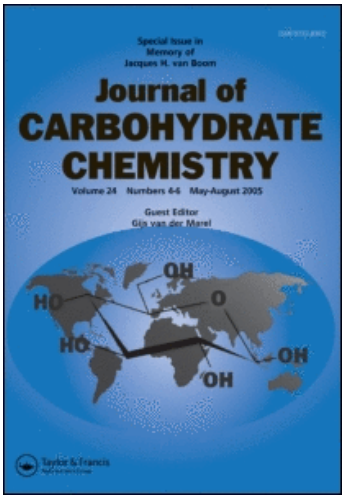

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PREARRANGED GLYCOSIDES, PART 10.[1] INTRAMOLECULAR GLYCOSYLATION WITH CELLOBIOSYL, LACTOSYL, AND MALTOSYL DONORS

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ABSTRACT

Acetyl protected 1,2-*O*-(1-methoxyethylidene)-disaccharides **1** of maltose, cellobiose, and lactose, respectively were converted *via* the corresponding benzyl protected couterparts **2**, the benzyl protected phenyl 2-*O*-acetyl- **3** and 2-*O*-unprotected 1-thio-glycoside disaccharides **4** into 2-*O*-succinoylated disaccharides **5**. The latter were esterified with benzyl 2-*O*-benzoyl-4,6-di-*O*-benzylidene-α-D-glucopyranoside (**6**) to afford succinyl linked derivatives **7** the benzylidene groups of which were regioselectively opened to give prearranged glycoside trisaccharides **8**. Intramolecular glycosylation of the latter with *N*-iodosuccinimide resulted in exclusive formation of the corresponding α-(1→4)-linked trisaccharides **9**. No influence of the donor moiety on the diastereoselectivity of the intramolecular glycosylation was observed.

INTRODUCTION

For the selective chemical synthesis of oligosaccharides, tethering of a glycosyl donor and a glycosyl acceptor prior to the formation of the interglycosidic bond and thus,

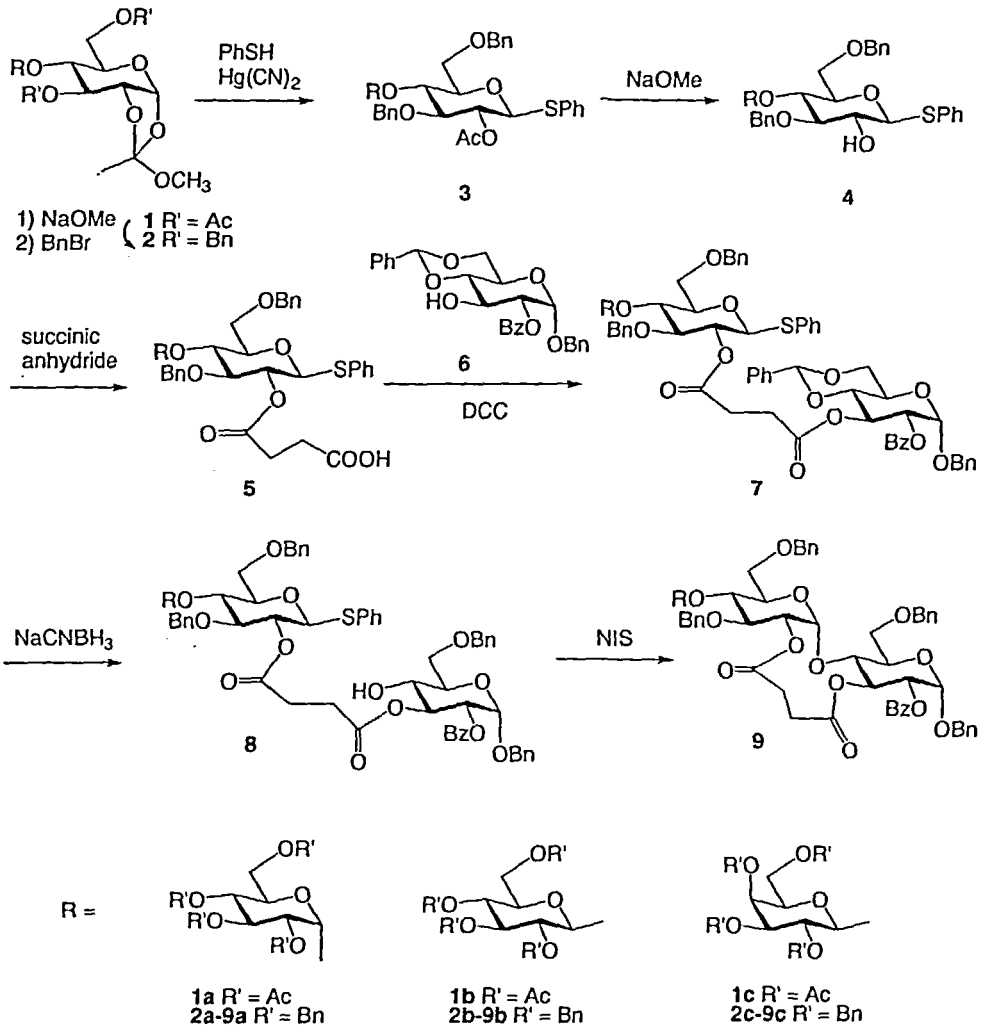
performing the glycosylation reactions intramolecularly is a powerful tool for controlling the anomeric selectivity and the regioselectivity of the condensation. In this respect, chemically performed intramolecular glycosylations resemble enzyme catalyzed glycosylations to some extent and may be regarded as biomimetic since for enzymatic condensations as well, *O*-glycosidic bond formation occurs intramolecularly by transferring an enzyme bound glycosyl moiety to the glycosyl acceptor substrate.[2] Furthermore, intramolecular glycosylations can lead to bridged saccharides which exhibit a restricted flexibility of the dihedral angles of the interglycosidic bonds, and thus, may show rather unusual conformations and binding capabilities to carbohydrate-binding proteins which are different from those of the non-tethered counterparts.[3] Acetal or silylene acetal groups[4] and anomeric carbonates[5] have been used as temporary tethers for intramolecular glycosylations although the latter approach has been shown to proceed intermolecularly as well.[5d] Furthermore, stable and persisting tethers which are not cleaved during the glycosylation step have been applied for that approach.[6] In the latter case, it has also been demonstrated that a double diastereoselection (*i.e.*, the relative configuration of the linked glycosyl donor and glycosyl acceptor) controls the anomeric outcome of the *O*-glycosidic bond formation.[7] Nevertheless, other factors like solvent, activation of the leaving group and especially distant blocking groups of the donor moiety, respectively, can influence the diastereoselectivity of intramolecular glycosylations.[7-9] In order to gain more insight into these factors we extended our recent work toward α-selective intramolecular glucosylations and galactosylations[9] to similar glycosylations with disaccaride donors in the malto-, lacto- and cellobiosyl series, respectively. This should show if a distant glycosyl group can influence the diastereoselectivity of intramolecular glycosylations as well - important information which would be essential for planning syntheses of larger oligosaccharides *via* prearranged glycosides.

RESULTS AND DISCUSSION

All prearranged glycosides **8** were prepared conventionally from the corresponding disaccharide orthoesters **1** as previously described[8,9] for succinyl linked

monosaccharides. In general, acetylated orthoesters **1** of maltose,[10] cellobiose, and lactose, respectively, were first prepared from the corresponding acetobromo disaccharides by treatment with 2,6-dimethylpyridine (DMAP) in methanol.[11] Deacetylation of the latter with methanolic ammonia[12] and rebenzylation (BnBr, NaH in DMF) of the intermediates gave crude benzylated orthoesters **2** which were used in the next step without further purification. Tedious chromatographic isolation of the latter was found to be impractical in these cases since treatment of compounds **2** with thiophenol and a catalytic amount of $Hg(CN)_2$ in acetonitrile[12] afforded crystalline phenyl 1-thio-disaccharides **3** which were easily purified by simple recrystallization. Thus, maltoside **3a**, cellobioside **3b**, and lactoside **3c** were obtained in 18%, 19%, and 22% overall yield, respectively. Next, deacetylation of the acetyl group gave 2-*O*-unprotected saccharides **4a** (96%), **4b** (97%), and **4c** (99%) which were treated with succinic anhydride in pyridine to give succinates **5a** (89%), **5b** (93%), and **5c** (85%), respectively. As glycosyl acceptor, benzyl 2-*O*-benzoyl-4,6-di-*O*-benzylidene-α-D-glucopyranoside[3a] (**6**) was chosen in order to establish conditions which were comparable to previously performed intramolecular glucosylations and galactosylations with monosaccharide donors. Condensation of disaccharides **5** with **6** afforded compounds **7a** (63%), **7b** (64%), and **7c** (61%) the benzylidene acetals of which were finally regioselectively opened with $NaCNBH_3$[13] to give the prearranged glycosides **8** in 73-79% yield.

All three prearranged glycosides **8** were cyclized with *N*-iodosuccinimide (NIS) to give the α-linked trisaccharides **9a** (64%), **9b** (65%), and **9c** (65%), respectively. In all cases, TLC of the crude reaction mixture revealed that no β-linked products were formed. The medium yields for conversions **8**→**9** were probably due to the formation of oligomeric products by intermolecular condensation. This was evident from TLC of the crude reaction mixtures which showed the presence of spots with low mobility. The α-linkage of the newly formed *O*-glycosidic bond between glucose residues 1 and 2 of compounds **9** was unambiguously proven by NMR spectroscopy. The coupling constants $J_{1',2'}$ were found to be in the range of 3.6-3.8 Hz which is significant for α-linked glucose residues. Furthermore, compounds **9** showed C,H-coupling constants of 170.6, 173.2, and 174.0 Hz, respectively, which are also typical for α-D-glucopyranosyl units.[16]



Compared to previously performed intramolecular α-(1→4)-selective glucosylations of 3,2'-succinyl linked disaccharides,[9] reaction of prearranged trisaccharide glycosides **8** proceeded with identical diastereoselectivity (*i.e.*, solely α-linked products **9** were formed). Thus, no influence of a glycosyl residue attached to the 4-position of the glycosyl donor could be observed here. Similarly, no neighboring group participation of the succinyl bridge which should lead to the formation of β-linked products was operative here. This is in contrast to the previous finding in the case of intramolecular rhamnosylations and mannosylations[7,8] where distant substituents in the

donor moiety of prearranged glycosides had a significant influence on the anomeric outcome of the respective intramolecular glycosylations. Therefore, it should be possible to extend intramolecular α-maltosylations, α-cellobiosylations, and α-lactosylations as performed here to the syntheses of other oligosaccharides containing these residues. Further examples are now under investigation.

EXPERIMENTAL

The NMR data were obtained from spectra measured in $CDCl_3$ solutions (with Me_4Si as internal standard) at 25 °C with a Bruker AMX 300 spectrometer. ^1H NMR signal assignments were made by first-order analysis of the spectra and by HH-COSY spectra. Of the two magnetically non-equivalent geminal protons at C-6, the one resonating at lower field was allocated H-6a and the one resonating at higher field H-6b. ^{13}C NMR assignments were made by mutual comparison of the spectra, by DEPT spectra, and by CH-COSY spectra. Optical rotations were measured at 25 °C with a Perkin-Elmer automatic polarimeter, Model 241. TLC was performed on precoated plastic sheets, Polygram SIL UV_{254}, 40 x 80mm (Macherey-Nagel) using appropriately adjusted mixtures of toluene-acetone. Detection was effected by UV light, where applicable, and by charring with 5% H_2SO_4 in ethanol. CC was performed by eluting from columns of Silica Gel 60 (Merck) with appropriately adjusted mixtures of toluene/acetone. Solutions in organic solvents were dried with anhydr Na_2SO_4 and concentrated at 2 kPa, <40 °C.

2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose (1a). A soln of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide[14] (15 g, 21.4 mmol), 2,6-dimethylpyridine (40 mL, 345 mmol) and Bu_4NBr (2 g, 6.2 mmol) in MeOH (20 mL) was stirred at rt for 22 h. The mixture was diluted with CH_2Cl_2 (150 mL) washed with aq $NaHCO_3$ soln and concentrated. Chromatography (*n*-hexane/acetone 3:1 v/v) of the residue and crystallisation from MeOH afforded **1a** (12.5 g, 64%): mp 162 °C (ref.[10] 163-164 °C).

2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-*O*-(1-

methoxyethylidene)-α-D-glucopyranose (1b). Treatment of a soln of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide[15] (25 g, 35.8 mmol), 2,6-dimethylpyridine (40 mL, 345 mmol) and Bu_4NBr (2 g, 6.2 mmol) in $MeOH/CH_2Cl_2$ (1:3 v/v, 80 mL) at rt for 2 days as described for **1a** and chromatography (*n*-hexane/acetone 3:1 v/v) afforded **1b** (14.3 g, 61%) as a colorless foam: $[\alpha]_D$ +39.2° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.62 (d, 1 H, $J_{1,2}$ = 4.1 Hz, H-1), 4.57 (d, 1 H, $J_{1',2'}$ = 7.9 Hz, H-1'), 3.25 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$) significant signals δ 102.3 (C-1'), 96.8 (C-1).

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.6): C, 49.85; H, 5.89. Found: C, 49.64; H, 5.82.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-acetyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose (1c). Treatment of a soln of 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl bromide[12] (25 g, 35.8 mmol), 2,6-dimethylpyridine (40 mL, 345 mmol) and Bu_4NBr (2 g, 6.2 mmol) in $MeOH/CH_2Cl_2$ (1:3 v/v, 80 mL) at rt for 2 days as described for **1a** afforded **1c** (21.4 g, 92%): mp 133 °C (MeOH), $[\alpha]_D$ +14.0° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.66 (d, 1 H, $J_{1,2}$ = 5.1 Hz, H-1), 5.53 (dd, 1 H, $J_{2,3}$ = 2.7 Hz, $J_{3,4}$ = 1.3 Hz, H-3), 5.38 (dd, 1 H, $J_{3',4'}$ = 3.5 Hz, $J_{4',5'}$ = 1.0 Hz, H-4'), 5.19 (dd, 1 H, $J_{1',2'}$ = 8.0 Hz, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.01 (dd, 1 H, H-3'), 4.61 (d, 1 H, H-1'), 4.31 (dd, 1 H, H-2), 4.26 (dd, 1 H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = -12.0 Hz, H-6a), 4.15-4.08 (m, 3 H, H-6b,6a',6b'), 3.95 (dt, 1 H, $J_{5',6'}$ = 6.7 Hz, H-5'), 3.86 (m, 1 H, H-5), 3.65 (br.d, 1 H, H-4), 3.30 (s, 3 H, OCH_3).

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.6): C, 49.85; H, 5.89. Found: C, 49.53; H, 5.81.

2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose (2a). A soln of **1a** (10 g, 15.4 mmol), saturated methanolic NH_3 soln (20 mL) in MeOH (40 mL) was stirred at rt for 5 days and concentrated. The residue was dissolved in DMF (100 mL) and added dropwise with cooling to a soln of BnBr (17 mL, 143.1 mmol) and NaH (3.5 g, 145.8 mmol) in DMF (100 mL). The mixture was stirred at rt for 2 days, diluted with CH_2Cl_2 (200 mL) and poured into water. The organic layer was separated, washed with water and concentrated. Coevaporation of toluene from the residue afforded crude **2a** (9.1 g).

2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-1,2-*O*-(1-

methoxyethylidene)-α-D-glucopyranose (2b). Treatment of **1b** (10 g, 15.4 mmol) in MeOH (40 mL) with saturated methanolic NH_3 soln (15 mL) followed by NaH (5 g, 208.3 mmol), BnBr (30 mL, 252.6 mmol) in DMF (200 mL) as described for compound **2a** afforded crude **2b** (6.7 g).

2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-1,2-*O*-(1-methoxyethylidene)-α-D-glucopyranose (2c). Treatment of **1c** (15 g, 23.1 mmol) in MeOH (40 mL) with saturated methanolic NH_3 soln (20 mL) followed by NaH (5 g, 208.3 mmol), BnBr (30 mL, 252.6 mmol) in DMF (200 mL) as described for compound **2a** afforded crude **2c** (9.0 g).

Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (3a). A soln of crude **2a** (9.1 g), thiophenol (2 mL, 19.6 mmol) and $HgBr_2$ (250 mg, 0.69 mmol) in MeCN (50 mL) was stirred at 65 °C for 3 h cooled to rt and concentrated. The residue was dissolved in CH_2Cl_2, washed with aq $NaHCO_3$ soln and concentrated. Crystallisation of the residue from EtOH afforded **3a** (2.83 g, 18% with respect to **1a**): mp 149 °C (EtOH); $[\alpha]_D$ +4.8° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.50 (d, 1 H, $J_{1',2'}$ = 3.7 Hz, H-1'), 4.92-4.74 (m, 5 H, $PhCH_2$), 4.65-4.41 (m, 7 H, H-1, $PhCH_2$), 4.30 (d, 1 H, $PhCH_2$), 4.10 (t, 1 H, J = 9 Hz, H-4'), 3.90 (t, 1 H, J = 9 Hz, H-3'), 3.85-3.50 (m, 9 H, H-2,3,4,5,6,5', 6'), 3.45 (dd, 1 H, $J_{2',3'}$ = 10.0 Hz, H-2'), 2.10 (s, 3 H, CH_3).

Anal. Calcd for $C_{62}H_{64}O_{11}S$ (1017.3): C, 73.21; H, 6.34. Found: C, 73.04; H, 6.29.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-2-*O*-acetyl-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (3b). Treatment of crude **2b** (6.7 g) with thiophenol (1.1 mL, 10.8 mmol) and $HgBr_2$ (140 mg, 0.39 mmol) in MeCN (30 mL) for 5 h at 65 °C and workup as described for compound **3a** gave **3b** (1.87 g, 19% with respect to **1b**): mp 135 °C (EtOH); $[\alpha]_D$ +11.0° (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.03-4.97 (m, 2 H, H-2, $PhCH_2$), 4.91-4.75 (m, 5 H, $PhCH_2$), 4.64-4.54 (m, 3 H, H-1, $PhCH_2$), 4.50-4.36 (m, 5 H, H-1', $PhCH_2$), 2.10 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) significant signals δ 102.6 (C-1'), 86.0 (C-1).

Anal. Calcd for $C_{62}H_{64}O_{11}S$ (1017.3): C, 73.21; H, 6.34. Found: C, 73.01; H, 6.27.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-2-*O*-acetyl-3,6-

di-*O*-benzyl-1-thio-β-D-glucopyranoside (3c). Treatment of crude **2c** (9.0 g) with thiophenol (2 mL, 19.6 mmol) and $HgBr_2$ (250 mg, 0.69 mmol) in MeCN (50 mL) for 3 h at 65 °C and workup as described for compound **3a** gave **3c** (2.37 g, 22% with respect to **1c**): mp 96 °C (EtOH); $[\alpha]_D$ -5.1° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.02-4.97 (m, 2 H, H-2, $PhCH_2$), 4.80-4.70 (m, 4 H, $PhCH_2$), 4.62 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.55-4.35 (m, 5 H, H-1', $PhCH_2$), 3.59 (t, 1 H, $J_{3,4}$ = 9 Hz, H-3), 2.00 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) significant signals δ 103.0 (C-1'), 85.9 (C-1).

Anal. Calcd for $C_{62}H_{64}O_{11}S$ (1017.3): C, 73.21; H, 6.34. Found: C, 73.06; H, 6.20.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (4a). A soln of **3a** (4.57 g, 4.5 mmol) and a catalytic amount of NaOMe in $MeOH/CH_2Cl_2$ (1:1 v/v, 100 mL) was stirred at rt for 24 h, neutralized with ion exchange resin (H^+ form) and concentrated to give **4a** (4.20 g, 96%) as a colorless foam: $[\alpha]_D$ -3.3° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.52 (d, 1 H, $J_{1',2'}$ = 3.7 Hz, H-1'), 4.91-4.86 (m, 2 H, $PhCH_2$), 4.80-4.72 (m, 3 H, $PhCH_2$), 4.62-4.42 (m, 7 H, H-1, $PhCH_2$), 4.29 (d, 1 H, $PhCH_2$), 3.90 (dd, 1 H, $J_{2',3'}$ = 9.8 Hz, $J_{3',4'}$ = 9.0 Hz, H-3'), 3.50 (dd, 1 H, H-2').

Anal. Calcd for $C_{60}H_{62}O_{10}S$ (975.2): C, 73.90; H, 6.41. Found: C, 73.68; H, 6.32.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (4b). Treatment of a soln of **3b** (4.61 g, 4.53 mmol) in $MeOH/CH_2Cl_2$ (4:1 v/v, 100 mL) with a catalytic amount of NaOMe at rt for 24 h as described for compound **4a** afforded **4b** (4.29 g, 97%): mp 119 °C (EtOH); $[\alpha]_D$ -4.0° (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.07 (d, 1 H, $PhCH_2$), 4.89 (d, 1 H, $PhCH_2$), 4.84-4.69 (m, 5 H, H-1, $PhCH_2$), 4.58-4.38 (m, 7 H, H-1', $PhCH_2$); ^{13}C NMR ($CDCl_3$) significant signals δ 102.6 (C-1'), 87.3 (C-1).

Anal. Calcd for $C_{60}H_{62}O_{10}S$ (975.2): C, 73.90; H, 6.41. Found: C, 73.59; H, 6.35.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-1-thio-β-D-glucopyranoside (4c). Treatment of a soln of **3c** (3.38 g, 3.32 mmol) in $MeOH/CH_2Cl_2$ (1:1 v/v, 100 mL) with a catalytic amount of NaOMe at rt for 33 h as described for compound **4a** afforded **4c** (3.20 g, 99%): mp 101 °C (EtOH); $[\alpha]_D$ -10.8° (*c* 0.24, $CHCl_3$); ^1H NMR ($CDCl_3$) significant signals δ 5.07 (d, 1 H, $PhCH_2$), 4.96 (d, 1 H,

$PhCH_2$), 4.83-4.74 (m, 2 H, $PhCH_2$), 4.70-4.65 (m, 3 H, $PhCH_2$), 4.56-4.50 (m, 3 H, H-1, $PhCH_2$), 4.44 (d, 1 H, $J_{1',2'}$ = 7.7 Hz, H-1'), 4.40 (d, 1 H, $PhCH_2$), 4.37-4.24 (m, 2 H, $PhCH_2$), 2.50 (bs, 1 H, OH); ^{13}C NMR ($CDCl_3$) significant signals δ 102.8 (C-1'), 87.4 (C-1).

Anal. Calcd for $C_{60}H_{62}O_{10}S$ (975.2): C, 73.90; H, 6.41. Found: C, 73.76; H, 6.34.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-succinyl-1-thio-β-D-glucopyranoside (5a). A soln of **4a** (3.20 g, 3.28 mmol), succinic anhydride (2.63 g, 26.24 mmol) and a catalytic amount of DMAP (ca. 20 mg) in pyridine (80 mL) was stirred at 85 °C for 48 h and concentrated. The residue was dissolved in CH_2Cl_2 (100 mL) washed with aq HCl and $NaHCO_3$ soln and concentrated. Chromatography (toluene/ethyl acetate/acetic acid 10:1:0.1 v/v) of the residue afforded **5a** (3.13 g, 89%) as a colorless foam: $[\alpha]_D$ +29.7° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.44 (d, 1 H, $J_{1',2'}$ = 3.7 Hz, H-1'), 5.09 (dd, 1 H, $J_{1,2}$ = 9.8 Hz, $J_{2,3}$ = 8.6 Hz, H-2), 4.88 (d, 1 H, J = -11.0 Hz, $PhCH_2$), 4.79 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.77 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.75 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.58 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.56 (d, 1 H, J = -12.4 Hz, $PhCH_2$), 4.55 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.53 (d, 1 H, J = -11.9 Hz, $PhCH_2$), 4.50-4.43 (m, 4 H, $PhCH_2$), 4.32 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.11 (t, 1 H, $J_{4,5}$ = 9.4 Hz, H-4), 3.91 (t, 1 H, $J_{3',4'}$ = 9.5 Hz, H-3'), 3.90-3.82 (m, 2 H, H-6a,6b), 3.81 (t, 1 H, $J_{3,4}$ = 9.3 Hz, H-3), 3.81-3.76 (m 1 H, H-5), 3.75-3.52 (m, 1 H, $J_{5',6a'}$ = 3.6 Hz, $J_{5',6b'}$ = 2.0 Hz, H-5'), 3.73 (t, 1 H, $J_{4',5'}$ = 9.6 Hz, H-4'), 3.57 (dd, 1 H, $J_{6a',6b'}$ = -11.1 Hz, H-6a'), 3.48 (dd, 1 H, $J_{2',3'}$ = 9.8 Hz, H-2'), 3.38 (dd, 1 H, H-6b'), 2.55-2.37 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 176.7 (COOH), 170.4 ($COCH_2CH_2$), 97.4 (C-1'), 85.7 (C-1), 84.4 (C-3), 81.8 (C-3'), 79.4 (C-2'), 79.2 (C-5), 77.5 (C-4'), 73.4 (C-4), 71.8 (C-2), 71.0 (C-5'), 69.1 (C-6), 68.4 (C-6'), 29.2, 29.0 (CH_2CH_2).

Anal. Calcd for $C_{64}H_{66}O_{13}S$ (1075.3): C, 71.49; H, 6.19. Found: C, 71.35; H, 6.09.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-succinyl-1-thio-β-D-glucopyranoside (5b). Treatment of a soln of **4b** (2.26 g, 2.73 mmol), succinic anhydride (2.19 g, 21.84 mmol) and a catalytic amount of DMAP (ca. 20 mg) in pyridine (80 mL) at 85 °C for 52 h and workup as described for compound **5a** afforded **5b** (2.73 g, 93%) as a colorless foam: $[\alpha]_D$ +8.2° (*c* 1.7, $CHCl_3$); ^1H NMR

($CDCl_3$) δ 5.02 (d, 1 H, $J_{2,3}$ = 9.0 Hz, H-2), 4.90 (d, 1 H , J = -11.0 Hz, $PhCH_2$), 4.89 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.83 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.78 (bs, 3 H, $PhCH_2$), 4.74 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.63 (d, 1 H, $J_{1,2}$ = 9.9 Hz, H-1), 4.62 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.55 (bs, 2 H, $PhCH_2$), 4.44 (d, 1 H, J = -11.6 Hz, $PhCH_2$), 4.42 (d, 1 H, $J_{1',2'}$ = 9.2 Hz, H-1'), 4.31 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 3.95 (t, 1 H, $J_{4,5}$ = 9.1 Hz, H-4), 3.86 (t, 1 H, $J_{3',4'}$ = 9.2 Hz, H-3'), 3.80-3.75 (m, 2 H, H-6a,6b), 3.77 (t, 1 H, $J_{2',3'}$ = 9.3 Hz, H-2'), 3.75-3.58 (m, 1 H, $J_{5',6a'}$ = 3.7 Hz, $J_{5',6b'}$ = 1.8 Hz, H-5'), 3.73 (t, 1 H, $J_{4',5'}$ = 9.4 Hz, H-4'), 3.60 (t, 1 H, $J_{3,4}$ = 8.8 Hz, H-3), 3.56 (dd, 1 H, $J_{6a',6b'}$ = -11.5 Hz, H-6a'), 3.50-3.46 (m, 1 H, H-5), 3.37 (dd, 1 H, H-6b'), 2.60-2.45 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 176.8 (COOH), 170.5 ($COCH_2CH_2$), 102.6 (C-1'), 85.8 (C-1), 81.9 (C-3), 81.8 (C-3'), 79.7 (C-2'), 79.8 (C-5), 77.3 (C-4'), 76.6 (C-4), 75.2, 74.4, 74.3, 73.3, 73.2 72.6 ($PhCH_2$), 71.8 (C-2), 71.1 (C-5'), 68.6 (C-6), 68.3 (C-6'), 28.8, 29.0 (CH_2CH_2).

Anal. Calcd for $C_{64}H_{66}O_{13}S$ (1075.3): C, 71.49; H, 6.19. Found: C, 71.65; H, 5.98.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-succinyl-1-thio-β-D-glucopyranoside (5c). Treatment of a soln of **4c** (3.2 g, 3.28 mmol), succinic anhydride (2.63 g, 26.24 mmol) and a catalytic amount of DMAP (ca. 20 mg) in pyridine (80 mL) at 85 °C for 24 h and workup as described for compound **5a** afforded **5c** (3.0 g, 85%) as a colorless foam: $[\alpha]_D$ -2.0° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 4.99 (dd, 1 H, $J_{2,3}$ = 8.9 Hz, H-2), 4.94 (2 d, 2 H, J = -11.2 Hz, J = -12.9 Hz, $PhCH_2$), 4.82 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.76 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.69 (bd, 2 H, $PhCH_2$), 4.62 (d, 1 H, $J_{1,2}$ = 9.8 Hz, H-1), 4.58 (s, 1 H, $PhCH_2$), 4.53 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.47 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.43 (d, 1 H, $J_{1',2'}$ = 9.3 Hz, H-1'), 4.37 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 4.29 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 4.20 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 3.93 (t, 1 H, $J_{4,5}$ = 9.3 Hz, H-4), 3.89 (bd, 1 H, H-4'), 3.79-3.74 (m, 3 H, H-2',6a,6b), 3.61 (t, 1 H, $J_{3,4}$ = 8.7 Hz, H-3), 3.51-3.48 (m, 1 H, H-5), 3.47-3.41 (m, 2 H, H-3',6a'), 3.38-3.34 (m, 1 H, H-5'), 3.31-3.27 (m, 1 H, H-6b'), 2.62-2.35 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 176.8 (COOH), 170.5 ($COCH_2CH_2$), 103.1 (C-1'), 85.9 (C-1), 82.4 (C-3'), 82.0 (C-3), 79.9 (C-2'), 79.7 (C-5), 76.6 (C-4), 75.3, 74.6, 74.5 ($PhCH_2$), 73.6 (C-4'), 73.4, 73.1 ($PhCH_2$), 73.0 (C-5'), 71.7 (C-2), 68.4 (C-6), 68.1 (C-6'), 29.0, 28.8 (CH_2CH_2).

Anal. Calcd for $C_{64}H_{66}O_{13}S$ (1075.3): C, 71.49; H, 6.19. Found: C, 71.44; H, 6.15.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (7a). DCC (160 mg, 0.75 mmol) was added at rt to a soln of **5a** (0.81 g, 0.75 mmol), benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside[3a] (**6**) (350 mg, 0.75 mmol) and a catalytic amount of DMAP (ca. 10 mg) in CH_2Cl_2 (50 mL), the mixture was stirred for 15 h and filtered through a layer of Celite. The filtrate was washed with aq HCl and $NaHCO_3$ soln and concentrated. Chromatography (toluene/acetone 30:1 v/v) of the residue afforded **7a** (0.72 g, 63%) as a colorless foam: $[\alpha]_D$ +61.8° (*c* 1.07, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.86 (t, 1 H, $J_{3Glc,4Glc}$ = 9.9 Hz, H-3_{Glc}), 5.50 (s, 1 H, PhCH), 5.46 (d, 1 H, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.28 (d, 1 H, $J_{1Glc,2Glc}$ = 3.7 Hz, H-1_{Glc}), 5.08 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.0 Hz, H-2_{Glc}), 4.95 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, H-2), 4.88 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.79 (d, 1 H, J = -10.7 Hz, $PhCH_2$), 4.78 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.76 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.73 (d, 1 H, J = -11.6 Hz, $PhCH_2$), 4.60 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.56 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.55 (d, 1 H, J = -12.4 Hz, $PhCH_2$), 4.54 (d, 1 H, $J_{1,2}$ = 10.2 Hz, H-1), 4.50 (s, 3 H, $PhCH_2$), 4.49 (d, 1 H, J = -11.7 Hz, $PhCH_2$), 4.45 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.33 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.27 (dd, 1 H, $J_{6aGlc,6bGlc}$ = -10.1 Hz, H-$6a_{Glc}$), 4.12-4.00 (m, 2 H, $J_{5Glc,6aGlc}$ = 4.9 Hz, H-$4,5_{Glc}$), 3.90 (t, 1 H, $J_{3',4'}$ = 9.4 Hz, H-3'), 3.88-3.59 (m, 7 H, $J_{5',6a'}$ = 3.3 Hz, H-3,4',5,5',6a,6b,$6b_{Glc}$), 3.71 (t, 1 H, $J_{4Glc,5Glc}$ = 9.8 Hz, H-4_{Glc}), 3.56 (dd, 1 H, $J_{6a',6b'}$ = -10.8 Hz, H-6a'), 3.43 (dd, 1 H, H-6b'), 2.57-2.26 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 171.0, 170.4 ($\underline{C}OCH_2CH_2$), 165.8 (PhCO), 101.6 (PhCH), 97.2 (C-1'), 95.9 (C-1_{Glc}), 85.8 (C-1), 84.4 (C-3), 81.8 (C-3'), 79.4 (C-2'), 79.1, 79.0 (C-5, C-4_{Glc}), 77.6 (C-4'), 75.5, 75.0, 73.6 ($PhCH_2$), 73.4 (2 C, C-4, $PhCH_2$), 73.3 (2 C, $PhCH_2$), 72.2 (C-2_{Glc}), 71.7 (C-2), 71.1 (C-5'), 70.0 ($PhCH_2$), 69.2 (C-3_{Glc}), 69.0 (C-6), 68.8 (C-6_{Glc}).68.3 (C-6'), 62.8 (C-5_{Glc}), 29.0, 28.4 ($CO\underline{C}H_2CH_2$).

Anal. Calcd for $C_{91}H_{90}O_{19}S$ (1519.8): C, 71.92; H, 5.97. Found: C, 72.11; H, 6.05.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (7b). Treatment of a soln of **5b** (0.83 g, 0.77

mmol), **6** (0.36 g, 0.77 mmol) and a catalytic amount of DMAP (ca. 10 mg) in CH_2Cl_2 (60 mL) with DCC (160 mg, 0.77 mmol) at rt for 16 h as described for compound **7a** afforded **7b** (0.75 g, 64%) as a colorless foam: $[\alpha]_D$ +4.0° (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.84 (t, 1 H, $J_{3Glc,4Glc}$ = 10.0 Hz, H-3_{Glc}), 5.50 (s, 1 H, PhCH), 5.29 (d, 1 H, $J_{1Glc,2Glc}$ = 3.8 Hz, H-1_{Glc}), 5.06 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.0 Hz, H-2_{Glc}), 4.93 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 4.91 (d, 1 H, J = -11.7 Hz, $PhCH_2$), 4.90-4.85 (m, 1 H, $J_{2,3}$ = 9.2 Hz, H-2), 4.85-4.77 (m, 4 H, $PhCH_2$), 4.73 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.70 (s, 2 H, $PhCH_2$), 4.57 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.55 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 4.51 (2 d, 1 H, $J_{1,2}$ = 10.0 Hz, J = -10.7 Hz, H-1, $PhCH_2$), 4.46 (d, 1 H, J = -11.5 Hz, $PhCH_2$), 4.40 (d, 1 H, $J_{1',2'}$ = 9.0 Hz, H-1'), 4.36 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.27 (dd, 1 H, $J_{6aGlc,6bGlc}$ = -10.2 Hz, H-$6a_{Glc}$), 4.10-4.00 (m, 1 H, $J_{5Glc,6aGlc}$ = 5.0 Hz, $J_{5Glc,6bGlc}$ = 9.8 Hz, H-5_{Glc}), 3.90 (t, 1 H, $J_{4,5}$ = 9.1 Hz, H-4), 3.87 (t, 1 H, $J_{3',4'}$ = 9.4 Hz, H-3'), 3.84-3.78 (m, 2 H, $J_{5',6a'}$ = 3.4 Hz, $J_{5',6b'}$ = 1.9 Hz, H-5',6b$_{Glc}$), 3.77-3.72 (m, 4 H, H-4',4$_{Glc}$,6a,6b), 3.75 (t, 1 H, $J_{2',3'}$ = 9.2 Hz, H-2'), 3.55 (dd, 1 H, $J_{6a',6b'}$ = -10.8 Hz, H-6a'), 3.52 (t, 1 H, $J_{3,4}$ = 9.0 Hz, H-3), 3.44-3.40 (m, 2 H, H-5,6b'), 28.8, 29.0 (CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 171.3, 170.5 ($COCH_2CH_2$), 165.7 (PhCO), 102.8 (C-1'), 101.5 (PhCH), 95.8 (C-1_{Glc}), 85.9 (C-1), 81.9 (C-3), 81.8 (C-3'), 79.7 (2 C, C-2', C-5), 79.1 (C-4_{Glc}), 77.4 (C-4'), 76.6 (C-4), 75.4, 74.9, 74.4, 73.3, 73.1, 72.4 ($PhCH_2$), 72.2 (C-2_{Glc}), 71.7 (C-2), 71.3 ($PhCH_2$), 71.2 (C-5'), 69.2 (C-3_{Glc}), 68.9 (C-6_{Glc}), 68.5 (C-6), 68.2 (C-6'), 62.8 (C-5_{Glc}), 28.8, 29.0 (CH_2CH_2).

Anal. Calcd for $C_{91}H_{90}O_{19}S$ (1519.8): C, 71.92; H, 5.97. Found: C, 71.85; H, 6.11.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (7c). Treatment of a soln of **5c** (0.78 g, 0.73 mmol), **6** (0.34 g, 0.73 mmol) and a catalytic amount of DMAP (ca. 10 mg) in CH_2Cl_2 (30 mL) with DCC (150 mg, 0.73 mmol) at rt for 17 h as described for compound **7a** afforded **7c** (0.68 g, 61%) as a colorless foam: $[\alpha]_D$ +40.9° (*c* 1.75, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.88 (t, 1 H, $J_{3Glc,4Glc}$ = 9.9 Hz, H-3_{Glc}), 5.51 (s, 1 H, PhCH), 5.29 (d, 1 H, $J_{1Glc,2Glc}$ = 4.0 Hz, H-1_{Glc}), 5.07 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.0 Hz, H-2_{Glc}), 4.94 (d, 1 H, J = -11.6 Hz, $PhCH_2$), 4.90 (d, 1 H, J = -11.7 Hz, $PhCH_2$), 4.88-4.82 (m, 4 H, H-2, $PhCH_2$), 4.82 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.76 (d, 1 H, J = -11.0 Hz, $PhCH_2$), 4.69 (bs, 1 H, $PhCH_2$),

4.55 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.53 (d, 1 H, J = -11.5 Hz, $PhCH_2$), 4.52 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.51 (d, 1 H, J = -10.7 Hz, $PhCH_2$), 4.46 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.41 (d, 1 H, $J_{1',2'}$ = 9.0 Hz, H-1'), 4.37 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 4.27 (dd, 1 H, $J_{6aGlc,6bGlc}$ = -10.0 Hz, H-$6a_{Glc}$), 4.08 (dt, 1 H, $J_{5Glc,6aGlc}$ = 5.0 Hz, $J_{5Glc,6bGlc}$ = 9.9 Hz, H-5_{Glc}), 3.90-3.86 (m, 2 H, H-4,4'), 3.80-3.69 (m, 5 H, $J_{4Glc,5Glc}$ = 9.8 Hz, H-2',4_{Glc},6a,6b,$6b_{Glc}$), 3.52 (t, 1 H, $J_{3,4}$ = 8.9 Hz, H-3), 3.47-3.39 (m, 4 H, H-3',5,5',6a'), 3.37-3.30 (m, 1 H, H-6b'), 2.55-2.44 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 171.1, 170.3 ($COCH_2CH_2$), 165.8 (PhCO), 102.9 (C-1'), 101.6 (PhCH), 95.9 (C-1_{Glc}), 85.9 (C-1), 82.4 (C-3'), 82.0 (C-3'), 79.9 (C-2'), 79.6 (C-5'), 79.1 (C-4_{Glc}), 76.6 (C-4'), 75.3, 74.7, 74.6 ($PhCH_2$), 73.6 (C-4'), 73.4, 73.1 ($PhCH_2$), 73.0 (C-5'), 72.6 ($PhCH_2$), 72.3 (C-2_{Glc}), 70.0 ($PhCH_2$), 71.6 (C-2'), 69.2 (C-3_{Glc}), 68.8 (C-6_{Glc}), 68.3 (C-6'), 62.8 (C-5_{Glc}), 68.1 (C-6'), 29.1, 29.0 (CH_2CH_2).

Anal. Calcd for $C_{91}H_{90}O_{19}S$ (1519.8): C, 71.92; H, 5.97. Found: C, 72.03; H, 6.03.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (8a). A soln of HCl (saturated in Et_2O) was added at rt to a suspension of **7a** (0.65 g, 0.43 mmol), $NaCNBH_3$ (0.34 g, 5.38 mmol) and molecular sieves (3 Å) in THF (20 mL) until the evolution of H_2 has ceased. The mixture was diluted with CH_2Cl_2, filtered through a layer of Celite, washed with aq $NaHCO_3$ soln and water and concentrated. Chromatography (toluene/acetone 20:1 v/v) of the residue afforded **8a** (0.49 g, 75%) as a colorless foam: $[\alpha]_D$ +58.0° (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.63 (dd, 1 H, $J_{3Glc,4Glc}$ = 9.2 Hz, H-3_{Glc}), 5.45 (d, 1 H, $J_{1',2'}$ = 3.6 Hz, H-1'), 5.25 (d, 1 H, $J_{1Glc,2Glc}$ = 3.7 Hz, H-1_{Glc}), 5.03 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.2 Hz, H-2_{Glc}), 5.00 (t, 1 H, $J_{2,3}$ = 10.0 Hz, H-2), 4.88 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.79 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.78 (d, 1 H = -11.1 Hz, $PhCH_2$), 4.76 (d, 1 H, J = -12.4 Hz, $PhCH_2$), 4.61 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.60 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.57 (d, 1 H, $J_{1,2}$ = 7.6 Hz, H-1), 4.56 (s, 2 H, $PhCH_2$), 4.52 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 4.51 (d, 1 H, J = -11.6 Hz, $PhCH_2$), 4.50 (bs, 4 H, $PhCH_2$), 4.45 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.33 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.06 (t, 1 H, $J_{4,5}$ = 9.1 Hz, H-4), 4.00-3.93 (m, 1 H, $J_{5Glc,6aGlc}$ = 4.1 Hz, H-5_{Glc}), 3.90-3.85 (m, 1 H, H-3'), 3.83-3.71 (m, 8 H, H-3,4_{Glc},5,5',6a,6b,$6a_{Glc}$,$6b_{Glc}$), 3.63 (zm, 1 H, H-4'), 3.50 (dd, 1 H, $J_{2',3'}$ = 9.8 Hz, H-2'), 3.43 (bd, 1 H, H-6b'), 2.93-2.24 (m, 4 H,

CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 172.3, 171.1 ($COCH_2CH_2$), 165.7 (PhCO), 97.2 (C-1'), 95.2 ($C\text{-}1_{Glc}$), 85.7 (C-1), 84.5 (C-3), 81.9 (C-3'), 79.4 (C-2'), 77.6 (C-4'), 75.5, 75.0, 73.7 ($PhCH_2$), 73.6 (3 C, $C\text{-}3_{Glc}$, C-4, $PhCH_2$), 73.4, 73.3 (1 C, 2 C, $PhCH_2$), 71.9, 71.3 (2 C, 1 C, C-2, C-5, $C\text{-}2_{Glc}$), 71.2 (C-5'), 70.5 ($C\text{-}5_{Glc}$), 70.1 ($C\text{-}4_{Glc}$), 69.6 ($PhCH_2$), 69.3, 69.0 ($C\text{-}6_{Glc}$, C-6), 68.3 (C-6'), 29.3, 29.1 (CH_2CH_2).

Anal. Calcd for $C_{91}H_{92}O_{19}S$ (1521.8): C, 71.82; H, 6.09. Found: C, 72.00; H, 6.10.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (8b). Treatment of compound **7b** (0.62 g, 0.41 mmol), $NaCNBH_3$ (0.32 g, 5.13 mmol) and molecular sieves (3 Å) in THF (20 mL) with HCl as described for compound **8a** afforded **8b** (0.46 g, 73%) as a colorless foam: $[\alpha]_D$ +12.8° (*c* 0.69, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.67 (t, 1 H, $J_{3Glc,4Glc}$ = 9.8 Hz, $H\text{-}3_{Glc}$), 5.26 (d, 1 H, $J_{1Glc,2Glc}$ = 3.8 Hz, $H\text{-}1_{Glc}$), 5.07 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.2 Hz, $H\text{-}2_{Glc}$), 4.90 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.81 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.78 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.75 (bd, 2 H, $PhCH_2$), 4.63 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.61-4.50 (m, 6 H, $PhCH_2$), 4.55 (d, 1 H, $J_{1,2}$ = 8.9 Hz, H-1), 4.47 (d, 1 H, J = -10.8 Hz, PhCH), 4.46 (d, 1 H, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.43 (t, 1 H, $J_{2,3}$ = 9.2 Hz, H-2), 4.38 (d, 2 H, J = -12.0 Hz, $PhCH_2$), 4.30 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 3.99 (dt, 1 H, $J_{5Glc,6aGlc}$ = 6.0 Hz, $J_{5Glc,6bGlc}$ = 9.8 Hz, $H\text{-}5_{Glc}$), 3.90 (t, 1 H, $J_{4,5}$ = 9.3 Hz, H-4), 3.88-3.83 (m, 2 H, H-3',5'), 3.81 (t, 1 H, $J_{4Glc,5Glc}$ = 9.6 Hz, $H\text{-}4_{Glc}$), 3.80-3.72 (m, 5 H, H-2',6a,6b,$6a_{Glc}$,$6b_{Glc}$), 3.68-3.63 (m, 1 H, H-4'), 3.58 (t, 1 H, $J_{3,4}$ = 9.2 Hz, H-3), 3.57-3.52 (m, 1 H, H-6a'), 3.48-3.43 (m, 2 H, $J_{5',6b'}$ = 1.9 Hz, $J_{6a',6b'}$ = -10.6 Hz, H-5,6b'), 2.85-2.33 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 172.2, 171.0 ($COCH_2CH_2$), 165.7 (PhCO), 103.1 (C-1'), 95.1 ($C\text{-}1_{Glc}$), 85.9 (C-1), 82.1 (C-3), 81.9 (C-3'), 79.6 (2 C, C-2', C-5), 77.4 (C-4'), 76.3 (C-4), 75.4, 75.1, 73.8 ($PhCH_2$), 73.5 (2 C, $PhCH_2$, $C\text{-}3_{Glc}$), 73.4, 73.2 (1 C, 2 C, $PhCH_2$), 69.7 ($PhCH_2$), 71.5 (C-2), 71.3 (C-5'), 71.2 ($C\text{-}2_{Glc}$), 70.4 ($C\text{-}5_{Glc}$), 70.1 ($C\text{-}4_{Glc}$), 69.2 ($C\text{-}6_{Glc}$), 68.5 (C-6), 68.3 (C-6'), 29.1, 29.2 (CH_2CH_2).

Anal. Calcd for $C_{91}H_{92}O_{19}S$ (1521.8): C, 71.82; H, 6.09. Found: C, 72.01; H, 6.11.

Phenyl 2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-*O*-[3-(2-*O*-benzoyl-1,6-di-*O*-benzyl-α-D-glucopyranos-3-yloxycarbonyl)propanoyl]-1-thio-β-D-glucopyranoside (8c). Treatment of compound **7c** (0.58 g, 0.38 mmol),

$NaCNBH_3$ (0.30 g, 4.75 mmol) and molecular sieves (3 Å) in THF (20 mL) with HCl as described for compound **8a** afforded **8c** (0.45 g, 79%) as a colorless foam: $[\alpha]_D$ +44.4° (*c* 0.75, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.66 (t, 1 H, $J_{3Glc,4Glc}$ = 9.7 Hz, H-3_{Glc}), 5.26 (d, 1 H, $J_{1Glc,2Glc}$ = 3.7 Hz, H-1_{Glc}), 5.06 (dd, 1 H, $J_{2Glc,3Glc}$ = 10.3 Hz, H-2_{Glc}), 4.93 (d, 1 H, J = -11.5 Hz, $PhCH_2$), 4.90 (bt, 1 H, $J_{2,3}$ = 9.2 Hz, H-2), 4.82 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.75 (bd, 2 H, J = -12.8 Hz, $PhCH_2$), 4.71 (d, 1 H, J = -11.7 Hz, $PhCH_2$), 4.67 (d, 1 H, J = -11.9 Hz, $PhCH_2$), 4.64 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 4.61 (bd, 2 H, $PhCH_2$), 4.59 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.55 (d, 1 H, $J_{1,2}$ = 8.8 Hz, H-1), 4.54 (s, 1 H, $PhCH_2$), 4.52 (d, 1 H, J = -11.4 Hz, $PhCH_2$), 4.44 (d, 1 H, $J_{1',2'}$ = 10.0 Hz, H-1'), 4.38 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.28 (d, 1 H, J = -11.9 Hz, $PhCH_2$), 4.20 (d, 1 H, J = -11.7 Hz, $PhCH_2$), 3.90 (zm, 1 H, H-4'), 3.98 (dt, 1 H, $J_{5Glc,6aGlc}$ = 5.9 Hz, $J_{5Glc,6bGlc}$ = 9.7 Hz, H-5_{Glc}), 3.82 (t, 1 H, $J_{4Glc,5Glc}$ = 9.5 Hz, H-4_{Glc}), 3.78-3.73 (m, 5 H, H-2',6a,6b, $6a_{Glc}$,$6b_{Glc}$), 3.55 (t, 1 H, $J_{3,4}$ = 8.9 Hz, H-3), 3.48-3.41 (m, 4 H, H-3',5,6a',6b'), 3.39-3.28 (m, 1 H, $J_{5',6b'}$ = 4.6 Hz, H-5'), 2.68-2.39 (m, 4 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 172.4, 171.1 ($COCH_2CH_2$), 165.8 (PhCO), 103.0 (C-1'), 95.2 (C-1_{Glc}), 85.8 (C-1), 82.5 (C-3'), 82.1 (C-3), 79.9, 79.6 (C-2', C-5), 76.5 (C-4), 75.4, 74.6, 73.7 (1 C, 2 C, 1 C, $PhCH_2$), 73.6, (2 C, C-3_{Glc}, C-4'), 73.4 ($PhCH_2$), 73.0 (C-5'), 72.6 ($PhCH_2$), 71.8 (C-2), 71.4 (C-2_{Glc}), 70.5 (C-5_{Glc}), 70.1 (C-4_{Glc}), 69.6 ($PhCH_2$), 69.3 (C-6_{Glc}), 68.3 (C-6), 68.1 (C-6'), 29.4, 29.3 (CH_2CH_2).

Anal. Calcd for $C_{91}H_{92}O_{19}S$ (1521.8): C, 71.82; H, 6.09. Found: C, 71.80; H, 6.15.

Benzyl *O*-[2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside] 3,2'-Succinate (9a). A suspension of **8a** (0.24 g, 0.16 mmol) and molecular sieves (3 Å) in CH_2Cl_2 (12 mL) was stirred at rt under Ar for 15 min. and then cooled to –30 °C. NIS (0.18 g, 0.79 mmol) was added followed by TMSOTf (7 μL, 40 μmol). The mixture was stirred for 10 min., neutralized with pyridine, diluted with CH_2Cl_2, and filtered. The filtrate was washed with aq $NaHCO_3$, aq $Na_2S_2O_3$ soln, water and concentrated. Chromatography (toluene/ethyl acetate 15:1 v/v) of the residue afforded compound **9a** (0.14 g, 64%), as a colorless foam: $[\alpha]_D$ +54.4° (*c* 1.50, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.84 (dd, 1 H, $J_{3,4}$ = 9.1 Hz, H-3), 5.60 (d, 1 H, $J_{1'',2''}$ = 3.6 Hz, H-1''), 5.25 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.19 (d, 1 H, $J_{1',2'}$ = 3.6 Hz, H-1'), 4.95 (dd, 1 H, $J_{2,3}$ = 10.3 Hz, H-2), 4.92 (d, 1

H, J = -10.9 Hz, $PhCH_2$), 4.88 (bd, 1 H, H-2'), 4.82 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.81 (d, 1 H, J = -10.8 Hz, $PhCH_2$), 4.75 (d, 1 H, J = -12.4 Hz, $PhCH_2$), 4.65 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.64 (d, 2 H, J = -10.9 Hz, $PhCH_2$), 4.56 (d, 2 H, J = -11.1 Hz, $PhCH_2$), 4.54 (d, 2 H, J = -12.2 Hz, $PhCH_2$), 4.48 (d, 2 H, J = -11.6 Hz, $PhCH_2$), 4.46 (d, 1 H, J = -12.5 Hz, $PhCH_2$), 4.41 (d, 1 H, J = -10.7 Hz, $PhCH_2$), 4.32 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.17-4.07 (m, 3 H, H-3',4',5'), 4.04-3.79 (m, 2 H, H-3'',4), 3.91 (t, 1 H, $J_{4,5}$ = 8.9 Hz, H-4), 3.81 (dd, 1 H, $J_{6a'',6b''}$ = -10.9 Hz, H-6a''), 3.74-3.56 (m, 6 H, $J_{5'',6a''}$ = 3.5 Hz, H-4'',5'',6a,6a',6b,6b'), 3.53 (dd, 1 H, $J_{2'',3''}$ = 9.9 Hz, H-2''), 3.45 (bd, 1 H, H-6b''), 2.62-2.54 (m, 1 H, CH_2CH_2), 2.39-2.35 (m, 2 H, CH_2CH_2), 2.29-2.22 (m, 1 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 170.4, 170.1 ($COCH_2CH_2$), 165.6 (PhCO), 99.8 (C-1', $J_{C\text{-}1',1'\text{-}H}$ = 170.6 Hz), 97.3 (C-1''), 95.0 (C-1), 82.0 (C-3''), 80.4 (2 C, C-3',C-4), 79.5 (C-2''), 77.6 (C-4''), 75.6, 74.9 ($PhCH_2$), 74.6 (C-2'), 74.3, 73.5, 73.3, 73.2 (1 C, 2 C, 1 C, 1 C, $PhCH_2$), 72.6 (C-4'), 71.6 (C-2), 71.5 (C-3), 71.2 (2 C, C-5', C-5''), 70.2 (C-5), 69.8 ($PhCH_2$), 68.8 (C-6), 68.2, 68.1 (C-6', C-6''), 30.3, 30.4 (CH_2CH_2).

Anal. Calcd for $C_{85}H_{86}O_{19}$ (1411.6): C, 72.32; H, 6.14. Found: C, 72.11; H, 6.09.

Benzyl *O*-[2,3,4,6-Tetra-*O*-benzyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside] 3,2'-Succinate (9b). Treatment of compound **8b** (0.26 g, 0.17 mmol), NIS (0.19 g, 0.85 mmol), TMSOTf (7 μL, 40 μmol) and molecular sieves (3 Å) in CH_2Cl_2 (12 mL) as described for compound **9a** afforded **9b** (0.16 g, 65%), as a colorless faom: $[\alpha]_D$ +38.3° (*c* 1.75, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.90 (dd, 1 H, $J_{3,4}$ = 9.2 Hz, H-3), 5.26 (d, 1 H, $J_{1,2}$ = 3.8 Hz, H-1), 5.20 (d, 1 H, $J_{1',2'}$ = 3.8 Hz, H-1'), 4.99 (dd, 1 H, $J_{2,3}$ = 10.2 Hz, H-2), 4.90 (d, 1 H, J = -11.2 Hz, $PhCH_2$), 4.83 (d, 1 H, J = -11.3 Hz, $PhCH_2$), 4.80 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.75 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.72 (dd, 1 H, $J_{2',3'}$ = 9.6 Hz, H-2'), 4.63 (d, 1 H, J = -10.9 Hz, $PhCH_2$), 4.60-4.48 (m, 8 H, $PhCH_2$), 4.42-4.39 (m, 1 H, H-4'), 4.38-4.30 (m, 4 H, H-1'', $PhCH_2$), 4.01-3.98 (m, 1 H, H-5'), 3.95-3.90 (m, 1 H, H-3'), 3.92 (t, 1 H, $J_{4,5}$ = 9.0 Hz, H-4), 3.88-3.80 (m, 3 H, H-2'',3'',6a''), 3.82 (dd, 1 H, $J_{6a,6b}$ = -12.3 Hz, H-6a), 3.79-3.72 (m, 2 H, $J_{5,6a}$ = 4.8 Hz, $J_{5,6b}$ = 9.8 Hz, H-5,5''), 3.70-3.66 (m, 1 H, H-4''), 3.68-3.59 (m, 3 H, H-6b,6a',6b'), 3.47 (bd, 1 H, $J_{6a'',6b''}$ = -10.4 Hz, H-6b''), 2.60-2.51 (m, 1 H, CH_2CH_2), 2.40-2.34 (m, 2 H, CH_2CH_2), 2.28-2.21 (m, 1 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.3 ($COCH_2CH_2$), 165.6 (PhCO), 103.0 (C-1''), 99.6 (C-1', $J_{C\text{-}1',1'\text{-}H}$ =

173.2 Hz), 95.2 (C-1), 82.0 (C-3''), 80.4 (C-4), 79.7 (C-2''), 78.0 (C-3'), 77.4 (C-4''), 75.5 ($PhCH_2$), 75.4 (C-4'), 75.0 ($PhCH_2$), 74.5 (2 C, C-2', $PhCH_2$), 73.6, 73.5, 73.2 (1 C, 1 C, 2 C, $PhCH_2$), 71.7 (C-5'), 71.5 (2 C, C-2, C-3), 71.3 (C-5''), 70.1 (C-5), 69.7 (C-6), 69.6 ($PhCH_2$), 68.5 (C-6''), 67.7 (C-6'), 30.3, 30.4 (CH_2CH_2).

Anal. Calcd for $C_{85}H_{86}O_{19}$ (1411.6): C, 72.32; H, 6.14. Found: C, 72.28; H, 6.18.

Benzyl *O*-[2,3,4,6-Tetra-*O*-benzyl-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-α-D-glucopyranosyl-(1→4)-2-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside] 3,2'-Succinate (9c). Treatment of compound **8c** (0.26 g, 0.17 mmol), NIS (0.19 g, 0.86 mmol), TMSOTf (11 µl, 40 µmol) and molecular sieves (3 Å) in CH_2Cl_2 (12 mL) as described for compound **9a** afforded **9c** (0.16 g, 65%), as a colorless faom: $[\alpha]_D$ +47.7° (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 5.87 (dd, 1 H, $J_{3,4}$ = 9.0 Hz, H-3), 5.26 (d, 1 H, $J_{1,2}$ = 3.7 Hz, H-1), 5.19 (d, 1 H, $J_{1',2'}$ = 3.8 Hz, H-1'), 5.00 (d, 1 H, J = -10.2 Hz, $PhCH_2$), 4.97 (d, 1 H, J = -11.6 Hz, $PhCH_2$), 4.96 (dd, 1 H, $J_{2,3}$ = 10.2 Hz, H-2), 4.84 (d, 1 H, J = -11.4 Hz, $PhCH_2$), 4.77 (d, 1 H, J = -12.2 Hz, $PhCH_2$), 4.73 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.72 (d, 1 H, J = -12.0 Hz, $PhCH_2$), 4.71 (dd, 1 H, $J_{2',3'}$ = 9.6 Hz, H-2'), 4.67 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 4.57 (d, 1 H, J = -11.4 Hz, $PhCH_2$), 4.56 (d, 1 H, J = -11.4 Hz, $PhCH_2$), 4.46 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 4.39-4.36 (m, 3 H, H-1'', $PhCH_2$), 4.36 (d, 1 H, J = -12.1 Hz, $PhCH_2$), 4.35 (d, 1 H, J = -10.7 Hz, $PhCH_2$), 4.25 (d, 1 H, J = -11.8 Hz, $PhCH_2$), 3.94-3.87 (m, 5 H, H-3',4,4',4'',5'), 3.81 (dd, 1 H, $J_{6a,6b}$ = -13.0 Hz, H-6a), 3.77-3.73 (m, 3 H, $J_{5,6a}$ = 4.9 Hz, $J_{5,6b}$ = 9.9 Hz, H-2'',5,6a''), 3.65 (bd, 1 H, H-6b), 3.54 (bd, 2 H, H-6a',6b''), 3.44-3.36 (m, 3 H, H-3'',5'',6b'), 2.72-2.60 (m, 2 H, CH_2CH_2), 2.53-2.40 (m, 2 H, CH_2CH_2); ^{13}C NMR ($CDCl_3$) δ 170.5, 170.1 ($COCH_2CH_2$), 165.6 (PhCO), 103.0 (C-1''), 99.6 (C-1', $J_{C\text{-}1',1'\text{-}H}$ = 174.0 Hz), 95.0 (C-1), 80.4 (C-3'), 82.5 (C-3''), 80.0 (C-2''), 77.3 (C-4), 76.5 (C-4'), 75.3, 74.6 (2 C, 1 C, $PhCH_2$), 73.9 (C-2'), 73.5 (C-4''), 73.4, 73.3 ($PhCH_2$), 73.1 (2 C, C-5'', $PhCH_2$), 72.5 ($PhCH_2$), 71.7 (C-5), 71.6 (C-2), 71.4 (C-3), 70.3 (C-5'), 69.7 ($PhCH_2$), 68.2, 68.1, 68.0 (C-6,6',6''), 30.3, 30.4 (CH_2CH_2).

Anal. Calcd for $C_{85}H_{86}O_{19}$ (1411.6): C, 72.32; H, 6.14. Found: C, 72.57; H, 6.09.

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