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Synthesis of α-D-Man*p*-(1→3)-[β-D-Glc*p*NAc-(1→4)]-[α-D-Man*p*-(1→6)]-β-D-Man*p*-(1→4)-β-D-Glc*p*NAc-(1→4)-[α-L-Fuc*p*-(1→6)]-D-Glc*p*NAc, a core glycoheptaose of a "bisected" complex-type glycan of glycoproteins*

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ABSTRACT

A synthesis of α-D-Man*p*-(1→3)-[β-D-Glc*p*NAc-(1→4)]-[α-D-Man*p*-(1→6)]-β-D-Man*p*-(1→4)-β-D-Glc*p*NAc-(1→4)-[α-L-Fuc*p*-(1→6)]-D-Glc*p*NAc was achieved by employing benzyl *O*-(3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-*O*-(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 as a key glycosyl acceptor. Highly stereoselective mannosylation was performed by taking advantage of the 2-*O*-acetyl group in the mannosyl donors. The α-L-fucopyranosyl residue was also stereoselectively introduced by copper(II)-mediated activation of methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside.

INTRODUCTION

Since our successful synthesis[2a] of the undecasaccharide of a biantennary complex-type glycan of a glycoprotein, our experiments have been directed toward the development of a stereocontrolled route[2b] for the synthesis of "bisected" complex-type glycans of a glycoprotein. We describe herein a synthesis of a fucosylated glycoheptaose **2**, the core structure of a typical "bisected" complex type glycan **1** with two antennae.

Retrosynthetic analysis of the target **2** led us to design two glycosyl donors, **3** and **5**, for the purposes of α-D-mannosylation and α-L-fucosylation, respectively, as well as a linear glycotetraoside **4** for use as a glycosyl acceptor. The latter compound may, in turn, be readily obtained from glycotetraoside **15**, which was prepared[2b] as a versatile key intermediate useful for a "bisected" glycan project.

RESULTS AND DISCUSSION

In order to design an efficient α-D-mannosyl donor **3**, we chose the following as leaving groups: X = chloro, methylthio, and trichloroacetimidyl. All these functional-

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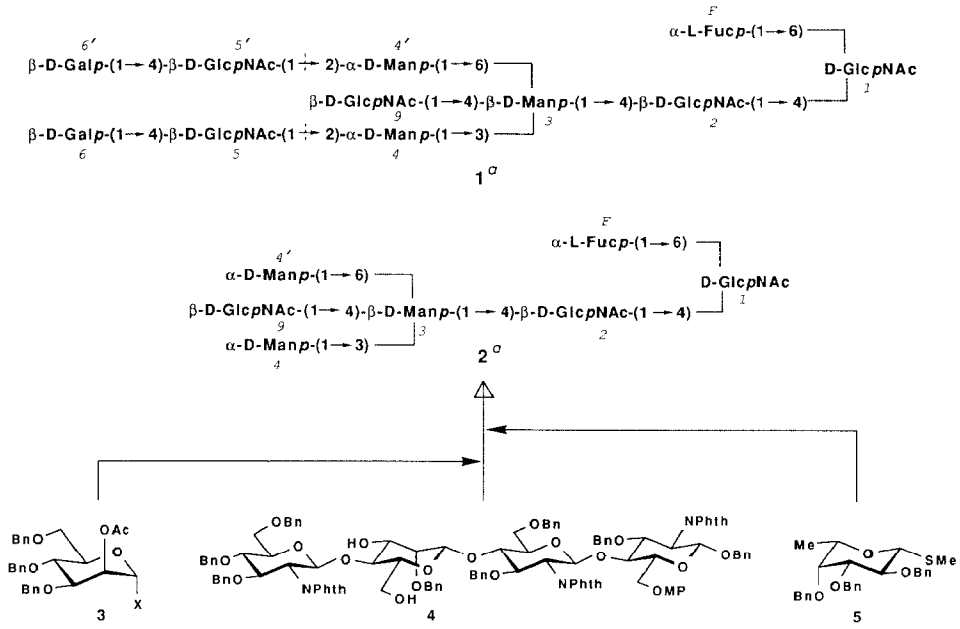
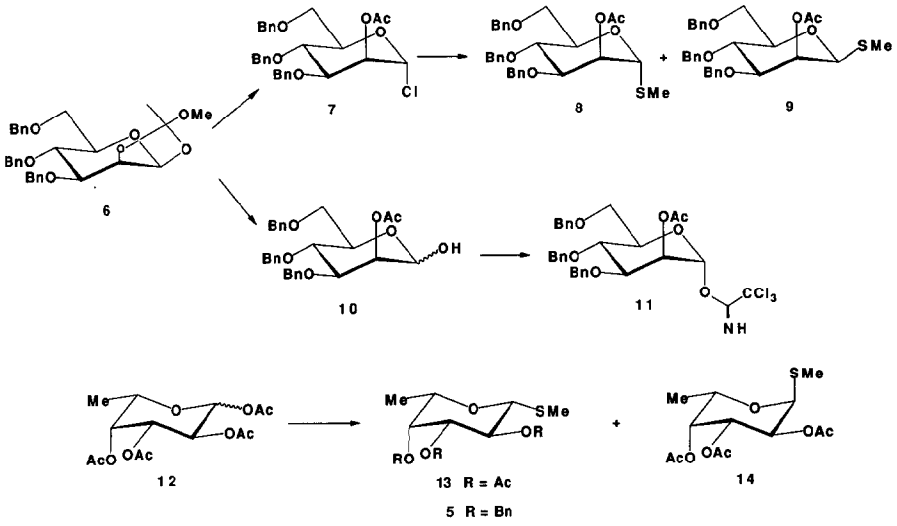


Scheme 1

[a] Numbering of the monosaccharide residues for compounds **1** and **2** is made in conformity with recent articles (see refs. 14 and 20).

ities were readily introduced starting from orthoester **6** as shown in Scheme 2. Treatment of **6** with chlorotrimethylsilane in dichloromethane gave a quantitative yield[3] of glycosyl chloride **7**, which was directly treated with tributyltin methylsulfide[4] in the presence of tin(IV) chloride to give the methyl α-thioglycoside **8** and its β-isomer **9**, in yields of 91 and 3%, respectively. Upon treatment with 60% aq. acetic acid, compound **6** gave the hemiacetal **10**, which, in turn, was converted in 96% yield to trichloroacetimidate **11** in the presence of trichloroacetonitrile[5] and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). A fucosyl donor **5** was obtained in three steps in 51% overall yield from tetraacetate **12** in the usual way: (*i*) tributyltin methylsulfide and tin(IV) chloride[4], (*ii*) sodium methoxide in methanol, (*iii*) sodium hydride and benzyl bromide in DMF.

Next, conversion of a linear glycotetraoside **15** into a key glycosyl acceptor **4** was studied. The three allyl ether functions of compound **15** were removed by sequential treatment[6] with tris(triphenylphosphine)rhodium(I) chloride and 1,4-diazabicyclo[2.2.2]octane (DABCO) in toluene–aq. ethanol and mercury(II) chloride and mercury(II) oxide in aq. acetone to give hemiacetal **16** in 79% yield. Acetylation of compound **16** gave an 89% yield of triacetate **17** as a 1:9 mixture of α- and β-anomers, and then chemoselective deacetylation of acetate **17** with $NH_2NH_2 \cdot AcOH$ in DMF according to Excoffier *et al.*[7] gave a 77% yield of hemiacetal **18** that was smoothly converted into β-imidate **19** in the presence of trichloroacetonitrile and DBU. The boron trifluoride etherate promoted[8] reaction of the imidate **19** with benzyl alcohol subsequently gave an



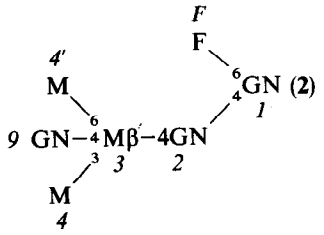
Scheme 2

87% yield of the desired glycoside **20** from hemiacetal **18**. In order to confirm the structure, compound **20** was deprotected stepwise into free glycotetraose **24** as follows. First, the *N*-phthaloyl and *O*-acetyl groups were removed by heating compound **20** under reflux in 10:1 ethanol–hydrazine hydrate[9] for 24 h, and the product was *N*-acetylated to give compound **22**. Further *O*-acetylation gave compound **23** in 60% total yield from compound **20**. Removal of the *p*-methoxyphenyl group by ammonium cerium(IV) nitrate in 8:1 acetonitrile–water[10], deacetylation with sodium methoxide in methanol, and finally hydrogenolysis of benzyl group, afforded glycotetraose **24**. ^{1}H-N.m.r. data (Table I) of compound **24** confirmed the structure of the key intermediate **15**, as well as that of **20**. Deacetylation of compound **20** could not be efficiently achieved under basic conditions, such as sodium methoxide in methanol or lithium hydroxide and hydrogen peroxide. However, the acidic conditions reported by Lemieux *et al.*[9] for deacetylation in the presence of phthalimido functions proved superior to the basic conditions that were explored in this specific case. Treatment of compound **20** with a mixture of hydrochloric acid and acetone at 80° gave a 59% yield of the desired diol **4**. The modest efficiency of this process was largely due, no doubt, to partial cleavage of the glycosidic linkages. The conversion of alcohol **16** into benzyl glycoside **4** was nonetheless achieved in five steps in 32% overall yield. In order to develop a more practical route to compound **4**, the triol **16** was directly reacted with trichloroacetonitrile and DBU for 30 min at −55° to give the *β*-trichloroacetimidate **21**, which upon treatment with boron trifluoride etherate and benzyl alcohol at −23°, gave compound **4** in 84% overall yield. The structure of compound **4** was assigned from the ^{1}H-n.m.r. data which showed three signals for three anomeric protons H-1[1,2,9] as three doublets with $^3J_{H,H}$ 7.9–8.6 Hz at δ 5.202, 5.160, and 4.972, respectively. Efficient glycosylations with glycosyl donors

TABLE I

^{1}H-N.m.r. data (500 MHz) for the deblocked compounds **2**, **24**, **34** and **35**[a]

Compound[b]	*Temp.* (°)	1^1	1^2	1^3	1^9	$1^{4'}$	1^4	1^F	2^3	$2^{4'}$	2^4	5^F	6^F	*NHAc*
GN−4Mβ−4GN−4GN (**24**) *9 3 2 1*	23	5.176(*α*) 4.682(*β*)	4.592 (7.8,*α*) 4.583(*β*)		4.531 (8.3)				4.093 (2.7)					2.051, 2.024 (Ac × 2),(Ac × 1)
	50	5.182 (2.4) 4.690 (8.3)	4.605 (8.1) 4.596 (8.1)	4.748(s)	4.544 (8.3)				4.089 (2.9)					
4′ M ^{6} ^{4}Mβ−4GN−4GN (**34**) GN *3 2 1* *9*	23	5.175 (2.2)	4.597 (7.6) 4.588 (8.1)		4.530 (8.5)	4.892(s)			4.106 (d, $J_{2,3}$ 2.4)	(3.958)				2.065, 2.023 (Ac × 2),(Ac × 1)
	50	5.181 (3.0) 4.690 (8.0)	4.603 (8.0) 4.593 (8.0)	4.735(s)	4.539 (8.3)	4.889 (1.5)			4.102 (d, $J_{2,3}$ 3.4)	3.952				
4′ M ^{6} *9* GN−^{4}Mβ−4GN−4GN (**35**) ^{3} *3 2 1* M *4*	23	5.177 (2.5)	4.590 (7.3,*α*) 4.583 (8.3,*β*)		4.503 (8.3)	4.931 (1.2)	5.216 (1.2)		4.172 (hhw 5)		4.140 (hhw 8)			2.064, 2.043, 2.023



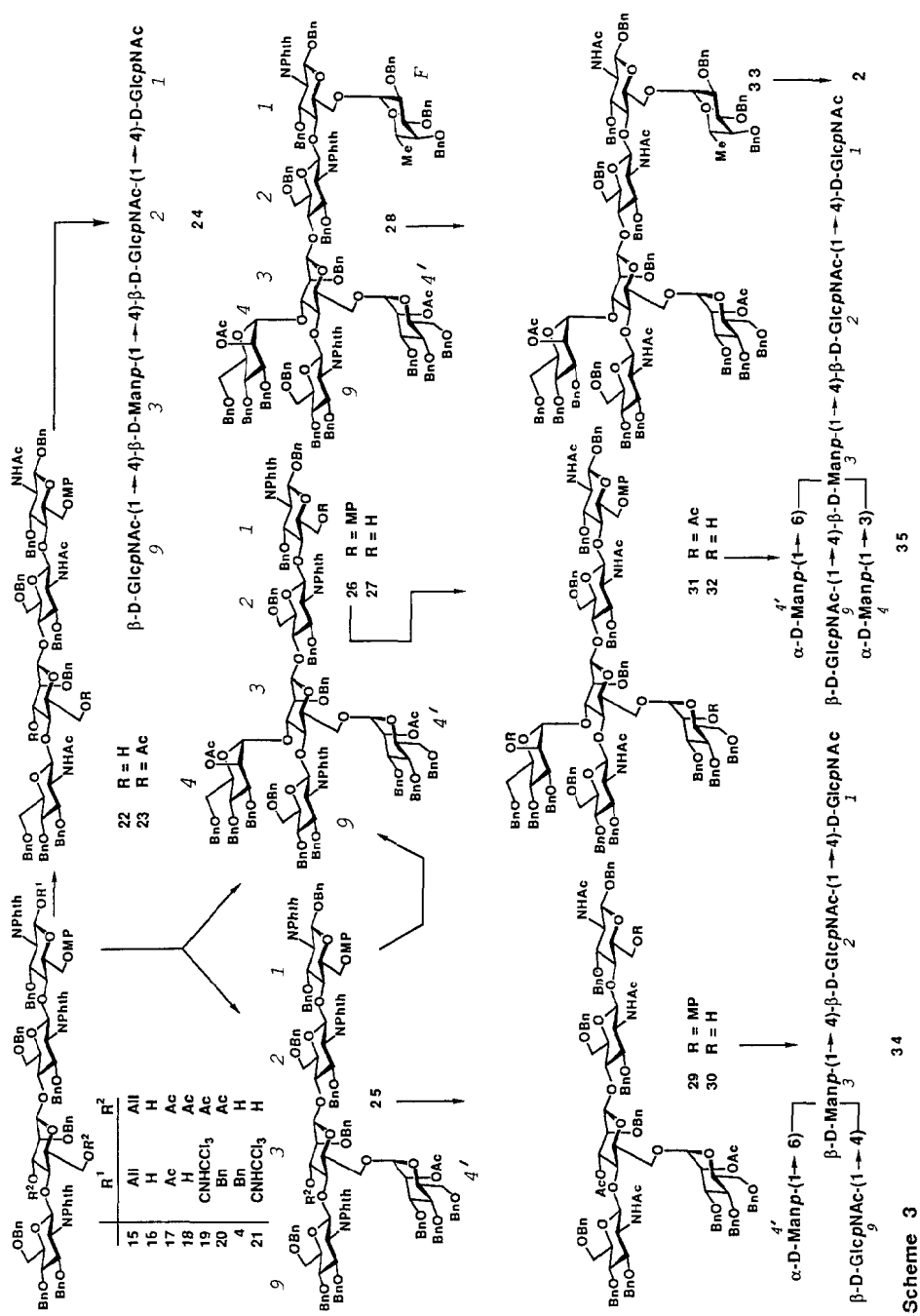
	50	5.180 (2.2)	4.603 (8.1)	4.733(s)		4.928 (1.5)	5.207 (1.5)		4.166 3.971 (d, $J_{2,3}$ 2.9)	4.134 (dd, $J_{1,2}$ 1.6, $J_{2,3}$ 3.3)			
		4.689 (8.2)	4.593 (8.2)										
	23	5.165 (2.7)			4.502 (8.1)	4.930 (1.3)	5.216 (hhw 3)	4.873 (3.5) 4.882 (3.0)	4.173 hhw 4	4.134 (hhw 7)	4.088 (q, 6.7)	1.205 (6.1) 1.194 (6.8)	2.078. 2.042, 2.023
	50	5.171 (2.9)	4.651 (7.0)	4.733(s)		4.930 (1.5)	5.207 (1.5)	4.873 (3.9)	4.167 (d, 2.7)	4.133 (dd, 1.8, 3.3)	4.078 (q, 6.8)		
		4.682 (~8)						4.882 (3.1)					

[a] Measured in D_2O using *tert*-BuOH as the internal reference (δ 1.230). Values in parentheses are the associated coupling constants reported in Hz. [b] GN = β-D-Glc*p*-NAc, Mβ = β-D-Man*p*, M = α-D-Man*p*, and Fuc = α-L-Fuc*p*

carrying hydroxy groups have also been observed in other cases[11].

Having prepared the designed intermediates **3**, **4**, **5**, **7**, **8** and **11** for the construction of the target glycoheptaose **2**, glycosylation of the key glycosyl acceptor **4** with mannosyl donors **7**, **8**, and **11** was studied. Silver triflate promoted glycosylation of compound **4** with chloride **7** was shown to be most efficient, in our hands, to give the monoglycosylated **25** and diglycosylated product **26** in 34 and 37% yield, respectively. Other methods of glycosylation were also examined, but these failed to improve the efficiency of the reaction. For example, benzeneselenenyl triflate promoted[12] glycosylation with methyl thioglycoside **8** afforded compound **25** and **26** in 24 and 35% yield, respectively, while boron trifluoride etherate promoted glycosylation with trichloroacetimidate **11** afforded **25** and **26** in 17 and 27% yield, respectively. Activation of mannosyl chloride **7** with mercury(II) bromide and mercury(II) cyanide gave **25** and **26** in 61 and 15% yield, respectively. Structure of compound **26** was assigned from the 2D ^{1}H-n.m.r. data that contained signals for H-2^4 and H-2$^{4'}$ at δ 5.873 and 5.320, along with the signals for H-1^4 and H-1$^{4'}$ at δ 5.154 and 4.929. These data, together with reasonable $^3J_{H,H}$ values, were in good agreement with the data for related synthetic compounds[13,14]. ^{13}C-N.m.r. data for compound **26** contained signals for C-1^4 and C-1$^{4'}$ at δ 100.3 and 98.4, respectively, in reasonable agreement with previous observations[14,15]. The structure of the monoglycosylated compound **25** was readily assigned also from ^{1}H- and ^{13}C-n.m.r. data, which revealed signals for H-2$^{4'}$ and H-1$^{4'}$ at δ 5.218 and 4.871, respectively, as well as a signal for C-1$^{4'}$ at δ 99.0. These results of the glycosylation of compound **4** seem to reflect a considerable steric impediment for the approach of an electrophilic mannosyl donor to O-3^3 of the β-mannosyl residue of compound **4** in comparison to the previous observation[14,16].

Following its separation from the desired diglycosylated product **26**, monoglycosylated glycopentaoside **25** was again submitted to various glycosylation conditions. The highest efficiency (65% conversion, based on consumed **25**) was obtained by the benzeneselenenyl triflate promoted glycosylation with methyl β-thiomannopyranoside **9**. Use of other donors **7**, **8**, and **11** in combination with the aforementioned promotors gave, respectively, 36, 0, and 54% conversion to the desired glycohexaoside **26**. Therefore, by using two successive glycosylations, acceptor **4** was at best converted into the desired product **26** in 59% overall yield. The *p*-methoxyphenyl protective group was then removed by ammonium cerium(IV) nitrate[10] to give alcohol **27** in 74% yield. This transformation was easily confirmed by the disappearance in its ^{1}H-n.m.r. spectrum of the signal for methyl protons of the *p*-methoxyphenyl group in compound **27**, which appeared as a singlet at δ 3.738 in compound **26**. The crucial α-L stereoselective glycosylation of compound **27** with methyl thioglycoside **5** was achieved in the presence of copper(II) bromide and tetrabutylammonium bromide[17] in 5:1 dichloroethane–DMF to give a completely protected glycoheptaoside **28** in 77% yield. The β-L stereoisomer of **28** could not be detected in the reaction mixture. Successful introduction of the L-fucosyl unit could be confirmed in the ^{1}H-n.m.r. spectrum of compound **28** which contained a signal for H-6^F at δ 0.933 as a doublet; however, the configuration at C-1^F could not be determined at this point, but was assigned after the complete deprotection


R¹ R²
15 All All
16 H H
17 Ac Ac
18 H Ac
19 CNHCCl3 Ac
20 Bn Ac
4 Bn H
21 CNHCCl3 H
22 R = H
23 R = Ac
β-D-GlcpNAc-(1→4)-β-D-Manp-(1→4)-β-D-GlcpNAc-(1→4)-D-GlcpNAc
26 R = MP
27 R = H
28
29 R = MP
30 R = H
31 R = Ac
32 R = H
α-D-Manp-(1→6)
β-D-Manp-(1→4)-β-D-GlcpNAc-(1→4)-D-GlcpNAc
β-D-GlcpNAc-(1→4)
α-D-Manp-(1→3)
34
35

Scheme 3

of compound **28**. All protective groups of **28** were removed in a stepwise manner as follows. Removal of the *N*-phthaloyl and *O*-acetyl groups with hydrazine hydrate in ethanol, followed by *N*- and *O*-acetylation with acetic anhydride and DMAP in pyridine, afforded compound **33**, which revealed in its ^{1}H-n.m.r. spectrum five singlets for methyl protons of the *O*- and *N*-acetyl groups at δ 2.181, 1.954, 1.904, 1.769, and 1.589. Deacetylation of **33** with sodium methoxide in methanol, and hydrogenolysis of the benzyl groups in methanol, gave the target glycoheptaose **2**. ^{1}H-N.m.r. spectral data (Figure 1 and Table I), which confirmed all configurational assignments at C-1^A, C-1$^{A'}$, and C-1^F for compound **28**, were in reasonable agreement with those[18] of the closely related glycans isolated from glycoproteins. Two key intermediates **25** and **27** were also completely deblocked in a similar sequence of reactions to give free glycopentaose **34** and glycohexaose **35**, respectively. Their ^{1}H-n.m.r. data (Table I) also confirmed the configurational assignments of newly introduced anomeric carbon atoms.

In summary, L-fucosylated core glycoheptaose **2** of the "bisected" complex-type glycan **1** was synthesized by employing glycotetraoside **4** as the key glycosyl acceptor. In synthetic experiments directed toward "bisected" glycan **1**, the key intermediate **26**, after deacetylation, should be a promising glycosyl acceptor for further chain elongation of the glycan at O-2^A and O-2$^{A'}$ of the two mannosyl residues.

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 A.S.T.M.). Flash chromatography was performed on columns of Wakogel C-300 (200–300 mesh A.S.T.M.). T.l.c. and high-performance (h.p.) t.l.c. were performed on Silica Gel-60 F_{254} (Merck). Molecular sieves 4A and AW-300 (acid stable, pore size 3Å) were purchased, respectively, from Nakarai Chemicals and Gasukuro Kogyo, Inc. N.m.r. spectra were recorded with either a JEOL GX500 [^{1}H(500 MHz)] or FX90Q [^{1}H (90 MHz) and ^{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. Values of δ_H (D_2O) are expressed in p.p.m. downfield from the reference to internal Me_3COH (δ1.230).

Methyl 2-O-acetyl-3,4,6-tri-O-benzyl-1-thio-α- and β-D-mannopyranoside (**8**) *and* **9**). — A solution of compound **6** (3.01 g, 5.93 mmol, ref. 19) and TMSCl (1.13 mL, 8.96 mmol) in CH_2Cl_2 (40 mL) was stirred for 40 min at 40°. The solvent was then evaporated *in vacuo*, and residual volatiles were co-evaporated with toluene to quantitatively give **7** (ref. 3). To a mixture of compound **7** and Bu_3SnSMe (2.2 mL, 7.6 mmol) in $(ClCH_2)_2$ (40 mL) was added $SnCl_4$ (0.9 mL, 7.7 mmol) at 0°. After stirring for 20 min at 20°, the mixture was diluted with EtOAc, washed with aq. KF, and filtered through Celite. The organic layer was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 4:1 toluene–EtOAc to give **8** (2.82 g, 91%) and **9** (94 mg, 3.0%). Analytical samples of **8**

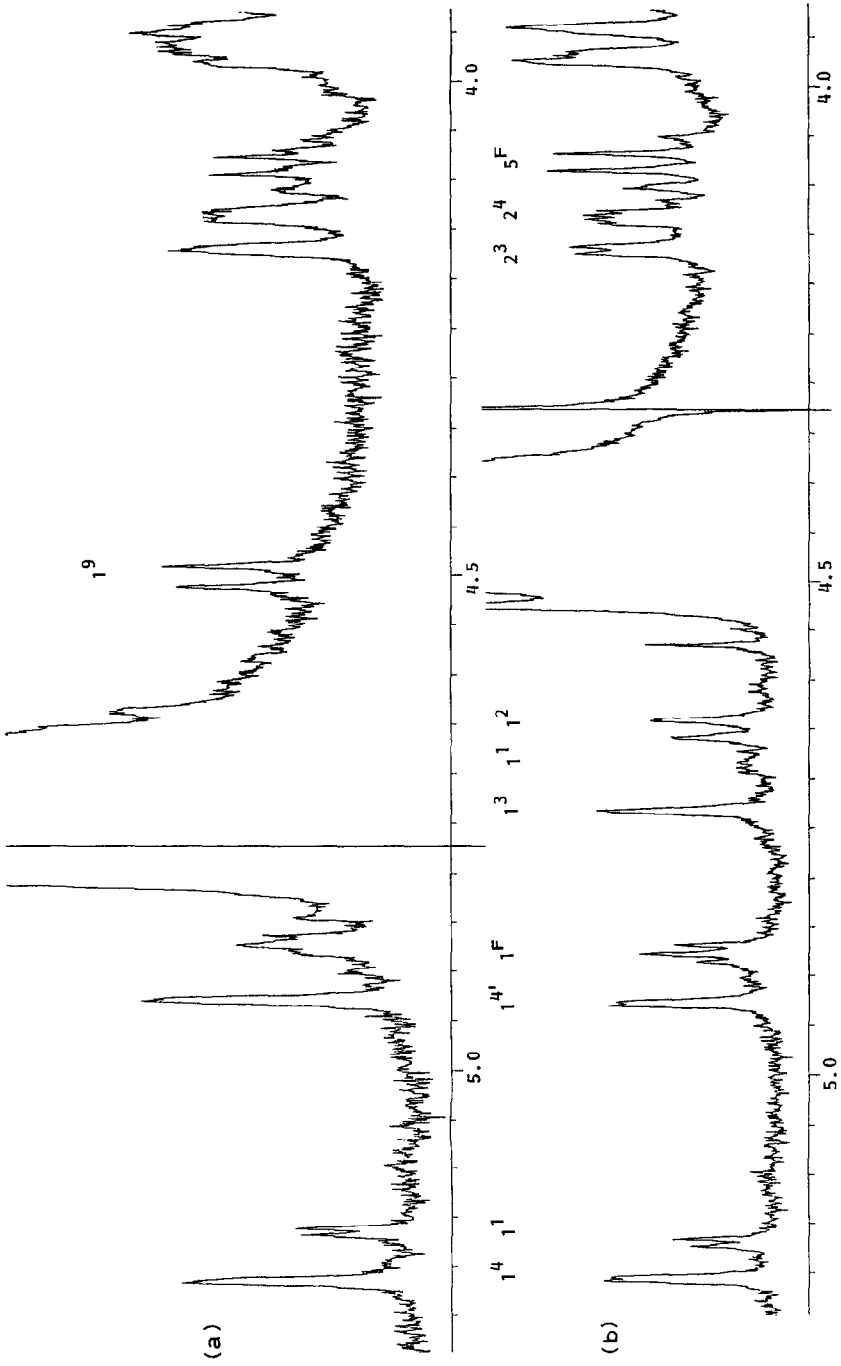


Fig. 1. Partial ^{1}H-n.m.r. spectrum (500 MHz) for compound **2** in D_2O (*tert*-BuOH, δ 1.230): (a) at 23°, (b) at 50°.

and **9** were further purified by semi-preparative h.p.l.c. (a Senshu Pak SSC-Silica-430-N column, 10 × 300 mm, UV 254 nm) using 5:1 hexane–EtOAc. Compound **8** had $[\alpha]_D$ +81.3° (*c* 1.0); R_F 0.55 (2:1 hexane–EtOAc); n.m.r. data: δ_H 7.4–7.1 (m, 15 H, C_6H_5 × 3), 5.435 (dd, 1 H, $J_{1,2}$ 1.2, $J_{2,3}$ 2.8 Hz, H-2), 5.194 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.850 and 4.481 (2 d, 2 H, *J* 10.7 Hz, CH_2Ph), 4.677 and 4.522 (2 d, 2 H, *J* 11.0 Hz, CH_2Ph), 4.675 and 4.498 (2 d, 2 H, *J* 13.0 Hz, CH_2Ph), 4.125 (ddd, 1 H, $J_{4,5}$ 9.2, $J_{5,6}$ 4.5, $J_{5,6'}$ 1.8 Hz, H-5), 3.94–3.90 (m, 2 H, H-3 and H-4), 3.825 (dd, 1 H, $J_{5,6}$ 4.5, $J_{6,6'}$ 10.7 Hz, H-6), and 3.699 (dd, 1 H, $J_{5,6'}$ 1.8, $J_{6,6'}$ 10.7 Hz, H-6'), and 2.151 and 2.125 (2 s, 6 H, SCH_3 and $COCH_3$); δ_C 170.2 ($COCH_3$), 83.9 ($^1J_{C,H}$ 166 Hz, C-1), 21.0 ($COCH_3$), and 13.8 (SCH_3).

Anal. Calc. for $C_{30}H_{34}O_6S$: C, 68.94; H, 6.56; S, 6.13. Found: C, 68.73; H, 6.55; S, 6.19.

Compound **9** had $[\alpha]_D$ −45.9° (*c* 0.9); R_F 0.48 (2:1 hexane–EtOAc); n.m.r. data: δ_H 7.4–7.1 (m, 15 H, C_6H_5 × 3), 5.649 (dd, 1 H, $J_{1,2}$ 0.9, $J_{2,3}$ 3.4 Hz, H-2), 4.858 and 4.520 (2 d, 2 H, *J* 10.7 Hz, CH_2Ph), 4.767 and 4.492 (2 d, 2 H, *J* 11.0 Hz, CH_2Ph), 4.627 and 4.565 (2 d, 2 H, *J* 12.2 Hz, CH_2Ph), 4.571 (d, 1 H, $J_{1,2}$ 0.9 Hz, H-1), 3.798 (dd, 1 H, $J_{5,6}$ 1.8, $J_{6,6'}$ 11.0 Hz, H-6), 3.747 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.8 Hz, H-4), 3.738 (dd, 1 H, $J_{5,6'}$ 5.5, $J_{6,6}$ 11.0 Hz, H-6'), 3.675 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.8 Hz, H-3), 3.513 (ddd, 1 H, $J_{4,5}$ 9.8, $J_{5,6}$ 1.8, $J_{5,6'}$ 5.5 Hz, H-5), 2.257 (s, 3 H, SCH_3), and 2.198 (s, 3 H, $COCH_3$); δ_C 170.4 ($COCH_3$), 83.4 ($^1J_{C,H}$ = 151 Hz, C-1), 20.9 ($COCH_3$), and 14.2 (SCH_3).

2-O-Acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl trichloroacetimidate (**11**). — A solution of compound **6** (452 mg, 892 μmol) in 60% aq. AcOH (40 mL) was stirred for 2 h at 20° and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 5:1 toluene–EtOAc to give **10** (432 mg, 98%); n.m.r. data: δ_C 170.3 ($COCH_3$), 92.2 ($^1J_{C,H}$ 170 Hz, C-1), and 20.9 ($COCH_3$). To a solution of compound **10** (123 mg, 249 μmol) in $(ClCH_2)_2$ (1 mL) was added successively Cl_3CCN (0.3 mL, 3.0 mmol) and DBU (10 μL, 0.07 mmol) at −5° under Ar. After stirring for 10 min, the mixture was directly chromatographed on SiO_2 using 6:1 toluene–EtOAc to give **11** (156 mg, 98%): $[\alpha]_D$ +36.3° (*c* 0.9); R_F 0.57 (3:1 toluene–EtOAc); n.m.r. data: δ_H 8.673 (s, 1 H, C=N*H*), 7.4–7.1 (m, 15 H, C_6H_5 × 3), 6.298 (d, 1 H, $J_{1,2}$ = 1.8 Hz, H-1), 5.494 (t, 1 H, $J_{1,2} = J_{2,3}$ = 2.1 Hz, H-2), 4.871 and 4.536 (2 d, 2 H, *J* 11.3 Hz, CH_2Ph), 4.731 and 4.580 (2 d, 2 H, *J* 11.3 Hz, CH_2Ph), 4.676 and 4.507 (2 d, 2 H, *J* 12.2 Hz, CH_2Ph), 3.838 (dd, 1 H, $J_{5,6}$ 3.9, $J_{6,6'}$ 11.2 Hz, H-6), 3.715 (dd, 1 H, $J_{5,6'}$ 1.7, $J_{6,6'}$ 11.2 Hz, H-6'), and 2.185 (s, 3 H, $COCH_3$); δ_C 170.0 ($COCH_3$), 160.0 ($CNHCCl_3$), 95.5 ($^1J_{C,H}$ 178 Hz, C-1), and 20.9 ($COCH_3$).

Anal. Calc. for $C_{31}H_{32}NO_7Cl_3$: C, 58.46; H, 5.06; N, 2.20. Found: C, 58.25; H, 5.13; N, 2.30.

Methyl 2,3,4-tri-O-acetyl-1-thio-β- and α-L-fucopyranoside (**13** *and* **14**). — To a mixture of compound **12** (3.3 g, 10 mmol) and Bu_3SnSMe (3.8 g, 10.5 mmol) in $(ClCH_2)_2$ (40 mL) was added dropwise $SnCl_4$ (1.4 mL, 10 mmol) at 0°. After stirring for 4 h at 20°, the mixture was concentrated *in vacuo*, and the residue was dissolved in EtOAc. The solution was washed with aq. KF and filtered through Celite. The filtrate was washed with aq. NaCl and dried ($MgSO_4$), and the solvent was evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 2:1 hexane–EtOAc to give **13** (1.8 g, 56%) and **14** (1.1 g, 34%).

Compound **13** had m.p. 139–141° (EtOAc–hexane); $[\alpha]_D$ −0.7° (*c* 1.1); R_F 0.43 (2:1 hexane–EtOAc); n.m.r. data: δ_H 4.35 (d, 1 H, $J_{1,2}$ 9.4 Hz, H-1), 2.19, 2.17, 2.07, and 1.99 (4 s, 12 H, SCH_3 and COCH_3 × 3), and 1.22 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calc. for $C_{13}H_{20}O_7S$: C, 48.74; H, 6.29; S, 10.01. Found: C, 48.75; H, 6.27; S, 9.87.

Compound **14** had m.p. 80–81° (EtOAc–hexane); $[\alpha]_D$ −222.3° (*c* 1.2); R_F 0.50 (2:1 hexane–EtOAc); n.m.r. data: δ_H 5.27 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 2.16, 2.07, 2.05, and 1.99 (4 s, 12 H, SCH_3 and COCH_3 × 3), and 1.17 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6).

Anal. Calc. for $C_{13}H_{20}O_7S$: C, 48.74; H, 6.29; S, 10.01. Found: C, 48.82; H, 6.28; S, 10.07.

*Methyl 2,3,4-tri-*O*-benzyl-1-thio-β-*L*-fucopyranoside* (**5**). — A solution of compound **13** (27.2 g, 85 mmol) in 0.16M NaOMe–MeOH (350 mL) was stirred for 4 h at 20°, and then concentrated *in vacuo*. To a solution of the residue in DMF (200 mL) was added portionwise NaH (60% oil dispersion, 16 g, 320 mmol). After stirring for 30 min at 20°, benzyl bromide (38 mL, 320 mmol) was added dropwise to the mixture at −5–0°. The mixture was stirred for 16 h at 20°, then it was poured into ice water and extracted with EtOAc. The organic layer was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 10:1 hexane–EtOAc to give **5** (33.5 g, 90%): $[\alpha]_D$ −0.2° (*c* 1.5); R_F 0.50 (4:1 hexane–EtOAc); n.m.r. data: δ_H 7.4–7.2 (m, 15 H, 3 Ph), 4.300 (d, 1 H, $J_{1,2}$ 9.7 Hz, H-1), 3.840 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9.4 Hz, H-2), 3.622 (d, 1 H, $J_{3,4}$ 2.8 Hz, H-4), 3.572 (dd, 1 H, $J_{2,3}$ 9.5, $J_{3,4}$ 2.8 Hz, H-3), 3.499 (q, 1 H, $J_{5,6}$ 6.4 Hz, H-5), 2.206 (s, 3 H, SCH_3), and 1.211 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6).

Anal. Calc. for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94; S, 6.90. Found: C, 72.44; H, 6.91; S, 6.65.

O-(*3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl-(1→4)-*O*-(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-*D*-glucopyranose* (**16**). — To a solution of compound **15** (ref. 2b) (781 mg, 408 μmol) in 7:3:1 EtOH–toluene–H_2O (50 mL) was added $(Ph_3P)_3RhCl$ (196 mg, 211 μmol) and DABCO (105 mg, 937 μmol). After stirring for 5 h at 85°, the mixture was concentrated *in vacuo*. A mixture of the residue, $HgCl_2$ (1.840 g, 776 mmol), and HgO (232 mg, 1.07 mmol) in 10:1 acetone–H_2O (50 mL) was stirred for 2 days at 20°. After dilution with $CHCl_3$, the mixture was washed with aq. KI and filtered through Celite. The organic layer was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 2:1 toluene–EtOAc to give **16** (573 mg, 79%); $[\alpha]_D$ +49.8° (*c* 0.8); R_f 0.46 (1:1 toluene–EtOAc); n.m.r. data: δ_H 7.80–6.65 (m, 51 H, aromatic), 3.738 (s, 3 H, OCH_3); δ_C 100.4 (C-1^3), 98.6, 97.5 (C-$1^{2,9}$), and 92.5 (C-1^1).

Anal. Calc. for $C_{104}H_{99}N_3O_{25}\cdot H_2O$; C, 69.05; H, 5.63; N, 2.32. Found: C, 68.85; H, 5.57; N, 2.16.

O-*(3,4,6-Tri-*O*-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-*O*-(3,6-di-*O*-acetyl-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*-glucopyranosyl acetate* (**17**). — A solution of compound **16** (487 mg, 272 μmol) in 1:1 pyridine–Ac_2O (4 mL) was stirred for 7 h at 20°, concentrated *in vacuo*, and the volatiles were co-evaporated with toluene. The residue was chromatographed on SiO_2 using 4:1 toluene–EtOAc and then further purified by preparative t.l.c. using 3:1 toluene–EtOAc to give **17** (417 mg, 80%) and α-anomer of **17** (48 mg, 9%).

Compound **17** had $[\alpha]_D$ +38.0° (*c* 1.0); R_f 0.49 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.6 (m, 51 H, aromatic), 6.132 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1^1), 5.154 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-2^{2*}), 5.131 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1^{9*}), 4.728 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 9.3 Hz, H-3^3), 4.496 (s, 1 H, H-1^3), 3.724 (s, 3 H, OCH_3), and 1.934, 1.852, and 1.544 (3 s, 9 H, COCH_3 × 3); δ_C 100.7 (C-1^3), 97.4 and 97.1 (C-1^{2,9}), and 90.1 (C-1^1).

Anal. Calc. for $C_{110}H_{105}N_3O_2$: C, 68.92; H, 5.52; N, 2.19. Found: C, 68.67; H, 5.58; N, 2.14.

The α-anomer of **17** had $[\alpha]_D$ +62.9° (*c* 1.1); R_f 0.44 (2:1 toluene–EtOAc); n.m.r. data: δ_H 6.111 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1^1), 5.247 and 5.148 (2 d, 2 H, $J_{1,2}$ 8.2 Hz, H-1^{2,9}), 3.746 (s, 3 H, OCH_3), 2.040, 1.933 and 1.629 (3 s, 9 H, COCH_3 × 3).

Anal. Calc. for $C_{110}H_{105}N_3O_2$: C, 68.92; H, 5.52; N, 2.19. Found: C, 68.94; H, 5.57; N, 2.22.

O-*(3,4,6-Tri-O-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-O-(3,6-di-O-acetyl-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-*D*-glucopyranose* (**18**). — To a solution of compound **17** (20 mg, 11 μmol) in DMF (0.5 mL) was added NH_2NH_2·AcOH (3.8 mg, 41 μmol), and the mixture was stirred for 30 min at 50° and then diluted with EtOAc. The solution was washed successively with H_2O, aq. $NaHCO_3$, and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 2:1 toluene–EtOAc to give **18** (15 mg, 77%): $[\alpha]_D$ +50.7° (*c* 0.9); R_f 0.27 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.7–6.6 (m, 51 H, aromatic), 5.216–5.121 (m, 3 H, H-1^{1,2,9}), 3.740 (s, 3 H, OCH_3), 1.928 and 1.546 (2 s, 6 H, COCH_3 × 2).

Anal. Calc. for $C_{108}H_{103}N_3O_{27}$: C, 69.18; H, 5.54; N, 2.24. Found: C, 68.80; H, 5.60; N, 2.27.

Benzyl O-*(3,4,6-tri-O-benzyl-2-deoxy-2-phthalimido-β-*D*-glucopyranosyl)-(1→4)-O-(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* (**4**). — *Procedure A* (via **19** and **20**). To a solution of compound **18** (54 mg, 29 μmol) in $(ClCH_2)_2$ (0.7 mL) was added Cl_3CCN (120 μL, 1.2 mmol) and DBU (2 μL, 0.01 mmol) at −5° under Ar. After stirring for 20 min at 0°, the mixture was directly chromatographed on SiO_2 using 3:1 toluene–EtOAc to give **19** (59 mg): R_f 0.34 (3:1 toluene–EtOAc); n.m.r. data: δ_H 8.403 (s, 1 H, C=N*H*), 7.7–6.6 (m, 51 H, aromatic), 6.252 (d, 1 H, $J_{1,2}$ 8.1 H, H-1^1), 3.739 (s, 3 H, OCH_3), and 1.934 and 1.557 (2

* The assignments with asterisk may be interchanged.

s, 6 H, $COCH_3$ × 2). To a mixture of AW-300 molecular sieves (50 mg) and benzyl alcohol (23 μL, 0.23 mmol) in $(ClCH_2)_2$ (1 mL) was added successively a solution of compound **19** (59 mg) in $(ClCH_2)_2$ (0.5 mL) and $BF_3{\cdot}Et_2O$ (7 μL, 0.06 mmol) at −20° under Ar. After stirring for 20 min at −20°, 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 ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 3:1 toluene–EtOAc to give **20** (49 mg, 87% from **18**) and recovered **18** (4 mg, 7%).

Compound **20** had R_F 0.47 (3:1 toluene–EtOAc); n.m.r. data: δ_C 100.8 (C-1^3), and 97.5 and 97.0 (in a ratio of 2:1. C-$1^{1,2,9}$).

A solution of compound **20** (106 mg, 54 μmol) in 50:2:1 acetone–H_2O–conc. HCl (1 mL) was stirred for 24 h at 80°, and then concentrated *in vacuo*. The residue was dissolved in EtOAc, and the solution was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was purified by chromatography on Bio-Beads S-X3 (200 mL) using toluene, and then by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 1:1 hexane–EtOAc to give **4** (56 mg, 59%).

Procedure B (via **21**). To a solution of compound **16** (124 mg, 69.2 μmol) in CH_2Cl_2 (1.6 mL) was added Cl_3CCN (330 μL, 3.3 mmol) and DBU (3μL, 0.02 mmol) at −55° under Ar. After stirring for 30 min at −55°, the mixture was directly chromatographed on SiO_2 using 2:1 toluene–EtOAc to give **21** (110 mg) that was used immediately for the next step.

Compound **21** had R_F 0.31 (2:1 toluene–EtOAc); n.m.r. data: δ_H 8.406 (s, 1 H, C=N*H*), 6.253 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1^1), and 3.744 (s, 3 H, OCH_3).

To a mixture of AW-300 molecular sieves (110 mg) and benzyl alcohol (99 μL, 0.96 mmol) in $(ClCH_2)_2$ (1.5 mL) was added successively a solution of compound **21** (108 mg, 55.8 μmol) in $(ClCH_2)_2$ (1 mL) and $BF_3{\cdot}Et_2O$ (23 μL, 0.19 mmol) at −20° under Ar. After stirring for 5 min at −20°, 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 ($MgSO_4$). The solvent was then evaporated *in vacuo*. The residue was chromatographed on SiO_2 using 5:4 hexane–EtOAc and further purified by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 1:1 hexane–EtOAc to give **4** (84 mg, 80%) and recovered **16** (6 mg, 6%).

Compound **4** had $[\alpha]_D$ +38.9° (*c* 1.6); R_F 0.34 (2:1 toluene–EtOAc); n.m.r. data: δ_H 7.8–6.6 (m, 56 H, aromatic), 5.202 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^2), 5.160 (d, 1 H, $J_{1,2}$ 8.5 Hz, H-1^9), 4.972 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1^1), 3.754 (s, 3 H, OCH_3), and 3.422 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.5 Hz, H-3^3); δ_C 100.6 (C-1^3), 98.6, 97.4, and 96.9 (C-$1^{1,2,9}$), 61.3 (C-6^3), 56.4, 55.8, 55.7, and 55.6 (C-$2^{1,2,9}$ and OCH_3).

Anal. Calc. for $C_{111}H_{105}N_3O_{25}$: C, 70.88; H, 5.63; N, 2.23. Found: C, 70.76; H, 5.80; N, 2.18.

Deprotection of compound **20** *to* **24** *via* **22** *and* **23**. — A solution of compound **20** (13 mg, 6.4 μmol) in 10:1 EtOH–$NH_2NH_2{\cdot}H_2O$ (1.5 mL) was heated for 24 h under reflux. T.l.c. examination revealed formation of a new spot on t.l.c. at R_F 0.40 (50:15:1

toluene–EtOH–THF). After evaporation of the mixture *in vacuo*, a solution of the residue in MeOH (1 mL) and Ac_2O (0.1 mL) was stirred for 1 h at 20°, giving a new spot on t.l.c. at R_F 0.67 (50:15:1 toluene–EtOH–THF). The volatiles were co-evaporated several times with toluene, and the residue was chromatographed on Bio-Beads S-X4 (30 mL) in toluene to give **22** (11 mg, 100%); n.m.r. data: δ_H 7.4–7.1 (m, 40 H, 8 Ph), 6.74–6.65 (m, 5 H, N*H*Ac and C_6H_4OMe), 5.584 (d, 1 H, *J* 8.2 Hz, N*H*Ac), 5.170 (d, 1 H, *J* 8.9 Hz, N*H*Ac), 3.743 (s, 3 H, OCH_3), 2.002, 1.821, and 1.674 (3 s, 9 H, NHCOCH_3 × 3).

A solution of compound **22** (6.0 mg, 3.7 μmol) in 1:1 pyridine–Ac_2O (1 mL) containing DMAP (1 mg) was stirred for 24 h at 20°, at the end of which time the volatiles were co-evaporated several times with 1:1 MeOH–toluene *in vacuo*. The residue was chromatographed on Bio-Beads S-X4 (30 mL) using toluene and then further purified by h.p.l.c. on a Senshu-Pak SSC-Silica-4301-N column (10 × 300 mm) using 50:1 $CHCl_3$–EtOH to give **23** (3.8 mg, 60% from **20**): $[\alpha]_D$ −31.1° (*c* 0.4); R_F 0.34 (30:1 $CHCl_3$–EtOH); n.m.r. data: δ_H 7.5–7.1 (m, 40 H, 8 Ph), 6.750 (d, 1 H, *J* 9.7 Hz, N*H*Ac), 6.714 and 6.644 (2 d, 4 H, *J* 9.2 Hz, C_6H_4OMe), 5.752 and 5.131 (2 d, 2 H, *J* 8.2 Hz, N*H*Ac × 2), 3.740 (s, 3 H, OCH_3), 2.008, 1.937, 1.928, 1.838, and 1.645 (5 s, 15 H, NHCOCH_3 × 3 and OCOCH_3 × 2).

To a stirred solution of compound **23** (3.7 mg, 2.2 μmol) in 8:1 CH_3CN–H_2O (0.9 mL) was added $(NH_4)_2Ce(NO_3)_6$ (8.7 mg, 16 μmol) at −5°. The mixture was stirred for 1 h at −5°, giving a new spot on t.l.c. at R_F 0.37 (20:1 $CHCl_3$–EtOH). At the end of this time, the mixture was diluted with EtOAc. The solution was washed successively with H_2O, aq. $NaHCO_3$, and aq. NaCl and dried ($MgSO_4$). The solvent was then evaporated *in vacuo*, and the residue was dissolved in MeOH (1 mL) and M NaOMe in MeOH (10 μL). After stirring the solution for 16 h at 20°, t.l.c. examination revealed a new spot at R_F 0.26 (20:1 $CHCl_3$–EtOH). The mixture was then treated with Amberlyst-15 [H^+] resin and filtered through Celite. The filtrate was concentrated *in vacuo*, and a mixture of the residue and 10% Pd–C (3 mg) in MeOH (1 mL) was stirred under H_2 for 16 h at 20°, then for 1 h at 50°, at the end of which time it was cooled and filtered through Celite. The filtrate was concentrated *in vacuo*, and the residue was chromatographed on Bio Gel P-4 (20 mL) using H_2O to give **24** (1.7 mg, 98%); $[\alpha]_D$ −2.1° (*c* 0.2, H_2O); R_F 0.35 (100:30:10:10:3 EtOH–H_2O–BuOH–pyridine–AcOH).

Benzyl O-*(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→6)-O-[(3,4,6-tri-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-O-(2-O-benzyl-β-D-mannopyranosyl)-(1→4)-O-(3,6-di-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-O-benzyl-2-deoxy-2-phthalimido-6-O-p-methoxyphenyl-β-D-glucopyranoside* (**25**) *and benzyl* O-*(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→6)-O-[(3,4,6-tri-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-O-[(2-O-acetyl-3,4,6-tri-O-benzyl-α-D-mannopyranosyl)-(1→3)]-O-(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-2-phthalimido-6-O-p-methoxyphenyl-β-D-glucopyranoside* (**26**). — *Procedure A.* To a mixture of 4A molecular sieves (150 mg) and AgOTf (29 mg, 0.11 mmol) was added successively a solution of compound **4** (10.5 mg, 5.6

μmol) in $(ClCH_2)_2$ (1.5 mL) and a solution of compound **7** (29 mg, 57 μmol) in $(ClCH_2)_2$ (0.5 mL) at −23° under Ar. After stirring for 1 h at −23°, an additional portion of compound **7** (29 mg), dissolved in $(ClCH_2)_2$ (0.5 mL), was added. The mixture was stirred for an additional 24 h at 0–20°, diluted with EtOAc, and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$, H_2O, and aq. NaCl and dried ($MgSO_4$). The solvents were evaporated *in vacuo*. The residue was chromatographed on Bio-Beads S-X3 (200 mL) using toluene and then purified by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 5:4 hexane–EtOAc to give **25** (4.4 mg, 34%) and **26** (5.8 mg, 37%).

Procedure B. A mixture of 4A molecular sieves (150 mg), PhSeCl (28 mg, 0.15 mmol) and AgOTf (46 mg, 0.18 mmol) in $(ClCH_2)_2$ (0.5 mL) was stirred for 10 min at −5° under Ar. To this mixture was added a solution of compound **4** (21 mg, 11 μmol) and compound **8** (34 mg, 66 μmol) in $(ClCH_2)_2$ (1.5 mL) at −23° under Ar. After stirring for 2 h at −23°, an additional portion of compound **8** (38 mg, 73 μmol) in $(ClCH_2)_2$ (0.8 mL) was added, and the mixture was stirred for an additional 24 h at 0–20°, whereupon it was diluted with EtOAc and filtered through Celite. The filtrate was processed as described in Procedure A to give **25** (6.2 mg, 24%) and **26** (11.1 mg, 35%).

Procedure C. To a mixture of AW-300 molecular sieves (800 mg) and compound **4** (27 mg, 14 μmol) in $(ClCH_2)_2$ (0.75 mL) was added successively a solution of compound **11** (124 mg, 195 μmol) in $(ClCH_2)_2$ (1.25 mL) and $BF_3{\cdot}Et_2O$ (14 μL, 0.11 mmol) at −23° under Ar. After stirring for 8 h at −23°, a solution of compound **11** (34 mg, 54 μmol) in $(ClCH_2)_2$ (0.4 mL) was again added. The mixture was stirred for 24 h at 0–20°, neutralized with Et_3N, diluted with EtOAc, and filtered through Celite. The filtrate was processed as described in Procedure A to give **25** (5.7 mg, 17%) and **26** (11.2 mg, 27%).

Procedure D. To a mixture of 4A molecular sieves (75 mg), $Hg(CN)_2$ (57 mg, 0.23 mmol) and $HgBr_2$ (81 mg, 0.22 mmol) was added a solution of compound **4** (13.2 mg, 7 μmol) in $(ClCH_2)_2$ (0.3 mL) at 20° under Ar. After stirring for 30 min at 20°, a solution of compound **7** (29 mg, 56 μmol) in $(ClCH_2)_2$ (0.3 mL) was added, and the mixture was stirred for 24 h at 20°. To this mixture was added an additional portion of compound **7** (27 mg, 54 μmol) in $(ClCH_2)_2$ (0.3 mL). After stirring for 24 h at 20°, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was processed as described in Procedure A to give **25** (10.1 mg, 61%) and **26** (2.9 mg, 15%). Compound **25** had $[\alpha]_D$ +40.3° (*c* 0.8); R_F 0.28 (5:4 hexane–EtOAc); n.m.r. data: δ_H 7.7–6.4 (m, 71 H, aromatic), 5.218 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.3 Hz, H-$2^{4'}$), 5.188 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1^{9*}), 5.138 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-2^{2*}), 4.939 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^1), 4.933 (d, 1 H, J = 12.5 Hz, CH_2Ph), 4.871 (d, 1 H, $J_{1,2}$ = 1.5 Hz, H-$1^{4'}$), 3.745 (s, 3 H, OCH_3), 2.913 (m, 1 H, H-5^3), and 1.572 (s, 3 H, $COCH_3$); δ_C 101.4 (C-1^3), 99.0 (C-$1^{4'}$), 97.3 and 96.9 (in a ratio of 1:2, C-$1^{1,2,9}$), 56.5, 55.9, 55.7, and 55.6 (C-$2^{1,2,9}$ and OCH_3), and 20.4 ($COCH_3$).

Anal. Calc. for $C_{140}H_{135}N_3O_{31}{\cdot}H_2O$: C, 70.84; H, 5.82; N, 1.77. Found: C, 70.88; H, 5.99; N, 1.84.

Compound **26** had $[\alpha]_D$ +22.5° (*c* 1.0); R_F 0.25 (5:4 hexane–EtOAc); n.m.r. data: δ_H 7.7–6.5 (m, 86 H, aromatic), 5.873 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1 Hz, H-2^4), 5.320 (bs, 1 H, hhw = 4.9 Hz, H-$2^{4'}$), 5.180 and 5.146 (2 d, 2 H, $J_{1,2}$ 8.2 Hz, H-$1^{2,9}$), 5.154 (d, 1 H, $J_{1,2}$ 1.5

Hz, H-1^4), 4.937 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^1), 4.929 (s, 1 H, H-1^4'), 4.483 (t, 1 H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4^3), 3.738 (s, 3 H, OCH_3), 3.627 (d, 1 H, $J_{2,3}$ 2.8 Hz, H-2^3), 3.339 (dd, 1 H, $J_{2,3}$ 2.8, $J_{3,4}$ 9.6 Hz, H-3^3), 2.576 (m, 1 H, H-5^3), and 2.322 and 1.634 (2 s, 6 H, COCH_3 × 2); δ_H 101.1 (C-1^3), 100.3 (C-1^4), 98.4 (C-1^4'), 97.4, 96.9 and 96.6 (C-1^{1,2,9}, 56.5, 55.9, 55.7 and 55.6 (C-2^{1,2,9} and OCH$_3$), and 21.4 and 20.6 (COCH$_3$ × 2).

Anal. Calc. for $C_{169}H_{165}N_3O_{37}$: C, 71.72; H, 5.88; N, 1.48. Found: C, 71.95; H, 5.92; N, 1.23.

Conversion of compound **25** *into* **26**. — *Procedure A*. A mixture of 4A molecular sieves (100 mg), PhSeCl (19 mg, 97 μmol), and AgOTf (23 mg, 91 μmol) in $(ClCH_2)_2$ (0.5 mL) was stirred for 10 min at −5°. To this mixture was added a solution of compound **25** (7.3 mg, 3.1 μmol) in $(ClCH_2)_2$ (0.5 mL), and then a solution of compound **9** (28 mg, 53 μmol) in $(ClCH_2)_2$ (1.25 mL) was slowly added during 3 h at −23° under Ar. After stirring for 24 h at 0–20°, the mixture was diluted with EtOAc and filtered through Celite. The filtrate was processed as described above to give **26** (3.3 mg, 38%) and recovered **25** (3.0 mg, 41%).

Procedure B. A mixture of 4A molecular sieves (120 mg), PhSeCl (15 mg, 76 μmol) and AgOTf (17 mg, 68 μmol) in $(ClCH_2)_2$ (1 mL) was stirred for 10 min at −5°. To this mixture was added a solution of compound **25** (7.5 mg, 3.2 μmol), followed by a solution of compound **8** (15 mg, 28 μmol) in $(ClCH_2)_2$ (1 mL) slowly at −23° under Ar. After stirring for 24 h at 0–20°, the mixture was processed as described in Procedure A to give only recovered **25** (4.4 mg, 59%).

Procedure C. To a stirred mixture of 4A molecular sieves (135 mg) and AgOTf (13 mg, 50 μmol) in $(ClCH_2)_2$ (0.6 mL) was added a solution of compound **25** (7.9 mg, 3.3 μmol) in $(ClCH_2)_2$ (0.3 mL) and a solution of compound **7** (23 mg, 45 μmol) in $(ClCH_2)_2$ (0.7 mL) at −23° under Ar. After stirring for 24 h at 0–20°, the mixture was processed as described in Procedure A to give **26** (2.7 mg, 29%) and recovered **25** (1.9 mg, 20%).

Procedure D. To a mixture of AW-300 molecular sieves (200 mg) and compound **25** (4.6 mg, 2.0 μmol) in $(ClCH_2)_2$ (0.3 mL) was added $BF_3{\cdot}Et_2O$ (3 μL, 0.02 mmol) and then a solution of compound **11** (85 mg, 133 μmol) in $(ClCH_2)_2$ (0.7 mL) slowly during 2 h at −23°. After stirring for 24 h at 0–20°, the mixture was neutralized with Et_3N, diluted with EtOAc, and filtered through Celite. The filtrate was processed as described in Procedure A to give **26** (1.6 mg, 29%) and recovered **25** (2.1 mg, 46%).

Benzyl O-*(2-O-acetyl-3,4,6-tri-*O-*benzyl-α-*D-*mannopyranosyl)-(1→6)-*O-*[(3,4,6-tri-*O-*benzyl-2-deoxy-2-phthalimido-β-*D-*glucopyranosyl)-(1→4)]-*O-*[(2-O-acetyl-3,4,6-tri-*O-*benzyl-α-*D-*mannopyranosyl)-(1→3)]-*O-*(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-2-phthalimido-β-*D-*glucopyranoside* (**27**). To a solution of compound **26** (12.3 mg, 4.35 μmol) in 8:1 CH_3CN–H_2O (1.8 mL) was added $(NH_4)_2Ce(NO_3)_6$ (12 mg, 21 μmol) at −5°. After stirring for 1 h at −5°, the mixture was diluted with $(ClCH_2)_2$ and washed with aq. $NaHCO_3$. The aq. phase was back-extracted with EtOAc and $(ClCH_2)_2$. Combined organic layer was washed with aq. NaCl and dried ($MgSO_4$), and the solvents were evaporated *in vacuo*. The residue was purified by h.p.l.c. on a Senshu-Pak SSC-Silica-4301-N column (10 × 300 mm) using 1:1 hexane–EtOAc to give

27 (8.7 mg, 74%); $[\alpha]_D$ +13.5° (*c* 0.5); R_F 0.29 (1:1 hexane–EtOAc); n.m.r. data: δ_H 7.8–6.5 (m, 82 H, aromatic), 5.873 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1 Hz, H-2^4), 5.329 (s, 1 H, hhw 4.9 Hz, H-$2^{4'}$), 5.193 and 5.188 (2 d, 2 H, $J_{1,2}$ 8.2 Hz, H-$1^{2,9}$), 5.152 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^4), 4.951 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^1), 4.950 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-$1^{4'}$), 3.645 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2^3), 3.337 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.6 Hz, H-3^3), 2.586 (m, 1 H, H-5^3), and 2.320 and 1.636 (2 s, 6 H, $COCH_3$ × 2).

Anal. Calc. for $C_{162}H_{159}N_3O_{26}\cdot 0.5\ H_2O$: C, 71.19; H, 5.90; N, 1.54. Found: C, 70.78; H, 6.06; N, 1.89.

Glycosylation of alcohol **27** *with thioglycoside* **5**. — To a stirred mixture of 4A molecular sieves (80 mg), $CuBr_2$ (9.5 mg, 44 μmol) and Bu_4NBr (13 mg, 41 μmol) in 5:1 $(ClCH_2)_2$–DMF (0.2 mL) was added a solution of compound **27** (4.1 mg, 1.5 μmol) in 5:1 $(ClCH_2)_2$–DMF (0.3 mL) and a solution of compound **5** (11 mg, 23 μmol) in 5:1 $(ClCH_2)_2$–DMF (0.1 mL) at 20° under Ar. After stirring for 48 h at 20°, the mixture was diluted with $(ClCH_2)_2$ and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl and dried ($MgSO_4$). The solvents were then evaporated *in vacuo*. The residue was chromatographed on Bio-Beads S-X3 (37 mL) in toluene and then purified by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 1:1 hexane–EtOAc to give benzyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-[(3,4,6-tri-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)]-*O*-[(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)]-*O*-(2-*O*-benzyl-β-D-mannopyranosyl-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside **28** (3.6 mg, 77%) and recovered **27** (0.5 mg, 12%).

Compound **28** had $[\alpha]_D$ +10.1° (*c* 0.2); R_F 0.37 (5:4 hexane–EtOAc); n.m.r. data: δ_H 7.8–6.5 (m, 97 H, aromatic), 5.843 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.1 H, H-2^4), 5.332 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^2), 5.324 (s, 1 H, H-$2^{4'}$), 5.181 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1^9), 5.158 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^4), 4.954 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-$1^{4'}$), 4.899 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1^1), 3.345 (dd, 1 H, $J_{2,3}$ 2.8, $J_{3,4}$ 10.1 Hz, H-3^3), 2.585 (ddd, 1 H, $J_{4,5}$ 9.5, $J_{5,6}$ 1.5, $J_{5,6'}$ 3.1 Hz, H-5^3), 2.308 and 1.602 (2 s, 6 H, $COCH_3$ × 2), and 0.933 (d, 3 H, $J_{5,6}$ 6.7 Hz, H-6^F).

Conversion of compound **25** *into free glycopentaose* **34** *via* **29** *and* **30**. — A solution of compound **25** (4.1 mg, 1.7 μmol) in 10:1 EtOH–$NH_2NH_2\cdot H_2O$ (0.55 mL) was stirred for 24 h at 80°, at the end of which time, it was concentrated *in vacuo*. The residue was co-evaporated with toluene–EtOH several times and then dissolved in 1:1 pyridine–Ac_2O (0.6 mL) containing DMAP (1 mg). After stirring for 24 h at 20°, the mixture was concentrated, with co-evaporation of the remaining volatiles with toluene–EtOH. The residue was purified by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 40:1 $CHCl_3$–EtOH to give **29** (2.5 mg, 68%); $[\alpha]_D$ −10.8° (*c* 0.3), R_F 0.39 (30:1 $CHCl_3$–EtOH); n.m.r. data: δ_H 7.5–7.1 (m, 55 H, 11 Ph), 6.802 (d, 1 H, *J* 9.5 Hz, N*H*Ac), 6.697 and 6.621 (2 d, 4 H, *J* 9.2 Hz, C_6H_4OMe), 6.124 (d, 1 H, *J* 8.2 Hz, N*H*Ac), 5.334 (s, 1 H, hhw 5 Hz, H-$2^{4'}$), 5.021 (d, 1 H, *J* 8.2 Hz, N*H*Ac), 4.883 (s, hhw 2,5 Hz, H-$1^{4'}$), 3.734 (s, 3 H, OCH_3), 2.001, 1.950, 1.915, 1.763, and 1.582 (5 s, 15 H, $COCH_3$ × 5).

To a solution of compound **29** (2.5 mg, 12 μmol) in 8:1 CH_3CN–H_2O (0.9 mL) was added $(NH_4)_2Ce(NO_3)_6$ (4.2 mg, 7.7 μmol) at −5°. After stirring for 2 h at −5°, the

mixture was diluted with EtOAc and washed with aq. $NaHCO_3$ and aq. NaCl. The organic layer was dried ($MgSO_4$), and the solvent was evaporated *in vacuo* to give crude **30**, R_F 0.27 (30:1 $CHCl_3$–EtOH), that was dissolved in 0.02M NaOMe–MeOH (1 mL). After stirring for 16 h at 20°, t.l.c. examination revealed a new spot at R_F 0.21 (30:1 $CHCl_3$–EtOH). The mixture was neutralized with Amberlyst-15 [H^+] resin and filtered through Celite. The filtrate was concentrated *in vacuo*. A mixture of the residue and 10% Pd–C (3.0 mg) in MeOH (1 mL) was stirred under H_2 for 2 days at 20°, then for 1 h at 50°. The mixture was diluted with MeOH and filtered through Celite. The filtrate was concentrated *in vacuo*. The residue was purified by successive chromatography on Sephadex G-25 (30 mL) and Bio Gel P-4 (20 mL) using H_2O to give **34** (0.7 mg, 66%), $[\alpha]_D$ +3° (*c* 0.07, H_2O); R_F 0.50 (100:30:10:10:3 EtOH–H_2O–BuOH–pyridine–AcOH); for ^{1}H-n.m.r. data: see Table I.

Conversion of compound **26** *into free glycohexaose* **35** *via* **31** *and* **32**. — A solution of compound **26** (2.5 mg, 0.88 μmol) in 5:1 EtOH–$NH_2NH_2 \cdot H_2O$ (0.6 mL) was stirred for 24 h at 80° and then evaporated to dryness. The remaining volatiles were co-evaporated with toluene–EtOH *in vacuo*. The residue was dissolved in 1:1 pyridine–Ac_2O (0.3 mL) containing DMAP (0.5 mg), and the solution was stirred for 24 h at 20°. After evaporation of the solvent *in vacuo*, the residue was chromatographed successively on Bio-Beads S-X4 (30 mL) and S-X3 (30 mL) in toluene, and further purified by h.p.l.c. on a Senshu Pak SSC-Silica-4301-N column (10 × 300 mm) using 40:1 $CHCl_3$–EtOH to give **31** (1.6 mg, 70%): $[\alpha]_D$ −6.7° (*c* 0.2); R_F 0.49 (30:1 $CHCl_3$–EtOH); n.m.r. data: δ_H 7.3–7.0 (m, 70 H, 14 Ph), 6.880 (d, 1 H, *J* 9.0 Hz, N*H*Ac), 6.693 and 6.622 (2 d, 4 H, *J* 9.2 Hz, C_6H_4OMe), 6.075 (d, 1 H, *J* 9.5 Hz, N*H*Ac), 5.770 (s, 1 H, hhw 5 Hz, H-2^4), 5.335 (s, 1 H, hhw 5 Hz, H-2$^{4'}$), 5.278 (s, 1 H, H-1^4), 4.955 (d, 1 H, 9.5 Hz, N*H*Ac), 4.848 (s, 1 H, H-1$^{4'}$), 3.728 (s, 3 H, OCH_3), 2.192, 1.979 (6 H), 1.787, and 1.599 (4 s, 15 H, COCH_3 × 5).

A solution of compound **31** (1.6 mg, 0.62 μmol) in 0.02M NaOMe–MeOH (1 mL) was stirred for 20 h at 20°, then neutralized with Amberlyst-15 [H^+] resin and filtered through Celite. The filtrate was concentrated *in vacuo* to give **32**, R_F 0.41 (30:1 $CHCl_3$–EtOH). To a solution of **32** in 8:1 CH_3CN–H_2O (1 mL) was added $(NH_4)_2Ce(NO_3)_6$ (8 mg, 15 μmol) at −5°. After stirring for 1.5 h, the mixture was processed as described above. A mixture of the product, R_F 0.24 (30:1 $CHCl_3$–EtOH), and 10% Pd–C (3 mg) in MeOH (1 mL) was stirred under H_2 for 16 h at 20°, and then for 1 h at 50°. Work-up as usual afforded a crude product which was purified by Bio Gel P-4 (20 mL) in H_2O to give **35** (0.6 mg, 84%): $[\alpha]_D$ +9° (*c* 0.06, H_2O); R_F 0.48 (100:30:10:10:3 EtOH–H_2O–BuOH–pyridine–AcOH); for ^{1}H-n.m.r. data: see Table I.

Conversion of **28** *into free glycoheptaose* **2** *via* **33**. — A solution of compound **28** (3.0 mg, 0.96 μmol) in 10:1 EtOH–$NH_2NH_2 \cdot H_2O$ (0.2 mL) was stirred for 24 h at 80°, at the end of which time, it was concentrated *in vacuo*. The residue was dissolved in 1:1 Ac_2O–pyridine (1.0 mL) containing DMAP (0.5 mg). The solution was stirred for 24 h at 20°, and the solvent was evaporated. The residual volatiles were co-evaporated with toluene–EtOH. The residue was purified by h.p.l.c. on a Hitachi GL-P-220 column (2 ×

60 cm) in $CHCl_3$ to give **33** (2.6 mg, 96%): $[\alpha]_D$ −18° (*c* 0.3); R_F 0.48 (30:1 $CHCl_3$–EtOH); n.m.r. data: δ_H 7.5–6.9 (m, 85 H, 17 Ph), 6.412 (d, 1 H, *J* 9.0 Hz, N*H*Ac), 6.061 (d, 1 H, *J* 9.5 Hz, N*H*Ac), 5.765 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.5 Hz, H-2^4), 5.327 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.5 Hz, H-2$^{4'}$), 5.280 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^4), 5.030 (d, 1 H, *J* 8.5 Hz, N*H*Ac), 2.181, 1.954, 1.904, 1.769, and 1.589 (5 s, 15 H, COCH_3), and 0.902 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6^F).

A solution of compound **33** (2.7 mg, 0.94 μmol) in 0.02M NaOMe–MeOH (1 mL) was stirred for 48 h at 20°, neutralized with Amberlyst-15 [H^+] resin, and filtered through Celite. The filtrate was concentrated *in vacuo*. A mixture of the residue, R_F 0.34 (30:1 $CHCl_3$–EtOH), and 10% Pd–C (4 mg) in MeOH (1 mL) was stirred under H_2 for 16 h at 20° and for 1 h at 50°. The mixture was processed as previously described, and the product was purified by Sephadex G-25 (28 mL) using H_2O as the eluent to give **2** (1.1 mg, 96%); R_F 0.35 (100:30:10:10:3 EtOH–H_2O–BuOH–pyridine–AcOH); for ^{1}H-n.m.r. data, see Table I.

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