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Synthesis of an appropriately protected core glycotetraoside, a key intermediate for the synthesis of "bisected" complex-type glycans of a glycoprotein*

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ABSTRACT

A stereocontrolled synthetic route to a glycotetraoside, allyl *O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-*O*-(3,6-di-*O*-allyl-2-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-*O*-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-*p*-methoxyphenyl-2-phthalimido-β-D-glucopyranoside, an important intermediate for the synthesis of "bisected" complex type glycans of glycoproteins has been established by employing two glycosyl donors, 3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl trichloroacetimidate and 4-*O*-acetyl-3,6-di-*O*-allyl-2-*O*-benzyl-α-D-mannopyranosyl bromide, and a glycosyl acceptor, allyl *O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-*p*-methoxyphenyl-2-phthalimido-β-D-glucopyranoside.

INTRODUCTION

"Bisected" complex-type glycans of glycoproteins such as **1** have been isolated from rather restricted sources such as hematopoietic cells[2], kidney[3], oviduct[4], malignant tissues[5], and abnormal skin fibroblasts[6]. A "bisecting" *N*-acetyl-D-glucosamine (GlcNAc) residue which modulates[7] conformational aspects of complex type glycans, is added[8] to the glycan by the action of the enzyme, (1→4)-β-D-mannosyl-glycoprotein (1→4)-*N*-acetyl-β-D-glucosaminyltransferase (EC 2.4.1.144). As part of our continuing project[9] on the synthesis of the glycan portion of a glycoprotein, we report herein the synthesis of a key tetrasaccharide **3** that corresponds to a linear core sequence **2**. Compound **3** is suitably protected to introduce additional glycans and also a peptide chain at residue GlcNAc-**1** and Man-**3** in later stages of synthesis. Retrosynthetic considerations led us to design a GlcNAc donor **4**, a Man donor **5**, and a chitobiosyl glycosyl acceptor **6**, where appropriate choices of R^1, R^2, and R^3 are made in keeping with the overall synthetic design shown in Scheme 1. It is to be noted that different approaches[10,11] to the synthesis of these "bisected" glycooligoses have recently been reported.

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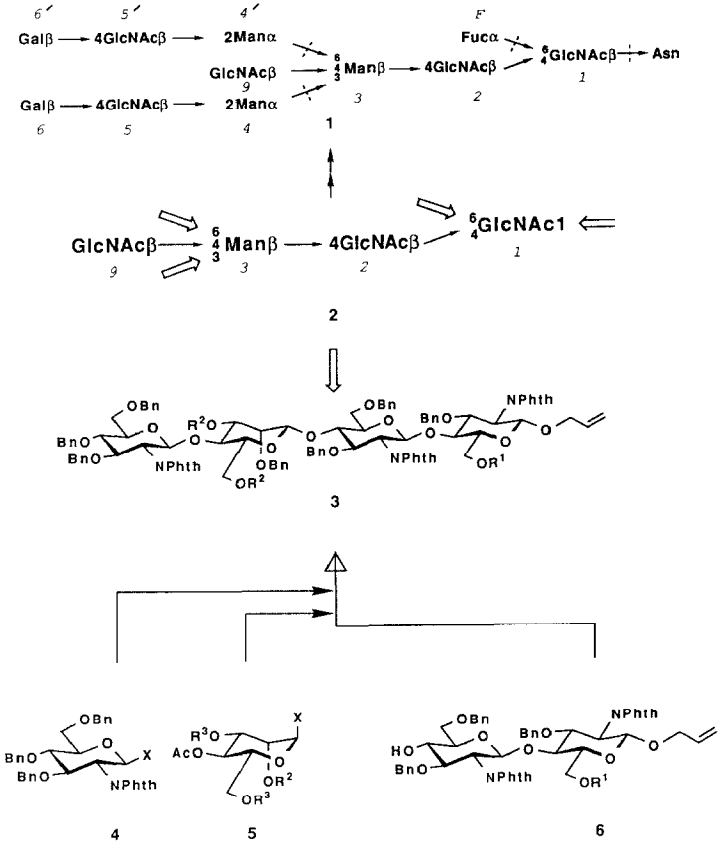
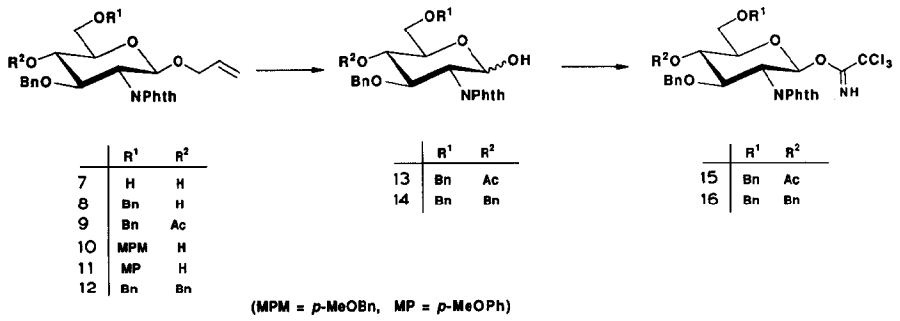


Scheme 1

RESULTS AND DISCUSSION

As a chitobiose derivative **6** with either *p*-methoxybenzyl or *p*-methoxyphenyl for R^1 seemed promising for our intended use, we first prepared the necessary monosaccharide synthons **10**, **11**, **15**, and **16** from diol **7** (ref. 12) (Scheme 2). Site-selective alkylation of compound **7** was performed using the stannyl method[13] to give both the benzyl ether **8**, a precursor of a glycosyl donor **15**, and the *p*-methoxybenzyl ether **10**, a glycosyl acceptor, in 76 and 62% yield, respectively. Another glycosyl acceptor **11** was prepared in 84% yield from compound **7** by the Mitsunobu reaction[14]. Compound **8** was converted into the glycosyl donor **15** in three steps in 66% overall yield via compounds **9** and **13**: [(*i*) Ac_2O–pyridine, (*ii*) $PdCl_2$–AcONa–aq. AcOH[15], and (*iii*) Cl_3CCN–DBU[16] in (CH_2Cl_2)]. Similarly, compound **7** was converted in three steps in 55% overall yield into trichloroacetimidate **16** that corresponds to a GlcNAc donor **4**, which is designed to introduce a GlcNAc residue **9** in the final target **1** (Scheme 1).



	R¹	R²
7	H	H
8	Bn	H
9	Bn	Ac
10	MPM	H
11	MP	H
12	Bn	Bn

	R¹	R²
13	Bn	Ac
14	Bn	Bn

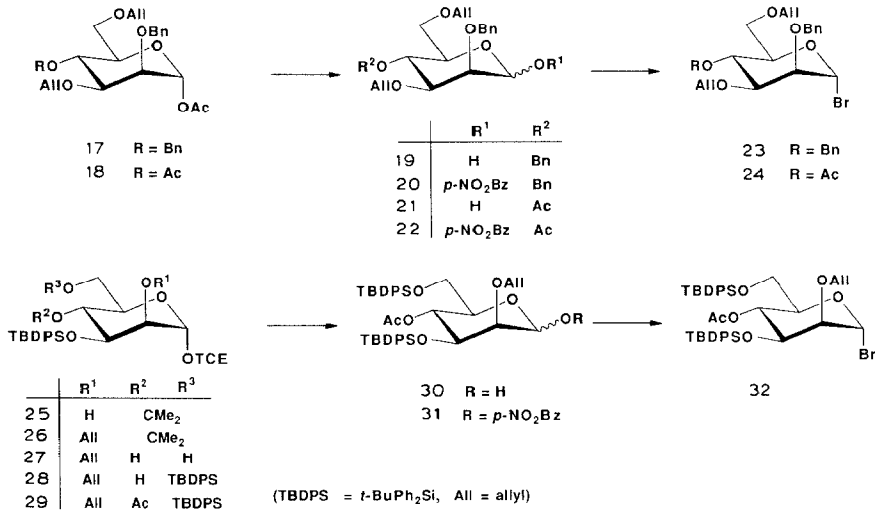
	R¹	R²
15	Bn	Ac
16	Bn	Bn

Scheme 2

Having prepared all the required GlcNAc synthons, the design of the Man synthons **5** was then undertaken. Since compound **5** should behave as a β-D-mannosyl donor[17], protecting group R^2 was chosen as either benzyl or allyl, and R^3 was selected as either allyl or silyl, respectively, in designing the mannosyl synthons **24** and **32**. Mannosyl donor **24** has already been reported by Paulsen and co-workers[10] in their synthetic study on a "bisected" glycotetraose closely related to our target. We prepared bromide **24** in a slightly modified route from compound **18** in three steps: (*i*) MeOH–Et_3N–H_2O–THF, (*ii*) *p*-NO_2BzCl in pyridine, and (*iii*) HBr in CH_2Cl_2. Another mannosyl donor **32** was prepared in a straightforward manner in 17% overall yield from 2,2,2-trichloroethyl-4,6-*O*-isopropylidene-α-D-mannopyranoside[18] via compounds **25**, **26**, **27**, **28**, **29**, **30**, and **31** in an eight-step sequence: (*i*) *tert*-$BuPh_2SiCl$–imidazole in DMF, (*ii*) allyl iodide–Bu_4NI–KH in DMF, (*iii*) 70% aq. AcOH, (*iv*) *tert*-$BuPh_2SiCl$–imidazole in DMF, (*v*) Ac_2O–pyridine, (*vi*) Zn–AcOH, (*vii*) *p*-NO_2BzCl–pyridine, and (*viii*) HBr–CH_2Cl_2.

Having prepared all the required monosaccharide synthons, coupling between the glycosyl acceptor **10** and the glycosyl donor **15** was first examined in the presence of either borontrifluoride etherate[19] or trimethylsilyl triflate[20], each together with powdered molecular sieves in 1,2-dichloroethane at −20°; however, the desired disaccharide **33** could not be isolated, presumably due to the acid-sensitive nature of the *p*-methoxybenzyl group of **10**, despite the fact that the *p*-methoxybenzyl group has been reported to be stable under silver triflate–collidine promoted glycosylation conditions[11]. However, when the same reaction was performed on **10** at −70°, the disaccharide **33** could be isolated in only 27% yield. Since the *p*-methoxybenzyl group was not found to be entirely compatible with Lewis acid promoted glycosylation conditions, another, more acid-stable glycosyl acceptor, compound **11**, was chosen. To our satisfaction, the borontrifluoride etherate promoted glycosylation of **11** with the glycosyl donor **15** proceeded smoothly at −23° to give a 77% yield of the desired product **34** that was subsequently saponified with NaOMe–MeOH to give alcohol **35** in 94% yield.

Having prepared a suitable glycosyl acceptor **35** that corresponds to the reducing-end disaccharide in target **1**, introduction of the β-D-Man residue was now examined.

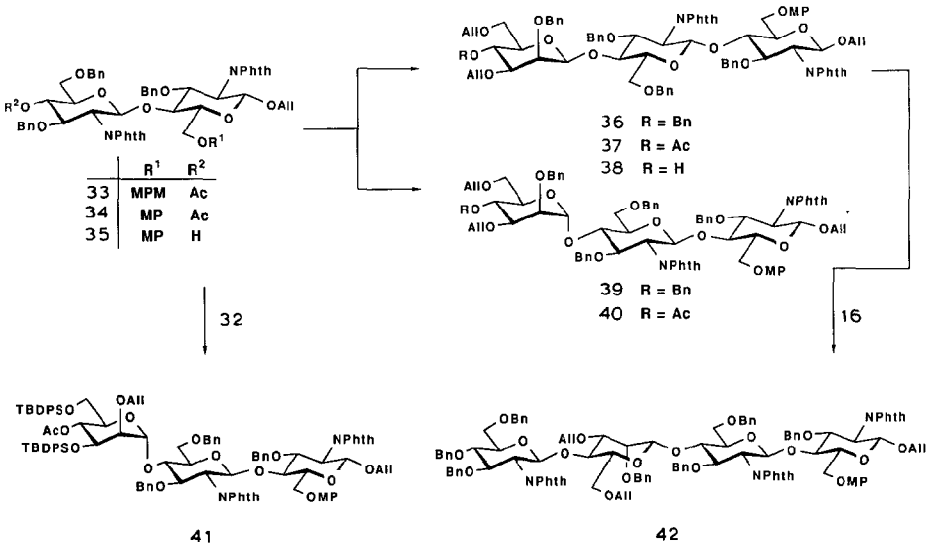


Scheme 3

We first studied the well established[12] β-Man donor **23**, which is readily available in three steps from the anomeric acetate **17** (ref. 21). Upon reaction of the bromide **23** with the acceptor **35** in the presence of silver silicate[22], β-glycoside **36** and α-glycoside **39** were obtained in 36 and 26% yield, respectively, in good agreement with our previous observation[12]. The configuration at C-1^3 in compounds **36** and **39** was deduced from the ^{13}C-n.m.r. data[23], which contained a signal for C-1^3 at δ 101.5 with $^1J_{C,H}$ 154 Hz for compound **36** and another at δ 100.2 with $^1J_{C,H}$ 172 Hz for compound **39**. These assignments were also confirmed by the ^{1}H-n.m.r. data of compound **36** which showed characteristic upfield signals[10] of H-3^3 and H-5^3 at δ 3.240 and 3.273, respectively.

The crucial glycosylation of the acceptor **35** with the donor **24** was achieved under the same conditions to afford the desired β-glycoside **37** and α-glycoside **40** in 48 and 19% yield, respectively. The configuration at C-1^3 in compounds **37** and **40** was again deduced from the ^{13}C-n.m.r. data, which showed a signal for C-1^3 at δ 101.1 with $^1J_{C,H}$ 158 Hz for compound **37**, and a signal at δ 100.2 with $^1J_{C,H}$ 174 Hz for compound **40**. The configuration at C-1^3 for compound **37** was also confirmed by the 2D-n.m.r. data, which revealed a characteristic high-field signal for H-3^3 at δ 3.188. Due to the presence of the 4-*O*-acetyl group in the donor **24** in place of the 4-*O*-benzyl group in the donor **23**, the β:α ratio of the glycosylation products was improved from 1.38:1 to 2.53:1 for the donor **24**, a result which is in agreement with the observation previously made by van Boeckel and his co-workers[24].

Another glycosyl donor **32**, upon reaction with the acceptor **35** under the same conditions, did afford a 60% yield of the α-glycoside **41**. Unexpectedly no β-isomer could be detected. This stereochemical outcome which resulted from changing the protective groups at *O*-2, *O*-3, and *O*-6 in the donor **32** from those of **24** might be



Scheme 4

explained by a neighboring-group interaction of the 2-*O*-allyl π-system between the C-1 cationic center from the β-face to hinder the approach of the nucleophilic alcohol **35** from the β-face of the molecule. Although a similar interaction between a 2-*O* substituent with a π-system and a cationic anomeric center has been recently reported[25] in furanosyl systems, no such example in pyranoses, to the best of the authors' knowledge, has been reported.

Saponification of compound **37** with $LiOH–H_2O_2$ in THF gave a quantitative yield of alcohol **38**, which in turn was glycosylated with a donor **16** in the presence of borontrifluoride etherate to afford a 92% yield of the desired key intermediate **42**. The structure of compound **42** was reasonably confirmed by 2D-n.m.r. and ^{13}C-n.m.r. spectroscopic data.

In conclusion, a linear key tetrasaccharide **42** for the synthesis of a "bisected" complex-type glycan such as **1** has been synthesized in a stereocontrolled way according to the design shown in Scheme 1.

EXPERIMENTAL

General. — Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Column chromatography was performed on Silica Gel-60 (Merck 70–230 mesh). Flash chromatography was performed on columns of Wakogel C-300 (200–300 mesh). T.l.c. and high-performance (h.p.) t.l.c. was performed an Silica Gel-60 F_{254} (Merck). Molecular sieves 4A and AW-300 (acid stable, pore size 3Å) were purchased from Nakarai Chemicals and Gasukuro Kogyo, Inc., respectively. N.m.r. spectra were recorded with

either JEOL GX500 [^{1}H(500 MHz)] or FX90Q [^{13}C (22.50 MHz)] spectrometers. The values of δ_C and δ_H are expressed in p.p.m. downfield from the signal for internal Me_4Si, for solutions in $CDCl_3$, unless noted otherwise.

Allyl 3-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**7**). — A solution of allyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside[12] (10.0 g, 19.0 mmol) in 80% aq. CH_3CO_2H (200 mL) was stirred for 1.5 h at 80°, and the solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 20:1 $CHCl_3$–MeOH to give **7** (6.56 g, 79%): $[\alpha]_D$ +40.3° (*c* 0.6); R_F 0.61 (10:1 $CHCl_3$–MeOH); n.m.r. data: δ_H 7.72–6.80 (m, 9 H, aromatic) and 5.88–5.44 (m, 1 H, C*H*=CH_2); δ_C 97.6 ($^1J_{C,H}$ 162 Hz, C-1), 62.6 (C-6), and 55.6 (C-2).

Anal. Calc. for $C_{24}H_{25}NO_7$: C, 65.59; H, 5.73; N, 3.19. Found: C, 65.74; H, 5.82; N, 3.03.

Allyl 3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**8**). — A mixture of compound **7** (8.8 g, 20 mmol) and $(Bu_3Sn)_2O$ (8.9 g, 15 mmol) in toluene (200 mL) was stirred for 4 h at 140° under continuous azeotropic removal of water, and then toluene (100 mL) was evaporated. To the remaining reaction mixture was added benzyl bromide (7.1 mL, 60 mmol) and Bu_4NBr (3.2 g, 10 mmol) at 20°. After stirring for 19 h at 90° under Ar, additional benzyl bromide (7.1 mL) and Bu_4NBr (3.2 g) were added. The mixture was stirred for 22 h at 90° and then concentrated *in vacuo*. A solution of the residue in EtOAc (600 mL) was stirred with 10% aq. KF (300 mL), and the precipitated Bu_3SnF was filtered through Celite. The organic layer was washed with water and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 10:1 toluene–EtOAc to give **8** (8.0 g, 76%), $[\alpha]_D$ +33.8° (*c* 0.7); R_F 0.47 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.8 (m, 14 H, aromatic) and 5.91–5.47 (m, 1 H, C*H*=CH_2); δ_C 97.4 ($^1J_{C,H}$ 162 Hz, C-1) and 55.4 (C-2).

Anal. Calc. for $C_{31}H_{31}NO_7$: C, 70.30; H, 5.90; N, 2.65. Found: C, 69.85; H, 5.99; N, 2.54.

Allyl 4-O-acetyl-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (**9**). — A solution of compound **8** (7.7 g, 14.5 mmol) in pyridine (40 mL) and Ac_2O (40 mL) was stirred for 17 h at 20° and concentrated *in vacuo*. The residue was chromatographed on SiO_2 using 10:1 toluene–EtOAc to give **9** (8.2 g, 98%), $[\alpha]_D$ +64.4° (*c* 0.5); R_F 0.49 in (5:1 toluene–EtOAc); n.m.r. data: δ_H 7.7–6.7 (m, 14 H, aromatic), 5.87–5.43 (m, 1 H, C*H*=CH_2), and 1.95 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{33}H_{33}NO_8$: C, 69.34; H, 5.82; N, 2.45. Found: C, 69.37; H, 5.87; N, 2.34.

Allyl 3-O-benzyl-2-deoxy-6-O-p-methoxybenzyl-2-phthalimido-β-D-glucopyranoside (**10**). — A mixture of compound **7** (307 mg, 0.70 mmol) and $(Bu_3Sn)_2O$ (450 mg, 0.75 mmol) in toluene (20 mL) was stirred for 2 h at 140° under continuous azeotropic removal of water. To the cooled solution was added *p*-methoxybenzyl chloride (0.5 mL, 3.7 mmol) and Bu_4NBr (16 mg, 0.05 mmol). The mixture was stirred under reflux, and the volatiles were evaporated *in vacuo*. The residue was processed as described for compound **8** and chromatographed on SiO_2 using 2:1 hexane–EtOAc to give **10** (243 mg, 62%): $[\alpha]_D$ +25.6° (*c* 1.5); R_F 0.46 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.8 (m,

13 H, aromatic), 5.71–5.60 (m, 1 H, C*H*=CH_2), 5.175 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.746 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 3.819 (s, 3 H, OCH_3), and 2.967 (d, 1 H, *J* 2.4 Hz, *H*O-4); δ_C 97.3 (C-1), 69.5 (C-6), and 55.3 and 55.1 (OCH_3 and C-2).

Anal. Calc. for $C_{32}H_{33}NO_8$. C, 68.68; H, 5.94; N, 2.50. Found: C, 68.39; H, 5.97; N, 2.48.

*Allyl 3-*O*-benzyl-2-deoxy-6-*O*-*p*-methoxyphenyl-2-phthalimido-β-*D*-glucopyranoside* (**11**). — To a stirred mixture of compound **7** (5.0 g, 11 mmol), *p*-methoxyphenol (4.3 g, 34 mmol), and Ph_3P (9.0 g, 34 mmol) in CH_2Cl_2 (100 mL) was added DEAD (diethyl azodicarboxylate, 3 mL, 20 mmol), and the mixture was stirred for 24 h at 20° under Ar. The reaction mixture was diluted with EtOAc, washed with aq. $NaHCO_3$ and aq. NaCl, and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 5:1 toluene–EtOAc to give **11** (5.2 g, 84%): m.p. 89–91° (EtOAc–hexane); $[\alpha]_D$ +21.8° (*c* 1.0); R_F 0.33 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.8 (m, 13 H, aromatic), 5.71–5.60 (m, 1 H, C*H*=CH_2), 5.221 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.702 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.553 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 3.772 (s, 3 H, OCH_3), and 2.555 (d, 1 H, *J* 3.4 Hz, *H*O-4); δ_C 97.5 (C-1), 68.9 (C-6), and 55.7 and 55.6 (C-2 and OCH_3).

Anal. Calc. for $C_{31}H_{31}NO_8 \cdot 0.5\ H_2O$: C, 67.14; H, 5.82; N, 2.53. Found: C, 67.40; H, 5.92; N, 2.50.

*Allyl 3,4-6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranoside* (**12**). — To a stirred mixture of Ag_2O (1.77 g, 7.63 mmol), KI (0.66 g, 4.0 mmol), and compound **7** (333 mg, 0.76 mmol) in DMF (7 mL) was added dropwise benzyl bromide (0.9 mL, 8.0 mmol) at −5°–0°. After stirring for 1 h at 5°, the mixture was diluted with Et_2O and washed with aq. $NaCHO_3$, aq. NaCl, and dried ($MgSO_4$), and the volatiles were evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 10:1 toluene–EtOAc to give **12** (339 mg, 72%): $[\alpha]_D$ +50.9° (*c* 1.0); R_F 0.66 (4:1 toluene–EtOAc); n.m.r. data: δ_H 7.70–6.80 (m, 19 H, aromatic) and 5.65–5.48 (m, 1 H, C*H*=CH_2); δ_C 97.5 (C-1) and 55.9 (C-2).

Anal. Calc. for $C_{38}H_{37}NO_7$: C, 73.65; H, 6.02; N, 2.26. Found: C, 73.45; H, 6.06; N, 2.27.

*4-*O*-Acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*D*-glucopyranose* (**13**). — To a stirred solution of compound **9** (8.2 g, 14 mmol) in 95% aq. AcOH (100 mL) was added $PdCl_2$ (2.8 g, 16 mmol) and AcONa (2.8 g, 34 mmol). The mixture was stirred for 2 h at 70° and concentrated *in vacuo*. The residue was dissolved in EtOAc (300 mL), washed with aq. $NaHCO_3$, and filtered through Celite. The organic layer was dried ($MgSO_4$) and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 3:1 toluene–EtOAc to give **13** (6.3 g, 83%): m.p. 102–104° (hexane–EtOAc), $[\alpha]_D$ +82.6° (*c* 0.6); R_F 0.35 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.80–6.80 (m, 14 H, aromatic) and 1.98 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{30}H_{29}NO_8$: C; 67.78; H, 5.50; N, 2.64. Found: C, 68.02; H, 5.65; N, 2.50.

Conversion of compound **13** *into 4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl trichloroacetimidate* (**15**). To a solution of compound **13** (1.01

g, 1.89 mmol) in $(ClCH_2)_2$ (5 mL) was added CCl_3CN (1.9 mL, 19 mmol) and DBU (57 μL, 3.8 mmol) at $-5°$. The mixture was stirred for 1 h at 0° and then directly chromatographed on SiO_2 using 4:1 hexane–EtOAc to give **15** (1.03 g, 81%): R_F 0.42 (5:1 toluene–EtOAc); n.m.r. data: δ_H 8.580 (s, 1 H, C=N*H*), 7.680–6.870 (m, 14 H, aromatic), 6.439 (d, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 5.262 (t, 1 H, $J_{3,4} = J_{4,5} = 9.5$ Hz, H-4), and 1.942 (s, 3 H, $COCH_3$); δ_C 94.1 (C-1), 69.1 (C-6), 54.6 (C-2), and 20.8 ($COCH_3$).

*3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl trichloroacetimidate* (**16**). — A mixture of compound **12** (2.41 g, 3.89 mmol), $PdCl_2$ (1.25 g, 7.05 mmol), and AcONa (1.22 g, 14.9 mmol) in 95% aq. AcOH (25 mL) was stirred for 20 h at 20° and then concentrated *in vacuo*. The residue was processed as described for compound **13** and chromatographed on SiO_2 using 6:1 toluene–EtOAc to give **14** (1.84 g, 82%): R_F 0.28 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.7–6.8 (m, 19 H, aromatic).

To a solution of **14** (708 mg, 1.22 mmol) in $(ClCH_2)_2$ (3.5 mL) was added Cl_3CCN (1.3 mL, 13 mmol) and DBU (44 μL, 0.29 mmol) at 0° under Ar. The mixture was stirred for 16 h at 20° and was then directly chromatographed on SiO_2 using 4:1 toluene–EtOAc to give **16** (814 mg, 92%): $[\alpha]_D$ +75.3° (*c* 1.2); R_F 0.66 (3:1 toluene–EtOAc); n.m.r. data: δ_H 8.543 (s, 1 H, C=N*H*), 7.75–6.80 (m, 19 H, aromatic), 6.418 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1), 4.851 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.811 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.676 (d, 1 H, *J* 11.9 Hz, CH_2Ph), 4.671 (d, 1 H, *J* 11.0 Hz, CH_2Ph), 4.578 (d, 1 H, *J* 11.9 Hz, CH_2Ph), and 4.465 (d, 1 H, *J* 12.2 Hz, CH_2Ph).

Anal. Calc. for $C_{37}H_{33}N_2O_7Cl_3$: C, 61.38; H, 4.59; N, 3.87; Cl, 14.69. Found: C, 61.24; H, 4.74; N, 3.92; Cl, 14.65.

*3,6-Di-*O*-allyl-2,4-di-*O*-benzyl-*D*-mannopyranose* (**19**). — A solution of compound **17** (ref. 12) (8.8 g, 18.3 mmol) in THF (60 mL) was diluted with 4:1:3 MeOH–H_2O–Et_3N (180 mL), stirred for 19 h at 20°, and then concentrated *in vacuo*. The residue was chromatographed in 5:1 toluene–EtOAc to give **19** (6.8 g, 85%): $[\alpha]_D$ +31.0° (*c* 1.1); R_F 0.45 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.32 (s, 10 H, aromatic) and 6.14–5.71 (m, 2 H, $CH=CH_2$ × 2).

Anal. Calc. for $C_{26}H_{32}O_6$: C, 70.89; H, 7.32. Found: C, 70.90; H, 7.38.

*3,6-Di-*O*-allyl-2,4-di-*O*-benzyl-α and β-*D*-glucopyranosyl p-nitrobenzoate* (**20α** and **20β**). — To a cooled solution of compound **19** (1.02 g, 2.3 mmol) in CH_2Cl_2 (20 mL) was added pyridine (2 mL) and *p*-nitrobenzoyl chloride (520 mg, 2.8 mmol) with stirring. The mixture was stirred for 15 h at 20° and then diluted with CH_2Cl_2 (80 mL), washed successively with dil. HCl, H_2O, aq. $NaHCO_3$, and H_2O. The organic layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 20:1 toluene–EtOAc to give **20α** (1.13 g, 83%) and **20β** (233 mg, 17%). Compound **20α** had $[\alpha]_D$ +52.5° (*c* 0.6); R_F 0.52 (10:1 toluene–EtOAc); n.m.r. data: δ_H 8.40–8.00 (m, 4 H, $C_6H_4NO_2$), 7.34 (s, 10 H, C_6H_5 × 2), 6.48 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 6.16–5.70 (m, 2 H, $CH=CH_2$ × 2); δ_C 93.5 ($^1J_{C,H}$ 176 Hz, C-1).

Anal. Calc. for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 67.20; H, 5.98; N, 2.35.

Compound **20β** had R_F 0.43 (10:1 toluene–EtOAc); n.m.r. data: δ_H 8.40–8.04 (m, 4 H, $C_6H_4NO_2$), 7.34 (s, 10 H, C_6H_5 × 2), 6.14–5.68 (m, 2 H, $CH=CH_2$ × 2), and 5.91 (d,

1 H, $J_{1,2}$ 1.5 Hz, H-1); δ_C 94.1 ($^1J_{C,H}$ 162 Hz, C-1).

Anal. Calc. for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 67.37; H, 5.99; N, 2.35.

4-O-Acetyl-3,6-di-O-allyl-2-O-benzyl-α and β-D-mannopyranosyl p-*nitrobenzoate* (**22α** and **22β**). — A solution of compound **18** (18.6 g, 42.7 mmol) in THF (117 mL) was diluted with 4:3:1 MeOH–Et_3N–H_2O (352 mL), stirred for 16 h at 20°, and the solvent was evaporated *in vacuo*. The remaining volatiles in the residue were co-evaporated with EtOH, and then with toluene, to give crude **21** (18.1 g): R_F 0.44 (2:1 toluene–EtOAc); n.m.r. data: δ_H 5.221 (t, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4) and 2.039 (s, 3 H, $COCH_3$).

The crude **21** (16.8 g, 37 mmol) was treated with *p*-nitrobenzoyl chloride (8.8 g, 47 mmol) as described for compound **20**. Chromatography on SiO_2 using 3:1 hexane–EtOAc gave **22α** (15.8 g, 73%) and **22β** (0.9 g, 3.6%).

Compound **22α** had m.p. 82–84° (EtOH): $[\alpha]_D$ +46.0° (*c* 1.6); n.m.r. data: δ_H 8.323–8.157 (m, 4 H, $C_6H_4NO_2$), 7.415–7.261 (m, 5 H, C_6H_5), 6.444 (d, 1 H, $J_{1,2}$ 2.1 Hz, H-1), 5.899–5.791 (m, 2 H, $CH=CH_2 \times 2$), 5.423 (t, 1 H, $J_{3,4} = J_{4,5} = 9.7$ Hz, H-4), 4.827 and 4.788 (d, 2 H, *J* 12.5 Hz, CH_2Ph), 3.917 (t, 1 H, $J_{1,2} = J_{2,3} = 2.5$ Hz, H-2), 3.852 (dd, 1 H, $J_{2,3}$ 3.1 Hz, $J_{3,4}$ 9.2 Hz, H-3), and 2.099 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{28}H_{31}NO_{10}$: C, 62.10; H, 5.77; N, 2.59. Found: C, 62.09; H, 5.79; N, 2.56.

Compound **22β** had $[\alpha]_D$ −46.0° (*c* 0.9); R_F 0.57 (3:1 toluene–EtOAc); n.m.r. data: δ_H 8.273–8.163 (m, 4 H, $C_6H_4NO_2$), 7.352–7.209 (m, 5 H, C_6H_5), 6.018 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.928–5.801 (m, 2 H, $CH=CH_2 \times 2$), 5.350 (t, 1 H, $J_{3,4} = J_{4,5} = 8.0$ Hz, H-4), 4.881 and 4.769 (2 d, 2 H, *J* 12.2 Hz, CH_2Ph), and 2.086 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{28}H_{31}NO_{10}$: C, 62.10; H, 5.77; N, 2.59. Found: C, 62.13; H, 5.98; 2.32.

Conversion of compound **20** *into 3,6-di-O-allyl-2,4-di-O-benzyl-α-D-mannopyranosyl bromide* (**23**). — To a solution of a 5:1 mixture[12] of compound **20α** and **20β** (6.6 g, 11 mmol) in CH_2Cl_2 (100 mL) was added saturated HBr–CH_2Cl_2 (30 mL) with ice-cooling. The mixture was stirred for 20 min at 0°, and the precipitated *p*-nitrobenzoic acid was filtered off through Celite. The filtrate was evaporated *in vacuo* to give **23**: R_F 0.64 (10:1 toluene–EtOAc) at −40°. The compound was used for the next reaction without further purification.

Conversion of compound **22** *into 4-O-acetyl-3,6-di-O-allyl-2-O-benzyl-α-D-mannopyranosyl bromide* **24**: — Compound **22** (2.15 g, 3.97 mmol) was treated as described for compound **20** to give **24** (ref. 10): R_F 0.52 (5:1 toluene–EtOAc) at −20°. The compound was used immediately for the reaction which follows.

*2,2,2-Trichloroethyl 3-O-*tert*-butyldiphenylsilyl-4,6-O-isopropylidene-α-D-mannopyranoside* (**25**). — To a solution of 2,2,2-trichloroethyl 4,6-*O*-isopropylidene-α-D-mannopyranoside[18] (204 mg, 580 μmol) in DMF (0.5 mL) was added imidazole (40 mg, 588 μmol), and a solution of *tert*-$BuPh_2SiCl$ (0.15 mL, 577 μmol) in DMF (2 mL). The mixture was stirred for 48 h, diluted with Et_2O, and washed successively with H_2O, aq. $NaHCO_3$, and aq. NaCl. The organic layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 20:1 toluene–

EtOAc to give **25** (240 mg, 71%) and recovered diol (55 mg, 27%).

Compound **25** had $[\alpha]_D$ +59.3° (*c* 0.9); R_F 0.25 (20:1 toluene–EtOAc); R_F 0.19 (5:1 hexane–EtOAc); n.m.r. data: δ_H 7.75–7.28 (m, 10 H, C_6H_5 × 2), 5.016 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 4.086 and 3.973 (2 d, 2 H, *J* 11.5 Hz, CH_2CCl_3), 1.461 and 1.287 (2 s, 6 H, $C(CH_3)_2$), and 1.104 (s, 9 H, $C(CH_3)_3$; δ_C 100.8 (C-1), 99.7 (CMe_2), and 96.3 (CCl_3).

Anal. Calc. for $C_{27}H_{35}O_6Cl_3Si \cdot 0.17\ C_6H_5CH_3$: C, 55.88; H, 6.05. Found: C, 55.87; H, 6.12.

Acetylation of compound **25** with Ac_2O and pyridine gave 2,2,2-trichloroethyl 2-*O*-acetyl-3-*O*-*tert*-butyldiphenylsilyl-4,6-*O*-isopropylidene-α-D-mannopyranoside: $[\alpha]_D$ +35.1° (*c* 1.1); R_F 0.24 (5:1 hexane–EtOAc); n.m.r. data: δ_H 7.75–7.30 (m, 10 H, C_6H_5 × 2), 4.928 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.4 Hz, H-2), 4.848 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.134 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 9.5 Hz, H-3), 4.060 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4), 4.054 and 3.915 (2 d, 2 H, *J* 11.5 Hz, CH_2CCl_3), 2.188 (s, 3 H, $COCH_3$), 1.469 and 1.259 (2 s, 6 H, $C(CH_3)_2$), and 1.042 (s, 9 H, $C(CH_3)_3$).

Anal. Calc. for $C_{29}H_{37}O_7Cl_3Si \cdot 0.14\ C_6H_5CH_3$: C, 55.85; H, 5.96. Found: C, 55.88; H, 6.23.

*2,2,2-Trichloroethyl 2-*O*-allyl-3-*O*-*tert*-butyldiphenylsilyl-4,6-*O*-isopropylidene-α-D-mannopyranoside* (**26**). — To a stirred solution of compound **25** (146 mg, 247 μmol) in DMF (1.5 mL) was added KH (35% oil dispersion, 34 mg, 0.30 mmol), Bu_4NI (9 mg, 25 μmol), and allyl iodide (0.23 mL, 2.5 mmol) at −40°. The mixture was stirred for 16 h at 20° under Ar, at the end of which time methanol (0.1 mL) was added. The mixture was stirred for 30 min at 20°, diluted with Et_2O, and washed successively with H_2O, and aq. NaCl. The organic layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 6:1 hexane–EtOAc to give **26** (70 mg, 45%) and recovered **25** (34 mg, 24%).

Compound **26** had $[\alpha]_D$ +41.0° (*c* 1.1); R_F 0.49 (20:1 toluene–EtOAc); n.m.r. data: δ_H 7.86–7.30 (m, 10 H, C_6H_5 × 2), 5.90–5.80 (m, 1 H, $CH{=}CH_2$), 4.898 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.169 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 9.7 Hz, H-3), 4.119 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4), 4.076 and 3.940 (2 d, 2 H, *J* 11.7 Hz, CH_2CCl_3), 3.795 (dd, 1 H, $J_{5,6}$ 10.0, $J_{6,6'}$ 10.5 Hz, H-6), 3.749 (dd, 1 H, $J_{5,6'}$ 5.4, $J_{6,6'}$ 10.5 Hz, H-6'), 3.519 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6'}$ 5.4, $J_{5,6}$ 9.9 Hz, H-5), 3.417 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 2.6 Hz, H-2), 1.427 and 1.249 (2 s, 6 H, $C(CH_3)_2$), and 1.094 (s, 9 H, $C(CH_3)_3$).

*2,2,2-Trichloroethyl 2-*O*-allyl-3-*O*-*tert*-butyldiphenylsilyl-α-D-mannopyranoside* (**27**). — A solution of compound **26** (90 mg, 0.14 mmol) in 70% aq. AcOH (1 mL) was stirred for 1 h at 70°, and the solvent was then evaporated *in vacuo*. Traces of AcOH were removed by co-evaporation with toluene, and the residue was chromatographed on SiO_2 using 2:1 toluene–EtOAc to give **27** (81 mg, 96%): $[\alpha]_D$ +38.9° (*c* 0.3); R_F 0.54 (1:1 toluene–EtOAc); n.m.r. data: δ_H 7.85–7.30 (m, 10 H, C_6H_5 × 2), 6.10–5.60 (m, 1 H, $CH{=}CH_2$), 4.946 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 3.408 (t, 1 H, *J* 1.8 Hz, H-2), and 1.115 (s, 9 H, $C(CH_3)_3$).

Anal. Calc. for $C_{27}H_{35}O_6Cl_3Si$: C, 54.96; H, 5.98. Found: C, 54.73; H, 6.21.

*2,2,2-Trichloroethyl 4-*O*-acetyl-2-*O*-allyl-3,6-di-*O*-tert-butyldiphenylsilyl-α-D-mannopyranoside* (**29**). — To a mixture of compound **27** (240 mg, 0.41 mmol) and

imidazole (51 mg, 0.76 mmol) in DMF (0.5 mL) was added a solution of *tert*-$BuPh_2SiCl$ (0.13 mL, 0.50 mmol) in DMF (2.5 mL). The mixture was stirred for 24 h at 20° under Ar, diluted with Et_2O, and washed successively with H_2O, aq. $NaHCO_3$, and aq. NaCl. The organic layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo* to give crude **28** (357 mg): n.m.r.data: δ_H 7.80–7.30 (m, 20 H, C_6H_5 × 4), 5.90–5.80 (m, 1 H, $CH{=}H_2$), 4.950 (d, 1 H, $J_{1,2}$ 1-7 Hz, H-1), 1.101 (s, 9 H, $C(CH_3)_3$, and 1.054 (s, 9 H, $C(CH_3)_3$). Crude **28** was dissolved in 1:1 pyridine–Ac_2O (4 mL), and the mixture was stirred for 16 h at 20° and evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 20:1 hexane–EtOAc to give **29** (284 mg, 82%): $[\alpha]_D$ +29.1° (*c* 1.7); R_F 0.45 (10:1 hexane–EtOAc); n.m.r. data: δ_H 7.73–7.30 (m, 20 H, C_6H_5 × 4), 5.800 (m, 1 H, $CH{=}CH_2$, 5.25 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.8 Hz, H-4), 4.936 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.312 (dd, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 9.8 Hz, H-3), 4.161 and 3.939 (2 d, 2 H, *J* 11.2 Hz, CH_2CCl_3), 3.776 (dd, 1 H, $J_{5,6}$ 7.1, $J_{6,6'}$ 11.2 Hz, H-6), 3.656 (ddd, 1 H, $J_{5,6'}$ 2.0 $J_{5,6}$ 7.1, $J_{4,5}$ 9.8 Hz, H-5), 3.563 (dd, 1 H, $J_{5,6'}$ 2.0, $J_{6,6'}$ 11.2 Hz, H-6'), 3.315 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 2.9 Hz, H-2), 1.619 (s, 3 H, $COCH_3$), 1.041 (s, 9 H, $C(CH_3)_3$), and 1.027 (s, 9 H, $C(CH_3)_3$).

Anal. Calc. for $C_{45}H_{55}O_7Cl_3Si_2$: C, 62.09; H, 6.37. Found: C, 62.36; H, 6.57.

Conversion of compound **29** *into 4-*O*-acetyl-2-*O*-allyl-3,6-di-*O*-*tert*-butyldiphenylsilyl-α-*D*-mannopyranosyl bromide* **32** via **30** *and* **31**. — To a solution of compound **29** (80 mg, 93 μmol) in 5:2 THF–AcOH (2 mL) was added Zn powder (79 mg, 1.2 mmol) at 0°. After stirring for 16 h at 20°, additional Zn powder (90 mg, 1.4 mmol) was added. After stirring for an additional 15 h at 20°, the mixture was diluted with Et_2O and filtered through Celite. The filtrate was washed with cold aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 10:1 hexane–EtOAc to give **30** (40 mg, $\alpha{:}\beta$ = 5:1, 60%): $[\alpha]_D$ +12.1° (*c* 1.9); R_F 0.22 (5:1 hexane–EtOAc); n.m.r. data: δ_H 5.298 (t, 0.17 H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4β), 5.217 (t, 0.83 H, $J_{3,4} = J_{4,5}$ = 9.5 Hz, H-4α), 5.042 (d, 0.83 H, $J_{1,2}$ 1.7 Hz, H-1α), 5.038 (d, 0.17 H, $J_{1,2}$ 1.5 Hz, H-1β), 4.312 (dd, 0.83 H, $J_{2,3}$ 3.2, $J_{3,4}$ 9.5 Hz, H-3α), 3.332 (dd, 0.17 H, $J_{1,2}$ 1.5, $J_{2,3}$ 2.2 Hz, H-2β), 3.183 (t, 0.83 H, $J_{1,2} = J_{2,3}$ = 2.5 Hz, H-2α), 1.580 (s, 3 H, $COCH_3$), 1.016 (s, 9 H, $C(CH_3)_3$), and 1.007 (s, 9 H, $C(CH_3)_3$).

To a solution of compound **30** (82 mg, 0.11 mmol) in pyridine (1 mL) was added *p*-nitrobenzoyl chloride (85 mg, 0.46 mmol). The mixture was stirred for 20 h at 20° and processed as described for **20**. The product was chromatographed on SiO_2 in 5:1 hexane–EtOAc to give **31** (82 mg, 83%): R_F 0.40 and 0.35 (5:1 hexane–EtOAc); n.m.r. data: δ_H 6.304 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 1.682 (s, 3 H, $COCH_3$), 1.052 (s, 9 H, $C(CH_3)_3$), and 0.995 (s, 9 H, $C(CH_3)_3$).

Compound **31** (75 mg, 86 μmol) was treated as described for compound **23** to give crude **32** (77 mg): R_F 0.50 (5:1 hexane–EtOAc) at −20°. The product was used for the next step without further purification.

Allyl O-(*4-*O*-acetyl-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-p-methoxybenzyl-2-phthalimido-β-*D*-glucopyranoside* (**33**). — To a stirred mixture of powdered AW-300 molecular sieves (0.2 g) and $BF_3{\cdot}Et_2O$ (3 μL, 8 μmol) was added dropwise a mixture of compound **10** (34 mg, 60 μmol) and compound **15** (37 mg, 55 μmol) in CH_2Cl_2 (1.5 mL) at −70° under Ar. After stirring

for 1.5 h at −70°, the mixture was neutralized with Et_3N at −70°, diluted with EtOAc, and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was purified by preparative t.l.c. using 4:1 toluene–EtOAc to give **33** (16 mg, 27%): $[\alpha]_D$ +30.6° (*c* 0.8); R_F 0.46 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.9–6.8 (m, 27 H, aromatic), 5.593 (m, 1 H, C*H*=CH_2), 5.307 (d, 1 H, $J_{1,2}$ 8.3 Hz, H-1^2), 5.151 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4^2), 4.979 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1^1), 4.830 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.600 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 3.772 (s, 3 H, OCH_3), and 1.924 (s, 3 H, COCH_3); δ_C 97.4 and 97.3 (C-1^{1,2}), 56.5, 55.9, 55.3 (C-2^{1,2} and O*C*H$_3$), and 20.9 (CO*C*H$_3$).

Anal. Calc. for $C_{60}H_{60}N_2O_{15}$: C, 69.39; H, 5.64; N, 2.61. Found: C, 69.01; H, 5.68; N, 2.56.

Allyl O-(*4-O-acetyl-3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-*D-*glucopyranosyl)-(1→4)-3-O-benzyl-2-deoxy-6-O-*p-*methoxyphenyl-2-phthalimido-β-*D-*glucopyranoside* (**34**). — To a mixture of AW-300 molecular sieves (3 g) and compound **11** (427 mg, 783 μmol) in $(ClCH_2)_2$ (6 mL) was added successively a solution of compound **15** (1.54 g, 2.27 mmol) in $(ClCH_2)_2$ (19 mL) and $BF_3{\cdot}Et_2O$ (0.18 mL, 1.5 mmol) at −23° under Ar. After stirring for 10 min at −23°, the mixture was neutralized with NEt_3, diluted with EtOAc, and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, aq. NaCl and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 6:1 toluene–EtOAc to give **34** (631 mg, 77%): $[\alpha]_D$ +61.5° (*c* 1.0); R_F 0.41 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.7 (m, 27 H, aromatic), 5.582 (m, 1 H, C*H*=CH_2), 5.281 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^2), 5.112 (dd, 1 H, $J_{3,4}$ 9.0, $J_{4,5}$ 10.0 Hz, H-4^2), 5.041 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^1), 4.989 (m, 1 H, CH=CH_2), 4.925 (m, 1 H, CH=CH_2), 4.860 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.559 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.535 (d, 1 H, *J* 11.9 Hz, CH_2Ph), 4.477 (d, 1 H, *J* 12.8 Hz, CH_2Ph), 4.452 (d, 1 H, *J* 11.9 Hz, CH_2Ph), 4.390 (dd, 1 H, $J_{2,3}$ 10.7, $J_{3,4}$ 8.9 Hz, H-3^2), 4.294 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.268 (dd, 1 H, $J_{1,2}$ 8.2, $J_{2,3}$ 10.7 Hz, H-2^2), 3.911 (dd, 1 H, $J_{5,6'}$ 1.5, $J_{6,6'}$ 10.7 Hz, H-6), 3.851 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 10.7 Hz, H-6$'^1$), 3.792 (s, 3 H, OCH_3), 3.619 (ddd, 1 H, $J_{4,5}$ 10.0, $J_{5,6'}$ 3.5, $J_{5,6}$ 5.2 Hz, H-5^2), 3.570 (dd, 1 H, $J_{5,6'}$ 3.5, $J_{6,6'}$ 11 Hz, H-6$'^2$), 3.491 (m, 1 H, H-5^1), 3.479 (dd, 1 H, $J_{5,6}$ 5.2, $J_{6,6'}$ 11 Hz, H-6^2), and 1.903 (s, 3 H, COCH_3): δ_C 97.4 and 97.3 (C-1^{1,2}), 56.5 and 55.8 (in a ratio of 1:2, C-2^{1,2} and O*C*H$_3$), and 20.8 (CO*C*H$_3$).

Anal. Calc. for $C_{61}H_{58}N_2O_{15}$: C, 69.18; H, 5.52; N, 2.64. Found: C, 69.26; H, 5.52; N, 2.72.

Allyl O-*(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-*D-*glucopyranosyl)-(1→4)-3-O-benzyl-2-deoxy-6-O-*p-*methoxyphenyl-2-phthalimido-β-*D-*glucopyranoside* (**35**). — A solution of compound **34** (548 mg, 517 μmol) in 0.005M NaOMe–MeOH (9 mL) was stirred for 16 h at 20°, at the end of which time 0.1M NaOMe–MeOH (0.5 mL) was added. The mixture was stirred for an additional 7 h, neutralized with Amberlyst -15 [H^+] resin, and filtered through Celite. The filtrate was concentrated *in vacuo*. The residue was chromatographed on SiO_2 using 4:1 toluene–EtOAc to give **35** (491 mg, 94%): $[\alpha]_D$ +35.0° (*c* 1.1); R_F 0.57 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.7 (m, 27 H, aromatic), 5.582 (m, 1 H, C*H*=CH_2), 5.272 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 5.038 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^1), 4.989 (m, 1 H, CH=CH_2), 4.928 (m, 1 H, CH=CH_2), 4.811 (d, 1 H, *J* 12.5

Hz, CH_2Ph), 4.740 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.520 (s, 2 H, CH_2Ph), 4.636 (d, 1 H, *J* 12.2 Hz, CH_2Ph), 4.457 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 3.791 (s, 3 H, OCH_3), and 3.000 (d, 1 H, $J_{4,OH}$ 2.1 Hz, HO-4^2); δ_C 97.4 and 97.1 (C-1^{1,2}), and 56.2 and 55.7 (in a ratio of 1:2, C-2^{1,2}, and OCH_3).

Anal. Calc. for $C_{59}H_{56}N_2O_{14}$: C, 69.67; H, 5.55; N, 2.75. Found: C, 69.53; H, 5.57; N, 2.72.

Allyl O-*(3,6-di-*O*-allyl-2,4-di-*O*-benzyl-β and α-*D*-mannopyranosyl-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*p*-methoxyphenyl-2-phthalimido-β-*D*-glucopyranoside* (**36** and **39**). — To a stirred mixture of 4A molecular sieves (1 g), Ag silicate (1 g), and compound **35** (176 mg, 173 μmol) in CH_2Cl_2 (3 mL) was added dropwise a solution of compound **23** (360 mg, 710 μmol) in CH_2Cl_2 (4 mL) at −5° under Ar. After stirring for 16 h at 0–20°, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was concentrated *in vacuo*, and the residue was chromatographed on SiO_2 using 5:1 toluene–EtOAc to give **36** (89 mg, 36%), **39** (70 mg, 28%), and recovered **35** (45 mg, 26%). An analytical sample of compound **36** was obtained after further purification by h.p.l.c. on a Senshu Pak. SSC-Silica-4301-N column (10 × 300 mm) in 3:1 toluene–EtOAc.

Compound **36** had $[\alpha]_D$ +29.0° (*c* 1.4), R_F 0.24 (5:1 toluene–EtOAc); n.m.r. data: δ_H 7.80–6.70 (m, 37 H, aromatic), 5.871, 5.718, and 5.577 (3 m, 3 H, $CH=CH_2$ × 3), 3.773 (s, 3 H, OCH_3), 3.273 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 4.4, $J_{5,6'}$ 1.0 Hz, H-5^3), 3.240 (dd, 1 H, $J_{2,3}$ 2.9, $J_{3,4}$ 9.5 Hz, H-3^3), δ_C 101.5 ($^1J_{C,H}$ 154 Hz, C-1^3), 97.4 and 97.0 (C-1^{1,2}), and 56.6 and 55.6 (in a ratio of 1:2, C-2^{1,2} and OCH_3).

Anal. Calc. for $C_{85}H_{86}N_2O_{19}\cdot C_6H_{14}$: C, 71.63; H, 6.60; N,1.84. Found: C, 71.70; H, 6.75; N, 1.80.

Compound **39** had $[\alpha]_D$ +47.7° (*c* 1.2); R_F 0.32 (5:1 toluene–EtOAc); n.m.r. data: δ_H 7.80–6.70 (m, 37 H, aromatic), 5.876 (m, 2 H, $CH=CH_2$ × 2), 5.568 (m, 1 H, $CH=CH_2$), 5.188 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1^2), and 3.778 (s, 3 H, OCH_3); δ_C 100.2 ($^1J_{C,H}$ 172 Hz, C-1^3), 97.1 (C-1^{1,2}), and 56.5 and 55.7 (in a ratio of 1:2, C-2^{1,2} and OCH_3).

Anal. Calc. for $C_{85}H_{86}N_2O_{19}$: C, 70.92; H, 6.02; N, 1.95. Found: C, 70.55; H, 6.03; N, 1.99.

Allyl O-*(4-*O*-acetyl-3,6-di-*O*-allyl-2-*O*-benzyl-β and α-*D*-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl-(1→4)-3-*O*-benzyl-2-deoxy-6-*p*-methoxyphenyl-2-phthalimido-β-*D*-glucopyranoside* (**37** *and* **40**). — To a stirred mixture of 4A molecular sieves (16 g), Ag silicate (16 g), and compound **35** (4.06 g, 3.99 mmol) in $(ClCH_2)_2$ (48 mL) was added dropwise a solution of compound **24** (6.6 g, 15 mmol) in $(ClCH_2)_2$ (16 mL) at −5°–0° under Ar. After stirring for 3 h at 20°, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$), and the solvents were evaporated *in vacuo*. The residue was chromatographed on SiO_2, first using 2:1 hexane–EtOAc, then using 6:1 toluene–EtOAc to give **37** (2.63 g, 48%), **40** (1.05 g, 19%), and recovered **35** (930 mg, 23%).

Compound **37** had $[\alpha]_D$ +20.8° (*c* 1.1); R_F 0.23 (5:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.7 (m, 32 H, aromatic), 5.750 (m, 2 H, $CH=CH_2$ × 2), 5.585 (m, 1 H,

C*H*=CH$_2$), 5.261 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^2), 5.207 (m, 1 H, CH=C*H*$_2$), 5.145 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4^3), 5.043 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^1), 4.939 (d, 1 H, *J* 12.5 Hz, C*H*$_2$Ph), 4.871 (d, 1 H, *J* 12.8 Hz, C*H*$_2$Ph), 4.829, 4.781, 4.554 (3 d, 3 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.536 (s, 1 H, H-1^3), 4.499 (d, 1 H, *J* 12.8 Hz, C*H*$_2$Ph), 4.458 (d, 1 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.347 (d, 1 H, *J* 12.5 Hz, C*H*$_2$Ph), 3.765 (s, 3 H, OC*H*$_3$), 3.720 (d, 1 H, $J_{2,3}$ 2.7 Hz, H-2^3), 3.188 (dd, 1 H, $J_{2,3}$ 2.7, $J_{3,4}$ 9.5 Hz, H-3^3), and 2.006 (s, 3 H, COC*H*$_3$): δ_C 101.1 ($^1J_{C,H}$ 158 Hz, C-1^3), 97.4 and 97.0 ($^1J_{C,H}$ 165 Hz, C-1^{1,2}), 56.6 and 55.7 (in a ratio of 1:2, C-2^{1,2} and OC*H*$_3$), and 21.0 (CO*C*H$_3$).

Anal. Calc. for $C_{80}H_{82}N_2O_{20}$: C, 69.05; H, 5.94; N, 2.01. Found: C, 68.68; H, 6.04; N, 2.02.

Compound **40** had $[\alpha]_D$ +45.8° (*c* 1.1); R_F 0.28 (5:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.7 (m, 32 H, aromatic), 5.840 (m, 1 H, C*H*=CH$_2$), 5.792 (m, 1 H, C*H*=CH$_2$), 5.574 (m, 1 H, C*H*=CH$_2$), 5.279 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.0 Hz, H-4^3), 5.216 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 5.020 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^1), 3.792 (s, 3 H, OC*H*$_3$), and 2.064 (s, 3 H, COC*H*$_3$); δ_C 100.2 ($^1J_{C,H}$ 174 Hz, C-1^3), 97.1 ($^1J_{C,H}$ 159 Hz, C-1^{1,2}), 56.4 and 55.6 (in a ratio of 1:2, C-2^{1,2} and OC*H*$_3$), and 21.0 (CO*C*H$_3$).

Anal. Calc. for $C_{80}H_{82}N_2O_{20}$: C, 69.05; H, 5.94; N, 2.01. Found: C, 68.89; H, 6.09; N, 1.82.

Allyl O-*(3,6-di-*O*-allyl-2-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-p-methoxyphenyl-2-phthalimido-β-*D*-glucopyranoside* (**38**). — To a solution of compound **37** (1.355 g, 974 μmol) in THF (19.5 mL) was added successively M aq. LiOH (1.2 mL, 1.2 mmol) and 31% aq. H_2O_2 (3.3 mL) at −5°. The mixture was stirred for 16 h at 20°, diluted with EtOAc, washed successively with H_2O, aq. KI and aq. NaCl, and dried ($MgSO_4$), and the solvents were evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 3:1 toluene–EtOAc to give **38** (1.297 g, 98%): $[\alpha]_D$ +14.9° (*c* 0.9); R_F 0.42 in 2:1 toluene–EtOAc; n.m.r. data: δ_H 7.8–6.7 (m, 32 H, aromatic), 5.860 (m, 1 H, C*H*=CH$_2$), 5.745 (m, 1 H, C*H*=CH$_2$), 5.584 (m, 1 H, C*H*=CH$_2$), 5.260 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^2), 5.038 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^1), 4.922 and 4.876 (2 d, 2 H, *J* 12.8 Hz, C*H*$_2$Ph), 4.813 and 4.768 (2 d, 2 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.551 and 4.453 (2 d, 2 H, *J* 12.2 Hz, C*H*$_2$Ph), 4.522 (s, 1 H, H-1^3), 4.494 and 4.351 (2 d, 2 H, *J* 12.8 Hz, C*H*$_2$Ph), 3.768 (s, 3 H, OC*H*$_3$), 3.705 (d, 1 H, $J_{2,3}$ 2.8 Hz, H-2^3), 3.234 (td, 1 H, $J_{4,5}$ 9.5, $J_{5,6} = J_{5,6'}$ = 5.0 Hz, H-5^3), 3.054 (dd, 1 H, $J_{2,3}$ 2.7, $J_{3,4}$ 9.5 Hz, H-3^3), and 2.781 (d, 1 H, $J_{4,OH}$ 1.0 Hz, *H*O-4^3).

Anal. Calc. for $C_{78}H_{80}N_2O_{19}$: C, 69.42; H, 5.98; N, 2.08. Found: C, 69.19; H, 6.12; N, 2.03.

Allyl O-*(4-*O*-acetyl-2-*O*-allyl-3,6-di-*O*-tert-butyldiphenylsilyl-α-*D*-mannopyranosyl-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-3-*O*-benzyl-2-deoxy-6-*O*-p-methoxyphenyl-2-phthalimido-β-*D*-glucopyranoside* (**41**). — To a stirred mixture of 4A molecular sieves (160 mg), Ag silicate (160 mg), and compound **35** (89 mg, 87 μmol) in $(ClCH_2)_2$ (2 mL) was added dropwise a solution of compound **32** (80 mg, 0.10 mmol) in $(ClCH_2)_2$ (2 mL) at −5° under Ar. After stirring for 16 h at 20°, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was processed as described for compound **37**, and chromatography of the crude product

on SiO_2 using 3:1 hexane–EtOAc, then with 5:1 toluene–EtOAc, gave **41** (90 mg, 60%) and recovered **35** (29 mg, 33%).

Compound **41** had $[\alpha]_D$ +66.1° (*c* 1.1); R_F 0.59 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.7 (m, 47 H, aromatic), 5.659 (m, 1 H, C*H*=CH$_2$), 5.571 (m, 1 H, C*H*=CH$_2$), 5.470 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.7 Hz, H-4^3), 5.195 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 5.190 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1^3), 5.008 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1^1), 4.825 and 4.462 (2 d, 2 H, *J* 12.8 Hz C*H*$_2$Ph), 4.550 and 4.298 (2 d, 2 H, *J* 11.9 Hz, C*H*$_2$Ph), 4.086 and 4.001 (2 d, 2 H, *J* 11.9 Hz, C*H*$_2$Ph), 3.759 (s, 3 H, OC*H*$_3$), 3.158 (t, 1 H, $J_{1,2} = J_{2,3}$ = 2.5 Hz, H-2^3), 1.749 (s, 3 H, COC*H*$_3$), 0.998 (s, 9 H, C(C*H*$_3$)$_3$), and 0.988 (s, 9 H, C(C*H*$_3$)$_3$); δ_C 98.2 ($^1J_{C,H}$ 172 Hz, C-1^3), 97.0 ($^1J_{C,H}$ 165 Hz, C-1^{1,2}), 55.9, 55.7 and 55.6 (C-2^{1,2} and OC*H*$_3$).

Anal. Calc. for $C_{102}H_{108}N_2O_{20}Si_2 \cdot H_2O$: C, 69.76: H, 6.31; N, 1.60. Found: C, 69.70; H, 6.22; N, 1.62.

Allyl O-*(3,4,6-tri*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→4)*-O-*(3,6-di*-O-*allyl-2*-O-*benzyl-β*-D-*mannopyranosyl)-(1→4)*-O-*(3,6-di*-O-*benzyl-2-deoxy-2-phthalimido-β*-D-*glucopyranosyl)-(1→4)-3*-O-*benzyl-2-deoxy-6*-O-p-*methoxyphenyl-2-phthalimido-β*-D-*glucopyranoside* (**42**). — To a stirred mixture of AW-300 molecular sieves (340 mg) and compound **38** (121 mg, 70 μmol) in $(ClCH_2)_2$ (1 mL) was added successively a solution of compound **16** (179 mg, 248 μmol) in $(ClCH_2)_2$ (1 mL) and $BF_3 \cdot Et_2O$ (7.8 μL, 63 μmol) at −23° under Ar. After stirring for 10 min at −23°, the mixture was neutralized with Et_3N, diluted with EtOAc, and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$), and the solvents were evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 4:1 toluene–EtOAc to give **42** (161 mg, 94%): $[\alpha]_D$ +17.4° (*c* 0.9); R_F 0.45 (3:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.6 (m, 51 H, aromatic), 5.681, 5.566 and 5.326 (3 m, 3 H, C*H*=CH$_2$ × 3), 5.349 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1^9), 5.184 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^2), 5.009 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^1), 4.346 (s, 1 H, H-1^3), 3.938 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.2 Hz, H-4^3), 3.756 (s, 3 H, OC*H*$_3$), 3.638 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2^3), 3.248 (d, 1 H, $J_{6,6'}$ 11.3 Hz, H-6^3), 3.152 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.2 Hz, H-3^3), 3.117 (dd, 1 H, $J_{5,6} = 4.9 = J_{6,6'}$, 11.3 Hz, H-6'^{3}), and 3.012 (ddd, 1 H, $J_{4,5}$ 9.2, $J_{5,6}$ 4.9, $J_{5,6'}$ 1.0 Hz, H-5^3), δ_C 101.1 (C-1^3), 97.8, 97.5 and 97.1 (C-1^{1,2,9}).

Anal. Calc. for $C_{113}H_{111}N_3O_{25}$: C, 71.02; H, 5.85; N,2.20. Found: C, 70.66; H, 5.84; N, 2.28.

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