Halobenzoyl groups in glycosylation: effect on stereoselectivity and reactivity of glycosyl donors*

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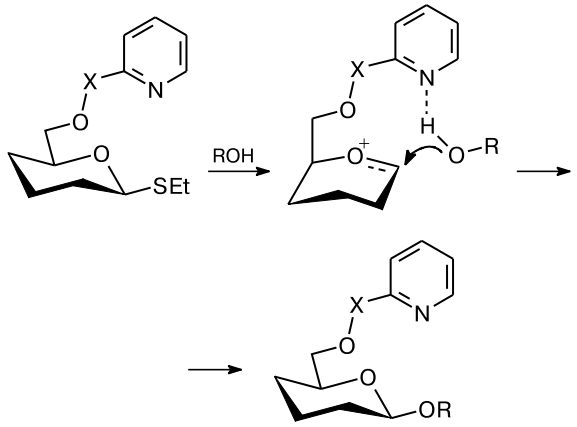
Described herein is the synthesis and evaluation of a series of glycosyl donors equipped with halobenzoyl substituents at O(4) and O(6) to study their properties in glycosylations. Among possible effects that may include carbonyl participation or H-bond mediated aglycone delivery, our results indicate that halobenzoyls act *via* a different mode.

Key words: carbohydrates, glycosylation, stereoselectivity, thioglycosides, activation.

The necessity to perform glycosylation reactions with complete stereoselectivity has been the major hurdle that consistently captured the attention of many carbohydrate chemists. The Kochetkov laboratory has made a number of seminal contributions to the glycosylation method development[1] introducing many significant improvements into this research field.[2] Many factors affect the outcome of chemical glycosylations.[3] For instance, the stereoselectivity of glycosylation can be profoundly influenced by protecting groups.[4] Neighboring protecting groups at O(2), traditionally known as participating groups for the synthesis of 1,2-*trans* glycosides,[5] can now assist in the formation of either 1,2-cis[6] or 1,2-*trans* glycosides.[7] Remote protecting groups at positions O(3), O(4), and/or O(6) may also affect the stereoselectivity by means of participation,[8] conformational restriction,[9] H-bond mediated aglycone delivery (*vide infra*),[10] steric hindrance,[11] and/or electron withdrawal.[12]

Recently, our laboratory has been investigating the stereodirecting effect of remote picolinyl (Pic) and picoloyl (Pico) substituents. Picolinyl at O(2) formally participates at the anomeric center and gives 1,2-*trans* glycosides *via* the six-membered ring intermediate.[7b] The action of the remote picolinyl and related picoloyl substituents is totally different. Not being able to participate at the anomeric center directly, picolinyl nitrogen forms the hydrogen bond with the incoming glycosyl acceptor (Scheme 1). As a result, a very high facial selectivity, always *syn* in respect to the picolinyl substituent at O(6), is observed.[10] This, rather unexpected involvement of remote picolinyl substituents, was termed as H-bond-mediated aglycone delivery (HAD).

Scheme 1



X = CH_2 (picolinyl), C=O (picoloyl)

The HAD approach has already been successfully applied to the stereoselective synthesis of glucosides, galactosides, rhamnosides,[10] and mannosides[13] by our group, arabinofuranosides by the Young group,[14] and 2-deoxy glycosides by Mong and co-workers.[15] The utility of this approach was extended to the synthesis of a β-mannan[13] and a series of linear and branched α-glucans (up to a pentasaccharide).[16a] Recently, K. Le Mai Hoang and X.-W. Liu reported on HAD involving 2-cyanobenzyl group neighboring the anomeric center.[16b] More recently, we investigated the effect of various leaving groups (*S*-phenyl, *S*-tolyl, *S*/*O*-imidates) and devised an effective α-glycosylation protocol with bromine activation at ambient temperature.[17] In conjunction with this effort, herein we report our first attempt to diversify protecting groups that may have an effect on the stereoselectivity of glycosylation. This study was prompted by an idea of us-

* On the occasion of the 100th anniversary of the birth of Academician N. K. Kochetkov (1915—2005).

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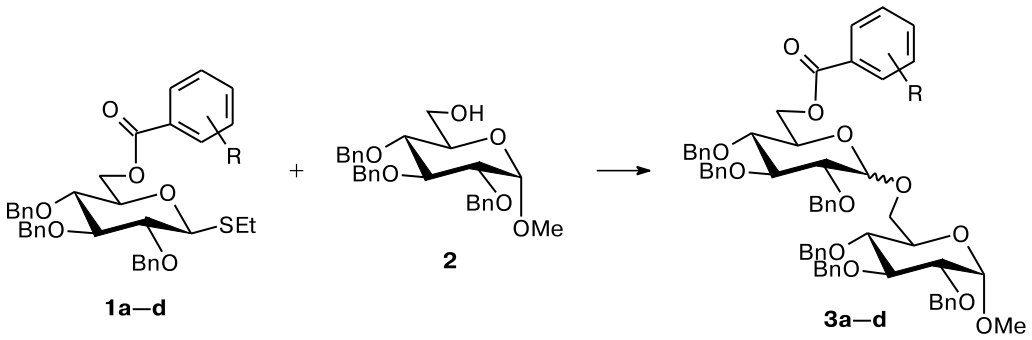
Scheme 2



R = 2-F (**a**), 3-F (**b**), 4-F (**c**), H (**d**)

Reagents and conditions: promoter, 1,2-dichloroethane, molecular sieves 4 Å, −30 °C→20 °C.

ing the fluorinated benzoyl substituents in lieu of picoloyl substituents that are prone to side reactions with excess electrophile in glycosylation.[10] We anticipated that the electronegative fluorine would act as the hydrogen bond acceptor site and hence would promote H-bond mediated *syn*-stereoselectivity like in the traditional HAD reactions with picoloyl groups.

To probe this concept, we obtained 6-*O*-(2-fluorobenzoyl) glycosyl donor **1a** and investigated its reactivity and stereoselectivity using glycosyl acceptor **2**[18] under standard HAD reaction conditions[10] (Scheme 2). It should be noted that HAD reactions give higher *syn*-selectivity in high dilution conditions (5 mmol L^{-1}), yet the high dilution has practically no effect on the reaction rate. Occasionally, HAD-mediated reactions proceed even faster in high dilution. This trend drastically differs from reactions with conventional glycosyl donors that are incapable of HAD, although stereoselectivity enhancement at lower concentrations has been observed in other applications.[19] Consistently with previous observations made with HAD, glycosidation of glycosyl donor **1a** with glycosyl acceptor **2** in high dilution (glycosyl donor concentration of 5 mmol L^{-1}) or regular concentration (glycosyl donor concentration of 50 mmol L^{-1}) conditions proceeded equally fast. Disaccharide **3a** was obtained in 6 h in both cases in a high yield of 91—95% (Table 1, entries *1* and *2*). The stereoselectivity in these experiments was very dissimilar, but it was opposite to that expected from the HAD-mediated reactions. Thus, both experiments preferentially gave α-linked disaccharide **3a**, anti-selectivity in respect to the fluorobenzoyl substituent, and the high dilution experiment was much more selective (α : β = 7.2 : 1, entry *1* *versus* α : β = 2.3 : 1, entry *2*). Likewise, 3-fluorobenzoyl (**1b**) and 4-fluorobenzoyl (**1c**) glycosyl donors gave comparable results in terms of reactivity, yield, and stereoselectivity (see Table 1, entries *3—6*). Conversely, reac-

Table 1. Glycosylation of glycosyl acceptor **2** with glycosyl donors **1a—d**

Entry	Glycosyl donor	Donor concentration /mmol L^{-1}	Promoter	*t*/h	Product	Yield (%) (α : β)
1	**1a**	5	DMTST	6	**3a**	91 (7.2 : 1)
2	**1a**	50	DMTST	6	**3a**	95 (2.3 : 1)
3	**1b**	5	DMTST	5	**3b**	87 (8.2 : 1)
4	**1b**	50	DMTST	20	**3b**	92 (3.1 : 1)
5	**1c**	5	DMTST	6	**3c**	85 (5.4 : 1)
6	**1c**	50	DMTST	8	**3c**	85 (2.9 : 1)
*7**	**1d**	5	DMTST	72	**3d**	68 (4.9 : 1)
*8**	**1d**	50	DMTST	72	**3d**	58 (2.8 : 1)
*9**	**1b**	5	IDCP	72	**3b**	47 (3.1 : 1)
10	**1b**	5	NIS/TfOH	1	**3b**	87 (9.0 : 1)
11	**1b**	5	NIS/TMSOTf	3	**3b**	95 (7.3 : 1)
12	**1b**	5	NIS/TESOTf	5	**3b**	94 (9.7 : 1)

Note. DMTST is dimethyl(methylthio)sulfonium trifluoromethanesulfonate, IDCP is iodonium dicollidine perchlorate, NIS is *N*-iodosuccinimide, TfOH is triflic acid, TMSOTf is trimethylsilyl triflate, TESOTf is triethylsilyl triflate.
* Incomplete reaction.

tions of glycosyl donor **1d**[20] equipped with unsubstituted 6-*O*-benzoyl substituent were very sluggish under these reaction conditions and failed to go to completion even after 72 h (entries *7* and *8*). Although the stereoselectivity trend with glycosyl donor **1d** was similar, stereoselectivity provided by glycosyl donor **1d** was lower than that observed with fluorinated glycosyl donors **1a**—**c**, particularly evident in the high dilution experiment (*cf.* entries *1*, *3*, *5*, and *7*).

In attempt to optimize the reaction conditions, we selected glycosyl donor **1b** that gave the best results in the preliminary experiments with dimethyl(methylthio)sulfonium trifluoromethanesulfonate (DMTST). Having investigated various promoters (see Table 1, entries *9*—*12*) we observed no drastic difference in stereoselectivity and yields. However, the decrease in stereoselectivity obtained with iodonium dicollidine perchlorate (IDCP), that is known to favor the formation of α-linked products, was somewhat puzzling (entry *9*). Reactions with NIS/TfOH, NIS/TMSOTf and NIS/TESOTf (NIS is *N*-iodosuccinimide; TfOH, TMSOTf, and TESOTf are triflic acid and its trimethylsilyl and triethylsilyl ethers, respectively), all of which are amongst the strongest promoters for thioglycosides, proceeded swiftly and provided **3b** in high yields and stereoselectivities (entries *10*—*12*: yield 87—95%, $\alpha : \beta = (7.3—9.7) : 1$).

The preliminary set of experiments indicates that fluorinated 6-*O*-benzoyl group can enhance the reactivity of glycosyl donors and provide higher α-stereoselectivity in glycosylation reactions in comparison to that of 6-*O*-benzoylated donor. Although the stereoselectivity observed is not consistent with the general concept of the HAD, we cannot entirely rule out a possibility of HAD from the α-face of the oxacarbenium intermediate ring (Fig. 1, structure **A**). Other modes of action can be also anticipated: the formal participation of the carbonyl *via* acyloxonium **B** or the formal coordination to fluorine (intermediate **C**).

To delineate between the possible pathways and probe the reaction mechanism we set up a number of test experiments. We initially thought that if the aglycone delivery is occurring *via* the bottom face (see Fig. 1, intermediate **A**), α-donor **4** would help to obtain enhanced β-selectivity (Scheme 3, equation (2) and Table 2, entries *13*, *14*). However, no significant difference was detected, and the slight enhancement of β-selectivity could be indicative of the departed leaving group blocking the bottom face and hence shielding it from the nucleophilic attack. To gain a better insight, we performed glycosylation of TMS-protected glycosyl acceptor **5** (see Scheme 3, equation (2) and Table 2, entry *15*)[21], which has a profound effect on HAD-mediated reactions. That is because the TMS-group excludes the possibility of H-bonding between the glycosyl donor and the glycosyl acceptor components.[10] In this application, no difference was observed in comparison to the earlier experiments with glycosyl acceptor **2** indicating that the selectivity observed is not due to the HAD from the bottom face. Hence, we believe that the intermediate **A** can be excluded from further consideration.

We cannot completely rule out the possibility of the acyloxonium intermediate **B** formation. The result of glycosylation of glycosyl acceptor **2** with glycosyl donor **6** (see Scheme 3, equation (3)) indicates the importance of the carbonyl group. Although its actual mode of action can relate to electronic factors or the restricted rotation of ester *versus* ether at O(6). This may be somewhat insignificant with unsubstituted benzoyl/benzyl, but becomes much more profound in the substituted derivatives. We believe that intermediate **C** offers a viable explanation of the enhanced stereoselectivity and reactivity. In this context, 3-fluorobenzylated glycosyl donor **6** has no such effect (or a much weaker effect) due to the much more flexible nature of methylene *versus* carbonyl. The role of the halogen may also relate to its ability to repel the nucleophile from the top face either electronically or sterically.

Since the role of 6-*O*-fluorobenzoyl *via* the HAD is unlikely, we decided to investigate other halogenated benzoyls to acquire possible relationships between electronegativity, bulkiness, stereoselectivity, and reactivity. Therefore, we obtained a series of glycosyl donors equipped with all positional isomers of chlorinated and brominated 6-*O*-benzoyl group (glycosyl donors **1e**—**j**) (Scheme 4, Table 3). It should be noted that in all cases faster reactions and higher α-stereoselectivity were observed in high dilution experiments. Therefore, only these experiments are presented in Table 3 and more detail (including experiments

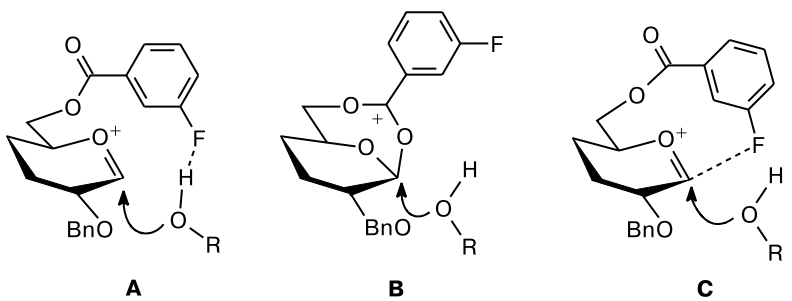
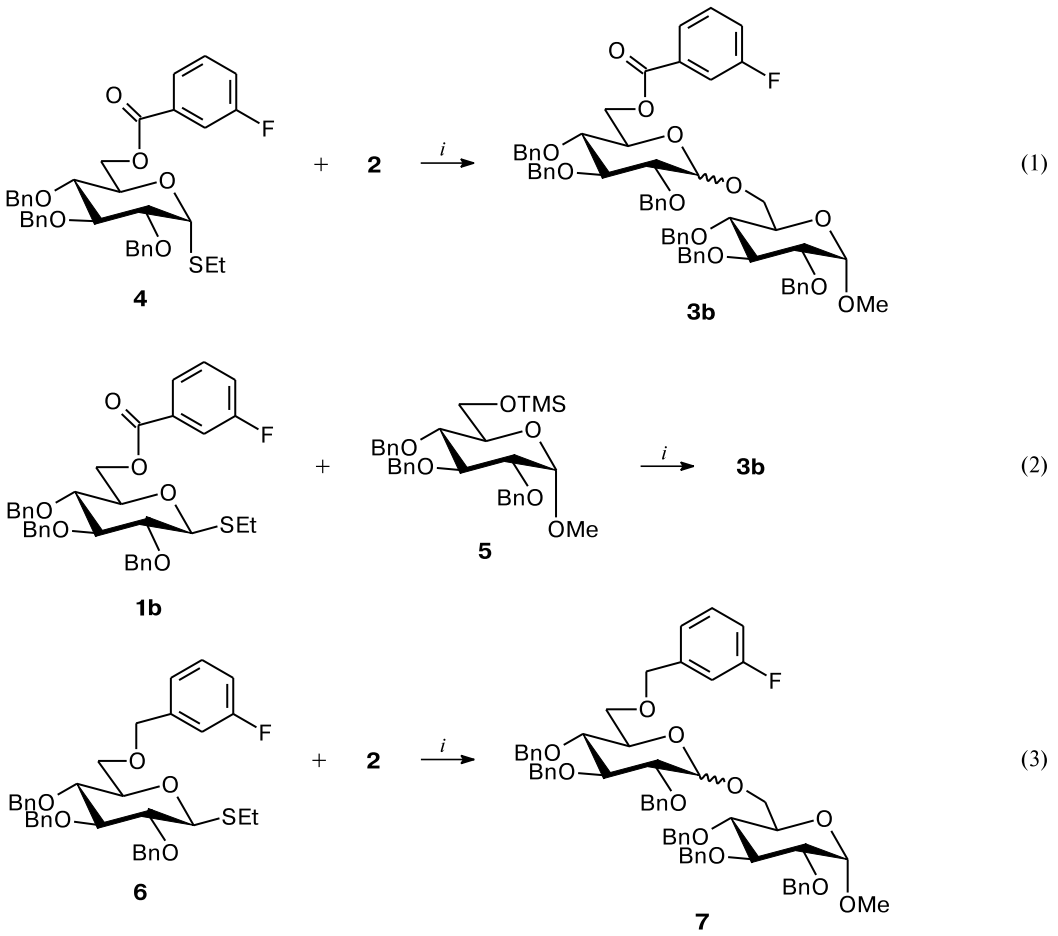


Fig. 1. Possible modes of action of 6-*O*-fluorobenzoyl group in glycosylation.

Scheme 3



Reagents and conditions: *i*. promoter (see Table 2), 1,2-dichloroethane, molecular sieves 4 Å, −30 °C→20 °C.

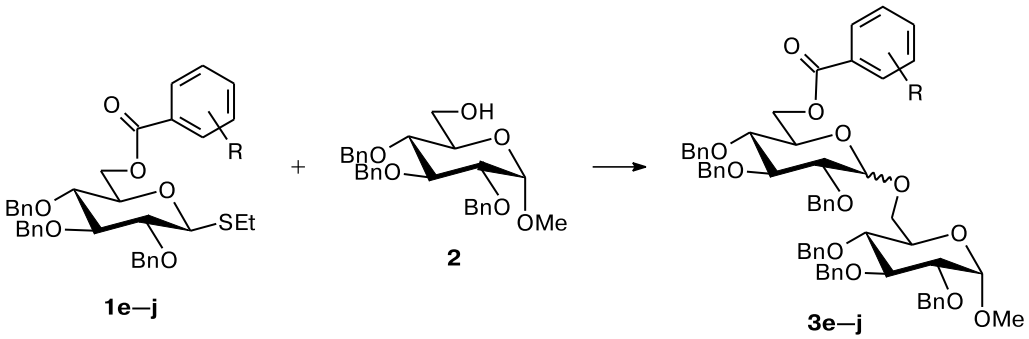
under regular conditions) is given in Experimental. Thus, glycosidation of 6-*O*-(2-chlorobenzoyl) glycosyl donor **1e** with glycosyl acceptor **2** gave good α-selectivity and the corresponding disaccharide **3e** was isolated in 95% yield with α : β = 6.9 : 1 (see Table 3, entry *18*). Similarly, 3- (**1f**) and 4-chlorobenzoylated (**1g**) glycosyl donors gave high α-selectivity and excellent yields (yields of 91 and 90%, α : β = 7.3 : 1 and 6.0 : 1, respectively; see entries *19* and *20*, respectively). A very similar set of results was obtained with a series of bromobenzoyl derivatives (entries *21—23*). The results in Tables 1 and 3 indicate that the presence of a halogen in the benzoyl ring at O(6) has a profound effect on the donor reactivity in comparison to that of 6-*O*-benzoylated counterpart. However, the nature of the halogen and even its position on the benzoyl ring has practically effect on neither the stereoselectivity nor reactivity.

Table 2. Probing the glycosylation mechanism*

Entry	Glycosyl donor	Donor concentration /mmol L^{-1}	Glycosyl acceptor	Promoter	*t*/h	Product	Yield (%) (α : β)
13	**4**	5	**2**	DMTST	4	**3b**	98 (5.8 : 1)
14	**1b**	5	**5**	NIS/TfOH	2.5	**3b**	90 (9.0 : 1)
15	**1b**	5	**5**	DMTST	8	**3b**	70 (5.7 : 1)
16	**6**	5	**2**	DMTST	3	**7**	61 (1.2 : 1)
17	**6**	50	**2**	DMTST	4.5	**7**	85 (1 : 1.3)

* Reaction conditions: 1,2-dichloroethane, molecular sieves 4 Å, −30 °C→20 °C.

Scheme 4



R = 2-Cl (**e**), 3-Cl (**f**), 4-Cl (**g**), 2-Br (**h**), 3-Br (**i**), 4-Br (**j**)

Reagents and conditions: DMTST, 1,2-dichloroethane, molecular sieves 4 Å, −30 °C→20 °C.

To diversify this further, we investigated the effect of halobenzoyl group at O(4) on glycosylation (Scheme 5). For this purpose, we obtained a range of glycosyl donors **8a**—**f** (the key results are summarized in Table 4). Again, faster reactions and higher stereoselectivities were observed in high dilution experiments. All of the 4-*O*-halobenzoyl glycosyl donors **8a**—**e** showed insignificant β-selectivity: α : β ratio range from 1 : 1.4 to 1 : 2.7 (see Table 4, entries *24*—*28*). Note that 4-*O*-benzoyl glycosyl donor **8f**[22] gave stereoselectivity (entry *29*) comparable with halobenzoyl glycosyl donors **8a**—**e**, yet much slower reaction.

Table 3. 6-*O*-Halobenzoyl (**1e**—**g**) and 6-*O*-bromobenzoyl (**1h**—**j**) glycosyl donors in glycosylation of glycosyl acceptor **2***

Entry	Glycosyl donor	*t*/h	Product	Yield (%) (α : β)
18	**1e**	9	**3e**	95 (6.9 : 1)
19	**1f**	6	**3f**	91 (7.3 : 1)
20	**1g**	6	**3g**	90 (6.0 : 1)
21	**1h**	6	**3h**	96 (5.5 : 1)
22	**1i**	5	**3i**	87 (6.1 : 1)
23	**1j**	4	**3j**	96 (7.9 : 1)

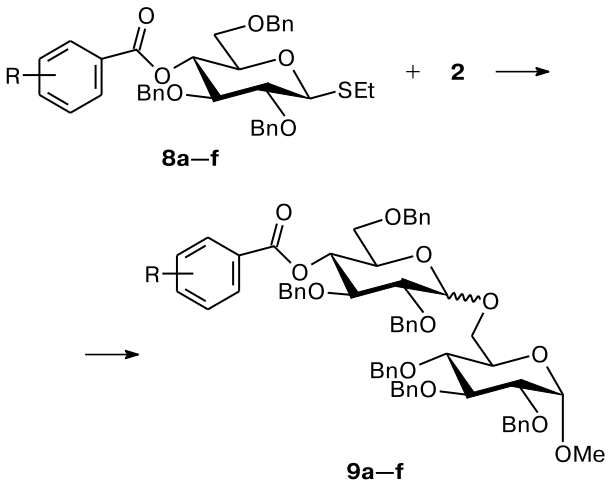
* Concentration of glycosyl donor is 5 mmol L^{-1}.

Table 4. 4-*O*-Halobenzoyl glycosyl donors **8a**—**f** in glycosylation of glycosyl acceptor **2***

Entry	Glycosyl donor	*t*/h	Product	Yield (%) (α : β)
24	**8a**	6	**9a**	98 (1 : 1.4)
25	**8b**	6	**9b**	81 (1 : 2.4)
26	**8c**	5	**9c**	83 (1 : 2.0)
27	**8d**	6	**9d**	75 (1 : 2.7)
28	**8e**	4	**9e**	95 (1 : 2.5)
*29***	**8f**	72	**9f**	64 (1 : 3.0)

* Concentration of glycosyl donor is 5 mmol L^{-1}.
** Incomplete reaction.

Scheme 5



R = 2-F (**a**), 3-F (**b**), 4-F (**c**), 2-Br (**d**), 3-Br (**e**), H (**f**)

Reagents and conditions: DMTST, 1,2-dichloroethane, molecular sieves 4 Å, −30 °C→20 °C.

In conclusion, we observed a very unusual effect of halobenzoyl substituents on the reactivity and stereoselectivity of thioglucosyl donors. The effect varies drastically from the expected disarming effect of electron-withdrawing substituents that would be expected less reactive in glycosylations. We already performed a variety of mechanistic experiments and ruled out the involvement of HAD in enhancing the reactivity and controlling the stereoselectivity. Further studies to elucidate the exact nature of this unusual participation of halobenzoyl substituents in glycosylation are currently underway in our laboratory.

Experimental

The reactions were performed using commercial reagents (Aldrich or Acros) and the ACS grade solvents were purified and dried according to standard procedures. Column chromatography was performed on silica gel 60 (EM Science, 70—230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254} (EM Science). The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40 °C. Dichloromethane and 1,2-dichloroethane were distilled from CaH_2 directly prior to application. Molecular sieves (4 Å), used for reactions, were crushed and activated *in vacuo* at 390 °C during 8 h in the first instance and then for 2—3 h at 390 °C directly prior to application. Optical rotations were measured at Jasco P-1020 polarimeter. ^{1}H NMR spectra were recorded at 300 MHz (Bruker Avance 300), ^{13}C NMR spectra were recorded at 75 MHz (Bruker Avance 300) or at 125 MHz (Bruker ARX-500) in $CDCl_3$. The ^{1}H chemical shifts are referenced to the residual solvent signal ($CHCl_3$, δ_H 7.27) and the ^{13}C chemical shifts are referenced to the central signal of $CDCl_3$ (δ_C 77.23). High resolution fast-atom bombardment (FAB) mass spectrometry were made with the a JMS-700 (JEOL MStation).

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-fluorobenzoyl)-1-thio-β-D-glucopyranoside (1a). 2-Fluorobenzoic acid (112 mg, 0.80 mmol), 3-(3-dimethylaminopropyl)-1-ethylcarbodiimide hydrochloride (EDC) (115 mg, 0.60 mmol), and DMAP (12 mg, 0.10 mmol) were added to a stirred solution of ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**10**)[23] (200 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~50 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL) and water (2×10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1a** as a white amorphous solid (226 mg, 92%). R_f 0.70 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +21.6 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, $SC\underline{H}_2CH_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 8.8 Hz); 3.55 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.7 Hz); 4.34 (dd, 1 H, H(6a), $J_{5,6a}$ = = 4.8 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.52 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.5 Hz); 4.70 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.7 Hz); 4.79 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.9 Hz); 7.02—7.32 (m, 17 H, aromatic); 7.43 (m, 1 H, aromatic); 7.84 (dd, 1 H, aromatic, J = 7.6 Hz). ^{13}C NMR, δ: 15.3, 25.1, 64.2, 75.3, 75.7, 79.1, 77.1, 77.8, 81.9, 85.2, 86.8, 117.0, 117.3, 118.6, 118.7, 124.1, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 132.4, 134.8, 134.9, 137.8, 138.0, 138.5, 164.3. MS (FAB), *m/z*: 639.2196 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-fluorobenzoyl)-1-thio-β-D-glucopyranoside (1b). 3-Fluorobenzoic acid (283 mg, 2.02 mmol), EDC (291 mg, 1.52 mmol), and DMAP (24 mg, 0.20 mmol) were added to a stirred solution of compound **10** (500 mg, 1.01 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1b** as a white amorphous solid (561 mg, 90%). R_f 0.70 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{26}$ +35.9 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, $SC\underline{H}_2CH_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 8.7 Hz); 3.55 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.8 Hz); 4.34 (dd, 1 H, H(6a), $J_{5,6a}$ = = 5.0 Hz, $J_{6a,6b}$ = 12.0 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.52 (dd, 1 H, H(6b), $J_{5,6b}$ = 2.6 Hz); 4.69 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 11.8 Hz); 4.79 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.1 Hz); 7.16—7.35 (m, 17 H, aromatic); 7.61 (dd, 1 H, aromatic, J = 9.3 Hz); 7.74 (dd, 1 H, aromatic, J = 6.6 Hz). ^{13}C NMR, δ: 15.4, 25.3, 64.3, 75.4, 75.8, 76.1, 77.1, 77.9, 81.9, 85.3, 86.8, 116.6, 116.9, 120.2, 120.5, 125.6, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.2, 132.2, 132.3, 137.7, 138.0, 138.4, 164.3. MS (FAB), *m/z*: 639.2183 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(4-fluorobenzoyl)-1-thio-β-D-glucopyranoside (1c). 4-Fluorobenzoic acid (170 mg, 1.21 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg, 0.61 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1c** as a white amorphous solid (351 mg, 94%). R_f 0.70 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{26}$ +48.2 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, $SC\underline{H}_2CH_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 9.1 Hz); 3.58 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.7 Hz); 4.35 (dd, 1 H, H(6a), $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 10.8 Hz); 4.52 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.5 Hz); 4.68 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.79 (dd, 2 H, CH_2Ph, ^2J = = 10.2 Hz); 4.87 (dd, 2 H, $C\underline{H}_2$Ph, ^2J = 10.2 Hz); 7.04 (dd, 2 H, aromatic, J = 8.7 Hz); 7.16—7.35 (m, 15 H, aromatic); 7.96 (dd, 2 H, aromatic, J = 5.5 aromatic). ^{13}C NMR, δ: 15.3, 25.3, 64.1, 75.4, 75.8, 76.1, 77.2, 77.4, 77.8, 81.9, 85.3, 86.8, 115.6, 115.9, 126.2, 126.4, 128.0, 128.1 (3 C), 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (2 C), 130.2, 132.3, 132.4, 137.7, 138.0, 138.4, 165.4. MS (FAB), *m/z*: 639.2187 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-chlorobenzoyl)-1-thio-β-D-glucopyranoside (1e). 2-Chlorobenzoic acid (190 mg, 1.22 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg, 0.61 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1e** as a white amorphous solid (345 mg, 90%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +19.0 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, $SC\underline{H}_2CH_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 8.8 Hz); 3.58 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.8 Hz);

4.38 (dd, 1 H, H(6a), $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.57 (dd, 1 H, H(6b), $J_{5,6b}$ = 2.0 Hz); 4.70 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 7.18—7.38 (m, 18 H, aromatic); 7.75 (dd, 1 H, aromatic, J = 8.2 Hz). ^{13}C NMR, δ: 15.3, 25.1, 64.4, 75.4, 75.7, 76.1, 77.1, 77.8, 81.9, 85.2, 86.8, 126.7, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (4 C), 129.8, 131.3, 131.9, 132.9, 134.1, 137.7, 138.0, 138.4, 165.4. MS (FAB), *m/z*: 655.1892 $[M + Na]^+$. Calculated for $C_{36}H_{37}ClO_6SNa$: 655.1897.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-chlorobenzoyl)-1-thio-β-D-glucopyranoside (1f). 3-Chlorobenzoic acid (190 mg, 1.22 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg, 0.61 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1f** as a white amorphous solid (368 mg, 96%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{26}$ +43.4 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.24 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 9.0 Hz); 3.58 (m, 2 H, H(4), H(5)), 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.6 Hz); 4.32 (dd, 1 H, H(6a), $J_{5,6a}$ = 5.1 Hz, $J_{6a,6b}$ = 10.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.54 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.7 Hz); 4.69 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 7.16—7.34 (m, 16 H, aromatic); 7.46 (dd, 1 H, aromatic, J = 8.0 Hz); 7.83 (dd, 1 H, aromatic, J = 7.8 Hz); 7.90 (dd, 1 H, aromatic, J = 1.8 Hz). ^{13}C NMR, δ: 15.4, 25.3, 64.4, 75.3, 75.8, 76.1, 77.1, 77.8, 81.9, 85.3, 86.8, 127.9, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (4 C), 129.8 (2 C), 131.8, 133.3, 134.6, 137.6, 137.9, 138.4, 165.4. MS (FAB), *m/z*: 655.1887 $[M + Na]^+$. Calculated for $C_{36}H_{37}ClO_6SNa$: 655.1897.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(4-chlorobenzoyl)-1-thio-β-D-glucopyranoside (1g). 4-Chlorobenzoic acid (190 mg, 1.22 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg, 0.61 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1g** as a white amorphous solid (377 mg, 98%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +30.5 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 8.8 Hz); 3.57 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.7 Hz); 4.35 (dd, 1 H, H(6a), $J_{5,6a}$ = 4.7 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.53 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.5 Hz); 4.68 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.1 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 7.18—7.35 (m, 17 H, aromatic); 7.87 (dd, 1 H, aromatic, J = 6.8 Hz). ^{13}C NMR, δ: 15.4, 25.3, 64.2, 75.3, 75.8, 76.1, 77.1, 77.8, 81.9, 85.3, 86.8, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.5 (3 C), 128.6 (2 C), 128.7 (4 C), 128.9 (2 C), 131.2 (2 C), 137.6, 137.9, 138.4, 139.7, 165.4. MS (FAB), *m/z*: 655.1885 $[M + Na]^+$. Calculated for $C_{36}H_{37}ClO_6SNa$: 655.1897.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(2-bromobenzoyl)-1-thio-β-D-glucopyranoside (1h). 2-Bromobenzoic acid (243 mg, 1.21 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~70 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1h** as a white amorphous solid (383 mg, 93%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +19.8 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.23 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.41 (dd, 1 H, H(2), $J_{2,3}$ = 8.8 Hz); 3.58 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.8 Hz); 4.38 (dd, 1 H, H(6a), $J_{5,6a}$ = 4.9 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.45 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.57 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.7 Hz); 4.70 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.7 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 7.20—7.32 (m, 17 H, aromatic); 7.61 (m, 1 H, aromatic); 7.73 (m, 1 H, aromatic). ^{13}C NMR, δ: 15.3, 25.2, 64.5, 75.4, 75.7, 76.1, 77.1, 77.9, 81.9, 85.2, 86.8, 122.1, 127.3, 127.9, 128.0 (2 C), 128.1, 128.2, 128.3 (2 C), 128.5 (2 C), 128.6 (2 C), 128.7 (4 C), 131.7, 131.8, 131.9, 132.9, 134.6, 137.7, 138.0, 138.4, 165.4. MS (FAB), *m/z*: 699.1390 $[M + Na]^+$. Calculated for $C_{36}H_{37}BrO_6SNa$: 699.1391.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-bromobenzoyl)-1-thio-β-D-glucopyranoside (1i). 3-Bromobenzoic acid (406 mg, 2.02 mmol), EDC (291 mg, 1.52 mmol), and DMAP (24 mg, 0.20 mmol) were added to a stirred solution of compound **10** (500 mg, 1.01 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1i** as a white amorphous solid (619 mg, 91%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +34.8 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.24 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.43 (dd, 1 H, H(2), $J_{2,3}$ = 9.2 Hz); 3.56 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.6 Hz); 4.31 (dd, 1 H, H(6a), $J_{5,6a}$ = = 5.3 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.46 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.53 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.8 Hz); 4.68 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.9 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.7 Hz); 7.17—7.34 (m, 16 H, aromatic); 7.62 (d, 1 H, aromatic, J = 8.1 Hz); 7.87 (d, 1 H, aromatic, J = 7.8 Hz); 7.87 (d, 1 H, aromatic, J = 1.5 Hz). ^{13}C NMR, δ: 15.4, 25.3, 64.4, 75.3, 75.8, 76.1, 77.1, 77.8, 81.9, 85.3, 86.8, 122.6, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (4 C), 130.1, 131.9, 132.8, 136.2, 137.6, 138.0, 138.3, 165.4. MS (FAB), *m/z*: 699.1380 $[M + Na]^+$. Calculated for $C_{36}H_{37}BrO_6SNa$: 699.1391.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(4-bromobenzoyl)-1-thio-β-D-glucopyranoside (1j). 4-Bromobenzoic acid (243 mg, 1.21 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **10** (300 mg,

0.61 mmol) in CH_2Cl_2 (15 ml) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~70 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **1j** as a white amorphous solid (405 mg, 99%). R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +28.6 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.22 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.68 (m, 2 H, $SC\underline{H}_2CH_3$); 3.42 (dd, 1 H, H(2), $J_{2,3}$ = 8.9 Hz); 3.57 (m, 2 H, H(4), H(5)); 3.69 (dd, 1 H, H(3), $J_{3,4}$ = 8.8 Hz); 4.34 (dd, 1 H, H(6a), $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 11.9 Hz); 4.45 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.53 (dd, 1 H, H(6b), $J_{5,6b}$ = 1.3 Hz); 4.68 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.86 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 7.17—7.34 (m, 16 H, aromatic); 7.62 (d, 2 H, aromatic, J = 8.6 Hz); 7.87 (d, 1 H, aromatic, J = 8.5 Hz). ^{13}C NMR, δ: 15.4, 25.3, 64.2, 75.3, 75.8, 76.1, 77.1, 77.8, 81.9, 85.3, 86.8, 128.0 (3 C), 128.1, 128.2, 128.3 (2 C), 128.4, 128.5 (2 C), 128.6 (2 C), 128.7 (4 C), 128.9, 131.4 (2 C), 131.8 (2 C), 137.6, 138.0, 138.4, 165.4. MS (FAB), *m/z*: 699.1385 $[M + Na]^+$. Calculated for $C_{36}H_{37}BrO_6SNa$: 699.1391.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-fluorobenzoyl)-1-thio-α-D-glucopyranoside (4). 3-Fluorobenzoic acid (102 mg, 0.73 mmol), EDC (104 mg, 0.54 mmol), and DMAP (12 mg, 0.10 mmol) were added to a stirred solution of ethyl-2,3,4-tri-*O*-benzyl-1-thio-α-D-glucopyranoside[24] (180 mg, 0.36 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **4** as a white amorphous solid (211 mg, 95%). R_f 0.80 (ethyl acetate—hexane, 2 : 3, (v/v)), $[\alpha]_D^{27}$ +131.4 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.26 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.48 (m, 2 H, $SC\underline{H}_2CH_3$); 3.57 (dd, 1 H, H(2), $J_{4,5}$ = 9.0 Hz); 3.86 (dd, 2 H, H(2), $J_{2,3}$ = 9.5 Hz); 3.94 (dd, 1 H, H(3), $J_{3,4}$ = 9.3 Hz); 4.42 (dd, 1 H, H(5), $J_{5,6a}$ = 3.2 Hz, $J_{5,6b}$ = 6.7 Hz); 4.51 (m, 2 H, H(6a), H(6b)); 4.71 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.7 Hz); 4.77 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 4.91 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.8 Hz); 5.40 (d, 1 H, H(1), $J_{1,2}$ = = 5.3 Hz); 7.21—7.41 (m, 17 H, aromatic); 7.65 (d, 1 H, aromatic, J = 9.3 Hz); 7.77 (d, 1 H, aromatic, J = 7.6 Hz). ^{13}C NMR, δ: 14.9, 23.8, 64.1, 69.1, 72.5, 75.2, 76.0, 77.4, 79.8, 82.7, 83.0, 116.5, 116.8, 120.2, 120.4, 125.4, 125.5, 127.9, 128.0, 128.1, 128.2 (2 C), 128.3 (2 C), 128.6 (3 C), 128.7, 130.1, 130.2, 132.1, 132.2, 137.8, 137.9, 138.5, 165.2. MS (FAB), *m/z*: 639.2180 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,4-tri-*O*-benzyl-6-*O*-(3-fluorobenzyl)-1-thio-α-D-glucopyranoside (6). 3-Fluorobenzyl bromide (153 mg, 0.81 mmol) and NaH (60% dispersion in mineral oil, 49 mg, 1.20 mmol) were added to a solution of compound **10** (200 mg, 0.40 mmol) in DMF (5.0 mL) and the resulting mixture was stirred at room temperature for 3 h. The reaction mixture was quenched with ice-water (~5 mL), stirred for 30 min, and then extracted with ethyl acetate—diethyl ether (1 : 1 (v/v), 3×20 mL). The combined organic extract (~60 mL) was washed with cold water (3×10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **6** as a white amorphous solid (212 mg, 87%). R_f 0.78 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ +3.55 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.28 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.72 (m, 2 H, $SC\underline{H}_2CH_3$); 3.37—3.46 (m, 2 H, H(2), H(5), $J_{2,3}$ = 8.6 Hz); 3.52—3.72 (m, 4 H, H(3), H(4), H(6a), H(6b), $J_{3,4}$ = 8.9 Hz); 4.43 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.50 (br.s, 2 H, C$\underline{H}_2$Ph); 4.67 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 13.1 Hz); 4.79 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 4.85 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.9 Hz); 6.91 (m, 1 H, aromatic); 7.03 (m, 2 H, aromatic); 7.13—7.34 (m, 16 H, aromatic). ^{13}C NMR, δ 15.4, 25.2, 69.5, 72.7, 72.8, 75.3, 75.9, 78.1, 79.2, 81.9, 85.2, 86.8, 114.3, 114.4, 114.6, 114.7, 123.1, 127.8, 127.9 (2 C), 128.0 (2 C), 128.5 (2 C), 128.6 (4 C), 129.9, 130.1, 138.1 (2 C), 138.6, 141.0, 141.1, 161.5. MS (FAB), *m/z*: 625.2397 $[M + Na]^+$. Calculated for $C_{36}H_{39}FO_5SNa$: 625.2400.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-fluorobenzoyl)-1-thio-β-D-glucopyranoside (8a). 2-Fluorobenzoic acid (170 mg, 1.21 mmol), EDC (176 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**11**)[25] (300 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~75 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **8a** as a white amorphous solid (342 mg, 92%). R_f 0.75 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{26}$ −32.0 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.49 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.92 (m, 2 H, $SC\underline{H}_2CH_3$); 3.69 (dd, 1 H, H(2), $J_{2,3}$ = 9.0 Hz); 3.77 (m, 2 H, H(6a), H(6b)); 3.84 (dd, 1 H, H(5), $J_{5,6b}$ = 3.7 Hz); 3.93 (dd, 1 H, H(3), $J_{3,4}$ = 9.2 Hz); 4.63 (br.s, 2 H, C$\underline{H}_2$Ph); 4.69 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.87 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.2 Hz); 4.97 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 5.44 (dd, 2 H, C$\underline{H}_2$Ph, $J_{4,5}$ = 9.6 Hz); 7.19—7.53 (m, 17 H, aromatic); 7.62 (m, 1 H, aromatic); 7.91 (dd, 1 H, aromatic, J = 7.6 Hz). ^{13}C NMR, δ: 15.3, 25.3, 70.0, 71.8, 73.7, 75.6, 75.8, 77.7, 81.7, 83.9, 85.3, 117.0, 117.3, 118.3, 118.5, 124.1, 124.2, 127.6, 127.7, 127.8 (2 C), 128.0 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 132.4, 134.8, 134.9, 137.9, 138.0, 138.1, 163.5. MS (FAB), *m/z*: 639.2182 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3-fluorobenzoyl)-1-thio-β-D-glucopyranoside (8b). 3-Fluorobenzoic acid (170 mg, 1.21 mmol), EDC (176 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **11** (300 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~75 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **8b** as a white amorphous solid (326 mg, 87%). R_f 0.75 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{26}$ −50.8 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.43 (t, 3 H, $SCH_2C\underline{H}_3$, J = 7.4 Hz); 2.87 (m, 2 H, $SC\underline{H}_2CH_3$); 3.69 (dd, 1 H, H(2), H(6a), H(6b), $J_{2,3}$ = 8.9 Hz); 3.77 (dd, 1 H, H(5), $J_{5,6b}$ = 4.5 Hz); 3.85 (dd, 1 H, H(3), $J_{3,4}$ = 9.1 Hz); 4.53 (br.s, 2 H, C$\underline{H}_2$Ph); 4.63 (d, 1 H, H(1),

$J_{1,2}$ = 9.8 Hz); 4.78 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.3 Hz); 4.92 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 5.34 (dd, 1 H, H(4), $J_{4,5}$ = 9.6 Hz); 7.17—7.48 (m, 17 H, aromatic); 7.62 (dd, 1 H, aromatic, J = 9.3 Hz); 7.77 (dd, 1 H, aromatic, J = 7.7 Hz). ^{13}C NMR, δ: 15.3, 25.3, 70.0, 72.0, 73.7, 75.5, 75.8, 77.5, 81.8, 83.5, 85.3, 116.6, 116.9, 120.2, 120.5, 125.6, 127.7, 127.8 (2 C), 128.1 (2 C), 128.3 (2 C), 128.4 (2 C), 128.5 (2 C), 128.6 (2 C), 130.1, 130.2, 131.8, 131.9, 137.8, 137.9, 164.3. MS (FAB), m/z: 639.2197 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(4-fluorobenzoyl)-1-thio-β-D-glucopyranoside (8c). 4-Fluorobenzoic acid (170 mg, 1.21 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **11** (300 mg, 0.61 mmol) in CH_2Cl_2 (20 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~100 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL) and water (2×20 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **8c** as a white amorphous solid (344 mg, 92%). R_f 0.75 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ −42.8 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.43 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.87 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.64 (dd, 1 H, H(2), H(6a), H(6b), $J_{2,3}$ = = 8.9 Hz); 3.78 (dd, 1 H, H(5), $J_{5,6b}$ = 4.6 Hz); 3.85 (dd, 1 H, H(3), $J_{3,4}$ = 9.1 Hz); 4.53 (br.s, 2 H, C$\underline{H}_2$Ph); 4.63 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.77 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.3 Hz); 4.91 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 5.33 (dd, 1 H, H(4), $J_{4,5}$ = 9.7 Hz); 7.10—7.49 (m, 17 H, aromatic); 7.96—8.00 (m, 2 H, aromatic). ^{13}C NMR, δ: 15.3, 25.3, 70.1, 71.8, 73.7, 75.5, 75.8, 77.8, 81.8, 83.7, 85.3, 115.5, 115.8, 126.0 (3 C), 127.7, 127.8 (2 C), 128.1 (2 C), 128.2 (2 C), 128.4 (4 C), 128.5 (2 C), 128.6 (2 C), 132.4, 132.5, 137.9 (2 C), 137.9, 164.5. MS (FAB), m/z: 639.2183 $[M + Na]^+$. Calculated for $C_{36}H_{37}FO_6SNa$: 639.2192.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(2-bromobenzoyl)-1-thio-β-D-glucopyranoside (8d). 2-Bromobenzoic acid (245 mg, 1.22 mmol), EDC (175 mg, 0.92 mmol), and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **11** (300 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~70 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane) to afford the title compound **8d** as a white amorphous solid (323 mg, 79%). R_f 0.71 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ −24.9 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.37 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.81 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.57 (dd, 1 H, H(2), $J_{2,3}$ = 8.9 Hz); 3.67—3.75 (m, 3 H, H(5), H(6a), H(6b)); 3.81 (dd, 1 H, H(3), $J_{3,4}$ = 9.1 Hz); 4.52 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.7 Hz); 4.57 (d, 1 H, H(1), $J_{1,2}$ = 9.7 Hz); 4.76 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.2 Hz); 4.85 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.2 Hz); 5.31 (dd, 1 H, H(4), $J_{4,5}$ = 9.6 Hz); 7.17—7.41 (m, 17 H, aromatic); 7.55 (dd, 1 H, aromatic, J = 7.6 Hz); 64 (dd, 1 H, aromatic, J = 7.9 Hz). ^{13}C NMR, δ: 15.3, 25.3, 70.2, 72.3, 73.8, 75.5, 75.7, 77.5, 81.7, 83.7, 85.3, 122.1, 127.3, 127.7, 127.8, 127.9 (2 C), 128.0 (2 C), 128.1, 128.4 (2 C), 128.5 (2 C), 128.6 (4 C), 131.6, 131.7, 132.9, 134.6, 137.9, 138.0, 138.1, 165.0. MS (FAB), m/z: 699.1398 $[M + Na]^+$. Calculated for $C_{36}H_{37}BrO_6SNa$: 699.1391.

Ethyl 2,3,6-tri-*O*-benzyl-4-*O*-(3-bromobenzoyl)-1-thio-β-D-glucopyranoside (8e). 3-Bromobenzoic acid (245 mg, 1.22 mmol), EDC (175 mg, 0.92 mmol) and DMAP (15 mg, 0.12 mmol) were added to a stirred solution of compound **11** (300 mg, 0.61 mmol) in CH_2Cl_2 (15 mL) and the resulting mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with CH_2Cl_2 (~70 mL) and washed with saturated aqueous $NaHCO_3$ (15 mL) and water (2×15 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel as described above to afford the title compound **8e** as a white amorphous solid (332 mg, 81%). R_f 0.71 (ethyl acetate—hexane, 2 : 3 (v/v)), $[\alpha]_D^{27}$ −50.1 (*c* 1, $CHCl_3$). ^{1}H NMR, δ: 1.43 (t, 3 H, SCH$_2$C$\underline{H}_3$, J = 7.4 Hz); 2.87 (m, 2 H, SC$\underline{H}_2$CH$_3$); 3.60—3.66 (m, 3 H, H(2), H(6a), H(6b), $J_{2,3}$ = 8.9 Hz); 3.76 (dd, 1 H, H(5), $J_{5,6a}$ = = 4.5 Hz); 3.84 (dd, 1 H, H(3), $J_{3,4}$ = 9.1 Hz); 4.52 (br.s, 2 H, C$\underline{H}_2$Ph); 4.63 (d, 1 H, H(1), $J_{1,2}$ = 9.8 Hz); 4.77 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 11.4 Hz); 4.92 (dd, 2 H, C$\underline{H}_2$Ph, ^2J = 10.4 Hz); 5.33 (dd, 1 H, H(4), $J_{4,5}$ = 9.7 Hz); 7.16—7.50 (m, 16 H, aromatic); 7.72—7.76 (m, 1 H, aromatic); 7.89 (dd, 1 H, aromatic, J = 7.8 Hz); 8.01 (m, 1 H, aromatic). ^{13}C NMR, δ: 15.3, 25.3, 70.0, 71.9, 73.7, 75.4, 75.8, 77.7, 81.9, 83.4, 85.3, 122.6, 127.7, 127.8 (3 C), 128.1, 128.2 (2 C), 128.4 (4 C), 128.5, 128.6 (4 C), 130.0, 131.7, 132.8, 136.2, 137.8, 137.9, 164.2. MS (FAB), m/z: 699.1383 $[M + Na]^+$. Calculated for $C_{36}H_{37}BrO_6SNa$: 699.1391.

Synthesis of disaccharides (general procedure). A mixture of a glycosyl donor (0.05 mmol), glycosyl acceptor (0.038 mmol), and freshly activated molecular sieves (4 Å, 200 mg) in 1,2-dichloroethane (1 mL for glycosyl donor concentration of 50 mmol L^{-1} or 10 mL for glycosyl donor concentration of 5 mmol L^{-1}) was stirred under argon for 1 h. The mixture was then cooled to −30 °C and promoter (DMTST (0.1 mmol) or IDCP (0.1 mmol) or mixtures NIS (0.1 mmol)—TfOH (0.01 mmol) or NIS (0.1 mmol)—TMSOTf (0.01 mmol) or NIS (0.1 mmol)—TESOTf (0.01 mmol), see Tables 1—4) was added. Cooling was removed and the resulting mixture was allowed to warm to room temperature. Upon completion, the solid was filtered off and successively washed with CH_2Cl_2. The combined filtrate (~30—40 mL) was washed with saturated aqueous $Na_2S_2O_3$ (10 mL) and water (3×10 mL). The organic phase was separated, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient elution with ethyl acetate—hexane). Anomeric ratios (or anomeric purity) were determined by comparison of the integral intensities of relevant signals in ^{1}H NMR spectra.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(2-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3a) was obtained as a colorless syrup from glycosyl donor **1a** and glycosyl acceptor **2** in the presence of DMTST. Yields and anomeric ratios are given in Table 1 (entries *1* and *2*). R_f 0.64 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), m/z: 1041.4193 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(3-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3b) was obtained as a colorless syrup from glycosyl donor **1b** and glycosyl acceptor **2** in the presence of various promoters. Yields and anomeric ratios obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 1 (entries *3*, *4*, *9—12*) and Table 2 (entries *13* (using glycosyl donor **4**), *14*, and *15*). Under regular concentration reaction conditions (50 mmol L^{-1})

following yields and anomeric ratios were achieved: 92%, $\alpha:\beta = 1.3:1$ in the presence of IDCP; 81%, $\alpha:\beta = 3.4:1$ in the presence of NIS/TfOH; 85%, $\alpha:\beta = 2.8:1$ in the presence of NIS/TMSOTf; 89%, $\alpha:\beta = 2.9:1$ in the presence of NIS/TESOTf. R_f 0.65 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1041.4200 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(4-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3c) was obtained as a colorless syrup from glycosyl donor **1c** and glycosyl acceptor **2** in the presence of DMTST. Yields and anomeric ratios are given in Table 1 (entries *5* and *6*). R_f 0.65 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1041.4103 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-benzoyl-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3d) was obtained as a colorless syrup from glycosyl donor **1d** and glycosyl acceptor **2** in the presence of DMTST.[22] Yields and anomeric ratios are given in Table 1 (entries *7* and *8*).

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(2-chlorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyde (3e) was obtained as a colorless syrup from glycosyl donor **1e** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *18*). Under regular concentration reaction conditions (50 mmol L^{-1}) following yield and anomeric ratio were achieved: 92%, $\alpha:\beta = 2.8:1$. R_f 0.64 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1057.3900 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}ClNa$: 1057.3906.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(3-chlorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3f) was obtained as a colorless syrup from glycosyl donor **1f** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *19*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 88%, $\alpha:\beta = 2.1:1$. R_f 0.64 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1057.3905 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}ClNa$: 1057.3906.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(4-chlorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3g) was obtained as a colorless syrup from glycosyl donor **1g** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *20*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 98%, $\alpha:\beta = 2.7:1$. R_f 0.64 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1057.3897 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}ClNa$: 1057.3906.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(2-bromobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3h) was obtained as a colorless syrup from glycosyl donor **1h** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *21*). Under regular concentration reaction conditions (50 mmol L^{-1}) following yield and anomeric ratio were achieved: 72%, $\alpha:\beta = 2.8:1$. R_f 0.63 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1101.3407 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}BrNa$: 1101.3401.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(3-bromobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3i) was obtained as a colorless syrup from glycosyl donor **1i** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *22*). Under regular concentration reaction conditions (50 mmol L^{-1}) following yield and anomeric ratio were achieved: 96%, $\alpha:\beta = 2.6:1$. R_f 0.63 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1101.3400 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}BrNa$: 1101.3401.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(4-bromobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3j) was obtained as a colorless syrup from glycosyl donor **1j** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 3 (entry *23*). Under regular concentration reaction conditions (50 mmol L^{-1}) following yield and anomeric ratio were achieved: 96%, $\alpha:\beta = 3.3:1$. R_f 0.63 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1101.3395 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}BrNa$: 1101.3401.

Methyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-(3-fluorobenzyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (7) was obtained as a colorless syrup from glycosyl donor **6** and glycosyl acceptor **2** in the presence of DMTST. Yields and anomeric ratios are given in Table 2 (entries *16* and *17*). R_f 0.72 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1027.4418 $[M + Na]^+$. Calculated for $C_{62}H_{65}O_{11}FNa$: 1027.4408.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-(2-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9a) was obtained as a colorless syrup from glycosyl donor **8a** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *24*). Under regular concentration reaction conditions (50 mmol L^{-1}) following yield and anomeric ratio were achieved: 96%, $\alpha:\beta = 1:1$. R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1041.4194 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-(3-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9b) was obtained as a colorless syrup from glycosyl donor **8b** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *25*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 51%, $\alpha:\beta = 1:1.6$. R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1041.4199 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-(4-fluorobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9c) was obtained as a colorless syrup from glycosyl donor **8c** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *26*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 96%, $\alpha:\beta = 1:1.6$. R_f 0.69 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1041.4189 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}FNa$: 1041.4201.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-(2-bromobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9d) was obtained as a colorless syrup from glycosyl donor **8d** and glycosyl acceptor **2** in the presence of DMTST. Yield and ano-

meric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *27*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 53%, $\alpha : \beta = 1 : 2.8$. R_f 0.67 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1101.3409 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}BrNa$: 1101.3401.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-(3-bromobenzoyl)-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9e) was obtained as a colorless syrup from glycosyl donor **8e** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *28*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 86%, $\alpha : \beta = 1 : 3.1$. R_f 0.67 (ethyl acetate—hexane, 2 : 3 (v/v)). MS (FAB), *m/z*: 1101.3402 $[M + Na]^+$. Calculated for $C_{62}H_{63}O_{12}BrNa$: 1101.3401.

Methyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-benzoyl-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (9f)[22] was obtained as a colorless syrup from glycosyl donor **8f** and glycosyl acceptor **2** in the presence of DMTST. Yield and anomeric ratio obtained under high dilution reaction conditions (5 mmol L^{-1}) are given in Table 4 (entry *29*). Under regular concentration reaction conditions (50 mmol L^{-1}) the following yield and anomeric ratio were achieved: 55%, $\alpha : \beta = 1 : 2.4$.

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