A Catalytic and Stereoselective Glycosylation with β-Glycosyl Fluorides

by **Teruaki Mukaiyama***, **Kazuya Takeuchi**, **Hideki Jona**, **Hisashi Maeshima**, and **Terunobu Saitoh**

Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162-8601

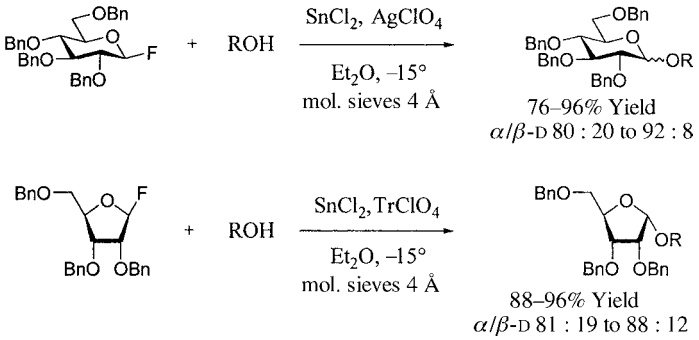
Dedicated to Prof. Dr. *Albert Eschenmoser* on the occasion of his 75th birthday

A catalytic and stereoselective glycosylation of several glycosyl acceptors with β-D-glycosyl fluoride was successfully performed in the presence of a catalytic amount of trityl tetrakis(pentafluorophenyl)borate ($TrB(C_6F_5)_4$) or trifluoromethanesulfonic acid (TfOH). When $TrB(C_6F_5)_4$ was used as a catalyst in the solvent pivalonitrile/(trifluoromethyl)benzene 1:5, the glycosylation proceeded smoothly to afford the glycosides in high yields with high β-D-stereoselectivities (see *Table 3*). Further, the glycosylation by the armed-disarmed strategy in the presence of this catalyst was established (see *Table 4*). Similarly, glycosylation catalyzed by the strong protic acid TfOH afforded the corresponding β-D-glycosides in good-to-excellent yields on treating β-D-glycosyl fluorides having a 2-*O*-benzoyl group with various glycosyl acceptors including thioglycosides (see *Tables 6* and *7*).

1. Introduction. – The development of stereoselective glycosylation reactions is one of the most fundamental topics in carbohydrate chemistry. Among the syntheses of glycosides including oligosaccharides, the *König-Knorr* reaction was commonly employed for a long time; however, the problematic use of a stoichiometric amount of heavy-metal salt or the unfavorably drastic reaction conditions have not yet been eluded. In the last 20 years, various types of superb glycosyl donors combined with activators have been developed [1] for the use in the classical *König-Knorr*-type reaction, and the following glycosyl donors were efficiently employed in the synthesis of saccharide chains: thioglycosides, glycosyl sulfoxides, glycosyl trichloroacetimidates, glycosyl phosphites, glycosyl phosphates, or other glycosyl donors having P-containing leaving groups, and pentenyl glycosides. In 1981, it was found in our laboratory that α-D-glycosides could be prepared with high stereoselectivities on treating β-D-glycosyl fluorides with various hydroxy compounds, including glycosyl acceptors, in the presence of stannous chloride ($SnCl_2$)/silver perchlorate ($AgClO_4$) [2] or $SnCl_2$/trityl perchlorate ($TrClO_4$) [3] as catalysts (*Scheme 1*). Glycosyl fluorides having a strong C–F bond are more stable donors than the corresponding chlorides or bromides due to their high bond-dissociation energy (C–F: 552/kJ · mol^{-1}, C–Cl: 397 ± 29/kJ · mol^{-1}, C–Br: 280 ± 21/kJ · mol^{-1}) [4]. On the other hand, glycosyl fluorides are efficiently activated by the above-mentioned combined-catalyst systems. Preparative methods involving glycosyl fluorides combined with suitable activators were widely studied by many research groups [5]. Activators such as SiF_4 [6], Me_3SiOTf [6], TiF_4 [7], $BF_3 \cdot OEt_2$ [8], Tf_2O [9], $[MCl_2(Cp)_2]/AgClO_4$ (M = Ti, Zr, Hf; cp = cyclopentadienyl) [10], $[GaClMe_2]$ [11], $Yb(OTf)_3$ [12], and $La(ClO_4)_3 \cdot n\,H_2O$ [13] promoted the glycosylation of various glycosyl acceptors and allowed the synthesis of many complex oligosac-

charide chains. Several examples involving activation of the glycosyl fluoride by a stoichiometric amount of the activator were studied; in comparison, only a few studies concerning catalytic glycosylation with glycosyl fluorides were reported [6][8][13]. And, to the best of our knowledge, a catalytic and stereoselective glycosylation of various free alcohols with glycosyl fluorides has not yet been reported.

Scheme 1



In the last decade, our interests were focused on developing catalytic and stereoselective glycosylations by choosing suitable combinations of glycosyl donors and catalysts. We already reported that several glycosyl donors such as 1-*O*-acylglycosides, sugars with a 1-OH or 1-*O*-$SiMe_3$ group, 1-*O*-(phenoxycarbonyl)glycosides, and thioglycoside could be activated in a catalytic manner [14]. In view of these results, the exploration of a useful method for the catalytic activation of glycosyl fluorides was undertaken, and the use of a catalytic amount of trityl tetrakis(pentafluorophenyl)borate ($TrB(C_6F_5)_4$) [15] or trifluoromethanesulfonic acid (TfOH) [16] was shown to activate the glycosyl fluorides efficiently, allowing the synthesis of the corresponding β-D-glycopyranosides in good yields with high stereoselectivities.

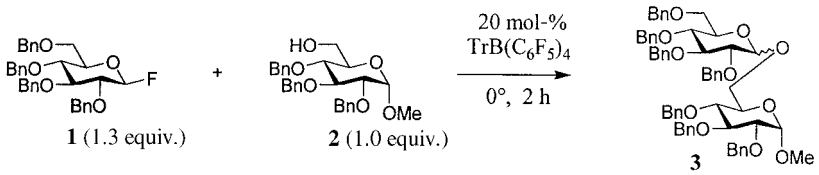
2. Results and Discussion. – 2.1. *Trityl Tetrakis(pentafluorophenyl)borate-Catalyzed Glycosylation with β-D-Glycosyl Fluorides.* Since our first report on the activation of 1-*O*-acetyl sugars by the triphenylcarbenium ion (trityl cation; Tr^+) in a catalytic manner [17], we focused our investigations on the effect of the counter anion of the trityl salt. Thus, $TrB(C_6F_5)_4$ turned out to work catalytically by activating, quite smoothly, various types of glycosyl donors such as sugars with a 1-OH group [18], glycosyl phenyl carbonates [19], and thioglycosides [20]. To establish further the usefulness of this catalyst, the catalytic activation of the anomeric C–F bond was now studied.

First, the effects of an added dehydrating agent, an additive, and of the solvent on the $TrB(C_6F_5)_4$-catalyzed glycosylation were examined in the model reaction of 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl fluoride (**1**) with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**) (*Table 1*). In the presence of 20 mol-% of $TrB(C_6F_5)_4$, the use of *Drierite* and pivalonitrile (^{t}BuCN) [20] apparently enhanced the rate of this reaction giving **3** (*Table 1*, *Entries 4* and *9*).

Table 1. *Effects of Dehydrating Agents and Solvents on the $TrB(C_6F_5)_4$-Catalyzed Glycosylation of* **2** *by* **1**[a])

Entry	Dehydrating agent[b])	Solvent	Yield/%	α/β-D[c])
1	molecular sieves 3 Å	CH_2Cl_2	41	49 : 51
2	molecular sieves 4 Å	CH_2Cl_2	9	–
3	molecular sieves 5 Å	CH_2Cl_2	38	50 : 50
4	*Drierite*	CH_2Cl_2	*42*	49 : 51
5	–	CH_2Cl_2	17	47 : 53
6	–	Et_2O	9	–
7	–	toluene	5	–
8	–	EtCN	51	13 : 87
9	–	^{t}BuCN/CH_2Cl_2 5 : 1	89	10 : 90

[a])



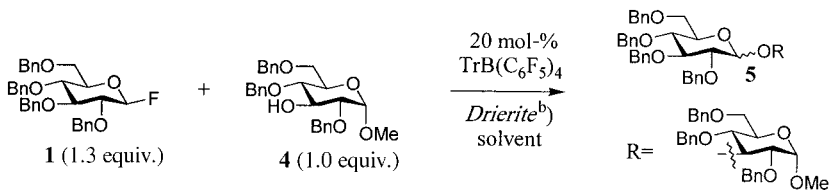
[b]) With 50 mg on a 0.1-mmol scale of the reaction. [c]) Ratio determined by HPLC analysis.

Next, to expand the applicability of this reaction, various solvent mixtures and reaction temperatures were examined in the reaction of **1** with methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**4**), the latter exhibiting lower nucleophilicity than **2** (*Table 2*). The β-D-selectivity was nearly the same when the ratio of pivalonitrile to CH_2Cl_2 was reduced from 5 : 1 to 1 : 10 (*Table 2*, *Entries 1* and *2*), while the yield of **5** increased when (trifluoromethyl)benzene ($PhCF_3$; 'benzotrifluoride') was used as a cosolvent for pivalonitrile. Recently, it was reported [21] that $PhCF_3$ is not only a useful alternative solvent for reactions currently conducted in CH_2Cl_2, but also is a

Table 2. *Effects of Solvents and Temperatures on the $TrB(C_6F_5)_4$-Catalyzed Glycosylation of* **4** *by* **1**[a])

Entry	Solvent	Temp./°	Time/h	Yield/%	α/β-D[c])
1	^{t}BuCN/CH_2Cl_2 5 : 1	0	4	80	17 : 83
2	^{t}BuCN/CH_2Cl_2 1 : 10	0	4	75	20 : 80
3	^{t}BuCN/toluene 1 : 10	0	4	90	17 : 83
4	^{t}BuCN/$PhCF_3$ 1 : 10	0	4	94	17 : 83
5	^{t}BuCN/$PhCF_3$ 1 : 5	0	4	95	18 : 82
6	^{t}BuCN/$PhCF_3$ 1 : 1	0	4	81	16 : 84
7	^{t}BuCN/$PhCF_3$ 1 : 5	– 10	14	93	9 : 91

[a])

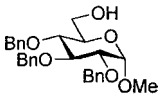
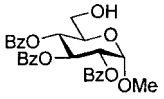
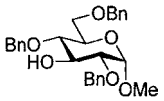
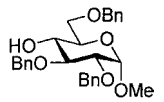


[b]) With 100 mg on a 0.1-mmol scale of the reaction. [c]) Ratio determined by HPLC analysis.

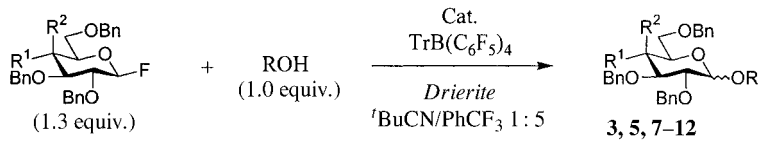
stable solvent with relatively low toxicity. When the reaction was carried out at $-10°$ for 14 h (*Table 2*, *Entry 7*), the stereoselectivity was further improved. Several examples using a catalytic amount of $TrB(C_6F_5)_4$ are listed in *Table 3*. In all cases, the desired β-D-gluco- and β-D-galactopyranosides **7**–**12** were obtained from **1** or **6** in good-to-high yields with high stereoselectivities.

In 1988, *Fraser-Reid* and co-workers introduced the so-called 'armed-disarmed' chemoselective glycosylation strategy; that is, a C(2)-ether-protected pentenyl glyco-

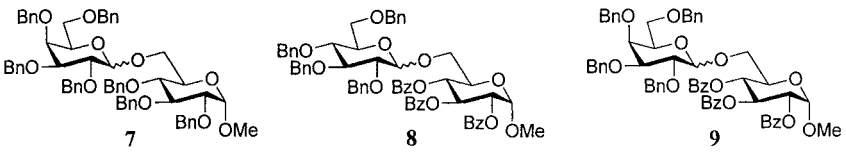
Table 3. *Syntheses of β-D-Gluco- and β-D-Galactopyranosides by $TrB(C_6F_5)_4$-Catalyzed Glycosylation of* **1** *or* **6**[a])

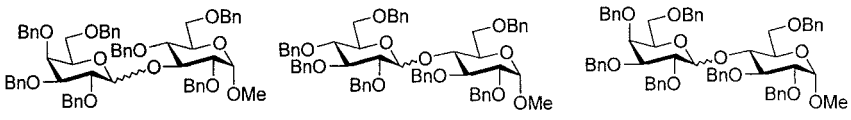
ROH	Donor	Cat./mol-%	Temp./°	Time/h	Product[b])	Yield/%	α/β-D[b])
	**1**	20	−10	4	**3**	91	3:97
	1	10	0	1.5	**3**	96	5:95
	6	20	−10	4	**7**	97	11:89
	**1**	20	−10	4	**8**	95	8:92
	1	10	0	1.5	**8**	95	11:89
	6	20	−10	4	**9**	89	18:82
	**1**	20	−10	14	**5**	93	9:91
	1	20	0	4	**5**	95	18:82
	6	20	−10	14	**10**	81	22:78
	6	20	−15	18	**10**	85	19:81
	**1**	20	−10	16	**11**	63	9:91
	1	20	0	6	**11**	82	16:84
	6	20	−10	17	**12**	70	28:72
	6	20	−15	24	**12**	71	23:77

[a])



1 R^1=BnO, R^2=H (Glc)
6 R^1=H, R^2=BnO (Gal)



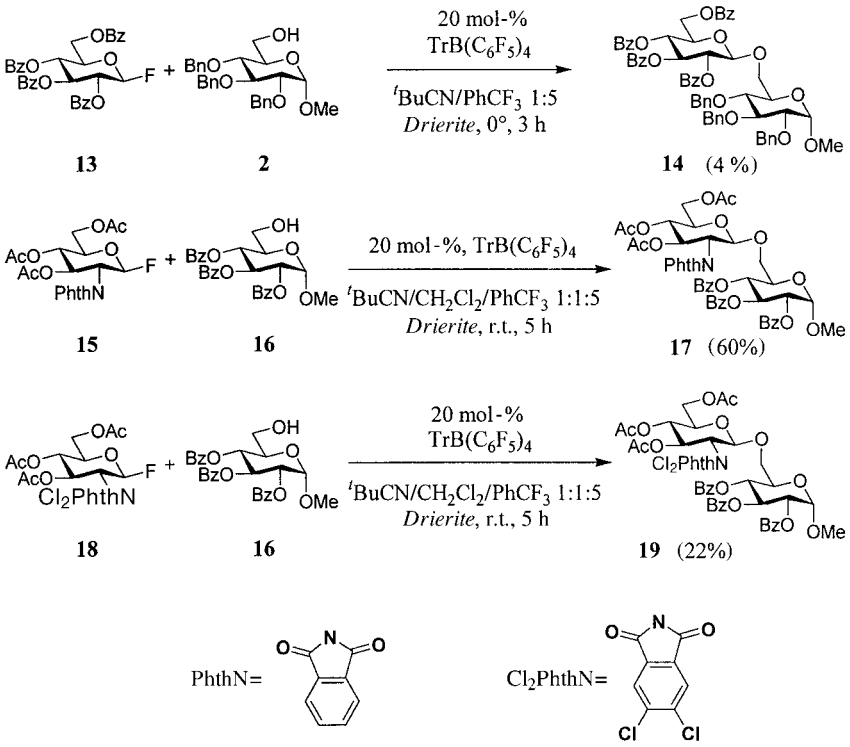


[b]) Ratio determined by HPLC analysis.

side was chemoselectively coupled with a benzoylated pentenyl glycoside [22]. Chemoselective glycosylations have also been developed for other types of glycosides, for example, thioglycosides, selenoglycosides, glycals, and 2,6-anhydro-2-thiosugars; as concerns glycosyl fluorides, it was firstly reported by *Castillon* and co-workers a chemoselective glycosylation with glycosyl fluorides by using $[HfCl_2(Cp)_2]/AgX$ (X = OTf, ClO_4) promoter system [23] to give the corresponding disaccharide in a good yield, and later, *Ley* and co-workers reported a successful chemoselective glycosylation based on their cyclic acetal protecting-group strategy [24].

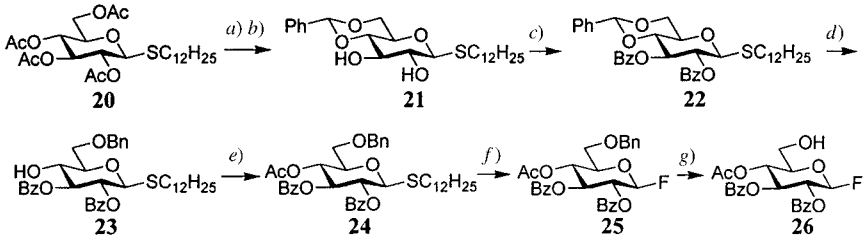
We decided to study the application of the $TrB(C_6F_5)_4$-catalyzed glycosylation reaction to the ordinary armed-disarmed glycosylation strategy. At first, the reactivities of several disarmed glycosyl fluorides were examined by applying the above glycosylation conditions to the reaction of the glycosyl fluorides **13**, **15**, and **18** with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**) or methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**16**) (*Scheme 2*). Thus, the reactivity of the disarmed glycosyl acceptor **2** dramatically decreased, and only 4% of the corresponding disaccharide **14** were obtained. Also, the reactivity of the glucosamine derivative **18** carrying a dichlorophthaloyl (Cl_2Phth) protecting group decreased compared to that of the corresponding phthaloyl (Phth) derivative **15**, furnishing **19** and **17** in 22 and 60% yield, respectively. These results indicate that the chemoselective glycosylation of glycosyl fluorides according to the armed-disarmed strategy is feasible. Subsequently, the

Scheme 2



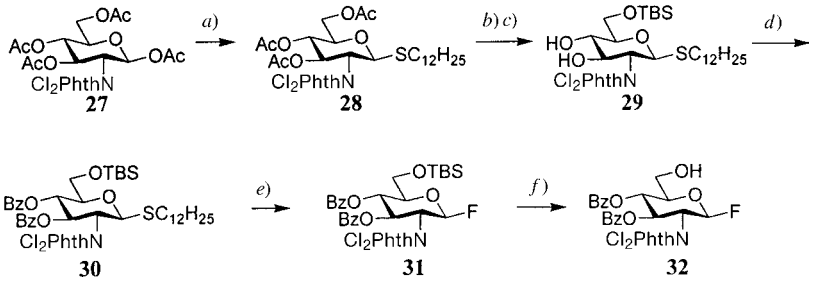
starting disarmed sugars **26**, **32**, and **37** were successfully prepared from **20** *via* **21**–**25**, from **27** *via* **28**–**31**, and from **28** *via* **33**–**36**, respectively, as shown in *Schemes 3*, *4*, and *5* (see *Exper. Part*). Indeed, chemoselective glycosylation proceeded when fluoride **1** (armed) and fluorides **26**, **32**, and **37** (disarmed) were used to afford the corresponding disaccharides **38**–**40** in high yields with high stereoselectivities (*Table 4*).

Scheme 3



a) Cat. NaOMe, CH_2Cl_2/MeOH. *b*) $PhCH(OMe)_2$, camphorsulfonic acid (CSA), DMF; 2 steps, 63%. *c*) BzCl, Py, cat. 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2; 89%. *d*) CF_3COOH, Et_3SiH, CH_2Cl_2; 61%. *e*) Ac_2O, Py, cat. DMAP, CH_2Cl_2; 96%. *f*) *N*-Bromosuccinimide (NBS), (diethylamino)sulfur trifluoride (DAST), CH_2Cl_2; 31%. *g*) H_2, 10% PdOH/C, CH_2Cl_2; 90%.

Scheme 4



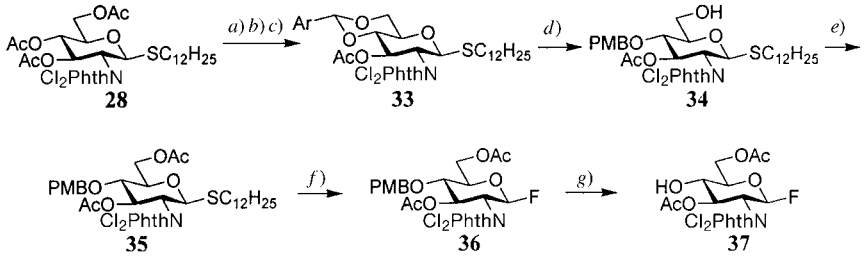
TBS = ^{t}BuMe$_2$Si; for Cl_2Phth, see *Scheme 2*

a) $BF_3 \cdot OEt_2$, $C_{12}H_{25}SH$, CH_2Cl_2; 84%. *b*) Cat. NaOMe, CH_2Cl_2/MeOH. *c*) ^{t}BuMe$_2$Si, 1*H*-imidazole, DMF, 2 steps; 70%. *d*) BzCl, Py, cat. DMAP, CH_2Cl_2; 99%. *e*) NBS, DAST, CH_2Cl_2; 92%. *f*) aq. HF soln./MeCN; 48%.

2.2. *Trifluoromethanesulfonic-Acid-Catalyzed Glycosylation with β-*D*-Glycosyl Fluorides.* On reviewing the methods of glycosylation by glycosyl fluorides, no reports on protic-acid activation could be found. Applying the concept of hard and soft acids and bases (HSAB) rules, however, the proton (H^+) is considered to be fluorophilic because of its hard character and should act as a catalyst for glycosylation by glycosyl fluoride. Indeed, glycosyl fluorides were activated by a catalytic amount of TfOH (5 mol-%), and *β*-D-glycopyranosides were obtained in good to excellent yields on treatment with several glycosyl acceptors.

First, 5 mol-% of protic-acid catalysts such as CF_3COOH, $MeSO_3H$, or TfOH were employed in the reaction of 2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl fluoride (**1**)

Scheme 5



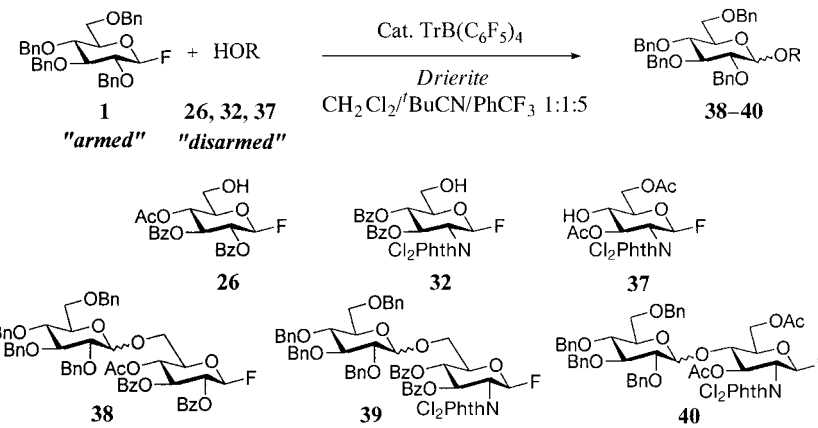
Ar = 4-MeOC$_6$H$_4$; PMB = 4-MeOC$_6$H$_4$CH$_2$; for Cl$_2$Phth, see *Scheme 2*

a) Cat. NaOMe, CH_2Cl_2/MeOH. *b*) *p*-Anisaldehyde dimethyl acetal, cat. CSA, DMF. *c*) Ac_2O, cat. DMAP, Py; 3 steps 50% (based on 59% conversion). *d*) $NaBH_3CN$, Me_3SiCl, THF/MeCN; 80%. *e*) Ac_2O, cat. DMAP, Py/CH_2Cl_2; 99%. *f*) NBS, DAST, CH_2Cl_2; 93%. *g*) DDQ, CH_2Cl_2/H_2O; 70%.

Table 4. *Chemoselective TrB(C$_6$F$_5$)$_4$-Catalyzed Glycosylation of Glycosyl Fluorides* **26**, **32**, *and* **37** *by* **1**[a])

Entry	Acceptor	Cat./mol-%	Temp./°	Time/h	Product	Yield/%	α/β-D[b])
1	**26**	20	0	3	**38**	80	17:83
2	**32**	10	−35 to −10°	21	**39**	86	9:91
3	**37**	10	−35 to −15°	15	**40**	84	8:92

[a])



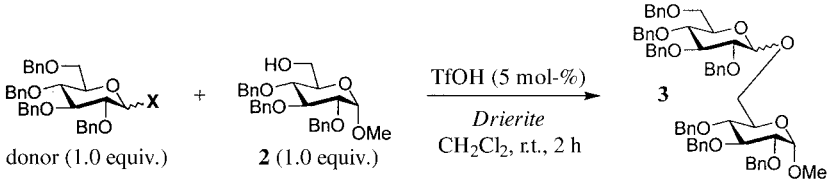
[b]) Ratio determined by HPLC analysis.

with methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**). TfOH efficiently accelerated the glycosylation by **1** in CH_2Cl_2 at room temperature to give 83% yield of the corresponding disaccharide (*Table 5*, *Entry 4*), while CF_3COOH and $MeSO_3H$ did not. Next, various donors that possess other types of leaving groups were examined under the same conditions to evaluate the suitability of the protic-acid-catalyzed glycosylation (*Table 5*). Interestingly, glycosyl bromide and chloride were not activated efficiently, in contrast to the glycosyl fluorides (*Table 5*, *Entries 1–4*). Glycosyl acetate and carbonate and the sugar with a 1-OH group (*Table 5*, *Entries 5–7*) reacted with acceptors and furnished the desired disaccharide **3** in moderate yields (not optimized). Since thioglycoside was not activated at all under the same conditions (*Table 5*,

Table 5. *TfOH-Catalyzed Glycosylation of* **2** *of by Various Glycosyl Donors*[a])

Entry	X	Yield/%	α/β-D[b])	*Entry*	X	Yield/%	α/β-D[b])
1	Br (α)	9	45 : 55	*5*	OH (mix)	51	73 : 27
2	Cl (α)	6	52 : 48	*6*	OAc (α)	75	68 : 32
3	F (α)	87	66 : 34	*7*	OCOOPh (β)	61	72 : 28
4	F (β)	83	67 : 33	*8*	SEt (β)	0	–

[a])



[b]) Ratios determined by HPLC analysis.

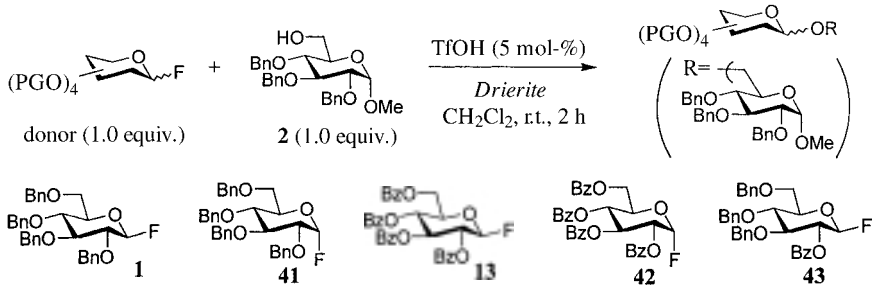
Entry 8), the present reaction should be applicable to the orthogonal glycosylation methodology (*vide infra*).

To study the influence of the protecting groups of the glycosyl donors, differently protected glycosyl fluorides were examined under the above reaction conditions (*Table 6*). Both armed sugars **1** and **41** (*Table 6*, *Entries 1* and *2*) reacted smoothly with **2** in the presence of 5 mol-% TfOH (see also *Table 5*), while disarmed sugars **13** and **42** gave poor results (*Table 6*, *Entries 3* and *4*). On the other hand, 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-protected glycosyl fluoride **43** [25] was efficiently activated and gave the corresponding glycoside stereoselectively in good yield (*Table 6*, *Entry 5*). Thus, the reactivity of the glycosyl fluoride increased drastically just by changing the 3,4,6-*O*-

Table 6. *TfOH-Catalyzed Glycosylation of* **2** *by Differently Protected Glycosyl Fluorides*[a])

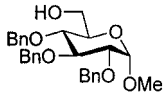
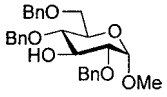
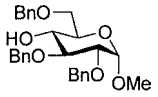
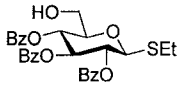
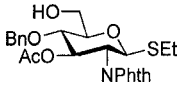
Entry	Donor	Product yield/%	α/β-D[b])
1	**1**	83 (for P6, see **1**)	67 : 33[b])
2	**41**	87 (for P6, see **1**)	66 : 34[b])
3	**13**	11 (for P6, see **13**)	β-D
4	**42**	0	–
5	**43**	80 (for P6, see **43**)	β-D
6[c])	**43**	97 (for P6, see **43**)	β-D

[a])

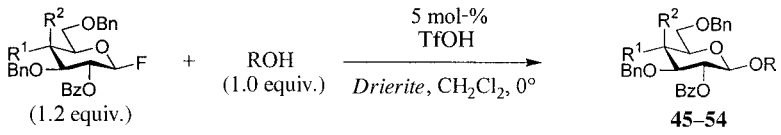


[b]) Ratio determined by HPLC analysis. [c]) With 1.2 equiv. of donor at 0° for 4 h.

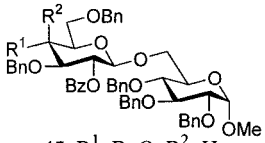
Table 7. *TfOH-Catalyzed β-D-Selective Glycosylation of Various Glycosyl Acceptors by Glycosyl Donors* **43** *and* **44**[a])

Entry	Acceptor (ROH)	Donor	Time/h	Product	Yield/%
1		**43**	4	**45**	97
		44	2.5	**46**	93
2		**43**	6	**47**	87
		44	9	**48**	87
3		**43**	18	**49**	67
		44	12	**50**	70
4		**43**	5	**51**	85
		44	1.5	**52**	81
5		**43**	8	**53**	81
		44	3.5	**54**	71

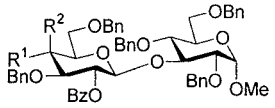
[a])



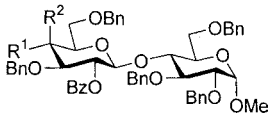
43 R^1=BnO, R^2=H (Glc)
44 R^1=H, R^2=BnO (Gal)



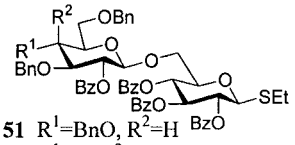
45 R^1=BnO, R^2=H
46 R^1=H, R^2=BnO



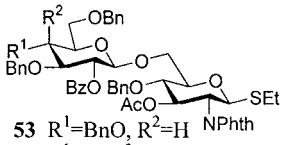
47 R^1=BnO, R^2=H
48 R^1=H, R^2=BnO



49 R^1=BnO, R^2=H
50 R^1=H, R^2=BnO



51 R^1=BnO, R^2=H
52 R^1=H, R^2=BnO



53 R^1=BnO, R^2=H
54 R^1=H, R^2=BnO

benzoyl protecting groups to benzyl ones [26] (*Table 6*, *Entries 4* and *5*). Also the neighboring-group participation worked well, resulting in a 1,2-*trans* glycosidic bond. Optimization of the reaction conditions (0°, 1.2 equiv. of donor **43**, 1 equiv. of acceptor **2**) raised the yield to 97% (*Entry 6*).

To illustrate further the efficiency of the TfOH-catalyzed glycosylation, several examples are summarized in *Table 7*. Indeed, glycosylation by the β-D-glucosyl fluoride **43** or the β-D-galactosyl fluoride **44** gave the corresponding disaccharides in good-to-excellent yields with β-D-configuration, as expected. It is remarkable that orthogonal glycosylation [27] with thioglycosides proceeded to give the disaccharides in good yields without damaging the thioglycosidic linkage at the reducing terminus (*Table 7*, *Entries 4* and *5*).

Thus, a catalytic and stereoselective glycosylation by the β-D-glycosyl fluorides **43** and **44** of several glycosyl acceptors was successfully carried out in the presence of 5 mol-% of TfOH furnishing the corresponding disaccharides in high yields with the expected stereoselectivitiy. It should be noted that the present reaction is the first example of an activation of the anomeric C–F bond by a catalytic amount of protic acid.

3. Conclusion. – A catalytic and β-D-selective glycosylation reaction with β-D-glycosyl fluorides was successfully carried out in the presence of a catalytic amount of trityl tetrakis(pentafluorophenyl)borate ($TrB(C_6F_5)_4$) or trifluoromethanesulfonic acid (TfOH). It is interesting to note that an α-D-selective glycosylation took place on treating a β-D-glycosyl fluoride with glycosyl acceptors in the presence of such combined activators as $SnCl_2/AgClO_4$ in Et_2O as solvent [2]. Thus, very convenient methods for the stereoselective preparation of both α- and β-D-glycosides are now established starting simply from β-D-glycosyl fluorides.

The present research is partially supported by *Grant-in-Aids for Scientific Research* from the Ministry of Education, Science, Sports, and Culture. We thank *Asahi Glass Engineering Co. Ltd.* for providing $TrB(C_6F_5)_4$ and Mr. *Ohsawa*, *Banyu Pharmaceutical Company*, for many mass-spectrometry analyses.

Experimental Part

General. All reactions were carried out under Ar in dried glassware, unless otherwise noted. CH_2Cl_2 and pivalonitrile were distilled from P_2O_5 and then from CaH_2 and dried (molecular sieves, 4 Å). Toluene and (trifluoromethyl)benzene were distilled from P_2O_5 and dried (molecular sieves, 4 Å). Dry THF and Et_2O were purchased from *Kanto Chemical*. Powdered and pre-dried (at 260°/0.1 Torr) molecular sieves 3 Å, 4 Å, and 5 Å were used in glycosylation reactions. Sufficiently crashed and pre-dried (at 260°/0.1 Torr) *Drierite* from *W. A. Hammond Drierite Company* was used in the glycosylations. All reagents were purchased from *Tokyo Kasei Kogyo*, *Kanto Chemical*, or *Aldrich* and used without further purification, unless otherwise noted. Column chromatography (CC): silica gel *60* (*Merck*) or *Wakogel B5F*. HPLC: *Hitachi LC-Organizer*, *L-4000* UV detector, *L-6200* intelligent pump, and *D-2500* chromato-integrator with *Shodex SIL-5B* (normal phase; 120 Å, 5 μm, 4.6 × 250 mm) and *YMC J'sphere M80* (reversed phase; 80 Å, 4 μm, 4.6 × 250 mm). M.p.: *Yanaco-MP-S3* micro melting-point apparatus. Optical rotations: *Jasco-DIP-360* or *Jasco-P-1020* digital polarimeter. IR Spectra: *Horiba-FT-300* infrared spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Jeol-JNM-EX300L*, *Jeol-JNM-LA-400*, and *Jeol-JNM-LA-500* FT-NMR spectrometers; $CDCl_3$ solns. with $SiMe_4$ and $CHCl_3$ as internal standard; δ in ppm, *J* in Hz. High-resolution MS: *Jeol-JMS-SX102A* instrument with 4-nitrobenzyl alcohol as matrix.

Glycosylation with Catalyst $TrB(C_6F_5)_4$: General Procedure (GP($TrB(C_6F_5)_4$)). To a stirred suspension of $TrB(C_6F_5)_4$ (18.5 mg, 0.02 mmol) and *Drierite* (100 mg) in $PhCF_3$/^{t}BuCN 5:1 (3.0 ml), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**2**; 46.5 mg, 0.10 mmol) and 2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl fluoride (**1**; 70.5 mg, 0.13 mmol) in $PhCF_3$/^{t}BuCN 5:1 (1.5 ml) were added successively at –10°. The mixture was stirred for 4 h at –10°. Then the reaction was quenched by adding sat. aq. $NaHCO_3$ soln. (10 ml). The mixture was filtered through *Celite* and extracted with CH_2Cl_2 (3×). The combined org. layer was washed with brine, dried (Na_2SO_4), and evaporated, and the resulting residue purified by prep. TLC (silica gel): *methyl 2,3,4-tri*-O-

benzyl-6-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*glucopyranosyl)*-α-D-glucopyranoside (**3**; 89.6 mg, 90.8%). The ratio was determined by HPLC (hexane/AcOEt): α/β-D 3:97. For data, see [28].

Methyl 2,4,6-Tri-O-*benzyl-3*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*glucopyranosyl)*-α-D-*glucopyranoside* (**5**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −10° for 14 h. Yield 93%, α/β-D 9:91. For data, see [29].

Methyl 2,3,4-Tri-O-*benzyl-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*galactopyranosyl)*-α-D-*glucopyranoside* (**7**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −10° for 14 h. Yield 97%, α/β-D 11:89. For data, see [30].

Methyl 2,3,4-Tri-O-*benzoyl-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*glucopyranosyl)*-α-D-*glucopyranoside* (**8**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −10° for 4 h. Yield 95%, α/β-D 8:92. For data, see [31].

Methyl 2,3,4-Tri-O-*benzoyl-6*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*galactopyranosyl)*-α-D-*glucopyranoside* (**9**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −10° for 4 h. Yield 89%, α/β-D 18:82. For data, see [31].

Methyl 2,4,6-Tri-O-*benzyl-3*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*galactopyranosyl)*-α-D-*glucopyranoside* (**10**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −15° for 18 h. Yield 85%, α/β-D 19:81.

Data of β-D-**10**: White crystals. M.p. 100–102°. $[\alpha]_D^{23} = +18.1$ ($c = 1.0$, $CHCl_3$). IR (KBr): 2916, 2870, 1458, 1365, 1157, 1072, 740, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.28 (*s*, 3 H); 3.45 (*dd*, *J* = 8.5, 4.9, 1 H); 3.49 (*dd*, *J* = 9.8, 3.7, 1 H); 3.52–3.74 (*m*, 7 H); 3.76 (*dd*, *J* = 9.4, 3.4, 1 H); 3.86 (*dd*, *J* = 9.5, 7.9, 1 H); 3.98–4.03 (*m*, 1 H); 4.30–4.38 (*m*, 4 H); 4.40 (*d*, *J* = 11.9, 1 H); 4.44 (*d*, *J* = 3.5, 1 H); 4.51 (*d*, *J* = 12.2, 1 H); 4.59 (*d*, *J* = 11.3, 1 H); 4.62–4.70 (*m*, 2 H); 4.77 (*d*, *J* = 12.2, 1 H); 4.80 (*d*, *J* = 12.2, 1 H); 4.93 (*d*, *J* = 11.6, 1 H); 4.96–5.07 (*m*, 2 H); 4.98 (*d*, *J* = 7.9, 1 H–C(1′)); 7.00–7.56 (*m*, 35 H). ^{13}C-NMR ($CDCl_3$): 55.0; 67.9; 68.5; 69.5; 72.6; 72.7; 73.4; 73.6; 73.8; 74.0; 74.8; 74.9; 75.2; 75.7; 80.3; 81.0; 82.5; 98.0; 102.7; 127.2; 127.3; 127.4; 127.6; 127.70; 127.74; 127.8; 127.9; 128.0; 128.1; 128.2; 128.30; 128.33; 128.36; 128.39; 128.9; 137.9; 138.0; 138.2; 138.7; 139.2. HR-MS: 1009.4495 ($C_{62}H_{66}NaO_{11}^+$, $[M+Na]^+$; calc. 1009.4503).

Methyl 2,3,6-Tri-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*glucopyranosyl)*-α-D-*glucopyranoside* (**11**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −10° for 16 h. Yield 63%, α/β-D 9:91. For data, see [28].

Methyl 2,3,6-Tri-O-*benzyl-4*-O-*(2,3,4,6-tetra*-O-*benzyl*-D-*galactopyranosyl)*-α-D-*glucopyranoside* (**12**). According to *GP (TrB(C$_6$F$_5$)$_4$)*, at −15° for 24 h. Yield 71%, α/β-D 23:77. For data, see [32].

Disarmed Sugar **26** (see *Scheme 3*). *Dodecyl 4,6*-O-*Benzylidene-1-thio-*β-D-*glucopyranoside* (**21**). To a soln. of dodecyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**20**) [33] (3.69 g, 6.76 mmol) in CH_2Cl_2 (10 ml) and MeOH (20 ml), 28% NaOMe (261 mg, 1.35 mmol) in MeOH was added at 0°. After stirring for 30 min at r.t., the mixture was acidified with *Amberlite® IR-120* cation exchange resin (until *ca.* pH 5). After filtration of the mixture and removal of the solvent, the residue was dried *in vacuo*. The crude product obtained was used without further purification. To a soln. of the crude product and camphorsulfonic acid (CSA; 0.470 g, 2.03 mmol) in DMF (34 ml) benzaldehyde dimethyl acetal (1.21 ml, 8.11 mmol) was added at r.t. After stirring for 5 h at *ca.* 20 Torr, sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, washed with H_2O and brine, dried (Na_2SO_4), and evaporated and the residue purified by CC (hexane/AcOEt 5:1 → 3:1): **21** (1.93 g, 63.0%). White solid. M.p. 96–98°. $[\alpha]_D^{23} = -37.1$ ($c = 1.1$, $CHCl_3$). IR (KBr): 3425, 2924, 2854, 1720, 1281, 1257, 1111, 1088, 987, 702. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.3, 3 H); 1.14–1.40 (*m*, 18 H); 1.41–1.68 (*m*, 2 H); 2.69 (*t*, *J* = 7.5, 2 H); 3.35–3.57 (*m*, 3 H); 3.63–3.82 (*m*, 2 H); 4.31 (*dd*, *J* = 10.5, 4.8, 1 H); 4.40 (*d*, *J* = 9.9, 1 H); 5.51 (*s*, 1 H); 7.33–7.40 (*m*, 3 H); 7.46–7.50 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 14.0; 22.6; 28.8; 29.1; 29.3; 29.4; 29.5; 29.6; 29.9; 30.5; 31.4; 31.8; 68.5; 70.4; 73.2; 74.4; 80.3; 86.6; 101.8; 126.3; 128.2; 129.2; 136.9. HR-MS: 475.2505 ($C_{25}H_{40}NaO_5S^+$, $[M+Na]^+$; calc. 475.2494).

Dodecyl 2,3-Di-O-*benzoyl-4,6*-O-*benzylidene-1-thio-*β-D-*glucopyranoside* (**22**). To a soln. of **21** (6.00 g, 13.3 mmol) and DMAP (162 mg, 1.30 mmol) in CH_2Cl_2 (67 ml), pyridine (2.6 ml, 31.9 mmol) and BzCl (3.30 ml, 29.3 mmol) were added successively at 0°. After stirring for 12 h at r.t., sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with sat. aq. $CuSO_4$ soln., H_2O, and brine, dried (Na_2SO_4) and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): **22** (7.80 g, 89%). White solid. M.p. 99–102°. $[\alpha]_D^{23} = +7.2$ ($c = 1.3$, $CHCl_3$). IR (KBr): 2924, 2854, 1720, 1265, 1095, 987, 702. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, *J* = 6.6, 3 H); 1.15–1.39 (*m*, 18 H); 1.40–1.70 (*m*, 2 H); 2.67–2.77 (*m*, 2 H); 3.70–3.78 (*m*, 1 H); 3.83–3.97 (*m*, 2 H); 4.45 (*dd*, *J* = 10.2, 4.8, 1 H); 4.80 (*d*, *J* = 9.9, 1 H); 5.51 (*dd*, *J* = 9.9, 9.9, 1 H); 5.55 (*s*, 1 H); 5.81 (*dd*, *J* = 9.9, 9.3, 1 H); 7.27–7.61 (*m*, 11 H); 7.92–8.13 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 14.1; 22.7; 28.7; 29.1; 29.3; 29.4; 29.5; 29.6; 30.3; 31.9; 68.5; 70.97; 71.00; 73.2; 78.7; 84.7; 101.4; 126.1; 128.2; 128.26; 128.32; 128.4; 129.0; 129.1; 129.3; 129.7; 129.8; 130.2; 133.1; 133.2; 133.7; 136.7; 165.3; 165.6. HR-MS: 683.3010 ($C_{39}H_{48}NaO_7S^+$, $[M+Na]^+$; calc. 683.3018).

Dodecyl 2,3-Di-O-*benzoyl-6*-O-*benzyl-1-thio-*β-D-*glucopyranoside* (**23**). To a soln. of **22** (6.00 g, 9.10 mmol) and Et_3SiH (7.30 ml, 45.4 mmol) in CH_2Cl_2 (30 ml), CF_3COOH (4.20 ml, 54.5 mmol) was added at 0°. After stirring for 2 h at r.t., sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with sat. aq. $CuSO_4$ soln., H_2O, and brine, dried (Na_2SO_4), and evaporated, and the residue

purified by CC (hexane/AcOEt 3:1): **23** (3.60 g, 61.0%). Colorless oil. $[\alpha]_D^{23} = +33.6$ ($c = 1.1$, $CHCl_3$). IR (neat): 3448, 2954, 2931, 2870, 1736, 1705, 1288, 1250, 1103, 1065, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (t, $J = 6.8$, 3 H); 1.20–1.45 (m, 18 H); 1.50–1.61 (m, 2 H); 2.68–2.75 (m, 2 H); 3.69–3.74 (m,1 H); 3.83–3.89 (m, 2 H); 3.97 (dd, $J = 9.3$, 9.0, 1 H); 4.60 (d, $J = 12.0$, 1 H); 4.65 (d, $J = 12.0$, 1 H); 4.68 (d, $J = 9.5$, 1 H); 5.44 (dd, $J = 9.5$, 9.5, 1 H); 5.50 (dd, $J = 9.5$, 9.0, 1 H); 7.25–7.51 (m, 11 H); 7.94–7.97 (m, 4 H). ^{13}C-NMR ($CDCl_3$): 14.1; 22.7; 28.7; 29.1; 29.3; 29.46; 29.54; 29.6; 30.1; 31.9; 60.4; 70.1; 70.2; 70.9; 73.7; 77.5; 78.7; 83.7; 127.7; 127.8; 128.29; 128.33; 128.40; 128.44; 129.0; 129.3; 129.8; 129.9; 130.1; 130.2; 133.3; 137.6; 165.3; 167.0. HR-MS: 685.3193 ($C_{39}H_{50}NaO_7S^+$, $[M + Na]^+$; calc. 685.3175).

*Dodecyl 4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-*O*-benzyl-1-thio-β-*D*-glucopyranoside* (**24**). To a soln. of **23** (1.16 g, 1.75 mmol) and DMAP (43 mg, 0.35 mmol) in CH_2Cl_2 (8.8 ml) and pyridine (0.42 ml, 5.2 mmol), Ac_2O (0.33 ml, 3.3 mmol) was added at r.t. After stirring for 12 h, sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with sat. aq. $CuSO_4$ soln., H_2O, and brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): **24** (1.19 g, 96%). Colorless foam. $[\alpha]_D^{24} = +44.5$ ($c = 1.1$, $CHCl_3$). IR (KBr): 2916, 2854, 1728, 1273, 1227, 1095, 1065, 710. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (t, $J = 6.3$, 3 H); 1.20–1.40 (m, 18 H); 1.50–1.64 (m, 2 H); 1.84 (s, 3 H); 2.65–2.80 (m, 2 H); 3.64–3.66 (m, 2 H); 4.52–4.64 (m, 1 H); 4.54 (d, $J = 11.7$, 1 H); 4.61 (d, $J = 11.7$, 1 H); 4.70 (d, $J = 9.9$, 1 H); 5.33 (dd, $J = 9.9$, 9.6, 1 H); 5.45 (dd, $J = 9.9$, 9.6, 1 H); 5.66 (dd, $J = 9.6$, 9.6, 1 H); 7.25–7.39 (m, 9 H); 7.46–7.53 (m, 2 H); 7.88–7.96 (m, 4 H). ^{13}C-NMR ($CDCl_3$): 14.1; 20.5; 22.7; 28.8; 29.1; 29.3; 29.48; 29.55; 29.60; 29.63; 30.0; 31.9; 69.0; 69.3; 70.5; 73.6; 74.4; 77.7; 83.8; 127.7; 127.8; 128.4; 128.9; 129.2; 129.76; 129.81; 133.2; 133.3; 137.7; 165.1; 165.8; 169.5. HR-MS: 727.3265 ($C_{41}H_{52}NaO_8S^+$, $[M + Na]^+$; calc. 727.3281).

*4-*O*-Acetyl-2,3-di-*O*-benzoyl-6-*O*-benzyl-β-*D*-glucopyranosyl Fluoride* (**25**). To a soln. of **24** (170 mg, 0.241 mmol) in CH_2Cl_2 (4.8 ml), (diethylamino)sulfur trifluoride (DAST; 0.0480 ml, 0.362 mmol) and *N*-bromosuccinimide (NBS; 55.7 mg, 0.313 mmol) were added at −23°. After stirring for 5 h at r.t., sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with H_2O and brine, dried (Na_2SO_4), and evaporated, and the residue purified by prep. TLC (hexane/AcOEt 2:1): **25** (39.5 mg, 31%). White crystals. M.p. 131–132°. $[\alpha]_D^{24} = +86.9$ ($c = 1.1$, $CHCl_3$). IR (KBr): 1736, 1273, 1111, 710. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.87 (s, 3 H); 3.69 (d, $J = 4.3$, 2 H); 4.03 (m, 1 H); 4.55 (d, $J = 11.9$, 1 H); 4.62 (d, $J = 11.9$, 1 H); 5.44–5.66 (m, 4 H); 7.27–7.41 (m, 9 H); 7.49–7.55 (m, 2 H); 7.92–7.99 (m, 4 H). ^{13}C-NMR ($CDCl_3$): 20.5; 68.1; 68.5; 71.3; 71.7; 71.9; 72.0; 73.56; 73.60; 73.65; 106.56 (d, $J = 219.5$, C(1)); 127.8; 127.9; 128.40; 128.44; 128.6; 128.7; 129.81; 129.84; 133.5; 137.4; 164.8; 165.6; 169.3.

*4-*O*-Acetyl-2,3-di-*O*-benzoyl-β-*D*-glucopyranosyl Fluoride* (**26**). To a soln. of **25** (37.2 mg, 0.0712 mmol) in CH_2Cl_2 (3 ml), 20% PdOH/C (*Aldrich*) was added at r.t. under Ar. After purging with H_2 (1 atm) and stirring for 5 h, H_2 was removed. Then the catalyst was filtered off, the mixture evaporated, and the residue purified by prep. TLC (hexane/AcOEt 1:1): **26** (27.8 mg, 90%). White crystals. M.p. 169–170°. $[\alpha]_D^{23} = +113.3$ ($c = 1.1$, $CHCl_3$). IR (KBr): 1736, 1273, 1111. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.00 (s, 3 H); 2.40–2.50 (br., 1 H); 3.73–3.78 (m, 1 H); 3.85–3.92 (m, 2 H); 5.44 (dd, $J = 9.5$, 9.3, 1 H); 5.48–5.73 (m, 4 H; half of the d of H_α–C(1) was detected, $J = 6.4$); 7.38 (d, $J = 7.6$, 2 H); 7.41 (d, $J = 7.6$, 2 H); 7.50–7.58 (m, 2 H); 7.93–8.00 (m, 2). ^{13}C-NMR ($CDCl_3$): 20.6; 61.2; 67.7; 71.5 (d, $J = 28.1$, C(2)); 71.75; 71.83; 71.9; 74.6; 106.6 (d, $J = 218.9$, C(1)); 128.44; 128.49; 128.54; 128.6; 129.8; 129.9; 133.6; 164.8; 165.5; 169.9. HR-MS: 455.1109 ($C_{22}H_{21}FNO_8^+$, $[M + Na]^+$; calc. 455.1118).

Disarmed Sugar **32** (see *Scheme 4*). *Dodecyl 3,4,6-Tri-*O*-acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-1-thio-β-*D*-glucopyranoside* (**28**). To a soln. of 1-acetoxy-3,4,6-tri-*O*-acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-β-D-glucopyranoside (**27**) [34] (84.3 g, 154 mmol) in CH_2Cl_2 (310 ml), dodecane-1-thiol (44.3 ml, 185 mmol) and $BF_3 \cdot OEt_2$ (22.8 ml, 185 mmol) were added successively at 0°. After stirring for 24 h at r.t., sat.aq. $NaHCO_3$ soln. was added. The mixture was extracted with AcOEt, the extract washed with H_2O and brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 3:1 → 1:1): **28** (89.5 g, 84.0%). White crystals. M.p. 117–118°. $[\alpha]_D^{24} = +44.0$ ($c = 1.1$, $CHCl_3$). IR (KBr): 2923, 2854, 1751, 1720, 1380, 1226, 1041. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (t, $J = 6.6$, 3 H); 1.18–1.40 (m, 18 H); 1.40–1.62 (m, 2 H); 1.88 (s, 3 H); 2.04 (s, 3 H); 2.11 (s, 3 H); 2.54–2.72 (m, 2 H); 3.87 (ddd, $J = 9.8$, 4.7, 2.2, 1 H); 4.17 (dd, $J = 12.3$, 2.2, 1 H); 4.31 (dd, $J = 12.3$, 4.7, 1 H); 4.34 (dd, $J = 9.8$, 9.3, 1 H); 5.17 (dd, $J = 10.2$, 10.5, 1 H); 5.42 (d, $J = 10.5$, 1 H); 5.76 (dd, $J = 10.2$, 9.3, 1 H); 7.93 (s, 1 H); 7.95 (s, 1 H). ^{13}C-NMR ($CDCl_3$): 14.1; 20.5; 20.6; 20.8; 28.7; 29.1; 29.3; 29.50; 29.56; 29.61; 29.64; 30.3; 31.9; 54.1; 62.2; 68.6; 71.5; 75.9; 81.1; 125.8; 169.4; 170.2; 170.7. HR-MS: 710.1911 ($C_{32}H_{43}Cl_2NNaO_9S^+$, $[M + Na]^+$; calc. 710.1933).

*Dodecyl 6-*O*-[(*tert*-Butyl)dimethylsilyl]-2-deoxy-2-(4,5-dichlorophthalimido)-1-thio-β-*D*-glucopyranoside* (**29**). To a soln. of **28** (34.7 g, 49.7 mmol) in CH_2Cl_2 (90 ml) and MeOH (10 ml), 28% NaOMe (2.9 g, 14.9 mmol) in MeOH was slowly added at r.t. After stirring for 30 min, TsOH was added (until *ca.* pH 5), the

solvent evaporated, and the residue dried *in vacuo*. The crude product thus obtained was used in the next step without further purification. To a soln. of the crude product in DMF (100 ml), 1*H*-imidazole (3.70 g, 54.7 mmol) and ^{t}BuMe$_2$SiCl (8.20 g, 54.7 mmol) were successively added at r.t. After stirring for 5 h, sat. aq. NaHCO$_3$ soln. was added, the mixture extracted with Et$_2$O, the extract washed with H$_2$O and brine, dried (Na$_2$SO$_4$), and evaporated, and the residue purified by CC (hexane/AcOEt 3:1): **29** (23.4 g, 70.0%). Colorless oil. $[\alpha]_D^{24} = -12.4$ ($c = 1.1$, CHCl$_3$). IR (neat): 2947, 2908, 2862, 1774, 1713. ^{1}H-NMR (500 MHz, CDCl$_3$): 0.01 (*s*, 6 H); 0.76 (*t*, $J = 6.8$, 3 H); 0.79 (*s*, 9 H); 1.07–1.19 (*m*, 18 H); 1.28–1.42 (*m*, 2 H); 1.91–2.54 (*m*, 2 H); 2.66 (br. *s*, 1 H); 3.39–3.45 (*m*, 1 H); 3.50 (*dd*, $J = 9.5$, 8.9, 1 H); 3.57–3.62 (br., 1 H); 3.71 (*dd*, $J = 10.1$, 7.1, 1 H); 3.88 (*dd*, $J =$ 10.1, 4.5, 1 H); 4.03 (*dd*, $J = 10.4$, 9.2, 1 H); 4.24 (*dd*, $J = 9.5$, 9.2, 1 H); 5.13 (*d*, $J = 10.4$, 1 H); 7.79 (*s*, 1 H); 7.81 (*s*, 1 H). ^{13}C-NMR (CDCl$_3$): −5.5; 14.1; 18.2; 22.7; 25.8; 28.7; 29.1; 29.3; 29.50; 29.54; 29.57; 29.61; 29.65; 29.8; 31.9; 55.4; 65.2; 72.2; 75.4; 81.0; 139.1. HR-MS: 698.2451 ($C_{32}H_{51}Cl_2NNaO_6SSi^+$, $[M+Na]^+$; calc. 698.2481).

Dodecyl 3,4-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)dimethylsilyl]-2-deoxy-2-(4,5-dichlorophthalimido)-1-thio-β*-D-*glucopyranoside* (**30**). To a soln. of **29** (4.00 g, 5.90 mmol) and DMAP (73.0 mg, 0.60 mmol) in CH$_2$Cl$_2$ (24 ml), pyridine (2.40 ml, 29.7 mmol) and BzCl (2.70 ml, 23.4 mmol) were added successively at r.t. After stirring for 12 h, sat. aq. NaHCO$_3$ soln. was added, the mixture extracted with Et$_2$O, the extract washed with H$_2$O and brine, dried (Na$_2$SO$_4$), and evaporated, and the residue purified by CC (hexane/AcOEt 15:1): **30** (5.20 g, 99.4%). Colorless oil. $[\alpha]_D^{24} = +37.7$ ($c = 1.4$, CHCl$_3$). IR (neat): 2962, 2862, 1720, 1373, 1265, 1034, 841. ^{1}H-NMR (500 MHz, CDCl$_3$): 0.01 (*s*, 6 H); 0.84 (*s*, 9 H); 0.85 (*t*, $J = 6.7$, 3 H); 1.20–1.28 (*m*, 18 H); 1.40–1.60 (*m*, 2 H); 2.58–2.64 (*m*, 1 H); 2.69–2.76 (*m*, 1 H); 3.79 (*dd*, $J = 11.6$, 5.2, 1 H); 3.83 (*dd*, $J = 11.6$, 2.5, 1 H); 3.91 (*ddd*, $J = 9.5$, 5.2, 2.5, 1 H); 4.52 (*dd*, $J = 10.7$, 10.4, 1 H); 5.51 (*d*, $J = 10.4$, 1 H); 5.53 (*dd*, $J = 9.8$, 9.5, 1 H); 6.16 (*dd*, $J = 10.7$, 9.8, 1 H); 7.25 (*dd*, $J = 7.3$, 7.3, 2 H); 7.32 (*dd*, $J = 7.3$, 7.3, 2 H); 7.40 (*dd*, $J = 7.3$, 7.3, 1 H); 7.46 (*dd*, $J = 7.3$, 7.3, 1 H); 7.74 (*d*, $J = 7.3$, 2 H); 7.78 (*s*, 1 H); 7.88 (*d*, $J = 7.3$, 2 H); 7.93 (*s*, 1 H). ^{13}C-NMR (CDCl$_3$): −5.4; 14.1; 18.3; 22.7; 25.8; 28.8; 29.1; 29.3; 29.5; 29.59; 29.62; 29.65; 31.9; 54.5; 62.8; 69.8; 72.3; 79.4; 80.6; 125.69; 125.73; 128.3; 128.5; 129.1; 129.7; 129.8; 130.3; 130.8; 133.2; 133.3; 139.1; 139.3; 165.0; 165.8. HR-MS: 906.3016 ($C_{46}H_{59}Cl_2NNaO_8SSi^+$, $[M+Na]^+$; calc. 906.3005).

3,4-Di-O-*benzoyl-6*-O-*[(*tert-*butyl)dimethylsilyl]-2-deoxy-2(4,5-dichlorophthalimido)-β*-D-*glucopyranosyl Fluoride* (**31**). As described for **25**, with **30** (2.00 g, 2.30 mmol), CH$_2$Cl$_2$ (45 ml), DAST (0.479 ml, 3.40 mmol), and NBS (523 mg, 2.90 mmol). The residue was purified by CC (hexane/AcOEt 10:1): **31** (1.47 g, 92.0%). White amorphous solid. $[\alpha]_D^{24} = +49.2$ ($c = 1.1$, CHCl$_3$). IR (KBr): 1736, 1381, 1265, 1111, 841, 710. ^{1}H-NMR (400 MHz, CDCl$_3$): 0.01 (*s*, 6 H); 0.84 (*s*, 9 H); 3.74–3.92 (*m*, 2 H); 3.95–4.03 (*m*, 1 H); 4.57 (*ddd*, $J = 12.7$, 10.7, 7.8, 1 H); 5.64 (*dd*, $J = 9.8$, 9.5, 1 H); 6.12 (*dd*, $J = 10.7$, 9.5, 1 H); 6.17 (*dd*, $J = 52.5$, 7.8, 1 H); 7.22–7.49 (*m*, 6 H); 7.71–7.75 (*m*, 2 H); 7.86–7.91 (*m*, 4 H). ^{13}C-NMR (CDCl$_3$): −5.5; 14.2; 18.3; 25.6; 25.8; 55.4 (*d*, $J = 24.1$, C(2)); 62.2; 69.0; 70.6 (*d*, $J = 10.1$, C(3)); 75.1 (*d*, $J = 5.0$, C(4)); 104.3 (*d*, $J = 215.6$, C(1)); 125.8; 128.2; 128.4; 128.9; 129.7; 129.8; 129.9; 130.4; 133.4; 133.5; 139.4; 164.9; 165.6; 165.8. HR-MS: 724.1290 ($C_{34}H_{44}Cl_2FNNaO_8Si^+$, $[M+Na]^+$; calc. 724.1312).

3,4-Di-O-*benzoyl-2-deoxy-2-(4,5-dichlorophthalimido)-β*-D-*glucopyranosyl Fluoride* (**32**). To a soln. of **31** (4.70 g, 6.70 mmol) in MeCN (66 ml), 46% aq. hydrofluoric acid (3.5 ml) was added at r.t. After stirring for 40 min, sat. aq. NaHCO$_3$ was added, the mixture extracted with Et$_2$O, the extract washed with H$_2$O and brine, dried (Na$_2$SO$_4$), and evaporated, and the residue purified by CC (hexane/AcOEt 10:1): **32** (1.90 g, 48.0%). White crystals. M.p. 124–126°. $[\alpha]_D^{24} = +61.1$ ($c = 1.2$, CHCl$_3$). IR (KBr): 1782, 1713, 1373, 1257, 1095, 710. ^{1}H-NMR (400 MHz, CDCl$_3$): 2.50–2.75 (br., 1 H); 3.80 (*dd*, $J = 12.9$, 3.9, 1 H); 3.94 (*dd*, $J = 12.9$, 1.7, 1 H); 4.27–4.30 (*m*, 1 H); 4.65 (*ddd*, $J = 12.4$, 10.7, 7.8, 1 H); 5.61 (*dd*, $J = 9.9$, 9.3, 1 H); 6.25 (*dd*, $J = 52.4$, 7.8, 1 H); 6.28 (*dd*, $J = 10.5$, 9.9, 1 H); 7.25–7.57 (*m*, 6 H); 7.77–7.79 (*m*, 2 H); 7.90–7.96 (*m*, 4 H). ^{13}C-NMR (CDCl$_3$): 55.2 (*d*, $J = 23.8$, C(2)); 60.9; 68.9; 70.0 (*d*, $J = 10.3$, C(3)); 74.6 (*d*, $J = 4.1$, C(4)); 104.2 (*d*, $J = 216.0$, C(1)); 125.7; 125.8; 128.0; 128.2; 128.4; 128.5; 129.8; 129.9; 130.3; 133.6; 133.8; 139.5; 165.5; 165.6; 165.8. HR-MS: 610.0433 ($C_{28}H_{20}Cl_2FNNaO_8^+$, $[M+Na]^+$; calc. 610.0448).

Disarmed Sugar **37** (see *Scheme 5*). *Dodecyl 3*-O-*Acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-4,6*-O-*(4-methoxybenzylidene)-1-thio-β*-D-*glucopyranoside* (**33**). To a soln. of **28** (35.1 g, 51.0 mmol) in CH$_2$Cl$_2$ (90 ml) and MeOH (10 ml), 28% NaOMe (2.9 g, 15.2 mmol) in MeOH was added at r.t. After stirring for 30 min, the mixture was acidified with TsOH (until *ca.* pH 5), the solvent evaporated, and the residue dried *in vacuo*. The crude product thus obtained was used without further purification. To a soln. of the crude product and CSA (3.60 g, 15.3 mmol) in DMF (100 ml), *p*-anisaldehyde dimethyl acetal (10.4 ml, 61.2 mmol) was added at r.t. and stirred at *ca.* 20 Torr for 5 h. Then pyridine (41.0 ml, 510 mmol), DMAP (1.20 g, 5.10 mmol), and Ac$_2$O (29.0 ml, 306 mmol) were added successively. After stirring for further 12 h, sat. aq. NaHCO$_3$ soln. was added, the mixture extracted with Et$_2$O, the org. layer washed with sat. aq. CuSO$_4$ soln., H$_2$O, and brine, dried (Na$_2$SO$_4$), and evaporated, and the residue purified by CC (hexane/AcOEt 5:1): **33** (11.8 g, 50% yield based on 59%

conversion) as white crystals and 41% of recovered **28**. **33**: M.p. 45–48°. $[\alpha]_D^{22} = +4.0$ ($c = 1.1$, $CHCl_3$). IR (KBr): 2924, 1728, 1373, 1227, 1095, 1034. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (t, $J = 6.4$, 3 H); 1.08–1.40 (m, 18 H); 1.40–1.54 (m, 2 H); 1.90 (s, 3 H); 2.55–2.73 (m, 2 H); 3.80 (s, 3 H); 3.74–3.85 (m, 3 H); 4.30 (dd, $J = 10.5$, 9.9, 1 H); 4.40 (m, 1 H); 5.50 (s, 1 H); 5.50 (d, $J = 10.5$, 1 H); 5.83 (dd, $J = 9.9$, 9.0, 1 H); 6.88 (d, $J = 8.8$, 2 H); 7.38 (d, $J = 8.8$, 2 H); 7.92 (s, 1 H); 7.95 (s, 1 H). ^{13}C-NMR ($CDCl_3$): 14.1; 20.6; 22.7; 28.6; 29.1; 29.3; 29.45; 29.55; 29.60; 29.63; 30.4; 31.9; 54.7; 55.2; 68.4; 70.5; 78.9; 81.6; 101.6; 113.5; 125.6; 125.7; 127.5; 129.2; 130.2; 130.7; 139.2; 139.4; 160.1; 165.4; 165.8; 170.3. HR-MS: 744.2169 ($C_{36}H_{45}Cl_2NNaO_8S^+$, $[M + Na]^+$; calc. 744.2141).

*Dodecyl 3-*O*-Acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-4-*O*-(4-methoxybenzyl)-1-thio-β-*D*-glucopyranoside* (**34**). To a suspension of **33** (10.9 g, 14.1 mmol) and 3 Å molecular sieves (10.9 g) in THF (150 ml) and MeCN (110 ml), $NaBH_3CN$ (8.10 g, 129 mmol) was added at 0°. Then Me_3SiCl (20.0 ml, 158 mmol) was slowly added at 0° within 30 min. After stirring for 2 h, H_2O was added and the mixture poured into sat. aq. $NaHCO_3$ soln. The mixture was extracted with AcOEt, the extract washed with brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 3:1): **34** (8.70 g, 80%). Colorless oil. $[\alpha]_D^{21} = +3.2$ ($c = 1.5$, $CHCl_3$). IR (neat): 2916, 2854, 1720, 1373, 1242, 1080, 1041. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (t, $J = 6.6$, 3 H); 1.10–1.40 (m, 18 H); 1.40–1.55 (m, 2 H); 2.56–2.68 (m, 2 H); 3.81 (s, 3 H); 3.70–3.83 (m, 4 H); 4.23 (dd, $J =$ 10.5, 10.2, 1 H); 4.51 (d, $J = 11.7$, 1 H); 4.56 (d, $J = 11.7$, 1 H); 5.41 (d, $J = 10.5$, 1 H); 5.61 (dd, $J = 10.5$, 8.5, 1 H); 6.88 (d, $J = 6.3$, 2 H); 7.26 (d, $J = 5.4$, 2 H); 7.92 (s, 1 H); 7.95 (s, 1 H). ^{13}C-NMR ($CDCl_3$): 14.1; 20.7; 22.7; 28.7; 29.1; 29.4; 29.53; 29.59; 29.63; 29.7; 30.2; 31.9; 54.1; 55.3; 70.1; 71.6; 73.5; 74.0; 77.7; 80.9; 113.9; 125.7; 129.5; 130.3; 130.8; 139.2; 139.5; 159.4; 165.5; 165.9; 171.0. HR-MS: 746.2303 ($C_{36}H_{47}Cl_2NNaO_8S^+$, $[M + Na]^+$; calc. 746.2297).

*Dodecyl 3,6-Di-*O*-acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-4-*O*-(4-methoxybenzyl)-1-thio-β-*D*-glucopyranoside* (**35**). To a soln. of **34** (5.00 g, 6.50 mmol) and DMAP (79 mg, cat.) in CH_2Cl_2 (20 ml) and pyridine (4.2 ml), Ac_2O (0.90 ml, 9.8 mmol) was added at 0°. After stirring for 3 h at r.t., sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with sat. aq. $CuSO_4$ soln., H_2O, and brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): **35** (5.30 g, 99%). Colorless oil. $[\alpha]_D^{21} = +64.1$ ($c = 1.1$, $CHCl_3$). IR (neat): 2908, 2854, 1743, 1380, 1218, 1041. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (t, $J = 6.6$, 3 H); 1.08–1.40 (m, 18 H); 1.40–1.54 (m, 2 H); 1.87 (s, 3 H); 1.92 (s, 3 H); 2.57–2.72 (m, 2 H); 3.55–3.62 (m, 2 H); 3.80 (s, 3 H); 3.77–3.86 (m, 1 H); 4.33 (dd, $J = 10.5$, 9.8, 1 H); 4.47 (d, $J = 11.7$, 1 H); 4.52 (d, $J =$ 11.7, 1 H); 5.17 (dd, $J = 9.8$, 9.5, 1 H); 5.40 (d, $J = 10.5$, 1 H); 5.75 (dd, $J = 9.8$, 9.5, 1 H); 6.87 (d, $J = 8.3$, 2 H); 7.25 (d, $J = 8.6$, 2 H); 7.95 (s, 1 H); 7.97 (s, 1 H). ^{13}C-NMR ($CDCl_3$): 14.1; 20.4; 20.6; 22.6; 28.6; 29.0; 29.3; 29.45; 29.49; 29.51; 29.55; 29.60; 30.1; 31.8; 54.2; 55.2; 68.6; 69.5; 71.6; 73.1; 80.8; 113.6; 125.7; 129.4; 129.7; 130.2; 130.6; 139.2; 139.4; 159.2; 165.2; 165.7; 169.5; 170.3. HR-MS: 788.2407 ($C_{38}H_{49}Cl_2NNaO_9S^+$, $[M + Na]^+$; calc. 788.2403).

*3,6-Di-*O*-acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-4-*O*-(4-methoxybenzyl)-β-*D*-glucopyranosyl Fluoride* (**36**). To a soln. of **35** (4.10 g, 5.40 mmol) in CH_2Cl_2 (100 ml), DAST (1.10 ml, 8.10 mmol) and NBS (1.25 g, 7.02 mmol) were added at −23°. After stirring for 5 h at r.t., the mixture was poured into sat. aq. $NaHCO_3$ soln. and extracted with CH_2Cl_2, the extract washed with H_2O and brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 4:1): **36** (2.70 g, 93%). White crystals. M.p. 119–124°. $[\alpha]_D^{22} = +84.7$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1759, 1720, 1381, 1227, 1111, 1034. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.88 (s, 3 H); 2.10 (s, 3 H); 3.72–3.90 (m, 2 H); 3.80 (s, 3 H); 4.23–4.39 (m, 2 H); 4.49 (dd, $J = 12.0$, 1.8, 1 H); 4.55 (d, $J = 11.7$, 1 H); 4.61 (d, $J = 11.7$, 1 H); 5.73 (dd, $J = 10.6$, 8.7, 1 H); 6.08 (dd, $J = 52.5$, 7.8, 1 H); 6.87 (d, $J = 8.6$, 2 H); 7.18 (d, $J = 8.6$, 2 H); 7.95 (s, 2 H). ^{13}C-NMR ($CDCl_3$): 20.6; 20.8; 55.4 (d, $J = 26.4$, C(2)); 62.2; 72.6; 72.7; 73.0 (d, $J =$ 5.8); 74.4; 74.8; 104.0 (d, $J = 214.8$, C(1)); 114.0; 125.8; 129.0; 129.7; 130.4; 139.6; 159.6; 165.7; 170.1; 170.6. HR-MS: 583.0825 ($C_{26}H_{24}Cl_2NO_9^+$, M^+; calc. 583.0812).

*3,6-Di-*O*-acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-β-*D*-glucopyranosyl Fluoride* (**37**). To a soln. of **36** (2.00 g, 3.40 mmol) in CH_2Cl_2 (64.4 ml) and H_2O (3.6 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 932 mg, 4.10 mmol) at r.t. After stirring for 12 h, sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with H_2O and brine, dried (Na_2SO_4), and evaporated, and the residue purified by CC (hexane/AcOEt 2:1): **37** (2.70 g, 93%). White crystals. M.p. 186–188°. $[\alpha]_D^{22} = +95.3$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1720, 1380, 1218, 1110, 1049. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.90 (s, 3 H); 2.10 (s, 3 H); 3.68–3.83 (m, 3 H); 4.47 (ddd, $J = 12.6$, 10.2, 7.8, 1 H); 5.20 (dd, $J = 9.6$, 9.3, 1 H); 5.80 (dd, $J = 10.2$, 9.3, 1 H); 6.09 (dd, $J = 52.5$, 7.8, 1 H); 7.96 (s, 1 H); 7.97 (s, 1 H). ^{13}C-NMR ($CDCl_3$): 20.4; 20.6; 55.1 (d, $J = 23.6$, C(2)); 60.9; 68.3; 69.8 (d, $J = 9.4$, C(3)); 74.2 (d, $J = 4.4$, C(4)); 104.1 (d, $J = 216.4$, C(1)); 125.9; 130.3; 139.7; 165.6; 170.1; 170.2. HR-MS: 486.0142 ($C_{18}H_{16}Cl_2FNNaO_8^+$, $[M + Na]^+$; calc. 486.0153).

4-O-*Acetyl-2,3-di*-O-*benzoyl-6*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)-β*-D-*glucopyranosyl Fluoride* (**38**). According to *GP (TrB(C_6F_5)$_4$)*, at 0° for 3 h. Yield 80%, α/β-D 17:83. **38** (β-D): White crystals. M.p. 163–164°. $[\alpha]_D^{22} = +48.1$ ($c = 0.85$, $CHCl_3$). IR (KBr): 3032, 2877, 1736, 1273, 1095, 1072, 741, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.44–3.52 (*m*, 2 H); 3.61–3.75 (*m*, 4 H); 3.80–3.84 (*m*, 1 H); 4.08–4.15 (*m*, 2 H); 4.48 (*d*, *J* = 7.9, H–C(1′)); 4.52 (*d*, *J* = 10.7, 1 H); 4.53 (*d*, *J* = 12.2, 1 H); 4.54 (*d*, *J* = 10.7, 1 H); 4.62 (*d*, *J* = 12.2, 1 H); 4.72 (*d*, *J* = 10.7, 1 H); 4.79 (*d*, *J* = 11.0, 1 H); 4.83 (*d*, *J* = 10.7, 1 H); 4.95 (*d*, *J* = 11.0, 1 H); 5.00 (*d*, *J* = 10.7, 1 H); 5.33 (*dd*, *J* = 9.5, 8.9, 1 H); 5.46–5.60 (*m*, 1 H); 5.54 (*dd*, *J* = 53.7, 6.1, 1 H); 5.65 (*dd*, *J* = 8.5, 8.5, 1 H); 7.10–7.60 (*m*, 26 H); 7.92 (*s*, 1 H); 7.93 (*d*, *J* = 7.0, 2 H); 7.97 (*s*, 1 H); 7.98 (*d*, *J* = 7.0, 2 H). ^{13}C-NMR ($CDCl_3$): 20.4; 68.2; 68.7; 69.1; 71.5 (*d*, *J* = 29.0, C(2)); 71.8 (*d*, *J* = 8.3, C(3)); 73.4; 73.8 (*d*, *J* = 3.6, C(4)); 74.66; 74.74; 74.8; 75.6; 76.6; 77.5; 82.1; 84.5; 104.1; 106.6 (*d*, *J* = 219.0, C(1)); 127.58; 127.62; 127.65; 127.75; 127.86; 127.90; 128.30; 128.34; 128.43; 128.48; 128.6; 128.7; 129.8; 129.9; 133.5; 138.0; 138.4; 138.5; 164.9; 165.5; 169.5. HR-MS: 977.3538 ($C_{56}H_{55}FNaO_{13}^+$, $[M+Na]^+$; calc. 977.3524).

3,4-Di-O-*benzoyl-2-deoxy-2-(4,5-dichlorophthalimido)-6*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)-β*-D-*glucopyranosyl Fluoride* (**39**). According to *GP (TrB(C_6F_5)$_4$)*, at −35 to −10° for 21 h. Yield 86%, α/β-D 9:91. **39** (β-D): White crystals. M.p. 150–151°. $[\alpha]_D^{24} = +38.7$ ($c = 1.2$, $CHCl_3$). IR (KBr): 2924, 2854, 1728, 1381, 1273, 1103, 1072, 741, 710. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.32–3.41 (*m*, 2 H); 3.45–3.70 (*m*, 4 H); 3.80 (*dd*, *J* = 10.3, 7.6, 1 H); 4.07 (*d*, *J* = 10.3, 1 H); 4.15–4.22 (*m*, 1 H); 4.38 (*d*, *J* = 7.6, H–C(1′)); 4.37–4.49 (*m*, 3 H); 4.57 (*ddd*, *J* = 12.2, 10.7, 7.6, 1 H); 4.61 (*d*, *J* = 11.0, 1 H); 4.69 (*d*, *J* = 11.0, 1 H); 4.72 (*d*, *J* = 10.7, 1 H); 4.85 (*d*, *J* = 11.0, 1 H); 4.91 (*d*, *J* = 11.0, 1 H); 5.47 (*dd*, *J* = 9.8, 9.2, 1 H); 6.12 (*dd*, *J* = 10.7, 9.2, 1 H); 6.17 (*dd*, *J* = 52.5, 7.6, 1 H); 7.05–7.45 (*m*, 26 H); 7.66 (*d*, *J* = 7.3, 2 H); 7.79–7.83 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 55.3 (*d*, *J* = 23.8, C(2)); 68.5; 68.7; 69.5; 70.3 (*d*, *J* = 11.8, C(3)); 73.4; 73.8 (*d*, *J* = 5.5, C(4)); 74.8; 74.9; 75.6; 77.5; 82.1; 84.5; 104.1; 104.2 (*d*, *J* = 209.2, C(1)); 125.8; 127.5; 127.6; 127.7; 128.20; 128.23; 128.31; 128.36; 128.46; 129.67; 129.72; 129.77; 129.84; 130.3; 133.55; 133.59; 138.0; 138.4; 138.6; 139.5; 165.1; 165.5. HR-MS: 1132.2871 ($C_{62}H_{54}Cl_2FNNaO_{13}^+$, $[M+Na]^+$; calc. 1132.2854).

3,6-Di-O-*acetyl-2-deoxy-2-(4,5-dichlorophthalimido)-4*-O-*(2,3,4,6-tetra*-O-*benzyl-β*-D-*glucopyranosyl)-β*-D-*glucopyranosyl Fluoride* (**40**). According to *GP (TrB(C_6F_5)$_4$)*, at −35 to −15° for 15 h. Yield 84%, α/β-D 8:92. **40** (β-D): White crystals. M.p. 62–65°. $[\alpha]_D^{24} = +37.0$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1751, 1728, 1373, 1234, 1103, 1065, 741, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.87 (*s*, 3 H); 1.99 (*s*, 3 H); 3.43–3.55 (*m*, 2 H); 3.60–3.81 (*m*, 5 H); 3.98–4.10 (*m*, 2 H); 4.36–4.43 (*m*, 1 H); 4.46 (*d*, *J* = 7.3, H–C(1′)); 4.50–4.57 (*m*, 2 H); 4.63 (*d*, *J* = 12.2, 1 H); 4.71 (*d*, *J* = 10.7, 1 H); 4.79 (*d*, *J* = 11.0, 1 H); 4.82 (*d*, *J* = 10.7, 1 H); 4.94 (*d*, *J* = 11.0, 1 H); 4.98 (*d*, *J* = 10.7, 1 H); 5.10 (*dd*, *J* = 10.1, 9.5, 1 H); 5.76 (*dd*, *J* = 10.0, 9.5, 1 H); 6.07 (*dd*, *J* = 52.2, 7.6, 1 H); 7.10–7.40 (*m*, 20 H); 7.94 (*s*, 2 H). ^{13}C-NMR ($CDCl_3$): 20.3; 20.5; 55.1 (*d*, *J* = 23.8, C(2)); 68.9; 70.5 (*d*, *J* = 9.3, C(3)); 73.36; 73.41; 73.5; 74.7; 74.8; 74.9; 75.7; 77.5; 82.0; 84.5; 103.9 (*d*, *J* = 217.2, C(1)); 104.0; 125.8; 127.57; 127.61; 127.69; 127.74; 127.8; 127.9; 130.3; 138.3; 138.4; 138.5; 165.5; 169.4; 170.1. HR-MS: 1008.2584 ($C_{52}H_{50}Cl_2FNNaO_{13}^+$, $[M+Na]^+$; calc. 1008.2541).

2-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl Fluoride* (**44**). To a soln. of ethyl 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-1-thio-β-D-*galactopyranoside* [35] (90.7 mg, 0.15 mmol) in CH_2Cl_2 (1.3 ml), DAST (0.020 ml, 0.17 mmol) was added at −23°. After stirring for 2 h at r.t., sat. aq. $NaHCO_3$ soln. was added. The mixture was extracted with Et_2O, the extract washed with H_2O and brine, dried (Na_2SO_4), and evaporated, and the residue purified by prep. TLC (hexane/AcOEt 3:1): **44** (51.5 mg, 61.8%). Colorless oil. $[\alpha]_D^{24} = +45.0$ ($c = 0.99$, $CHCl_3$). IR (neat): 1728, 1265, 1111, 1057, 741, 702. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.66–3.81 (*m*, 4 H); 3.99–4.04 (*m*, 1 H); 4.43–4.67 (*m*, 5 H); 4.95 (*d*, *J* = 11.4, 1 H); 5.28 (*dd*, *J* = 53.1, 6.3, 1 H); 5.71 (*ddd*, *J* = 12.0, 9.6, 6.6, 1 H); 7.14–7.61 (*m*, 18 H); 8.02 (*d*, *J* = 7.2, 2 H). ^{13}C-NMR ($CDCl_3$): 63.4; 71.5 (*d*, *J* = 24.3, C(2)); 71.9; 73.6; 74.1; 74.4; 78.3 (*d*, *J* = 9.3, C(3)); 107.5 (*d*, *J* = 217.4, C(1)); 127.66; 127.73; 127.81; 127.9; 128.0; 128.3; 128.4; 128.5; 129.6; 129.9; 133.2; 137.3; 137.6; 138.0; 165.1. HR-MS: 579.2170 ($C_{34}H_{33}FNaO_6^+$, $[M+Na]^+$; calc. 579.2159).

Glycosylation with Catalyst TfOH: General Procedure (GP(TfOH)). To a stirred suspension of *Drierite* (100 mg), 2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl fluoride (**43**; 66.8 mg, 0.12 mmol), and methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (46.5 mg, 0.10 mmol) in CH_2Cl_2 (2.5 ml), TfOH (0.75 mg in toluene, 0.04 ml, 5.0 μmol) was added dropwise at 0°. The mixture was stirred for 4 h at 0° and then the reaction quenched by adding sat. aq. $NaHCO_3$ soln. (2 ml). The mixture was diluted with AcOEt and 1N HCl, the aq. layer extracted with AcOEt, the combined org. layer washed with H_2O and brine, dried ($MgSO_4$), and evaporated, and the resulting residue purified by prep. TLC (silica gel): *methyl 6*-O-*(2*-O-*benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-2,3,4-tri*-O-*benzyl-α*-D-*glucopyranoside* (**45**; 97.2 mg, 97.1%). White solid. M.p. 131–133°. $[\alpha]_D^{21} = +26.5$ ($c = 1.1$, $CHCl_3$). IR (KBr): 1720, 1273, 1072, 746, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.19 (*s*, 3 H); 3.37 (*dd*, *J* = 9.5, 9.2, 1 H); 3.43 (*dd*, *J* = 9.5, 3.7, 1 H); 3.53–3.58 (*m*, 1 H); 3.63–3.74 (*m*, 3 H);

3.76 (*dd*, *J* = 10.6, 1.5, 1 H); 3.81 (*dd*, *J* = 9.5, 8.9, 1 H); 3.86 (*dd*, *J* = 9.5, 9.2, 1 H); 4.13 (*d*, *J* = 9.2, 1 H); 4.27 (*d*, *J* = 11.0, 1 H); 4.43 (*d*, *J* = 11.0, 1 H); 4.47 (*d*, *J* = 3.4, 1 H); 4.52 (*d*, *J* = 7.9, H–C(1′)); 4.54–4.62 (*m*, 5 H); 4.65 (*d*, *J* = 11.0, 1 H); 4.67 (*d*, *J* = 11.0, 1 H); 4.72 (*d*, *J* = 12.2, 1 H); 4.73 (*d*, *J* = 11.0, 1 H); 4.78 (*d*, *J* = 10.7, 1 H); 4.87 (*d*, *J* = 11.0, 1 H); 5.35 (*dd*, *J* = 9.5, 7.9, 1 H); 6.98–7.03 (*m*, 2 H); 7.10–7.35 (*m*, 30 H); 7.42–7.47 (*m*, 1 H); 7.90–7.95 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 54.9; 68.0; 69.4; 73.3; 73.4; 73.6; 74.6; 75.0; 75.1; 75.40; 75.44; 77.4; 78.0; 79.6; 81.9; 82.8; 97.9; 101.2; 127.37; 127.43; 127.56; 127.63; 127.65; 127.78; 127.81; 127.84; 127.97; 127.99; 128.1; 128.20; 128.23; 128.30; 128.33; 128.38; 128.40; 129.7; 132.9; 137.7; 137.8; 138.12; 138.15; 138.19; 138.82: HR-MS: 1023.4271 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Methyl 6-O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-2,3,4-tri*-O-*benzyl-α*-D-*glucopyranoside* (**46**). According to *GP (TfOH)*, for 2.5 h. Yield 93%. White crystals. M.p. 133–135°. $[\alpha]_D^{22} = +23.3$ (c = 1.0, $CHCl_3$). IR (KBr): 1720, 1265, 1111, 1065, 741, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.14 (*s*, 3 H); 3.35 (*dd*, *J* = 9.7, 9.2, 1 H); 3.40 (*dd*, *J* = 9.5, 2.6, 1 H); 3.55–3.69 (*m*, 6 H); 3.86 (*dd*, *J* = 9.5, 9.2, 1 H); 3.98–4.00 (*m*, 1 H); 4.07–4.12 (*m*, 1 H); 4.34 (*d*, *J* = 11.0, 1 H); 4.38–4.51 (*m*, 5 H); 4.42 (*d*, *J* = 2.6, 1 H); 4.54–4.72 (*m*, 5 H, including H–C(1′)); 4.80 (*d*, *J* = 11.0, 1 H); 4.96 (*d*, *J* = 11.6, 1 H); 5.71 (*dd*, *J* = 10.1, 7.6, H–C(2′)); 7.02–7.40 (*m*, 32 H); 7.46 (*dd*, *J* = 7.4, 7.4, 1 H); 7.94 (*d*, *J* = 7.4, 2 H). ^{13}C-NMR ($CDCl_3$): 54.8; 67.6; 68.4; 69.4; 71.6; 72.4; 73.2; 73.4; 73.6; 74.4; 74.5; 75.4; 77.4; 79.7; 79.8; 81.8; 97.6; 101.6; 127.3; 127.4; 127.5; 127.6; 127.70; 127.75; 127.83; 128.0; 128.1; 128.2; 128.3; 128.4; 129.7; 130.0; 132.7; 137.5; 137.7; 138.1; 138.2; 138.4; 138.8; 165.0. HR-MS: 1023.4303 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Methyl 3-O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-2,4,6-tri*-O-*benzyl-α*-D-*glucopyranoside* (**47**). According to *GP (TfOH)*, for 6 h. Yield 87%. Colorless oil. $[\alpha]_D^{20} = +26.5$ (c = 0.89, $CHCl_3$). IR (KBr): 1728, 1458, 1365, 1265, 1095, 741, 702. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.25 (*s*, 3 H); 3.30 (*dd*, *J* = 9.5, 3.1, 1 H); 3.51 (*dd*, *J* = 9.8, 8.9, 1 H); 3.54–3.68 (*m*, 4 H); 3.71 (*dd*, *J* = 11.0, 4.3, 1 H); 3.76–3.82 (*m*, 1 H); 3.86 (*dd*, *J* = 8.9, 8.5, 1 H); 3.87–3.92 (*m*, 1 H); 4.24 (*d*, *J* = 12.2, 1 H); 4.34 (*d*, *J* = 3.1, 1 H); 4.35 (*dd*, *J* = 9.5, 8.9, 1 H); 4.43 (*d*, *J* = 12.2, 1 H); 4.45–4.55 (*m*, 4 H); 4.58 (*d*, *J* = 12.2, 1 H); 4.63 (*d*, *J* = 10.7, 1 H); 4.70 (*d*, *J* = 11.0, 1 H); 4.79 (*d*, *J* = 11.0, 1 H); 4.82 (*d*, *J* = 10.7, 1 H); 5.13 (*d*, *J* = 11.0, 1 H); 5.21 (*d*, *J* = 7.9, H–C(1′)); 5.40 (*dd*, *J* = 8.9, 7.9, 1 H); 7.08–7.18 (*m*, 10 H); 7.18–7.32 (*m*, 20 H); 7.37 (*dd*, *J* = 7.6, 7.6, 2 H); 7.53 (*dd*, *J* = 7.6, 7.6, 1 H); 7.99 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR ($CDCl_3$): 54.9; 68.5; 68.7; 69.6; 73.4; 74.6; 74.9; 75.0; 75.1; 75.2; 75.7; 78.0; 78.4; 80.9; 83.1; 97.6; 100.1; 127.3; 127.5; 127.6; 127.77; 127.83; 127.9; 128.0; 128.18; 128.21; 128.29; 128.32; 128.34; 128.38; 129.7; 130.0; 137.84; 137.88; 137.94; 138.0; 138.4; 138.7; 165.2. HR-MS: 1023.4284 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Methyl 3-O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-2,4,6-tri*-O-*benzyl-α*-D-*glucopyranoside* (**48**). According to *GP (TfOH)*, for 9 h. Yield 87%. Colorless oil. $[\alpha]_D^{23} = +19.9$ (c = 1.0, $CHCl_3$). IR (neat): 2870, 1728, 1597, 1496, 1458, 1103, 748, 701. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.26 (*s*, 3 H); 3.28 (*dd*, *J* = 9.7, 3.4, 1 H); 3.44–3.54 (*m*, 2 H); 3.55–3.75 (*m*, 6 H); 4.08–4.20 (*m*, 3 H); 4.24–4.38 (*m*, 4 H); 4.41 (*d*, *J* = 12.0, 1 H); 4.46 (*d*, *J* = 12.2, 1 H); 4.53 (*d*, *J* = 12.4, 1 H); 4.58 (*d*, *J* = 11.7, 1 H); 4.61 (*d*, *J* = 11.2, 1 H); 4.69 (*d*, *J* = 12.4, 1 H); 5.02–5.15 (*m*, 2 H); 5.09 (*d*, *J* = 8.0, H–C(1′)); 5.76 (*dd*, *J* = 10.0, 8.0, 1 H); 6.90–7.60 (*m*, 33 H); 8.02 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR ($CDCl_3$): 14.1; 21.0; 54.8; 60.3; 67.7; 68.3; 69.5; 71.4; 72.6; 72.9; 73.5; 73.6; 74.8; 75.1; 75.4; 77.7; 79.9; 80.5; 97.8; 100.8; 127.2; 127.3; 127.5; 127.6; 127.7; 127.84; 127.86; 127.88; 128.0; 128.1; 128.21; 128.26; 128.30; 128.32; 128.9; 129.8; 130.1; 132.9; 137.7; 137.8; 137.9; 138.0; 138.2; 138.7; 165.3. HR-MS: 1023.4303 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Methyl 4-O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-2,3,6-tri*-O-*benzyl-α*-D-*glucopyranoside* (**49**). According to *GP (TfOH)*, for 18 h. Yield 67%. White crystals. M.p. 124–127°. $[\alpha]_D^{17} = +26.1$ (c = 1.0, $CHCl_3$). IR (KBr): 1720, 1273, 1103, 1049, 740, 701. ^{1}H-NMR (500 MHz, $CDCl_3$): 3.25 (*s*, 3 H); 3.37 (*dd*, *J* = 10.7, 1.8, 1 H); 3.39–3.43 (*m*, 2 H); 3.48–3.55 (*m*, 2 H); 3.60 (*dd*, *J* = 9.5, 9.2, 1 H); 3.57–3.64 (*m*, 1 H); 3.69 (*dd*, *J* = 11.0, 1.8, 1 H); 3.73 (*dd*, *J* = 9.5, 9.2, 1 H); 3.83–3.92 (*m*, 2 H); 4.27 (*d*, *J* = 12.2, 1 H); 4.37 (*d*, *J* = 12.2, 1 H); 4.48 (*d*, *J* = 9.2, 1 H); 4.51 (*d*, *J* = 3.5, 1 H); 4.51–4.59 (*m*, 3 H); 4.62 (*d*, *J* = 12.2, 1 H); 4.65 (*d*, *J* = 7.9, H–C(1′)); 4.70 (*d*, *J* = 11.3, 1 H); 4.73 (*d*, *J* = 12.2, 1 H); 4.787 (*d*, *J* = 11.0, 1 H); 4.793 (*d*, *J* = 11.3, 1 H); 5.08 (*d*, *J* = 11.3, 1 H); 5.23 (*dd*, *J* = 9.5, 7.9, 1 H); 7.05–7.15 (*m*, 5 H); 7.18–7.34 (*m*, 22 H); 7.32–7.43 (*m*, 5 H); 7.53–7.57 (*m*, 1 H); 7.88 (*dd*, *J* = 8.5, 1.5, 2 H). ^{13}C-NMR ($CDCl_3$): 55.2; 67.8; 68.7; 69.5; 73.38; 73.47; 73.50; 74.2; 74.8; 75.0; 75.2; 75.4; 78.1; 78.9; 80.2; 82.8; 98.3; 100.3; 127.0; 127.3; 127.5; 127.6; 127.67; 127.70; 127.81; 127.84; 127.90; 127.98; 128.03; 128.06; 128.18; 128.23; 128.27; 128.34; 128.38; 128.5; 129.7; 129.8; 133.1; 137.7; 137.9; 138.0; 138.3; 138.4; 139.6; 164.8. HR-MS: 1023.4271 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Methyl 4-O-*(2*-O-*Benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-2,3,6-tri*-O-*benzyl-α*-D-*glucopyranoside* (**50**). According to *GP (TfOH)*, for 12 h. Yield 70%. White solid. M.p. 118–121°. $[\alpha]_D^{22} = +32.0$ (c = 1.0, $CHCl_3$). IR (KBr): 2916, 2877, 1728, 1458, 1365, 1265, 1095, 1049, 741, 702. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.25 (*s*, 3 H); 3.32–3.56 (*m*, 7 H); 3.59 (*dd*, *J* = 10.7, 3.2, 1 H); 3.78–3.90 (*m*, 2 H); 3.96–4.04 (*m*, 1 H); 4.22 (*d*, *J* =

12.2, 1 H); 4.23 (*d*, *J* = 11.7, 1 H); 4.34 (*d*, *J* = 11.7, 1 H); 4.41 (*d*, *J* = 12.4, 1 H); 4.50 (*d*, *J* = 3.6, 1 H); 4.54 (*d*, *J* = 7.8, H–C(1′)); 4.50–4.70 (*m*, 4 H); 4.72–4.84 (*m*, 2 H); 4.96–5.10 (*m*, 2 H); 5.60 (*dd*, *J* = 10.0, 7.8, 1 H); 7.00–7.50 (*m*, 32 H); 7.51–7.80 (*m*, 1 H); 7.89 (*d*, *J* = 8.3, 2 H). ^{13}C-NMR ($CDCl_3$): 55.2; 67.8; 68.0; 69.5; 71.2; 72.4; 72.5; 73.27; 73.33; 73.4; 73.5; 74.6; 75.3; 76.5; 78.8; 79.9; 98.3; 100.6; 126.9; 127.40; 127.44; 127.5; 127.65; 127.68; 127.75; 127.84; 127.89; 127.91; 128.0; 128.1; 128.22; 128.26; 128.29; 128.31; 128.35; 129.8; 129.9; 132.9; 137.7; 138.0; 138.4; 138.7; 139.5; 164.9. HR-MS: 1023.4301 ($C_{62}H_{64}NaO_{12}^+$, $[M+Na]^+$; calc. 1023.4295).

Ethyl 2,3,4-Tri-O-*benzoyl-6*-O-*(2*-O-*benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-1-thio-β*-D-*glucopyranoside* (**51**). According to *GP (TfOH)*, for 5 h. Yield 85%. Colorless foam. $[\alpha]_D^{21} = 26.2$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1728, 1265, 1095, 709. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.04 (*t*, *J* = 7.3, 3 H); 2.42 (*dq*, *J* = 12.5, 7.3, 1 H); 2.52 (*dq*, *J* = 12.5, 7.3, 1 H); 3.48–3.54 (*m*, 1 H); 3.65–3.80 (*m*, 4 H); 3.81 (*dd*, *J* = 9.2, 8.9, 1 H); 3.93–3.98 (*m*, 1 H); 4.01 (*dd*, *J* = 11.6, 1.5, 1 H); 4.44 (*d*, *J* = 12.2, 1 H); 4.52–4.57 (*m*, 2 H); 4.62 (*d*, *J* = 9.8, 1 H); 4.65 (*d*, *J* = 11.0, 1 H); 4.67 (*d*, *J* = 8.2, H–C(1′)); 4.73 (*d*, *J* = 11.0, 1 H); 4.79 (*d*, *J* = 11.0, 1 H); 5.28 (*dd*, *J* = 8.9, 8.2, 1 H); 5.33 (*dd*, *J* = 9.8, 9.5, 1 H); 5.39 (*dd*, *J* = 9.8, 9.5, 1 H); 5.79 (*dd*, *J* = 9.5, 9.5, 1 H); 7.18–7.50 (*m*, 26 H); 7.52–7.58 (*m*, 1 H); 7.75 (*dd*, *J* = 7.3, 1.5, 2 H); 7.86 (*dd*, *J* = 8.2, 1.2, 2 H); 7.91 (*dd*, *J* = 8.5, 1.5, 2 H); 8.06 (*dd*, *J* = 8.6, 1.5, 2 H). ^{13}C-NMR ($CDCl_3$): 14.7; 23.8; 60.3; 68.0; 68.4; 69.5; 70.5; 73.4; 73.6; 74.0; 74.9; 75.06; 75.15; 77.7; 78.2; 82.8; 83.2; 101.0; 127.6; 127.7; 127.9; 128.17; 128.25; 128.30; 128.35; 128.6; 128.8; 129.1; 129.6; 129.8; 129.9; 133.0; 133.1; 133.2; 133.4; 137.7; 137.8; 137.9; 165.0; 165.1; 165.3; 165.6. HR-MS: 1095.3625 ($C_{63}H_{60}NaO_{14}S^+$, $[M+Na]^+$; calc. 1095.3601).

Ethyl 2,3,4-Tri-O-*benzoyl-6*-O-*(2*-O-*benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-1-thio-β*-D-*glucopyranoside* (**52**). According to *GP (TfOH)*, for 1.5 h. Yield 81%. Colorless foam. $[\alpha]_D^{24} = +12.9$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1728, 1265, 1095, 710. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.97 (*t*, *J* = 7.3, 3 H); 2.35 (*dq*, *J* = 12.5, 7.3, 1 H); 2.45 (*dq*, *J* = 12.5, 7.3, 1 H); 3.46–3.60 (*m*, 3 H); 3.62 (*dd*, *J* = 10.1, 2.8, 1 H); 3.71 (*dd*, *J* = 11.6, 7.6, 1 H); 3.90–4.05 (*m*, 3 H); 4.30 (*d*, *J* = 11.9, 1 H); 4.33 (*d*, *J* = 11.9, 1 H); 4.44 (*d*, *J* = 12.2, 1 H); 4.55–4.68 (*m*, 4 H, including H–C(1′)); 4.94 (*d*, *J* = 11.6, 1 H); 5.30 (*dd*, *J* = 9.8, 9.8, 1 H); 5.37 (*dd*, *J* = 9.8, 9.5, 1 H); 5.65 (*dd*, *J* = 10.1, 7.9, H–C(2′)); 5.78 (*dd*, *J* = 9.5, 9.5, 1 H); 7.20–7.60 (*m*, 27 H); 7.75 (*d*, *J* = 7.6, 2 H); 7.83 (*d*, *J* = 7.3, 2 H); 7.90 (*d*, *J* = 7.3, 2 H); 8.05 (*d*, *J* = 7.6, 2 H). ^{13}C-NMR ($CDCl_3$): 14.6; 23.9; 53.4; 67.9; 68.3; 69.5; 70.6; 71.6; 71.7; 72.2; 73.5; 74.1; 74.4; 78.1; 79.9; 83.1; 101.2; 127.5; 127.6; 127.75; 127.82; 128.1; 128.20; 128.23; 128.26; 128.4; 128.6; 128.8; 129.1; 129.6; 129.7; 129.8; 130.1; 132.9; 133.0; 133.1; 133.3; 137.5; 137.7; 138.3; 165.0; 165.2; 165.3; 165.6. HR-MS: 1095.3586 ($C_{63}H_{60}NaO_{14}S^+$, $[M+Na]^+$; calc. 1095.3601).

Ethyl 3-O-*Acetyl-6*-O-*(2*-O-*benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*glucopyranosyl)-4*-O-*benzyl-2-deoxy-2-phthalimido-1-thio-β*-D-*glucopyranoside* (**53**). According to *GP (TfOH)*, for 8 h. Yield 81%. White crystals. M.p. 157–160°. $[\alpha]_D^{21} = +17.6$ ($c = 1.2$, $CHCl_3$). IR (KBr): 1720, 1381, 1265, 1227, 1095, 710. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.08 (*t*, *J* = 7.3, 3 H); 1.67 (*s*, 3 H); 2.46 (*dq*, *J* = 12.5, 7.3, 1 H); 2.58 (*dq*, *J* = 12.5, 7.3, 1 H); 3.55–3.62 (*m*, 1 H); 3.66 (*dd*, *J* = 10.1, 8.2, 1 H); 3.67–3.73 (*m*, 1 H); 3.75–3.86 (*m*, 5 H); 4.17 (*dd*, *J* = 11.0, 1.2, 1 H); 4.23 (*dd*, *J* = 10.4, 10.0, 1 H); 4.37 (*d*, *J* = 11.3, 1 H); 4.47 (*d*, *J* = 11.3, 1 H); 4.598 (*d*, *J* = 12.2, 1 H); 4.600 (*d*, *J* = 10.4, 1 H); 4.65 (*d*, *J* = 7.9, H–C(1′)); 4.68 (*d*, *J* = 10.7, 1 H); 4.69 (*d*, *J* = 12.2, 1 H); 4.75 (*d*, *J* = 11.0, 1 H); 4.82 (*d*, *J* = 10.7, 1 H); 5.37 (*dd*, *J* = 9.2, 7.9, 1 H); 5.40 (*d*, *J* = 10.4, 1 H); 5.74 (*dd*, *J* = 10.0, 8.2, 1 H); 7.04–7.43 (*m*, 22 H); 7.50–7.55 (*m*, 1 H); 7.67–7.74 (*m*, 2 H); 7.78–7.85 (*m*, 2 H); 8.02 (*dd*, *J* = 8.2, 1.2, 2 H). ^{13}C-NMR ($CDCl_3$): 14.9; 20.4; 23.8; 54.1; 67.9; 68.7; 73.6; 73.8; 73.9; 74.4; 74.96; 74.99; 75.3; 76.6; 78.0; 78.6; 80.4; 82.8; 101.1; 123.4; 123.5; 127.3; 127.6; 127.8; 127.9; 128.20; 128.26; 128.34; 128.4; 129.7; 131.2; 131.7; 133.0; 134.0; 134.2; 137.75; 137.78; 138.1; 165.0; 167.4; 167.6; 169.9. HR-MS: 1044.3619 ($C_{59}H_{59}NNaO_{13}S^+$, $[M+Na]^+$; calc. 1044.3605).

Ethyl 3-O-*Acetyl-6*-O-*(2*-O-*benzoyl-3,4,6-tri*-O-*benzyl-β*-D-*galactopyranosyl)-4*-O-*benzyl-2-deoxy-2-phthalimido-1-thio-β*-D-*glucopyranoside* (**54**). According to *GP (TfOH)*, for 3.5 h. Yield 71%. Colorless oil. $[\alpha]_D^{22} = +11.8$ ($c = 1.0$, $CHCl_3$). IR (KBr): 1720, 1381, 1095, 748, 710. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.03 (*t*, *J* = 7.3, 3 H); 1.67 (*s*, 3 H); 2.40 (*dq*, *J* = 12.5, 7.3, 1 H); 2.55 (*dq*, *J* = 12.5, 7.3, 1 H); 3.56–3.72 (*m*, 6 H); 3.75 (*dd*, *J* = 11.2, 4.9, 1 H); 4.02–4.05 (*m*, 1 H); 4.14–4.18 (*m*, 1 H); 4.20 (*dd*, *J* = 10.4, 10.4, 1 H); 4.37 (*d*, *J* = 9.6, 1 H); 4.40–4.52 (*m*, 4 H); 4.60 (*d*, *J* = 8.0, H–C(1′)); 4.62–4.68 (*m*, 2 H); 5.00 (*d*, *J* = 11.6, 1 H); 5.37 (*d*, *J* = 10.4, 1 H); 5.66–5.74 (*m*, 2 H); 7.00–7.10 (*m*, 2 H); 7.10–7.45 (*m*, 20 H); 7.54 (*dd*, *J* = 7.3, 7.3, 1 H); 7.57–7.62 (*m*, 2 H); 7.75–7.85 (*m*, 2 H); 8.02 (*d*, *J* = 7.3, 2 H). ^{13}C-NMR ($CDCl_3$): 14.7; 20.4; 23.6; 54.0; 67.6; 68.4; 71.6; 71.7; 72.3; 73.5; 73.6; 73.9; 74.3; 74.4; 76.5; 78.5; 79.9; 80.2; 101.4; 123.4; 123.5; 127.4; 127.5; 127.6; 127.8; 127.9; 128.16; 128.18; 128.22; 128.26; 128.4; 129.8; 130.1; 131.7; 132.8; 133.9; 134.2; 137.5; 137.8; 138.4; 165.1; 167.3; 167.5; 169.9. HR-MS: 1044.3602 ($C_{59}H_{59}NNaO_{13}S^+$, $[M+Na]^+$; calc. 1044.3605).

REFERENCES

[1] K. Toshima, K. Tatsuta, *Chem. Rev.* **1993**, *93*, 1503; K. Suzuki, T. Nagasawa, *J. Synth. Org. Chem. Jpn*. **1992**, *50*, 378.
[2] T. Mukaiyama, Y. Murai, S. Shoda, *Chem. Lett*. **1981**, 431.
[3] T. Mukaiyama, Y. Hashimoto, S. Shoda, *Chem. Lett*. **1983**, 935.
[4] 'Handbook of Chemistry and Physics', 72nd Edition, 9–105.
[5] M. Shimizu, H. Togo, M. Yokoyama, *Synthesis* **1998**, 799.
[6] S. Hashimoto, M. Hayashi, R. Noyori, *Tetrahedron. Lett*. **1984**, *25*, 1379.
[7] M. Kreuzer, J. Thiem, *J. Carbohydr. Chem*. **1986**, *149*, 347.
[8] H. Kunz, W. Sager, *Helv. Chim. Acta* **1985**, *68*, 283.
[9] H. P. Wessel, *Tetrahedron Lett*. **1990**, *31*, 6863.
[10] T. Matsumoto, H. Maeta, K. Suzuki, G. Tsuchihashi, *Tetrahedron Lett*. **1988**, *29*, 3567, 3571, 3575.
[11] S. Kobayashi, K. Koide, M. Ohno, *Tetrahedron Lett*. **1990**, *31*, 2435.
[12] S. Hosono, W.-S. Kim, H. Sasai, M. Shibasaki, *J. Org. Chem*. **1995,** *60*, 4.
[13] W.-S. Kim, S. Hosono, H. Sasai, M. Shibasaki, *Tetrahedron Lett*. **1995**, *36*, 4443.
[14] T. Mukaiyama, T. Ishikawa, H. Uchiro, *Chem. Lett.* **1997**, 389; K. Takeuchi, S. Higuchi, T. Mukaiyama, *Chem. Lett.* **1997**, 969; T. Mukaiyama, M. Yamada, S. Suda, *Chem. Lett.* **1992**, 1401; T. Mukaiyama, K. Miyazaki, H. Uchiro, *Chem. Lett.* **1998**, 635; H. Uchiro, T. Mukaiyama, *Chem. Lett.* **1997**, 121.
[15] K. Takeuchi, T. Mukaiyama, *Chem. Lett*. **1998**, 555.
[16] T. Mukaiyama, H. Jona, K. Takeuchi, *Chem. Lett*. **2000**, in press.
[17] T. Mukaiyama, S. Kobayashi, S. Shoda, *Chem. Lett*. **1984**, 907.
[18] H. Uchiro, T. Mukaiyama, *Chem. Lett*. **1996**, 79; K. Takeuchi, S. Higuchi, T. Mukaiyama, *Chem. Lett*. **1997**, 969.
[19] T. Mukaiyama, K. Miyazaki, H. Uchiro, *Chem. Lett*. **1998**, 635.
[20] H. Uchiro, T. Mukaiyama, *Chem. Lett*. **1997**, 121.
[21] A. Ogawa, D. P. Curran, *J. Org. Chem*. **1997**, *62*, 450.
[22] D. R. Mootoo, P. Konradsson, U. Udodong, B. Fraser-Reid, *J. Am. Chem. Soc*. **1988**, *110*, 5583.
[23] M. I. Barrena, R. Echarri, S. Castillon, *Synlett* **1996**, 675.
[24] L. Green, B. Hinzen, S. J. Ince, P. Langer, S. V. Ley, S. L. Warriner, *Synlett* **1998**, 440.
[25] J. T. Randolph, S. J. Danishefsky, *J. Am. Chem. Soc*. **1995**, *117*, 5693.
[26] K. Takeuchi, T. Tamura, T. Mukaiyama, *Chem. Lett*. **2000**, 122.
[27] O. Kanie, Y. Ito, T. Ogawa, *J. Am. Chem. Soc*. **1994**, *116*, 12073.
[28] K. Fukase, A. Hasuoka, I. Kinoshita, Y. Aoki, S. Kusumoto, *Tetrahedron* **1995**, *51*, 4923.
[29] K. Tsuboyama, K. Takeda, K. Torii, M. Ebihara, J. Shimizu, A. Suzuki, N. Sato, K. Furuhata, H. Ogura, *Chem. Pharm. Bull*. **1990**, *38*, 636.
[30] Y. D. Vanker, P. S. Vanker, M. Behrendt, R. R. Schmidt, *Tetrahedron* **1991**, *47*, 9985.
[31] H. Uchiro, N. Kurusu, T. Mukaiyama, *Israel J. Chem*. **1997**, *37*, 87.
[32] A. Marra, J. Esnault, A. Veyrières, P. Sinaÿ, *J. Am. Chem. Soc.* **1992**, *114*, 6354.
[33] H. Matsui, J. Furukawa, T. Awano, N. Nishi, N. Sakairi, *Chem. Lett*. **2000**, 326.
[34] M. Lergenmüller, Y. Ito, T. Ogawa, *Tetrahedron* **1998**, *54*, 1381.
[35] K. I. Eklind, H. R. Loenn, A. U. E. Tiden, Jap. Pat. 8-512026 (1996).

Received May 2, 2000