-arom), 138.1, 138.3, 138.5, 138.8, and 138.9 (C-arom); HRMS: Calcd for $C_{47}H_{54}O_7SNa$ 785.3489; Found: $(MNa)^+$ *m/z* 785.3488.

*(2*S*)-Methoxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-1-methoxy-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**11a**)

Colorless oil; R_f 0.31 (1:6 ethyl acetate-hexane); $[\alpha]^{21}_{D}$ +23.3° (*c* 0.78, $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ): 1.10 and 1.17 (two s, 6H, $C(CH_3)_2$), 2.12 (dd, $J_{1a',2'}$ = 9.3, $J_{1a',1b'}$ = 15.3, 1H, H(1a′)), 2.31(s, 3H, CH_3), 2.44 (d, $J_{1b',2'}$ = 0, $J_{1a',1b'}$ = 15.3, 1H, H(1b′)), 3.31 (s, 3H, OCH_3), 3.37 (d, $J_{1b',2'}$ = 0, $J_{1a',2'}$ = 9.3, 1H, H(2′)), 3.45 (s, 3H, OCH_3), 3.61 (d, $J_{2,3}$ = 9.0, 1H, H(2)), 3.73 (dd, $J_{5,6a}$ = 1.1, $J_{6a,6b}$ = 8.0, 1H, H(6a)), 3.74 (m, 2H, H(6b), H(5)), 3.80 (dd, $J_{3,4}$ = 9.0, $J_{4,5}$ = 4.2, 1H, H(4)), 4.17 (br t, $J_{3,4} = J_{2,3}$ = 9.0, 1H, H(3)), 4.48 and 4.53 (two d, J_{AB} = 11.9, 2H, CH_2Ph), 4.65 and 4.88 (two d, J_{AB} = 10.8, 2H, CH_2Ph), 4.87 and 5.03 (two d, J_{AB} = 11.1, 2H, CH_2Ph), 4.89 and 4.94 (two d, J_{AB} = 11.0, 2H, CH_2Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 21.2, 24.2, and 26.7 (3 CH_3), 34.8 (CH_2), 48.2 (OCH_3), 54.3 (*C*$(CH_3)_2$), 60.6 (OCH_3), 69.0, 73.8, 75.0, 75.3, and 75.5 (5 OCH_2 groups), 71.9, 78.6, 82.5, 83.8, and 83.9 (5 CHOR groups), 101.6 (*C*(OCH_3)O), 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 129.3, 137.6, 138.1, and 138.3 (CH-arom), 138.4, 138.5, 138.6, 138.7, and 138.8 (C-arom); HRMS: Calcd for $C_{50}H_{56}SO_7$ 800.3746; Found: M^+ *m/z* 799.3644.

*(2*R*)-Methoxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-1-methoxy-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**11b**)

Colorless oil; R_f 0.29 (1:6 ethyl acetate-hexane); $[\alpha]^{21}_{D}$ +13.2° (*c* 0.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ): 1.18 and 1.25 (two s, 6H, $C(CH_3)_2$), 2.10 (dd, $J_{1a',2'}$ = 10.9, $J_{1a',1b'}$ = 14.9, 1H, H(1a′)), 2.30 (s, 3H, CH_3), 2.67 (dd, $J_{1b',2'}$ = 1.2, $J_{1a',1b'}$ = 14.9, 1H, H(1b′)), 3.31 and 3.33 (two s, 6H, 2 OCH_3 groups), 3.50 (dd, $J_{1b',2'}$ = 1.2, $J_{1a',2'}$ = 10.9, 1H, H(2′)), 3.70 (d, $J_{2,3}$ = 9.1, 1H, H(2)), 3.71 (m, 2H, H(4), H(5)), 3.74 (dd, $J_{5,6a}$ = 1.2, $J_{6a,6b}$ = 10.6, 1H, H(6a)), 3.85 (dd, $J_{6a,6b}$ = 10.6, $J_{5,6b}$ = 3.1, 1H, H(6b)), 4.15 (br t, $J_{3,4}$ = $J_{2,3}$ = 9.1, 1H, H(3)), 4.50 and 4.56 (two d, J_{AB} = 11.9, 2H, CH_2Ph), 4.60 and 4.86 (two d, J_{AB} = 10.9, 2H, CH_2Ph), 4.84 and 4.90 (two d, J_{AB} = 11.0, 2H, CH_2Ph), 4.87 and 4.94 (two d, J_{AB} = 10.9, 2H, CH_2Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 21.6, 23.1, and 27.2 (3 CH_3 groups), 30.8 (CH_2), 47.5 (OCH_3), 53.4 ($C(CH_3)_2$), 60.8 (OCH_3), 69.6, 73.7, 75.5, 75.6, and 76.1 (5 OCH_2 groups), 72.3, 78.9, 82.9, 83.8, and 84.1 (5 CHOR groups), 101.4 (*C*(OCH_3)O), 127.2, 127.3, 127.4, 127.5, 127.6, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 128.9, and 129.3 (CH-arom), 137.6, 138.4, 138.6, 138.8 and 138.9 (C-arom); HRMS: Calcd for $C_{50}H_{56}SO_7$ 800.3746; Found: M^+ *m/z* 799.3644.

*(2*S*)-Methoxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**12a**)

Colorless oil; R_f 0.35 (1:7 ethyl acetate-hexane); $[\alpha]^{19}_{D}$ −15.5° (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$, δ): 1.12 and 1.18 (two s, 6H, $C(CH_3)_2$), 1.92 (ddd, $J_{1b',2'}$ = 10.6, $J_{1a',1b'}$ = 13.0, $J_{1b',1}$ = 2.3, 1H, H(1b′)), 1.98 (ddd, $J_{1a',2'}$ = 2.6, $J_{1a',1b'}$ = 13.0, $J_{1a',1}$ = 10.6, 1H, H(1a′)), 2.28 (s, 3H, CH_3), 3.33 (t, $J_{3,4}$ = $J_{4,5}$ = 9.2, 1H, H(4)), 3.37 (s, 3H, OCH_3), 3.45 (br d, $J_{1,2}$ = 9.2, $J_{1b',1}$ = 2.3, $J_{1a',1}$ = 10.6, 1H, H(1)), 3.48 (dd, $J_{1b',2'}$ = 10.6, $J_{1a',2'}$ = 2.6,1H, H(2′)), 3.65 (t, $J_{2,3}$ =$J_{1,2}$ = 9.2, 1H, H(2)), 3.72 (m, 1H, H(3)), 3.73 (m, 2H, H(6a), H(6b)), 4.55 and 4.63 (two d, J_{AB} = 12.2, 2H, CH_2Ph), 4.61 and 4.86 (two d, J_{AB} = 10.9, 2H, CH_2Ph), 4.68 and 4.88 (two d, J_{AB} = 11.2, 2H, CH_2Ph), 4.89 and 4.92 (two d, J_{AB} = 3.56, 2H, CH_2Ph), 7.30 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 21.6, 24.4, and 26.6 (3 CH_3 groups), 34.1 (CH_2), 33.7 (*C*(CH_3)$_2$), 61.8 (OCH_3), 69.9, 73.9, 75.4, 75.6, and 75.9 (5 OCH_2 groups), 76.6, 79.1, 79.2, 83.0, 83.7, and 87.9 (6 CHOR groups), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.2, 129.3, 129.4, 137.4, 137.7, 137.9, and 138.1 (CH-arom), 138.2, 138.5, 138.7, 138.9, and 140.9 (C-arom); HRMS: Calcd for $C_{47}H_{54}O_6SNa$, 769.3539; Found: $(MNa)^+$ *m/z* 769.3539.

*(2*S*)-Methoxy-1-*C*-[2,3,4,6-tetra-*O*-benzyl-1-hydroxy-β-D-glucopyranosyl]-3-(*p*-tolyl)sulfonylpropane (***13a**)

Colorless oil; R_f 0.25 (1:5 ethyl acetate-hexane); $[\alpha]^{21}_{D}$ +2.52° (*c* 1.79, $CHCl_3$); IR (neat, ν, cm^{-1}): 3430 br (OH);^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.53 (dd, $J_{1a',2'}$ = 2.3, $J_{1a',1b'}$ = 14.4, 1H, H(1a′)), 2.07 (dd, $J_{1b',2'}$ = 11.1, 1H, H(1b′)), 2.28 (s, 3H, CH_3), 2.82 (dd, $J_{3a',2'}$ = 7.1, $J_{3a',3b'}$ = 13.5, 1H, H(3a′)), 2.98 (dd, $J_{3b',2'}$ = 4.1, 1H, H(3b′)), 3.22 (br d, $J_{2,3}$ = 9.6, 1H, H(2)), 3.28 (s, 3H, OCH_3), 3.61 (dd, $J_{5,6a}$ =1.9, $J_{6a,6b}$ = 10.9, 1H, H(6a)), 3.62 (br t, $J_{3,4}$ = $J_{4,5}$ = 9.6, 1H, H(4)), 3.72 (dd, $J_{5,6b}$ = 4.3, 1H, H(6b)), 3.98 (dddd, 1H, H(2′)), 4.03 (ddd, 1H, H(5)), 4.05 (br t, 1H, H(3)), 4.48 and 4.52 (two d, J_{AB} = 12.2, 2H, C*H₂*Ph), 4.58 and 4.87 (two d, J_{AB} = 14.1, 2H, C*H₂*Ph), 4.60 and 4.85 (two d, J_{AB} = 11.0, 2H, C*H₂*Ph), 4.88 and 4.90 (two d, J_{AB} = 10.7, 2H, C*H₂*Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 21.2 (CH_3), 38.4 and 40.1 (2 CH_2 groups), 57.1 (OCH_3), 69.6, 73.8, 75.2, 75.8, and 76.0 (5 OCH_2 groups), 71.3, 77.7, 89.2, 83.6, and 83.9 (5 CHOR groups), 97.9 (*C*(OH)O), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 128.5, 128.6, 129.8, 130.6, (CH-arom), 132.5, 136.6, 138.2, 138.4, 138.5 and 138.8 (C-arom); HRMS: Calcd for $C_{45}H_{50}O_7SNa$ 757.3175; Found: $(MNa)^+$ *m/z* 757.3175.

*(2*S*)-Methoxy-1-*C*-[2,3,4,6-tetra-*O*-benzyl-1-methoxy-β-D-glucopyranosyl]-3-(*p*-tolyl)sulfonylpropane* **(14a)**

Colorless oil; R_f 0.33 (1:5 ethyl acetate-hexane); $[\alpha]^{21}_D$ +27.13° (*c* 0.81, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 2.10 (dd, $J_{1a',2'}$ = 8.1, $J_{1a',1b'}$ = 14.6, 1H, H(1a′)), 2.15 (dd, $J_{1b',2'}$ = 4.7, 1H, H(1b′)), 2.26 (s, 3H, CH_3), 3.05 (dd, $J_{3a',2'}$ = 6.3, $J_{3a',3b'}$ = 13.5, 1H, H(3a′)), 3.07 (dd, $J_{3b',2'}$ = 4.7, 1H, H(3b′)), 3.20 and 3.23 (two s, 6H, 2 OCH_3 groups), 3.60 (m, 1 H, H(2′)), 3.63 (d, $J_{2,3}$ = 9.0, 1 H, H(2)), 3.64 (dd, $J_{3,4}$ =9.0, $J_{4,5}$ = 10.1, 1H, H(4)) 3.65 (m, 1H, H(6a)), 3.67 (m, 1 H, H(5)), 3.75 (dd, $J_{5,6b}$ = 3.5, $J_{6a,6b}$ = 10.7, 1H, H(6b)), 4.08 (br t, 1H, H(3)), 4.48 and 4.55 (two d, J_{AB} = 12.1, 2H, C*H₂*Ph), 4.60 and 4.87 (two d, J_{AB} = 10.8, 2H, C*H₂*Ph), 4.70 and 4.75 (two d, J_{AB} = 10.9, 2H, C*H₂*Ph), 4.85 and 4.88 (two d, J_{AB} = 5.8, 2H, C*H₂*Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 21.4 (CH_3), 34.9 and 39.2 (2 CH_2), 47.9 and 57.4 (2 OCH_3), 69.4, 73.7, 75.5, 75.8, and 76.1 (5 OCH_2 groups), 72.4, 77.1, 78.9, 82.2, and 83.8 (5 CHOR groups), 100.7 (*C*(OCH_3)O), 127.3, 127.4, 127.5, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.4, 129.7, 130.6, 132.9, 136.4, (CH-arom), 138.1, 138.3, 138.5, 138.6, 138.7 and 138.8 (C-arom); HRMS: Calcd for $C_{46}H_{52}O_7SNa$ 771.3331; Found: $(MNa)^+$ *m/z* 771.3331.

*(2*S*)-Methoxy-1-*C*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-3-(*p*-tolyl)sulfonylpropane* **(15a)**

Colorless oil; R_f 0.29 (1:5 ethyl acetate-hexane); $[\alpha]^{21}_D$ +5.72° (*c* 0.24, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, δ): 1.87 (ddd, $J_{1a',1'}$ = 4.5, $J_{1a',2'}$ = 8.5, $J_{1a',1b'}$ = 14.2, 1H, H(1a′)), 2.07 (ddd, $J_{1b',1'}$ = 2.7, $J_{1b',2'}$ = 6.9, 1H, H(1b′)), 2.31 (s, 3H, CH_3), 3.05 (dd, $J_{3a',2'}$ = 6.5, $J_{3a',3b'}$ = 13.4, 1H, H(3a′)), 3.11 (dd, $J_{3b',2'}$ = 5.2, 1H, H(3b′)), 3.30 (s, 3H, OCH_3), 3.31 (m, 1 H, H-4), 3.35 (ddd, $J_{1,2}$ = 9.6, 1H, H(1)), 3.39 — 3.65 (m, 6H, H(5), H(2′), H(2), H(3), H(6a), and H(6b)), 4.52 and 4.58 (two d, J_{AB} = 12.3, 2H, C*H₂*Ph), 4.59 and 4.89 (two d, J_{AB} = 9.7, 2H, C*H₂*Ph), 4.66 and 4.82 (two d, J_{AB} = 10.8, 2H, C*H₂*Ph), 4.87 and 4.91 (two d, J_{AB} = 11.2, 2H, C*H₂*Ph), 7.28 (m, 24H, H-arom); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 20.9 (CH_3), 34.6 and 38.7 (2 CH_2 groups), 57.0 (OCH_3), 69.4, 73.9, 75.4, 75.6, and 76.0 (5 OCH_2 groups), 76.4, 77.5, 78.9, 79.3, 82.6 and 87.8 (6 CHOR groups), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 129.6, 130.0, 130.1 and 133.2

(CH-arom), 136.0, 138.0, 138.1, 138.2, 138.3 and 138.6 (C-arom); HRMS: Calcd for $C_{45}H_{50}O_6SNa$ 741.3225; Found: $(MNa)^+$ *m/z* 741.3224.

*(2*S*)-Hydroxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**16a**)

Colorless oil; R_f 0.19 (1:4 ethyl acetate-hexane); $[\alpha]^{21}_D$ −23.2° (*c* 0.43, $CHCl_3$); IR (neat, ν, cm $^{-1}$): 3467 br (OH); ^{1}H NMR ($CDCl_3$, δ): 1.30 and 1.37 (two s, 6H, $C(CH_3)_2$), 1.95 (ddd, $J_{1a',2'}$ = 4.9, $J_{1a',1b'}$ = 15.0, $J_{1a',1}$ = 7.9, 1H, H(1a′)), 2.23 (ddd, $J_{1b',2'}$ = 5.8, $J_{1a',1b'}$ = 15.0, $J_{1b',1}$ = 2.8, 1H, H(1b′)), 2.26 (s, 3H, CH_3), 3.27 (br t, $J_{1a',2'}$ = 4.9, $J_{1b',2'}$ = 5.8, 1H, H(2′)), 3.33 (t, $J_{1,2}$ = $J_{2,3}$ = 9.2, 1H, H(2)), 3.45 (br s, 1H, OH), 3.46 (ddd, $J_{4,5}$ = 9.5, $J_{5,6a}$ = 1.9, $J_{5,6b}$ = 4.9, 1H, H(5)), 3.56 (dd, $J_{3,4}$ = 8.9, $J_{4,5}$ = 9.5, 1H, H(4)), 3.58 (dd, $J_{5,6b}$ = 4.9, $J_{6a,6b}$ = 10.8, 1H, H(6b)), 3.64 (dd, $J_{5,6a}$ = 1.9, $J_{6a,6b}$ = 10.8, 1H, H(6a)), 3.72 (dd, $J_{3,4}$ =8.9, $J_{2,3}$ = 9.2, 1H, H(2)), 3.88 (ddd, $J_{1,2}$ = 9.2, $J_{1a',1}$ =7.9, $J_{1b',1}$ = 2.8, 1H, H(1)), 4.48 and 4.58 (two d, J_{AB} = 12.2, 2H, C*H₂*Ph), 4.52 and 4.56 (two d, J_{AB} = 11.1, 2H, CH_2Ph), 4.79 and 4.86 (two d, J_{AB} = 10.9, 2H, CH_2Ph), 4.85 and 4.87 (two d, J_{AB} = 11.0, 2H, CH_2Ph), 7.30 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 21.1, 27.8, and 28.4 (3 CH_3), 33.6 (CH_2), 65.3 ($C(CH_3)_2$), 73.5, 74.9, 75.0, 75.5, and 78.4 (5 OCH_2 groups), 60.2, 68.9, 76.6, 78.4, 82.2, and 87.2 (6 CHOR groups), 126.9, 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 129.7, 131.8, 133.1, 136.4, 137.5, 137.9, and 138.1 (CH-arom), 138.2, 138.5, 138.7, 138.9, and 140.9 (C-arom); HRMS: Calcd for $C_{46}H_{52}O_6SNa$, 755.3382; Found: $(MNa)^+$ *m/z* 755.3382.

*(2*R*)-Hydroxy-3-methyl-1-*C*-[2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl]-3-(*p*-tolylsulfanyl)butane* (**16b**)

Colorless oil; R_f 0.25 (1:4 ethyl acetate-hexane); $[\alpha]^{21}_D$ +15.5° (*c* 0.10, $CHCl_3$); IR (neat, ν, cm $^{-1}$): 3458 br (OH); ^{1}H NMR ($CDCl_3$, δ): 1.15 and 1.24 (two s, 6H, $C(CH_3)_2$), 1.61 (ddd, $J_{1a',2'}$ = 2.8, $J_{1a',1b'}$ = 13.7, $J_{1a',1}$ = 10.6, 1H, H(1a′)), 1.83 (ddd, $J_{1b',2'}$ = 12.4, $J_{1a',1b'}$ = 13.7, $J_{1b',1}$ = 2.0, 1H, H(1b′)), 2.20 (s, 3H, CH_3), 2.85 (br.s, 1H, OH), 2.95 (ddd, $J_{4,5}$ = 9.5, $J_{5,6a}$ = 7.9, $J_{5,6b}$ = 1.6, 1H, H(5)), 3.06 (dd, $J_{6a,6b}$ =10.9, $J_{5,6b}$ = 1.6, 1H, H(6b)), 3.28 (br t, $J_{1,2}$ = $J_{2,3}$ = 9.0, 1H, H(2)), 3.38 (dd, $J_{1b',2'}$ = 12.4, $J_{1a'2'}$ =2.8, 1H, H(2′)), 3.42 (m, 1H, H(6a)), 3.60 (br t, $J_{4,5}$ = $J_{3,4}$ = 9.5, 1H, H(4)), 3.62 (ddd, $J_{1a',1}$ = 10.6, $J_{1b',1}$ = 2.0, $J_{1,2}$ = 9.0, 1H, H(1)), 3.66 (br t, $J_{2,3}$ = 9.0, $J_{3,4}$ = 9.5, 1H, H(3)), 4.45 (two d, J_{AB} = 12.4, 2H, CH_2Ph), 4.55 and 4.80 (two d, J_{AB} = 10.7, 2H, CH_2Ph), 4.63 and 4.86 (two d, J_{AB} = 11.4, 2H, CH_2Ph), 4.62 and 4.84 (m, 2H, CH_2Ph), 7.30 (m, 24H, H-arom); ^{13}C NMR ($CDCl_3$, δ): 20.9, 26.3, and 26.9 (3 CH_3), 34.9 (CH_2), 72.5 ($C(CH_3)_2$), 68.0, 73.4, 74.9, 75.0, and 75.6 (5 OCH_2 groups), 61.2, 76.6, 78.3, 78.5, 81.8, and 87.4 (6 CHOR groups), 127.6, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 129.6, 129.8, 130.7, 131.5, 133.7, 136.2, 136.8, and 137.5 (CH-arom), 138.0,138.1, 138.2, 138.3, and 138.6, (C-arom); HRMS: Calcd for $C_{46}H_{52}O_6SNa$, 755.3382; Found: $(MNa)^+$ *m/z* 755.3382.

Reference

1. Fiser, M.; Fiser, L. F. P. *Reagents for Organic Synthesis*, Vol. 5; Wiley: New York, 1975; p. 523.