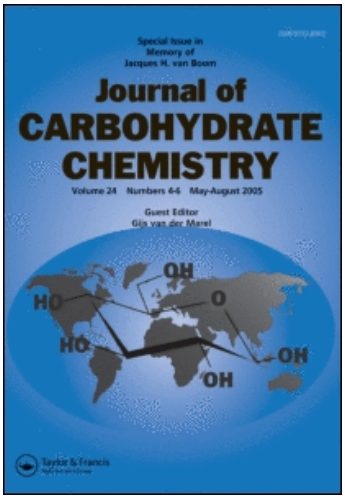

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Scope and Applications of "Active and Latent" Thioglycosyl Donors. Part 4

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SCOPE AND APPLICATIONS OF "ACTIVE AND LATENT" THIOGLYCOSYL DONORS. PART 4[1,2]

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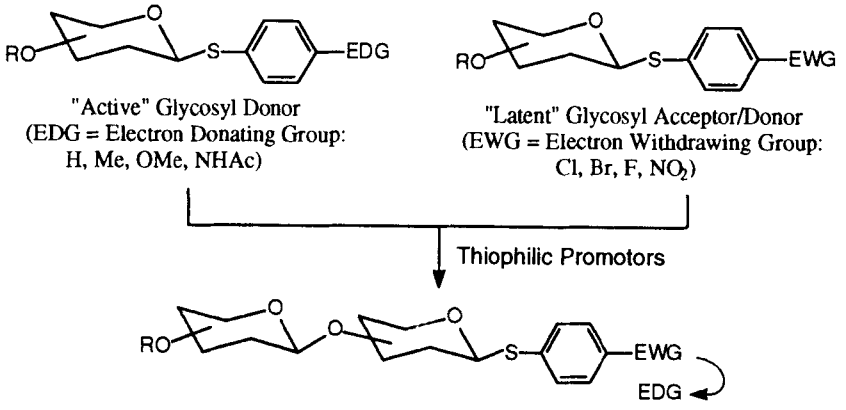
ABSTRACT

The relative reactivity of various thioglycosyl donors having ethyl, phenyl, or *para*-substituted phenyl groups with electron donating (*N*-Ac) or electron withdrawing (NO_2) substituents were compared using 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**) as standard glycosyl acceptor. The reactivity order was found to decrease from ethyl > phenyl > *p*-acetamidophenyl > *p*-nitrophenyl. In the latter situation, when the thioglycosyl donor was also equipped with "disarming" ester protecting groups, they were found to be inert or inactive toward common thiophilic promotors. Alternatively, it was possible to selectively activate the "armed" perbenzylated *p*-nitrophenyl 1-thio-β-D-galactopyranoside (**21**) in the presence of the corresponding "disarmed" perbenzoylated *p*-nitrophenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (**15**) which served as the glycosyl acceptor. When both "armed" perbenzylated thioglycosides **7** and **25** were used as thioglycosyl donor and thioglycosyl acceptor, respectively, the milder thiophilic promotor methyl triflate was required for chemoselective activation. These results further demonstrate the potential of "armed and disarmed" "active and latent" thioglycosides in blockwise oligosaccharide syntheses.

INTRODUCTION

After we[2] first published that "active and latent" (Scheme 1) *para*-substituted phenyl 1-thioglycosides could be used as efficient glycosyl donors[4] of controllable reactivity, other groups have confirmed[5] and exploited these findings with aryl sulfoxides,[6] allyl *vs.* vinyl glycosides,[7] and bulky alkyl thioglycosides.[8] Several aspects of these studies

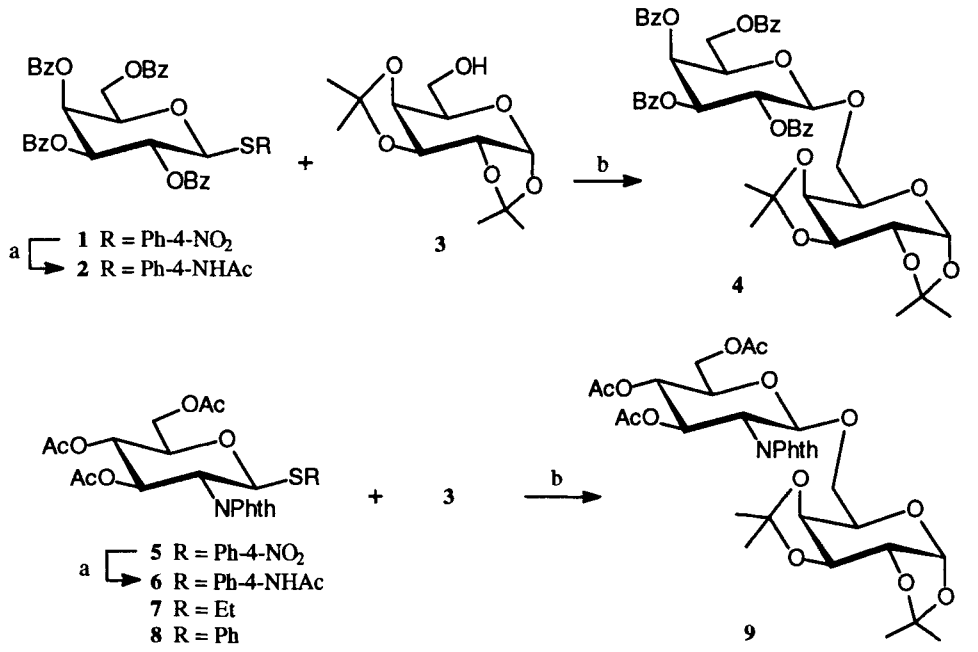


Scheme 1. Iterative "Active-Latent" glycosylation strategy. Note that the R-protecting groups could either be "arming" or "disarming".

have been recently reviewed.[9] Thus, the active and latent thioglycosylation strategy can nicely complement the armed-disarmed strategy[10] by further controlling the reactivity of the glycosyl donors from the aglycone rather than from the glycone themselves. The present work further defines the scope and limitations of the strategy. Scheme 1 below shows the general strategy and its application in blockwise oligosaccharide synthesis.

RESULTS AND DISCUSSION

In order to study the flexibility of the "active-latent" glycosylation strategy introduced by us,[2] we first investigated the glycosylation behavior of different thioglycosyl donors with the acceptor 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**3**) (Scheme 2). The thioglycosides chosen as donors were the fully benzoylated 4-nitrophenyl 1-thio-β-D-galactopyranoside **1** and 4-nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5**), as well as the corresponding 4-acetamidophenylthio glycosides **2** and **6**. Compound **1** was obtained by benzoylation (BzCl, pyridine, 89%) of 4-nitrophenyl 1-thio-β-D-galactopyranoside,[2b] whereas compound **5** was synthesized from 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose[11] by reaction with 4-nitrothiophenol under the catalytic action of tin(IV) chloride. Compounds **2** and **6** were obtained by reduction with $SnCl_2$[2a] and acetylation of **1** and **5**, respectively. When active-disarmed 4-acetamidophenyl thioglycosyl donors **2** and **6** were treated with glycosyl acceptor **3** using



Scheme 2. *Reagents and conditions:* (a) *i*: $SnCl_2$, EtOH, 70 °C, 2 h; *ii:* Ac_2O, pyridine, 70% for **2**, 93% for **6**; (b) NIS-TfOH, CH_2Cl_2, -30 °C, 94% for **4** and 77-92% for **9** (see Table 1 for details).

only a catalytic amount of TfOH (0.2 equiv) in dichloromethane, no glycosylation products were observed. However, formation of disaccharides **4** (94%) and **9** (80%), respectively, were rapidly achieved in high yields when TfOH was present in equimolar amounts with respect to the thioglycosyl donor (Table 1). As expected,[2] coupling latent-disarmed 4-nitrophenyl thioglycosides **1** and **5** with the same acceptor **3** did not take place even when equimolar amounts of triflic acid were used.

In order to further assess the "unreactivity" of disarmed 4-nitrophenyl thioglycosides in glycosylation reactions, an equimolar mixture of **1** and **2** was treated with acceptor **3** under the same reaction conditions described above. Thin-layer chromatography of this competitive experiment revealed the rapid disappearance of the active donor **2** while 4-nitrophenyl thioglycoside **1** remained unaffected. The relative reactivity of the 4-acetamidophenyl thioglycosides with respect to the widely used ethyl and phenyl thioglycosyl donors was then qualitatively evaluated. Ethyl 1-thio- and phenyl 1-thio-glucosaminides **7**[12] and **8**[13] were synthesized from 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-

Table 1. Glycosylation between thioglycosyl donors **1**, **2**, **5-8** with acceptor **3**.

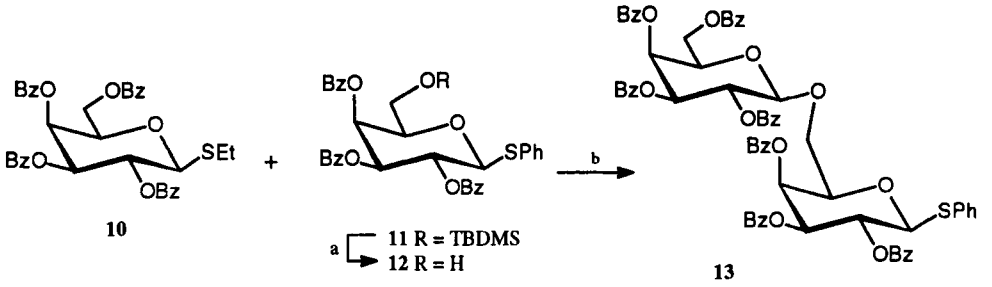
Entry[a]	Donor	NIS-TfOH[b]	Time (min)	Compound (Yield %)[c]
1	**1**	1.8/1.2	NR	-
2	**2**	1.8/1.2	10	**4** (94)
3	**5**	1.8/1.2	NR	-
4	**6**	1.8/1.2	20	**9** (80)
5	**7**	1.8/0.2	20	**9** (92)
6	**8**	1.8/0.6	25	**9** (77)

a. Reactions were performed at -30 °C in CH_2Cl_2 and with a 1.2:1.0 molar ratio of donor *vs.* acceptor.
b. Molar ratios relative to acceptor **3**.
c. After purification by silica gel column chromatography.

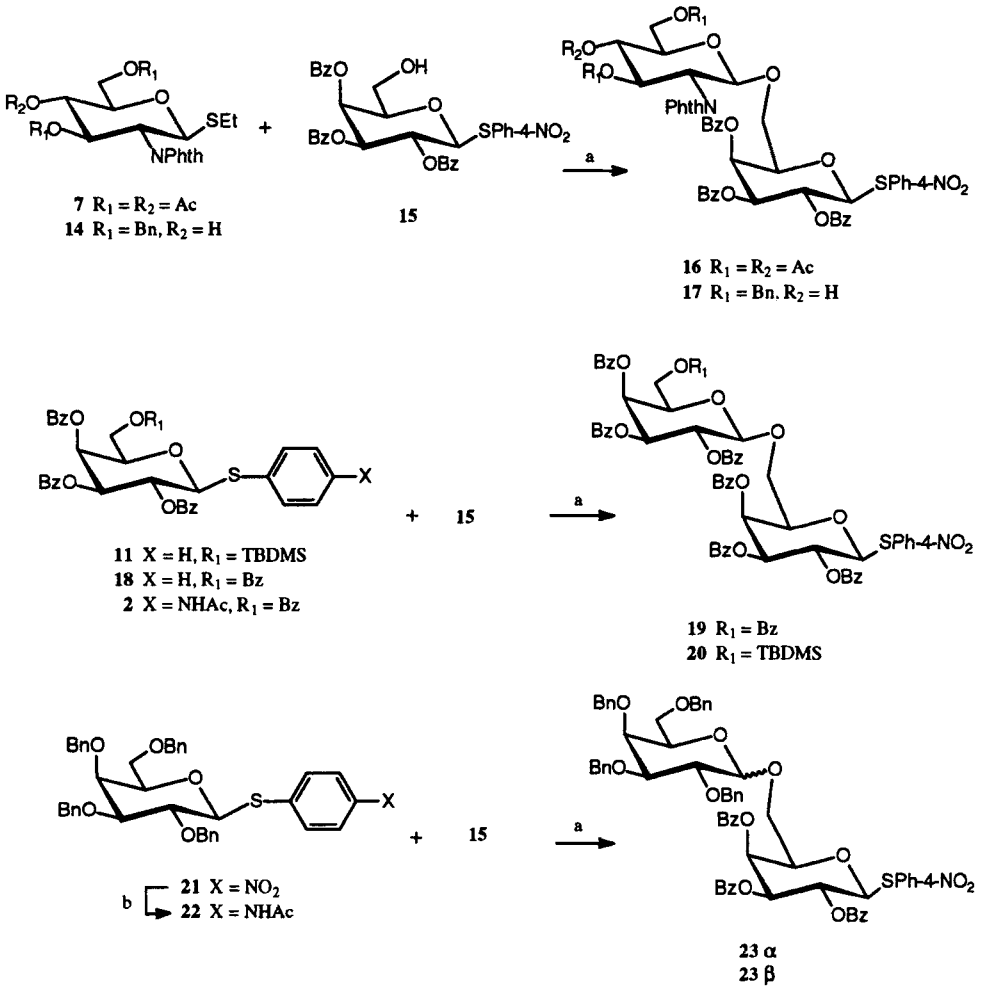
phthalimido-β-D-glucopyranose by reaction with ethanethiol or thiophenol, respectively, under the catalytic action of tin(IV) chloride in excellent yields and with complete stereocontrol. Glycosylations of **7** and **8** with **3** were performed using only catalytic amounts of TfOH. As judged from TLC, **7** reacted slightly faster than **8**, as expected. The higher reactivity of ethyl thioglycosides than phenyl thioglycosides was further established by treating perbenzoylated ethyl 1-thio-β-D-galactopyranoside donor **10** with phenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside **12** as acceptor (Scheme 3). The reaction was complete within 5 min and disaccharide **13** was obtained in 89% yield. Self condensation or cyclization of the acceptor **12** was not detected. From these results, the relative reactivity of thioglycosyl donors can be estimated as: SEt > SPh > SPhNHAc > $SPhNO_2$.

Considering the observed differences in reactivities between ethyl and phenyl thioglycosyl donors, it was anticipated that selective activation could also be achieved when active 4-acetamidophenyl thioglycosyl donors were used in the presence of latent 4-nitrophenyl thioglycosides acting as acceptors. For this purpose, 4-nitrophenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside **15**[2b] was initially used as the acceptor (Scheme 4).

First, ethyl 2-deoxy-2-phthalimido-1-thio-β-D-glucopyranosides **7**[12] and **14** and phenyl 1-thio-β-D-galactopyranoside derivatives **11** and **18** were arbitrarily chosen as disarmed-active donors to be used in the glycosylation reactions with latent-acceptor **15**.



Scheme 3. *Reagents and conditions:* (a) Et_2O, HCl, MeOH, 97%; (b) NIS-TfOH, CH_2Cl_2, -30 °C, 89%.



Scheme 4. *Reagents and conditions:* (a) NIS-TfOH, CH_2Cl_2, -30 °C (see Table 2 for yields); (b) *i*: $SnCl_2$, EtOH, 70 °C, 2 h; *ii:* Ac_2O, pyridine, 91%.

NIS-TfOH mediated glycosidations of donors **7, 14, 11,** and **18** with **15** afforded the corresponding disaccharides **16, 17, 19, 20** in high yields (78-89%) with complete β–stereocontrol (Table 2).

In the next steps, the relative reactivities of armed and disarmed (active) 4-acetamidophenyl 1-thioglycosides were established using perbenzoylated 4-nitrophenyl 1-thioglycoside **15** as the acceptor (disarmed-latent) (Scheme 4). To this end, fully benzoylated and benzylated 4-acetamidophenyl 1-thio-β-D-galactopyranosides **2** and **22** were glycosylated with **15** using TfOH in a 1.5:1 molar ratio relative to the acceptor. Similar to the results obtained from **11** and **18**, glycosidation of disarmed-active galactoside **2** with **15** gave disaccharide **19** in 87 % yield (Table 2). Similarly and as expected, armed donor **22** also allowed rapid formation of disaccharide **23** in high yield (92%) albeit as a 3:1 α,β anomeric mixture (Table 2).

To complete the evaluation of the relative reactivities of disarmed-latent 4-nitrophenyl thioglycosyl acceptors, glycosidation of 4-nitrophenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside **21** was examined using the acceptor **15**. Consumption of acceptor **15** took place within 1 h and, similar to its reaction with **22**, an anomeric mixture of disaccharide **23** was isolated (76% yield) as a 4:1 mixture of the α,β-anomers.

Interestingly, none of the reactions performed using alcohol **15** as an acceptor and NIS-TfOH as promotors yielded detectable amounts of product resulting from self-condensation or products containing 1,6-anhydro derivatives.[5] From the results obtained in the glycosylation reactions using **15** as acceptor, several conclusions can be drawn. Overall, these reactions showed that the decreased nucleophilicity of the sulfur atom in perbenzoylated (disarmed-latent) 4-nitrophenyl 1-thioglycosides, such as **15**, allowed chemoselective activation of, not only disarmed-active ethyl 1-thio- and phenyl 1-thioglycosyl donors, but also of armed 4-acetamidophenyl 1-thioglycosyl donors and even of armed-latent 4-nitrophenyl 1-thioglycosyl donors leading to the formation of disaccharides in high to excellent yields (76-92%) when NIS-TfOH were used as promotors. These findings further extend similar observations by Sliedregt *et al.*[5] who recently studied the coupling of disarmed-latent 4-nitrophenyl 2,3,4,tri-*O*-benzoyl-1-thio-β-D-glucopyranoside with the corresponding armed ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside and disarmed ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-glucopyranoside donors using IDCP and NIS-TfOH as promotors, respectively. In both cases, glycosylation products were observed but the coupling was efficient only in the second case.

Table 2. Glycosylation reactions between thioglycosyl donors **2**, **7**, **11**, **14**, **18**, **21**, **22** and acceptor **15** (Scheme 4).

Entry	Donor[a]	NIS-TfOH[b]	Time (min)	Compounds (yield %)[c]	α/β
1	**7**	1.8/0.2	15	**16** (78)	β
2	**14**	1.8/0.2	10	**17** (89)	β
3	**18**	1.8/0.6	20	**19** (81)	β
4	**11**	1.8/0.6	25	**20** (79)	β
5	**2**	1.8/1.2	25	**19** (87)	β
6	**22**	1.8/1.2	25	**23** (92)	3:1
7	**21**	1.8/1.2	25	**23** (76)	4:1

a. Reactions were performed at -30 °C in CH_2Cl_2 and a 1.2:1.0 molar ratios of donor to acceptor.
b. Molar ratios relative to acceptor **15**.
c. Isolated yield after purification by silica gel column chromatography.

In addition, it should be noticed that the reaction between donor **21** and acceptor **15** constitutes the first example of coupling of two so-called "latent" thioaryl glycosides. This result further confirmed the validity of the "armed-disarmed" glycosylation strategy even when the nucleophilicity of both acceptor and donor is decreased by the presence of an electron withdrawing nitro functionality in the aryl group of the aglycone. The ability of perbenzylated 4-nitrophenyl 1-thioglycosides to work as glycosyl donors was previously observed,[5] but only with non-thioglycoside acceptors in glycosylation mediated by DMTST. These authors carried out the reaction of perbenzylated 4-nitrophenyl 1-thio-β-D-glucopyranoside with acceptor **3** and isolated the corresponding disaccharide in 75% yield.

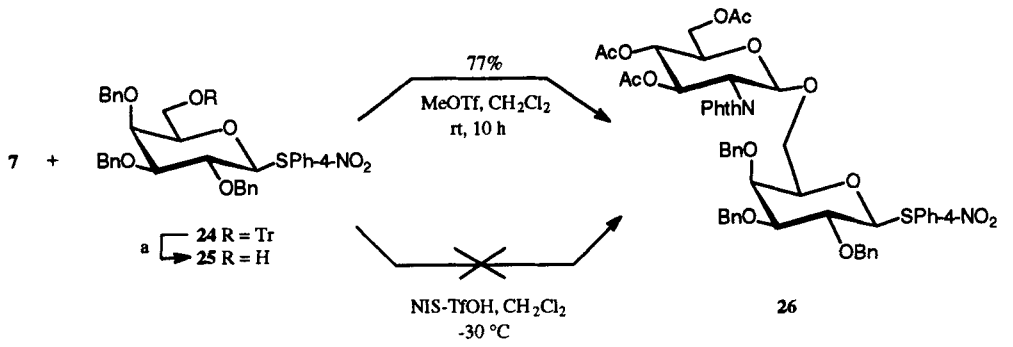
Considering these last results, glycosylation reactions with an "armed-latent" glycosyl acceptor were examined. This situation was previously addressed by Sliedregt *et al.*[5] who studied the coupling of fully benzylated ("armed") and fully benzoylated

("disarmed") ethyl 1-thio-β-D-glucopyranoside with 4-nitrophenyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside **25** using IDCP and NIS-TfOH as promotors, respectively. In both cases, they found that the corresponding disaccharides were formed but only in low yields and with concomitant intramolecular cyclization of the acceptor (1,6-anhydro derivative). 4-Nitrophenyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside **25** was synthesized to be used as "armed-latent" acceptor. Attempts to prepare this compound using the method suggested by Ohrui *et al.*[14] was not successful in our hands because benzylation of 6-*O*-*tert*-butyldimethylsilyl galactoside led to concomitant cleavage of the 6-*O*-silyl group under the basic conditions giving perbenzylated galactoside as the major product. Thus, compound **25** was prepared starting from 4-nitrophenyl 1-thio-β-D-galactopyranoside by tritylation, benzylation (86%) and by detritylation (95%) of the resulting **24**. Glycosylation of "disarmed" ethyl thioglycosyl donor **7** with acceptor **25** using NIS-TfOH as promotor led to a complex mixture that was not further investigated. However, the coupling took place smoothly when the less thiophilic methyl triflate promotor was used (CH_2Cl_2, rt) to give disaccharide **26** in 77% yield (Scheme 5).

As demonstrated from reaction between **21** with **15** (entry 7, Table 2), compound **21** could be used directly as a glycosyl donor without manipulating the anomeric center in further glycosylation reactions with disarmed 4-nitrophenyl thioglycosyl donors, allowing the preferential formation of a 1,2-*cis* linkage. On the other hand, disaccharide **20** is a versatile compound because chain-elongation can be performed at the non-reducing end (C-6') by removing the silyl protecting group and also at the reducing-end (C-1) by conversion of the nitro group (latent) into an acetamido group (active). The above results further substantiate earlier observations reported by Garegg and coworkers,[4] who first described the usefulness and versatility of thioglycosides in oligosaccharide syntheses before the advent of NIS-TfOH as a promotor.

EXPERIMENTAL

General methods. Melting points were measured with a Gallenkamp apparatus and are uncorrected. Optical rotations were recorded on a Perkin Elmer 241 polarimeter at room temperature. NMR spectra were recorded for $CDCl_3$ solutions on a Bruker AMX 500, Varian XL 300, or Gemini 200 spectrometers at 500, 300 and 200 MHz for protons and 125.7, 75.4 and 50.3 MHz for carbons, respectively. Proton chemical shifts (ppm) are given relative to internal chloroform (7.24 ppm) and carbon chemical shifts (ppm) are



Scheme 5. *Reagents and conditions:* (a) *p*-TsOH, CH_2Cl_2, MeOH, rt, 30 min, 95%.

referred to internal $CDCl_3$ (77.0 ppm). Mass spectra were obtained using a VG 7070-E spectrometer (EI and CI) or Kratos IIH instrument (FAB-glycerol). Xenon was used as the carrier in FAB-MS experiments. Thin-layer chromatography (TLC) was performed using silica Gel 60-F254 glass plates. The developed TLC plates were dipped in a solution of ceric ammonium sulfate (1% v/v) in 10% aqueous sulfuric acid, and heated to 150-200 °C.

4-Nitrophenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (1). To a solution of 4-nitrophenyl 1-thio-β-D-galactopyranoside[2b] (0.5 g, 1.6 mmol) in dry pyridine (8 mL), was added benzoyl chloride (1.1 mL, 9.6 mmol) and a catalytic amount of 4-dimethylaminopyridine. The solution was stirred at 0 °C for 1 h, and was then allowed to reach rt. After 3 h, the reaction mixture was quenched with ice water and extracted with methylene chloride (2 x 10 mL). The extracts were successively washed with sodium hydrogen carbonate, water and brine. The organic phase was dried (sodium sulfate), filtered, concentrated under reduced pressure and coevaporated with toluene (2 x 20 mL). The residue was crystallized from 1:1 diethyl ether-hexane (10 mL) to afford **1** (1.03 g) in 89% yield as needles: mp 157-159 °C; $[\alpha]_D$ +76.5° (*c* 1.0, $CHCl_3$); IR (film) 3067, 2966, 1727, 1600, 1582, 1518, 1452, 1342, 1269, 1099, 1069, 910, 852, 711 cm^{-1}; ^1H NMR δ 8.03 - 7.19 (m, 24H, aromatic), 6.03 (dd, 1H, $J_{4,5} < 1.0$ Hz, H-4), 5.82 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 5.66 (dd, 1H, $J_{3,4} = 3.3$ Hz, H-3), 5.17 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1), 4.64 (dd, 1H, $J_{5,6a} = 7.2$, $J_{6a,6b} = 11.3$ Hz, H-6a), 4.53(dd, 1H, $J_{5,6b} = 4.5$ Hz, H-6b), 4.47 (m, 1H, H-5); ^{13}C NMR δ 165.9, 165.3(2C), 165.1 (C=O), 146.9 (C-para), 141.5 (C-ipso), 133.9-123.7 (C-aromatic), 84.6 (C-1), 75.6 (C-5), 72.5 (C-3), 68.2 (C-4), 67.5 (C-2), 62.6 (C-6); CI-

MS (ether) *m/z* (ion, relative intensity) 733.7 ($[M]^+$, 3.3%), 579.2 ($[M-HSPhNO_2]^+$, 100%).

Anal. Calcd for $C_{40}H_{31}O_{11}NS$ (733.75): C, 65.48; H, 4.26; N, 1.91; S, 4.37. Found: C, 65.61; H, 4.46; N, 1.92; S, 4.20.

4-Acetamidophenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (2). To a solution of **1** (300 mg, 0.41 mmol) in absolute ethanol (20 mL) was added tin dichloride ($SnCl_2 2H_2O$) (460 mg, 20 mmol). The reaction mixture was stirred at 70 °C for 2 h. After cooling, the reaction mixture was poured onto ice-water. The pH of the solution was adjusted to 7 by addition of sodium hydrogen carbonate. The resulting mixture was extracted with ethyl acetate (3 x 20 mL). The extracts were washed successively with saturated sodium hydrogen carbonate and water. The organic phase was dried (sodium sulfate) and concentrated under reduced pressure. The resulting crude residue was acetylated with pyridine-acetic anhydride (4:2 mL) for 2 h at rt. Standard work-up gave a residue that was purified by silica gel column chromatography (ethyl acetate-hexane, 1:1) to give **2** (230 mg) as a white solid in 70% yield: mp 119-121 °C; $[\alpha]_D$ +91.0° (*c* 0.96, $CHCl_3$); IR (KBr) 3344, 3065, 2970, 1716, 1594, 1522, 1452,, 1396, 1269, 1178, 909, 834, 711 cm^{-1}; ^1H NMR δ 8.02 - 7.18 (m, 24H, aromatic), 5.98 (dd, 1H, $J_{4,5}$ <1.0 Hz, H-4), 5.72 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.57 (dd, 1H, $J_{3,4}$ = 2.7 Hz, H-3), 4.95 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.64 (dd, 1H, $J_{5,6a}$ = 6.0 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 4.41 - 4.34 (m, 2H, H-5,6b), 1.83 (s, 3 H, Me); ^{13}C NMR δ 168.2 (C=O, NHAc), 166.0, 165.4, 165.3, 165.1 (C=O), 138.7-119.6 (C-aromatic), 86.0 (C-1), 75.0 (C-5), 72.9 (C-3), 68.3 (C-4), 67.8 (C-2), 62.4 (C-6), 24.6 (Ac); CI-MS (ether) *m/z* (ion, relative intensity) 745.8 ($[M]^+$, 1.7%), 579 ($[M+1-HSPhNHAc]^+$, 4.5%).

Anal. Calcd for $C_{42}H_{35}NO_{10}S$ (745.80): C, 67.64; H, 4.73; N, 1.88; S, 4.30. Found: C, 67.57; H, 5.00; N, 1.86; S, 4.17.

4-Nitrophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (5). Tin(IV) chloride (1.0 mL) was added to a stirred mixture of 1,3,4,6,-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose[11] (1.0 g, 2.09 mmol), 4-nitrothiophenol (650 mg, 2.5 mmol) and ground molecular sieves (1.0 g, 4 Å) in dichloromethane (10 mL) at 0 °C. The solution was stirred at rt for 4 h and filtered through a layer of celite, washed with ice-cold, 1 M sulfuric acid, aqueous sodium hydrogen carbonate, and water. The organic phase was dried (sodium sulfate), concentrated in vacuum, and coevaporated with toluene to give a crude product that was crystallized from diethyl ether-methylene chloride

to afford **5** (1.09 g) as needles in 91% yield: mp 217 °C; $[\alpha]_D$ +65.7 (*c* 1.0, $CHCl_3$); IR (film) 1749, 1719, 1580, 1518, 1379, 1342, 1230, 1077, 1039 cm^{-1}; ^1H NMR δ 8.11 - 7.48 (m, 8H, aromatic), 5.85 (d, 1H, $J_{1,2}$ = 10.6 Hz, H-1), 5.81 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.13 (dd, 1H, $J_{4,5}$ = 10.2 Hz, H-4), 4.39 (dd, 1H, $J_{2,3}$ = 10.2 Hz , H-2), 4.29 (dd, 1H, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.20 (dd, 1H, H-6b), 3.98 (ddd, 1H, $H_{5,6a}$ = 5.2, $H_{5,6b}$ = 2.3 Hz, H-5), 2.10, 2.02, 1.82 (3s, 9H, 3 OAc); ^{13}C NMR δ 170.4, 170.0, 169.4 (C=O), 168.4, 167.7 (C=O, Phth), 147.0-123.8 (C-aromatic), 81.9 (C-1), 76.2 (C-5), 71.3 (C-3), 68.4 (C-4), 62.1 (C-6), 53.3 (C-2), 20.9, 20.6, 20.4 (*Me*CO); CI-MS (ether) *m/z* (ion, relative intensity) 420 ($[M+1-SPhNO_2]^+$, 6.3%), 358 ($[M+1-HSPhNO_2\text{-}AcOH]^+$, 11.3%).

Anal. Calcd for $C_{26}H_{28}N_2O_{10}S$ (572.24): C, 54.54; H, 4.23; N, 4.89; S, 5.60. Found: C, 54.57; H, 4.41; N, 4.76; S, 5.77.

4-Acetamidophenyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (6). To a solution of **5** (1 g, 1.75 mmol) in absolute ethanol (30 mL) was added tin dichloride ($SnCl_2 2H_2O$) (1.84 g, 5.25 mmol). The reaction mixture was stirred at 70 °C for 2.5 h. The reaction mixture was then cooled and poured onto ice-water. The pH of the solution was adjusted to 7-8 by addition of sodium hydrogen carbonate. The resulting mixture was extracted with ethyl acetate (3 x 40 mL) which was successively washed with saturated sodium hydrogen carbonate and water. The organic phase was dried (sodium sulfate) and concentrated under reduced pressure. The resulting crude residue was then acetylated with pyridine-acetic anhydride (4:2 mL) at rt overnight. Standard work-up gave a residue that was purified by column chromatography (ethyl acetate-hexane 3:5) to give **6** (864 mg, 93%) as a solid: mp 185.0 °C; $[\alpha]_D$ +25.1° (*c* 1.0, $CHCl_3$); IR (KBr) 3328, 1748, 1718, 1592, 1525, 1495, 1380, 1234, 1039, 912, 726 cm^{-1}; ^1H NMR δ 7.86 - 7.72 (m, 4H, Phth), 7.41 - 7.30 (m, 4H, SPhNHAc), 5.74 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 5.59 (d, 1H, $J_{1,2}$ = 10.5 Hz, H-1), 5.08 (dd, 1H, $J_{4,5}$ = 10.1 Hz, H-4), 4.26 (dd, 1H, $J_{2,3}$ =10.3 Hz, H-2), 4.25 - 4.12 (m, 2H, H-6a, H-6b), 3.84 (ddd, 1H, $J_{4,5}$ = 10.2 $J_{5,6a}$ = 2.6, $J_{5,6b}$ = 5.0 Hz, H-5), 2.15, 2.08, 1.99, 1.80 (4s,4 x Ac), 1.62 (br, 1H, NH); ^{13}C NMR δ 170.7, 170.1, 169.4, 168.5 (C=O), 167.8, 167.0 (C=O Phth), 138.7-119.9 (aromatic), 83.1 (C-1), 75.9 (C-5), 71.6 (C-3), 68.6 (C-4), 62.1 (C-6), 53.5 (C-2), 24.6, 20.8, 20.6, 20.4 (*Me*CO). (+)FAB-MS (glycerol) *m/z* (ion, relative intensity) 585.2 ($[M+1]^+$, 5.9 %); 418.1 ($[M-HSPhNHAc]^+$, 1.2%).

Anal. Calcd for $C_{28}H_{28}N_2O_{10}S$ (584.58): C, 57.53; H, 4.83; N, 4.79; S, 5.48. Found: C: 57.48; H, 4.76; N, 4.86; S, 5.58.

Ethyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (10). Tin(IV) chloride (0.5 mL) was added to a stirred mixture of 1,2,3,4,6-penta-*O*-benzoyl-β-D-galactopyranose (701 mg, 1 mmol), ethanethiol (0.5 mL, 6.75 mmol), and ground molecular sieves (4Å, 1 g) in methylene chloride (10 mL) at 0 °C. After 1 h at rt, the mixture was filtered through a layer of celite, washed with ice-cold 1 M sulfuric acid, aqueous sodium hydrogen carbonate and water, dried (sodium sulfate), and concentrated. The residue was purified by silica gel column chromatography (ethyl acetate-hexane, 1:4) to afford **10** (531 mg) in 83% yield: mp 101 - 102 °C; $[\alpha]_D$ +110.2° (*c* 1.0, $CHCl_3$); ^1H NMR δ 8.10 - 7.18 (20H, aromatic), 6.00 (dd, 1H, $J_{4,5}$ <1.0 Hz, H-4), 5.85 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.60 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 4.86 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 4.65 (m, 1H, H-6a), 4.59 - 4.30 (m, 2H, H-5,6b); ^{13}C NMR δ 165.1, 165.7, 165.5, 165.4 (C=O), 133.5-128.3 (C-aromatic), 88.2 (C-1), 82.9 (C-5), 81.1 (C-3), 77.9 (C-4), 70.2 (C-2), 63.5 (C-6); CI-MS (ether) gave *m/z* (ion, relative intensity) 640.9 ($[M]^+$, 2.7%), 578.9 ($[M-EtSH]^+$, 100%).

Anal. Calcd for $C_{36}H_{32}O_9S$ (640.68): C, 67.49; H, 5.03. Found: C, 67.54; H, 5.01.

Phenyl 2,3,4-tri-*O*-benzoyl-6-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-galactopyranoside (11). To a solution of phenyl 1-thio-β-D-galactopyranoside[15] (0.5 g, 1.84 mmol) in dry pyridine (8 mL) was added *tert*-butyldimethylsilyl chloride (332 mg, 2.21 mmol) at 0 °C. The reaction mixture was stirred at rt for 3 h and then concentrated under reduced pressure and coevaporated with toluene. The residue was dissolved in dry pyridine (5 mL) and benzoyl chloride (776 μL, 6.62 mmol) was then added at 0 °C. After 3.5 h at rt, the reaction mixture was poured onto ice and extracted with chloroform (3 x 10 mL). The extracts were collected, washed with saturated sodium hydrogen carbonate and brine, dried (sodium sulfate) and evaporated to dryness under reduced pressure. The residue was purified by radial chromatography (2 mm plate) (ethyl acetate-hexane, 1:3) to give **11** (951 mg) in 74% yield. Compound **11** was crystallized from ethanol: mp 86 - 88 °C; $[\alpha]_D$ +103° (*c* 1.0, $CHCl_3$); IR (film) 3065, 2941, 2857, 1729, 1602, 1452, 1316, 1269, 1102 cm^{-1}; ^1H NMR δ 7.97 - 7.16 (m , 20H, aromatic), 5.94 (dd, 1H, $J_{4,5}$ = 0.8 Hz, H-4), 5.69 (dd, 1H, $J_{2,3}$ = 9.9 Hz, H-2), 5.56 (dd, 1H, $J_{3,4}$ = 3.1 Hz, H-3), 4.98 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 4.06 (ddd, 1H, $J_{5,6a}$ = 6.0 Hz, $J_{5,6b}$ = 7.4 Hz, H-5), 3.86 (dd, 1H, $J_{6a,6b}$ = 10.3 Hz, H-6a), 3.77 (dd, 1H, H-6b), 0.83 (s, 9H, *tert*-butyl), -0.02, -0.07 (2 s, 2 x SiMe); ^{13}C NMR δ 165.5, 165.2, 165.1 (C=O), 133.9-128.2 (C-aromatic), 85.8 (C-1), 78.0 (C-5), 73.4 (C-3), 68.2 (C-2), 68.1 (C-4), 61.1 (C-6), 25.8 (3C, $SiCMe_3$), 18.2 (CMe_3), -5.5, -5.6 ($SiMe_2$); CI-MS (ether) gave *m/z* (ion, relative intensity) 699.2 ($[M]^+$, 5.3%), 588.9 ($[M-HSPh]^+$, 100%).

Anal. Calcd for $C_{39}H_{41}O_{10}NSSi$ (698.85): C, 67.02; H, 6.06; S, 4.59. Found: C, 66.78; H, 6.11; S, 4.61.

Phenyl 2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (12). A solution of **11** (698 mg, 1 mmol) in ethyl ether (20 mL) was added to a freshly prepared hydrogen chloride solution obtained by dropwise addition of acetyl chloride (1 mL) into methanol (20 mL). The reaction mixture was stirred at rt for 30 min and then neutralized with Amberlite IR-45 (OH^-) and concentrated. The crude residue was purified by column chromatography (ethyl acetate-hexane, 1:5) to afford **11** (566 mg) in 97% yield: $[\alpha]_D$ +123° (*c* 1.0, $CHCl_3$); ^1H NMR δ 7.99 - 7.09 (m, 20H, aromatic), 5.80 (d, 1H, $J_{4,5} < 1.0$ Hz, H-4), 5.77 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 5.56 (dd, 1H, $J_{3,4} = 3.2$ Hz, H-3), 5.00 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1), 4.07 (ddd, 1H, $J_{5,6a} = 6.6$, $J_{5,6b} = 6.5$ Hz, H-5), 3.88 (dd, 1H, $J_{6a,6b} = 11.9$ Hz, H-6a), 3.65 (dd, 1H, H-6b), 2.50 (bs, 1H, OH); ^{13}C NMR δ 166.4, 165.5, 165.2 (C=O), 134.1-128.3 (C-aromatic), 85.5 (C-1), 77.9 (C-5), 73.2 (C-3), 68.8 (C-2), 68.0 (C-4), 60.8 (C-6); CI-MS (ether) gave *m/z* (ion, relative intensity) 584 (M^+, 1.5%), 475 ($[M-HSPh]^+$, 13.5%).

Anal. Calcd for $C_{33}H_{28}O_8S$ (584.61): C, 67.79; H, 4.83. Found: C, 67.39; H, 4.76

Phenyl 2,3,4,6-tetra-*O*-benzoyl-1-thio-β-D-galactopyranoside (18). To a solution of 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl bromide[16] (6.65 g, 10.08 mmol), tetrabutyl ammonium hydrogen sulfate (TBAHS) (5.1 g, 1.5 equiv), and thiophenol (2.08 mL, 20.16 mmol, 2 equiv) in ethyl acetate (100 mL) was added 1M aqueous sodium carbonate (100 mL). The two phase reaction mixture was stirred vigorously at rt for 50 min. The mixture was diluted with ethyl acetate (100 mL) and the organic layer was washed with saturated sodium hydrogen carbonate, water (3 x 50 mL), dried (sodium sulfate), filtered and concentrated under reduced pressure. The residue was purified by column chromatography (ethyl acetate-hexane, 1:3) to give **18** (6.64 g) in 96%yield: $[\alpha]_D$ +92.2° (*c* 1.0, $CHCl_3$); IR (film) 3065, 2960, 1727, 1600, 1451, 1268, 1100, 1069, 1027 cm^{-1}; ^1H NMR δ 8.05 - 7.10 (25H, aromatic), 6.00 (dd, 1H, $J_{4,5} < 1.0$ Hz, H-4), 5.77 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 5.60 (dd, 1H, $J_{3,4} = 3.2$ Hz, H-3), 5.04 (d, 1H, $J_{1,2} = 9.7$ Hz, H-1), 4.64 (m, 1H, H-6a), 4.48 - 4.41 (m, 2H, H-5,6b); ^{13}C NMR δ 166.0, 165.4, 165.3, 165.1 (C=O), 138.9-123.2 (C-aromatic), 85.8 (C-1), 75.1 (C-5), 72.9 (C-3), 67.3 (C-2), 67.8 (C-4), 62.5 (C-6); CI-MS (ether) gave *m/z* (ion, relative intensity) 688.8 ($[M]^+$, 1.9%), 579.0 ($[M-SPh]^+$, 95%).

Anal. Calcd for $C_{40}H_{32}O_8S$ (688.75): C, 69.76; H, 4.68; S, 4.65. Found: C, 69.78; H, 4.81; S, 4.61.

4-Nitrophenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (21). To a solution of 4-nitrophenyl 1-thio-β-D-galactopyranoside (634 mg, 2.0 mmol) in dry dimethyl formamide (5 mL) were added a sodium hydride dispersion (50% in oil, 768 mg, 16 mmol) and then benzyl bromide (1.46 mL, 12 mmol) at 0 °C. The mixture was warmed up to rt and stirred for 4 h. Methanol (1 mL) was added and the solution was diluted with toluene-ether (100 mL, 3:1), and washed with 5% HCl (2 x 50 mL), dried, and concentrated under reduced pressure. The residue was crystallized from ether-hexane (20 mL, 1:1) to give **21** (1.09 g) in 81% yield: mp 99 - 100 °C; $[\alpha]_D$ -34.0° (*c* 1.0, $CHCl_3$); IR (KBr) 3063, 3030, 2887, 1595, 1579, 1514, 1544, 1343, 1091, 910, 851, 740, 699 cm^{-1}; ^1H NMR δ 7.86 (d, 2H, $J_{m,o}$ = 9.0 Hz, H-meta), 7.58 (d, 2H, H-ortho), 7.35 - 7.26 (m, 22H, aromatic), 4.77 - 4.43 (m, 8H, 4 x C*H*$_2$Ph), 4.73 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 4.01 (d, 1H, $J_{4,5}$ < 1.0 Hz, H-4), 4.00 (dd, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.67 - 3.61 (4H, H-3, H-5,6a,6b); ^{13}C NMR δ 165.1 (C=O), 145.9 (C-para), 144.4 (C-ipso), 138.3 - 123.8 (C-aromatic), 84.7 (C-1), 84.2 (C-5), 84.0 (C-3), 76.7 (C-4), 75.8, 74.7, 73.7 (*C*H$_2$Ph), 73.3 (C-2), 72.7 (OCH$_2$), 68.7 (C-6); CI-MS (ether) gave *m/z* (ion, relative intensity) 525.0 ($[M+1-HSPhNO_2]^+$, 0.8%).

Anal. Calcd for $C_{40}H_{39}NO_7S$ (677.82): C, 70.88; H, 5.80; N, 2.07; S, 4.73. Found: C, 71.07; H, 6.00; N, 2.07; S, 4.76.

4-Acetamidophenyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (22). To a solution of **21** (660 mg, 0.97 mmol) in absolute ethanol (8 mL) was added tin dichloride ($SnCl_2 2H_2O$) (1.31 g, 5.81 mmol). The reaction mixture was stirred at 70 °C for 2.5 h and then cooled and poured onto ice-water. The pH of the solution was adjusted to 7 by addition of sodium hydrogen carbonate. The resulting mixture was extracted with ethyl acetate (3 x 20 mL). The extracts were washed successively with saturated sodium hydrogen carbonate and water. The organic phase was dried (sodium sulfate) and concentrated under reduced pressure. The crude residue was then directly acetylated with pyridine-acetic anhydride (2.5:5 mL) for 2 h at rt. Standard work-up gave a residue that was purified by column chromatography (ether) to afford **21** (294.4 mg) in 91% yield: mp 146 - 148 °C; $[\alpha]_D$ -4.0° (*c* 1.0, $CHCl_3$), $[\alpha]_{365(Hg)}$ -19.0° (*c* 1.0, $CHCl_3$); IR (KBr) 3300, 3031, 2881, 1673, 1592, 1527, 1495, 1454, 1396, 1313 cm^{-1}; ^1H NMR δ 7.54 - 7.25 (m, 22H, aromatic), 7.04 (s, 1H, NH), 4.95 - 4.36 (m, 8H, 4 x AB system, 4 x C*H*$_2$Ph), 4.55 (d, 1H, $J_{1,2}$ = 9.7 Hz, H-1), 3.95 (d, 1H, $J_{3,4}$ = 2.4, $J_{4,5}$ < 1.0 Hz, H-4), 3.86 (dd, 1H, $J_{2,3}$ = 9.4 Hz, H-2), 3.63 - 3.55 (4H, H-3,5,6a,6b), 1.78 (s, 3H, Me); ^{13}C NMR δ 168.1 (C=O), 138.7-119.9 (C-aromatic), 84.5 (C-1), 84.09 (C-5), 77.2 (C-4), 75.6 , 74.4, 73.5 (*C*H$_2$Ph),

73.5 (C-2), 72.6 (CH_2Ph), 68.7 (C-6), 24.6 (Ac); CI-MS (ether) gave *m/z* (ion, relative intensity) 689.9 ($[M]^+$, 1.8%), 540 ($[M-SPhNHAc]^+$, 1.6%).

Anal. Calcd for $C_{42}H_{43}NO_6S$ (689.87): C, 73.12; H, 6.28; N, 2.03; S, 4.65. Found: C, 72.86; H, 6.56; N, 2.03; S, 449.

4-Nitrophenyl 2,3,4-tri-*O*-benzyl-6-*O*-trityl-1-thio-β-D-galactopyranoside (24). Trityl chloride (1.05 g, 3.78 mmol) was added to a solution of 4-nitrophenyl 1-thio-β-D-galactopyranoside (1 g, 3.15 mmol) in pyridine (15 mL). The mixture was stirred at rt 16 h. The solution was concentrated under reduced pressure. The residue was dissolved in dry *N,N*-dimethylformamide (18 mL) and then sodium hydride (50% in oil, 680 mg, 14.18 mmol) was slowly added followed by benzyl bromide (1.69 mL, 14.18 mmol) at 0 °C. The mixture was allowed to reach rt. After 15 h, methanol (5 mL) was added to destroy the excess benzyl bromide. After 45 min, the solution was neutralized with acetic acid, diluted with dichloromethane (60 mL), washed with water (2 x 50 mL), dried, and concentrated. Column chromatography (ethyl acetate-hexane 1:5) of the residue gave **24** (2.24 g) in 86% yield: mp 136 - 137 °C; $[\alpha]_D$ +3.5° (*c* 0.97, $CHCl_3$); IR (film) 3050, 2890, 1585, 1514, 1451, 1339 cm^{-1}; ^1H NMR δ 7.83 - 7.80 (m, 2H, Ph-meta, $J_{o,m}$ = 9.0 Hz), 7.56 - 7.53 (m, 2H, Ph-ortho, $J_{o,m}$ = 9.0 Hz), 7.39 - 7.10 (m, 30H, aromatic), 4.84 (AB system, 1H, $J_{a,b}$ =11.0 Hz, H-a), 4.73 - 4.62 (m, 4H, 2 x CH_2Ph), 4..65 (d, 1H, $J_{1,2}$ = 9.5 Hz, H-1), 4.50 (AB system, 1H, J = 11.0 Hz, H-b), 3.96 (dd, 1H, $J_{1,2}$ = 9.5, $J_{2,3}$ = 9.5 Hz, H-2), 3.89 (d, 1H, $J_{3,4}$ = 2.6, $J_{4,5}$ < 1.0 Hz, H-4), 3.56 (dd, 1H, $J_{3,4}$ = 2.6 Hz, H-3), 3.53 - 3.20 (m, 3H, H-5, H-6a,6b); ^{13}C NMR δ 145.7-123.7 (C-aromatic), 85.5 (C-1), 83.9 (C-3), 77.8 (C-5), 76.6 (C-2), 75.7, 74.4 (CH_2Ph), 73.5 (C-4), 72.8 (CH_2Ph) 62.8 (C-6); (+)-FAB-MS gave *m/z* (relative intensity) 830.27 ($[M+1]^+$, 2%,), 570.18 ($[M-Ph_3COH]^+$ 12%).

Anal. Calcd for $C_{52}H_{47}O_7NS$ (829.30): C, 75.25; H, 5.71; N, 1.69; S, 3.86. Found: C, 75.18; H, 5.79; N, 1.89; S, 3.61.

4-Nitrophenyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (25). To a solution of **24** (2.0 g, 2.41 mmol) in methanol-dichloromethane (30 mL, 1:1 v/v) was added *p*-toluenesulfonic acid (20 mg, 0.12 mmol). The mixture was stirred at rt for 30 min. Triethylamine (1 mL) was added and the reaction mixture was stirred for an additional 15 min. Evaporation and coevaporation with toluene (2 x 10 mL) under reduced pressure gave a residue that was purified by column chromatography (ethyl acetate-hexane, 2:7) to give **25** (1.34 g) in 95% yield: mp 129 - 130 °C; $[\alpha]_D$ -29.5° (*c* 0.78, $CHCl_3$); IR (film) 3448, 3031, 2890, 1585, 1513, 1453, 1340, 1083 cm^{-1}; ^1H NMR δ 7.96 - 7.91 (m, 2H, $J_{o,m}$

= 9.0 Hz Ph-meta,), 7.60 - 7.55 (m, 2H, $J_{o,m}$ = 9.0 Hz , Ph-ortho), 7.41 - 7.23 (m, 15H, aromatic), 5.00 (AB system, 1H, $J_{a,b}$ = 11.2 Hz, H-a), 4.77 - 4.68 (m, 4H, 2 x CH_2Ph), 4.72 (d, 1H, $J_{1,2}$ = 8.9 Hz, H-1), 4.61 (AB system, 1H, $J_{a,b}$ = 11.2 Hz, H-b), 4.01 (dd, 1H, $J_{2,3}$ = 9.5 Hz, H-2), 3.91 (d, 1H, $J_{4,5}$ < 1.0 Hz, H-4), 3.63 (dd, 1H, $J_{3,4}$=2.6 Hz, H-3), 3.88 - 3.51 (m, 3H, H-5,6a,6b), 1.59 (bs, 1H, OH); ^{13}C NMR δ 145.9 - 123.9 (C-aromatic), 85.6 (C-1), 84.1 (C-3), 79.1 (C-5), 76.7 (C-2), 75.8, 74.5 (*C*H_2Ph), 73.12 (C-4), 72.9 (*C*H_2Ph), 62.1(C-6); CI-MS (ether) gave *m/z* (ion, relative intensity) 570.3 ([M-H_2O]$^+$, 1.1%), 433.2 ([M-HSPhNO_2]$^+$, 15.2%), 325 ([M-HSPhNO_2-BnOH]$^+$, 13.1%), 219 ([M-HSPhNO_2-2xPhCH_2O]$^+$, 32.8%).

Anal. Calcd for $C_{33}H_{33}O_7NS$ (587.69): C, 67.44; H, 5.66; N, 2.38; S, 5.46. found: C, 67.18; H, 5.79; N, 2.35; S, 5.61.

General procedure for the glycosylation reactions. Synthesis of disaccharides 4, 9, 13, 16, 17, 19, 20, 23, 26. A solution of the glycosyl acceptor (**3**, **12**, **15** and **25**), the glycosyl donor (**1**, **2**, **5-8**, **10**, **11**, **18**, **21**, and **22**) and pulverized molecular sieves (4Å, 150 mg) in dry methylene chloride (2 mL) was stirred under nitrogen at rt for 3 h. After cooling at -30 °C, NIS-TfOH or methyl triflate (MeOTf) were added. The reactions were complete after 10-25 min for reactions with NIS-TfOH and 10 h for reaction with methyl triflate. The reaction mixture was then diluted with dichloromethane (10 mL) and filtered through celite. The filtrate was washed with 10% aqueous sodium thiosulfate (10 mL), saturated aqueous sodium hydrogen carbonate (2 x 10 mL), and brine (10 mL). The solution was dried (sodium sulfate), concentrated and the residue purified by column chromatography.

***O*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside (4).** Compounds **2** (100 mg, 0.134 mmol) and **3** (29 mg, 0.11 mmol) were reacted with NIS (46 mg, 0.20 mmol) and TfOH (13 μL) for 10 min. Column chromatography (ethyl acetate-hexane, 3:1) of the crude residue gave **4** (87 mg) as a solid in 94% yield: mp 87 - 89 °C; $[\alpha]_D$ +50° (*c* 1.0, $CHCl_3$); IR (KBr) 2051, 1729, 1602, 1452, 1266, 1111, 1069, 1027 cm^{-1}; ^{1}H NMR δ 8.09 - 7.19 (m, 20H, aromatic), 5.92 (dd, 2H, $J_{4,5}$ = 0.9 Hz, H-4'), 5.79 (dd, 1H, $J_{2',3'}$ = 10.4 Hz, H-2'), 5.58 (dd, 1H, $J_{3',4'}$ = 3.4 Hz, H-3'), 5.39 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.99 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.65 (dd, 1H, $J_{5',6a'}$ = 6.4 Hz, $J_{6a',6b'}$ = 11.0 Hz, H-6a'), 4.40 (dd, 1H, $J_{5',6b'}$ = 6.8 Hz, H-6b'), 4.39 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.32 (m, 1H, H-5'), 4.20 (dd, 1H, $J_{2,3}$ = 2.4 Hz, H-2), 4.09 (dd, 1H, $J_{4,5}$ = 1.5 Hz, H-4), 5.58 (dd, 1H, $J_{3,4}$ = 3.4 Hz, H-3), 4.64 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 4.03 (m, 1H, H-5),

3.88 (m, 2H, H-6a,6b), 1.37, 1.22, 1.19, 1.17 (4s, 12H, 2 x C*Me*$_2$); ^{13}C NMR δ 166.0, 165.5, 165.3 (C=O), 147.0-124.4 (aromatic), 109.2 (*C*Me$_2$), 108.4 (*C*Me$_2$), 101.7 (C-1), 96.1 (C-1'), 71.5, 70.9, 70.5, 70.3, 69.6, 68.1, 67.4, 62.0 (C-2,3,4,5,2',3',4',5'), 68.4 (C-6), 63.0 (C-6).

Anal. Calcd for $C_{46}H_{46}NO_{15}$ (838.864): C, 65.86; H, 5.53. Found: C, 65.89; H, 5.58.

O-(3,4,6-Tri-O-Acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (9). Method **A**: Compounds **6** (72 mg, 0.144 mmol) and **3** (30 mg, 0.12 mmol) were treated with NIS (48mg, 0.216 mmol) and TfOH (13 μL) for 20 min. Column chromatography of the crude residue (2% ethanol in dichloromethane) gave disaccharide **9** in 80% yield.

Method **B**: Compounds **7** (132 mg, 0.28 mmol) and **3** (60 mg, 0.23 mmol) were treated with NIS (93 mg, 0.41 mmol) and TfOH (4 μL) for 15 min. Similar purification to that describe above gave **9** (156 mg) in 92% yield.

Method **C**: Compounds **8** (66 mg, 0.144 mmol) and **3** (30 mg, 0.12 mmol) were treated with NIS (48 mg, 0.216 mmol) and TfOH (6.5 μL) for 25 min. Purification as above gave **9** in 77% yield.

Compound **9** had: mp 216 - 217 °C; $[\alpha]_D$ -27.2° (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.80 (m, 2H, Phth), 7.67 (m, 2H, Phth), 5.82 (dd, 1H, $J_{3',4'}$ = 9.1 Hz, H-3'), 5.42 (d, 1H, $J_{1',2'}$ = 8.5 Hz, H-1'), 5.14 (dd, 1H, $J_{4',5'}$ = 10.2 Hz, H-4'), 5.07 (d, 1H, $J_{1,2}$ = 5.1 Hz, H-1), 4.37 (dd, 1H, $J_{3,4}$ = 7.9 Hz, H-3), 4.32 (dd, 1H, $J_{6a',6b'}$ = 12.4 Hz, H-6a'), 4.28 (dd, 1H, $J_{2',3}$= 10.6 Hz, H-2'), 4.13 (dd, 1H, $J_{5,6b'}$ = 2.4 Hz, H-6b'), 4.06 (dd, 1H, $J_{2,3}$ = 2.4 Hz, H-2), 3.96 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 3.93 (m, 2H, H-6a, H-6b), 3.86 (ddd, 1H, $J_{5',6a'}$ = 4.6 Hz, H-5'), 3.67 (m, 1H, H-5), 2.09, 2.00, 1.84 (3s, 9H, 3 x OAc), 1.37 (s, 3H, Me), 1.21 (s, 3H, Me), 0.99 (s, 6H, 2 x Me); ^{13}C NMR δ 170.7, 170.1, 169.5 (C=O), 109.2 (*C*Me$_2$), 107.9 (*C*Me$_2$), 99.3 (C-1'), 95.8 (C-1), 71.5 (C-5'), 70.8 (C-4), 70.6 (C-3'), 70.6 (C-3), 70.1 (C-2), 69.3 (C-6), 69.0 (C-4'), 67.4 (C-5), 62.0 (C-6'), 54.5 (C-2'), 25.8, 25.3, 24.6, 24.2 (C*Me*$_2$), 20.7, 20.6, 20.4 (OAc).); CI-MS (ether) gave *m/z* (ion, relative intensity) 678.3 ([M+1]$^+$, 63.1 %).

Anal. Calcd for $C_{32}H_{39}NO_{15}$ (677.64): C, 56.68; H, 5.80; N, 2.06. Found: C, 56.69; H, 5.98; N, 1.88.

Phenyl O-(2,3,4,6-tetra-O-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-O-benzoyl-1-thio-β-D-galactopyranoside (13). Compound **10** (92 mg, 0.14 mmol) and **12** (70 mg, 0.12 mmol) were treated with NIS (48 mg, 0.216 mmol) and TfOH (2.1 μL) for 5

min. Column chromatography (ethyl acetate-hexane, 3:7) of the crude residue gave **13** (124 mg) in 89% yield: mp 87 - 89 °C; $[\alpha]_D$ +54.3° (*c* 1.2, $CHCl_3$); IR (film) 3065, 2934, 1726, 1602, 1451, 1315, 1268, 1177, 1105, 1069, 1027 cm^{-1}; ^1H NMR δ 8.11 - 7.20 (m, 40H, aromatic), 6.00 (d, 1H, $J_{4,5}$, < 1.0 Hz H-4), 5.89 (d, 1H, H-4'), 5.73 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 5.58 (dd, 1H, $J_{3,4}$ = 3.0 Hz, H-3), 5.57 (H-3'), 5.42 (H-2'), 5.32 (H-1'), 5.02 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.56 - 4.48 (m, 2H, H-5',6a'), 4.32 (dd, 1H, $J_{5',6b'}$ = 3.3, $J_{6a',6b'}$ = 12.2 Hz, H-6b'), 4.30 (m, 1H, H-5), 3.96 (dd, 1H, $J_{5,6a}$ =7.3, $J_{6a,6b}$ = 9.6 Hz, H-6a), 3.80 (dd, 1H, $J_{5,6b}$ = 5.8 Hz, H-6b); ^{13}C NMR δ 165.9, 165.8, 165.7, 165.4, 165.3, 165.1 (C=O), 134.3-128.1 (C-aromatic), 106.0 (C-1'), 85.7 (C-1), 82.1 (C-2'), 81.7 (C-5'), 77.4 (C-3'), 76.0 (C-5), 73.2 (C-3), 70.4 (C-4'), 68.2 (C-4), 67.9 (C-2), 65.1 (C-6), 63.7 (C-6'). (+)FAB-MS (glycerol) gave *m/z* (ion, relative intensity) 1163.3 ($[M]^+$, 2.3%), 1053.4 ($[M+1-HSPhNO_2,]^+$, 5.4%).

Anal. Calcd for $C_{67}H_{54}O_{17}S$ (11633.22): C, 69.18; H, 4.68. Found: C, 69.37; H, 4.98.

4-Nitrophenyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (16). Compounds **7** (110 mg, 0.21 mmol) and **15** (107 mg. 0.17 mmol) were treated with NIS (69 mg, 0.30 mmol) and TfOH (3.0 μL) for 15 min. Column chromatography (ethyl acetate-hexane, 3:2) of the crude residue gave **16** (137 mg, 78 % yield) as a solid: mp 135 - 136 °C; $[\alpha]_D$ +81.2° (*c* 1.2, $CHCl_3$); ^1H NMR δ 8.20 - 7.15 (m, 19H, aromatic), 5.79 (d, 1H, H-4), 5.68 (dd, 1H, $J_{3',4}$= 9.1 Hz, H-3'), 5.64 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 5.52 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 5.46 (d, 1H, $J_{1',2'}$ = 8.5 Hz, H-1'), 5.14 (dd, 1H, $J_{4',5'}$ = 10.1 Hz, H-4'), 5.01 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.33 (dd, 1H, $J_{2',3'}$ = 9.8 Hz, H-2'), 4.23 (m, 2H, H-6b, H-5'), 4.21 (dd, 1H, $J_{5,6a}$ = 2.3 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 3.94 (dd, 1H, $J_{5',6a'}$ = 2.4 Hz, $J_{6a',6b'}$ = 11.2 Hz, H-6a'), 3.79 (dd, 1H, $J_{5,6b'}$ = 7.4 Hz, H-6b'), 3.74 (m, 1H, H-5), 2.08, 2.00, 1.85 (3 x Ac); ^{13}C NMR δ 170.6, 170.1, 169.4 (C=O, Ac), 165.2, 165.1, 165.0 (C=O, Bz), 147.0-123.6 (C-aromatic), 98.2 (C-1'), 84.2 (C-1), 77.1 (C-5'), 72.5 (C-3), 72.1 (C-5), 70.7 (C-3'), 68.7 (C-4',6'), 68.5 (C-4), 67.4 (C-2), 61.7 (C-6), 54.4 (C-2'), 20.7, 20.5, 20.4 (Ac); (+)FAB-MS (glycerol) gave *m/z* (ion, relative intensity) 892.3 ($[M-HSPhNO_2]^+$, 5.7%), 612.1 ($[M-C_{20}H_{21}NO_{10}]^+$, 12.5%).

Anal. Calcd for $C_{53}H_{46}NO_{19}S$ (1046.99): C, 60.80; H, 4.43; N, 2.70; S, 3.06. Found: C, 60.60; H, 4.61; N, 2.58; S, 3.07.

4-Nitrophenyl *O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (17). Compounds **14** (70 mg, 0.13 mmol) and **15** (69 mg. 0.11 mmol) were treated with NIS (44.5 mg, 0.20 mmol)

and TfOH (2 μL) for 10 min. Column chromatography (ethyl acetate-hexane, 1:3) of the crude residue gave **17** (116 mg) in 89% yield: mp 103 - 105 °C; $[\alpha]_D$ +71.3° (*c* 1.3, $CHCl_3$); IR (film) 3480, 3064, 3030, 2917, 1775, 1721, 1599, 1582, 1518, 1545, 1390, 1341, 1270, 1083, 1069, 1027 cm^{-1}; ^1H NMR δ 8.16 - 6.91 (m, 19H, aromatic), 5.76 (d, 1H, $J_{4,5}$ < 1.0 Hz, H-4), 5.59 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 5.47 (dd, 1H, $J_{3,4}$ = 3.2 Hz, H-3), 5.22 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.90 (d, 1H, $J_{1,2}$ = 9.9 Hz, H-1), 4.72 - 4.49 (AB system, 4H, 2 x CH_2Ph), 4.19 - 4.13 (m, 3H, H-2',3',5'), 3.88 (dd, 1H, $J_{5',6a'}$ = 3.2 Hz, $J_{6a',6b'}$ = 12.2 Hz, H-6a'), 3.81(dd, 1H, $J_{5,6a}$ = 7.8, $J_{5,6b}$ = 9.5 Hz, H-5), 3.73 - 3.68 (m, 3H, H-6a,6b,6b'), 3.57 (dd, 1H, $J_{3',4'}$ = 4.9 Hz, $J_{4',5'}$ = 9.6 Hz, H-4'); ^{13}C NMR δ 165.2, 165.1, 165.1 (C=O), 147.1-123.3 (C-Aromatic), 98.6 (C-1'), 84.4 (C-1), 78.5 (C-5'), 77.2 (C-3'), 74.4 (C-5), 74.3, 73.8 (CH_2Ph), 73.5 (C-4'), 70.6 (C-6), 68.5 (C-4), 68.3 (C-6'), 67.5 (C-2).

Anal. Calcd for $C_{61}H_{52}O_{19}N_2S$ (1101.15): C, 66.53; H, 4.76; N, 2.55; S, 2.91. Found: C, 66.74; H, 5.00; N, 2.49; S, 3.06.

4-Nitrophenyl *O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (19). Method **A:** Compounds **18** (100 mg, 0.145 mmol) and **15** (76 mg. 0.12 mmol) were treated with NIS (49 mg, 0.216 mmol) and TfOH (6.4 μL) for 20 min. Column chromatography (ethyl acetate-hexane, 3:5) gave **19** (118 mg) in 81% yield.

Method **B:** Compounds **2** (40 mg, 0.053 mmol) and **15** (27.5 mg, 0.044 mmol) were treated with NIS (18mg, 0.08 mmol) and TfOH (4.6 μL) for 25 min. Purification as above gave **19** (46.2 mg) in 87% yield.

Compound **19** had: mp 143 - 145 °C; $[\alpha]_D$ +108° (*c* 1.0, $CHCl_3$); IR (film) 1729, 1600, 1518, 1451, 1342, 1286, 1093 cm^{-1}; ^1H NMR δ 8.12 - 7.19 (m, 39H, aromatic), 5.95 (d, 2H, H-4,4'), 5.82 (dd, 1H, $J_{2',3'}$ = 10.5 Hz, H-2'), 5.74 (dd, 1H, $J_{2,3}$ = 9.8 Hz, H-2), 5.58 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.56 (dd, 1H, $J_{3',4'}$ = 3.3 Hz, H-3'), 5.00 (d, 1H, $J_{1,2}$ = 9.8 Hz, H-1), 4.91 (d, 1H, $J_{1',2'}$ = 8.0 Hz, H-1'), 4.48 - 4.27 (m, 4H, H-5,5',6a',6b'), 4.16 (dd, 1H, $J_{5,6a}$ = 4.2 Hz, $J_{6a,6b}$ = 10.5 Hz, H-6a), 3.92 (dd, 1H, $J_{5,6b}$ = 7.5 Hz, H-6b); ^{13}C NMR δ 165.9, 165.5, 165.2, 165.1, 168.1 (C=O), 146.9-123.8 (C-aromatic), 101.4 (C-1'), 84.7 (C-1), 77.1 (C-5), 72.54 (C-3), 71.7 (C-3'), 71.4 (C-5'), 69.6 (C-2'), 68.5, 68.0 (C-4,4'), 68.1 (C-6), 67.5 (C-2), 61.8 (C-6'). (+)FAB-MS (glycerol) gave *m/z* (ion, relative intensity) 1208.2 ($[M+1]^+$, 1.2%), 1053.3 ($[M+1-HSPhNO_2]^+$, 6.6%).

Anal. Calcd for $C_{67}H_{53}NO_{19}S$ (1208.16): C, 66.60; H, 4.42; N, 1.16. Found: C, 66.32; H, 4.47; N, 1.28.

4-Nitrophenyl *O*-(2,3,4,-tri-*O*-benzoyl-6-*tert*-butyldimethylsilyl-β-D-galacto-pyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (20). Compounds **11** (60 mg, 0.086 mmol) and **15** (45 mg. 0.072 mmol) were treated with NIS (29 mg, 0.130 mmol) and TfOH (3.2 μL) for 20 min. Column chromatography (0.5% ethanol in dichloromethane) of the crude residue gave **20** (70 mg) in 79% yield: mp 109 - 112°C; $[\alpha]_D$ +128.2° (*c* 1.1, $CHCl_3$); IR (film) 3067, 2939, 2856, 1731, 1601, 1515, 1451, 1281, 1101, 1070 cm^{-1}; ^1H NMR δ 8.12 - 7.19 (m, 34H, aromatic), 5.94 (d, 1H, $J_{4,5} < 1.0$ Hz, H-4,), 5.89 (d, 1H, $J_{4',5'} < 1.0$ Hz, H-4'), 5.74 (dd, 1H, $J_{2',3'} = 10.4$ Hz, H-2'), 5.73 (dd, 1H, $J_{2,3} = 9.8$ Hz, H-2), 5.56 (dd, 1H, $J_{3,4} = 3.3$ Hz, H-3), 5.44 (dd, 1H, $J_{3',4'} = 3.4$ Hz , H-3'), 4.96 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1) , 4.83 (d, 1H, $J_{1',2'} = 7.9$ Hz, H-1'), 4.30 (ddd, 1H, $J_{5,6a} = 4.2$ Hz, $J_{5,6b} = 7.4$ Hz, H-5), 4.14 (dd, 1H, $J_{6a,6b} = 10.6$ Hz, H-6a), 3.94 (ddd, 1H, $J_{5',6a'} = 5.8$ Hz, $J_{5',6b'} = 8.0$ Hz, H-5'), 3.88 (dd, 1H, H-6b), 3.76 (dd, 1H, $J_{6a',6b'} = 9.9$ Hz, H-6a'), 3.60 (dd, 1H, H-6b), 0.77 (s, $SiCMe_3$), -0.04, -0.17 (s, 2 x SiMe); ^{13}C NMR δ 165.6, 165.4, 165.3, 165.3, 168.2, 168.1 (C=O), 147.0-123.8 (C-aromatic), 101.5 (C-1'), 84.8 (C-1), 77.3 (C-5), 74.2 (C-5'), 72.6 (C-3), 72.0 (C-3'), 70.0 (C-2), 68.6 (C-4), 68.1 (C-6), 67.65 (C-4'), 67.6 (C-2'), 60.5 (C-6'), 25.7 (3 x Me_3), 25.4 (SiC), 18.1 ($SiCH_3$).

Anal. Calcd for $C_{66}H_{53}NO_{19}SSi$ (1218.37): C, 65.06; H, 5.21; N, 1.15. Found: C, 65.23 H, 5.17; N, 1.27.

4-Nitrophenyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-galactopyranosyl)-(1→6)-2,3,4-tri-*O*-benzoyl-1-thio-β(α)-D-galactopyranoside (23α,β). Method A: Compounds **21** (81.6 mg, 0.12 mmol) and **15** (63 mg. 0.1 mmol) were treated with NIS (40 mg, 0.18 mmol) and TfOH (8.8 μL) for 65 min. Column chromatography (ethyl acetate-hexane, 1:4) of the crude residue gave **23** (87.9 mg) in 76% yield as ≈ 4/1 mixture of α/β anomers as judged from the ^1H NMR spectrum.

Method B: Compound **22** (33 mg, 0.048 mmol) and **15** (25 mg, 0.040 mmol) were treated with NIS (16 mg, 0.072 mmol) and TfOH (4.2 μL) for 25 min. Purification as above gave **23** (42 mg) in 92% yield as an ≈ 3/1 mixture of α/β anomers as judged from the ^1H NMR spectrum. Radial chromatography on silica gel (1 mm plate) (1% *tert*-butyl alcohol in methylene chloride) gave:

Compound **23α:** $[\alpha]_D$ +62.0° (*c* 1.0, $CHCl_3$); ^1H NMR δ 8.13 - 7.20 (m, 39H, aromatic), 5.94 (d, 1H, $J_{4,5} < 1.0$ Hz, H-4), 5.73 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 5.59 (dd, 1H, $J_{3,4} = 3.4$ Hz, H-3), 5.00 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1) , 4.90 - 4.64 (m, 6H, 3 CH_2Ph), 4.79 (d, 1H, $J_{1',2'} = 3.7$ Hz, H-1'), 4.38 - 4.32 (m, 3H, H-5, CH_2Ph), 4.02 (dd, 1H, $J_{2',3'} = 10.5$

Hz, H-2'), 3.99 (m, 1H, H-5'), 3.89 (d, 1H, $J_{4',5'} < 1.0$ Hz, H-4'), 3.87 (dd, 1H, $J_{3',4'} < 1.0$ Hz, H-3'), 3.86 (dd, 1H, $J_{5,6a} = 6.1$, $J_{6a,6b} = 11.0$ Hz, H-6a), 3.73 (dd, 1H, $J_{5,6b} = 7.3$ Hz, H-6b), 3.50 (dd, 1H, $J_{5',6a'} = 6.3$ Hz, $J_{6a',6b'} = 9.3$ Hz, H-6a'), 3.44 (dd, 1H, $J_{5',6b'} = 6.5$ Hz, H-6b'); ^{13}C NMR δ 165.4, 165.3, 165.1 (C=O), 147.0-123.7 (C-Aromatic), 98.8 (C-1'), 84.3 (C-1), 79.0 (C-3'), 76.5 (C-5), 74.9 (C-5'), 74.8 (C-4'), 73.7, 73.4 , 73.2 (*C*H_2Ph), 72.7 (C-3), 69.9 (C-2'), 69.2 (C-6'), 68.7 (C-4), 67.7 (C-2), 67.4 (C-6).

Anal. Calcd for $C_{67}H_{62}NO_{15}S$ (1152.287): C, 69.84; H, 5.34; N, 1.22; S, 2.78. Found: C, 70.00; H, 5.59; N, 1.09; S, 2.86.

Compound **23β:** had: $[\alpha]_D$ +70.2° (*c* 1.2, $CHCl_3$); ^{1}H NMR δ 8.13 - 7.20 (m, 39H, aromatic), 5.90 (d, 1H, $J_{4,5} < 1.0$ Hz, H-4,), 5.79 (dd, 1H, $J_{2,3} = 9.9$ Hz, H-2), 5.58 (dd, 1H, $J_{3,4} = 3.4$ Hz, H-3), 5.13 (d, 1H, $J_{1,2} = 9.9$ Hz, H-1), 5.00 - 4.64 (m, 6H, 3 x C*H*$_2$Ph), 4.38 (d, 1H, $J_{1',2'} = 7.7$ Hz, H-1'), 4.40 - 4.33 (m, 3H, H-5', C*H*$_2$Ph), 3.98 (dd, 1H, $J_{5,6a} = 3.4$, $J_{6a,6b} = 11.4$ Hz, H-6a), 3.92 (dd, 1H, $J_{5,6b} = 8.0$ Hz, H-6b), 3.86 (d, 1H, $J_{4',5'} < 1.0$ Hz, H-4'), 3.85 (dd, 1H, $J_{2',3'} = 9.8$ Hz, H-2'), 3.79 - 3.49 (m, 2H, H-5', H-6a'), 3.48 (dd, 1H, $J_{3',4'} = 3.0$ Hz, H-3'), 3.39 (dd, 1H, $J_{5',6b'} = 9.3$ Hz, $J_{6a',6b'} = 11.9$ Hz, H-6b'); ^{13}C NMR δ 165.4, 165.2 (C=O), 146.7-123.9 (C-aromatic), 104.6 (C-1'), 84.2 (C-1), 82.2 (C-5'), 79.6 (C-2'), 77.6 (C-5), 75.4, 74.4, 73.5 (*C*H_2,Ph), 73.4 (C-3'), 73.2 (*C*H_2Ph), 73.2 (C-4'), 72.8 (C-3), 69.3 (C-6), 68.8 (C-4,6'), 67.7 (C-2).

4-Nitrophenyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-1-thio-β-D-galactopyranoside (26). Compounds **7** (70 mg, 0.145 mmol) and **25** (102 mg, 0.174 mmol) were treated with methyl triflate (196 μL, 1.74 mmol) for 10 h. Column chromatography (ethyl acetate-hexane, 2:5) gave **26** (113 mg, 77%) as a solid: mp 84 - 86 °C; $[\alpha]_D$ -3.5° (*c* 1.0, $CHCl_3$); IR (film) 3029, 2904, 1749, 1718, 1579, 1515, 1454, 1387, 1339, 1231, 1083, 1043 cm^{-1}; ^{1}H NMR) δ 7.93 - 7.22 (m, 23H, aromatic), 5.67 (dd, 1H, $J_{3',4'} = 9.2$ Hz, H-3'), 5.43 (d, 1H, $J_{1',2'} = 8.7$ Hz, H-1'), 5.16 (dd, 1H, $J_{4',5'} = 10.1$ Hz, H-4'), 4.90 - 4.60 (m, 6H, 3 x C*H*$_2$Ph), 4.62 (d, 1H, $J_{1,2} = 9.5$ Hz, H-1), 4.30 (dd, 1H, $J_{2',3'} = 10.6$ Hz, H-2'), 4.27 (dd, 1H, $J_{5',6a'} = 4.4$, $J_{6a',6b'} = 12.5$ Hz, H-6a'), 4.07 (dd, 1H, $J_{5,6b'} = 7.4$ Hz , H-6b'), 3.90 (dd, 1H, $J_{2,3} = 9.1$ Hz, H-2), 3.88 (dd, 1H, $J_{5,6a} = 3.0$, $J_{6a,6b} = 10.2$ Hz, H-6a), 3.82 (d, 1H, $J_{4,5} < 1.0$ Hz, H-4), 3.70 (m, 1H, H-5'), 3.53-3.45 (m, 2H, H-3,5), 2.03, 2.71, 1.84 (3s, 9H, 3 x Ac); ^{13}C NMR δ 170.6, 170.0, 169.4 (C=O), 145.9-123.6 (C-aromatic), 97.7 (C-1'), 85.4 (C-1), 83.8 (C-5), 77.6 (C-3), 76.3 (C-2), 75.6, 74.6, 72.5 (*C*H_2Ph), 73.1 (C-4), 71.9 (C-5'), 70.7 (C-3'), 68.6 (C-4'), 67.9 (C-6), 61.7 (C-6'), 54.6 (C-2'). 20.7, 20.5, 20.4 (Ac); (+)FAB-MS (glycerol) gave *m/z* (ion, relative intensity) 850.4 ([M-HSPhNO$_2$]$^+$, 0.7%).

Anal. Calcd for $C_{53}H_{52}O_{16}N_2S$ (1005.06): C, 63.33; H, 5.22; N, 2.79; S, 5.22. found: C, 63.28; H, 5.25; N, 2.82; S, 5.31.

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REFERENCES AND NOTES

1. Dedicated to the memory of Professor Akira Hasegawa.
2. For part 1-3, see, respectively: (a) R. Roy, F. O. Andersson and M. Letellier, *Tetrahedron Lett.*, **33**, 6053 (1992); (b) S. Cao, S. J. Meunier, F. O. Andersson, M. Letellier and R. Roy, *Tetrahedron: Asymmetry*, **5**, 2303 (1994); (c) S. Cao and R. Roy, *Tetrahedron Lett.*, **37**, 3421 (1996).
3. Visiting Professor from Instituto de Biotecnologia, Facultad de Ciencias, Universidad de Granada, Granada, Spain.
4. Previous accounts on thioglycosyl donors and their relative reactivity were initially described using mainly methyl triflate as the promotor: (a) B. A. Silwanis, F. Dasgupta and P. J. Garegg, Abstract No. CARB-92, 3rd Chemical Congress of North America, Toronto, Canada, June 5-10, 1988; (b) F. Dasgupta and P. J. Garegg, *Carbohydr. Res.*, **202**, 225 (1990); (c) P. Fügedi, P. J. Garegg, S. Oscarson, G. Rosén and B. A. Silvanis, *Carbohydr. Res.*, **211**, 157 (1991); (d) V. Pozsgay in *Carbohydrates, Synthetic Methods and Applications in Medicinal Chemistry*; H. Ogura, A. Hasegawa and T. Suami, Eds.; VCH-Kodansha, Tokyo, Japan, 1992, p 188.
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