New Phenyl 6,4'-Substituted-1-Thio-β-Maltosides, Building Blocks for The Synthesis of Linear and Branched Malto-oligosaccharides

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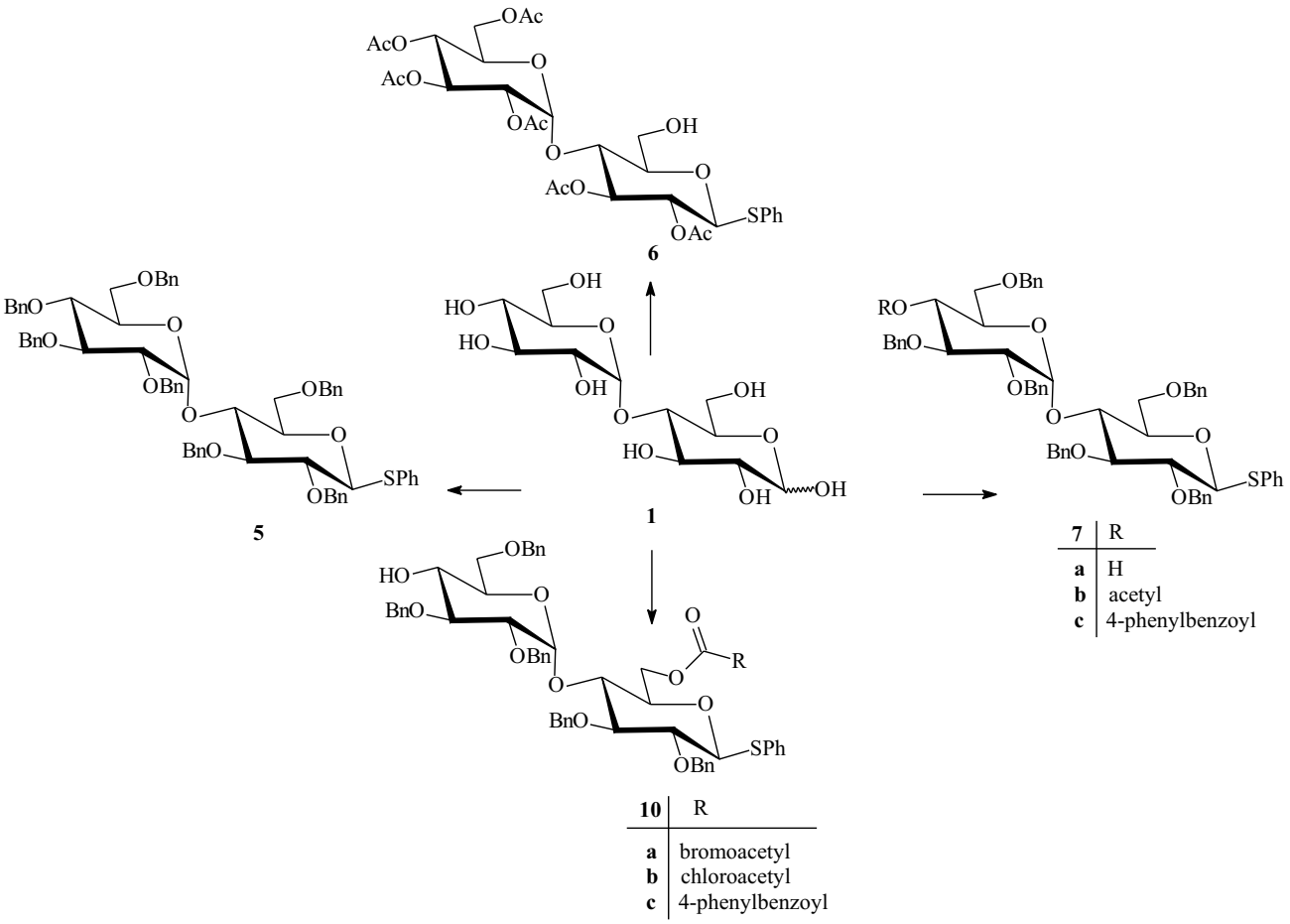
Abstract: An efficient strategy to synthesize a number of new phenylthio-maltoside derivatives in yields from 55 to 95% is described. These derivatives can be used as suitable building blocks for stepwise synthesis of starch derived malto-oligosaccharides.

Key words: phenyl 1-thio-β-maltoside, benzylidenation, silylation, benzylation, regioselective reductive cleavage

A practical and efficient strategy to achieve the chemical synthesis of a large number of complex oligosaccharides of interest for studies of starch biosynthesis and degradation requires a systematic approach based on a limited number of building blocks. Thioglycosides have received extensive attention due to their reactivity towards thiophiles[1] and their sensitivity to nucleophiles after conversion into glycosyl halides[2] thereby offering convenient possibilities for subsequent manipulations at the anomeric centre. Electrophilic[3] and radical[4] reactions have also been reported. Various methods for the preparation and use of these compounds have been reported.[5] We have previously reported a general method for removal of the thiophenyl protecting group at the anomeric position to generate a reducing sugar with the other original protecting groups still present.[6] On the other hand, the use of thioglycosides offer distinct advantages due to their relative stability under chemical conditions typically used for manipulation of other protective groups.[2a] Accordingly, the phenylthio group was selected as the protecting group for the anomeric center in the building blocks (Scheme 1). Based on this strategy, we report efficient methodologies including one-pot syntheses to obtain, in a multi-gram-scale, a set of maltose-derived building blocks (Scheme 1) that fulfil the requirements for efficient synthesis of complex α-1→4- and α-1→6-malto-oligosaccharides. Maltose was chosen as starting material because it is commercially available, cheap, and because it already contains an α-1→4- glycosidic bond thus saving one extra coupling reaction.

The per-*O*-acetylated phenyl 1-thio-β-maltoside **2a**[7,10] is the key intermediate for the synthesis of building block **5**.[7] Likewise, the per-*O*-acetylated pentachlorophenyl 1-β-maltoside **3**[9b] is the best suited precursor for the synthesis of per-*O*-acetylated 1,6-anhydromaltose,[9] which is important for the synthesis of the building block **6**.[7,8] Thus both compounds **2a** and **3** are mandatory for the synthesis of the desired building blocks, and improved and fast access to their synthesis in multi-gram-scale is required. Phase transfer catalysis (PTC) has been extensively used in the field of carbohydrate chemistry,[11,12] in particular to achieve nucleophilic substitutions at the anomeric center of glycosyl halides using a wide variety of nucleophiles[13] including aryloxides[14,15] and arylthiolates.[10,16] Therefore, our strategy for improved and fast access to the maltose derivatives **2a** and **3** (Scheme 2) is based on phase transfer catalysis (PTC). In a one-pot synthesis, β-maltose (**1**) was converted into hepta-*O*-acetyl-α-maltosyl bromide using acetic anhydride and hydrogen bromide in acetic acid,[17] and subsequently treated with thiophenol under PTC conditions using tetrabutylammonium hydrogen sulfate (TBAHS) as catalyst[10] to give **2a** in 55% yield, after chromatographic purification. A second one-pot synthesis was based on the same methodology, but using pentachlorophenol as the nucleophile, and provided compound **3** in 57% yield, without chromatographic treatment. NMR data and physical properties of both compounds **2a**[10] and **3**[9b] are consistent with the data previously reported.

The desired new building blocks **7a**–**c** were synthesized based on the use of cyclic acetal[18] using **2a** as the starting material. Quantitative conversion of **2a** into **2b** was achieved by deacetylation using sodium methoxide in methanol. Reaction of **2b** with α,α-dibromotoluene in pyridine[18c,d] under reflux and subsequent in situ acetylation to facilitate work-up gave the 4',6'-*O*-benzylidene derivative **4a** in 65% yield without chromatographic purification. The ^{1}H NMR spectrum of **4a** (Table 1, 2) revealed a 1-proton-singlet signal at δ = 5.47 ppm assignable to the methine proton of the benzylidene acetal function. The ^{13}C NMR spectrum (Table 3) showed the corresponding methine carbon resonating at δ = 101.5 ppm. Standard deacetylation of **4a** by treatment with sodium methoxide in methanol provided the related deacetylated product **4b** (Scheme 2) in quantitative yield. Benzylation of **4b** using benzyl bromide-sodium hydride in DMF afforded the corresponding benzylated product **4c** in 85% yield after purification by silica gel column chromatography. Reductive cleavage of the benzylidene acetal function of **4c** was performed regioselectively using sodium cyanoborohydride-HCl (gas)-diethyl ether in THF,[19]



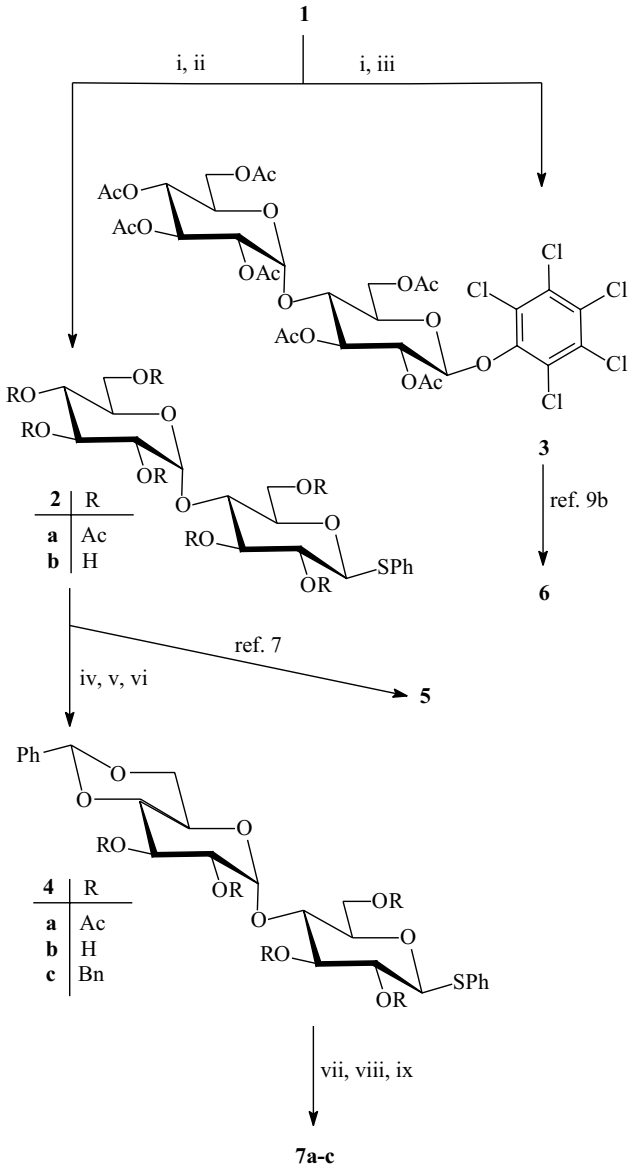
Maltose-derived building blocks

Scheme 1

resulting in the desired building block **7a** in 84% yield after chromatographic purification on silica gel. Acetylation of **7a** with acetic anhydride in pyridine provided the corresponding acetylated derivative **7b** quantitatively. Reaction of **7a** with biphenylcarbonyl chloride in CH_2Cl_2 in presence of 4-(dimethylamino)-pyridine (DMAP) gave the corresponding 4'-*O*-substituted phenylthio maltoside derivative **7c** in 97% yield after chromatographic purification

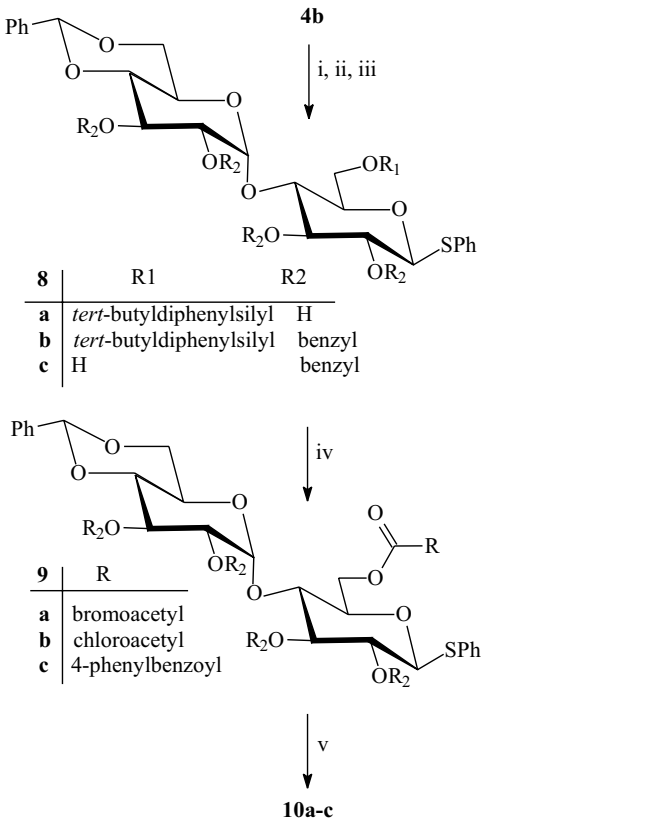
The additionally required new maltose-derived building blocks **10a**–**c** were obtained by selective silylation of **4b** with *tert*-butyldiphenylsilyl chloride in DMF in the presence of imidazole,[20] which provided the related 6-*O*-silylated derivative **8a** in 85% yield after chromatographic purification (Scheme 3). Attempted benzylation of compound **8a** using the DMF-NaH/benzyl bromide method was unsatisfactory due to the instability of the silyl group under these benzylation conditions. Instead, compound **8a** was successfully benzylated under PTC conditions using TBAHS as catalyst[10,21] to obtain **8b** in 56% yield. The silyl group of **8b** was removed by treatment with tetra-butylammonium fluoride in THF[19] to give **8c** quantitatively. Important characteristics of a suitable protecting group for the free 6-OH group of **8c** are its ability to survive during reductive cleavage of the benzylidene acetal function of **8c** concomitant with being readily removable under neutral or basic conditions. Haloacetyl (bromo- or chloroacetyl)[22] or 4-biphenylcarbonyl[23] protecting groups were found to fulfil these criteria. Treatment of **8c** with the appropriate carbonyl chloride in the presence of DMAP provided the desired products **9a**–**c** in good yield (Scheme 3). Regioselective reductive cleavage of the benzylidene acetal function of **9a**–**c** was successfully achieved by using the $NaBH_3CN$-HCl (gas)-diethyl ether system in THF[19] to give the desired building blocks **10a**–**c** in 63, 89 and 85% yield, respectively, after chromatographic treatment.

In conclusion, we have developed a multi-gram-scale practical strategy and an easy access to a number of building blocks including, (1) building block **6** with a free OH group at the 6-position for use as a glycosyl acceptor needed for introduction of α-1→6-glycosyl linkages, (2) building block **7** providing an access to the 4'-position of the non-reducing end for use as an acceptor suitable for introduction of α-1→4-glycosyl linkages, (3) building block **10** with a free 4'-position at the non-reducing end and simultaneously providing access to the 6-position to be used



Reagents and conditions: i) Ac_2O, 33% HBr-AcOH, r.t., 2 h; ii) TBAHS, thiophenol, 1M aq Na_2CO_3, r.t., 30 min, 55%; iii) TBAHS, pentachlorophenol, 1M aq Na_2CO_3, r.t., 30 min, 57%; iv) α,α-dibromotoluene, pyridine, 140 °C, 2 h, Ac_2O, r.t., overnight, 65%; v) MeONa-MeOH, r.t., 1 h, 100%; vi) NaH, DMF, benzyl bromide, r.t., overnight, 85%; vii) $NaBH_3CN$, THF, 4A MS-activated powder, HCl-Et_2O, 0 °C, 30 min, 84%; viii) Ac_2O, pyridine, r.t., 6 h, quant.; x) 4-phenylbenzoyl acid chloride, CH_2Cl_2, DMAP, −7 °C, 15 min, 97%

Scheme 2



Reagents and conditions: i) *tert*-butylchlorodiphenylsilane, DMF, imidazole, 20 °C, 45 min, 85%; ii) TBAHS, benzyl bromide, 50% aq NaOH, toluene, r.t., 3 days, 56%; iii) TBAF, THF, r.t., 1½ h, 95%; iv) acid chloride, CH_2Cl_2, DMAP, −7 °C, 15 min, 88−96%; v) $NaBH_3CN$, THF, 4Å MS-activated powder, HCl-Et_2O, 0 °C, 30 min, 63−89%

Scheme 3

for the introduction of an α-1→6-branch point in the α-1→4-glucan chain. The thiophenyl group present at the anomeric center of all selected building blocks can be easily removed to provide a free anomeric center, which may be activated and used as a glycosyl donor at any stage of the reaction sequences. The improved synthesis of both compounds **2a** and **3** constitutes a convenient and quick route to building blocks **5** and **6**. The availability of the building blocks here reported has made it possible to initiate a program for the synthesis of oligosaccharides which contain all major features of starch, i.e. the α-1→4 linkages and the α-1→6 branching point.

Mps were determined using a Mettler FP81 MBC Cell connected to a Mettler FP80 Central processor unit. Optical rotations were measured at 21 ± 2 °C with an Optical Activity Ltd AA-1000 Polarimeter. All reactions were monitored by TLC on aluminum sheets coated with silica gel $60F_{254}$ (0.2 mm thickness, E. Merck, Darmstadt, Germany) and the components present were detected by charring with 10% H_2SO_4 in MeOH. Column chromatography was carried out using silica gel 60 (particle size 0.040−0.063 mm, 230−400 mesh ASTM, E. Merck). Solvent extracts were dried with anhyd $MgSO_4$ unless otherwise specified. Microanalysis was performed at DB Lab-Danish Bioprotein A/S, Stenhuggervej 22, P.O. Box 829, DK-5230 Odense M, Denmark. The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 and 101 MHz, respectively. $CDCl_3$ was used as solvent (unless otherwise indicated), δ_H values are relative to internal TMS and δ_C values are referenced to the solvent [δ_C ($CDCl_3$) = 77.0; δ_C (CD_3OD) = 49.5; δ_C (Acetone-d_6) = 206 ppm]. FAB spectra were recorded on a Joel A505W mass spectrometer.

Compounds 2a and 3 under Conditions of Phase Transfer Catalysis using Bu_4NHSO_4 as Catalyst; General Procedure

A solution of 2,3,6,2',3',4',6'-hepta-*O*-acetyl-α-D-maltosyl bromide [prepared in situ from β-maltose monohydrate (**1**, 40 g, 0.11 mol)

Table 1 ^{1}H NMR Data ($CDCl_3$/TMS, δ_H in ppm) of Skeleton Protons[a] for Compounds **4a–c**, **7a–c**, **8a–c**, **9a–c** and **10a–c**

H	4a	4b[b]	4c	7a	7b	7c	8a[c]
1	4.71 d	4.56 d	4.67 d	4.69 d	4.70 d	4.73 d	4.80 d
2	4.79 t	3.21 dd	3.56 t	3.59 dd	3.57 dd	3.59 dd	3.39−3.48 m
3	5.29 t	3.60 t	3.82 t	3.82 t	3.81 t	3.85 t	3.73−3.88 m
4	4.94 dd	3.46 dd	3.81 t	4.10 dd	4.06 dd	4.11 t	3.73−3.88 m
5	3.72 m	3.36 td	3.62 m	3.60 m	3.61 td	3.66 td	3.61−3.69 m
6a	4.60 dd	3.64 m	3.90 dd	3.81 dd	3.83 dd	3.89 dd	4.05 dd
6b	4.24 dd	3.81 m	4.15 m	3.89 dd	3.87 dd	3.95 dd	4.08 dd
1’	5.33 d	5.13 d	5.67 d	5.63 d	5.58 d	5.61 d	5.24 d
2’	4.87 dd	3.49 dd	3.50 dd	3.44 dd	3.51 dd	3.61 dd	3.61−3.69 m
3’	5.44 t	3.75 t	4.00 t	3.75 t	3.86 t	4.06 t	3.73−3.88 m
4’	3.62 t	3.38 t	3.61 t	3.64 td	5.05 dd	5.36 dd	3.73−3.88 m
5’	3.83 td	3.78 m	3.86 m	3.77 m	3.87 m	4.09 m	3.39−3.48 m
6’a	3.71 t	3.67 m	3.62 m	3.56 dd	3.36 dd	3.46 dd	3.39−3.48 m
6’e	4.24 m	4.15 dd	4.15 m	3.49 dd	3.29 dd	3.38 dd	3.61−3.69 m
PhCH	5.47 s	4.48 s	5.53 s				5.57 s

H	8b	8c	9a	9b	9c	10a	10b	10c
1	4.74 d	4.74 d	4.68 d	4.68 d	4.72 d	4.68 d	4.68 d	4.73 d
2	3.51−3.59 m	3.52 dd	3.53 dd	3.53 dd	3.55 dd	3.53 dd	3.53 dd	3.58 dd
3	3.78 t	3.82 t	3.78 t	3.78 t	3.84 t	3.79 t	3.79 t	3.86 t
4	3.97−4.09 m	3.52 m	3.92 dd	3.91 dd	4.06 t	3.90 t	3.89 t	4.08 t
5	3.51−3.59 m	3.96 td	3.78 m	3.77 m	3.83 m	3.66 m	3.68 m	3.78 m
6a	3.97−4.09 m	3.85 dd	4.36 dd	4.37 dd	4.54 dd	4.38 dd	4.39 dd	4.52 dd
6b	3.97−4.09 m	4.01 m	4.66 dd	4.67 dd	4.90 dd	4.65 dd	4.66 dd	4.90 dd
1’	5.56 d	5.63 d	5.45 d	5.45 d	5.59 d	5.44 d	5.43 d	5.63 d
2’	3.48 dd	3.53 dd	3.51 dd	3.51 dd	3.54 dd	3.45 dd	3.44 dd	3.48 dd
3’	3.91 t	4.01 t	3.99 t	3.99 t	4.05 t	3.75 t	3.72 t	3.83 t
4’	3.51−3.59 m	3.62 t	3.61 t	3.61 t	3.61 t	3.59 td	3.59 td	3.67 td
5’	3.75 m	3.86 m	3.68 m	3.68 m	3.61 m	3.66 m	3.68 m	3.78 m
6’a	3.97−4.09 m	3.70 t	3.70 t	3.70 t	3.88 t	3.66 m	3.68 m	3.52 dd
6’e	3.51−3.59 m	4.33 dd	4.29 dd	4.28 dd	4.15 dd	3.72 m	3.68 m	3.59 dd
PhCH	5.56 s	5.54 s	5.53 s	5.53 s	5.49 s			

[a] Chemical shifts for the protecting groups are given in the Experimental.
[b] Recorded in CD_3OD.
[c] Recorded in acetone-d_6

Table 2 First-order Coupling Constants [*J* (Hz)] for $CDCl_3$ Solutions, unless otherwise stated

H	4a	4b[a]	4c	7a	7b	7c	8a[b]
1,2	9.8	9.7	9.7	9.7	9.7	9.7	9.8
2,3	9.0	9.0	9.2	8.9	8.6	8.8	nd
3,4	8.7	9.0	8.9	9.0	8.8	8.8	nd
4,5	9.7	9.6	9.2	9.5	9.5	9.2	nd
5,6a	2.6	2.3	nd	1.9	2.3	2.3	2.3
5,6b	4.7	4.6	3.6	4.0	4.3	4.3	3.8
6a,6b	12.0	12.0	11.1	11.1	11.2	11.1	11.5
1',2'	4.0	3.9	3.8	3.6	3.6	3.7	3.8
2',3'	10.2	9.6	9.4	9.7	9.8	9.6	nd
3',4'	9.9	9.4	9.3	9.7	9.4	9.2	nd
4',5'	9.6	9.4	9.3	9.7	10.1	10.1	nd
5',6'a	10.9	10.0	10.3	2.5	3.1	2.8	nd
5',6'b	4.7	4.9	nd	3.8	4.3	4.2	nd
6'a,6'e	10.9	10.0	10.3	10.2	10.7	10.7	nd

H	8b	8c	9a	9b	9c	10a	10b	10c
1,2	10.1	9.6	9.7	9.7	9.7	9.7	9.6	9.7
2,3	8.8	8.7	8.8	8.8	8.7	8.6	8.6	8.5
3,4	8.8	8.7	8.5	8.5	8.7	8.6	8.6	8.5
4,5	nd	nd	8.8	8.8	8.7	8.8	8.6	8.5
5,6a	nd	2.4	2.3	2.7	2.3	2.3	2.0	2.3
5,6b	nd	5.0	4.8	5.1	4.9	5.6	5.5	5.2
6a,6b	nd	11.7	11.8	11.8	11.9	11.8	11.8	12.0
1',2'	3.8	4.1	3.8	3.9	3.9	3.8	3.7	4.0
2',3'	9.6	9.4	9.4	9.3	9.5	9.6	9.6	9.7
3',4'	9.4	9.4	9.4	9.3	9.4	9.5	9.5	9.5
4',5'	nd	nd	nd	9.0	9.4	9.3	9.5	9.4
4',OH						2.8	2.1	2.5
5',6'a	nd	10.0	10.0	10.1	10.0	nd	nd	2.4
5',6'e	nd	4.7	4.3	4.1	4.6	nd	nd	3.7
6'a,6'e	nd	10.0	10.0	10.0	10.0	nd	nd	10.9

[a] Recorded in CD_3OD.
[b] Recorded in acetone-d_6.
nd: Not analyzed due to overlapping signals.

Table 3 ^{13}C NMR Data ($CDCl_3$/TMS; δ_C in ppm) of Skeleton Carbons[a] for Compounds **4a–c**, **7a–c**, **8a–c**, **9a–c** and **10a–c**

C	4a	4b[b]	4c	7a	7b	7c	8a[c]
1	84.9	89.3	87.2	87.2	87.3	87.3	88.4
2	70.7	73.4	80.9	80.9	80.8	80.9	82.2
3	76.5	79.3	86.8	86.7	86.5	86.4	79.8
4	72.5	81.1	71.8	72.5	73.6	74.4	71.7
5	63.5	80.5	78.4	78.7	78.8	78.8	74.8
6	62.5	62.5	73.4	69.1	97.1	69.5	63.9
1’	96.5	103.4	97.6	96.9	79.1	97.3	103.5
2’	70.8	74.8	78.8	78.9	79.1	79.1	81.9
3’	68.5	72.1	78.6	81.2	79.1	79.0	78.9
4’	78.8	82.5	82.3	71.3	70.6	71.2	73.1
5’	76.1	65.0	63.3	70.6	69.5	69.8	64.6
6’	68.4	69.8	68.9	69.6	68.7	68.8	69.3
PhCH	101.5	103.0	101.1				102.2

C	8b	8c	9a	9b	9c	10a	10b	10c
1	87.8	87.5	87.2	87.2	87.1	87.2	87.3	87.1
2	78.8	78.8	80.2	80.8	80.9	80.7	80.8	80.8
3	86.3	86.4	86.0	86.0	86.2	85.9	86.0	86.3
4	74.9	81.3	74.4	74.4	74.4	74.8	74.7	73.7
5	81.1	72.5	76.2	76.1	76.5	76.4	76.3	76.6
6	63.7	62.2	64.9	64.8	63.8	65.2	65.1	64.0
1’	98.3	98.1	98.5	98.4	98.6	97.8	97.8	97.6
2’	78.5	78.6	78.6	78.4	78.5	78.8	78.8	78.7
3’	79.6	78.8	79.0	78.5	78.6	81.0	81.0	81.2
4’	82.3	82.1	82.2	82.1	82.3	71.0	71.0	71.2
5’	63.4	63.4	63.6	63.6	63.7	71.4	71.4	71.2
6’	68.8	68.9	68.8	68.8	68.8	69.5	69.5	69.4
PhCH	101.1	101.1	101.3	101.3	101.3			

[a] Chemical shifts for the protecting groups are given in the Experimental.
[b] Recorded in CD_3OD.
[c] Recorded in acetone-d_6.

by the method of Kartha and Jennings[15]] in EtOAc (500 mL) was added gradually to a stirred mixture of Bu_4NHSO_4 (40 g, 0.12 mol), thiophenol (34 mL, 0.33 mol) and/or pentachlorophenol (87.9 g, 0.33 mol), and 1 M aq Na_2CO_3 (800 mL) at r.t. The two-phase mixture was vigorously stirred for 30 min at r.t. after which the organic phase was separated, successively washed with 1 M aq NaOH (3×100 mL), H_2O (3×100 mL), brine (50 mL), and dried. The solvent was evaporated in vacuo and the residue was chromatographed and/or crystallized**.**

Phenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (2a)

The obtained residue was chromatographed on silica gel (300 g). After an initial washing step with CH_2Cl_2 to remove all impurities, the column was eluted with CH_2Cl_2/EtOAc (9:1) to give **2a** as a white amorphous material. Yield: 44 g (55%); mp 99−100 °C [Lit.[10], mp 93−95 °C]; $[\alpha]_D$ +50.7 (*c* 1.31, $CHCl_3$); [Lit.,[10] $[\alpha]_D$ +47.4 (*c* 1.0, $CHCl_3$)].

Pentachlorophenyl 2,3,6-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-β-D-glucopyranoside (3)
The obtained residue was crystallized twice from EtOH to give **3** as a crystalline white solid. Yield: 54.9 g (57%); mp 170−171 °C [Lit.,[9b] mp 171−172 °C]; $[\alpha]_D$ +63.5 (*c* 1.41, $CHCl_3$); [Lit.,[9b] $[\alpha]_D$ +63 (*c* 0.5, $CHCl_3$)].

Phenyl 2,3,6-tri -*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (4a)
A stirred solution of **2b**[3] (5 g, 11.51 mmol) and α,α-dibromotoluene (2.5 mL, 15.1mmol) in dry pyridine (50 mL) was refluxed for 2 h at 140 °C, cooled to r.t. and Ac_2O (30 mL) gradually added with stirring for 24 h. The solvents were evaporated to dryness in vacuo and the last traces of solvents were removed by repeated co-evaporation with toluene (3 × 50 mL). EtOH (50 mL) was added to the residue and heated to dissolve oily impurities. After cooling to r.t., the resulting precipitate was collected by filtration and crystallized from EtOH to give **4a** as crystalline solid.

Yield: 4.2 g (65%); mp 196−197 °C; $[\alpha]_D$ +29.6 (*c* 0.82, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.99, 2.04, 2.05, 2.06, 2.09 (5 × s, 15H, 5 × $COCH_3$), 7.26−7.49 (m, 10H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.5, 20.6, 20.6, 20.7, 20.9 (5 × $COCH_3$), 126.1−136.7 (Ar-C), 169.5, 169.6, 170.1, 170.1, 170.7 (5 × $COCH_3$).

Anal. Calcd for $C_{35}H_{40}O_{15}S$ (732.76): C, 57.37; H, 5.50; S, 4.38. Found: C, 57.15; H, 5.58; S, 4.32.

Phenyl 4',6'-*O*-benzylidene-1-thio-β-maltoside (4b)
MeONa (30%) in MeOH (10 mL) was added gradually to a stirred suspension of **4a** (10 g, 13.1 mmol) in dry MeOH (100 mL) at r.t. Stirring was continued for 1 h at r.t. and the mixture neutralized by addition of Dowex 50W-X8 (H^+ form, 200−400 mesh, pre-washed with EtOH) resin. The resin was filtered off and washed with MeOH (4 × 50 mL). The residue obtained upon evaporation of the combined filtrates was co-evaporated with toluene (3 × 50 mL). The amorphous solid formed upon toluene treatment was collected by filtration and air-dried to give chromatographically pure **4b (**6.85 g, 100%) as a white amorphous material. An analytically pure sample was obtained by flash chromatography on silica gel CH_2Cl_2/MeOH (9:1); mp 95−97 °C; $[\alpha]_D$ +43.2 (*c* 0.75, MeOH).

^{1}H NMR (CD_3OD): δ = 7.16−7.50 (m, 10H, Ar-H).

^{13}C NMR (CD_3OD): δ = 127.6−139.1 (Ar-C).

Anal. Calcd for $C_{25}H_{30}O_{10}S$ (522.57): C, 57.46; H, 5.79; S, 6.14. Found: C, 57.24; H, 5.93; S, 6.21.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (4c)
A solution of **4b** (3.52 g, 6.74 mmol) in dry DMF (50 mL) was stirred with NaH (5.67 g, 60% in mineral oil) for 5 h at r.t. After cooling to 0 °C, benzyl bromide (11 mL) was added dropwise to the mixture and stirring was continued overnight at r.t. The mixture was cooled to 0 °C and excess NaH was decomposed by dropwise addition of MeOH (50 mL). The solution was concentrated in vacuo and diluted with EtOAc (200 mL) and H_2O (100 mL). The organic phase was separated, washed with H_2O (4 × 50 mL) and brine (25 mL), and dried. The solvent was evaporated and the residue chromatographed on silica gel (180 g) with 10−20% Et_2O in *n*-pentane to give **4c** as a colourless syrup.

Yield: 5.57 g (85%); $[\alpha]_D$ +3.6 (*c* 0.42, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.52, 4.69 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.55, 4.83 (2 × d, 2H, *J* = 10.3 Hz, PhCH_2), 4.59, 4.68 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.73, 4.89 (2 × d, 2H, *J* = 11.0 Hz, PhCH_2), 4.82, 4.90 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 7.12−7.61 (m, 35H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 73.9, 74.1, 75.2, 75.2, 75.2 (5 × PhCH_2), 126.0−138.6 (Ar-C).

MS (FAB): *m/z* = 995 $[M+Na]^+$.

Anal. Calcd for $C_{60}H_{60}O_{10}S$ (973.20): C, 74.05; H, 6.21; S, 3.29. Found: C, 73.92; H, 6.12; S, 3.15.

Phenyl 4-*O*-(4,6-*O*-Benzylidene-α-D-glucopyranosyl)-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (8a)
tert-Butylchlorodiphenylsilane (7.5 mL, 28.84 mmol) was added dropwise to a stirred solution of **4b** (4.2 g, 8 mmol) and imidazole (4.2 g, 61.69 mmol) in dry DMF (100 mL) maintained at 0 °C using an ice-bath. The ice-bath was removed and the mixture was stirred for 45 min at 15−20 °C and diluted with EtOAc (400 mL) and H_2O (100 mL). The organic phase was separated and washed with sat. $NaHCO_3$ (3 × 100 mL), H_2O (3 × 100 mL), brine (50 mL), and dried. The solvent was evaporated in vacuo and the residue chromatographed on silica gel (130 g) with 0−10% MeOH in $CHCl_3$ to obtain **8a** as a white amorphous material, crystalline from Et_2O/*n*-pentane.

Yield: 5.2 g (85%); mp 105−106 °C; $[\alpha]_D$ +28.9 (*c* 0.73, $CHCl_3$).

^{1}H NMR (Acetone-d_6): δ = 1.06 (s, 9H, Si[C(CH_3)$_3$]), 4.52 (d, 1H, *J* = 4.8 Hz, OH-2), 4.59 (d, 1H, *J* = 4.0 Hz, OH-3'), 5.23 (s, 1H, OH-2'), 5.52 (s, 1H, OH-3), 7.22−7.50 (m, 20H, Ar-H).

^{13}C NMR (Acetone-d_6): δ = 19.8 (Si[*C*(CH_3)$_3$]), 27.2 (Si[C(*C*H_3)$_3$]), 127.3−139.1 (Ar-C).

Anal. Calcd for $C_{41}H_{48}O_{10}SSi$ (760.98): C, 64.71; H, 6.36; S, 4.21. Found: C, 64.83; H, 6.26; S, 4.07.

Phenyl 2,3-*O*-Benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-(4,6-*O*-benzylidene 2,3-di-*O*-benzyl -α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (8b)
A solution of **8a** (9 g, 11.83 mmol) in toluene (175 mL) was added gradually to a stirred mixture of Bu_4NHSO_4 (6.54 g, 19.26 mmol), benzyl bromide (65 mL), and 50% aq NaOH (105 mL) at r.t. Stirring was continued for 3 days at r.t. after which the mixture was diluted with toluene (300 mL). The organic phase was separated and washed with H_2O (4 × 100 mL), and dried. The solvent was evaporated and the residue chromatographed on silica gel (210 g) with 0−20% Et_2O in *n*-pentane to obtain **8b** (7.44 g, 56%) as a gum. An analytical sample was obtained as a white powder from *n*-pentane; mp 54−56 °C; $[\alpha]_D$ +4.3 (*c* 0.33, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.08 (s, 9H, Si[C(CH_3)$_3$]), 4.51, 4.66 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.62, 4.87 (2 × d, 2H, *J* = 10.0 Hz, PhCH_2), 4.69, 4.85 (2 × d, 2H, *J* = 11.1 Hz, PhCH_2), 4.82, 4.90 (2 × d, 2H, *J* = 11.3 Hz, PhCH_2), 7.16−7.77 (m, 40H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 19.4 (Si[*C*(CH_3)$_3$]), 27.0 (Si[C(*C*H_3)$_3$]), 73.6, 74.5, 75.1, 75.4 (4 × Ph*C*H_2), 125.9−138.5 (Ar-C).

MS (FAB): *m/z* = 1143 $[M+Na]^+$.

Anal. Calcd for $C_{69}H_{72}O_{10}SSi$ (1121.48): C, 73.90; H, 6.47; S, 2.86. Found: C, 74.16; H, 6.67; S, 2.69.

Phenyl 2,3-di-*O*-Benzyl-4-*O*-(4,6-O-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (8c)
Tetrabutylammonium fluoride (1.1 M in THF, 20 mL) was added dropwise to a stirred solution of **8b** (10 g, 8.92 mmol) in THF (60 mL) at r.t. Stirring was continued for 1½ h at r.t. and the solvent was removed in vacuo. The residue was dissolved in EtOAc (300 mL) and H_2O (100 mL) and the organic phase separated, washed with H_2O (3 × 50 mL), sat. $NaHCO_3$ (3 × 50 mL), brine (50 mL), and dried. The solvent was evaporated and the residue chromatographed on silica gel (210 g) with 0−5% EtOAc in CH_2Cl_2 to give **8c** (7.5 g, 95%) as a foam. An analytical sample was crystallized from Et_2O/

n-pentane to obtain a white powder; mp 64−66 °C; $[\alpha]_D$ +13.4 (*c* 0.31, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.50, 4.71 (2 × d, 2H, *J* = 11.8 Hz, PhCH_2), 4.59, 4.86 (2 × d, 2H, *J* = 10.0 Hz, PhCH_2), 4.73, 4.91 (2 × d, 2H, *J* = 11.6 Hz, PhCH_2), 4.85, 4.89 (2 × d, 2H, *J* = 11.9 Hz, PhCH_2), 7.10−7.53 (m, 30H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 74.0, 74.2, 75.2, 75.4 (4 × Ph*C*H_2), 126.0−138.4 (Ar-C).

MS (FAB): *m/z* = 905 $[M+Na]^+$.

Anal. Calcd for $C_{53}H_{54}O_{10}S$ (883.07): C, 72.09; H, 6.16; S, 3.63. Found: C, 72.31; H, 6.32; S, 3.49.

6-*O*-Substituted Phenyl 1-Thio-β-maltosides (9a-c); General Procedure

A solution of the acid chloride (22.64 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise at -10 °C during a period of 10 min to a stirred solution of **8c** (5 g, 5.66 mmol) and DMAP (2.76 g, 22.64 mmol) in dry CH_2Cl_2 (75 mL) under Ar. The mixture was stirred for an additional 15 min at −10 °C to −7°C under Ar, after which solid $NaHCO_3$ (5 g) was added and diluted with EtOAc (200 mL). The mixture was filtered through a sand pad on a silica gel layer and the filtrate was washed successively with H_2O (50 mL), 1 N aq HCl (3 × 25 mL), 1 N aq NaOH (4 × 50 mL), H_2O (4 × 50 mL), and dried. The solvent was evaporated in vacuo to dryness and the last traces of solvents were removed by additional co-evaporation with toluene (3 × 50 mL). The resulting residue was purified by column chromatography on silica gel (130 g) with 30−40% Et_2O in *n*-pentane to give the products **9a-c**.

Phenyl 2,3-Di-*O*-benzyl-6-*O*-bromoacetyl-4-*O*-(4,6-di-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (9a)

Colourless syrup; yield: 5 g (88%). An analytical sample was crystallized from Et_2O/*n*-pentane to obtain a white amorphous solid; mp 52−54 °C; $[\alpha]_D$ +6.4 (*c* 0.49, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 3.83 (s, 2H, COCH_2Br), 4.49, 4.69 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.59, 4.86 (2 × d, 2H, *J* = 10.0 Hz, PhCH_2), 4.74, 4.89 (2 × d, 2H, *J* = 11.3 Hz, PhCH_2), 4.85 (s, 2H, PhCH_2), 7.15−7.56 (m, 30H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 25.6 (CO*C*H_2Br), 74.0, 74.4, 75.1, 75.3 (4 × Ph*C*H_2), 125.9−138.4 (Ar-C), 166.6 (*C*OCH_2Br).

MS (FAB): *m/z* = 1027 $[M+Na]^+$.

Anal. Calcd for $C_{55}H_{55}BrO_{11}S$ (1004.01): C, 65.80; H, 5.52; S, 3.19. Found: C, 65.96; H, 5.73; S, 3.31.

Phenyl 2,3-Di-*O*-benzyl-6-*O*-chloroacetyl-4-*O*-(4,6-di-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (9b)

Colourless syrup; yield: 4.9 g (90%). An analytical sample was crystallized from Et_2O/*n*-pentane to obtain a white amorphous solid; mp 48−49 °C; $[\alpha]_D$ +8.6 (*c* 0.77, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.05 (s, 2H, COCH_2Cl), 4.49, 4.69 (2 × d, 2H, *J* = 11.8 Hz, PhCH_2), 4.59, 4.87 (2 × d, 2H, *J* = 10.1 Hz, PhCH_2), 4.74, 4.89 (2 × d, 2H, *J* = 11.4 Hz, PhCH_2), 4.85 (s, 2H, PhCH_2), 7.14−7.56 (m, 30H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 40.6 (COCH_2Cl), 74.0, 74.4, 75.1, 75.3 (4 × PhCH_2), 125.9−138.3 (Ar-C), 166.7 (*C*OCH_2Cl).

MS (FAB): *m/z* = 981 $[M+Na]^+$.

Anal. Calcd for $C_{55}H_{55}ClO_{11}S$ (959.56): C, 68.84; H, 5.78; S, 3.34. Found: C, 69.11; H, 5.93; S, 3.47.

Phenyl 2,3-Di-*O*-benzyl-4-*O*-(4,6-di-*O*-benzylidene-2,3-di-*O*-benzyl-α-D-glucopyranosyl)-6-*O*-(4-phenylbenzoyl)-1-thio-β-D-glucopyranoside (9c)

White powder; yield: 5.7 g (96%). An analytical sample was crystallized from Et_2O/*n*-pentane to give a white crystalline material; mp 116−117 °C; $[\alpha]_D$ +18.3 (*c* 0.68, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.50, 4.73 (2 × d, *J* = 11.9 Hz, 2H, PhCH_2), 4.59, 4.87 (2 × d, *J* = 10.2 Hz, 2H, PhCH_2), 4.74, 4.89 (2H, 2 × d, *J* = 11.5 Hz, PhCH_2), 4.88 (s, 2H, PhCH_2), 7.08−8.14 (m, 39H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 74.1, 74.5, 75.1, 75.2 (4 × Ph*C*H_2), 126.0−145.8 (Ar-C), 165.8 (*C*OPhPh).

MS (FAB): *m/z* = 1085 $[M+Na]^+$.

Anal. Calcd for $C_{66}H_{62}O_{11}S$ (1063.28): C, 74.55; H, 5.88; S, 3.02. Found: C, 74.42; H, 5.66; S, 2.86.

Building Blocks 7a and 10a-c via Regioselective Reductive Cleavage of the Benzylidene Acetal Function of 4c and 9a-c; General Procedure

A solution of **4c** and/or **9a-c** (5.14 mmol) and $NaBH_3CN$ (3.23 g, 51.4 mmol) in dry THF (100 mL) was stirred with 4Å molecular sieves (3 g, activated powder) for 1 h at r.t.. After cooling to 0 °C, a solution of HCl in Et_2O was slowly added until the mixture became acidic (pH region 2−3, gas evolution). Stirring was continued for 30 min at 0 °C and the mixture was diluted with EtOAc (100 mL) and filtered through a Celite pad and a silica gel layer. The filtrate was washed successively with H_2O (3 × 150 mL), sat. $NaHCO_3$ (3 × 100 mL), H_2O (3 × 100 mL), and brine (50 mL), and dried. The solvent was evaporated in vacuo and the residue purified by column chromatography on silica gel (210 g) with 30−60% Et_2O in *n*-pentane to obtain **7a** and/or **10a-c**.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (7a)

Colourless syrup; yield: 4.21 g (84%); $[\alpha]_D$ +13.0 (*c* 1.0, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.38, 4.48 (2 × d, 2H, *J* = 12.2 Hz, PhCH_2), 4.49, 4.5 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.56, 4.57 (2 × d, 2H, *J* = 12.1 Hz, PhCH_2), 4.58, 4.84 (2 × d, 2H, *J* = 10.5 Hz, PhCH_2), 4.70, 4.86 (2 × d, 2H, *J* = 11.3 Hz, PhCH_2), 4.87, 4.92 (2 × d, 2H, *J* = 11.8 Hz, PhCH_2), 7.12−7.62 (m, 35H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 73.2, 73.2, 73.6, 74.2, 75.2, 75.3 (6 × Ph*C*H_2), 126.5−138.7 (Ar-C).

MS (FAB): *m/z* = 997 $[M+Na]^+$.

Anal. Calcd for $C_{60}H_{62}O_{10}S$ (975.21): C, 73.90; H, 6.41; S, 3.29. Found: C, 74.08; H, 6.55; S, 3.42.

Phenyl 2,3-Di-*O*-benzyl -6-*O*-bromoacetyl l-4-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (10a)

Colourless syrup; yield: 3.26 g (63%); $[\alpha]_D$ +14.0 (*c* 0.88, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.44 (d, 1H, *J* = 2.8 Hz, OH-4'), 3.76 (s, 2H, COCH_2Br), 4.46, 4.57 (2 × d, 2H, *J* = 12.0 Hz, PhCH_2), 4.53, 4.58 (2 × d, 2H, *J* = 12.2 Hz, PhCH_2), 4.61, 4.85 (2 × d, 2H, *J* = 10.0 Hz, PhCH_2), 4.70, 4.87 (2 × d, 2H, *J* = 11.4 Hz, PhCH_2), 4.87, 4.92 (2 × d, 2H, *J* = 11.7 Hz, PhCH_2), 7.15−7.56 (m, 30H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 25.7 (COCH_2Br), 73.3, 73.6, 74.4, 75.2, 75.2 (5 × Ph*C*H_2), 127.6-138.4 (Ar-C), 166.6 (*C*OCH_2Br).

MS (FAB): *m/z* = 1029 $[M+Na]^+$.

Anal. Calcd for $C_{55}H_{57}BrO_{11}S$ (1006.02): C, 65.67; H, 5.71; S, 3.19. Found: C, 65.91; H, 5.95; S, 2.99.

Phenyl 2,3-Di-*O*-benzyl-6-*O*-chloroacetyl-4-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (10b)
Colourless syrup; yield: 4.40 g (89%); $[\alpha]_D$ +15.6 (*c* 1.23, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.43 (d, 1H, *J* = 2.1 Hz, OH-4'), 3.97 (s, 2H, $COCH_2Cl$), 4.45, 4.58 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.53, 4.57 (2 × d, 2H, *J* = 11.8 Hz, $PhCH_2$), 4.61, 4.86 (2 × d, 2H, *J* = 10.4 Hz, $PhCH_2$), 4.70, 4.87 (2 × d, 2H, *J* = 11.2 Hz, $PhCH_2$), 4.87, 4.91 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 7.14−7.55 (m, 30H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 40.7 ($COCH_2Cl$), 73.4, 73.7, 74.4,75.3, 75.3 (5×$PhCH_2$), 127.7-138.4 (Ar-C), 166.8 ($COCH_2Cl$).

MS (FAB): *m/z* = 983 $[M+Na]^+$.

Anal. Calcd for $C_{55}H_{57}ClO_{11}S$ (961.57): C, 68.70; H, 5.98; S, 3.33. Found: C, 68.92; H, 6.13; S, 3.17.

Phenyl 2,3-Di-*O*-benzyl-6-*O*-(4-phenylbenzyol)-4-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (10c)
Colourless syrup; yield: 4.60 g (85%). An analytical sample was crystallized from Et_2O/*n*-pentane as a white amorphous material; mp 76−77°C; $[\alpha]_D$ +7.7 (*c* 0.74, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 2.53 (d, 1H, *J* = 2.5 Hz, 4'-OH), 4.35, 4.43 (2 × d, 2H, *J* = 12.4 Hz, $PhCH_2$), 4.48, 4.63 (2 × d, 2H, *J* = 11.6 Hz, $PhCH_2$), 4.60, 4.88 (2 × d, 2H, *J* = 10.0 Hz, $PhCH_2$), 4.75, 4.87 (2 × d, 2H, *J* = 11.3 Hz, $PhCH_2$), 4.91 (s, 2H, $PhCH_2$), 7.08−8.15 (m, 39H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 73.4, 73.5, 74.3, 75.2, 75.3 (5 × $PhCH_2$), 127.0−145.8 (Ar-C), 165.8 (*C*OPhPh).

MS (FAB): *m/z* = 1087 $[M+Na]^+$.

Anal. Calcd for $C_{66}H_{64}O_{11}S$ (1065.87): C, 74.37; H, 6.05; S, 3.01. Found: C, 74.52; H, 6.22; S, 2.82.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-1-thio-β-D-glucopyranoside (7b)
Ac_2O (5 mL) was added to a stirred solution of **7a** (5 g, 5.13 mmol) in dry pyridine (100 mL) and stirring was continued for 6 h at r.t., after which the solvents were evaporated in vacuo and the last traces of solvents removed by co-evaporation with toluene (3 × 50 mL). The residue was dissolved in EtOAc (150 mL), H_2O (50 mL), and the organic phase was separated, washed with sat. $NaHCO_3$ (4 × 50 mL), H_2O (3 × 50 mL), and brine (25 mL), and dried. Evaporation of the solvent to dryness afforded chromatographically pure **7b** as a colourless syrup; yield: 5.2 g (quant.); $[\alpha]_D$ +24.8 (*c* 0.40, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 1.81 (s, 3H, $COCH_3$), 4.34, 4.46 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.45, 4.57 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.54 (s, 2H, $PhCH_2$), 4.56, 4.76 (2 × d, 2H, *J* = 11.5 Hz, $PhCH_2$), 4.59, 4.84 (2 × d, 2H, *J* = 10.2 Hz, $PhCH_2$), 4.88 (s, 2H, $PhCH_2$), 7.11−7.60 (m, 35H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 20.8 ($COCH_3$), 73.3, 73.4, 73.5, 74.3, 75.0, 75.2 (6 × $PhCH_2$), 126.5−138.5 (Ar-C), 169.5 ($COCH_3$).

MS (FAB): *m/z* = 1039 $[M+Na]^+$.

Anal. Calcd for $C_{62}H_{64}O_{11}S$ (1017.25): C, 73.21; H, 6.34; S, 3.15. Found: C, 73.45; H, 6.60; S, 3.37.

Phenyl 2,3,6-Tri-*O*-benzyl-4-*O*-[4-*O*-(4-phenylbenzoyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl]-1-thio-β-D-glucopyranoside (7c)
Compound **7a** was converted into compound **7c** as described above for compounds **9a-c** and purified by column chromatography on silica gel with 20% EtOAc in *n*-pentane to give **7c** as a colourless syrup; yield: (97%); $[\alpha]_D$ −12.3 (*c* 0.83, $CHCl_3$).

^{1}H NMR ($CDCl_3$): δ = 4.35, 4.44 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.49, 4.58 (2 × d, 2H, *J* = 12.0 Hz, $PhCH_2$), 4.56 (s, 2H, $PhCH_2$), 4.59, 4.73 (2 × d, 2H, *J* = 11.5 Hz, $PhCH_2$), 4.61, 4.85 (2 × d, 2H, *J* = 10.2 Hz, $PhCH_2$), 4.90, 4.94 (2×d, 2H, *J* = 11.7 Hz, $PhCH_2$), 7.05−8.00 (m, 44 H, Ar-H).

^{13}C NMR ($CDCl_3$): δ = 73.4, 73.5, 73.6, 74.0, 75.1, 75.2 (6 × $PhCH_2$), 126.5−145.8 (Ar-C), 165.0 (*C*OPhPh).

MS (FAB): *m/z* = 1177 $[M+Na]^+$.

Anal. Calcd for $C_{73}H_{70}O_{11}S$ (1155.42): C, 75.89; H, 6.11; S, 2.78. Found: C, 76.03; H, 6.25; S, 2.65.

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