SYNTHESIS OF 2-AMINO-2-DEOXY-β-D-GALACTOPYRANOSYL-(1→4)-2-AMINO-2-DEOXY-β-D-GALACTOPYRANOSIDES: USING VARIOUS 2-DEOXY-2-PHTHALIMIDO-D-GALACTOPYRANOSYL DONORS AND ACCEPTORS

Jan VESELÝ[1a], Miroslav LEDVINA[1b,*], Jindřich JINDŘICH[2a], Tomáš TRNKA[3a] and David ŠAMAN[2b]

[a] *Department of Organic Chemistry, Charles University, Albertov 2030, 128 40 Prague 2, Czech Republic; e-mail:* [1] *jxvesely@natur.cuni.cz,* [2] *jindrich@natur.cuni.cz,* [3] *trnka@natur.cuni.cz*

[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic; e-mail:* [1] *ledvina@uochb.cas.cz,* [2] *saman@uochb.cas.cz*

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Dedicated with due respect to Professor Miloslav Černý on the occasion of his 75th birthday in recognition of his outstanding contributions to carbohydrate chemistry.

A systematic study is presented of the efficiency of the most common glycosylation methods using standard 2-deoxy-2-phthalimidogalactopyranosyl donors ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**3a**), 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl bromide (**4**), 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl fluoride (**5b**), *O*-(4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl) trichloroacetimidate (**7**) and ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**8**), pent-4-enyl 3,6-di-*O*-benzyl- and 3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**10a**) and (**10b**) and pent-4-enyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(trimethylsilyl)-β-D-galactopyranoside (**11**) as glycosyl acceptors in the synthesis of 2-amino-2-deoxy-β-D-galactopyranosyl-(1→4)-2-amino-2-deoxy-β-D-galactopyranosides **12**, **16a** and **17a**. It was found that due to a low reactivity of the axial OH(4) group of glycosyl acceptors, disaccharides **16b** and **17b** with α(1→4) bond were also formed. The unexpected intermolecular migration of ethylsufanyl group from the reducing end of glycosyl acceptor **8** the reducing end of the activated form of glycosyl donor **4** in the glycosylation step to give ethylsulfanyl derivative **3a** was proved. For preparation of the glycosyl donors and glycosyl acceptors with *galacto* configuration an approach based on epimerization of 4-*O*-mesyl derivatives of appropriate synthons with *gluco* configuration **2a** and **2b** was employed.

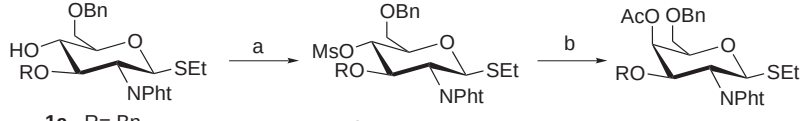
Keywords: Carbohydrates; Oligosaccharides; Aminosugars; D-Galactosamine; Phthalimide; Glycosyl donors; Glycosyl acceptors; Glycosylations; Peptidoglycan; Glycoproteins.

The β(1→4)-linked 2-amino-2-deoxy-D-hexopyranose moieties are frequently occurring structural units in various biologically important oligosaccharides and their glycoconjugates, which have multiple biological functions and activities, such as a play a key role in molecular recognition and interactions of the cell–cell, cell–bacteria, and cell–virus types[1–3]. In contrast to the large number of works devoted to the synthesis of oligosaccharides with β(1→4)-linked 2-amino-2-deoxy-D-glucopyranose units, the synthesis of analogous oligosaccharides with β(1→4)-linked 2-amino-2-deoxy-D-galactopyranose units has received only little attention so far. The β(1→4)-linked *N*-acetylglucosamine moieties form e.g. an important structural polysaccharide chitin[4], glycan part of peptidoglycan of bacterial cell walls[5,6] as well as the reducing end of glycan residues of *N*-glycoproteins[3]. A systematic study devoted to the use of the most common glycosylation methods for the formation of 1,2-*trans*-glycosidic bond in the synthesis of oligosaccharides with β(1→4)-linked 2-amino-2-deoxy-D-glucopyranose units was reported by Paulsen et al.[7] The β(1→4)-linked *N*-acetylgalactosamine to 3-*O*-sialosyl-β-D-galactopyranoside unit constitutes a core unit of gangliosides[8,9]. Due to the problem of formation of β(1→4) glycosidic bond between two D-galactosamine units only one article related to this topic describing synthesis of ganglioside lactams (i.e., stable analogs of ganglioside lactones) was published. This synthesis is based on the glycosylation of 2-amino-2-deoxy-3-*O*-(sialosyl-1′,2′-lactam)-β-D-galactopyranoside subunit or 2-azido-2-deoxy-3-*O*-sialosyl-β-D-galactopyranoside subunit as glycosyl acceptor in position OH(4) with peracetylated 2-deoxy-2-phthalimido-D-galactopyranosyl bromide as glycosyl donor[10]. Oligosaccharides consisting of β(1→4)-linked 2-amino-2-deoxygalactopyranose units are a group of compounds having a significant potential from both the synthetic and biological points of view. The 2-amino-2-deoxy-β-D-galactopyranose units have equatorially oriented glycosidic bond and axially oriented C(4)–O bond (i.e., inverted configuration at both linkage centers in comparison to the α-D-glucopyranose units, forming cyclodextrin molecules) and so they satisfy the basic criteria for cyclization[11]. Oligosaccharides consisting of β(1→4)-linked 2-acetamido-2-deoxy-D-galactopyranose units also seem to be potential mimics of natural ligands for activated receptor of NK (natural killer) cells, taking into account the fact that the binding activity of *N*-acetyl-D-galactosamine is higher than *N*-acetyl-D-glucosamine and in the case of chitooligomers this activity increases with elongation of the saccharide chain[12]. The above mentioned facts motivated us to focus our attention on the problem of synthesis of oligosaccharides consisting β(1→4)-linked 2-acetamido-2-deoxy-D-galactopyranose units.

RESULTS AND DISCUSSIONS

In the synthesis of an oligosaccharide consisting from β(1→4)-linked 2-amino-2-deoxy-D-galactopyranose units we were confronted with the problem of stereoselective formation of 1,2-*trans*-glycosidic bond between glycosyl donor and glycosyl acceptor bearing a free axially oriented OH group in position 4. A large number of procedures for the synthesis of 1,2-*trans*-di- and oligosaccharides are described. For the 1,2-*trans*-glycosidic linking of 2-amino-2-deoxyhexopyranoside residue, the Koenigs–Knorr, oxazoline and phthalimide methods are most often used[3,13,14]. The phthalimide method is the most preferred, because 2-deoxy-2-phthalimido-hexopyranoses with halogen, trichloroacetimidate or alkylsulfanyl group at C-1 seem to be the most efficient donors and show the highest stereoselectivity[3,7]. The axially oriented OH(4) group on the galactopyranose skeleton is in general found to be the least reactive[15]. Thus, we were been prompted to make a systematic comparative investigation of the most widely used glycosylation methods using the synthesis of model disaccharides.

For the preparation of appropriate glycosyl donors and acceptors of *galacto* configuration, the approach based on the inversion of configuration at C-4 of the corresponding synthons with *gluco* configuration[16–18] was applied (Scheme 1). We used the mesyl group as a leaving group and sodium acetate as a nucleophile, instead of a combination of trifluoromethanesulfonyl group with tetrabutylammonium or cesium acetate[16–18]. The more stable 4-*O*-mesyl derivatives **2a** and **2b** (in contrast to analogical 4-*O*-trifluoromethanesulfonyl derivatives) can be isolated and are useful synthons for reactions with other nucleophiles, which give the corresponding saccharide units with *galacto* configuration. Ethyl 3,6-di-*O*-benzyl-2-deoxy-4-*O*-mesyl-2-phthalimido-1-thio-β-D-glucopyranoside (**2a**) and ethyl 3-*O*-allyl-6-*O*-benzyl-2-deoxy-4-*O*-mesyl-2-phthalimido-1-thio-β-D-glucopyranoside (**2b**) were obtained by the reaction of either ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[19–21] (**1a**), or ethyl



1a, R= Bn
1b, R=All

2a, R=Bn
2b, R=All

3a, R=Bn
3b, R=All

a) MsCl, pyridine; b) NaOAc, DMSO

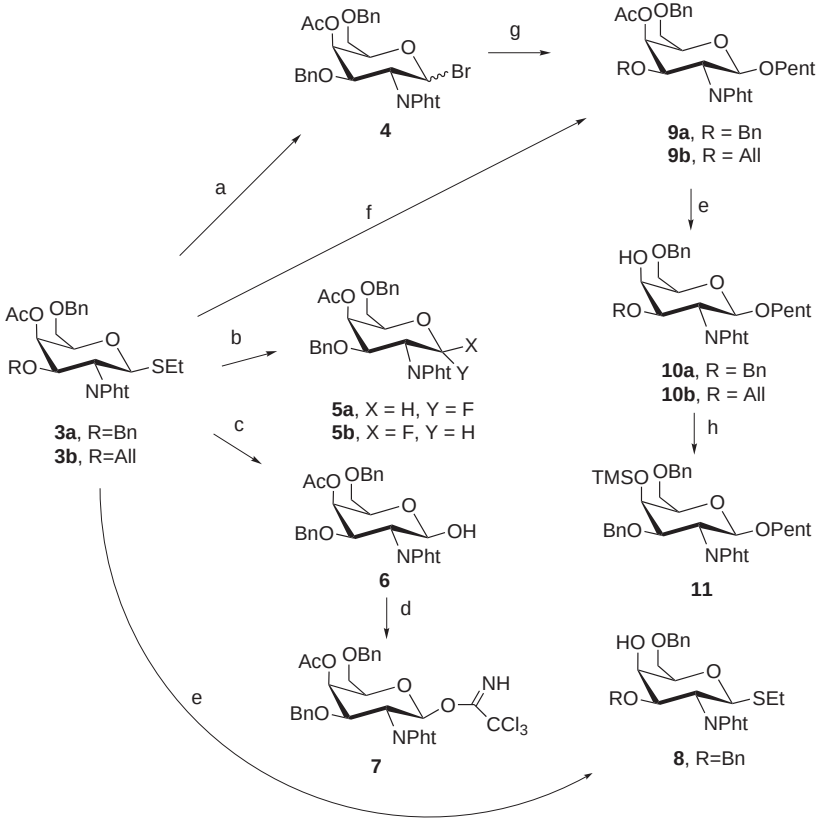
Ms = mesyl; Pht = phthaloyl

SCHEME 1

3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[18,20] (**1b**) with methanesufonyl chloride in pyridine. Mesylates **2a** and **2b** upon treatment with anhydrous sodium acetate in dry dimethyl sulfoxide at 130 °C, afforded the key compounds ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**3a**) and ethyl 4-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**3b**), respectively, in very good yields.

The attractive feature of thioglycosides in oligosaccharide synthesis is that they can be utilized directly as glycosyl donors by activation via sulfonium ion or readily converted into other glycosyl donors used in most common glycosylation methods[22] (i.e., glycosyl bromides, fluorides[23], glycosyl trichloroacetimidates[24] and pent-4-enyl (Pent) glycosides). The β-anomer of glycosyl bromide **4** was obtained by the reaction of ethyl thioglycoside **3a** with bromine in dichloromethane (Scheme 2). The reaction of ethyl thioglycoside **3a** with *N*-bromosuccinimide (NBS) and diethylaminosulfur trifluoride (DAST) in dichloromethane afforded a mixture of α- and β-glycosyl fluorides **5a** and **5b**, in the 1:15 ratio, which was separated by chromatography on a silica gel column. The β-anomer of trichloroacetimidate **7** was prepared from ethyl thioglycoside **3a** by splitting off the ethylsulfanyl group with *N*-iodosuccinimide (NIS) in a water–acetone mixture, to yield **6**, which was then converted to **7** by using a modified literature[25] procedure treatment with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene. The silver perchlorate promoted reaction of glycosyl bromide **4** with pent-4-en-1-ol in dichloromethane afforded pent-4-enyl glycoside **9a**. The pent-4-enyl glycoside **9b** was prepared directly from ethyl thioglycoside **3b** by methyl triflate-promoted condenzation with pent-4-en-1-ol in dichloromethane. Ethyl thioglycoside **8**, pent-4-enyl glycosides **10a** and **10b** and 4-*O*-trimethylsilyl derivative **11** were chosen as glycosyl acceptors for this comparative study. Compound **11** represents glycosyl acceptor suited for glycosylation with glycosyl fluorides and silicon-based catalysis[26]. Compounds **8**, **10a** and **10b** were prepared by Zemplén deacetylation from 4-*O*-acetates **3a**, **9a** and **9b** respectively. Silyl derivative **11** was obtained by reaction of compound **10a** with trimethylsilyl chloride and hexamethyldisilazane in a mixture of dichoromethane and pyridine.

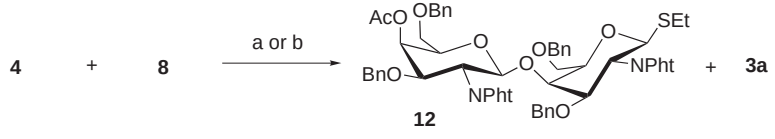
The results of the presented comparative investigation of the most widely used glycosylation methods using above specified glycosyl donors **3a**, **4**, **5b** and **7**, and glycosyl acceptors **8**, **10a**, **10b** and **11** in the synthesis of model disaccharides containing (1→4)-linked 2-amino-2-deoxygalactopyranose units are summarized in Table I. The silver triflate promoted glycosylation



a) Br_2, CH_2Cl_2; b) NBS, DAST in CH_2Cl_2, -35 °C; c) NIS, H_2O and acetone; d) CCl_3CN and DBU in toluene, 0°C and then r.t.; e) MeONa in MeOH; f) pent-4-en-1-ol and MeOTf in CH_2Cl_2; g) pent-4-en-1-ol and $AgClO_4$ in CH_2Cl_2; h) TMSCl and HMDS in CH_2Cl_2 and pyridine

SCHEME 2

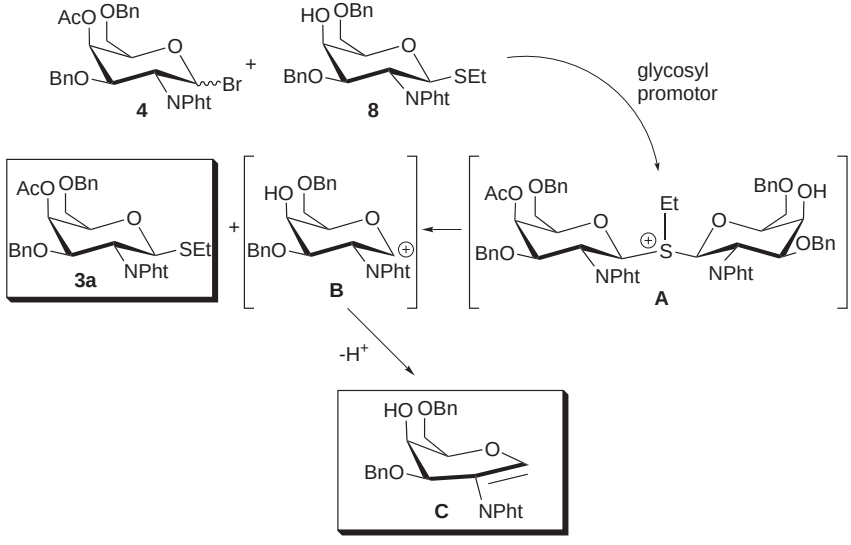
of ethyl thioglycoside **8** with glycosyl bromide **4** in dichloromethane at –45 °C in the presence of base gave the expected disaccharide **12** in a very low yield and ethyl thioglycoside **3a** was obtained as a major product (Scheme 3). The base, in the case of little reactive glycosyl acceptors acts as a glyco-



a) AgOTf, CH_2Cl_2, -45°C; b) $AgClO_4$, $AgCO_3$, CH_2Cl_2, r.t.

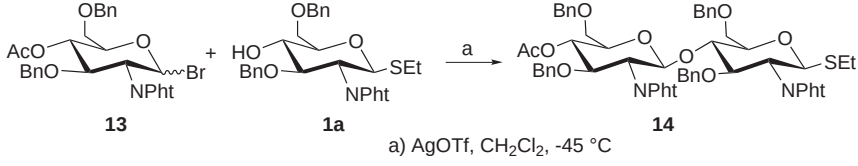
SCHEME 3

sylation inhibitor[27,28]. Application of the glycosidation procedure using silver perchlorate in the presence of silver carbonate[9], which acts as a scavenger of hydrogen bromide, did not lead to significant increase in the production of target compound **12** and ethyl glycoside **3a** was still a major product. The formation of unexpected ethyl thioglycoside **3a** can be interpreted as a result of low reactivity of axially oriented OH(4) group of glycosyl acceptor (Scheme 4). Due to this fact the activated form of glycosyl donor attacks mainly sulfur at the reducing end of glycosyl acceptor to give sulfonium ion **A**. The ion decomposes to form ethyl thioglycoside **3a** and carbocation **B**, which is stabilized by elimination to form glycal **C**. An analogous



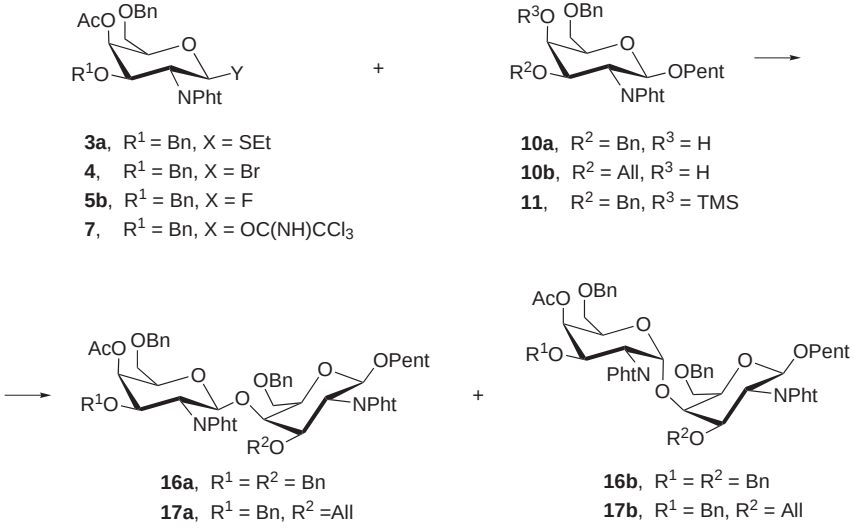
SCHEME 4

coupling of the corresponding synthons with *gluco* configuration followed the expected course, to afford disaccharide **14** in a very good yield (Scheme 5). The problem of intermolecular migration of ethylsulfanyl group was solved by using glycosyl acceptor having pent-4-enyl group at the reducing end.



SCHEME 5

Coupling of glycosyl bromide **4** with pent-4-enyl glycoside **10a** (Scheme 6) promoted with silver perchlorate in the presence of silver carbonate gave a mixture of β(1→4)- and α(1→4)-linked disaccharides **16a** and **16b**, respectively, in the 2.7:1 ratio, in a total yield of 78%. The use of ethyl thioglycoside **3a** as glycosyl donor activated with methyl triflate, by using the procedure as reported in the literature[20], led to an increase in the yield of α(1→4)-linked disaccharide **16b**, but the overall yield was low. The attempt



SCHEME 6

to couple β-glycosyl fluoride **5b** with pentenyl glycoside **10a** by using titanium tetrafluoride as glycosyl promotor[29] afforded, beside unreacted starting compounds, 24% of disaccharide **16a**, 17% of disaccharide **16b** and 15% of α-glycosyl fluoride **5a**. The same coupling carried out with the use of metallocene ($Cp_2ZrCl_2/AgClO_4$) as a catalyst[30,31] gave, in addition to unreacted starting compounds, 36% of disaccharide **16a** and 14% of disaccharide **16b**. Glycosylation using glycosyl fluorides as glycosyl donors and silicon-based catalysis[26], which employs the eminent affinity of silicon to fluorine, was unsuccessful. The trimethylsilyl triflate promoted reaction of **5b** with **10a** yielded a complex mixture from which the target disaccharide **16a** was isolated in a very low yield. Coupling of glycosyl trichloroacetimidate **7** with **10a** promoted with boron trifluoride etherate[7] afforded, in addition to unreacted glycosyl acceptor **10a**, 30% of disaccharide **16a** and 11% of disaccharide **16b**. A significant increase in stereoselectivity and efficiency of this glycosylation, i.e., formation of

β(1→4)- and α(1→4)-linked disaccharides **16a** and **16b** in the ratio 5:1 and 60% overall yield, was achieved by using trimethylsilyl triflate as a stronger Lewis acid. The replacement of benzyl protecting group in position OH(4) with less bulky allyl group did not have any positive effect. Silver perchlorate in the presence of silver carbonate promoted coupling of glycosyl bromide **4** with pentenyl glycoside **10b** gave, in addition to unreacted glycosyl acceptor **10b**, 17% of disaccharide **17a** and 11% of disaccharide **17b**.

Summarizing the results (Table I) revealed that the stereoselectivity and efficiency of glycosylation of D-galactosamine in comparison with D-glucosamine was lower, due to the low reactivity of axially oriented OH(4) group in a galactopyranose ring. The maximum overall yields of β(1→4)- and α(1→4)-linked disaccharides were obtained by silver perchlorate in the presence silver carbonate promoted glycosylation with glycosyl bromide. Quite a good stereoselectivity in favor of β(1→4)-linked disaccharides was achieved by Schmidt's trichloroacetimidate method.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Specific rotations were measured on a Perkin–Elmer 141 polarimeter at 22 °C and are given in deg cm^2 g^{-1}. Elemental analyses were performed using a Perkin–Elmer 2400 II instrument. NMR spectra were recorded on a Bruker Avance 500 spectrometer in the FT mode at 500.1 MHz (^{1}H) and at 125.8 MHz (^{13}C) in $CDCl_3$ or $(CD_3)_2SO$, using tetramethylsilane as internal standard for ^{1}H NMR spectra and $CDCl_3$ (δ 77.0) or $(CD_3)_2SO$ (δ 39.7) signals as standards for ^{13}C NMR spectra. For unambiguous assignment of signals in ^{13}C NMR spectra, ^{1}H- and ^{13}C-hetero-correlated 2D NMR spectra were measured by gHSQC and gHMBC techniques using the standard pulse sequences delivered by the producer of the spectrometer. The following typical parameters were used: spectral width in both f_1 and f_2 dimensions 5000 and 17 000 Hz, respectively, number of scans 16, number of increments in f_1 dimension 256, recycle delay 1 s, acquisition time 0.2 s, 90° pulse for ^{1}H was 12.5 μs, data matrix for processing 2048 × 2048 datapoints. For processing, shifted sinebell weighting function was used. Chemical shifts are given in ppm (δ-scale) and coupling constants (*J*) in Hz. Positive-ion FAB mass spectra were measured on a BeqG-geometry mass spectrometer ZAB-EQ (VG Analytical, Manchester, U.K.) using an M-Scan FAB gun (Xe, energy 8 keV) at an accelerating voltage of 8 kV. Samples were dissolved in chloroform or methanol, and a mixture of glycerol and thioglycerol or dimethyl sulfoxide was used as matrix. Thin-layer chromatography (TLC) was performed on DC-Alufolien Kieselgel 60 F_{254} (Merck, Darmstadt, Germany) or Silufol UV_{254} (Kavalier, Votice, Czech Republic) silica gel sheets. Preparative chromatography was performed on a silica gel column, particle size 40–60 μm (Fluka, Neu-Ulm, Switzerland). Analytical RP HPLC was performed using a Waters instrument (PDA detector, software Milennium 32; Milford, MA, U.S.A.) equipped with a Nova-Pak C18 column (150 × 3.9 mm), particle size 4 μm. Preparative RP HPLC was performed on a column (250 × 25 mm) filled with LiChrosorb RP-18, particle size 5 μm (Merck, Darmstadt, Germany). Solvents were evapo-

TABLE I
Comparison of the efficiency of a series of glycosyl donors and acceptors in standard glycosylation processes

Glycosyl donor	Glycosyl acceptor	Glycosyl promotor	Solvent	Temp., °C	Time	Products (anomeric configuration), %						
						12 (β)	**14** (β)	**16a** (β)	**16b** (α)	**17a** (β)	**17b** (α)	**3a**
4	**8**	AgOTf [a]	CH_2Cl_2	–45/–20	1.5 h	5						50
4	**8**	$AgClO_4/AgCO_3$	CH_2Cl_2	r.t.	8 h	17						55
13	**1a**	AgOTf [a]	CH_2Cl_2	–45	1.5 h		61					
4	**10a**	$AgClO_4/AgCO_3$	CH_2Cl_2	–15/r.t.	11 h			57	21			
3a	**10a**	MeOTf [a]	CH_2Cl_2	r.t.	48 h			42	21			
5b	**10a**	TiF_4	Et_2O	0/r.t.	18 h			24	17			
5b	**10a**	$Cp_2ZrCl_2/AgClO_4$	CH_2Cl_2	–20/r.t.	2 h			36	14			
5b	**11**	TMSOTf [a]	CH_3CN	–45/r.t.	3 d			11				
7	**10a**	$BF_3{\cdot}Et_2O$	CH_2Cl_2	r.t.	3 d			30	11			
7	**10a**	TMSOTf [a]	CH_2Cl_2	–45/r.t.	3 d			49	11			
4	**10b**	$AgClO_4/AgCO_3$	CH_2Cl_2	r.t.	8 h					17	11	

[a] Tf, trifluoromethanesulfonyl.

rated on a rotary vacuum evaporator at 40 °C. Analytical samples were dried at 6.5 Pa and 25 °C for 8 h.

Ethyl 3,6-Di-*O*-benzyl-2-deoxy-4-*O*-mesyl-2-phthalimido-1-thio-β-D-glucopyranoside (**2a**) and Ethyl 3-*O*-Allyl-6-*O*-benzyl-2-deoxy-4-*O*-mesyl-2-phthalimido-1-thio-β-D-glucopyranoside (**2b**)

Ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[19–21] (**1a**; 53.4 g, 100 mmol) or ethyl 3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[18,20] (**1b**; 48.4 g, 100 mmol) was dried at room temperature and 20 Pa for 6 h and then dissolved in pyridine (600 ml). Mesyl chloride (50 ml, 646 mmol) was slowly added under stirring and the mixture was stirred at room temperature for 24 h. Progress of the reaction was monitored by TLC in toluene–ethyl acetate (5:1). Toluene (3000 ml) was added and the mixture was washed with cool 1 M aqueous HCl (3 × 800 ml), water (3 × 600 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo.

Compound **2a**: Yield 58.7 g (96%) of a solid **2a**, chromatographically homogenous in the solvent system mentioned above. An analytical sample was prepared by crystallization from toluene–petroleum ether; m.p. 60–62 °C, $[\alpha]_D$ +76 (*c* 0.9, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{31}H_{33}NO_8S_2$ calculated: relative molecular mass 611.7, monoisotopic mass 611.2. ESI MS, *m/z*: 634.0 $[M + Na]^+$. For $C_{31}H_{33}NO_8S_2$ (611.7) calculated: 60.87% C, 5.44% H, 2.29% N, 10.48% S; found: 60.96% C, 5.56% H, 2.21% N, 10.31% S.

Compound **2b**: Yield 53.9 g (96%) of a syrupy compound **2b**, chromatographically homogenous in the solvent system mentioned above. An analytical sample was prepared by chromatography on a silica gel column in toluene–ethyl acetate (9:1), syrup; $[\alpha]_D$ +44 (*c* 0.5, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{27}H_{31}NO_8S_2$ calculated: relative molecular mass 561.7, monoisotopic mass 561.2. ESI MS, *m/z*: 584.1 $[M + Na]^+$, 600.1 $[M + K]^+$. For $C_{27}H_{31}NO_8S_2$ (561.7) calculated: 57.74% C, 5.56% H, 2.49% N, 11.42% S; found: 57.98% C, 5.71% H, 2.58% N, 11.14% S.

Ethyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**3a**) and Ethyl 4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**3b**)

Compound **2a** (15.3 g, 25 mmol) or compound **2b** (14.0 g, 25 mmol) and freshly melted sodium acetate (131 g, 1600 mmol) were dried in a flask equipped with a reflux condenser at room temperature and 20 Pa for 4 h and then the apparatus was flushed with argon (2×). Dry dimethyl sulfoxide (1400 ml) was added and the reaction mixture was stirred under argon atmosphere at 130 °C for 24 h. Progress of the reaction was monitored on TLC in toluene–ethyl acetate (5:1). The solvent was evaporated in vacuo at 90 °C and the residue was partitioned between toluene (1000 ml) and water (700 ml). Organic layer was separated, washed with water (2 × 700 ml), dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on a silica gel column (350 g) in toluene–ethyl acetate (7:1).

Compound **3a**: Yield 10.4 g (72%) of a syrupy compound **3a**; $[\alpha]_D$ +65 (*c* 0.6, chloroform), lit.[16] gives $[\alpha]_D$ +64 (*c* 1.0, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{32}H_{33}NO_7S$ calculated: relative molecular mass 575.7, monoisotopic mass 575.2. FAB MS, *m/z*: 514 $[M – EtSH + H]^+$. ESI MS, *m/z*: 598.3 $[M + Na]^+$, 614.1 $[M + K]^+$. For $C_{32}H_{33}NO_7S$ (575.7) calculated: 66.76% C, 5.78% H, 2.43% N, 5.57% S; found: 67.04% C, 5.89% H, 2.53% N, 5.49% S.

TABLE II
^{1}H NMR parameters of compounds **2a**–**8**[a]

Parameter	**2a**	**2b**	**3a**	**3b**	**4**[b]	**4**[c]	**5a**	**5b**	**6**	**7**	**8**
δ(H-1)	5.25 d	5.29 d	5.29 d	5.34 d	6.69 d	6.22 d	5.72 dd	5.85 dd	5.33 t	6.43 d	5.23 d
δ(H-2)	4.35 t	4.35 t	4.45 t	4.49 t	4.69 ddd	4.68 ddd	4.66 ddd	4.49 ddd	4.32 dd	4.65 dd	4.56 t
δ(H-3)	4.56 dd	4.43 dd	4.31 dd	4.37 dd	5.32 dd	4.24 dd	5.28 dd	4.34 dd	4.41 dd	4.45 dd	4.30 dd
δ(H-4)	4.75 dd	4.69 dd	5.71 dd	5.61 dd	5.89 dd	5.72 ddd	5.85 dd	5.67 dd	5.66 dd	5.74 bd	4.22 ddd
δ(H-5)	3.84 ddd	3.82 dd	3.96 ddd	3.96 ddd	4.53 dddd	4.01 ddd	4.47 bt	4.02 bt	3.97 dt	4.14 ddd	3.81 tt
δ(H-6a)	3.76 dd	3.74 dd	3.55 dd	3.53 dd	3.58 dd	3.56 dd	3.55 dd	3.61 dd	3.56 dd	3.60 dd	3.78 dd
δ(H-6b)	3.90 dd	3.89 dd	3.63 dd	3.62 dd	3.62 dd	3.65 dd	3.62 dd	3.68 dd	3.64 dd	3.68 dd	3.85 dd
J(1,2)	10.5	10.4	10.5	10.6	3.7	9.7	2.7	8.0	8.2	8.9	10.5
J(2,3)	10.2	10.2	10.6	10.6	11.6	10.7	11.6	11.1	11.0	11.0	10.4
J(3,4)	9.0	8.9	3.4	3.2	3.1	3.5	3.1	3.4	3.3	3.2	3.3
J(4,5)	10.0	9.9	1.2	1.2	1.3	1.3	0.9	1.2	1.2	1.2	1.0
J(5,6a)	5.3	5.4	7.2	7.0	6.8	7.1	6.7	6.9	6.4	7.2	5.0
J(5,6b)	2.3	2.3	5.8	5.9	6.0	5.8	6.0	5.9	6.2	5.7	5.2
J(6a,6b)	11.1	11.0	9.4	9.5	9.7	9.4	9.6	9.5	9.5	9.5	8.0

[a] Additional NMR parameters: **2a** – arom. H: 6.84–7.83 m, $OCH_2C_6H_5$: 4.40 d (1 H, *J* = 11.9), 4.63 s (2 H), 4.77 d (1 H, *J* = 11.9), OSO_2CH_3: 2.94 s (3 H), SCH_2CH_3: 2.60 dq (1 H, *J* = 3 × 7.5, 12.5), 2.68 dq (1 H, *J* = 3 × 7.5, 12.5), 1.17 t (3 H, *J* = 7.5); **2b** – arom. H: 7.26–7.93 m, $OCH_2C_6H_5$: 4.61 d (1 H, *J* = 11.9), 4.63 d (1 H, *J* = 11.9), OSO_2CH_3: 3.04 s (3 H), SCH_2CH_3: 2.62 dq (1 H, *J* = 3 × 7.4, 12.6), 2.70 dq (1 H, *J* = 3 × 7.4, 12.6), 1.20 t (3 H, *J* = 7.4), $OCH_2CH{=}CH_2$: 3.90 ddt (1 H, *J* = 1.4, 1.4, 6.2, 12.4), 4.16 ddt (1 H, *J* = 1.4, 1.4, 5.4, 12.4), 4.85 ddt (1 H, *J* = 1.2, 1.2, 1.5, 10.4), 5.02 dq (1 H, *J* = 3 × 1.6, 17.2), 5.58 dddd (1 H, *J* = 5.5, 6.2, 10.4, 17.2); **3a** – arom. H: 6.89–7.86 m, $OCH_2C_6H_5$: 4.26 d (1 H, *J* = 12.3), 4.48 d (1 H, *J* = 11.8), 4.59 d (1 H, *J* = 12.3), 4.60 d (1 H, *J* = 11.8), SCH_2CH_3: 2.61 dq (1 H, *J* = 3 × 7.5, 12.6), 2.68 dq (1 H, *J* = 3 × 7.5, 12.6), 1.18 t (3 H, *J* = 7.5), OAc: 2.14 s (3 H); **3b** – arom. H: 6.89–7.89 m, $OCH_2C_6H_5$: 4.48 d (1 H, *J* = 11.9), 4.58 d (1 H, *J* = 11.9), SCH_2CH_3: 2.65 dq (1 H, *J* = 3 × 7.5, 12.6), 2.71 dq (1 H, *J* = 3 × 7.5, 12.6), 1.21 t (3 H, *J* = 7.5), OAc: 2.12 s (3 H), $OCH_2CH{=}CH_2$: 3.80 ddt (1 H, *J* = 1.3, 1.3, 6.3, 12.9), 4.05 ddt (1 H, *J* = 1.5, 1.5, 5.1, 12.9), 4.94 ddt (1 H, *J* = 1.2, 1.2, 1.7, 10.3), 5.02 dq (1 H, *J* = 3 × 1.6, 17.3), 5.53 dddd (1 H, *J* = 5.1, 6.3, 10.3, 17.3); **4** – [b] α-anomer – $J_{1,5}$ = 0.8, $J_{2,4}$ = 0.5, arom. H: 6.89–7.90 m, $OCH_2C_6H_5$: 4.50 d (1 H, *J* = 9.1), 4.50 d (1 H, *J* = 12.0), 4.61 d (1 H, *J* = 12.0), 4.79 d (1 H, *J* = 9.1), OAc: 2.07 s (3 H); **4** – [c] β-anomer – $J_{2,4}$ = 0.5, arom. H: 6.89–7.90 m, $OCH_2C_6H_5$: 4.23 d (1 H, *J* = 12.5), 4.48 d (1 H, *J* = 11.9), 4.57 d (1 H, *J* = 12.5), 4.60 d (1 H, *J* = 11.9), OAc: 2.16 s (3 H); **5a** – $J_{H\text{-}1,F}$ = 53.7, $J_{H\text{-}2,F}$ = 30.0, arom. H: 7.09–7.86 m, $OCH_2C_6H_5$: 4.40 d (1 H, *J* = 10.1), 4.51 d (1 H, *J* = 12.0), 4.62 d (1 H, *J* = 12.0), 4.76 d (1 H, *J* = 10.1), OAc: 2.09 s (3 H); **5b** – $J_{H\text{-}1,F}$ = 53.4, $J_{H\text{-}2,F}$ = 12.8, arom. H: 6.92–7.84 m, $OCH_2C_6H_5$: 4.25 d (1 H, *J* = 12.3), 4.50 d (1 H, *J* = 11.9), 4.61 d (1 H, *J* = 12.3), 4.61 d (1 H, *J* = 11.9), OAc: 2.15 s (3 H); **6** – $J_{1,OH}$ = 8.2, arom. H: 6.93–7.87 m, $OCH_2C_6H_5$: 4.26 d (1 H, *J* = 12.1), 4.49 d (1 H, *J* = 12.0), 4.61 d (1 H, *J* = 12.1), 4.61 d (1 H, *J* = 12.0), OAc: 2.14s, OH: 3.18 bd (*J* = 8.2); **7** – arom. H: 6.90–7.88 m, $OCH_2C_6H_5$: 4.28 d (1 H, *J* = 12.0), 4.49 d (1 H, *J* = 12.0), 4.58 d (1 H, *J* = 12.3), 4.63 d (1 H, *J* = 12.3), OAc: 2.16s, NH: 8.57 bs; **8** – $J_{4,OH}$ = 1.0, $J_{5,OH}$ = 1.0, arom. H: 6.97–7.85 m, $OCH_2C_6H_5$: 4.34 d (1 H, *J* = 12.3), 4.61 s (2 H), 4.63 d (1 H, *J* = 12.3), SCH_2CH_3: 2.61 dq (1 H, *J* = 3 × 7.5, 12.5), 2.71 dq (1 H, *J* = 3 × 7.5, 12.5), 1.17 t (3 H, *J* = 7.5), OH: 2.61 t (1 H, *J* = 1.0).

Compound **3b**: Yield 8.5 g (65%) of a syrupy compound **3b**; $[\alpha]_D$ +33 (*c* 0.3, chloroform); lit.[18] gives $[\alpha]_D$ +24 (*c* 0.6, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{28}H_{31}NO_7S$ calculated: relative molecular mass 525.6, monoisotopic mass 525.2. FAB MS, *m/z*: 526 $[M + H]^+$, 548 $[M + Na]^+$. For $C_{28}H_{31}NO_7S$ (525.6) calculated: 63.98% C, 5.94% H, 2.66% N, 6.10% S; found: 64.17% C, 6.07% H, 2.72% N, 6.21% S.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α/β-D-galactopyranosyl Bromide (**4**)

Compound **3a** (576 mg, 1 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 10 ml) and then at room temperature and 20 Pa for 4 h. The apparatus was flushed with argon (2×) and dry dichloromethane (2 ml) was added through the septum. After dissolution, the mixture was cooled to 0 °C and 1 M solution of bromine in dry dichloromethane (1.1 ml, 1.1 mmol) was added through the septum. The mixture was stirred at 0 °C for 1 h. In the same apparatus the solvents were evaporated in vacuo (water pump) with exclusion of moisture. The residue was co-evaporated with toluene (3 × 10 ml) at 20 Pa, and lyophilized from benzene. Yield 590 mg (98%) of α/β-anomeric mixture (3:4) of compound **4**; $[\alpha]_D$ +77 (*c* 0.1, chloroform). The ratio of anomers was determined by ^{1}H NMR spectra. ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{30}H_{28}BrNO_7$ calculated: relative molecular mass 594.5, monoisotopic mass 593.1. FAB MS, *m/z*: 594 $[M + H]^+$. For $C_{30}H_{28}BrNO_7$ (594.5) calculated: 60.61% C, 4.75% H, 13.44% Br, 2.36% N; found: 66.89% C, 4.91% H, 13.32% Br, 2.38% N.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α-D-galactopyranosyl Fluoride (**5a**) and 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl Fluoride (**5b**)

Compound **3a** (1.73 g, 3.0 mmol) was dried at room temperature and 20 Pa for 4 h, then *N*-bromosuccinimide (1.07 g, 6.0 mmol) was added and drying was continued in an apparatus equipped with a septum for another 1 h. The apparatus was flushed with argon (2×) and dry dichloromethane (70 ml) was added trough the septum. After dissolution, the mixture was cooled to –45 °C and (diethylamino)sulfur trifluoride (DAST) (1 ml, 5.1 mmol) was added under stirring through the septum and the stirring was continued at –35 °C for 6 h. Saturated aqueous sodium hydrogencarbonate (30 ml) was added and the mixture was stirred at room temperature for another 1 h. The organic layer was separated, washed with water (3 × 15 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. Chromatography of the residue on silica gel column (80 g) in toluene–ethyl acetate (20:1) afforded 72 mg (5%) of α-anomer **5a** and 1.1 g (69%) of β-anomer **5b**.

Compound **5a**: Syrup; $[\alpha]_D$ +96 (*c* 0.2, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{30}H_{28}FNO_7$ calculated: relative molecular mass 533.5, monoisotopic mass 533.2. ESI MS, *m/z*: 514 $[M - F]^+$, 556 $[M + Na]^+$. For $C_{30}H_{28}FNO_7$ (533.5) calculated: 67.53% C, 5.29% H, 3.56% F, 2.63% N; found: 67.26% C, 5.55% H, 3.36% F, 2.48% N.

Compound **5b**: Solid; $[\alpha]_D$ +65 (*c* 0.1, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{30}H_{28}FNO_7$ calculated: relative molecular mass 533.5, monoisotopic mass 533.2. ESI MS, *m/z*: 514 $[M - F]^+$, 556 $[M + Na]^+$. For $C_{30}H_{28}FNO_7$ (533.5) calculated: 67.53% C, 5.29% H, 3.56% F, 2.63% N; found: 67.48% C, 5.43% H, 3.39% F, 2.54% N.

4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranose (**6**)

Compound **3a** (1.04 g, 1.8 mmol) and *N*-iodosuccinimide (930 mg, 4.1 mmol) were dissolved under stirring in a mixture acetone–water (4:1, 30 ml) at room temperature and stirring was continued for 12 h. The solvents were evaporated in vacuo and the residue was co-distilled with toluene (3 × 30 ml) and then dissolved in chloroform (30 ml). The solution was washed with 30% aqueous sodium thiosulfate (3 ml), water (2 × 3 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo, giving 950 mg (98%) of compound **6**; $[\alpha]_D$ +66 (*c* 0.3, chloroform). Compound **6** without specification of configuration on the anomeric centre is described in the literature[25] as a product of deallylation product of appropriate allyl glycoside; $[\alpha]_D$ +83 (*c* 0.6, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{30}H_{29}NO_8$ calculated: relative molecular mass 531.5, monoisotopic mass 531.5. FAB MS, *m/z*: 514 $[M - H_2O]^+$, 554 $[M + Na]^+$. For $C_{30}H_{29}NO_8$ (531.5) calculated: 67.79% C, 5.50% H, 2.64% N; found: 67.61% C, 5.61% H, 2.49% N.

O-(4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl) Trichloroacetimidate (**7**)

Compound **6** (870 mg, 1.6 mmol) was dried in an apparatus equipped with a septum at room temperature and 20 Pa for 4 h. The apparatus was flushed with argon (2×) and dry toluene (23 ml) was added through the septum. After dissolution, the mixture was cooled to 0 °C, and trichloroacetonitrile (2 ml, 9.6 mmol) and 1 M solution of DBU in toluene (320 µl, 0.32 mmol) were added through the septum. The stirring was then continued at room temperature for 24 h. Progress of the reaction was monitored on TLC in toluene–ethyl acetate (1:1). A saturated aqueous ammonium chloride (2 ml) was added. Organic layer was separated, washed with water (2 × 10 ml), then dried over anhydrous magnesium sulfate and evaporated in vacuo. Chromatography of the residue on a silica gel column (20 g) in toluene–ethyl acetate (20:1) afforded 680 mg (63%) of compound **7**; $[\alpha]_D$ +63 (*c* 0.2, chloroform). Compound **7** is described in[25] as incomplete characterized intermediate. ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{32}H_{29}Cl_3N_2O_8$ calculated: relative molecular mass 675.9, monoisotopic mass 674.1. FAB MS, *m/z*: 514 $[M - CCl_3CNHO]^+$, 697 $[M + H]^+$. For $C_{32}H_{29}Cl_3N_2O_8$ (675.9) calculated: 56.86% C, 4.32% H, 15.73% Cl, 4.14% N; found: 56.73% C, 4.45% H, 15.60% Cl, 4.08% N.

Ethyl 3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**8**)

Compound **3a** (576 mg, 1 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 5 ml) and then at room temperature and 20 Pa for 4 h. The apparatus was flushed with argon (2×), dry methanol (10 ml) and 1 M MeONa (100 µl, 0.1 mmol) were added through the septum and then the mixture was stirred at room temperature for 80 h. Progress of the reaction was monitored by TLC in toluene–ethyl acetate (5:1). The mixture was neutralized by addition of Dowex 50 (pyridinium form). The ion exchanger was filtered off, washed with methanol (20 ml) and the filtrate was evaporated in vacuo. Chromatography of the residue on a silica gel column (40 g) in the above mentioned solvent system gave 460 mg (80%) of a syrupy compound **8**, which was crystallized from ethanol to afford 444 mg (77%) of compound **8**; m.p. 112–113 °C, $[\alpha]_D$ + 58 (*c* 0.9, chloroform). ^{1}H NMR: see Table II, ^{13}C NMR: see Table V. For $C_{28}H_{31}NO_7S$ calculated: relative molecular mass 533.6, monoisotopic mass 533.2. FAB MS, *m/z*: 472 $[M - EtSH + H]^+$, 556 [M +

Na]$^+$. For $C_{30}H_{31}NO_6S$ (533.6) calculated: 67.53% C, 5.85% H, 2.63% N, 6.00% S; found: 67.61% C, 5.88% H, 2.61% N, 5.97% S.

Pent-4-enyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**9a**)

A mixture of silver perchlorate (1.4 g, 6.7 mmol) and molecular sieves 3 Å (3 g) was dried in an apparatus equipped with a septum at room temperature and 20 Pa for 4 h. The apparatus was flushed with argon (2×) and dry dichloromethane (30 ml) and pent-4-en-1-ol (2 ml, 19.4 mmol) were added through the septum and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –40 °C and a solution of glycosyl bromide **4**, freshly prepared from **3a** (2.4 g, 4 mmol) and dry dichloromethane (20 ml), was added through the septum under stirring during 10 min and stirring was continued at –20 °C for 12 h. A saturated aqueous sodium hydrogencarbonate (10 ml) was added at –20 °C and after warming to room temperature the mixture was diluted with dichloromethane (70 ml) and filtered through a Celite. The filtrate was washed with saturated aqueous sodium hydrogencarbonate (30 ml), water (3 × 30 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. Chromatography of the residue on silica gel column (140 g) in toluene–ethyl acetate (25:1) gave 2.2 g (90%) of a syrupy compound **9a**; $[\alpha]_D$ +39 (*c* 0.2, chloroform). ^{1}H NMR: see Table III, ^{13}C NMR: see Table V. For $C_{35}H_{37}NO_8$ calculated: relative molecular mass 599.7, monoisotopic mass 599.3. FAB MS, *m/z*: 600.8 [M + H]$^+$, 622.8 [M + Na]$^+$. For $C_{35}H_{37}NO_8$ (599.7) calculated: 70.10% C, 6.22% H, 2.34% N; found: 70.26% C, 6.34% H, 2.26% N.

Pent-4-enyl 4-*O*-Acetyl-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**9b**)

Compound **3b** (1.0 g, 2.0 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 15 ml) and then at room temperature and 20 Pa for 6 h. The apparatus was flushed with argon (2×) and dry dichloromethane (40 ml) was added through the septum. After dissolution, the mixture was cooled to –30 °C and methyl triflate (0.9 ml, 8.0 mmol) was added under stirring through the septum. The temperature was allowed to increase to 0 °C (during 15 min) and pent-4-en-1-ol (2 ml, 19.4 mmol) was added through the septum and stirring was then continued at room temperature for 6 h. Progress of the reaction was monitored by TLC in toluene–ethyl acetate (5:1). Pyridine (2 ml) was added and after 1 h stirring at room temperature the mixture was diluted with dichloromethane (30 ml). The solution was washed with saturated aqueous sodium hydrogencarbonate (30 ml), water (2 × 30 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. Chromatography of the residue on silica gel column (70 g) in toluene–ethyl acetate (20:1) gave 1.0 g (92%) of a syrupy compound **9b**; $[\alpha]_D$ +4 (*c* 0.4, chloroform). ^{1}H NMR: see Table III, ^{13}C NMR: see Table V. For $C_{31}H_{35}NO_8$ calculated: relative molecular mass 549.6, monoisotopic mass 549.2. FAB MS, *m/z*: 600.8 [M + H]$^+$, 622.8 [M + Na]$^+$. For $C_{31}H_{35}NO_8$ (549.6) calculated: 67.74% C, 6.42% H, 2.55% N; found: 67.68% C, 6.58% H, 22.49% N.

TABLE III
^{1}H NMR parameters of compounds **9**–**11**[a]

Parameter	**9a**	**9b**	**10a**	**10b**	**11**
δ(H-1)	5.13 d	5.15 d	5.09 d	5.12 d	5.11 d
δ(H-2)	4.39 dd	4.42 dd	4.45 dd	4.47 dd	4.57 dd
δ(H-3)	4.28 dd	4.34 dd	4.26 dd	4.28 dd	4.15 dd
δ(H-4)	5.67 dd	5.57 dd	4.16 d	4.15 bd	4.26 d
δ(H-5)	3.92 ddd	3.92 ddd	3.79–3.81 m	3.79 dd	3.71–3.76 m
δ(H-6a)	3.59 dd	3.57 dd	3.76–3.78 m	3.79 dd	3.64 m
δ(H-6b)	3.64 dd	3.63 dd	3.87–3.89 m	3.88 dd	3.71–3.76 m
δ(H-1a′)	3.39 ddd	3.43 ddd	3.39 dt	3.42 ddd	3.36 ddd
δ(H-1b′)	3.81 dt	3.84 dt	3.80 dt	3.82 dt	3.79 dt
δ(H-2′)	1.40–1.60 m	1.44–1.62 m	1.40–1.58 m	1.43–1.60 m	1.40–1.55 m
δ(H-3′)	1.75–1.92 m	1.79–1.93 m	1.77–1.92 m	1.80–1.93 m	1.74–1.87 m
δ(H-4′)	5.55 ddt	5.57 ddt	5.56 ddt	5.58 ddt	5.54 ddt
δ(H-5a′)	4.69 ddt	4.75 ddt	4.71 ddt	4.73 dq	4.68 ddt
δ(H-5b′)	4.73 ddt	4.72 ddt	4.74 ddt	4.75 ddt	4.72 ddt
J(1,2)	8.5	8.4	8.5	8.5	8.5
J(2,3)	11.1	11.2	10.9	11.0	11.1
J(3,4)	3.4	3.3	3.3	3.3	2.8
J(4,5)	1.2	1.2	[b]	0.0	0.0
J(5,6a)	7.0	6.8	[b]	5.8	[b]
J(5,6b)	5.8	6.0	[b]	8.2	[b]
J(6a,6b)	9.5	9.6	[b]	11.8	[b]

[a] Parameters of pent-4-enyl residue signed H-1′ to H-5′, typical values of coupling constants in pent-4-enyl residue: $J_{1a',2a'}$ = 6.3, $J_{1a',2b'}$ = 7.1, $J_{1b',2a'}$ = $J_{1b',2b'}$ = 6.2, $J_{1a',1b'}$ = 9.8, $J_{3a',4'}$ = $J_{3b',4'}$ = 6.6, $J_{3a',5a'}$ = $J_{3a',5a'}$ = 1.7, $J_{3a',5b'}$ = $J_{3b',5b'}$ = 1.4, $J_{4',5a'}$ = 17.0, $J_{4',5b'}$ = 10.3, $J_{5a',5b'}$ = 1.9. Additional NMR parameters and parameters of substituents: **9a** – arom. H: 6.89–7.87 m, $OCH_2C_6H_5$: 4.26 d (1 H, *J* = 12.4), 4.50 d (1 H, *J* = 11.9), 4.60 d (1 H, *J* = 11.9), 4.60 d (1 H, *J* = 12.4), OAc: 2.14 s; **9b** – arom. H: 7.28–7.89 m, $OCH_2C_6H_5$: 4.50 d (1 H, *J* = 11.9), 4.59 d (1 H, *J* = 11.9), OAc: 2.14 s, $OCH_2CH{=}CH_2$: 3.80 ddt (1 H, *J* = 1.3, 1.3, 6.3, 12.9), 4.06 ddt (1 H, *J* = 1.5, 1.5, 5.1, 12.9), 5.56 dddd (*J* = 5.1, 6.3, 10.4, 17.2), 4.95 ddt (*J* = 1.3, 1.3, 1.7, 10.4), 5.05 dq (*J* = 3 × 1.6, 17.2); **10a** – arom. H: 6.96–7.92 m, $OCH_2C_6H_5$: 4.34 d (1 H, *J* = 12.3), 4.64 d (1 H, *J* = 12.3), 4.62 s (2 H); **10b** – arom. H: 7.26–7.92 m, $OCH_2C_6H_5$: 4.62 s (2 H), $OCH_2CH{=}CH_2$: 3.88 ddt (1 H, *J* = 1.4, 1.4, 5.9, 12.9), 4.07 ddt (1 H, *J* = 1.4, 1.4, 5.5, 12.9), 5.65 ddt (1 H, *J* = 5.8, 5.8, 10.4, 17.2), 4.99 dq (1 H, *J* = 3 × 1.3, 10.4), 5.11 dq (1 H, *J* = 3 × 1.5, 17.2); **11** – arom. H: 6.92–7.83 m, $OCH_2C_6H_5$: 4.23 d (1 H, *J* = 12.1), 4.56 d (1 H, *J* = 11.9), 4.59 d (1 H, *J* = 11.9), 4.64 d (1 H, *J* = 12.1), $OSi(CH_3)_3$: 0.15 s (9 H). [b] Value not determined.

Pent-4-enyl 3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**10a**) and Pent-4-enyl 3-*O*-Allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**10b**)

Compound **9a** (1.2 g, 2.0 mmol) or compound **9b** (1.1 g, 2 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 10 ml) and then at room temperature and 20 Pa for 6 h. The apparatus was flushed with argon (2×) and dry methanol (40 ml) and 0.5 M MeONa in methanol (0.5 ml) were added through the septum. The mixture was stirred at room temperature for 7 days: Progress of the reaction was monitored on TLC in toluene–ethyl acetate (5:1). The mixture was neutralized by addition of Dowex 50 (pyridinium form), the ion exchanger was filtered off, washed with methanol (50 ml) and filtrate was evaporated in vacuo. The residue was chromatographed on a silica gel column (100 g) in toluene–ethyl acetate (10:1)

Compound **10a**: Yield 981 mg (88%) of a syrupy compound **10a**; $[\alpha]_D$ +33 (*c* 0.6, chloroform). ^{1}H NMR: see Table III, ^{13}C NMR: see Table V. For $C_{33}H_{35}NO_7$ calculated: relative molecular mass 557.6, monoisotopic mass 557.2. FAB MS, *m/z*: 558.2 $[M + H]^+$, 580.2 $[M + Na]^+$. For $C_{33}H_{35}NO_7$ (557.6) calculated: 71.08% C, 6.33% H, 2.51% N; found: 71.19% C, 6.41% H, 2.43% N.

Compound **10b**: Yield 822 mg (81%) of a syrupy compound **10b**; $[\alpha]_D$ +5 (*c* 0.4, chloroform). ^{1}H NMR: see Table III, ^{13}C NMR: see Table V. For $C_{29}H_{33}NO_7$ calculated: relative molecular mass 507.6, monoisotopic mass 507.2. FAB MS, *m/z*: 508.2 $[M + H]^+$, 530.7 $[M + Na]^+$. For $C_{29}H_{33}NO_7$ (507.6) calculated: 68.62% C, 6.55% H, 2.76% N; found: 68.49% C, 6.68% H, 2.64% N.

Pent-4-enyl 3,6-Di-*O*-benzyl-2-deoxy-2-phthalimido-4-*O*-(trimethylsilyl)-β-D-galactopyranoside (**11**)

Compound **10a** (160 mg, 0.3 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 5 ml) and then at room temperature and 20 Pa for 4 h. The apparatus was flushed with argon (2×), and dry dichloromethane (9 ml) and dry pyridine (4.5 ml) were added through the septum. After dissolution, 1,1,1,3,3,3-hexamethyldisilazane (130 µl, 0.6 mmol) and chlorotrimethylsilane (150 µl, 1.2 mmol) were added under stirring through the septum and stirring was continued at room temperature for 48 h. Progress of the reaction was monitored on TLC in toluene–ethyl acetate (5:1). The reaction mixture was evaporated in vacuo and the residue was chromatographed on a silica gel column (12 g) in toluene–ethyl acetate (20:1), to give 160 mg (88%) of a syrupy compound **11**; $[\alpha]_D$ +24 (*c* 0.02, chloroform). ^{1}H NMR: see Table III, ^{13}C NMR: see Table V. For $C_{36}H_{43}NO_7Si$ calculated: relative molecular mass 629.8, monoisotopic mass 629.3. ESI MS, *m/z*: 652 $[M + H]^+$. For $C_{36}H_{43}NO_7Si$ (629.8) calculated: 68.65% C, 6.88% H, 2.22% N; found: 68.41% C, 7.07% H, 2.11% N.

Ethyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-galactopyranoside (**12**)

Method A. A mixture of compound **8** (133 mg, 0.25 mmol) and silver trifluoromethanesulfonate (90 mg, 0.35 mmol) was dried in a flask equipped with a septum at room temperature and 20 Pa for 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (0.7 ml) was added through the septum. After dissolution, the mixture was cooled to –45 °C, and a solution of glycosyl bromide **4**, freshly prepared from **3a** (216 mg, 0.38 mmol) and

dry dichloromethane (0.6 ml), was added under stirring through the septum during 1 h. The mixture was stirred at –45 °C for another 1 h and at –20 °C for 30 min. Pyridine (0.5 ml) was added at –20 °C and after warming to room temperature the mixture was diluted with chloroform (5 ml) and filtered. The filtrate was washed with 0.5 M HCl (3 × 2 ml), saturated aqueous sodium hydrogencarbonate (3 × 2 ml) and water (3 × 2 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was separated by HPLC on silica gel C18 column in solvent system water–methanol (linear gradient 50→100%) to give 13 mg (5%) of a syrupy compound **12** and 72 mg (50%) of a syrupy compoud **3a**, which is identical in all respects ($[\alpha]_D$, MS, and NMR spectra) with the authentic compound **3a** described above.

Method B: A mixture of compound **8** (133 mg, 0.25 mmol), silver carbonate (276 mg, 1.0 mmol), silver perchlorate (62 mg, 0.3 mmol) and molecular sieves 4 Å (0.8 g) was dried in an apparatus equipped with a septum at room temperature and 20 Pa for 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (1.4 ml) was added through the septum. The mixture was stirred at room temperature for 1 h and a solution of glycosyl bromide **4**, freshly prepared from **3a** (216 mg, 0.38 mmol) and dry dichloromethane (0.6 ml), was added under stirring through the septum during 3 h. Stirring was continued at room temperature for another 10 h and then pyridine (1 ml) was added. The reaction mixture was worked up by the same procedure as is given in method *A* to afford 45 mg (17%) of a syrupy compound **12** and 38 mg (55%) of a syrupy compound **3a**.

Compound **12**: $[\alpha]_D$ +18 (*c* 0.1, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{60}H_{58}N_2O_{13}S$ calculated: relative molecular mass 1047.2, monoisotopic mass 1046.4. FAB MS, *m/z*: 877.4 $[M - (OBn \text{ and } EtS)]^+$, 1048.4 $[M + H]^+$, 1069.4 $[M + Na]^+$. For $C_{60}H_{58}N_2O_{13}S$ (1047.2) calculated: 68.82% C, 5.58% H, 2.68% N, 3.06% S; found: 69.07% C, 5.67% H, 2.74% N, 2.91% S.

Ethyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**14**)

Ethyl 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[20] (430 mg, 0.75 mmol) was dried in an apparatus equipped with a septum at room temperature and 20 Pa for 10 h. The apparatus was flushed with argon (2×) and dry dichloromethane (1.7 ml) was added through the septum. After dissolution, the mixture was cooled to 0 °C and 1 M solution of bromine in dry dichloromethane (0.8 ml) was added through the septum under stirring. Then the mixture was stirred at 0 °C for 1 h and then at room temperature for 1 h. In the same apparatus the solvents were evaporated in vacuo (water pump) with exclusion of moisture. The residue was co-evaporated with toluene (3 × 1.5 ml) at 20 Pa, added through the septum and the residue was dissolved in dry dichloromethane (1 ml). The solution of glycosyl bromide[20] **13** was used for the condenzation with **1a**.

A mixture of ethyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[19,20] (**1a**; 266 mg, 0.5 mmol) and silver trifluoromethanesulfonate (193 mg, 0.75 mmol) was dried in an apparatus equipped with a septum at room temperature and 20 Pa for 8 h. The apparatus was washed with argon (2×) and dry dichloromethane (1 ml) was added through the septum. After dissolution, the mixture was cooled to –45 °C and a solution of glycosyl bromide **13** was added through the septum under stirring during 1 h. Then the mixture was stirred at –45 °C for another 1 h and at –20 °C for 30 min. Pyridine (0.5 ml) was added at –20 °C and after warming to room temperature the mixture was diluted with chloroform (10 ml) and

filtered. The filtrate was washed with 0.5 M HCl (3 × 3 ml), saturated aqueous sodium hydrogencarbonate (3 × 3 ml), water (3 × 3 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. Chromatography of the residue on a silica gel column (30 g) in toluene–ethyl acetate (9:1) gave 320 mg (61%) of solid compound **14**; $[\alpha]_D$ +47 (*c* 1.3, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{60}H_{58}N_2O_{13}S$ calculated: relative molecular mass 1047.2, monoisotopic mass 1046.4. FAB MS, *m/z*: 877.4 [M – (OBn and EtS)]$^+$, 1048.4 [M + H]$^+$, 1069.4 [M + Na]$^+$. For $C_{60}H_{58}N_2O_{13}S$ (1047.2) calculated: 68.82% C, 5.58% H, 2.68% N; found: 69.09% C, 5.64% H, 2.67% N.

Pent-4-enyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**16a**) and Pent-4-enyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**16b**)

Method A: Compound **10a** (112 mg, 0.2 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Silver carbonate (320 mg, 1.16 mmol), silver perchlorate (67 mg, 0.32 mmol) and molecular sieves 4 Å (300 mg) were added and drying was continued at room temperature and 20 Pa for another

TABLE IV
^{1}H NMR parameters of compounds **12**–**17b**[a]

Parameter	12	14	16a	16b	16c	17a	17b
δ(H-1)	4.94 dd	5.10 m	4.88 d	4.90 d	4.93 d	5.03 d	5.03 d
δ(H-2)	4.11 t		4.02 dd	4.02 dd	4.05 dd	4.77 dd	4.38 dd
δ(H-3)	4.08 ddd	4.14–4.19 m	3.98 dd	4.03 dd	4.01 dd	4.08 dd	4.15 dd
δ(H-4)	4.05 dd		3.93 dd	3.94 dd	3.97 dd	4.32 dd	4.17 dd
δ(H-5)	3.65 ddd	3.34 ddd	3.60 ddd	3.64 ddd	3.64 ddd	3.53 dd	3.75 ddd
δ(H-6a)	3.70 dd	3.38 dd	3.73 dd	3.75 dd	3.74 dd	3.02 dd	3.78 dd
δ(H-6b)	3.84 dd	3.52 dd	3.90 dd	3.88 dd	3.89 dd	3.14 dd	3.88 dd
δ(H-1′)	5.32 d	5.33	5.28 d	5.44 d	5.24 d	5.30 d	5.81 d
δ(H-2′)	4.47 dd	4.27 dd	4.53 dd	4.69 dd	4.49 dd	4.76 dd	4.98 dd
δ(H-3′)	4.43 dd	4.77 dd	4.40 dd	5.95 dd	4.38 dd	5.61 dd	5.58 t
δ(H-4′)	5.67 dd	5.15 dd	5.66 dd	5.48 dd	5.64 dd	5.88 dd	4.45 dd
δ(H-5′)	3.87 ddd	3.66 ddd	3.88 ddd	4.08 ddd	3.86 dt	4.83 ddd	5.37 ddd
δ(H-6a′)	3.49 dd	3.44 dd	3.49 dd	4.04 dd		3.30 dd	4.26 dd
δ(H-6b′)	3.51 dd	3.54 dd	3.51 dd	4.17 dd	3.51 d	3.38 dd	4.33 dd
δ(H-1a″)	–	–	3.25 ddd	3.28 ddd	3.29 ddd	3.29 ddd	3.35 ddd
δ(H-1b″)	–	–	3.67 dt	3.71 dt	3.69 dt	3.50 dt	3.79 dd
δ(H-2″)	–	–		1.33–1.51 m	1.37–1.48 m	1.38–1.55 m	1.37–1.55 m
δ(H-3″)	–	–	1.60–1.82 m	1.68–1.81 m	1.73–1.82 m	1.76–1.87 m	1.74–1.88 m
δ(H-4″)	–	–	5.50 ddt	5.51 ddt	5.54 ddt	5.59 ddt	5.54 ddt
δ(H-5a″)	–	–	4.63 ddt	4.64 ddt	4.68 ddt	4.70 ddt	4.68 dq
δ(H-5b″)	–	–	4.68 ddt	4.69 ddt	4.71 ddt	4.76 ddt	4.71 dd

TABLE IV
(*Continued*)

Parameter	12	14	16a	16b	16c	17a	17b
J(1,2)	10.3	[b]	7.9	8.1	7.8	8.5	8.6
J(2,3)	10.3	[b]	11.0	10.1	11.1	11.1	10.8
J(3,4)	2.6	[b]	3.4	2.8	2.4	2.9	2.9
J(4,5)	1.0	9.3	1.0	0.0	1.0	0.0	1.3
J(5,6a)	5.5	4.0	5.9	6.0	6.1	8.6	6.0
J(5,6b)	6.1	1.3	5.7	5.4	5.5	6.1	5.9
J(6a,6b)	9.6	11.1	10.1	10.3	10.3	9.0	9.8
J(1′,2′)	8.1	8.4	8.4	8.4	8.4	3.3	4.7
J(2′,3′)	11.0	10.8	11.1	11.6	11.0	9.8	7.5
J(3′,4′)	3.2	9.0	3.4	3.4	3.4	3.1	7.9
J(4′,5′)	1.1	9.8	0.9	0.0	0.7	0.9	3.7
J(5′,6a′)	6.0	2.5	6.1	6.0	6.5	5.6	7.1
J(5′,6b′)	7.0	4.4	7.0	6.4	6.5	7.5	4.5
J(6a′,6b′)	9.2	9.9	9.2	9.8	[b]	9.1	11.8

[a] Parameters of pent-4-enyl residue signed H-1″ to H-5″, typical values of coupling constants in pent-4-enyl residue: $J_{1a'',2a''}$ = 6.1, $J_{1a'',2b''}$ = 7.3, $J_{1b'',2a''}$ = $J_{1b'',2b''}$ = 6.1, $J_{1a'',1b''}$ = 9.7, $J_{3a'',4''}$ = $J_{3b'',4''}$ = 6.7, $J_{3a'',5a''}$ = $J_{3a'',5a''}$ = 1.7, $J_{3a'',5b''}$ = $J_{3b'',5b''}$ = 1.2, $J_{4'',5a''}$ = 17.1, $J_{4'',5b''}$ = 10.2, $J_{5a'',5b''}$ = 2.1. Additional NMR parameters and parameters of substituents: **12** – $J_{1,3}$ = 1.3, arom. H: 6.56–8.10 m, $OCH_2C_6H_5$: 4.25 d (1 H, J = 12.5), 4.34 d (1 H, J = 12.7), 4.40 d (1 H, J = 11.8), 4.49 d (1 H, J = 11.8), 4.52 d (1 H, J = 12.7), 4.54 s (2 H), 4.60 d (1 H, J = 12.5), SCH_2CH_3: 2.45 dq (1 H, J = 3 × 7.4, 12.3), 2.60 dq (1 H, J = 3 × 7.4, 12.3), 1.32 t (3 H, J = 7.3), OAc: 2.17 s (3 H); **14** – arom. H: 6.80–7.88 m, $OCH_2C_6H_5$: 4.32 d (1 H, J = 12.1), 4.43 d (1 H, J = 11.8), 4.44 d (1 H, J = 11.9), 4.50 d (1 H, J = 12.3), 4.52 d (1 H, J = 11.8), 4.52 d (1 H, J = 11.9), 4.60 d (1 H, J = 12.1), 4.84 d (1 H, J = 12.3), SCH_2CH_3: 2.49 dq (1 H, J = 3 × 7.5, 12.5), 2.57 dq (1 H, J = 3 × 7.5, 12.5), 1.09 t (3 H, J = 7.5), OAc: 1.92 s (3 H); **16a** – arom. H: 6.52–7.80 m, $OCH_2C_6H_5$: 3.93 d (1 H, J = 12.8), 4.13 d (1 H, J = 12.8), 4.27 d (1 H, J = 12.0), 4.42 d (1 H, J = 11.8), 4.50 d (1 H, J = 11.8), 4.54 d (1 H, J = 11.9), 4.57 d (1 H, J = 11.9), 4.60 d (1 H, J = 12.0), OAc: 1.92 s (3 H); **16b** – arom. H: 6.63–7.75 m, $OCH_2C_6H_5$: 4.02 d (1 H, J = 12.7), 4.36 d (1 H, J = 12.7), 4.59 s (2 H), OAc: 1.87 s (3 H), 2.03 s (3 H), 2.20 s (3 H); **16c** – arom. H: 6.85–7.75 m, $OCH_2C_6H_5$: 4.25 d (1 H, J = 12.5), 4.42 d (1 H, J = 11.8), 4.50 d (1 H, J = 11.8), 4.55 d (1 H, J = 11.9), 4.57 d (1 H, J = 11.9), 4.58 d (1 H, J = 12.5), OAc: 2.15 s (3 H), $OCH_2CH{=}CH_2$: 3.47 ddt (1 H, J = 1.2, 1.2, 6.2, 12.8), 3.71 ddt (1 H, J = 1.4, 1.4, 5.8, 12.8), 5.30 ddt (1 H, J = 6.0, 6.0, 10.3, 17.2), 4.75 dq (1 H, J = 3 × 1.5, 10.3), 4.80 dq (1 H, J = 3 × 1.6, 17.2); **17a** – arom. H: 6.88–7.87 m, $OCH_2C_6H_5$: 4.15 d (1 H, J = 11.8), 4.16 d (1 H, J = 11.9), 4.18 d (1 H, J = 11.7), 4.32 d (1 H, J = 11.9), 4.40 d (1 H, J = 11.8), 4.59 d (1 H, J = 9.5), 4.71 d (1 H, J = 11.7), 4.87 d (1 H, J = 9.5), OAc: 2.06 s (3 H); **17b** – arom. H: 6.56–7.82 m, $OCH_2C_6H_5$: 4.06 d (1 H, J = 12.3), 4.34 d (1 H, J = 12.3), 4.61 d (1 H, J = 11.8), 4.67 d (1 H, J = 11.8), OAc: 2.03 s (3 H), 2.06 s (3 H), 2.16 s (3 H). [b] Value not determined.

TABLE V
^{13}C NMR chemical shifts of compounds **2a**–**11**[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6
2a	81.23	54.88	78.82	79.12	77.85	68.92
2b	81.23	54.92	78.68	77.88[b]	77.91[b]	68.90
3a	81.54	51.64	73.58	66.05	76.09	68.01
3b	81.76	51.70	74.03	66.28	76.20	68.13
4 α-anomer	90.40	54.66	71.39	65.52	72.84	67.30
4 β-anomer	78.70	56.13	72.92	65.64	77.30	67.47
5a	106.34	51.71	69.90	66.05	70.71	67.76
5b	104.96	52.95	72.25	65.30	72.52	67.56
6	93.29	54.69	72.81	65.90	72.54	68.11
7	94.36	51.86	72.80	65.62	73.33	67.33
8	81.02	51.01	75.63	65.74	77.15	69.16
9a	98.60	53.02	73.05	66.00	72.33	68.04
9b	98.77	53.06	73.37	66.19	72.44	68.17
10a	98.37	52.44	75.06	65.63	73.39	69.12
10b	98.51	52.51	75.23	65.84	73.45	69.19
11	98.78	52.45	[c]	67.55	73.87	68.80

[a] ^{13}C chemical shifts of aromatic carbons from protecting groups are not given. Additional ^{13}C NMR chemical shifts of substituents: **2a** – $OCH_2C_6H_5$: 74.91 t, 73.60 t, SCH_2CH_3: 24.11 t, 14.94 q, CH_3SO_2O: 38.63 q; **2b** – $OCH_2C_6H_5$: 73.56 t, SCH_2CH_3: 24.14 t, 14.95 q, CH_3SO_2O: 38.73 q, $OCH_2CH{=}CH_2$: 73.21 t, 133.42 d, 117.81 t; **3a** – $OCH_2C_6H_5$: 73.65 t, 70.96 t, SCH_2CH_3: 24.30 t, 14.88 q, OAc: 170.44 s, 20.95 q; **3b** – $OCH_2C_6H_5$: 73.63 t, SCH_2CH_3: 24.31 t, 14.90 q, OAc: 170.27 s, 20.86 q, $OCH_2CH{=}CH_2$: 70.16 t, 133.91 d, 117.52 t; **4** – α-anomer – $OCH_2C_6H_5$: 71.06 t, 73.66 t, OAc: 169.95 s, 23.89 q; **4** – β-anomer – $OCH_2C_6H_5$: 71.22 t, 73.72 t, OAc: 170.27 s, 23.89 q; **5a** – $J_{C\text{-}1,F}$ = 228.1, $J_{C\text{-}2,F}$ = 25.7, $J_{C\text{-}5,F}$ = 2.2, $OCH_2C_6H_5$: 73.64 t, 71.24 t, OAc: 170.07 s, 20.80 q; **5b** – $J_{C\text{-}1,F}$ = 214.3, $J_{C\text{-}2,F}$ = 21.5, $J_{C\text{-}3,F}$ = 9.4, $J_{C\text{-}5,F}$ = 5.0, $OCH_2C_6H_5$: 73.74 t, 71.28 t, OAc: 170.22 s, 20.78 q; **6** – $OCH_2C_6H_5$: 73.70 t, 71.20 t, OAc: 170.40 s, 20.91 q; **7** – $OCH_2C_6H_5$: 73.54 t, 71.28 t, OAc: 170.34 s, 20.87 q, $OC(NH)CCl_3$: 160.90 s, 93.21 s; **8** – $OCH_2C_6H_5$: 73.67 t, 71.24 t, SCH_2CH_3: 23.69 t, 14.87 q; **9a** – $OCH_2CH_2CH_2CH{=}CH_2$: 68.94 t, 28.41 t, 29.75 t, 137.71 d, 114.61 t; **9b** – $OCH_2C_6H_5$: 73.65 t, OAc: 170.31 s, 20.84 q, $OCH_2CH_2CH_2CH{=}CH_2$: 68.98 t, 28.48 t, 29.78 t, 137.74 d, 114.61 t, $OCH_2CH{=}CH_2$: 70.25 t, 133.98 d, 117.41 t; **10a** – $OCH_2C_6H_5$: 73.68 t, 71.29 t, $OCH_2CH_2CH_2CH{=}CH_2$: 68.57 t, 28.48 t, 29.81 t, 137.85 d, 114.53 t; **10b** – $OCH_2C_6H_5$: 73.70 t, $OCH_2CH_2CH_2CH{=}CH_2$: 68.60 t, 28.54 t, 29.83 t, 137.87 d, 114.54 t, $OCH_2CH{=}CH_2$: 70.37 t, 133.88 d, 117.86 t; **11** – $OCH_2C_6H_5$: 73.70 t, 72.23 t, $OCH_2CH_2CH_2CH{=}CH_2$: 68.80 t, 28.45 t, 29.80 t, 137.88 d, 114.49 t, $OSi(CH_3)_3$: 0.57 q. [b] Alternative assignment of chemical shifts. [c] Overlapped by solvent signal.

8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (5 ml) was added through the septum. The mixture was stirred at room temperature for 1 h, and a solution of glycosyl bromide **4**, freshly prepared from **3a** (230 mg, 0.4 mmol) and dichloromethane (4 ml), was added at –15 °C under stirring through the septum during 1 h and then the stirring was continued at room temperature for another 10 h. Progress of the reaction was monitored on TLC in toluene–ethyl acetate (5:1). Pyridine (1.5 ml) was added and after 1 h stirring at room temperature, the mixture was diluted with chloroform (12 ml) and filtered

TABLE VI
Characteristic ^{13}C NMR chemical shifts of compounds **12**–**17b**[a]

Carbon	**12**	**14**	**16a**	**16b**	**16c**	**17a**	**17b**
1	80.18	80.77	98.02	98.15	98.24	98.04	98.50
2	50.77	54.74	52.13	52.27	52.30	51.87	52.60
3	75.92	78.82	75.32	70.25	75.50	75.66	76.18
4	73.49	76.03	74.54	75.26	74.54	69.68	73.06
5	77.14	77.67	73.58	73.60	73.75	72.72	73.30
6	69.44	69.45	69.72	69.77	69.86	66.94	69.38
1′	99.5	97.09	99.86	99.85	99.64	97.62	104.62
2′	52.94	56.24	52.80	51.14	52.82	52.65	60.81
3′	72.72	76.87	72.69	67.81	72.79	70.68	72.74
4′	65.74	72.73	65.70	66.52	65.81	66.77	77.96
5′	71.67	73.42	71.57	75.26	71.69	68.19	69.03
6′	68.00	68.25	68.14	61.38	68.18	68.13	62.57
1″	–	–	67.95	68.19	67.93	67.24	68.67
2″	–	–	28.37	28.41	28.49	29.69	28.47
3″	–	–	29.75	29.76	29.82	29.96	29.79
4″	–	–	137.96	137.91	138.03	138.08	137.87
5″	–	–	114.34	114.39	114.38	114.48	114.49

[a] ^{13}C chemical shifts of aromatic carbons from protecting groups are not given. Additional ^{13}C NMR chemical shifts of substituents: **12** – $OCH_2C_6H_5$: 73.59 t, 72.74 t, 71.43 t, 71.03 t, SCH_2CH_3: 22.49 t, 14.63 q, OAc: 170.59 s, 21.03 q; **14** – $OCH_2C_6H_5$: 74.58 t, 73.90 t, 73.55 t, 72.67 t, SCH_2CH_3: 23.62 t, 14.86 q, OAc: 169.63 s, 20.89 q; **16a** – $OCH_2C_6H_5$: 73.34 t, 71.60 t, 70.93 t, 68.14 t, OAc: 170.58 s, 20.99 q; **16b** – $OCH_2C_6H_5$: 73.47 t, 71.91 t, OAc: 170.39 s, 170.35 s, 169.92 s, 20.74 q, 20.66 q, 20.57 q; **16c** – $OCH_2C_6H_5$: 73.62 t, 73.42 t, 71.00 t, OAc: 170.56 s, 20.97 q, $OCH_2CH{=}CH_2$: 71.34 t, 134.28 d, 117.63 t; **17a** – $OCH_2C_6H_5$: 73.46 t, 73.11 t, 71.36 t, 71.13 t, OAc: 170.28 s, 21.27 q; **17b** – $OCH_2C_6H_5$: 73.60 t, 71.97 t, OAc: 170.43 s, 170.39 s, 170.31 s, 20.78 q, 20.69 q, 20.50 q.

through Celite. The filtrate was evaporated. The residue was separated by chromatography on a silica gel column (15 g) in toluene–ethyl acetate (10:1) to give 122 mg (57%,) of a syrupy compound **16a** and 45 mg (21%) of a syrupy compound **16b**.

Method B: Compounds **3a** (234 mg, 0.4 mmol) and **10a** (112 mg, 0.2 mmol) were dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Crushed molecular sieves 4 Å (300 mg) were added and drying was continued at room temperature and 20 Pa for 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (4 ml) was added through the septum. After dissolution, methyl triflate (60 μl, 0.53 mmol) was added under stirring at room temperature through the septum and the stirring was continued at the same temperature for 2 days. Progress of the reaction was monitored as described in method *A*. The mixture was taken between chloroform (20 ml) and saturated aqueous sodium hydrogencarbonate (10 ml) and organic layer was separated, washed with water (2 × 5 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was separated by a column chromatography as described in method *A*, to give 90 mg (42%) of a syrupy compound **16a**, 45 mg (21%) of a syrupy compound **16b** and 25 mg (22%) of starting compound **10a**.

Method C: Compound **10a** (112 mg, 0.2 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml). Compound **5b** (213 mg, 0.4 mmol) was added and drying was continued at room temperature and 20 Pa for another 8 h. The apparatus was flushed with argon (2×) and the mixture was dissolved in dry diethyl ether (6 ml) added through the septum. The obtained solution was added through the septum to a stirred mixture of titanium(IV) fluoride (87 mg, 0.7 mmol) and molecular sieves 3 Å (1.5 g) under argon in an apparatus equipped with the septum at 0 °C. The stirring was then continued at room temperature for 18 h. Progress of the reaction was monitored as described in method *A*. The reaction mixture was worked up by the same procedure as is given in procedure *A*, to afford 51 mg (24%) of a syrupy compound **16a**, 36 mg (17%) of a syrupy compound **16b**, 31 mg (15%) of a syrupy compound **5a**, 23 mg (21%) of starting compound **10a** and 74 mg (35%) of starting compound **5b**.

Method D: Compound **10a** (112 mg, 0.2 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Compound **5b** (120 mg, 0.22 mmol) was added and the drying was continued at room temperature and 20 Pa for another 8 h. The apparatus was flushed with argon (2×) and the mixture was dissolved in dry dichloromethane (4 ml) added through the septum. The obtained solution was added through the septum to a stirred mixture of bis(cyclopentadienyl)zirconium dichloride (350 mg, 1.2 mmol), silver perchlorate (250 mg, 1.2 mmol) and crushed molecular sieves 4 Å (200 mg) in dry dichloromethane (4 ml) under argon and at –20 °C in a apparatus equipped with a septum. The mixture was stirred at –20 °C for 2 h, and then chloroform (20 ml) and saturated aqueous sodium hydrogencarbonate (6 ml) were added. After warming to room temperature the mixture was filtered and organic layer was separated, washed with water (2 × 10 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was separated by a column chromatography as described in method *A*, to give 77 mg (36%) of a syrupy compound **16a**, 30 mg (14%) of a syrupy compound **16b**, 40 mg (36%) of starting compound **10a** and 15 mg (13%) of starting compound **5b**.

Method E: Compounds **11** (126 mg, 0.2 mmol) and **5b** (213 mg, 0.4 mmol) were dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml). The apparatus was flushed with argon (2×) and dry acetonitrile (6 ml) was added through the septum. After dissolution, the mixture was cooled to –45 °C and trimethylsilyl trifluoro-

methanesulfonate (10 μl, 0.05 mmol) was added under stirring through the septum. The mixture was stirred at –20 °C for 2 h and than at room temperature for 3 days. Progress of the reaction was monitored as described in method *A*. The mixture was filtered through Celite, taken between toluene (30 ml) and saturated aqueous sodium hydrogencarbonate (10 ml), and organic layer was separated, washed with water (2 × 10 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. From the complex reaction mixture 24 mg (11%) of a syrupy compound **16a** was isolated by a column chromatography as described in method *A*, followed by HPLC separation on a silica gel column (5 μm) in hexane–ethyl acetate (3:1).

Method F: Compounds **7** (270 mg, 0.4 mmol) and **10a** (112 mg, 0.2 mmol) were dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Crushed molecular sieves 4 Å (300 mg) were added and drying was continued at room temperature and 20 Pa for 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (5 ml) was added through the septum. After dissolution, the mixture was cooled to –45 °C and 1 M solution of boron trifluoride etherate in dichloromethane (100 μl, 0.1 mmol) was added through the septum under stirring. Then the mixture was stirred at room temperature for 3 days. Progress of the reaction was monitored as described in method *A*. The mixture was taken between chloroform (20 ml) and saturated aqueous sodium hydrogencarbonate (10 ml), and organic layer was separated, washed with water (2 × 5 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was separated by a column chromatography as described in method *A*, to give 64 mg (30%) of a syrupy compound **16a**, 24 mg (11%) of a syrupy compound **16b** and 54 mg (48%) of starting compound **10a**.

Method G: Compounds **7** (270 mg, 0.4 mmol) and **10a** (112 mg, 0.2 mmol) were dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Crushed molecular sieves 4 Å (300 mg) were added and drying was continued at room temperature and 20 Pa for 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (5 ml) was added through the septum. After dissolution, the mixture was cooled to –45 °C and trimethylsilyl trifluoromethanesulfonate (80 μl, 0.4 mmol) was added under stirring through the septum. The mixture was stirred at the same temperature for 12 h and then at room temperature for 3 days. Progress of the reaction was monitored as described in method *A*. The mixture was filtered through Celite, partioned between chloroform (20 ml) and saturated aqueous sodium hydrogencarbonate (10 ml), and organic layer was separated, washed with water (2 × 5 ml), dried over anhydrous magnesium sulfate and evaporated in vacuo. The residue was separated by a column chromatography as described in method *A*, to give 105 mg (49%) of a syrupy compound **16a** and 24 mg (11%) of a syrupy compound **16b**.

Compound **16a**: $[\alpha]_D$ +13 (*c* 0.2, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{63}H_{62}N_2O_{14}$ calculated: relative molecular mass 1071.2, monoisotopic mass 1070.4. ESI MS, *m/z*: 1093.8 $[M + Na]^+$. For $C_{63}H_{62}N_2O_{14}$ (1071.2) calculated: 70.64% C, 5.83% H, 2.62% N; found: 70.28% C, 6.02% H, 2.51% N.

Compound **16b**: $[\alpha]_D$ +46 (*c* 0.7, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{63}H_{62}N_2O_{14}$ calculated: relative molecular mass 1071.2, monoisotopic mass 1070.4. ESI MS, *m/z*: 1093.5 $[M + Na]^+$. For $C_{63}H_{62}N_2O_{14}$ (1071.2) calculated: 70.64% C, 5.83% H, 2.62% N; found: 70.32% C, 5.91% H, 2.49% N.

Pent-4-enyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**17a**) and Pent-4-enyl 4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α-D-galactopyranosyl-(1→4)-3-*O*-allyl-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**17b**)

Compound **10b** (102 mg, 0.2 mmol) was dried in an apparatus equipped with a septum by co-distillation with dry benzene (3 × 3 ml), added through the septum. Silver carbonate (276 mg, 1 mmol), silver perchlorate (48 mg, 0.23 mmol) and molecular sieves 4 Å (300 mg) were added and drying was continued at room temperature and 20 Pa for another 8 h. The apparatus was flushed with argon (2×) and dry dichloromethane (3 ml) was added through the septum. The mixture was stirred at room temperature for 1 h and a solution of glycosyl bromide **4**, freshly prepared from **3a** (173 mg, 0.3 mmol), in dry dichloromethane (3 ml) was added under stirring through the septum during 1 h and the stirring was continued at room temperature for another 10 h. Progress of the reaction was monitored on TLC in toluene–ethyl acetate (5:1). Pyridine (1.5 ml) was added and after 1 h stirring at room temperature, the mixture was diluted with chloroform (12 ml) and filtered through Celite. The filtrate was evaporated. Chromatography of the residue on a silica gel column (15 g) in oluene–ethyl acetate (10:1) followed by HPLC separation on a silica gel column (5 μm) in hexane–ethyl acetate (4:1) afforded 35 mg (17%) of a syrupy compound **17a** and 22 mg (11%) of a syrupy compound **17b** and 42 mg (43%) of starting compound **10b**.

Compound **17a**: $[\alpha]_D$ –39 (*c* 0.2, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{59}H_{60}N_2O_{14}$ calculated: relative molecular mass 1021.1, monoisotopic mass 1020.4. ESI MS, *m/z*: 1043.3 $[M + Na]^+$. For $C_{59}H_{60}N_2O_{14}$ (1021.1) calculated: 69.40% C, 5.92% H, 2.74% N; found: 69.28% C, 6.10% H, 2.66% N.

Compound **17b**: $[\alpha]_D$ +128 (*c* 0.2, chloroform). ^{1}H NMR: see Table IV, ^{13}C NMR: see Table VI. For $C_{59}H_{60}N_2O_{14}$ calculated: relative molecular mass 1021.1, monoisotopic mass 1020.4. ESI MS, *m/z*: 1043.5 $[M + Na]^+$. For $C_{59}H_{60}N_2O_{14}$ (1021.1) calculated: 69.40% C, 5.92% H, 2.74% N; found: 69.33% C, 6.16% H, 2.62% N.

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