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TOTAL SYNTHESIS OF THE MOLLU-SERIES GLYCOSYL CERAMIDES α-D-Man*p*-(1→3)-β-D-Man*p*-(1→4)-β-D-Glc*p*-(1→1)-Cer AND α-D-Man*p*-(1→3)-[β-D-Xyl*p*-(1→2)]-β-D-Man*p*-(1→4)-β-D-Glc*p*-(1→1)-Cer*

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ABSTRACT

The mollu-series glycosphingolipids, *O*-α-D-mannopyranosyl-(1→3)-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-2-*N*-tetracosanoyl-(4*E*)-sphingenine and *O*-α-D-mannopyranosyl-(1→3)-*O*-[β-D-xylopyranosyl-(1→2)]-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-2-*N*-tetracosanoyl-(4*E*)-sphingenine, were synthesized for the first time by using 2,3,4-tri-*O*-acetyl-D-xylopyranosyl trichloroacetimidate, methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside, benzyl *O*-(4,6-di-*O*-benzyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside **9**, and (2*S*,3*R*,4*E*)-2-azido-3-*O*-(*tert*-butyldiphenylsilyl)-4-octadecene-1,3-diol **6** as the key intermediates. The hexa-*O*-benzyl disaccharide **9** was prepared by coupling two monosaccharide synthons, namely, 2,3-di-*O*-allyl-4,6-di-*O*-benzyl-α-D-mannopyranosyl bromide and benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside. It was demonstrated that azide **6** was highly efficient as a synthon for the ceramide part in the coupling with both glycotriaosyl and glycotetraosyl donors, particularly in the presence of trimethylsilyl triflate.

INTRODUCTION

Glycosphingolipids such as **1** and **2** were recently isolated from hepatopancreas[2], spermatozoa[3], and ova[4] of *Hyriopsis schlegelii*, and classified as mollu series glycosphingolipids[5]. The biological function of these glycosphingolipids in fresh water bivalves remains to be elucidated, but studies should be facilitated by the availability of synthetic samples. As part of our project on the synthesis of mannose-containing glycosphingolipids[6], we describe here stereocontrolled total syntheses of glycolipids **1** and **2**.

RESULTS AND DISCUSSION

Based upon retrosynthetic analysis, a synthetic plan for the target compounds

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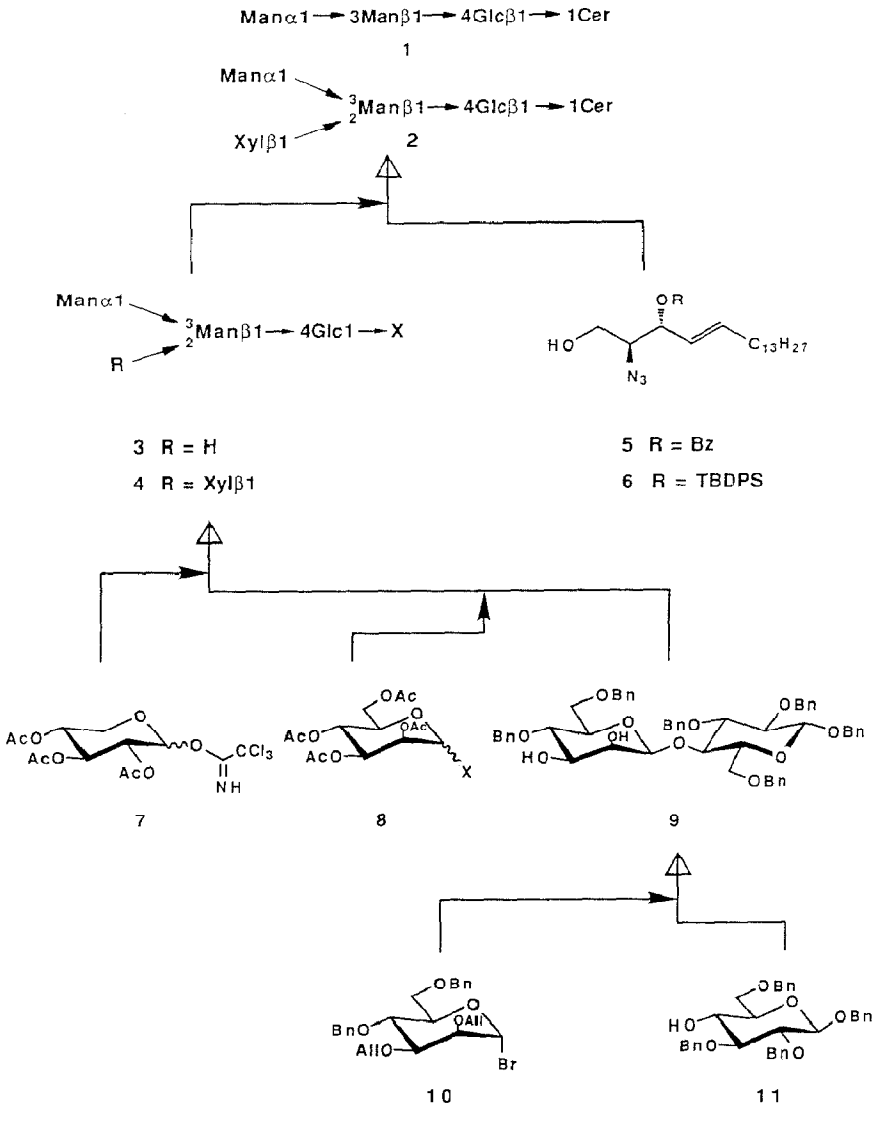
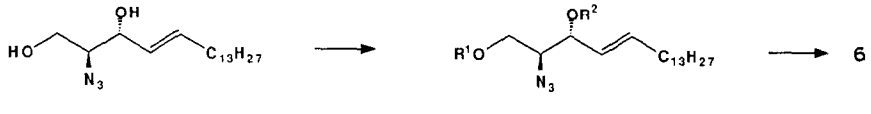


Scheme 1 { Bz = COPh, Bn = CH_2Ph
TBDPS = $SiBu^tPh_2$, All = CH_2-CH=CH_2

1 and **2** was designed as shown in Scheme 1. Synthons **5** and **6** were employed for the ceramide portion of **1** and **2** because of the high efficiency[7] previously observed in related couplings with glycosyl donors. Compound **5** was already known[7], and compound **6** was readily prepared as shown in Scheme 2.

The glycobiosyl synthon **9** was obtained from a mannosyl synthon **10** and a glucosyl synthon **11**. An immediate precursor **21** for the mannosyl synthon **10** was readily prepared in 6 steps from compound **15**, in 40% overall yield, via **16**, **17**, **18**,

19, and **20**. This sequence resulted from successive treatments with i) 2,2-dimethoxypropane and pyridinium *p*-toluenesulfonate in *N,N*-dimethylformamide(DMF)–acetone; ii) allyl bromide–tetrabutylammonium iodide–sodium hydride in DMF; iii) 67% aqueous acetic acid; iv) benzyl bromide–tetrabutylammonium iodide–sodium hydride in DMF; v) zinc in acetic acid–oxolane; and



12

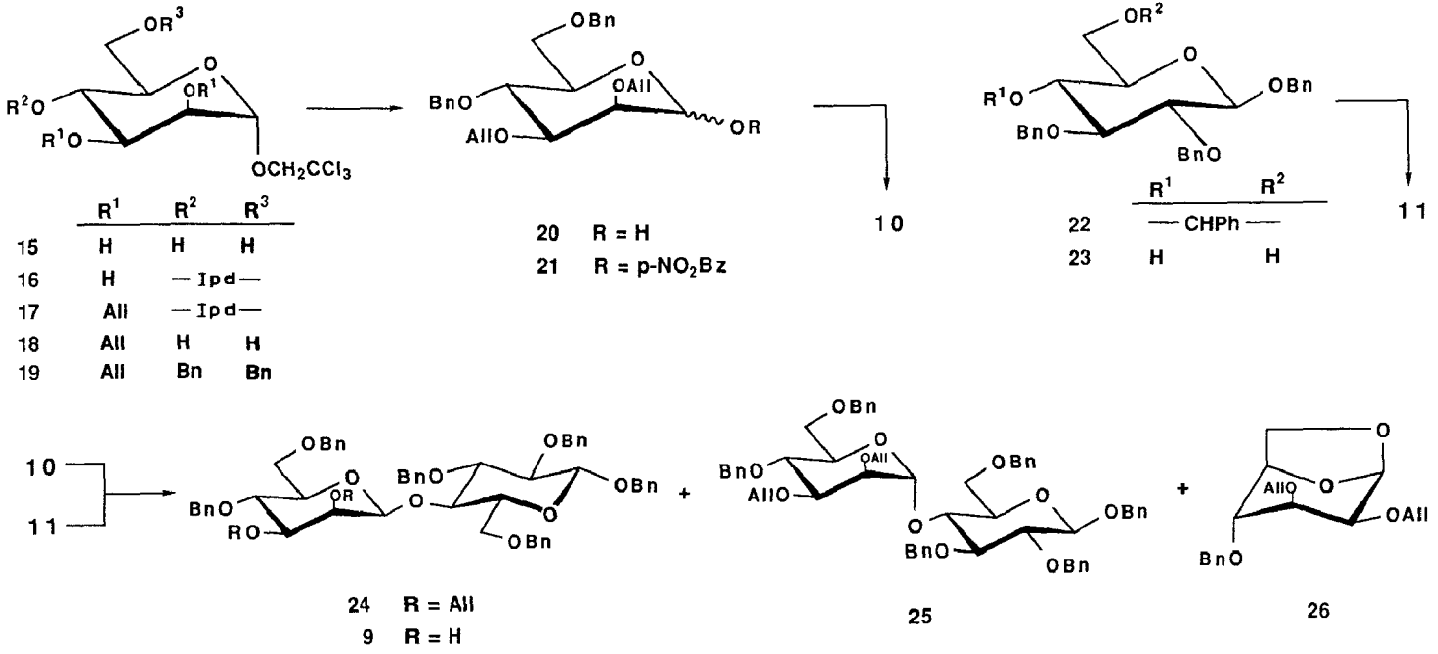
	R^1	R^2
13	Tr	H
14	Tr	TBDPS

Scheme 2

vi) 4-nitrobenzoyl chloride in pyridine. It is to be noted that both the allylation of diol **16** and the benzylation of diol **18** could only be achieved efficiently at −20° by using either allyl bromide or benzyl bromide and sodium hydride in the presence of added tetrabutylammonium iodide. The known glucosyl synthon **11** (ref. 8) was prepared from the benzylidene derivative **22** (ref. 9) via compound **23**, in 68% yield, by sequential treatment with aqueous acetic acid, bis(tributyltin) oxide[10], and benzyl bromide[11]. The conversion of compound **21** into the bromide **10** by treatment with hydrogen bromide and the subsequent reaction of **10** with the glycosyl acceptor **11** in the presence of silver silicate according to Paulsen *et al.*[12] afforded a 77% yield of a mixture of the desired β-(1→4)-linked product **24** and its α anomer **25** in a ratio of 1.1:1, together with 11% of the 1,6-anhydro derivative **26**. Configurations at C-1b for **24** and **25** were assigned as β-D and α-D, respectively, from the ^{13}C-n.m.r. spectra[13], which contained signals for C-1b at δ 100.6 with $^1J_{C,H}$ 154 Hz for compound **24** and at δ 100.4 with $^1J_{C,H}$ 171 Hz for compound **25**. The deallylation of **24** to compound **9** was smoothly achieved in 87% yield in two steps: i) Wilkinson's catalyst and 1,4-diazabicyclo[2.2.2]octane[14] in acetonitrile–ethanol–water[15], and ii) mercuric oxide–mercuric chloride in aqueous acetone[16]. An attempted deallylation of **24** to **9** by a palladium(II) chloride-mediated procedure gave only inferior results.

The monoglycosylation of the diol **9** was then examined, using the mannosyl donors **27** (ref. 17) and **28**. Cupric bromide–tetrabutylammonium bromide–silver triflate-promoted[18] coupling of **9** with the thioglycoside **27** in 1,2-dichloroethane gave the best result, affording a 67% yield of a 3:2 mixture of trisaccharides **29** and **31**. On the other hand, boron trifluoride etherate promoted glycosylation of **9** with the trichloroacetimidate **28** in 1,2-dichloroethane according to Schmidt[19] afforded a 90% yield of 1:3.1 mixture of **29** and **31**. Use of the conventional glycosyl halides in place of **27** or **28** did not improve the regioselectivity of the glycosylation in favor of O-3 (formation of **29**).

The positions of the new linkages were assigned by conversion of the tri-



	R^1	R^2	R^3
15	H	H	H
16	H	—Ipd—	
17	All	—Ipd—	
18	All	H	H
19	All	Bn	Bn

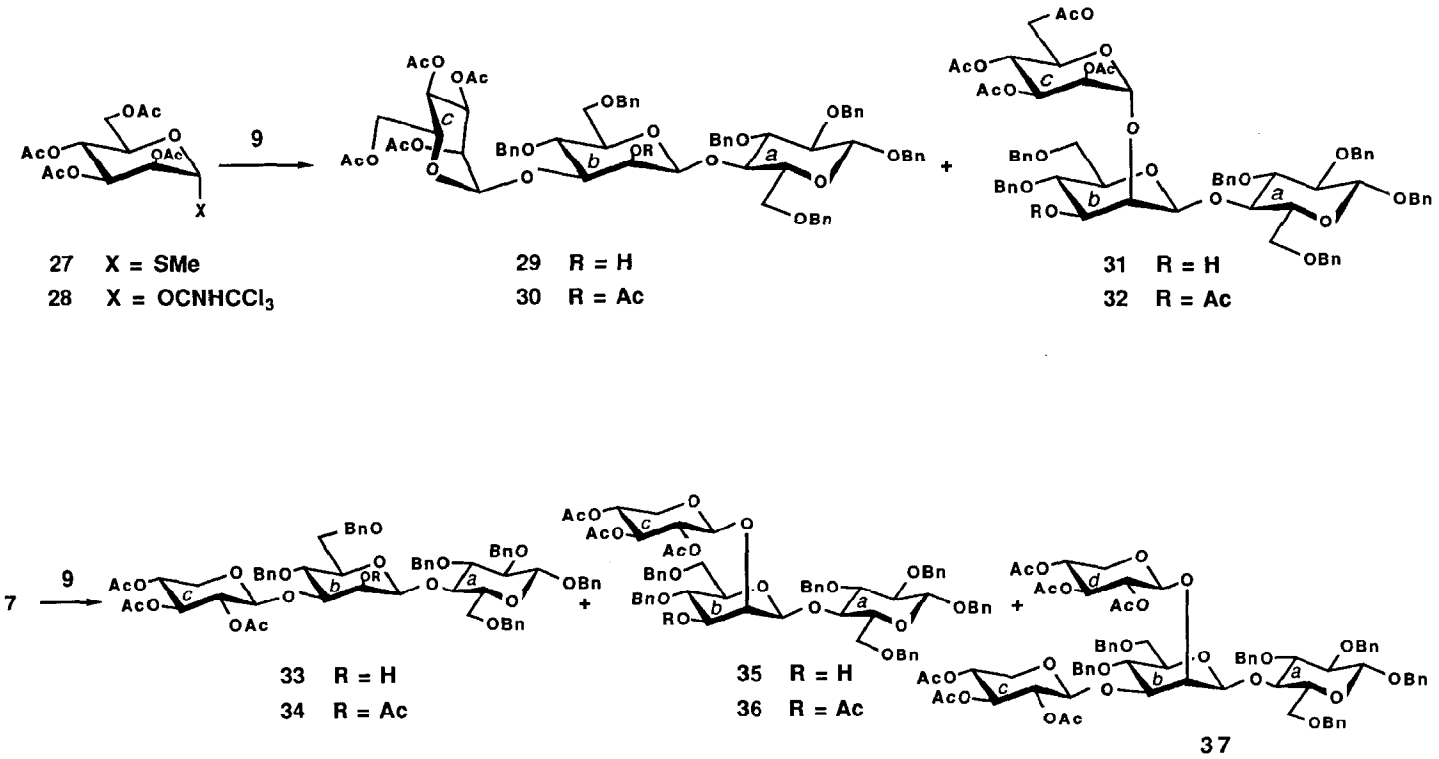
20 R = H
21 R = p-NO_2Bz

	R^1	R^2
22	—CHPh—	
23	H	H

24 R = All
9 R = H

25

26


9
27 X = SMe
28 X = OCNHCCl3
29 R = H
30 R = Ac
31 R = H
32 R = Ac
7
9
33 R = H
34 R = Ac
35 R = H
36 R = Ac
37

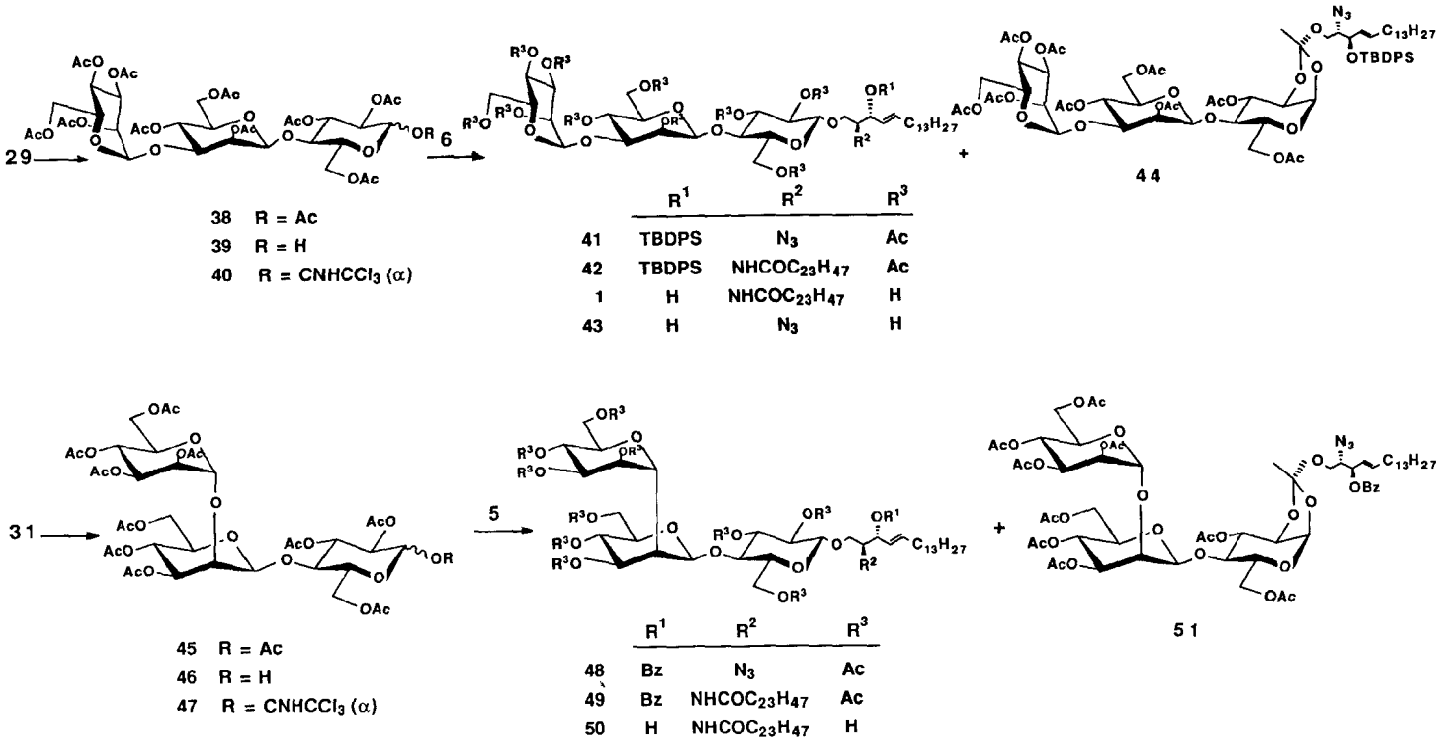
Scheme 4

saccharides into the acetates **30** and **32**. The ^{1}H-n.m.r. spectrum of compound **30** showed a deshielded signal for H-2b at δ 5.646 as a doublet with a $^3J_{2,3}$ value of 2.9 Hz, and for compound **32** a deshielded signal for H-3b at δ 4.857 as a double doublet with the $^3J_{2,3}$ and $^3J_{3,4}$ values of 2.8 and 10.0 Hz. The α configurations at C-1c for the trisaccharides **29** and **31** were evident from the mode of glycosylation, which employed the mannosyl donors **27** and **28** having a participating group at O-2, and confirmed by their ^{13}C-n.m.r. spectra, which contained signals for C-1c at δ 99.5 with a $^1J_{C,H}$ value of 175 Hz for compound **29** and at δ 98.4 with a $^1J_{C,H}$ value of 179 Hz for compound **31**.

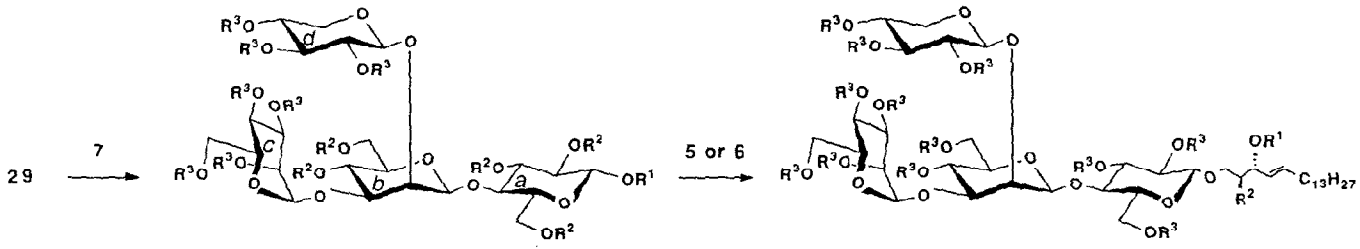
Since the imidate procedure for the coupling of a mannopyranosyl residue to diol **9** favored O-2 over O-3 by a ratio of 3:1, the substitution of a xylopyranosyl residue onto **9** by the imidate approach was next examined, with the expectation that the 1→2 linked trisaccharide **35** might be the major product. However, boron trifluoride etherate-promoted glycosylation of compound **9** with the imidate **7** showed no regioselectivity, but gave in 95% yield a 1.4:1.3:1 mixture of the products **33**, **35**, and **37**. The regiochemistry of the trisaccharides **33** and **35** was assigned on the basis of the ^{1}H-n.m.r. data of the acetate **34** (obtained from compound **33**), which showed a deshielded signal for H-2b at δ 5.284 as a doublet with a $^3J_{2,3}$ value of 2.6 Hz. The configuration at the newly introduced anomeric carbon atom (C-1c) of compound **33** was assigned as β-D- from the ^{1}H-n.m.r. spectrum, which showed a signal for H-1c at δ 4.337 as a doublet with a $^3J_{1,2}$ value of 6.9 Hz. The configuration at C-1c of compound **35** was also assigned as β-D- because the ^{13}C-n.m.r. spectrum showed signals for three anomeric carbon atoms at 102.5, 100.5, and 100.0 with $^1J_{C,H}$ values of 153–161 Hz.

The configurations at both C-1c and C-1d in compound **37** were expected to be β-D because of the presence of an acetyl group as a stereocontrolling auxiliary on O-2 of the glycosyl donor **7**. The ^{13}C-n.m.r. spectrum of **37**, however, revealed besides three signals at δ 102.5, 100.4, and 99.3 with $^1J_{C,H}$ values of 154 to 161 Hz that were assignable to three anomeric carbon atoms having the β-D configuration, a signal for an anomeric carbon atom at δ 95.3 with a $^1J_{C,H}$ value of 173 Hz. This could be rationalized as indicating that one β-xylopyranosyl residue in **37** had assumed the $^1C_4$ conformation. Further evidence was obtained by the deprotection of compound **37**, which smoothly afforded the free tetrasaccharide β-D-Xyl-(1→3)-[β-D-Xyl-(1→2)]-β-D-Man-(1→4)-D-Glc. The β-D configurations for the two xylopyranosyl residues were firmly assigned according to ^{1}H-n.m.r. data which showed a pair of doublets for H-1d at δ 4.610 and 4.582 with a $^3J_{1,2}$ value of 7.6 Hz, corresponding to the α-D and β-D configurations at C-1a, and a doublet for H-1c at δ 4.528 with $^3J_{1,2}$ value of 7.3 Hz.

To achieve a total synthesis of the target compound **1**, the conversion of trisaccharide **29** into the glycosyl donor **40** was performed in a conventional manner. First, hydrogenolysis of compound **29** in the presence of 10% Pd–C in methanol and subsequent acetylation gave an 81% yield of the completely acetylated product **38** as a 1:1 mixture of α and β-anomers at C-1a. This was further treated with


29
6
38 R = Ac
39 R = H
40 R = CNHCCl3 (α)
44
41 TBDPS N3 Ac
42 TBDPS NHCOC23H47 Ac
1 H NHCOC23H47 H
43 H N3 H
31
5
45 R = Ac
46 R = H
47 R = CNHCCl3 (α)
51
48 Bz N3 Ac
49 Bz NHCOC23H47 Ac
50 H NHCOC23H47 H

Scheme 5



	R^1	R^2	R^3
52	Bn	Bn	Ac
53	H	H	H
54	Ac	Ac	Ac
55	H	Ac	Ac
56	$CNHCCl_3$ (α)	Ac	Ac

	R^1	R^2	R^3
57	TBDPS	N_3	Ac
58	TBDPS	$NHCOC_{23}H_{47}$	Ac
2	H	$NHCOC_{23}H_{47}$	H
59	Bz	N_3	Ac
60	H	N_3	H

Scheme 6

hydrazine acetate according to Excoffier *et al.*[20] to yield 86% of hemiacetal **39**. Then, treatment of compound **39** with trichloroacetonitrile[19] in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) afforded an 88% yield of the α-imidate **40**. Boron trifluoride etherate-promoted glycosylation of acceptor **6** with **40** in 1,2-dichloroethane gave an orthoester (**44**) as the major product (59% yield), as well as the desired product **41** in 5% yield. However, when the orthoester **44** was treated with trimethylsilyl triflate[21] at 0°, compound **41** was formed in 40% yield. The choice of the promoter was crucial for this glycosylation. The use of trimethylsilyl triflate in place of boron trifluoride etherate gave the desired coupling product **41** directly in 51% yield from the imidate **40** and the glycosyl acceptor **6**. The configuration at C-1a of compound **41** was assigned from its ^{1}H-n.m.r. spectrum, which contained a signal for H-1a at δ 4.335 as a doublet with a $^3J_{1,2}$ value of 7.8 Hz. The structure of compound **41** was further confirmed by deprotection to **43**, the ^{1}H-n.m.r. spectrum of which showed three signals for three anomeric protons. These were at δ 4.920, doublet with a $^3J_{1,2}$ value of 1.7 Hz for H-1c, δ 4.560, singlet for H-1b, and δ 4.222, doublet with $^3J_{1,2}$ 7.8 Hz for H-1a.

The transformation of compound **41** into the target **1** was achieved via **42** in 34% overall yield as previously described for related compounds[7]. The azido group was reduced in the presence of Lindlar catalyst[22], and the resulting amino group was acylated with tetracosanoic acid, 2-chloro-2-methylpyridinium iodide, and tributylamine according to the Mukaiyama procedure[23] to give the fully protected hexotriaosyl ceramide **42**. Deprotection of compound **42** afforded the target glycosyl ceramide **1**.

As for the regioisomeric trisaccharide **31**, conversion into the imidate **47** was performed in four steps in 83% overall yield in the same way as discussed for the imidate **40**. Coupling of the imidate **47** with the benzoate **5** in the presence of boron trifluoride etherate gave a 32% yield of the desired compound **48**, along with a 10% yield of the orthoester **51**. Compound **48** was then converted into hexotriaosyl ceramide **50**, an isomer of the target **1**, in 24% overall yield.

The introduction of a β-D-xylopyranosyl residue into the partially protected trisaccharide **29** was achieved by the use of imidate **7** in the presence of boron trifluoride etherate to afford a 60% yield of the fully protected tetrasaccharide **52**. The presence of a xylosyl residue was evident from the ^{13}C-n.m.r. data, which revealed four signals for four anomeric carbon atoms. The configuration at C-1d was assigned by deprotection to the free tetrasaccharide **53**. The ^{1}H-n.m.r. spectrum of **53** in D_2O contained two signals for H-1d at δ 4.521 and 4.496, as a pair of doublets with $^3J_{1,2}$ values of 7.6 Hz, corresponding to the α-D- and β-D-configuration at the reducing end (C-1a).

The conversion of compound **52** into the imidate **56** was accomplished as discussed above for the imidates **40** and **47**, in four steps in 64% overall yield. The crucial coupling between the imidate **56** and acceptors **5** and **6** was performed in the presence of trimethylsilyl triflate, to give the fully protected products **57** and **59** in 68 and 64% yields, respectively. Finally, compound **57** was converted into the

target glycotetraosyl ceramide **2** via **58** in 32% overall yield. Compound **59** was transformed into the corresponding deblocked compound (**60**) and the structure was confirmed by ^{1}H-n.m.r. data.

The results discussed above demonstrated that trimethylsilyl triflate was superior to boron trifluoride etherate as a catalyst for the crucial coupling between the glycosyl imidates and glycosyl acceptors **5** and **6**. Since good agreement was observed between the ^{1}H-n.m.r. data for synthetic **1** and **2** with those for natural **1** and **2** (ref. 3), as well as data for related glycosphingolipids[24], the synthetic evidence, provided here for the first time, strongly supports the structures assigned to these mollu-series glycosphingolipids.

EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Ordinary column chromatography was performed on Silica Gel (Merck 70–230 mesh). For flash chromatography, columns of Wako-gel C-300 (200–300 mesh) were used. T.l.c. and high-performance (h.p.) t.l.c. were performed on Silica Gel 60 F_{254} (Merck). Molecular sieves were purchased from Nakarai Chemicals. N.m.r. spectra were recorded with JEOL GX400 (^{1}H, 400 MHz) and FX90Q (^{13}C, 22.50 MHz) spectrometers. Values of δ_C and δ_H are expressed in p.p.m. downfield from the signal for Me_4Si, measured directly for solutions in $CDCl_3$. For solutions in D_2O, δ_H was measured from internal Me_2CO (2.225 p.p.m.) or Me_3COH (1.230 p.p.m.), and δ_C from internal dioxane (67.4 p.p.m.) or MeOH (49.8 p.p.m.), respectively.

(2S,3R,4E)-2-azido-1-O-trityl-4-octadecene-1,3-diol (**13**). — A solution of compound[24a] **12** (107 mg, 330 μmol) and trityl chloride (109 mg, 390 μmol) in pyridine (2.0 mL) was stirred for 60 h at 20°, then for 14 h at 65° under argon, and diluted with EtOAc (80 mL). The solution was washed with aqueous $NaHCO_3$, aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 in 90:10:1 hexane–EtOAc–Et_3N and coevaporation of the fractions with toluene gave **13** (149 mg, 82%); $[\alpha]_D$ +6.6° (*c* 1.5); R_F 0.23 in 10:1 hexane–EtOAc; n.m.r. data: δ_H 7.5–7.2 (m, 15 H, Ph-H), 5.649 (td, 1 H, *J* 6.8, 15.4 Hz, H-5), 5.318 (dd, 1 H, *J* 7.2, 15.4 Hz, H-4), 4.192 (t, 1 H, *J* 5.6 Hz, H-3), 3.525 (q, 1 H, *J* 5.6 Hz, H-2), 3.314 (dd, 1 H, *J* 5.6, 12.0 Hz, H-1), 3.284 (dd, 1 H, *J* 5.6, 12.0 Hz, H-1′), 1.945 (q, 2 H, *J* 6.8 Hz, H-6), and 0.880 (t, 3 H, *J* 7.0 Hz, CH_2CH_3).

Anal. Calc. for $C_{37}H_{49}N_3O_2 \cdot 0.5\ C_6H_5CH_3$: C, 79.24; H, 8.87; N, 6.85. Found: C, 79.20; H, 8.81; N, 6.98.

(2S,3R,4E)-2-Azido-3-O-(tert-butyldiphenylsilyl)-4-octadecene-1,3-diol (**6**). — To a mixture of compound **13** (969 mg, 1.71 mmol) and imidazole (178 mg, 2.61 mmol) in *N,N*-dimethylformamide (DMF, 3 mL) was added a solution of *t*-$BuPh_2SiCl$ (790 μL, 3.1 mmol) in DMF (7 mL). The mixture was stirred for 44 h

at 20°, and diluted with Et_2O. The solution was washed with H_2O, dried ($MgSO_4$), and evaporated *in vacuo* to give crude **14**; R_F 0.72 in 10:1 hexane–EtOAc. A solution[25] of the compound in 3:2 HCOOH–Et_2O (2 mL) was stirred for 20 min at 20°, then diluted with EtOAc. The organic layer was washed with aqueous $NaHCO_3$, water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 5:1 hexane–Et_2O to give **6** (630 mg, 66%); $[\alpha]_D$ −65.8° (*c* 1.0); R_F 0.26 in 5:1 hexane–Et_2O; n.m.r. data: δ_H 7.75–7.6 (m, 4 H, Ph-H), 7.5–7.3 (m, 6 H, Ph-H), 5.421 (dd, 1 H, *J* 8.3, 15.4 Hz, H-4), 5.161 (td, 1 H, *J* 6.6, 15.4 Hz, H-5), 4.171 (dd, 1 H, *J* 4.1, 8.3 Hz, H-3), 3.583 (dd, 1 H, *J* 4.1, 7.5 Hz, H-2), 1.065 [s, 9 H, $C(CH_3)_3$], 0.882 (t, 3 H, *J* 6.6 Hz, CH_2CH_3).

Anal. Calc. for $C_{34}H_{53}N_3O_2Si$: C, 72.42; H, 9.47; N, 7.45. Found: C, 72.47; H, 9.47; N, 7.41.

2,2,2-Trichloroethyl 4,6-O-isopropylidene-α-D-mannopyranoside (**16**). — To an ice-cold solution of compound[6] **15** (13.35 g, 42.8 mmol) and 2,2-dimethoxypropane (DMP; 13.3 mL, 108 mmol), in DMF (207 mL)–acetone (68 mL) was added pyridinium *p*-toluenesulfonate[26] (PPTS, 747 mg). The mixture was stirred for 4 days at 5°, with the addition of further DMP (4.2 mL) at every 24 h interval. The reaction mixture was treated with Amberlite IRA 400, filtered through Celite, and evaporated *in vacuo*. The residue was crystallized from Et_2O–hexane to give **16** (12.8 g, 85%); m.p. 124–125°, $[\alpha]_D$ +57.4° (*c* 1.0, MeOH); R_F 0.31 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 5.116 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 4.239 (d, 1 H, *J* 11.2 Hz, CH_2CCl_3), 4.209 (m, 1 H, H-2), 4.112 (d, 1 H, *J* 11.2 Hz, CH_2CCl_3), 1.535 (s, 3 H, CCH_3), 1.435 (s, 3 H, CCH_3).

Anal. Calc. for $C_{11}H_{17}O_6Cl_3$: C, 37.58; H, 4.87. Found: C, 37.68; H, 4.95.

Acetylation of **16** gave a diacetate; n.m.r. data: δ_H 5.448 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.7 Hz, H-2), 5.303 (dd, 1 H, $J_{2,3}$ 3.7 Hz, $J_{3,4}$ 10.3 Hz, H-3), 5.011 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.232 (d, 1 H, *J* 11.5 Hz, CH_2CCl_3), 4.122 (d, 1 H, *J* 11.5 Hz, CH_2CCl_3), 4.070 (t, 1 H, *J* 10.5 Hz, H-4), 2.180, 2.043 (2 s, 6 H, $COCH_3$), 1.538, and 1.406 (2 s, 6 H, CCH_3).

2,2,2-Trichloroethyl 2,3-di-O-allyl-4,6-O-isopropylidene-α-D-mannopyranoside (**17**). — To a stirred mixture of compound **16** (12.0 g, 34.1 mmol), allyl bromide (58.8 mL, 682 mmol) and Bu_4NI (1.17 g, 3 mmol) in DMF (200 mL) was added NaH (60%, 3.26 g, 82 mmol) portionwise at −20 to −25° (dry ice–CCl_4 bath). The mixture was stirred for 4.5 h at −20 to −25°, and methanol was added dropwise to destroy the excess NaH. The mixture was diluted with Et_2O, washed with water, dried ($MgSO_4$), and evaporated *in vacuo*. Chromatography of the residue on SiO_2 in 12:1 toluene–EtOAc gave **17** (13.1 g, 89%); $[\alpha]_D$ +67.1° (*c* 1.4); R_F 0.38 in 12:1 toluene–EtOAc; n.m.r. data: δ_H 5.99–5.86 (m, 2 H, $CH_2CH{=}CH_2$), 5.053 (d, 1 H, *J* 1.5 Hz, H-1), 1.538, and 1.417 (2 s, 6 H, CCH_3).

Anal. Calc. for $C_{17}H_{25}O_6Cl_3$: C, 47.29; H, 5.84; Cl, 24.63. Found: C, 46.85; H, 5.79; Cl, 24.26.

2,2,2-Trichloroethyl 2,3-di-O-allyl-α-D-mannopyranoside (**18**). — A solution of compound **17** (3.56 g, 8.2 mmol) in 67% aqueous AcOH was stirred for 1 h at

70°, and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **18** (2.90 g, 91%); $[\alpha]_D$ +36.5° (*c* 0.8); R_F 0.25 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 6.0–5.85 (m, 2 H, $CH_2CH{=}CH_2$), 5.132 (d, 1 H, *J* 1.7 Hz, H-1).

Anal. Calc. for $C_{14}H_{21}O_6Cl_3$: C, 42.93; H, 5.40. Found: C, 42.54; H, 5.28.

*2,2,2-Trichloroethyl 2,3-di-*O*-allyl-4,6-di-*O*-benzyl-α-*D*-mannopyranoside* (**19**). — To a stirred mixture of compound **18** (2.12 g, 5.4 mmol), benzyl bromide (5.55 g, 32.5 mmol), and Bu_4NI (210 mg, 0.54 mmol) in DMF (40 mL) was added NaH (60%, 517 mg, 13 mmol) portionwise at −20° (dry ice–CCl_4 bath). Work-up as described for **17** and chromatography of the residue on SiO_2 in 2:1 toluene–EtOAc afforded **19** (2.35 g, 76%); $[\alpha]_D$ +64.2° (*c* 0.8); R_F 0.47 in 4:1 hexane–EtOAc; n.m.r. data: δ_H 6.0–5.9 (m, 2 H, CH_2-$CH{=}CH_2$), 5.135 (d, 1 H, *J* 1.8 Hz, H-1), 4.860 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.642 (d, 1 H, *J* 12.0 Hz, CH_2Ph), 4.527 (d, 1 H, *J* 12.0 Hz, CH_2Ph), 4.487 (d, 1 H, *J* 10.7 Hz, CH_2Ph), 4.219 (d, 1 H, *J* 11.6 Hz, CH_2CCl_3), 4.109 (d, 1 H, *J* 11.6 Hz, CH_2CCl_3).

Anal. Calc. for $C_{28}H_{33}O_6Cl_3$: C, 58.80; H, 5.82. Found: C, 58.78; H, 5.74.

*2,3-Di-*O*-allyl-4,6-di-*O*-benzyl-*D*-mannopyranose* (**20**). — A mixture of compound **19** (280 mg, 0.49 mmol) and Zn powder (420 mg, 6.4 mmol) in 2:5 AcOH–oxolane (7 mL) was stirred for 22 h at 20°, diluted with Et_2O, and filtered through Celite. The filtrate was washed with H_2O, aqueous $NaHCO_3$, aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 4:1 toluene–EtOAc to give **20** (174 mg, 81%); R_F 0.41 in 7:3 toluene–EtOAc; n.m.r. data: δ_H 7.4–7.2 (m, 10 H, Ph-H), and 6.02–5.88 (m, 2 H, $CH_2CH{=}CH_2$).

Anal. Calc. for $C_{26}H_{32}O_6 \cdot 0.1\ C_6H_5CH_3$: C, 71.30; H, 7.35. Found: C, 71.32; H, 7.41.

*2,3-Di-*O*-allyl-4,6-di-*O*-benzyl-*D*-mannopyranosyl p-nitrobenzoate* (**21**). — To a solution of compound **20** (3.7 g, 8.4 mmol) in pyridine (12 mL) was added *p*-nitrobenzoyl chloride (2.96 g, 16 mmol), portionwise at −5–0°. After the mixture was stirred for 2 h at 20°, water (2 mL) was added, stirring for was continued 20 min, and the mixture was diluted with EtOAc. This solution was washed with water, aqueous $NaHCO_3$, water, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 4:1 hexane–EtOAc to give **21α** (4.26 g, 86%) and **21β** (0.42 g, 8.5%).

Compound **21α** had m.p. 76–77° (EtOAc–hexane); $[\alpha]_D$ +66.5° (*c* 0.7); R_F 0.46 in 4:1 hexane–EtOAc; n.m.r. data: δ_H 8.285 (d, 2 H, *J* 8.9 Hz) and 8.158 (d, 2 H, *J* 8.9 Hz) for $COPhNO_2$, 6.463 (d, 1 H, *J* 1.9 Hz, H-1), and 6.04–5.91 (m, 2 H, CH_2-$CH{=}CH_2$).

Anal. Calc. for $C_{33}H_{35}NO_9$: C, 67.22; H, 5.98; N, 2.38. Found: C, 67.20; H, 5.91; N, 2.33.

Compound **21β** had $[\alpha]_D$ −16.9° (*c* 1.1); R_F 0.36 in 4:1 hexane–EtOAc; n.m.r. data: δ_H 5.927 (d, 1 H, *J* 1.2 Hz, H-1).

Anal. Found: C, 67.29; H, 5.90; N, 2.43.

*Benzyl 2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**11**). — A solution of com-

pound[9] **22** (660 mg, 1.2 mmol) in 80% aqueous AcOH (18 mL) was stirred for 1 h at 95°, then evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 EtOAc–toluene to give **23** (462 mg, 86%), $[\alpha]_D$ −40.3° (*c* 1.0); R_F 0.29 in 1:1 toluene–EtOAc.

A mixture of compound **23** (2.0 g, 4.4 mmol) and $(Bu_3Sn)_2O$ (2.7 g, 4.5 mmol) in toluene (80 mL) was stirred under reflux with continuous azeotropic removal of H_2O for 2 h, and then concentrated *in vacuo*. A mixture of the residue and Bu_4NBr (100 mg, 0.3 mmol) in benzyl bromide (15 mL) was stirred for 15 h at 90°, and then evaporated *in vacuo*. A solution of the residue in EtOAc was stirred with aqueous KF and filtered through Celite. The organic layer was separated, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 4:1 hexane–EtOAc to give **11** (1.9 g, 80%); m.p. 59–60° (hexane); $[\alpha]_D$ −40.3° (*c* 9.0); R_F 0.29 in 9:1 toluene–EtOAc; n.m.r. data: δ_H 7.2–7.4 (m, 20 H, Ph-H), 4.531 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1).

Anal. Calc. for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.19; H, 6.63.

Benzyl O-*(2,3-di-*O-*allyl-4,6-di-*O-*benzyl-β-* (**24**) *and -α-* (**25**) -D-*manno-pyranosyl)-(1→4)-2,3,6-tri-*O-*benzyl-β-*D-*glucopyranoside*. — To a saturated solution of HBr in CH_2Cl_2 (5 mL) was added dropwise a solution of compound **21** (10:1 mixture of α and β anomers; 1.44 g, 2.4 mmol) in CH_2Cl_2 (8 mL) at −15°. The mixture was stirred for 30 min at −15°, then hexane (4 mL) was added. This mixture was filtered through Celite and evaporated, and the residue was subjected to three additions and evaporations of benzene, to give unstable **10** (1.2 g); R_F (at −40°) 0.57 in 4:1 hexane–EtOAc. A stirred mixture of compound **11** (500 mg, 0.92 mmol), Ag silicate (2.5 g), and molecular sieves 4A (MS4A, 2.5 g) in CH_2Cl_2 (4.5 mL) was cooled to −45° (dry ice-MeCN bath), and to this was added dropwise a solution of the bromide (**10**) in CH_2Cl_2 (4.5 mL). The mixture was stirred for 15 h at 20°, diluted with EtOAc (80 mL), and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$, water, aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 9:1 toluene–EtOAc to give **24** (353 mg, 40%), **25** (329 mg, 37%), and **26** (33 mg, 4%). The use of toluene or nitromethane as the solvent for the reaction instead of CH_2Cl_2 afforded **24** and **25** in 16 and 48%, or 17 and 36% yields, respectively.

Compound **24** had $[\alpha]_D$ −8.1° (*c* 1.0); R_F 0.33 in 9:1 toluene–EtOAc; n.m.r. data: δ_H 7.5–7.0 (m, 30 H, Ph-H), 6.0–5.85 (m, 2 H, CH_2-C*H*=CH_2); δ_C 102.6 ($^1J_{C,H}$ 158 Hz, C-1a) and 100.6 ($^1J_{C,H}$ 154 Hz, C-1b).

Anal. Calc. for $C_{60}H_{66}O_{11} \cdot 0.33\ H_2O$: C, 74.36; H, 6.93. Found: C, 74.15; H, 6.76.

Compound **25** had m.p. 54–55° (toluene–hexane); $[\alpha]_D$ +4.0° (*c* 1.0); R_F 0.48 in 9:1 toluene–EtOAc; n.m.r. data: δ_H 7.5–7.0 (m, 30 H, Ph-H), 5.97–5.83 (m, 1 H, CH_2CH=CH_2), and 5.70–5.59 (m, 1 H, CH_2CH=CH_2); δ_C 102.1 ($^1J_{C,H}$ 159 Hz, C-1a) and 100.4 ($^1J_{C,H}$ 171 Hz, C-1b).

Anal. Calc. for $C_{60}H_{66}O_{11}$: C, 74.82; H, 6.91. Found: C, 74.45; H, 6.85.

Compound **26** had R_F 0.14 in 9:1 toluene–EtOAc; n.m.r. data: δ_H 7.5–7.3

(m, 5 H, Ph-H), 6.0–5.8 (m, 2 H, CH_2-C*H*=CH_2), 5.470 (s, 1 H, H-1), 5.33–5.16 (m, 4 H, CH=CH_2), 4.678 (d, 1 H, *J* 12.5 Hz, CH_2Ph), 4.640 (d, 1 H, *J* 12.5 Hz, CH_2Ph).

Benzyl O-(4,6-di-O-benzyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**9**). — A solution of compound **24** (2.6 g, 2.7 mmol) in 10:5:1 MeCN–EtOH–H_2O (180 mL) was stirred by passage of N_2 for 1 h at 70°. To this solution was then added $(Ph_3P)_3RhCl$ (849 mg, 918 μmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO; 436 mg, 3.89 mmol), and the mixture was stirred for 45 h at 85° under N_2, when t.l.c. revealed the product as a spot having R_F 0.40 in 9:1 toluene–EtOAc. The mixture was concentrated *in vacuo*, and the residual oil (4.5 g) was stirred with $HgCl_2$ (7.33 g, 27 mmol), and HgO (216 mg, 1.0 mmol) in 10:1 acetone–H_2O (125 mL) for 4 h at 25°. The suspension was filtered through Celite, the filtrate was concentrated *in vacuo*, the residue was dissolved in $CHCl_3$, and the solution was washed with 10% aqueous KI and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 7:3 toluene–EtOAc to give **9** (2.074 g, 87%); m.p. 112–113° (toluene–hexane); $[\alpha]_D$ −1.0° (*c* 1.0); R_F 0.20 in 7:3 toluene–EtOAc; n.m.r. data: δ_H 7.5–7.1 (m, 30 H, Ph-H), 4.678 (s, 1 H, H-1b), and 4.502 (d, 1 H, *J* 7.6 Hz, H-1a).

Anal. Calc. for $C_{54}H_{58}O_{11}$: C, 73.45; H, 6.62. Found: C, 73.31; H, 6.63.

Acetylation of **9** afforded a diacetate; n.m.r. data: δ_H 5.376 (d, 1 H, $J_{2,3}$ 3.1 Hz, H-2b), 4.886 (dd, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 9.8 Hz, H-3b), 4.788 (s, 1 H, H-1b), 4.460 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1a).

2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl trichloroacetimidate (**28**). — A solution of 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose[27] (3.5 g, 9 mmol) and $NH_2NH_2 \cdot AcOH$ (1.07 g, 1.7 mmol) in DMF (10 mL) was stirred for 10 min at 50° and, after cooling to 20°, diluted with EtOAc. The solution was washed with H_2O, aqueous $NaHCO_3$, aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 2:1 toluene–EtOAc to give 2,3,4,6-tetra-*O*-acetyl-D-mannopyranose as an oil (3.0 g, 96%); R_F 0.21 in 1:1 hexane–EtOAc. A solution of this oily hemiacetal (500 mg, 1.44 mmol) in $Cl(CH_2)_2Cl$ (2 mL), stirred under argon, was treated successively with CCl_3CN (2.1 g, 14.5 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 22 mg, 0.14 mmol) at 0°. After being stirred for 2 h at 0°, the mixture was directly chromatographed on SiO_2 in 1:1 hexane–EtOAc to give **28** (702 mg, 99%); $[\alpha]_D$ +46.5° (*c* 0.5); R_F 0.26 in 1:1 hexane–EtOAc; n.m.r. data: δ_H 8.783 (s, 1 H, C=N*H*), 6.281 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.475 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.9 Hz, H-2), 2.203, 2.087, 2.071, and 2.013 (4 s, 12 H, $COCH_3$); δ_C 94.7 ($^1J_{C,H}$ 179 Hz, C-1).

Anal. Calc. for $C_{16}H_{19}NO_8Cl_3$: C, 39.01; H, 4.09; N, 2.84. Found: C, 39.01; H, 4.06; N, 2.80.

Benzyl O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(4,6-di-O-benzyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**29**) *and benzyl O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→2)-O-(4,6-di-O-benzyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside* (**31**).

— (*A*). To a mixture of MS4A (1.6 g), silver triflate (AgOTf; 191 mg, 743 μmol), $CuBr_2$ (166 mg, 743 μmol), and Bu_4NBr (80 mg, 250 μmol) was added a solution of compound **27** (187 mg, 495 μmol) and compound **9** (243 mg, 275 μmol) in $Cl(CH_2)_2Cl$ (8 mL). The mixture was stirred for 6 h at 25°, then diluted with EtOAc and filtered. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 5:4 hexane–EtOAc to give **29** (134 mg, 40%), **31** (88 mg, 27%), and recovered **9** (70 mg, 29%).

(*B*). To a stirred mixture of compound **9** (111 mg, 126 μmol) and MS AW300 (300 mg) in $Cl(CH_2)_2Cl$ (4 mL) were added successively, at −20°, a solution of compound **28** (93 mg, 190 μmol) in $Cl(CH_2)_2Cl$ (4 mL) and then a solution of $BF_3 \cdot Et_2O$ (4.7 μL, 38 μmol) in $Cl(CH_2)_2Cl$ (1 mL). The reaction mixture was stirred for 1.5 h at −20°, then for 3 h at 20°, neutralized with Et_3N (20 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 5:1 CCl_4–acetone to give **29** (33 mg, 22%) and **31** (98 mg, 68%).

Compound **29** had $[\alpha]_D$ +7.7° (*c* 1.4); R_F 0.29 in 5:4 hexane–EtOAc and 0.53 in 4:1 CCl_4–acetone; n.m.r. data: δ_H 5.451 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3c), 5.300 (t, 1 H, $J_{3,4}$, $J_{4,5}$ 10.0 Hz, H-4c), 5.300 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.4 Hz, H-2c), 4.956 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1c), 4.585 (s, 1 H, H-1b), 4.484 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 2.145, 2.056, 2.048, and 1.996 (4 s, 12 H, $COCH_3$); δ_C 102.6 ($^1J_{C,H}$ 159 Hz, C-1a), 99.5 ($^1J_{C,H}$ 175 Hz, C-1c), 98.9 ($^1J_{C,H}$ 158 Hz, C-1b), 62.7 (C-6c), and 20.8 (4 C, $COCH_3$).

Anal. Calc. for $C_{68}H_{78}O_{20}$: C, 67.20; H, 6.48. Found: C, 66.80; H, 6.32.

Acetylation of **29** gave **30**; n.m.r. data: δ_H (C_6D_6), 5.770 (t, 1 H, $J_{3,4}$ 10.0 Hz, H-4c), 5.690 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.2 Hz, H-2c), 5.666 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.0 Hz, H-3c), 5.646 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2b), 5.292 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.761 (s, 1 H, H-1b), 1.982, 1.824, 1.698, 1.634, and 1.540 (5 s, 15 H, $COCH_3$).

Compound **31** had $[\alpha]_D$ −5.1° (*c* 1.6); R_F 0.47 in 4:1 CCl_4–acetone; n.m.r. data: δ_H 5.427 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.2 Hz, H-2c), 5.374 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 10.0 Hz, H-3c), 5.295 (t, 1 H, *J* 10.0 Hz, H-4c), 5.100 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 2.147, 2.021, 1.967, and 1.806 (4 s, 12 H, $COCH_3$); δ_C 102.7 ($^1J_{C,H}$ 158 Hz, C-1a), 99.4 ($^1J_{C,H}$ 158 Hz, C-1b), 98.4 ($^1J_{C,H}$ 179 Hz, C-1c), and 62.8 (C-6c).

Anal. Calc. for $C_{68}H_{78}O_{20}$: C, 67.20; H, 6.47. Found: C, 67.18; H, 6.37.

Acetylation of **31** gave **32**; n.m.r. data: δ_H 5.412 (dd, 1 H, $J_{2,3}$ 3.4 Hz, $J_{3,4}$ 10.0 Hz, H-3c), 5.401 (d, 1 H, $J_{2,3}$ 3.4 Hz, H-2c), 5.328 (t, 1 H, $J_{3,4}$, $J_{4,5}$ 10.0 Hz, H-4c), 4.882 (s, 1 H, H-1c), 4.857 (dd, 1 H, $J_{2,3}$ 2.8, $J_{3,4}$ 10.0 Hz, H-3b), 2.161, 2.012, 1.987, 1.979, and 1.794 (5 s, 15 H, $COCH_3$).

2,3,4-Tri-O-acetyl-α- and -β-D-xylopyranosyl trichloroacetimidate (**7α** *and* **7β**). — A solution of 1,2,3,4-tetra-*O*-acetyl-D-xylopyranose (2.48 g, 7.8 mmol) and $NH_2NH_2 \cdot AcOH$ (940 mg, 10.2 mmol) in DMF (8 mL) was stirred for 15 min at 55°. After cooling to 20° the mixture was diluted with EtOAc, washed with H_2O,

aqueous $NaHCO_3$, and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give 2,3,4-tri-*O*-acetyl-D-xylopyranose as an oil (1.6 g, 75%); R_F 0.36 in 1:1 toluene–EtOAc. To a solution of the oily hemiacetal (607 mg, 2.2 mmol) in $Cl(CH_2)_2Cl$ (8 mL), stirred under argon at −20°, was added CCl_3CN (3.2 g, 22 mmol) and DBU (34 mg, 0.22 mmol). The mixture was stirred for 4 h at −20°, then chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **7*α*** (770 mg, 82%) and **7*β*** (156 mg, 16%).

Compound **7*α*** had $[\alpha]_D$ +81.7° (*c* 1.9); R_F 0.39 in 2:1 hexane–toluene; n.m.r. data: δ_H 8.673 (s, 1 H, C=N*H*), 6.485 (d, 1 H, *J* 3.7 Hz, H-1), 5.582 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 9.8 Hz, H-3), 5.062 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.8 Hz, H-2), 4.001 (dd, 1 H, $J_{4,5}$ 6.2, $J_{5,5}$ 10.5 Hz, H-5*eq*), 3.795 (t, 1 H, *J* 10.5 Hz, H-5*ax*), 2.055 (s, 6 H, $COCH_3$), and 2.018 (s, 3 H, $COCH_3$).

Anal. Calc. for $C_{13}H_{16}NO_8Cl_3$: C, 36.97; H, 3.84; N, 3.34. Found: C, 37.31; H, 3.85; N, 3.15.

Compound **7*β*** had $[\alpha]_D$ −21.3° (*c* 0.5); R_F 0.28 in 2:1 hexane–EtOAc; n.m.r. data: δ_H 8.710 (s, 1 H, C=N*H*), 6.025 (d, 1 H, $J_{1,2}$ 4.4 Hz, H-1), 5.168 (t, 1 H, *J* 5.8 Hz, H-3), 5.126 (t, 1 H, *J* 5.0 Hz, H-2), 4.942 (q, 1 H, *J* 5.6 Hz, H-4), 4.304 (dd, 1 H, $J_{4,5}$ 3.9, $J_{5,5}$ 12.5 Hz, H-5*eq*), 3.705 (dd, 1 H, $J_{4,5}$ 5.5, $J_{5,5}$ 12.5 Hz, H-5*ax*), 2.111, 2.101, and 2.098 (3 s, 9 H, $COCH_3$).

Benzyl O-*(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1→3)-*O*-(4,6-di-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**33**), *benzyl* O-*(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1→2)-*O*-(4,6-di-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**35**), *and benzyl* O-*(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1→3)-*O*-[(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1→2)]-*O*-(4,6-di-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**37**). — To a stirred mixture of MS AW300 (500 mg) and compound **9** (126 mg, 143 μmol) in $Cl(CH_2)_2Cl$ (3 mL), cooled to −20° (dry ice–CCl_4 bath), was added a solution of compound **7** (96 mg, 0.23 mmol) in $Cl(CH_2)_2Cl$ (2 mL), then dropwise a solution of $BF_3 \cdot Et_2O$ (5.6 μL, 45 μmol) in $Cl(CH_2)_2Cl$ (1 mL). The reaction mixture was stirred for 1 h at −20°, then for 5 h at 20°, neutralized with Et_3N (20 μL), diluted with EtOAc, and filtered. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 hexane–EtOAc to give **33** (46 mg, 28%), **35** (43 mg, 26%), and **37** (41 mg, 20%).

Compound **33** had $[\alpha]_D$ −17.7° (*c* 0.7); R_F 0.27 in 2:1 hexane–oxolane; n.m.r. data: δ_H 5.140 (t, 1 H, *J* 8.5 Hz, H-3c), 4.935 (t, 1 H, *J* 8.1 Hz, H-2c), 4.920 (dt, 1 H, *J* 1.7, 8.5 Hz, H-4c), 4.643 (s, 1 H, H-1b), 4.509 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.337 (d, 1 H, $J_{1,2}$ 6.9 Hz, H-1c), 2.077, 2.064, and 2.031 (3 s, 9 H, $COCH_3$); δ_C 102.7 ($^1J_{C,H}$ 162 Hz, C-1a), 99.7 ($^1J_{C,H}$ 165 Hz, C-1), and 97.2 ($^1J_{C,H}$ 160 Hz, C-1).

Anal. Calc. for $C_{65}H_{72}O_{18}$: C, 68.41; H, 6.36. Found: C, 68.16; H, 6.38.

Acetylation of **33** gave **34**; n.m.r. data: δ_H 5.284 (d, 1 H, $J_{2,3}$ 2.6 Hz, H-2b), 5.146 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 8.5 Hz, H-3c), 2.081, 2.066, 2.041, and 2.015 (4 s, 12 H, $COCH_3$).

Compound **35** had $[\alpha]_D$ −37.3° (*c* 1.0); R_F 0.30 in 2:1 hexane–oxolane; n.m.r. data: δ_H 5.149 (t, 1 H, $J_{2,3}$, $J_{3,4}$ 8.1 Hz, H-3c), 2.056, 2.004, and 1.880 (3 s, 9 H, $COCH_3$); δ_C 102.5 ($^1J_{C,H}$ 158 Hz, C-1a), 100.5 ($^1J_{C,H}$ 153 Hz, C-1), 100.0 ($^1J_{C,H}$ 161 Hz, C-1), and 20.8 (3 C, $COCH_3$).

Anal. Calc. for $C_{65}H_{72}O_{18}$: C, 68.41; H, 6.36. Found: C, 68.08; H, 6.38.

Acetylation of **35** gave **36**; n.m.r. data: δ_H 4.803 (d, 1 H, $J_{1,2}$ 4.9 Hz, H-1c), 4.504 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 2.072, 2.012 (2 s, 6 H, $COCH_3$), and 1.897 (s, 6 H, $COCH_3$).

Compound **37** had $[\alpha]_D$ −52.9° (*c* 1.4); R_F 0.20 in 2:1 hexane–oxolane; n.m.r. data: δ_H 2.144, 2.086, 2.042, 2.012, 1.957, and 1.794 (6 s, 18 H, $COCH_3$); δ_C 102.5 ($^1J_{C,H}$ 161 Hz, C-1a), 100.4 ($^1J_{C,H}$ 154 Hz, C-1), 99.3 ($^1J_{C,H}$ 158 Hz, C-1), and 95.3 ($^1J_{C,H}$ 173 Hz, C-1).

Anal. Calc. for $C_{76}H_{86}O_{25}$: C, 65.23; H, 6.19. Found: C, 64.94; H, 6.21.

Deprotection of compound **37**. — A solution of compound **37** (11 mg, 7.9 μmol) in MeOH (1 mL) and a 0.1M solution of MeONa in MeOH (0.5 mL) was mixed and stirred for 16 h at 20°, when t.l.c. examination showed a single spot at R_F 0.76 in 11:2:1 EtOAc–EtOH–H_2O. The mxiture was neutralized with Amberlyst 15 resin, and filtered through Celite. The filtrate was concentrated *in vacuo*. A mixture of crude deacetylated product (10 mg) and 10% Pd–C (25 mg) in MeOH (1.5 mL) was stirred for 24 h at 20° and for 2 h at 50° under H_2, diluted with MeOH, and filtered through Celite. The filtrate was concentated *in vacuo* and the residue was chromatographed on Sephadex G-25 in H_2O to give the free tetrasaccharide β-D-Xyl*p*-(1→3)-[β-D-Xyl*p*-(1→2)]-β-D-Man*p*-(1→4)-D-Glc (4.5 mg, 97%); R_F 0.48 in 2:1:1 BuOH–AcOH–H_2O; n.m.r. data: δ_H D_2O, Bu^tOH, 60°), 5.212 (d, 0.3 H, $J_{1,2}$ 3.7 Hz, H-1aα), 4.781 (s, 0.3 H, H-1b), 4.777 (s, 0.7 H, H-1b), 4.651 (d, 0.7 H, $J_{1,2}$ 8.1 Hz, H-1aβ), 4.610 (d, 0.3 H, $J_{1,2}$ 7.6 Hz, H-1d), 4.582 (d, 0.7 H, $J_{1,2}$ 7.6 Hz, H-1d), 4.528 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1c), 4.386 (d, 0.7 H, $J_{2,3}$ 3.2 Hz, H-2b), and 4.381 (d, 0.3 H, $J_{2,3}$ 2.7 Hz, H-2b).

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-1,2,3,6-tetra-O-acetyl-D-glucopyranose (**38**). — A mixture of compound **29** (105 mg, 86 μmol) and 10% Pd–C (115 mg) in MeOH (2.5 mL) was stirred under H_2 for 16 h at 20°, then for 4 h at 45°, diluted with MeOH, and filtered through Celite. The filtrate was concentrated *in vacuo*. A solution of the residual oil (51 mg) in pyridine (2.5 mL)–Ac_2O (2.0 mL) was stirred for 18 h at 20°, then evaporated *in vacuo*. Chromatography of the residue on SiO_2 in 3:2 toluene–EtOAc gave **38** (68 mg, 81%) as a 1:1 mixture of α and β anomers; R_F 0.43 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 6.270 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.692 (d, 0.5 H, $J_{1,2}$ 8.5 Hz, H-1aβ), and 2.231–1.990 (20 s, 33 H, $COCH_3$).

Anal. Calc. for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63. Found: C, 49.49; H, 5.45.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-D-glucopyranose (**39**). — A mixture of compound **38** (65 mg, 67 μmol) and $NH_2NH_2 \cdot AcOH$ (7.4 mg, 80 μmol) in DMF (3.5 mL) was stirred for 10 min at 55°, and then diluted with EtOAc. The organic layer was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried

($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **37** (54 mg, 86%); R_F 0.21 in 3:2 EtOAc–toluene.

Anal. Calc. for $C_{38}H_{52}O_{26} \cdot H_2O$: C, 48.41; H, 5.77. Found: C, 48.35; H, 5.49.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl trichloroacetimidate (**40**). — To a solution of compound **39** (51 mg, 54 μmol) in $Cl(CH_2)_2Cl$ (2.0 mL), stirred under argon at −20° (dry ice–CCl_4 bath), was added CCl_3CN (55 μL, 0.54 mmol) and a solution of DBU (0.8 μL, 5 μmol) in $Cl(CH_2)_2Cl$ (0.5 mL). The mixture was stirred for 2 h at −20°, and then directly chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **40** (51 mg, 88%); $[\alpha]_D$ +18.5° (*c* 0.3); R_F 0.35 in 3:2 EtOAc–toluene; n.m.r. data: δ_H 8.670 (s, 1 H, C=N*H*), 6.492 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 4.645 (s, 1 H, H-1b), 2.228, 2.145, 2.125, 2.111 (6 H), 2.101, 2.082, 2.051, 2.020, and 1.992 (9 s, 30 H, $COCH_3$).

Anal. Calc. for $C_{40}H_{52}NO_{26}Cl_3$: C, 44.93; H, 4.90; N, 1.31. Found: C, 44.63; H, 4.90; N, 1.30.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl-(1→1)-(2S,3R,4E)-2-azido-3-O-(tert-butyldiphenylsilyl)-4-octadecene-1,3-diol (**41**) *and O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-3,6-di-O-acetyl-1,2-O-{(1R)-1-[(2S,3R,4E)-2-azido-3-(tert-butyldiphenylsilyloxy)-4-octadecenyloxy]ethylidene}-α-D-glucopyranose* (**44**). — (*A*). To a mixture of compound **6** (34 mg, 60 μmol) and MS AW300 (1 g) in $Cl(CH_2)_2Cl$ (1.5 mL), stirred under argon at −20°, was added a solution of compound **40** (48 mg, 45 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) and a solution of $BF_3 \cdot Et_2O$ (1.8 μL, 17 μmol) in $Cl(CH_2)_2Cl$ (0.5 mL). The mixture was stirred for 2 h at −20°, neutralized with Et_3N (10 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **41** (3.5 mg, 5%) and **44** (39 mg, 59%).

Compound **41** had $[\alpha]_D$ −43.7° (*c* 0.7); R_F 0.55 in 1:1 toluene–EtOAc; n.m.r. data: 5.388 (d, $J_{2,3}$ 2.7 Hz, H-2b), 4.976 (br. s, 2 H, H-1c, 2c), 4.531 (s, 1 H, H-1b), 4.335 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 2.203, 2.139, 2.120, 2.098 (6 H), 2.085, 2.058, 2.046, 1.987, and 1.872 (9 s, 30 H, $COCH_3$).

Anal. Calc. for $C_{72}H_{103}N_3O_{27}Si$: C, 58.80; H, 7.06; N, 2.86. Found: C, 58.98; H, 7.03; N, 2.78.

Compound **44** had R_F 0.39 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 5.603 (d, 1 H, $J_{1,2}$ 5.4 Hz, H-1a), 5.376 (dd, 1 H, *J* 8.2, 15.5 Hz, H-4')*, 5.152 (dt, 1 H, *J* 15.5, 6.9 Hz, H-5'), 4.980 (s, 1 H, H-1c), 4.711 (s, 1 H, H-1b), 2.209, 2.144, 2.125, 2.114, 2.094, 2.090, 2.068, 2.045, 1.992 (9 s, 27 H, $COCH_3$), 1.574 (s, 3 H, terminal CH_3), and 1.050 [s, 9 H, $C(CH_3)_3$].

*Primed locants are used for atoms in the sphingenine moiety.

(*B*). To a mixture of compound **6** (21 mg, 38 μmol) and MS4A (40 mg) in $Cl(CH_2)_2Cl$ (1.5 mL), stirred under argon at −20°; was added a solution of compound **40** (29 mg, 27 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL), then Me_3SiOTf (5.7 μL, 30 μmol). After being stirred for 2 h at −20°, the mixture was neutralized with Et_3N (33 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 toluene–EtOAc to give **41** (21 mg, 51%).

Rearrangement of compound **44** *to compound* **41**. — To a mixture of compound **44** (35 mg, 24 μmol) and MS4A (300 mg) in $Cl(CH_2)_2Cl$ (2.5 mL), stirred at 0° under argon, was added Me_3SiOTf (5.6 μL, 29 μmol). After being stirred for 2 h at 0°, the mixture was neutralized with Et_3N (20 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **41** (14 mg, 40%).

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-(2,4,6-tri-O-acetyl-β-D-mannopyranosyl)-(1→4)-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→1)-3-O-tert-butyldiphenylsilyl-2-N-tetracosanoyl-(4E)-sphingenine (**42**). — A mixture of compound **41** (13 mg, 8.8 μmol) and Lindlar catalyst (9.5 mg) in 1:1 EtOAc–EtOH (1.4 mL) was stirred for 46 h at 20° under H_2, diluted with EtOAc, and filtered through Celite. The filtrate was concentrated *in vacuo* to give a residual oil (14 mg), a solution of which in $Cl(CH_2)_2Cl$ (2.5 mL) was added dropwise to a stirred mixture of tetracosanoic acid (6.5 mg, 18 μmol), 2-chloro-1-methylpyridinium iodide (4.5 mg, 18 μmol), and Bu_3N (8.8 μL, 37 μmol) in $Cl(CH_2)_2Cl$ (0.8 mL) at 20°. The mixture was stirred for 3 h at 20° and diluted with EtOAc. The organic layer was washed with H_2O and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 toluene–EtOAc to give **42** (8 mg, 51%); $[\alpha]_D$ −25.5° (*c* 0.7); R_F 0.48 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 4.980 (br. s, 2 H, H-1c,2c), 4.532 (s, 1 H, H-1b), 4.406 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 2.12, 2.139, 2.122, 2.107, 2.100, 2.074, 2.049, 2.044, 1.988, and 1.963 (10 s, 30 H, $COCH_3$).

Anal. Calc. for $C_{96}H_{151}NO_{28}Si \cdot 1.5\ C_6H_5CH_3$: C, 66.16; H, 8.49. Found: C, 66.25; H, 8.09.

Deprotection of **42** *to form* **1**. — A mixture of compound **42** (6.4 mg, 3.5 μmol) in oxolane (2.0 mL) and a solution of M Bu_4NF in the same solvent (70 μL, 70 μmol) was stirred for 1 h at 20° and concentrated *in vacuo*. A solution of the residue in oxolane (1 mL) and 0.05M NaOMe in MeOH (2 mL) was then stirred for 20 h at 20°, neutralized with Amberlyst 15 resin, and evaporated *in vacuo*. The residue was purified by successive chromatography on Sephadex LH-20, preparative h.p.t.l.c., and chromatography on Sephadex LH-20, all in 12:6:1 $CHCl_3$–MeOH–H_2O to give *O*-α-D-mannopyranosyl-(1→3)-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-2-*N*-tetracosanoyl-(4*E*)-sphingenine **1** (2.6 mg, 65%); $[\alpha]_D$ −5.7° (*c* 0.3, pyridine); R_F 0.46 in 12:6:1 $CHCl_3$–MeOH–H_2O;

n.m.r. data: δ_H [99:1 $(CD_3)_2SO$–D_2O at 80°] 5.573 (td, 1 H, *J* 6.1, 15.4 Hz, H-5′), 5.387 (dd, 1 H, *J* 6.8, 15.4 Hz, H-4′), 4.925 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1c), 4.558 (s, 1 H, H-1b), 4.176 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 3.976 (d, 1 H, $J_{2,3}$ 2.9 Hz, H-2b); δ_H (C_5D_5N, 80°), 5.793 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1c), 5.146 (s, 1 H, H-1b), 4.724 (d, $J_{1,2}$ 7.9 Hz, H-1a).

Deprotection of compound **41** *to form* **43**. — A solution of compound **41** (11 mg, 7.0 μmol) in oxolane (2 mL) containing a solution of M Bu_4NF in the same solvent (115 μL, 115 μmol) was stirred for 2 h at 20° and evaporated *in vacuo*. The residue was then dissolved in oxolane (1 mL) plus 0.5M NaOMe–MeOH (2.5 mL). After being stirred for 16 h at 20°, the mixture was neutralized with Amberlyst 15 resin and evaporated *in vacuo*. The residue was purified by successive chromatography on Sephadex LH-20, preparative h.p.t.l.c., and finally chromatography on Sephadex LH-20, all in 12:6:1 $CHCl_3$–MeOH–H_2O, to give *O*-α-D-mannopyranosyl-(1→3)-*O*-β-D-mannopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→1)-(2*S*,3*R*,4*E*)-2-azido-4-octadecene-1,3-diol (**43**; 4.8 mg, 83%); $[\alpha]_D$ −13.1° (*c* 0.5, pyridine), R_F 0.57 in 12:6:1 $CHCl_3$–MeOH–H_2O; n.m.r. data: δ_H [99:1 $(CD_3)_2SO$–D_2O, 80°] 5.681 (td, 1 H, *J* 5.9, 15.5 Hz, H-5′), 5.450 (dd, 1 H, *J* 6.8, 15.5 Hz, H-4′), 4.920 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.560 (s, 1 H, H-1b), 4.222 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.079 (t, 1 H, *J* 5.9 Hz, H-3′), 3.969 (d, 1 H, $J_{2,3}$ 2.4 Hz, H-2b).

O-*(2,3,4,6-Tetra*-O-*acetyl*-α-D-*mannopyranosyl)*-*(1→2)*-O-*(3,4,6-tri*-O-*acetyl*-β-D-*mannopyranosyl)*-*(1→4)*-*1,2,3,6-tetra*-O-*acetyl*-D-*glucopyranose* (**45**). — A mixture of compound **31** (116 mg, 96.0 μmol) and 10% Pd–C (117 mg) in MeOH (2.5 mL) was stirred for 20 h at 20° under H_2, diluted with MeOH, and filtered through Celite. The filtrate was then concentrated *in vacuo*. A solution of the residue (54 mg) in pyridine (2.5 mL)–Ac_2O (2.0 mL) was stirred for 17 h at 20° and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 6:5 EtOAc–toluene to give **45** (89 mg, 96%) as a 3:7 mixture of α and β anomers; R_F 0.15 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 6.274 (d, 0.3 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.743 (d, 0.7 H, $J_{1,2}$ 8.1 Hz, H-1aβ), 4.944 (d, 0.7 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.901 (d, 0.3 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.523 (s, 1 H, H-1b).

Anal. Calc. for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63. Found: C, 49.72; H, 5.58.

O-*(2,3,4,6-Tetra*-O-*acetyl*-α-D-*mannopyranosyl)*-*(1→2)*-O-*(3,4,6-tri*-O-*acetyl*-β-D-*mannopyranosyl)*-*(1→4)*-*2,3,6-tri*-O-*acetyl*-D-*glucopyranose* (**46**). — A mixture of compound **45** (76 mg, 79 μmol) and $NH_2NH_2 \cdot AcOH$ (8.7 mg, 95 μmol) in DMF (2.5 mL) was stirred for 10 min at 50°, then diluted with EtOAc. The mixture was washed with H_2O, aqueous $NaHCO_3$, and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **46** (65 mg, 89%); R_F 0.17 in 3:2 EtOAc–toluene; n.m.r. data: δ_H 2.126–2.013 (m, 30 H, $COCH_3$).

Anal. Calc. for $C_{38}H_{52}O_{26}$: C, 49.35; H, 5.67. Found: C, 49.34; H, 5.63.

O-*(2,3,4,6-Tetra*-O-*acetyl*-α-D-*mannopyranosyl)*-*(1→2)*-O-*(3,4,6-tri*-O-*acetyl*-β-D-*mannopyranosyl)*-*(1→4)*-*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl trichloroacetimidate* (**47**). — To a solution of compound **46** (43 mg, 46 μmol) in

$Cl(CH_2)_2Cl$ (1.3 mL), stirred at −20° under argon, were added CCl_3CN (67 mg, 0.47 mmol) and DBU (0.7 mg, 5 μmol). The mixture was stirred for 2 h at −20°, then directly chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **47** (48 mg, 97%); $[\alpha]_D$ +16.5° (*c* 0.2); R_F 0.24 in 3:2 EtOAc–toluene; n.m.r. data: δ_H 8.672 (s, 1 H, C=N*H*), 6.501 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 4.942 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.562 (s, 1 H, H-1b), 2.150, 2.126 (6 H), 2.105 (6 H), 2.095, 2.076, 2.025, and 2.015 (6 H) (7 s, 30 H, $COCH_3$).

Anal. Calc. for $C_{40}H_{52}NO_{26}Cl_3 \cdot 0.1\ C_6H_5CH_3$: C, 45.33; H, 4.94; N, 1.30. Found: C, 45.63; H, 4.92; N, 1.24.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→2)-O-(3,4,6-tri-O-acetyl-β-D-mannopyransyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→1)-(2S,3R,4E)-2-azido-3-O-benzoyl-4-octadecene-1,3-diol (**48**) *and O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl-(1→2)-O-(3,4,6-tri-O-acetyl-β-D-mannopyranosyl-(1→4)-3,6-di-O-acetyl-1,2-O-{(1R)-1-[(2S,3R,4E)-2-azido-3-benzoyloxy-4-octadecenyloxy]ethylidene}-α-D-glucopyranose* (**51**). — To a mixture of compound **5** (26 mg, 62 μmol) and MS AW300 (700 mg) in $Cl(CH_2)_2Cl$ (1 mL), stirred at −20° under argon, was added a solution of compound **47** (48 mg, 45 μmol) in $Cl(CH_2)_2Cl$ (1.2 mL), and then $BF_3 \cdot Et_2O$ (1.8 μL, 17 μmol). The mixture was stirred for 2 h at −20°, neutralized with Et_3N (10 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 toluene–EtOAc to give **48** (20 mg, 32%) and **51** (6.0 mg, 10%).

Compound **48** had $[\alpha]_D$ −33.8° (*c* 0.7); R_F 0.42 in 1:1 toluene-EtOAc; n.m.r. data: δ_H 5.925 (td, 1 H, *J* 6.8, 14.8 Hz, H-5'), 5.594 (dd, 1 H, *J* 3.9, 8.1 Hz, H-3'), 5.540 (dd, 1 H, *J* 8.1, 14.8 Hz, H-4'), 4.916 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.589 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.492 (s, 1 H, H-1b), 2.147, 2.131, 2.121, 2.099, 2.076, 2.071, 2.061, 2.059, 2.022, 2.015 (10 s, 30 H, $COCH_3$), and 0.876 (t, 3 H, *J* 7.0 Hz, terminal CH_3).

Anal. Calc. for $C_{63}H_{89}N_3O_{28}$: C, 56.63; H, 6.72; N, 3.15. Found: C, 56.90; H, 6.72; N, 2.91.

Compound **51** had $[\alpha]_D$ −13.7° (*c* 0.3); R_F 0.37 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 5.932 (td, 1 H, *J* 6.6, 14.4 Hz, H-5'), 5.642 (d, 1 H, $J_{1,2}$ 5.1 Hz, H-1a), 5.012 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1c), 4.713 (s, 1 H, H-1b), 2.150, 2.120 (9 H), 2.096, 2.086, 2.040, 2.032, 2.009 (7 s, 27 H, $COCH_3$), 1.707 (s, 3 H, CCH_3 of orthoester), and 0.878 (t, 3 H, *J* 6.8 Hz, terminal CH_3).

Anal. Calc. for $C_{63}H_{89}N_3O_{28}$: C, 56.63; H, 6.72; N, 3.15. Found: C, 56.58; H, 6.61; N, 2.96.

Conversion of compound **48** *into compound* **50** *via* **49**. — A mixture of compound **48** (13 mg, 9.9 μmol) and Lindlar catalyst (8.8 mg) in 1:1 EtOAc–EtOH (1.2 mL) was stirred for 20 h at 20° under H_2, diluted with 1:1 EtOAc–EtOH, and filtered through Celite, and the filtrate was evaporated *in vacuo*. A solution of the residue (15 mg) in $Cl(CH_2)_2Cl$ (1.7 mL) was added dropwise to the mixture of tetracosanoic acid (7.3 mg, 20 μmol), 2-chloro-1-methylpyridinium iodide (5.1 mg,

20 μmol), and Bu_3N (9.9 μL, 42 μmol) in $Cl(CH_2)_2Cl$ (0.3 mL). The reaction mixture was stirred for 3 h at 20°, diluted with EtOAc, washed with water and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **49** (6.0 mg, 36%); $[\alpha]_D$ −17.0° (*c* 0.3), R_F 0.52) in 3:2 EtOAc–toluene; n.m.r. data: δ_H 8.012 (d, 2 H, *J* 7.3 Hz, COC_6H_5), 7.552 (t, 1 H, *J* 7.3 Hz, COC_6H_5), 7.442 (t, 2 H, *J* 7.3 Hz, COC_6H_5), 5.874 (td, 1 H, *J* 6.8, 14.9 Hz, H-5′), 5.737 (d, 1 H, *J* 9.3 Hz, N*H*), 5.514 (dd, 1 H, *J* 7.3, 14.9 Hz, H-4′), 4.907 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1c), 4.503 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.454 (s, 1 H, H-1b), 2.142, 2.128, 2.101, 2.090, 2.068, 2.062, 2.022 (6 H), 2.010, 1.979 (9 s, 30 H, $COCH_3$), and 0.879 (t, 6 H, *J* 7.0 Hz, terminal CH_3).

A mixture of compound **49** (5.0 mg, 30 μmol) in oxolane (1 mL) and 0.03M NaOMe–MeOH (3 mL) was stirred for 16 h at 20°, neutralized with Amberlyst 15 resin, and concentrated *in vacuo*. The residue was chromatographed on Sephadex LH-20 in 12:6:1 $CHCl_3$–MeOH–H_2O to give **50** (2.3 mg, 67%); $[\alpha]_D$ +9.2° (*c* 0.1, pyridine); R_F 0.39 in 12:6:1 $CHCl_3$–MeOH–H_2O; n.m.r. data [99:1 $(CD_3)_2SO$–D_2O, 60°]: δ_H 5.556 (td, 1 H, *J* 6.6, 15.4 Hz, H-5′), 5.367 (dd, 1 H, *J* 6.8, 15.4 Hz, H-4′), 5.078 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1c), 4.536 (s, 1 H, H-1b), 4.139 (d, 1 H, *J* 7.8 Hz, H-1a), and 3.925 (d, 1 H, $J_{2,3}$ 2.7 Hz, H-2b).

Benzyl O-*(2,3,4,6-tetra-*O*-acetyl-α-*D*-mannopyranosyl)-(1→3)-*O*-[(2,3,4-tri-*O*-acetyl-β-*D*-xylopyranosyl)-(1→2)]-*O*-(4,6-di-*O*-benzyl-β-*D*-mannopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**52**). — To a mixture of compound **29** (85 mg, 70 μmol) and MS AW300 (690 mg) in $Cl(CH_2)_2Cl$ (2.5 mL) stored at −20° under argon, was added dropwise a solution of compound **7** (68 mg, 0.16 mmol) in $Cl(CH_2)_2Cl$ (1 mL) and then a solution of $BF_3 \cdot Et_2O$ (4.0 μL, 32 μmol) in $Cl(CH_2)_2Cl$ (0.8 mL). After 3 h of stirring at −20°, a solution of compound **7** (64 mg, 0.15 mmol) in $Cl(CH_2)_2Cl$ (1 mL) was again added. After 6 h, the mixture was neutralized with Et_3N (20 μL), diluted with EtOAc, and filtered through Celite. The organic layer was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was successively chromatographed on SiO_2 in 5:4 hexane–EtOAc, then on Bio-beads SX-8 (2.2 cm × 1 m) in benzene to give **52** (62 mg, 60%); $[\alpha]_D$ −20.5° (*c* 1.4), R_F 0.22 in 5:4 hexane–EtOAc; n.m.r. data: δ_H 7.4–7.1 (m, 30 H, Ph-H), 2.092, 2.069, 2.061, 2.040, 1.985, 1.931, and 1.878 (7 s, 21 H, $COCH_3$); δ_C 102.5 ($^1J_{C,H}$ 158 Hz, C-1a), 100.1 (C-1), 99.9 (C-1), and 99.3 (C-1).

Anal. Calc. for $C_{79}H_{90}O_{27} \cdot 0.5\ H_2O$: C, 64.00; H, 6.19. Found: C, 63.89; H, 6.03.

Deprotection of compound **52** *to form* **53**. — A solution of **52** (22 mg, 15 μmol) in 0.04M NaOMe–MeOH (1.3 mL) was stirred for 14 h at 20°, neutralized with Amberlyst 15 resin, and concentrated *in vacuo*. A mixture of the residue and 10% Pd–C (25 mg) in MeOH (1.2 mL) was then stirred for 20 h at 20° under H_2, diluted with MeOH, and filtered through Celite. The filtrate was evaporated *in vacuo*, and the residue was chromatographed on Sephadex G-25 in H_2O to give **53** (7.7 mg, 83%); R_F 0.20 in 2:1:1 BuOH–AcOH–H_2O; n.m.r. data (D_2O, 60°): δ_H

5.209 (d, 0.35 H, $J_{1,2}$ 3.9 Hz, H-1aα), 5.126 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1c), 4.813 (s, 1 H, H-1b), 4.646 (d, 0.65 H, $J_{1,2}$ 8.1 Hz, H-1aβ), 4.521 (d, 0.35 H, $J_{1,2}$ 7.6 Hz, H-1d), 4.496 (d, 0.65 H, $J_{1,2}$ 7.6 Hz, H-1d), 4.244 (d, 0.35 H, $J_{2,3}$ 2.9 Hz, H-2b), 4.236 (d, 0.65 H, $J_{2,3}$ 2.9 Hz, H-2b), 4.042 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.4 Hz, H-2c).

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-O-(4,6-di-O-acetyl-β-D-mannopyranosyl)-(1→4)-1,2,3,6-tetra-O-acetyl-D-glucopyranose (**54**). — A mixture of compound **52** (73 mg, 50 μmol) and 10% Pd–C (81 mg) in MeOH (2 mL) was stirred for 26 h at 20° under H_2, diluted with MeOH, and filtered through Celite. The filtrate was concentrated *in vacuo*. A solution of the residue (44 mg) in pyridine (2.5 mL)–Ac_2O (2 mL) was then stirred for 6.5 h at 20°, and concentrated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **54** (49 mg, 83%) as a 1:2 mixture of α and β-anomers; R_F 0.17 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 6.250 (d, 0.33 H, $J_{1,2}$ 3.3 Hz, H-1aα) and 5.716 (d, 0.67 H, $J_{1,2}$ 8.3 Hz, H-1aβ).

Anal. Calc. for $C_{49}H_{66}O_{33}$: C, 49.75; H, 5.62. Found: C, 49.81; H, 5.46.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-O-(4,6-di-O-acetyl-β-D-mannopyranosyl)-(1→4)-2,3,6-tri-O-acetyl-α-D-glucopyranosyl trichloroacetimidate (**56**). — A mixture of compound **54** (20 mg, 17 μmol) and $NH_2NH_2 \cdot AcOH$ (2.0 mg, 21 μmol) in DMF (1.5 mL) was stirred for 15 min at 50°. After addition of further $NH_2NH_2 \cdot AcOH$ (2.0 mg), stirring was continued for 10 min at 55°, then the mixture was diluted with EtOAc. The solution was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **55** (17 mg, 88%); R_F 0.12 in 2:1 EtOAc–toluene.

A solution of **55** (15 mg, 13 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL), stirred at −20° under argon, was treated with CCl_3CN (13 μL, 0.13 mmol) and a solution of DBU (0.4 μL, 3 μmol) in $Cl(CH_2)_2Cl$ (0.2 mL). The mixture was stirred for 2.5 h at −20° and directly chromatographed on SiO_2 in 3:2 EtOAc–toluene to give **56** (14.5 mg, 88%); $[\alpha]_D$ −17.7° (*c* 1.1); R_F 0.22 in 3:2 EtOAc–toluene; n.m.r. data: δ_H 8.684 (s, 1 H, C=N*H*), 6.494 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 5.376 (d, 1 H, $J_{1,2}$ 6.3 Hz, H-1d), 5.031 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1c), 4.563 (s, 1 H, H-1b), 2.153, 2.134, 2.122, 2.108 (6 H), 2.093, 2.087, 2.074, 2.056, 2.043, 2.023, and 1.998 (11 s, 36 H, $COCH_3$).

Anal. Calc. for $C_{49}H_{64}NO_{32}Cl_3 \cdot 0.5\ C_6H_5CH_3$: C, 47.36; H, 5.15; N, 1.05. Found: C, 47.00; H, 5.15; N, 1.03.

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-O-(4,6-di-O-acetyl-β-D-mannopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→1)-(2S,3R,4E)-2-azido-3-O-(tert-butyldiphenylsilyl)-4-octadecene-1,3-diol (**57**). — To a mixture of compound **6** (13.4 mg, 24 μmol) and MS4A (500 mg) in $Cl(CH_2)_2Cl$ (1.5 mL), stirred at −20° under argon, was added successively a solution of compound **56** (21 mg, 17 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) and a solution of TMSOTf (3.9 μL, 20 μmol) in $Cl(CH_2)_2Cl$

(0.5 mL). After being stirred for 1 h at −20°, the mixture was neutralized with Et_3N (30 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 toluene–EtOAc to give **57** (17 mg, 60%); $[\alpha]_D$ −60.0° (*c* 0.8); R_F 0.32 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 7.7–7.6 (m, 4 H, Ph-H), 7.5–7.3 (m, 6 H, Ph-H), 2.150, 2.133, 2.114, 2.108, 2.090, 2.085 (9 H), 2.043, 1.996 (6 H), 1.874 (9 s, 36 H, $COCH_3$), 1.049 [s, 9 H, $C(CH_3)_3$], and 0.882 (t, 3 H, *J* 7.0 Hz, terminal CH_3).

Anal. Calc. for $C_{81}H_{115}N_3O_{33}Si$: C, 57.67; H, 6.87; N, 2.49. Found: C, 57.83; H, 6.70; N, 2.15.

Conversion of compound **57** *into* **2** *via compound* **58**. — A mixture of compound **57** (14 mg, 8.5 μmol) and Lindlar catalyst (17 mg) in 1:1 EtOAc–EtOH (1.4 mL) was stirred for 46 h at 20° under H_2, diluted with EtOAc, and filtered through Celite. Concentration of the filtrate *in vacuo* gave a residue (15 mg). A solution of this residue in $Cl(CH_2)_2Cl$ (1.8 mL) was then added to a mixture of tetracosanoic acid (6.3 mg, 17 μmol), 2-chloro-1-methylpyridinium iodide (4.3 mg, 17 μmol), and Bu_3N (8.1 μL, 36 μmol) in $Cl(CH_2)_2Cl$ (0.8 mL). The reaction mixture was stirred for 3 h at 20°, diluted with EtOAc, washed with water and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by chromatography on SiO_2 in 4:3 EtOAc–hexane and then by preparative h.p.t.l.c. in 2:1 EtOAc–hexane to give *O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-[(2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl)-(1→2)]-*O*-(4,6-di-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-(1→1)-3-*O*-(*tert*-butyldiphenylsilyl)-2-*N*-tetracosanoyl-(4*E*)-sphingenine **58** (8.2 mg, 49%); $[\alpha]_D$ −41.7° (*c* 0.4); R_F 0.62 in 2:1 EtOAc–hexane; n.m.r. data: δ_H 7.7–7.6 (m, 4 H, Ph-H), 7.45–7.3 (m, 6 H, Ph-H), 2.151, 2.141, 2.125, 2.118, 2.098, 2.094, 2.090, 2.048 (6 H), 2.010, 1.999, 1.968 (11 s, 36 H, $COCH_3$), 1.006 [s, 9 H, $C(CH_3)_3$], and 0.880 (t, 6 H, *J* 6.5 Hz, terminal CH_3).

A mixture of compound **58** (7.4 mg, 3.8 μmol) in oxolane (1.5 mL) and a solution of M Bu_4NF in oxolane (75 μL, 75 μmol) was stirred for 1 h at 20° under argon, and concentrated *in vacuo*. The residue was dissolved in THF (0.8 mL) and 0.05M NaOMe–MeOH (1.7 mL), and this solution was stirred for 22 h at 20°, neutralized with Amberlyst 15 resin, and concentrated *in vacuo*. The residue was purified by successive chromatography on Sephadex LH-20, preparative h.p.t.l.c., and chromatography on Sephadex LH-20, all in 12:6:1 $CHCl_3$–MeOH–H_2O, to give **2** (3.2 mg, 66%); $[\alpha]_D$ −14.8° (*c* 0.3, pyridine); R_F 0.42 in 12:6:1 $CHCl_3$–MeOH–H_2O; n.m.r. data: δ_H [99:1 $(CD_3)_2SO$–D_2O, 80°] 5.573 (td, 1 H, *J* 7.0, 15.0 Hz, H-5′), 5.385 (dd, 1 H, *J* 7.6, 15.0 Hz, H-4′), 4.948 (s, 1 H, H-1c), 4.659 (s, 1 H, H-1b), 4.432 (d, 1 H, $J_{1,2}$ 6.4 Hz, H-1d), 4.173 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1a), 4.064 (s, 1 H, H-2b), 2.051 (t, 2 H, *J* 7.6 Hz, $COCH_2CH_2$), and 0.857 (t, 6 H, *J* 6.7 Hz, terminal CH_3); δ_H (C_5D_5N, 80°) 5.886 (s, 1 H, H-1c), 5.275 (d, 1 H, $J_{1,2}$ 6.4 Hz, H-1d), 5.196 (s, 1 H, H-1b), and 4.680 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a).

O-(2,3,4,6-Tetra-O-acetyl-α-D-mannopyranosyl)-(1→3)-O-[(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-(1→2)]-O-(4,6-di-O-acetyl-β-D-mannopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→1)-(2S,3R,4E)-2-azido-3-O-benzoyl-4-octadecene-1,3-diol (**59**). — To a mixture of compound **5** (7.0 mg, 13 μmol) and MS4A (400 mg) in $Cl(CH_2)_2Cl$ (1.5 mL), stirred at −20° under argon, were added successively a solution of compound **56** (12 mg, 9.6 μmol) in $Cl(CH_2)_2Cl$ (1.5 mL) and a solution of TMSOTf (2.2 μL, 11.5 μmol) in $Cl(CH_2)_2Cl$ (0.3 mL). The mixture was stirred for 40 min at −20°, neutralized with Et_3N (20 μL), diluted with EtOAc, and filtered through Celite. The filtrate was washed with aqueous $NaHCO_3$ and aqueous NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on SiO_2 in 1:1 EtOAc–toluene to give **59** (9.4 mg, 64%); $[\alpha]_D$ −41.4° (*c* 0.8); R_F 0.34 in 1:1 toluene–EtOAc; n.m.r. data: δ_H 8.049 (d, 2 H, *J* 7.7 Hz, Ph-H), 7.579 (t, 1 H, *J* 7.7 Hz, Ph-H), 7.454 (t, 2 H, *J* 7.7 Hz, Ph-H), 5.924 (td, 1 H, *J* 6.8, 14.7 Hz, H-5′), 5.599 (dd, 1 H, *J* 3.9, 8.1 Hz, H-3′), 5.541 (dd, 1 H, *J* 8.1, 14.7 Hz, H-4′), 4.551 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1a), 4.434 (s, 1 H, H-1b), 2.149, 2.134, 2.114 (6 H), 2.091, 2.088, 2.079, 2.074, 2.057, 2.042, 2.004, 1.996 (11 s, 36 H, $COCH_3$), and 0.878 (t, 3 H, *J* 6.8 Hz, terminal CH_3).

Anal. Calc. for $C_{72}H_{101}N_3O_{34}$: C, 55.70; H, 6.56; N, 2.71. Found: C, 55.64; H, 6.35; N, 2.42.

Conversion of compound **59** *into compound* **60**. — A solution of compound **59** (6.5 mg, 4.2 μmol) in oxolane (0.75 mL) and 0.05M NaOMe–MeOH (1.75 mL) was stirred for 21 h at 20°, then neutralized with Amberlite 15 resin and concentrated *in vacuo*. The residue was chromatographed on Sephadex LH-20 in 12:6:1 $CHCl_3$–MeOH–H_2O to give **60** (3.9 mg, 98%); $[\alpha]_D$ −23.5° (*c* 0.4; pyridine); R_F 0.23 in 12:6:1 $CHCl_3$–MeOH–H_2O; n.m.r. data [99:1 $(CD_3)_2SO$–D_2O, 20°]: δ_H 5.660 (td, 1 H, *J* 7.0, 14.7 Hz, H-5′), 5.432 (dd, 1 H, *J* 7.0, 15.3 Hz, H-4′), 4.868 (s, 1 H, H-1c), 4.651 (s, 1 H, H-1b), 4.308 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1d), 4.191 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 4.070 (t, 1 H, *J* 6.0 Hz, H-3′), 4.045 (d, 1 H, $J_{2,3}$ 2.5 Hz, H-2b), 2.000 (m, 1 H, H-6′), and 0.856 (t, 3 H, *J* 6.7 Hz, terminal CH_3).

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