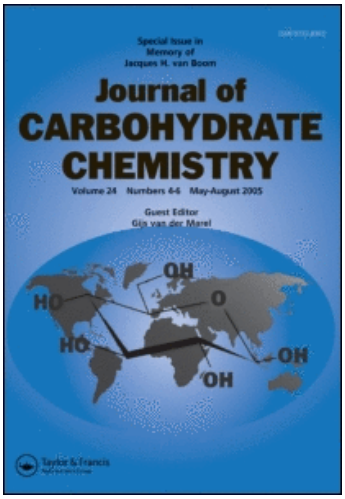

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A Comparison in the Efficiency of Six Standard 2-Amino-2-Deoxy-Glucosyl Donors for the Synthesis of (2-Deoxy-2-Phthalimido-β-D-Glucopyranosyl) (14)-β-D-Glucopyranosides.

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A COMPARISON IN THE EFFICIENCY OF SIX STANDARD 2-AMINO-2-DEOXY-GLUCOSYL DONORS FOR THE SYNTHESIS OF (2-DEOXY-2-PHTHALIMIDO-β-D-GLUCOPYRANOSYL) (1→4)-β-D-GLUCOPYRANOSIDES.

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ABSTRACT

A systematic study is presented for the most common methods used for the preparation of the disaccharide benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**9**) from "standard 2-amino-2-deoxyglucopyranosyl donors" **1-6** and benzyl 3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**7**) as an acceptor. It was found that the highest yield was obtained when the trichloroacetimidate derivative **1** was coupled to the 4 position of acceptor **7**. In an analogous manner, the disaccharides allyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6,-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**10**), benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**12**), and allyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-

phthalimido-β-D-glucopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (**14**) were prepared.

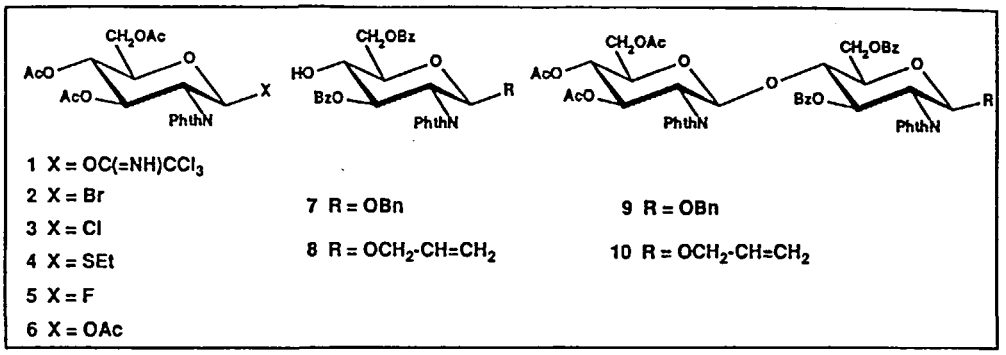
INTRODUCTION

A large number of procedures are reported in the literature for the synthesis of 1,2-*trans*-di- and oligosaccharides. Among the most widely used methods are the original Koenigs - Knorr glycosidation [2-4] and its modifications, [5-6] the imidate, [7] the thioglycoside [8] and the trimethylsilyl [9] coupling methods.

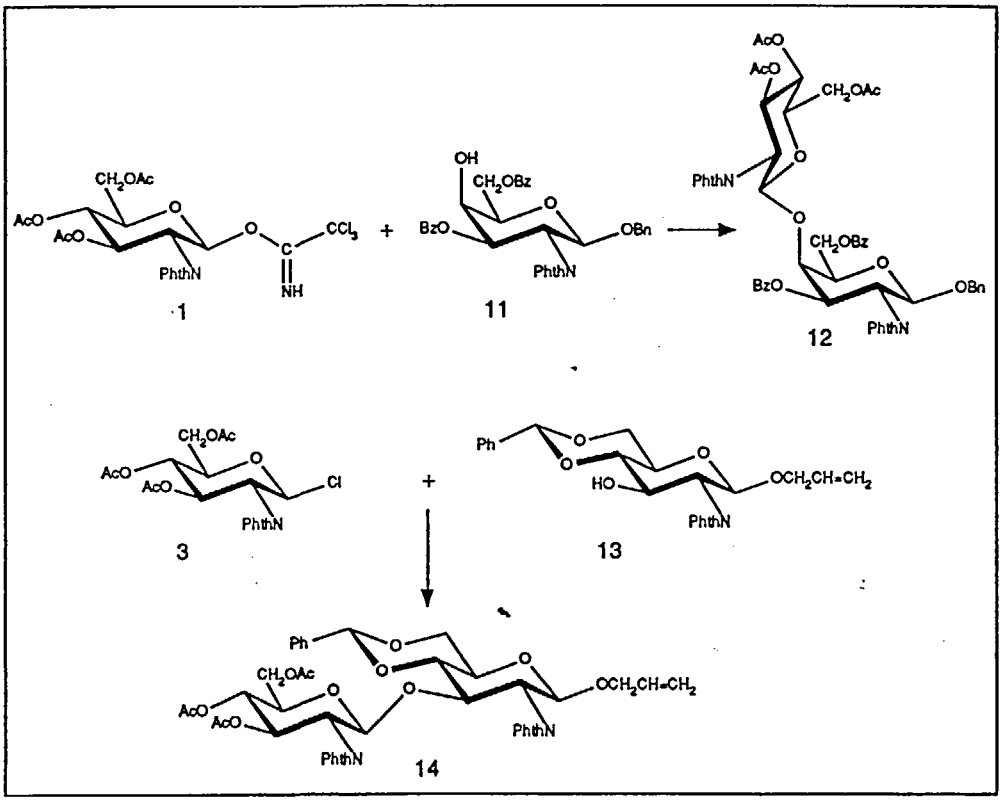
Systemization for optimum yield and stereospecificity is difficult, [10] since too many parameters in the experiments reported in literature vary. However, it has gradually become clear that the yield and product composition depend on various parameters such as the structure of the donor, the reactivity of the alcohol, the promoter and the solvent used. In this report we have directly compared the coupling efficiency on six glycosyl donors, which differ only in the leaving group at the anomeric carbon, with the same glycosyl acceptor.

RESULTS AND DISCUSSION

The three most important parameters determining the selectivity and the yield of a glycosidation reaction are the reactivity of the donor, the catalyst, and the specific acceptor. [3] Although 4- OH acceptors in general are usually found to be the least reactive, we have often been confronted with coupling reactions that involve the reaction of a donor to an acceptor bearing a free OH group on a 4-position. [11] Thus, we have been prompted to make a systematic comparative investigation of the most widely used methods for oligosaccharides synthesis to obtain the same target disaccharide, benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (*9*). The acceptor benzyl 3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (*7*) was chosen for this comparative study, since it is less reactive than a sugar with a free OH on the 3-position or having a free primary OH.



SCHEME I



SCHEME II

In the present investigation, benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**9**) was prepared in 69% yield by coupling 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate (**1**) to **7** in dichloromethane at -20 °C. An inspection of the ^{1}H NMR spectrum of **9** (see Experimental) reveals that there are two doublets for β-anomeric protons, together with the features of the two building blocks. No evidence for α-linked disaccharide was observed, either on TLC or in the ^{1}H NMR spectrum. Thus, coupling proceeds stereospecifically under the chosen conditions. This stereo-specificity is probably due to the presence of a bulky participating group in the 2- position of the donor.

The same coupled product (**9**) was obtained by a modification of the Koenigs - Knorr method developed by Banoub and Hanessian.[13] In this procedure, the glycosyl halide[15] **2** or **3** was added to a solution of the glucosamine acceptor[12] **7** in dichloromethane containing 4 Å molecular sieves and 1.2 equiv. of silver triflate. Disaccharide **9** was again formed but in a lower yield (~ 60%, see Table).

Thioglycosides may also be used directly as glycosyl donors. Recently, Garegg et al. [14] described the use of dimethyl(methylthio)sulfonium triflate (DMTST) as a highly thiophylic promoter in the synthesis of 1,2-*trans*-glycosides. Ethyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside[12] (**4**) was coupled to **7** by using DMTST as a promoter in dichloromethane at ambient temperature to yield the desired coupling product **9** in 57%.

In addition, 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose[14] (**6**) or the corresponding glucosyl fluoride [11] **5** was coupled to the acceptor **7** under acidic conditions using trimethylsilyl triflate (TMSOTf) in dichloromethane or absolute acetonitrile respectively (see Table) to give disaccharide **9**, in yields of 18% and 44% respectively.

A summary of the results shown in the following table reveals that the highest yield was obtained by Schmidt's trichloroacetimidate method [4] (Entry 1) while, the lowest was obtained by using the acetate method (Entry 6).

TABLE

Entry	Donor	Solvent	Catalyst	Time	Temp.	Yield%
1	1	CH_2Cl_2	BF_3Et_2O	0.5 h	-20 °C	69
2	3	CH_2Cl_2	AgOTf	2 h	-30 °C	62
3	2	CH_2Cl_2	AgOTg	1 h	-30 °C	60
4	4	CH_2Cl_2	DMTST	5 h	20 °C	57
5	5	CH_3CN	TMSOTf	24 h	0 °C	44
6	6	CH_2Cl_2	TMSOTf	16 h	20 °C	18

Since the trichloroacetimidate method was the most convenient to use, two additional derivatized disaccharides were prepared employing this method. Allyl *O*- (3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**10**) was prepared in 73% yield using the acceptor **8** and the donor **1**. The structure of the coupling product was confirmed by ^{1}H NMR.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate [6] (**1**) was coupled to benzyl 3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-galacto-pyranoside[12] (**11**) under acidic conditions. The product (72% yield) was found to be the fully protected chitobioside analogue, benzyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzoyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (**12**). The ^{1}H NMR spectrum of the product was in accordance with the assigned structure.

A final condensation reaction was between 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl chloride[15] (**3**) and the glucosyl acceptor[12] **13** were allowed to react in dichloromethane solution with silver triflate and sym-collidine, the coupled product, allyl *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (**14**) was obtained in 89% yield and identified as a β-linked disaccharide from its ^{1}H NMR spectrum.

The above mentioned allyl disaccharides (1→3) and (1→4) can be further used as building blocks for the synthesis of trisaccharides or even tetrasaccharides (as donors), through the method introduced by Nashed and Anderson.[16] Furthermore, the disaccharide **14** has potential as a glycosyl acceptor, by selective ring opening of the benzylidene ring.[17]

EXPERIMENTAL

General Procedure. Melting points were determined on a Buchi 510 and are uncorrected. Optical rotations were measured with a Perkin-Elmer Model 241 or 243 Polarimeter in a 10 cm cell at 589 nm. ^{1}H NMR (internal Me_4Si) were recorded with Bruker WM - 270 or WM - 400 Spectrometers. Elemental analyses were preformed at the University of Hamburg. TLC was performed on silica gel GF ^{254} (Merck). For column chromatography, silica gel 60, (70 - 230 mesh, ASTM, Merck) was used. The following solvent combinations (v/v) were utilized for thin-layer and column chromatography: A, 20:1 dichloromethane-acetone; B, 20:1 dichloromethane - methanol; C, 7:3:10 ethyl acetate - petroleum ether-toluene.

Preparation of Disaccharides having the sequence β-D-GlcpNPhth (1→4)-D-GlcpNPhth 9 and 10.

General Procedure for β - glycosidic coupling reactions. The glycosyl acceptor, glycosyl donor, and powdered 4 Å activated molecular sieves, were dried under vacuum (~0.01 torr) for 4 - 6 h. Dry nitrogen gas was passed through the flask and the solvent was added. The reaction mixture was stirred at ambient temperature for 20 min, then the catalyst was added to the cold mixture. The reaction mixture was diluted with dichloromethane, filtered over a Celite-bed, and the filtrate was washed with sodium hydrogen carbonate solution and water. The organic layer was dried over Na_2SO_4, filtered, concentrated to dryness, and subjected to column chromatography.

Benzyl O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (9).

Method [A]: Using a trichloroacetimidate derivative as a donor. A mixture of the β-trichloroacetimidate derivative **1** (500 mg, 0.90 mmol), glycosyl acceptor **7** (500 mg, 0.8 mmol), and powdered 4 Å activated molecular sieves (1.0 g), was subjected to the procedure for β-glycosidic coupling described above. Dichloromethane (20 mL) was added, the reaction mixture was stirred at ambient temp for 15 min, then boron trifluoride etherate at 20 °C was added followed by stirring for 30 min, when TLC showed complete disappearance of the starting materials. The product was isolated by conventional extraction. The solvent was evaporated, and the residue obtained was purified on a column of silica gel (using solvent **D** as an eluent) and recrystallized from ethyl acetate - *n*-hexane to give 580 mg (69%) of pure title compound; mp, 114 °C; $[\alpha]_D$ + 75° (*c* 0.5, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 - 7.00 (m, 23 H, $2C_6H_4$, $2C_6H_5CO$, and $C_6H_5CH_2$), 6.12 (dd, 1H, $J_{3',4'}$ = 8.6 Hz, $J_{2',3'}$ = 10.6 Hz, H - 3'), 5.65 (d, 1H, $J_{1',2'}$ = 8.2 Hz, H - 1'), 5.57 (dd, 1H, $J_{3,4}$ = 9.2 $J_{2,3}$ = 10.6 Hz,H - 3), 5.42 (d, 1H, $J_{1,2}$ = 8.2 Hz, H - 1), 4.98 (t, 1H, $J_{3,4}$ = 9.2 Hz, H - 4), 4.60 (ABq, 2H, J_{AB} = 12.2 Hz, $PhCH_2$), 4.40 (dd, 1H, $J_{3',4'}$ = 10.8 Hz, H - 4'), 4.67, 4.07 (dq, 2H, H - 6, 6'), 4.29 - 4.21 (m, 2H, H - 2, 2'), 3.90 (m, 1H, H - 5'), 3.80, 3.50 (dq, 2H, H - 6, 6'), 3.22 (m, 1H, H - 5), 2.00, 1.88, 1.77 (3 s, 9H, 3xAc).

Anal. Calcd for $C_{55}H_{48}N_2O_{18}$ (1024.98): C, 64.45; H, 4.74;N, 2.73. Found: C, 64.55; H, 4.85; N, 2.68.

Method [B]: Using a glycosyl chloride derivative as a donor. A mixture of the glycosyl acceptor **7** (486 mg, 0.8 mmol), silver trifluoromethanesulfonate (silver triflate) (334 mg, 1.3 mmol), and powdered 4 Å activated molecular sieves (450 mg), was subjected to the procedure for β-glycosidic coupling as described above, under exclusion of light, dichloromethane (10 mL), and sym-collidine (0.25 mL, 1.88 mmol) were added. The reaction mixture was stirred at ambient temperature for 20 min, at 30 °C, a solution of glycosyl chloride **3** (445 mg, 0.98 mmol) in dichloromethane (10 mL) was added dropwise during 2 h. The reaction mixture was allowed to attain room temperature until TLC (solvent C) showed complete reaction. The product was isolated by conventional extraction, the solvent was evaporated, and the residue obtained was purified on a column of silica gel (solvent **D**), furnishing 508 mg (62%) of **9**.

Method [C]: Using a glycosyl bromide derivative as a donor. A mixture of glycosyl acceptor **7** (240 mg, 0.4 mmol) silver triflate (170 mg, 0.66 mmol), and powdered 4 Å activated molecular sieves (300 mg), was subjected to the general procedure for β-glycosidic coupling described above. Dichloromethane (6 mL), and sym-collidine (0.15 mL, 1.1 mmol) were added. At -30 °C a solution of glycosyl bromide **2** (274 mg, 0.55 mmol) in dichloromethane (7 mL) was added dropwise over 1 h. The reaction mixture was allowed to attain ambient temp, when TLC (solvent C) showed complete reaction. The product was isolated by conventional extraction, the solvent was evaporated, and the residue obtained was purified on a column of silica gel (solvent D), affording 243 mg of **9** (60%).

Method [D]: Using a thioglycoside as a donor. A mixture of the glycosyl acceptor **7** (100 mg, 0.16 mmol), thioglycoside **4** (92 mg, 0.19 mmol), and powdered 4 Å activated molecular sieves (200 mg), was subjected to the general procedure for β-glycosidic coupling described above. Dichloromethane (3 mL) was added, the reaction mixture was stirred for 15 min, and dimethyl(methylthio)-sulfonium triflate (DMTST) (165 mg, 0.64 mmol) was added at room temperature. The reaction mixture was stirred for 5 h, in which time TLC (solvent C) indicated complete reaction. The product was isolated by conventional extraction, the solvent was evaporated, and the residue obtained was purified on a column of silica gel using solvent D as an eluent to give 96 mg (57%) of pure compound **9**.

Method [E]: Using a glycosyl fluoride derivative as a donor. A mixture of the glycosyl acceptor **7** (220 mg, 0.36 mmol), glycosyl fluoride **6** (344 mg, 0.78 mmol), was powdered 4 Å activated molecular sieves (520 mg) was subjected to the general procedure for β-glycosidic coupling described above. Absolute acetonitrile (10 mL) was added, the reaction mixture was stirred at 0 C° for 30 min, and trimethylsilyl triflate (TMSOTf) (70 μLm 0.28 mmol) was added. The reaction mixture was stirred for 24 h, when TLC showed complete reaction, triethylamine was added to neutralize the medium, and the product was isolated by conventional extraction. The solvent was evaporated, and the residue obtained was purified on a column of silica gel (solvent D), yield 163 mg (44%) of compound **9**.

Method [F]. Using a glycosyl acetate derivative as a donor. A mixture of glycosyl acceptor (**7**) (110 mg, 0.18 mmol) 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthal-

imido-β-D-glucopyranose (**6**) (186 mg, 0.39 mmol), and powdered 4 Å activated molecular sieves (250 mg) were subjected to the general procedure for β-glycosidic coupling which is described above. Absolute dichloromethane (6 mL) was added, and stirred 10 min at ambient temperature. Then trimethylsilyl triflate (40 μL, 0.22 mmol) was added. The reaction mixture was stirred overnight , when TLC showed complete reaction. After neutralization with triethylamine, the product was isolated by conventional extraction. The solvent was evaporated, and the residue obtained was purified on a column of silica gel using solvent **D** as an eluent, furnishing 67 mg (18%) of compound **9**.

Allyl O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzoyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (10). A mixture of β-trichloroacetimidate derivative **1** (278 mg, 0.5 mmol), glycosyl acceptor **8** (270 mg, 0.48 mmol), and powdered 4 Å activated molecular sieves (480 mg), were subjected to the general procedure for β-glycosidic coupling which is described above. Dichloromethane (7 mL) was added, and the reaction mixture was stirred at ambient temp for 30 min, cooled to -20 °C, and 0.1 M boron trifluoride etherate (0.22 mL, 0.022 mmol) was added. After 1 h TLC (solvent **C**) showed complete disappearance of the starting materials. Powdered sodium hydrogen carbonate was added to the reaction mixture and stirred for 10 min, filtered and washed with water. The organic layer was dried over anhydrous sodium sulfate, the solvent was concentrated, and the residue was purified on a column of silica gel using solvent **D** as an eluent and recrystallized from ethyl acetate - *n*-hexane to give 345 mg (73%) of the pure **10** : mp, 137 °C; $[\alpha]_D$ + 98.2° (*c* 0.55, chloroform); ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.97 - 7.10 (m, 18H, 2 C_6H_4.CO), 6.10 (dd, 1H, $J_{2',3'}$ = 9.0 Hz, J = 10.5 Hz, H - 3'), 5.72 - 5.55 (m, 1H, -CH =), 5.64 (d, 1H, $J_{1',2'}$ 8.5 Hz, H - 1'), 5.54 (dd, 1H, $J_{2,3}$ = 9.0, $J_{3,4}$ = 10.5 Hz, H - 3), 5.44 (d, 1H, $J_{1,2}$ = 8.0 Hz, H - 1), 5.09 - 4.94 (m, 3H, H - 4' and CH_2=), 4.62-3.93 (m, 6H, H - 6, 6, 4, 2', -OCH_2 -CH=), 3.93 - 3.89 (m, 1H, H - 5'), 3.80, 3.50 (dq, 2H, H - 6, 6'), 3.25 - 3.18 (m, 1H, H - 5), 2.91 (t, 1H, $J_{1,2}$ = 7.8 - 8.0 Hz, H - 2), 2.01, 1.88, 1.77 (3f s, 9H, 3xAc).

Anal. Calcd for $C_{51}H_{46}N_2O_{18}H_2O$ (992.95): C, 61.69; H, 4.87; N, 2.82. Found: C, 61.47; H, 4.85; N, 3.03.

Benzyl O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-O-benzoyl-2-deoxy-2-phthalimido-β-D-galactopyranoside (12). A mixture of the glycosyl acceptor **11** (150 mg, 0.25 mmol), the β-imidate derivative **1** (170 mg, 0.31 mmol), and powdered 4 Å activated molecular sieves (300 mg), were subjected to the general procedure for β-glycosidic coupling described above. Absolute dichloromethane (4 mL) was added, the reaction mixture was stirred at -20 °C for 15 min, and 0.1 M boron trifluoride etherate (0.2 mL, 0.02 mmol) was added. Stirring was continued for an additional 30 min, when TLC (solvent **C**) showed complete reaction. The product was isolated by conventional extraction, the solvent was evaporated, and the residue obtained was purified on a column of silica gel (using solvent **D** as an eluent). Recrystallization of the residue from ethyl acetate - *n*-hexane afforded 182 mg (72%) of **12**; mp, 152 °C; $[\alpha]_D$ + 28.2° (*c* 0.55, chloroform); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (t, 1H, $J_{3',4'}$ = 9l.8 Hz, H - 3'), 5.71 (dd, 1H, $J_{3,4}$ = 3.0, $J_{2,3}$ = 1.8 Hz, H - 3), 5.58 (d, 1H, $J_{1',2'}$ = 8.3 Hz, H - 1'), 5.32 (d, 1H, $J_{1,2}$ = 8.7 Hz, H - 1), 5.12 (t, 1H, $J_{3',4'}$ = 3.0, $J_{4,5}$ < 1 Hz, H - 4), 4.69 - 4.57 (dq, 2H, H - 6, 6'), 4.66 - 4.49 (ABq, 2H, J_{AB} = 12.0 Hz, $PhCH_2$), 4.54 - 4.43 (m, 2H, H - 2, 2'), 4.16 - 4.11 (m, 1H, H - 5'), 4.07 - 3.94 (dq, 2H, H - 6, 6'), 3.57 - 3.52 (m, 1H, H - 5), 2.07, 1.98, 1.85 (3s, 9H, 3xAc).

Anal. Calcd for $C_{55}H_{84}N_2O_{18}$ (1024.98): C, 64.45; H, 4.72; N, 2.73. Found: C. 63.81; H, 5.03; N, 2.54.

Allyl O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→3)-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (14). A mixture of the glycosyl acceptor **13** (250 mg, 0.51 mmol), trifluoromethane sulfonate (silver triflate) (209 mg, 0.81 mmol), and powdered 4 Å activated molecular sieves (350 mg), were subjected to the general procedure for β-glycosidic coupling described above. Dichloromethane (7 mL), and sym-collidine (0.16 mL, 1.75 mmol) were added. The reaction mixture was stirred at ambient temp for 20 min. At - 30 °C a solution of glycosyl chloride **3** (278 mg, 0.63 mmol) in dichloromethane (6 mL) was added dropwise over 2 h. The reaction mixture was allowed to attain room temperature, while being monitored by TLC (solvent **C**), until reaction was complete. The product was isolated by conventional extraction, the solvent was evaporated, and the residue obtained was purified on a column of silica gel

(solvent **D**) followed by recrystallization form ethyl acetate - *n*-hexane furnishing 445.5 mg (89%) of compound **14**: mp 217 °C; $[\alpha]_D$ + 19.3° (*c* 0.75, chloroform); ^{1}H NMR data (400 MHz, $CDCl_3$) δ 7.70 - 7.28 (m, 1H, $2C_6H_5CH$), 5.60 (s, 1H, PhCH), 5.52 (d, 1H, $J_{1',2'}$ = 8.8 Hz, H - 1'), 5.58 - 4.47 (m, 1H, -CH=), 5.50 (t, 1H, J = 10.2 Hz, H - 3'), 5.09 (t, 1H, $J_{3',4'}$ = 9.4 Hz, H - 4'), 5.04 (d, 1H, $J_{1,2}$ = 8.6 Hz, H - 1), 5.03 - 4.91 (m, 2H, CH_2=), 4.83 (dd, 1H, $J_{3,4}$ = 8.8, $J_{2,3}$ = 10.4 Hz, H - 3), 4.38 - 3.77 (m, 8H, H - 6, 6', H - 2 2', 6, 6', OCH_2 - CH=), 4.25 (dd, 1H, $J_{3,4}$ = 8.6, $J_{4,5}$ = 10.5 Hz, H - 4), 3.63 - 3.57 (m, 1H, H - 5'), 3.45 - 3.40 (m, 1H, H - 5), 2.03, 1.92, 1.70 (3 s, 9H, 3xAc).

Anal. Calcd for $C_{44}H_{43}N_2O_{16}$ (855.82): C, 61.75; H, 5.06; N, 3.27. Found: C, 61.57; H, 5.07; N, 3.33.

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