Synthesis of Glucose-Containing Linear Oligosaccharides Having $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$ Linkages Using Stereoselective Dehydrative Glycosylation

Shinkiti Koto,* Hisamitsu Haigoh, Sonoko Shichi, Motoko Hirooka, Teiko Nakamura, Chika Maru, Misuzu Fujita, Ayano Goto, Tomoko Sato, Masato Okada, Shonosuke Zen, Kazuo Yago,† and Fumiya Tomonaga†

School of Pharmaceutical Sciences, Kitasato University, Shirokane, Minato-ku, Tokyo 108

†Department of Pharmacy, Kitasato University Hospital, Kitasato, Sagamihara 228

(Received December 15, 1994)

Glycogen-storage-disease-relating linear tetra-, hexa-, and octasaccharides of D-glucose having $\alpha(1\rightarrow4)$ and $\alpha(1\rightarrow6)$ linkages were synthesized using a stereoselective dehydrative glycosylation with a reagent mixture of *p*-nitrobenzenesulfonyl chloride, silver trifluoromethanesulfonate, *N*,*N*-dimethylacetamide, and triethylamine. A cross-condensation of a quasi-stoichiometric amount of a donor and an acceptor of an octasaccharide, followed by deprotection, afforded a glucohexadecasaccharide.

Recent progress of the glycosylation methods[1] has brought forth recent syntheses[2] of megalosaccharides.[3] Dehydrative glycosylation (Eq. 1) using 1-OH sugar derivatives such as 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**1**, DOH) and acceptor (AOH) has an advantage over other glycosylations which inevitably require preparation and manipulation of reactive glycosyl donors.[1] Several reports,[4] including two-stage method,[5] have dealt with such glycosylations.

$$\mathrm{DOH} + \mathrm{AOH} \longrightarrow \mathrm{DOA} + \mathrm{H_2O} \qquad (1)$$

Among the glycosylation reagent systems so far studied by the authors, a reagent mixture (NSDT)[6] composed of *p*-nitrobenzenesulfonyl chloride (NSC), silver trifluoromethanesulfonate (STF), *N*,*N*-dimethylacetamide (DMA), and triethylamine (TEA) was shown to be suitable for stereoselective syntheses of glucotrisaccharides having α-D-glucopyranosidic linkages.[7] This paper reports the results of an application of NSDT for the synthesis of a megalosaccharide. The glucotetrasaccharide **2**[8—11] and the glucooctasaccharide **3**,[11] which are reported to be excreted by patients suffered from glycogen storage disease type II and type III[8—11] were synthesized (Chart 1). A cross-coupling between the donor **4** and the acceptor **5**, both of which were derived from the octasaccharide intermediate **6**, and subsequent deprotection processes furnished the linear glucohexadecaose **7**. No report dealing with megalosaccharide synthesis using dehydrative glycosylation has yet appeared.

We have reported that α-cross-coupling could be achieved using NSDT with good selectivity in the reaction between hemiacetal OH in the maltosyl donor **8** and less reactive 4-OH in the acceptor **9**, whereas a similar reaction of **8** with the acceptor **10** carrying primary 6-OH resulted in lower α-selectivity (Chart 2).[7] Taking this into account, we decided the synthetic plan for the construction of the octasaccharide **3**, component IV_1 of the urinary oligosaccharides,[11] and further elongation of the sugar chain using NSDT as shown in Fig. 1.

Maltotriose **11** was converted into an acceptor **12** having a primary OH in the nonreducing terminal D-glucopyranosyl residue. A cross-condensation of **12** with a donor **13**,[12] followed by deacetylation of an anomeric mixture of the condensates and subsequent chromatographic separation, gave the desired $\alpha(1\rightarrow6)$-linked tetrasaccharide acceptor **14** as a major product in a 36% yield. The sulfonate **15** formed in the reaction was converted to **12** through substitution of the sulfonyloxyl group with acetoxyl group, followed by deacetylation. Compound **14** was transformed into the tetrasaccharide donor **16** via the acetate **17**. An α-cross-coupling between **14** and **16** in the presence of seven molar amount of NSDT afforded **6** in a 35% yield with complete selectivity. The sulfonate **18** was converted into **14** in a marginal yield by a brief treatment with lithium aluminium hydride in 1,2-dimethoxyethane. After usual deprotection processes, **14** and **6** were transformed into **2** and **3**, respectively. ^{1}H and ^{13}C NMR spectra of **2** matched well with the published data.[13,14] ^{13}C NMR spectrum of **3** shows the presence

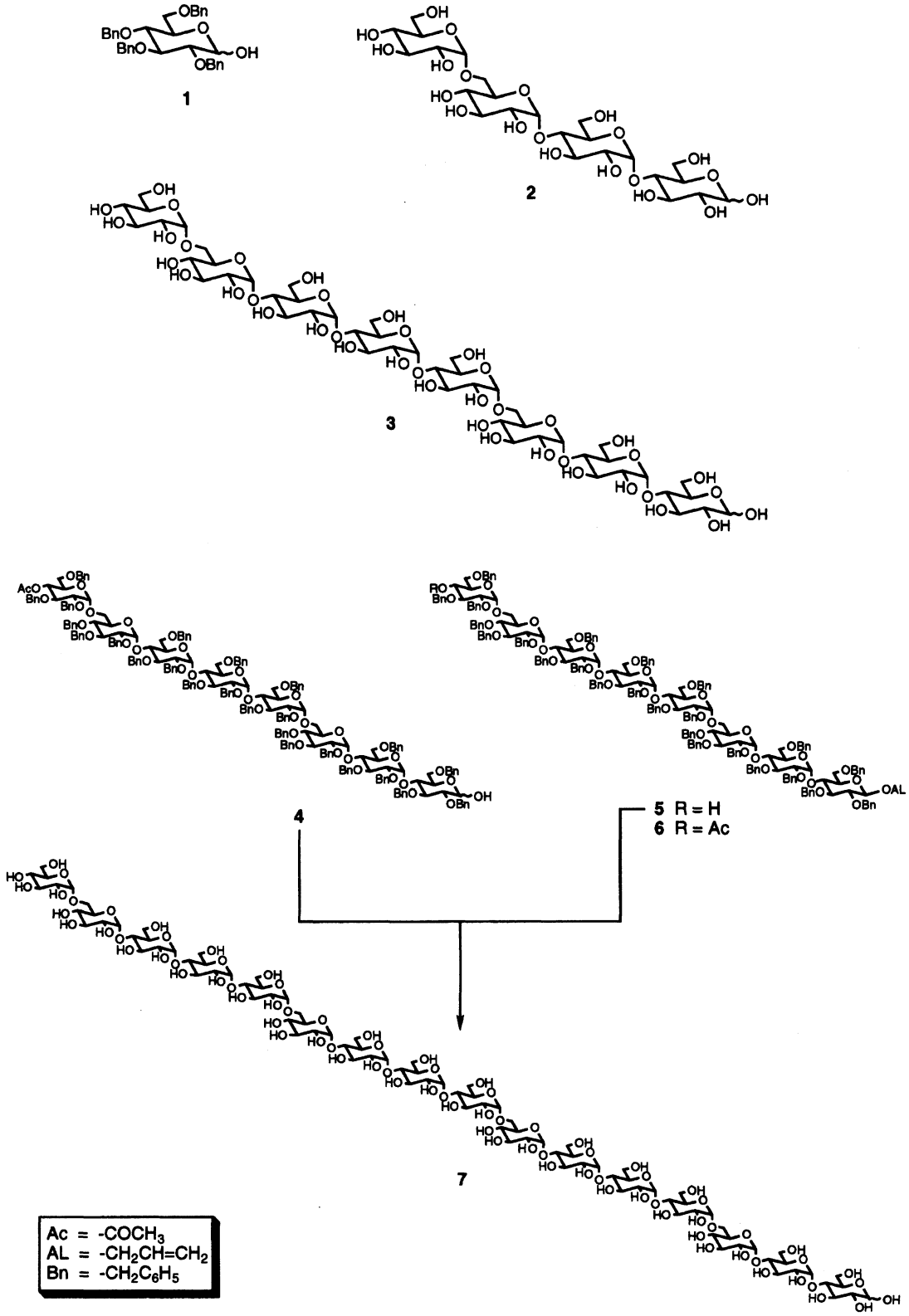

Chart 1.

of seven interglycosidic anomeric carbons. The splitting of the signals arising from the anomeric carbon of B-unit, observed at δ's of 102.2 and 102.3, reflects the anomeric configuration of the reducing A-unit. This is also the case in maltose **19**,[15] its homolog **11**,[7] and **2**. Compound **6** was converted into the donor **4** and the acceptor **5**. An α-cross-condensation of almost equimolar amounts of the partners, with the aid of ten molar amount of NSDT, furnished the anticipated compound **20** in a 35% yield with complete selectivity. ^{13}C NMR

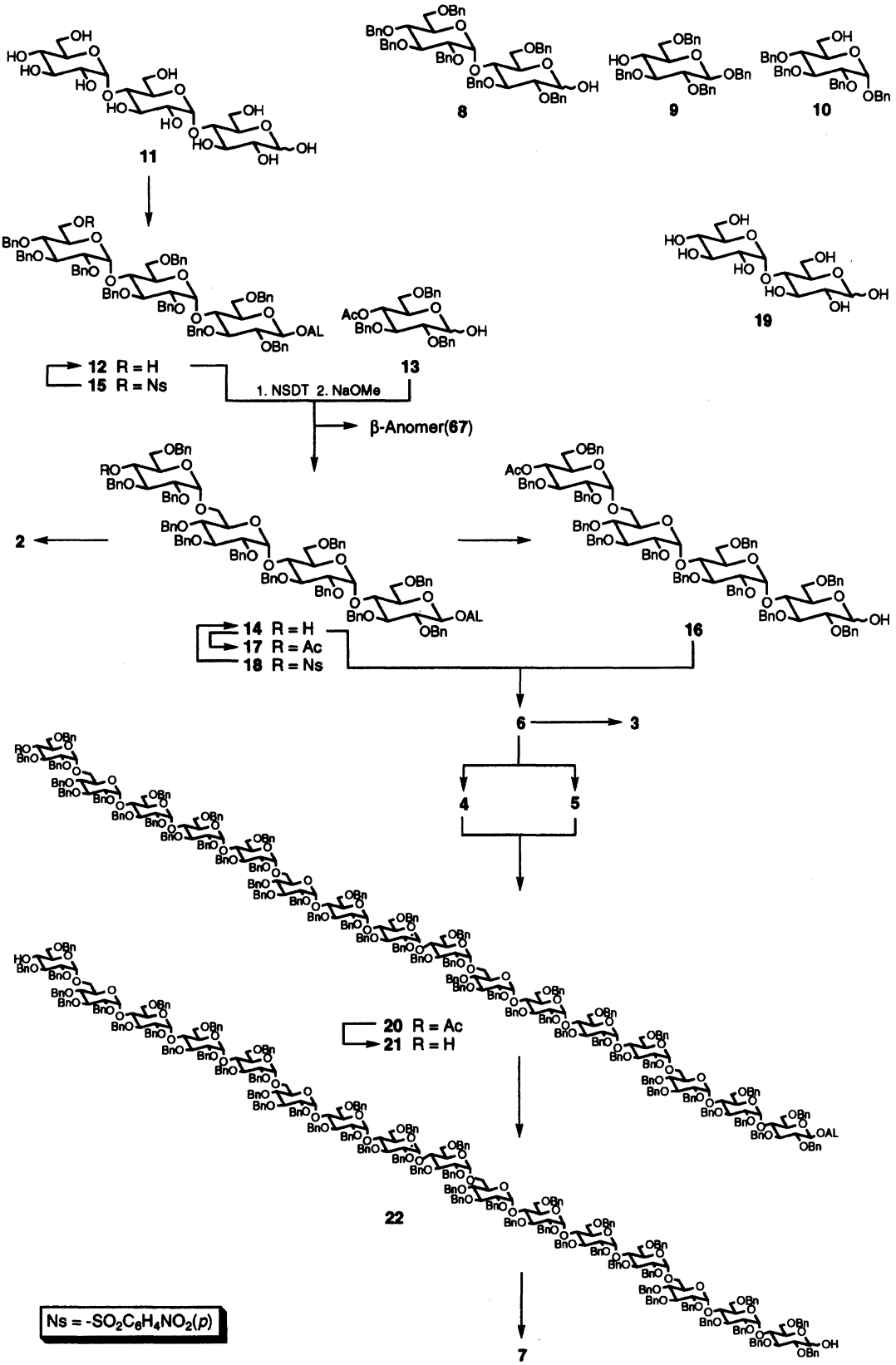

Chart 2.

spectra of **14**, **5**, and **20** show the progressive accumulation of the signals of the anomeric carbons for $\alpha(1\rightarrow4)$ linkages around 96.1 ppm. In the spectrum of **5**, the signal at 96.7 ppm, which is absent in that of **14**, arises from the inner $\alpha(1\rightarrow6)$ linkage in D-unit, in addition to the signal at 97.2 ppm for the anomeric carbon in the

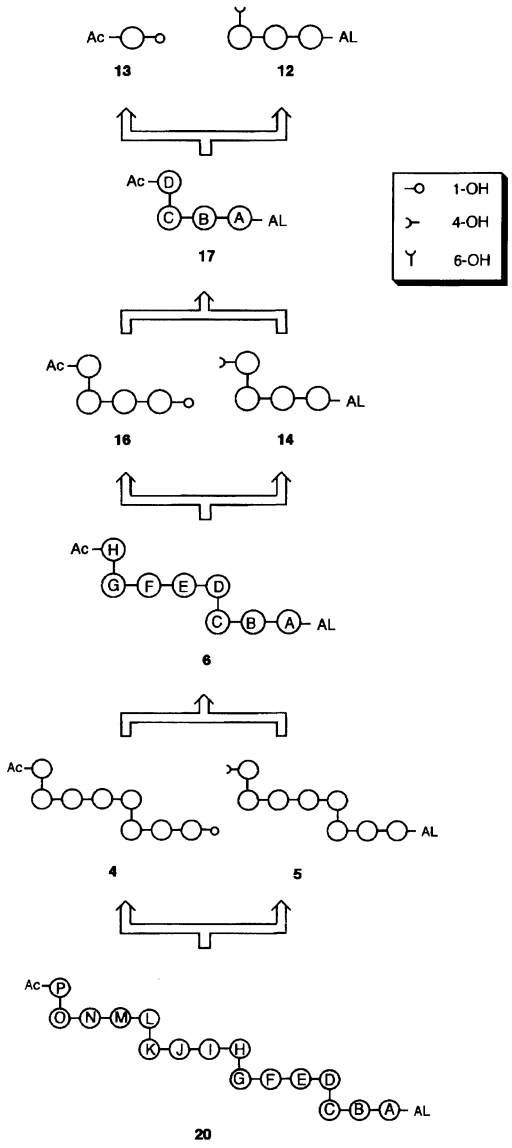

Fig. 1. A retro-synthetic scheme for the glucooctasaccharide **3** and the glucohexadecasaccharide **7**. A, B, ···, and P designate the sequential order of D-glucopyranosyl units from the reducing end to the nonreducing end. A horizontal line between large circles indicating α-D-Glc*p*(OBn)$_3$ or α-D-Glc*p*(OBn)$_4$ represents an α(1→4) linkage whereas a vertical one does α(1→6) linkage.

terminal H-unit having α(1→6) linkage. In the spectrum of **20**, the signal at 96.7 ppm with increased intensity suggests the presence ot three anomeric carbons of the inner D-, H-, and L-units with α(1→6) linkages. Unfortunately, the conventional deacetylation of **20** using sodium methoxide[16] encountered unexpected side reactions. Desired **21** was afforded only in a 34% yield. After mild deallylation[17] of **21**, the final hydrogenative debenzylation of the intermediary diol **22** yielded the free glucohexadecaose **7**; the amount was enough to confirm its structure by its DEPT spectrum.[18] The ^{13}C-DEPT spectrum of the methyne carbons for **7** shows that the increased intensity of the signal at 100.6 ppm arises from the three anomeric carbons of D-, H-, and L-units with the inner α(1→6) linkages of **7**. The signals for C1, C2, C3, and C5 in the A-unit of the major β-anomer of **7** can unambiguously be distinguished from noise peaks; the signals for C1 and C5 in A-unit of the minor α-anomer are not observed, however. The resemblance between the ^{13}C-DEPT spectral patterns of the methyne carbons for **3** and **7**, except the decreased intensity of the peaks arising from A-unit observed for **7**, indicates that the structure of **7** is homologous to that of **3**. The synthesis of a linear glucohexadecasaccharide with a repeating unit[19] was thus achieved using the NSDT method.

The tetrasaccharide **23** having the structure corresponding to the sequence of C–D–E–F in **3** was also synthesized. Maltotriose **11** was converted into a donor **24**[20] via the allyl route[17] and the 2-methoxyethyl route.[12] A cross-coupling of the acceptor **25**[21] with **24** mainly afforded the α-linked tetrasaccharide derivative **26** in a 32% yield (Chart 3). This was then hydrogenolyzed into the tetraose **23**. ^{13}C NMR shows the splitting of the signals of the anomeric carbon in B-unit[15] at δ's of 102.26 and 102.30, as observed in the case of *O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (isopanose).[7]

The hexasaccharide **27**, which was once postulated[11,22] as component IV$_{21}$ of the urinary saccharides, was synthesized via three individual approaches, as shown in Fig. 2. Among them, the best yield was obtained via the following approach (Chart 4). A cross-condensation was carried out using the isomaltose donor **28**[7] and the maltose acceptor **29** to give the α-condensate **30** in a 27% yield. Compound **30** was transformed into the donor **31**, which was then coupled with the acceptor **32** to yield compound **33** in a 24% yield with complete selectivity. ^{13}C NMR of the hexaose **27** obtained from **33** clearly shows the presence of five interglycosidic anomeric carbons. A pair of the split signals of the anomeric carbon of B-unit[15] is present at δ's of 102.1 and 102.2. Such a splitting is also present in the ^{13}C NMR of the tetrasaccharide **34** derived from **31**, as well as in that of the tetrasaccharide **35** described below. On the other hand, approaches employing the isomaltotriose donor **36** did not work well. Especially, its direct coupling with the maltotriose acceptor **37** afforded very little **33**.

The synthesis of another hexaose, the structure of which was once proposed as component IV$_3$[11,22] was then attempted (Fig. 2). The maltose donor **8**[7] was condensed with the isomaltose acceptor **38** to give **39** in a 48% yield as a main product, which was converted into the free tetrasaccharide **35** (Chart 5). The tetraose donor **40** having isomaltotriose moiety therein again exhibited a very weak reactivity. Its condensation with the maltose acceptor **32** gave the hexaose derivative **41**, but not enough for deprotection processes.

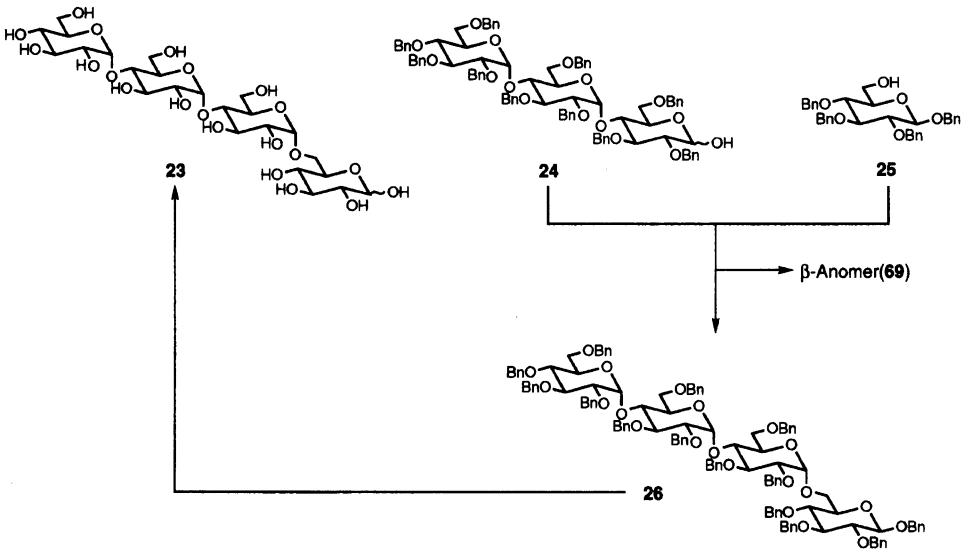

Chart 3.

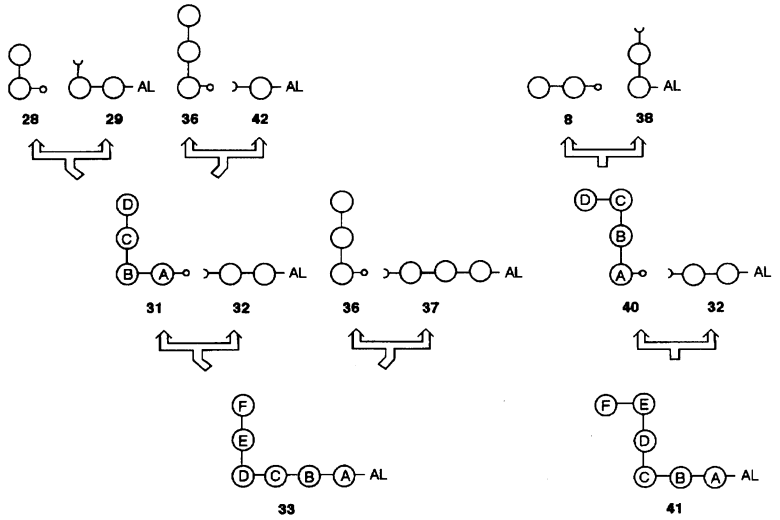

Fig. 2. A retro-synthetic scheme for glucohexasaccharides.

In conclusion, NSDT is capable of performing a dehydrative cross-condensation between both a donor and an acceptor of a linear glucooctasaccharide to form an $\alpha(1\rightarrow4)$ linkage with practically complete stereoselectivity.

Experimental

The solvent systems for column chromatography on silica gel (Kanto Chemical, No. 37047; gradient elution) and thin-layer chromatography on silical gel plate (Merck DC-Plastikfolien Kieselgel 60 F_{254}, Art. 5735) were benzene–ethyl acetate (BE), chloroform–methanol (CM), 1,2-dichloroethane–ethyl acetate (DE), hexane–ethyl acetate (HE), toluene–2-butanone (TB), and toluene–ethyl acetate (TE). The optical rotations were measured on a JASCO DIP-150 Digital Polarimeter at ca. 25 °C.

The donors **8**,[7] **13**,[12] and **28**,[7] the acceptor **42**,[23] and the intermediates **43**[7] and **44**[7] were prepared through the published methods (Chart 6). Similar to the preparation of benzyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**10**),[21] **25**[24] was prepared from benzyl β-D-glucopyranoside[25] via benzylation[26] and detritylation of **benzyl 6-*O*-trityl-β-D-glucopyranoside**, $[\alpha]_D$ −73° (*c* 0.2, $CHCl_3$) (lit,[27] $[\alpha]_D$ −50° (*c* 1.7, $CHCl_3$)). Found: C, 74.71; H, 6.39%. Calcd for $C_{32}H_{32}O_6$: C, 74.98; H, 6.29%. Compounds **11**, **19**, **45**, and **46** were the commercial products of Tokyo Kasei Kogyo Co., Inc. The other items were described earlier.[28]

Unless otherwise described, the ^1H and ^{13}C NMR spectra were recorded with a Varian VXR-300 spectrometer or a Varian XL-400 spectrometer, accompanied with the measurements of H,H-COSY, H,C-COSY, and DEPT spectra.[7,28] The value, 69.2 ppm, instead of the previously used 67.4 ppm, was taken as the chemical shift of 1,4-dioxane as the internal standard in D_2O.

Synthetic Blocks. Allyl *O*-(2,3-Di-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (47). The synthetic route[29] for **47** from **19** was modified for handiness as follows. The acetate **43**[29] (4.46 g), prepared from **19** through a 'one-pot'

Table 1. Results of Dehydrative Glycosylation (DOH+AOH→DOA)

No.	DOH[a]	AOH[a]	DOH/AOH	NSC[a]	STF[a]	DMA[a]	TEA[a]	DCM[a]	DOA	AONs[a]
	mg	mg	mol/mol	equiv[b]	equiv[b]	equiv[b]	equiv[b]	ml	%(α%)	%
1	**13**	**12**	1.30	1.7	1.7	3.4	1.7	5.90	**14**[c]+**67**[c]	**15**
	438.9	929.5							56 (65)	18
2	**16**	**14**	1.26	7.0	7.0	7.0	7.0	0.60	**6**	**18**
	122.5	97.1							35 (100)	29
3	**4**	**5**	0.94	10.0	10.0	10.0	10.0	0.40	**20**	**68**
	60.2	63.7							35 (100)	27
4	**24**	**25**	1.30	2.7	2.7	5.4	2.7	0.46	**26**+ **69**	
	154.4	45.7							54 (60)	—[d]
5	**28**	**29**	1.30	2.5	2.5	5.0	2.5	2.30	**30**+ **72**	**73**
	283.3	206.7							41 (67)	19
6	**36**	**42**	1.30	4.0	4.0	4.0	4.0	0.45	**30**	**74**
	77.9	20.9							13 (100)	20
7	**31**	**32**	0.97	6.0	6.0	6.0	6.0	2.50	**33**	**75**
	442.3	228.2							24 (100)	24
8	**36**	**37**	1.46	5.5	5.5	5.5	5.5	1.00	**33**	**76**
	158.6	104.7							8 (100)	15
9	**8**	**38**	1.18	3.0	3.0	6.0	3.0	3.00	**39**+ **77**	**78**
	189.2	151.8							58 (83)	31
10	**40**	**32**	0.88	7.0	7.0	7.0	7.0	0.65	**41**	**75**
	109.8	63.0							3 (100)	31

a) DOH = donor hemiacetal, AOH = acceptor alcohol, NSC = *p*-nitrobenzenesulfonyl chloride, STF = silver trifluoroethanesulfonate, DMA = *N*,*N*-dimethylacetamide, TEA = triethylamine, DCM = dichloromethane, AONs = *p*-nitrobenzenesulfonate of acceptor alcohol. b) To AOH. c) De-*O*-acetate of the cross-condensates. d) Not determined.

procedure,[7,30] was treated with methanolic sodium methoxide (0.14%, 46 ml), followed by chromatography (CM system) to give **48** (2.25 g, 90%), $[\alpha]_D$ +73° (*c* 1.0, H_2O) (lit,[31] $[\alpha]_D^{26}$ +63° (*c* 3.3, H_2O)); ^{1}H NMR (D_2O) δ=4.48 (d, J=8.0 Hz, H1^A), # 5.36 (d, J=4.0 Hz, H1^B); ^{13}C NMR (D_2O) δ=102.2 (C1^B), 103.7 (C1^A); 73.3, 121.4, 135.9 (AL). ## Found: C, 46.27; H, 6.86%. Calcd for $C_{15}H_{26}O_{11}\cdot 0.5H_2O$: C, 46.03; H, 6.95%. This (7.26 g) was then reacted with benzaldehyde dimethyl acetal (5.4 ml) in DMF## (70 ml) in the presence of TSA## (monohydrate, 0.36 g) at room temp overnight. After addition of TEA## (0.53 ml), evaporation and chromatography (CM system) yielded **allyl *O*-(4,6-*O*-benzylidene-α-D-glucopyranosyl)-(1→4)-β-D-glucopyranoside (49)** (7.00 g, 78%); $[\alpha]_D$ +26° (*c* 2.0, CH_3OH); ^{1}H NMR (D_2O) δ=4.50 (d, J=8.0 Hz, H1^A), 5.44 (d, J=4.0 Hz, H1^B), 5.72 (s, Bd);## ^{13}C NMR (D_2O) δ=63.2 (C6^A), 66.0 (C5^B), 70.6 (C6^B), 72.7 (C3^B), 74.9 (C2^B), 75.6 (C2^A), 77.0 (C5^A), 78.9 (C3^A), 79.6 (C4^A), 82.8 (C4^B), 103.0 (C1^B), 103.7 (C1^A), 104.4 (Bd); 73.3, 121.4, 135.9 (AL). Found: C, 55.96; H, 6.42%. Calcd for $C_{22}H_{30}O_{11}$: C, 56.16; H, 6.43%. To a stirred mixture of **49** (6.67 g), NaH (ca. 60% dispersion in oil, 14.2 g), and DMF (65 ml), benzyl bromide (42.2 ml) was added in drops at 0 °C. After stirring at 20 °C for 1.5 h, the processed reaction mixture was chromatographed (HE system) to give the pentabenzyl ether. This was then treated with TFA## (25 ml) in chloroform (50 ml) containing methanol (50 ml) at room temp for 6 h. Chromatography (TB system) furnished **47** (7.46 g, 63%); $[\alpha]_D$ +24° (*c* 1.4, $CHCl_3$) (lit,[29] $[\alpha]_D^{25}$ +23.6° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ=4.08 (t, J=9.0 Hz, H4^A), 4.50 (d, J=7.5 Hz, H1^A), 5.66 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=62.3 (C6^B), 68.7 (C6^A), 71.9 (C4^B), 72.3 (C4^A), 79.1 (C2^B), 81.1 (C3^B), 82.2 (C2^A), 84.8 (C3^A), 96.3 (C1^B), 102.5 (C1^A); 70.2, 117.3, 134.0 (AL). Found: C, 71.63; H, 6.80%. Calcd for $C_{50}H_{56}O_{11}$: C, 72.10; H, 6.80%.

Allyl *O*-α-D-Glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (50). Similar to the preparation of **48**, deacetylation of **51** (13.95 g) with methanolic sodium methoxide (0.24%, 100 ml), followed by chromatography (CM system), furnished **50** (7.36 g, 93%); $[\alpha]_D$ +99° (*c* 2.3, H_2O) (lit,[20] $[\alpha]_D^{20}$ +111.5° (*c* H_2O); ^{1}H NMR (D_2O) δ=4.34 (d, J=8.0 Hz, H1^A), 5.22 (2H, d, J=3.5 Hz, H1^B, H1^C); ^{13}C NMR (D_2O) δ=62.8

#D-Glucose units in the glucooligosaccharides dealt with are coded alphabetically starting from the reducing end toward the non-reducing end.

##AL = allyl, Bd = benzylidene, DCM = dichloromethane, DMA = *N*, *N*-dimethylacetamide, DMF = *N*, *N*-dimethylformamide, EBW = mixture of ethanol, benzene, and H_2O (7 : 3 : 1), ME = 2-methoxyethyl, Ns = *p*-nitrobenzenesulfonyl, NSC = *p*-nitrobenzenesulfonyl chloride, STF = silver trifluoromethanesulfonate, TEA = triethylamine, TFA = trifluoroacetic acid, TRC = tris(triphenylphosphine)rhodium(I) chloride, TSA = *p*-toluenesulfonic acid, Tr = trityl.

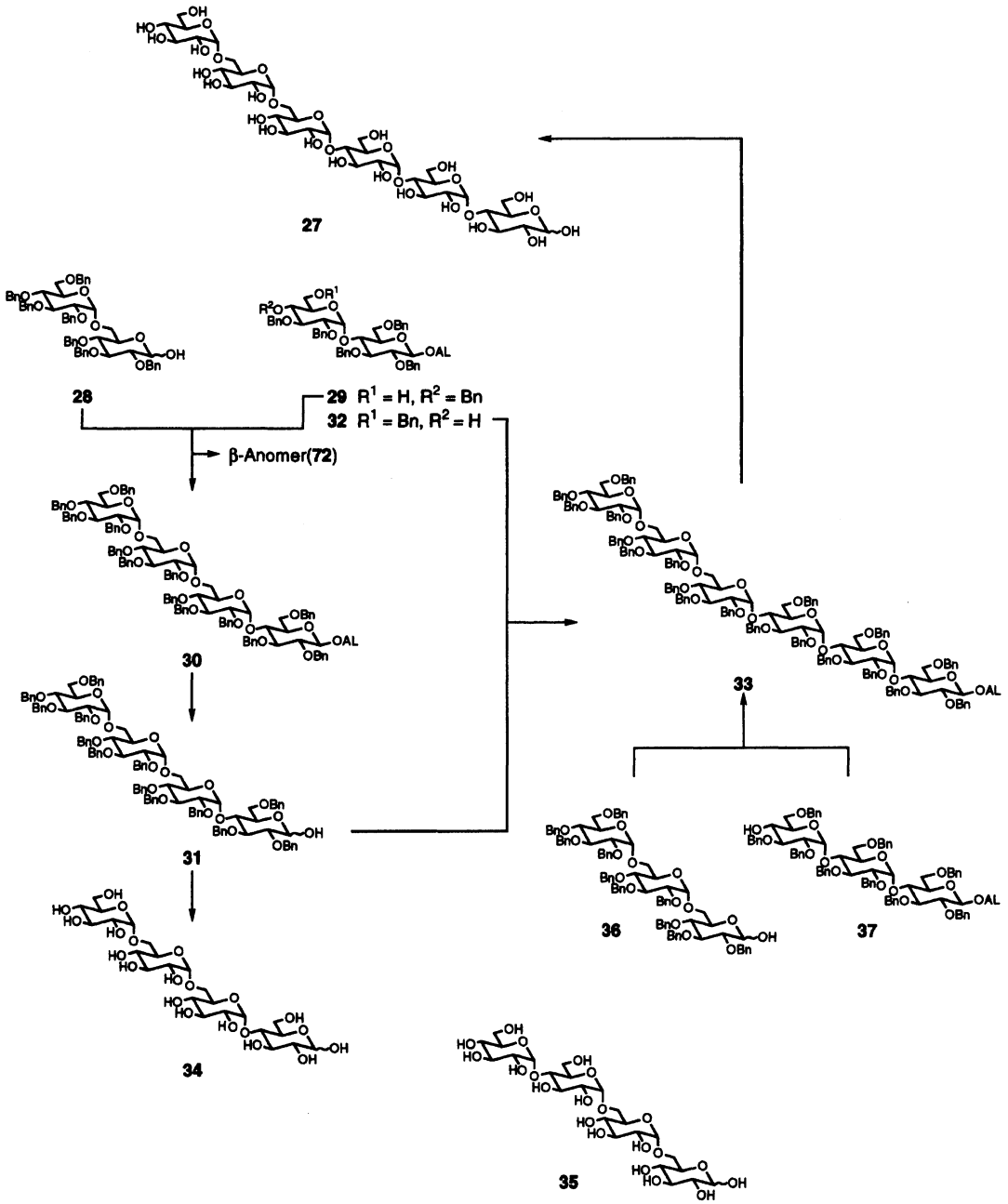

Chart 4.

(2C), 63.0 ($C6^A$, $C6^B$, $C6^C$); 71.6 ($C4^C$), 73.5 ($C5^B$), 73.8, 74.0 ($C2^B$, $C2^C$); 74.4 ($C5^B$), 75.0 ($C5^C$); 75.2, 75.6 ($C3^B$, $C3^C$); 75.3 ($C2^A$), 76.8 ($C5^A$), 78.5 ($C3^A$); 79.0, 79.2 ($C4^B$, $C4^C$); 101.9, 102.1 ($C1^B$, $C1^C$); 103.3 ($C1^A$); 73.0, 121.1, 135.6 (AL).

Found: C, 45.55; H, 6.67%. Calcd for $C_{21}H_{36}O_{16}\cdot 0.5H_2O$: C, 45.57, H, 6.74%.

Allyl *O*-α-D-Glucopyranosyl-(1→6)-*O*-α-D-glucopyranoside (52). Compound **44**[7] (2.65 g), obtained via the acetobromination[30] of **45**, was converted by treatment with methanolic sodium methoxide (0.12%, 17 ml), followed by chromatography (CM system), into **52** (1.12 g, 75%); $[\alpha]_D$ +35° (*c* 1.0, H_2O); ^{1}H NMR (D_2O) δ=4.46 (d, J=8.0 Hz, $H1^A$), 4.87 (d, J=3.5 Hz, $H1^B$); ^{13}C NMR (D_2O) δ=63.0 ($C6^B$), 68.0 ($C6^A$); 71.9, 72.0 ($C4^A$, $C4^B$); 74.1 ($C2^B$), 74.4 ($C5^B$), 75.7 (2C, $C2^A$, $C3^B$), 76.8 ($C5^A$), 78.6 ($C3^A$), 100.4 ($C1^B$), 103.9 ($C1^A$); 73.3, 121.3, 135.9 (AL).

Found: C, 45.87; H, 6.83%. Calcd for $C_{15}H_{26}O_{11}\cdot 0.5H_2O$: C, 46.03; H, 6.95%.

Allyl *O*-(4,6-*O*-Benzylidene-α-D-glucopyranosyl)-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-β-D-glucopyranoside (53). Similar to the preparation of **49**, acetalization of **50** (1.187 g) with benzaldehyde dimethyl acetal (0.99 ml) in DMF (23 ml) in the presence of TSA (monohydrate, 123 mg) furnished **53** (1.271 g, 92%); $[\alpha]_D$ +68° (*c* 2.4, H_2O); ^{1}H NMR (D_2O) δ=4.50 (d, J=8.0 Hz, $H1^A$), 5.38 (d, J=3.5, $H1^B$), 5.43 (d, J=3.5 Hz, $H1^C$), 5.73 (s, Bd); ^{13}C NMR ($CDCl_3$) δ=100.1 ($C1^B$), 101.0 ($C1^C$), 101.5 ($C1^A$), 102.6 (Bd); 71.5, 119.5, 134.2 (AL).

Found: C, 51.83; H, 6.22%. Calcd for $C_{28}H_{40}O_{16}\cdot H_2O$:

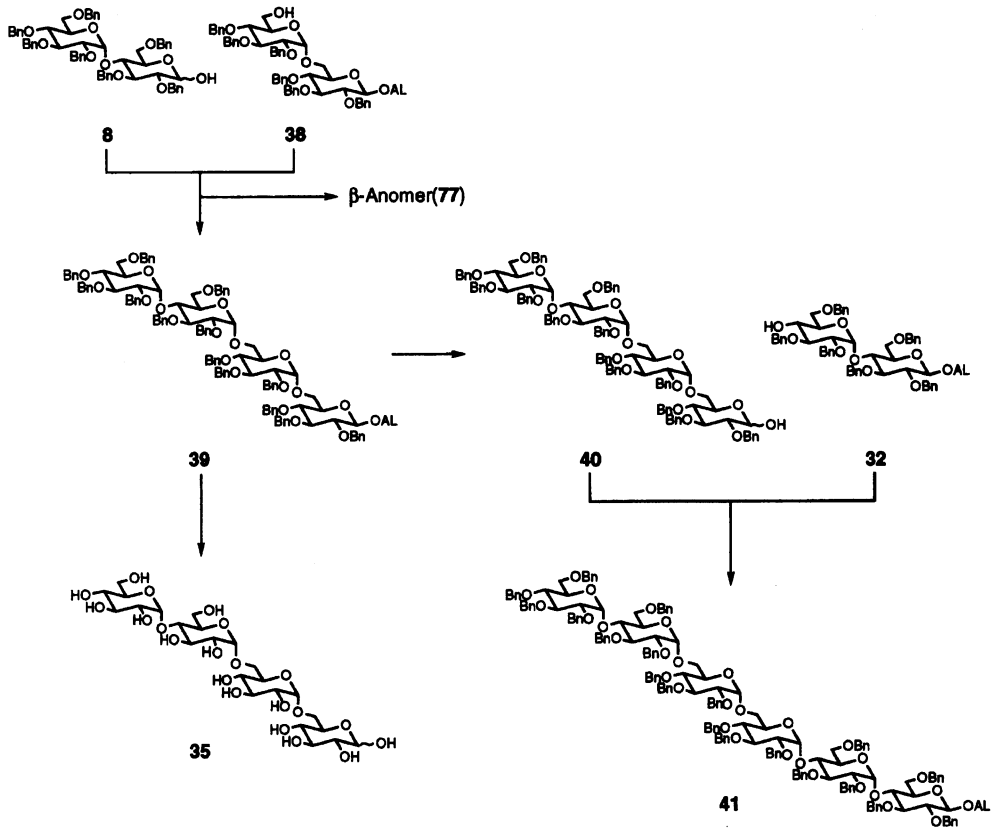

Chart 5.

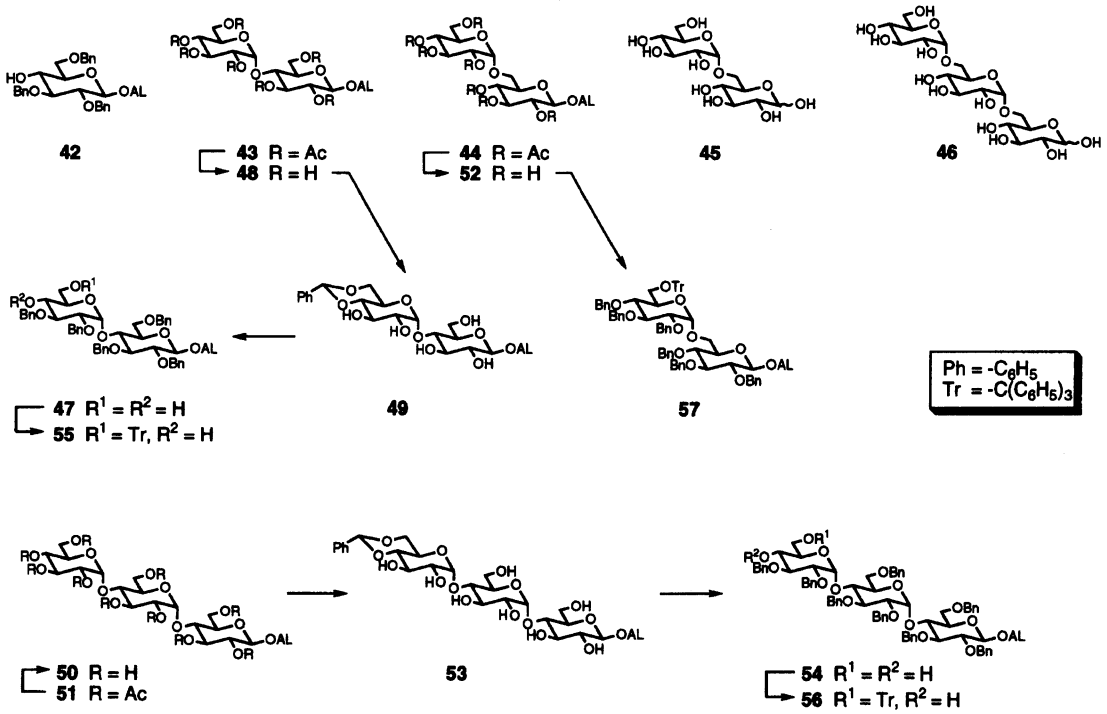

Chart 6.

C, 51.69; H, 6.51%.

Compound **50** (1.84 g, 38%) was recovered.

Allyl *O*-(2,3-Di-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (54). Analogous to the preparation of **47**, the acetal **53** (4.84 g) was treated with NaH (ca. 60% dispersion in oil, 11.6 g) and benzyl bromide (34.7 ml) in DMF (48 ml). The obtained

octabenzyl ether (10.1 g) was then transformed, by treatment with TFA (15 ml) in chloroform (36 ml) containing methanol (36 ml), into **54** (5.20 g, 54%); $[\alpha]_D$ +44° (*c* 0.4, $CHCl_3$); ^{1}H NMR (D_2O) δ=4.48 (d, J=7.5 Hz, H1^A); 5.61, 5.62 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=96.2, 96.4 (C1^B, C1^C); 102.6 (C1^A); 70.2, 117.3, 134.1 (AL).

Found: C, 72.38; H, 6.62%. Calcd for $C_{77}H_{84}O_{16}$: C, 73.08; H, 6.69%.

Prior to elution of **54**, the octabenzyl ether of **53** (4.1 g, 41%) which remained unhydrolyzed was collected.

Allyl *O*-(2,3-Di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (55). A mixture of **47** (7.46 g), trityl chloride (2.62 g), and pyridine (20 ml) was stirred at 75 °C for overnight. After addition of TEA[32] (20 ml) and evaporation to dryness, chromatography (TE system) afforded **55** (8.53 g, 89%); $[\alpha]_D$ +21° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=3.24 (dd, J=10.0, 4.5 Hz, H6a^B), 3.33 (dd, J=10.0, 4.0 Hz, H6b^B), 4.52 (d, J=7.5 Hz, H1^A), 5.64 (d, J=3.5 Hz, C1^B); ^{13}C NMR ($CDCl_3$) δ=63.5 (C6^B), 69.3 (C6^A), 96.2 (C1^B), 102.5 (C1^A); 70.1, 117.2, 134.1 (AL); 86.7, 143.7 (Tr).##

Found: C, 76.56; H, 6.68%. Calcd for $C_{69}H_{70}O_{11}$: C, 77.07; H, 6.56%.

Allyl *O*-(2,3-Di-*O*-benzyl-6-*O*-trityl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (56). In a similar manner, for the preparation of **55**, reaction of **54** (8.45 g) with trityl chloride (2.05 g) in pyridine (25 ml) at 70 °C overnight gave **56** (8.04 g, 80%); $[\alpha]_D$ +41° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=3.22 (dd, J=10.0, 3.5 Hz, H6a^C), 3.33 (dd, J=10.0, 3.0 Hz, H6b^C), 4.52 (d, J=7.5 Hz, H1^A); 5.59 (d, J=4.0 Hz), 5.68 (d, J=3.5 Hz) (H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=63.2 (C6^C); 96.2[7], 96.3[2] (C1^B, C1^C); 102.5 (C1^A); 70.1, 117.2, 134.1 (AL); 86.7, 143.7 (Tr).

Found: C, 76.20; H, 6.62%. Calcd for $C_{96}H_{98}O_{16}$: C, 76.74; H, 6.55%.

The unreacted **54** (1.18 g, 14%) was recovered.

Allyl *O*-(6-*O*-Trityl-α-D-glucopyranosyl)-(1→6)-*O*-α-D-glucopyranoside (57). Tritylation of **52** (1.07 g) with trityl chloride (0.92 g) and pyridine (2.0 ml), followed by chromatography (CM system), gave **57** (1.27 g, 73%); $[\alpha]_D$ +23° (*c* 0.4, CH_3OH–H_2O (1:1)); ^{1}H NMR (CD_3OD, δ_H=3.31) δ=4.36 (d, J=7.5 Hz, H1^A), 4.90 (d, J=3.5 Hz, H1^B); ^{13}C NMR (CD_3OD, δ_C=49.0), δ=65.0 (C6^B), 67.2 (C6^A), 99.5 (C1^B), 103.6 (C1^A); 71.3, 117.2, 135.6 (AL), 87.7, 145.6 (Tr).

Found: C, 62.05; H, 6.24%. Calcd for $C_{34}H_{40}O_{11}\cdot 2H_2O$: C, 61.81; H, 6.51%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (29). To a stirred mixture of **55** (8.5 g), NaH (ca. 60% dispersion in oil, 1.58 g), and DMF (50 ml), benzyl bromide (4.8 ml) was added in drops at 0 °C. Agitation at 20 °C for 1 h, processing, and chromatography using the HE system gave a hexabenzyl ether. This was then treated with TFA (8.0 ml) in chloroform (80 ml) containing methanol (80 ml) at room temp for overnight. Evaporation to dryness and chromatography with HE system afforded **29** (6.9 g, 73%); $[\alpha]_D$ +25° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.50 (d, J=7.5 Hz, H1^A), 5.64 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=96.4 (C1^B), 102.5 (C1^A); 70.2, 117.3, 134.1 (AL).

Found: C, 73.89; H, 6.74%. Calcd for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.77%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (12). Compound **56** (8.00 g) was reacted with NaH (ca. 60% in oil, 1.13 g) and benzyl bromide (3.17 ml) in DMF (50 ml) to give a nonabenzyl ether. Detritylation of this ether with TFA (8.0 ml) in chloroform (80 ml) containing methanol (80 ml) produced **12** (4.92 g, 68%); $[\alpha]_D$ +44° (*c* 1.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.50 (d, J=7.5 Hz, H1^A); 5.55, 5.60 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=96.2, 96.6 (C1^B, C1^C); 102.5 (C1^A); 70.2, 117.2, 134.1 (AL).

Found: C, 73.73; H, 6.60%. Calcd for $C_{84}H_{90}O_{16}$: C, 74.42; H, 6.69%.

Allyl *O*-(2,3,4-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (38). The trityl ether **57** (1.17 g) was benzylated with NaH (ca. 60% dispersion in oil, 2.19 g) and benzyl bromide (6.49 ml) in DMF (10 ml) to afford a hexabenzyl ether. This was subsequently treated with TFA (5 ml) in chloroform (23 ml) containing methanol (23 ml) to furnish **38** (1.29 g, 75%); $[\alpha]_D$ +35° (*c* 1.2, $CHCl_3$) (lit,[33] $[\alpha]_D^{25}$ +43.4° ($CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ=4.46 (d, J=7.5 Hz, H1^A), 4.98 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=61.9 (C6^B), 65.8 (C6^A), 97.0 (C1^B), 102.6 (C1^A); 70.2, 117.1, 134.0 (AL). Found: C, 73.96; H, 6.77%. Calcd for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.77%.

Allyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (32). A mixture of **47** (2.11 g), NaH (ca. 60% dispersion in oil, 204 mg), and benzyl chloride (42 ml) was stirred at 100 °C for 2 h. After addition of acetic acid under cooling and evaporation to dryness, chromatography with a TB system gave **32** (1.02 g, 44%); $[\alpha]_D$ +23° (*c* 0.9, $CHCl_3$) (lit,[31] $[\alpha]_D^{25}$ +21.6° (*c* 0.5, $CHCl_3$)); ^{1}H NMR ($CDCl_3$) δ=4.50 (d, J=8.0 Hz, H1^A), 5.68 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=70.6 (C4^B), 72.5 (C4^A), 96.5 (C1^B), 102.5 (C1^A); 70.2, 117.3, 134.1 (AL). Found: C, 74.01; H, 6.75%. Calcd for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.77%, **29** (0.48 g, 21%), and unreacted **47** (0.45 g, 21%).

Allyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (37). Analogously to the preparation of **32**, a controlled benzylation of **54** (2.77 g) with benzyl chloride (55 ml) in the presence of NaH (ca. 60% dispersion in oil, 263 mg) was performed to give **37** (1.50 g, 51%); $[\alpha]_D$ +41° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.50 (d, J=7.5 Hz, H1^A); 5.58, 5.67 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=96.4, 96.7 (C1^B, C1^C); 102.6 (C1^A); 70.2, 117.2, 134.1 (AL).

Found: C, 74.17; H, 6.88%. Calcd for $C_{84}H_{90}O_{16}$: C, 74.42; H, 6.69%.

The isomer **12** (0.69 g, 23%) and the diol **54** (0.45 g, 16%) were also isolated.

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tetra-*O*-acetyl-β-D-glucopyranoside (51). A mixture of **11** (9.77 g), acetic anhydride (50 ml), and pyridine (20 ml) was stirred at 70 °C overnight.

Processing and chromatography (TE system) gave a mixture (18.7 g, 98%) of ***O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-1,2,3,6-tetra-*O*-acetyl-α-** and **β-D-glucopyranoses** (**58** and **59**) (Chart 7). A sample (96 mg) was rechromatographed (TB system) to give **59** (65 mg); $[\alpha]_D$ +88° (*c* 1.5, $CHCl_3$) (lit,[34] $[\alpha]_D^{26}$ +89.5° (*c* 2.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=5.25, 5.39 (d, J=4.0 Hz each, $H1^B$, $H1^C$); 5.73 (d, J=7.5 Hz, H1); ^{13}C NMR ($CDCl_3$) δ=72.3, 73.3 ($C4^A$, $C4^B$); 91.2 ($C1^A$); 95.6, 95.9 ($C1^B$, $C1^C$). Found: C, 49.43; H, 5.62%. Calcd for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63%, and **58** (30 mg); $[\alpha]_D$ +118° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=5.30, 5.42 (d, J=4.0 Hz each, $H1^B$, $C1^C$); 6.24 (d, J=3.5 Hz, $H1^A$); ^{13}C NMR ($CDCl_3$) δ=72.5, 73.4 ($C4^A$, $C4^B$); 88.7 ($C1^A$); 95.6, 96.0 ($C1^B$, $C1^C$). Found: C, 49.47; H, 5.78%. Calcd for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63%. To a stirred solution of the mixture (11.2 g) of **58** and **59** in chloroform (34 ml), acetyl bromide (6.5 ml) and then cold H_2O (1.04 ml) were added under cooling. After stirring gently for 1.0 h, evaporation and co-evaporation with dry toluene gave a crude acetobromide;[35] this was then dissolved in cooled allyl alcohol (30 ml). After addition of Ag_2CO_3 (9.69 g), the mixture was stirred at room temp overnight, followed by chromatography (TE system), to give **51** (6.59 g, 59%); $[\alpha]_D$ +74° (*c* 1.5, $CHCl_3$) (lit,[20] $[\alpha]_D^{20}$ +75° (*c* 0.5, dioxane)); ^{1}H NMR ($CDCl_3$) δ=4.56 (d, J=7.5 Hz, H1); 5.25 (d, J=4.0 Hz), 5.39 (d, J=3.5 Hz) ($H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=72.5, 73.8 ($C4^A$, $C4^B$); 95.6, 95.7 ($C1^B$, $H1^C$); 98.9 ($C1^A$), 69.9, 117.6, 133.3 (AL).

Found: C, 51.03; H, 5.89%. Calcd for $C_{41}H_{56}O_{26}$: C, 51.04; H, 5.85%.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside (60). Analogously to the preparation of the corresponding allyl glycoside **51**, a mixture (4.68 g) of **58** and **59** was brominated with acetyl bromide (1.90 ml) and H_2O (0.42 ml) in chloroform (14.3 ml). The obtained bromide was treated with 2-methoxyethanol (13.8 ml) in the presence of Ag_2CO_3 (4.40 g) to give **60** (3.63 g, 76%), mp 73—75 °C; $[\alpha]_D$ +78° (*c* 2.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.60 (d, J=7.5 Hz, $H1^A$); 5.25 (d, J=4.0 Hz), 5.38 (d, J=3.5 Hz) ($H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=72.5, 73.8 ($C4^A$, $C4^B$); 95.6, 95.7 ($C1^B$, $H1^C$); 100.3 ($C1^A$); 59.0, 68.9, 71.5 (ME).##

Found: C, 50.22; H, 5.98%. Calcd for $C_{41}H_{58}O_{27}$: C, 50.10; H, 5.95%.

Allyl *O*-(2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tetra-*O*-acetyl-β-D-glucopyranoside (61). Compound **46** (1.00 g) was treated with acetic anhydride (5.0 ml) and pyridine (2.0 ml) at 70 °C to yield, after chromatography (TE system), an anomeric mixture of ***O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-acetyl-α-D-glucopyranosyl)-(1→6)-1,2,3,4-tetra-*O*-acetyl-α-** and **β-D-glucopyranose** (**62** and **63**) (1.81 g, 94%). A sample (50 mg) of a mixture of **62** and **63** was chromatographed (TB system) to give **63** (15 mg); $[\alpha]_D$ +94° (*c* 0.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=5.06, 5.10 (d, J=3.5 Hz each, $H1^B$, $H1^C$); 5.69 (d, J=8.5 Hz, $H1^A$); ^{13}C NMR ($CDCl_3$) δ=61.9 ($C6^C$); 66.0, 66.1 ($C6^A$, $C6^B$); 91.6 ($C1^A$); 95.6, 95.9 ($C1^B$, $H1^C$). Found: C, 49.91; H, 5.70%. Calcd for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63%. And **62** (33 mg); $[\alpha]_D$ +124° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=5.06, 5.10 (d, J=3.5 Hz each, $H1^B$, $H1^C$); 6.32 (d, J=4.0 Hz, $H1^A$); ^{13}C NMR ($CDCl_3$) δ=61.9 ($C6^C$); 66.0, 66.1 ($C6^A$, $C6^B$); 88.9 ($C1^A$); 95.4, 95.5 ($C1^B$, $C1^C$). Found: C, 49.55; H, 5.81%. Calcd for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63%. A convenient bromination[30] of a mixture (1.60 g) of **62** and **63** described above with acetyl bromide (0.68 ml) and H_2O (0.12 ml) in chloroform (5.2 ml) likewise furnished the intermediate, which was then converted, with allyl alcohol (3.3 ml) and Ag_2CO_3 (0.46 g), into **61** (0.80 g, 50%); $[\alpha]_D$ +116° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.56 (d, J=8.0 Hz, $H1^A$); 5.05, 5.13 (d, J=3.5 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=61.9 ($C6^C$); 66.0, 66.1 ($C6^A$,

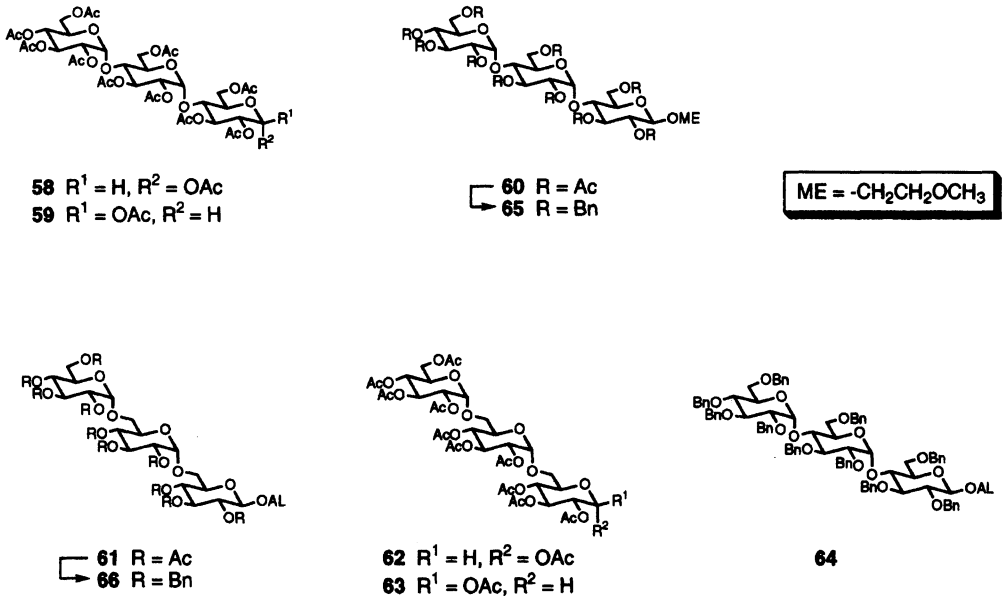

Chart 7.

$C6^B$); 95.3, 95.5 ($C1^B$, $C1^C$); 99.2 ($C1^A$); 69.8, 117.8, 133.4 (AL).

Found: C, 50.89; H, 5.92%. Calcd for $C_{41}H_{56}O_{26}$: C, 51.04; H, 5.85%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (64). A mixture of decaacetate **51** (0.77 g), crushed KOH (5.20 g), and benzyl chloride (11.2 ml) was stirred at 120 °C for 1.0 h. Processing and chromatography (HE system) yielded **64** (0.96 g, 83%); $[\alpha]_D$ +51° (*c* 1.9, $CHCl_3$) (lit,[20] $[\alpha]_D^{20}$ +47.7° (*c* 1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$); 5.58, 5.67 (d, J=3.5 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=72.8, 73.4 ($C4^A$, $C4^B$); 96.4, 96.9 ($C1^B$, $C1^C$); 102.6 ($C1^A$); 70.2, 117.2, 134.1 (AL).

Found: C, 75.61; H, 6.60%. Calcd for $C_{91}H_{96}O_{16}$: C, 75.60; H, 6.69%.

2-Methoxyethyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (65). The decaacetate **60** (390.0 mg) was reacted with bebzyl chloride (5.7 ml) and KOH (2.6 g), after chromatography (TB system), to afford **65** (385.9 mg, 66%); $[\alpha]_D$ +51° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$); 5.57, 5.65 (d, J=3.5 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=72.8, 73.5 ($C4^A$, $C4^B$); 96.3, 96.8 ($C1^B$, $C1^C$); 103.7 ($C1^A$); 58.9, 68.9, 71.8 (ME).

Found: C, 74.97; H, 6.75%. Calcd for $C_{91}H_{98}O_{17}$: C, 74.67; H, 6.75%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (66). An analogous reaction of **61** (0.54 g) with benzyl chloride (7.9 ml) and KOH (3.63 g) yielded **66** (0.55 g, 68%); $[\alpha]_D$ +59° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=4.42 (d, J=7.5 Hz, $H1^A$); 4.98, 5.04 (d, J=3.5 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=65.5, 65.8 ($C6^A$, $C6^B$); 68.5 ($C6^C$); 96.9, 97.2 ($C1^B$, $C1^C$); 102.6 ($C1^A$); 70.1, 117.0, 134.1 (AL).

Found: C, 75.75; H, 6.77%. Calcd for $C_{91}H_{96}O_{16}$: C, 75.60; H, 6.69%.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (24).** (a) A mixture of **64** (1.11 g), potassium *t*-butoxide[17] (0.65 g), and dimethyl sulfoxide (1.99 ml) was stirred at 120 °C for 1 h under N_2. The processed syrupy reaction mixture was stirred in 1,4-dioxane (7.7 ml) containing aq H_2SO_4 (16%, 0.64 ml) at 100 °C for 1 h, followed by chromatography (HE system) to give **24** (0.91 g, 84%); $[\alpha]_D$ +53° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) ($\alpha:\beta$=3:2) δ=5.24 (br, $H1^A\alpha$), 5.52 (d, J=3.5 Hz, $H1^C$), 5.66 (d, J=3.5 Hz, $H1^B\beta$), 5.68 (d, J=3.5 Hz, $H1^B\alpha$); ^{13}C NMR ($CDCl_3$) δ=90.9 ($C1^A\alpha$), 96.6 ($C1^C$), 96.8 ($C1^B\alpha$), 96.9 ($C1^B\beta$), 97.4 ($C1^A\beta$).

Found: C, 75.25; H, 6.73%. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60%.

(b) Agitation of **64** (747.1 mg) in aq acetic acid (90%) in the presence of $PdCl_2$[36] (20 mg) and sodium acetate (20 mg) at 60 °C for 1 h, followed by processing and chromatogtaphy yielded **23** (458.7 mg, 63%).

(c) A mixture of **64** (540.0 mg), TRC## (50 mg), and EBW## (5.0 ml)[37] was refluxed overnight. After evaporation to dryness, the resulting residue was stirred in acetone (8.0 ml) containing hydrochloric acid (3.7%, 0.20 ml) at 40 °C for 2 h. Evaporation to dryness and chromatography afforded the unreacted **64** (219.4 mg, 41%) and **24** (249.6 mg, 48%).

(d) To a stirring solution of **65** (59.8 mg) in dry DCM## (0.42 ml) at 20 °C, $TiCl_4$[12] (6.2 μl) was added. The resulting orange-colored solution was set aside for 5 min. After partition of the mixture between DCM and H_2O, the organic layer was washed with aq $NaHCO_3$ (5%), evaporated, and absorbed on a silica gel column, which was kept standing overnight. Elution with TB system afforded **24** (46.5 mg, 81%).

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranose (36).** Compound **66** (380.7 mg) was treated with $PdCl_2$[37] (25 mg) and sodium acetate (25 mg) in aq acetic acid to give **36** (258.9 mg, 70%); $[\alpha]_D$ +63° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) ($\alpha>\beta$) δ=5.12 (d, J=3.5 Hz, H1α); ^{13}C NMR ($CDCl_3$) δ=91.1 ($C1^A\alpha$), 96.8[5] ($C1^B\beta$), 96.8[9] ($C1^B\alpha$), 97.2 ($C1^B$), 97.3 (C1β).

Found: C, 75.30; H, 6.72%. Calcd for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60%.

Dehydrative Glycosylation. To a rubber-stoppered flask containing as acceptor, a donor, NSC## (Tokyo Kasei Kogyo Co., Inc., purified by passing swiftly through a silica-gel column eluted with benzene, followed by concentration and desiccation in vacuo over P_2O_5) and STF## (Aldrich Chemical Co., Inc.) was injected DCM## (Wako Pure Chemical Industries, Ltd., stored over molecular sieve 3A), followed by stirring at −40—0 °C until a whole syrup was dissolved to form a qausi to perfectly homogeneous solution. To a mixture with stirring below −40 °C (bath temp), DMA## (Wako Pure Chemical Industies, Ltd., distilled and stored over molecular sieve 3A) and TEA## (Wako Pure Chemical Industries, Ltd., distilled) were successively injected. Subsequent operations and processings including preliminary chromatography with TB system (gradient) were performed just as described before.[7] Each condensate thus obtained were purified through repeated chromatographies with TB system, occasionally with auxiliary uses of BE, DE, or TE systems, and at last with HE system.

Syntheses of Oligosaccharides Repeating Tetrasaccharide. Allyl *O*-(2,3,6-Tri-*O*-benzyl-α- and β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (14 and 67) (Chart 8). A dehydrative condensation between donor **13** (438.9 mg) and acceptor **12** (929.5 mg) was carried out in the presence of NSC (380.2 mg), STF (440.8 mg), DMA (320 μl), and TEA (240 μl) in DCM (5.90 ml) afforded **allyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (15)** (207.2 mg, 18%); $[\alpha]_D$ +56° (*c* 2.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ=4.48 (d, J=7.5 Hz, $H1^A$); 5.58, 5.61 (d, J=3.5 Hz each, $H1^B$ and $H1^C$); ^{13}C NMR ($CDCl_3$) δ=68.9 (2C, $C6^A$, $C6^B$), 69.7 ($C6^C$); 95.8, 96.0 ($C1^B$ and $C1^C$); 102.6 ($C1^A$); 70.2, 117.3, 134.0 (AL); 141.4, 150.5 (Ns). Found: C, 70.03; H, 6.33; N, 0.84%. Calcd for $C_{90}H_{93}NO_{20}S$: C, 70.16; H, 6.08; N, 0.91%. And a condensate mixture, which

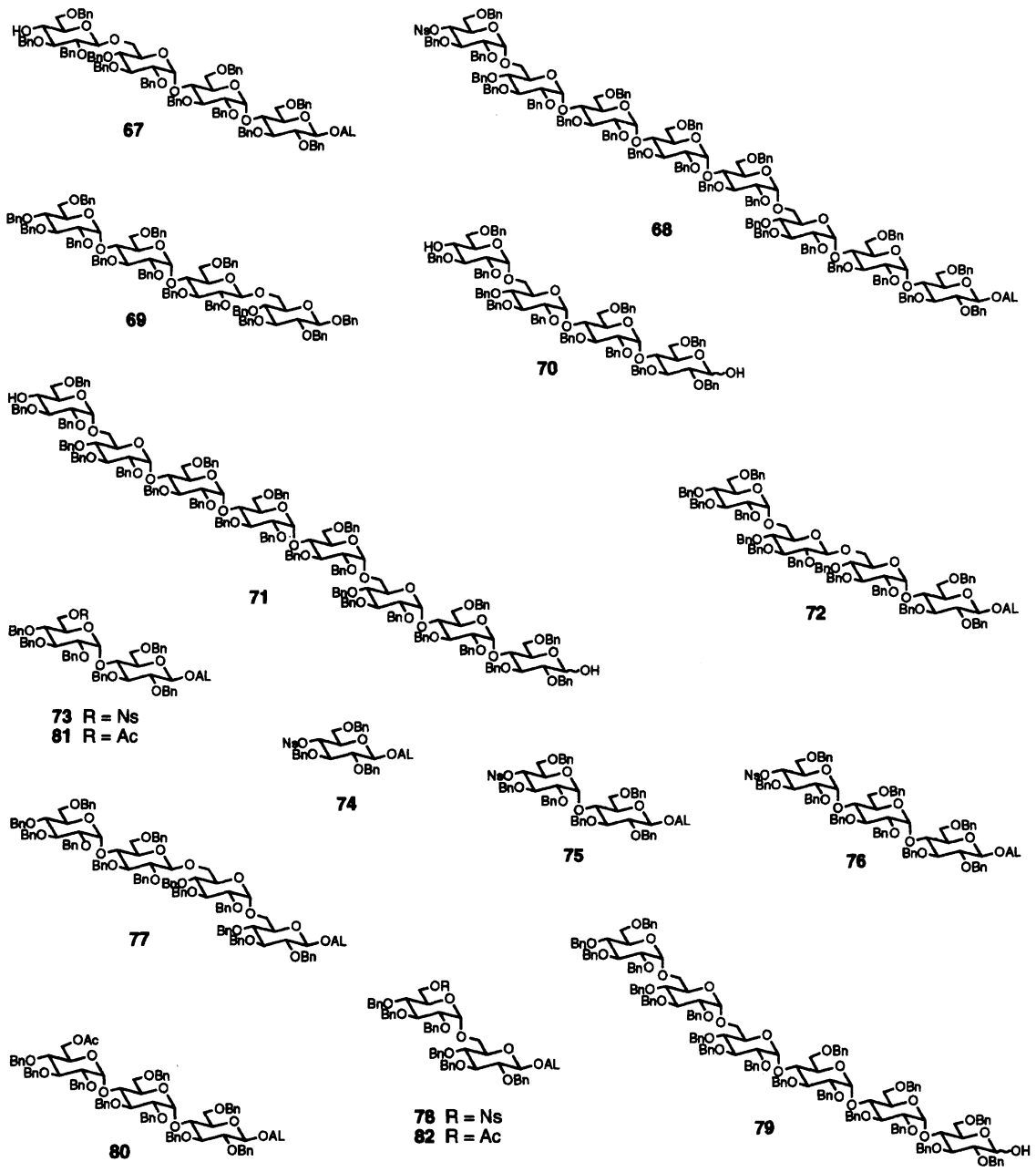

Chart 8.

was then treated with methanolic sodium methoxide (8%, 2.4 ml) in methanol (20 ml) containing acetone (20 ml) at room temp overnight. After quenching with acetic acid and evaporation to dryness, chromatogtaphy with TB system gave **14** (441.8 mg, 36%); $[\alpha]_D$ +58° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.52 (d, J=7.5 Hz, H1^A), 5.11 (d, J=3.5 Hz, H1^D); 5.60, 5.63 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=65.2 (C6^C), 70.6 (C4^D); 96.2, 96.3 (C1^B, H1^C); 97.2 (C1^D), 102.6 (C1^A); 70.2, 117.2, 134.1 (AL). And **67** (241.5 mg, 20%); $[\alpha]_D$ +39° (*c* 2.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.21 (d, J=7.5 Hz, H1^D), 4.48 (d, J=7.5 Hz, H1^A); 5.53, 5.74 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=68.2 (C6^C), 70.7 (C4^D); 96.4, 96.5 (C1^B, C1^C); 102.6 (C1^A), 103.6 (C1^D); 70.2, 117.2, 134.1 (AL).

Found: **14**, C, 74.45; H, 6.59% and **67**, C, 74.33; H, 6.64%. Calcd for $C_{111}H_{118}O_{21}$: C, 74.56; H, 6.65%.

Allyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-*O*-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (17). The tetrasaccharide derivative **14** (1.00 g) was treated with acetic anhydride (2.0 ml) in pyridine (6.0 ml) overnight. After quenching with ethanol (2 ml) under cooling, evaporation and chromatography (HE system) yielded **17** (1.02 g, 100%); $[\alpha]_D$ +67° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.77 (3H, s, Ac), 4.49 (d, J=8.0 Hz, H1^A), 5.04 (t, J=9.5 Hz, H4^D), 5.06 (d, J=3.5 Hz, H1^D); 5.59, 5.62 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=65.3 (C6^C), 70.5 (C4^D), 96.2 (2C, C1^B, C1^C), 97.1 (C1^D), 102.6 (C1^A); 20.8, 169.5 (Ac); 70.2, 117.2, 134.1 (AL).

Found: C, 73.88; H, 6.59%. Calcd for $C_{113}H_{120}O_{22}$: C,

74.16: H, 6.61%.

***O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (16).** The acetate **17** (0.98 g) was refluxed in EBW (60 ml) containing TRC (205 mg) overnight. After evaporation to dryness, the residue was stirred in acetone (40 ml) containing hydrochloric acid (3.7%, 0.80 ml) at 50 °C for 2 h. Evaporation and subsequent chromatography (HE system) gave **16** (0.75 g, 78%); $[\alpha]_D$ +69° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ($\alpha:\beta=2:1$) δ=1.80 (3H, s, Ac), 5.06 (t, J=9.5 Hz, $H4^D$), 5.09 (d, J=4.0 Hz, $H1^D$), 5.25 (d, J=3.5 Hz, $H1^A\alpha$), 5.57 (d, J=3.5 Hz, $H1^C$), 5.64 (d, J=3.5 Hz, $H1^B\beta$), 5.66 (d, J=3.5 Hz, $H1^B\alpha$); ^{13}C NMR ($CDCl_3$) δ=65.2 ($C6^C$), 70.3 ($C4^D$), 90.8 ($C1^A\alpha$), 96.1 ($C1^B\alpha$), 96.2 ($C1^B\beta$), 96.4 ($C1^C$), 97.0 ($C1^D$), 97.4 ($C1^A\beta$); 20.8, 169.5 (Ac).

Found: C, 73.47; H, 6.46%. Calcd for $C_{110}H_{116}O_{22}$: C, 73.80; H, 6.53%.

Allyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (6). A cross-condensation of donor **16** (122.5 mg) and acceptor **14** (97.1 mg) in the presence of NSC (84.3 mg), STF (97.8 mg), DMA (35.4 μl), and TEA (53.0 μl) in DCM (0.60 ml) furnished **allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (18)** (22.7 mg, 29%); $[\alpha]_D$ +71° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$), 4.89 (t, J=9.5 Hz, $H4^D$), 5.02 (d, J=3.5 Hz, $H1^D$); 5.61, 5.63 (d, J=3.5 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=65.6 ($C6^C$), 79.2 ($C4^D$); 96.0, 96.2 ($C1^B$, $C1^C$); 96.5 ($C1^D$), 102.6 ($C1^A$); 70.2, 117.2, 134.8 (AL); 142.7, 150.0 (Ns). Found: C, 71.26; H, 6.23; N, 0.77%. Calcd for $C_{117}H_{121}NO_{25}S$: C, 71.21; H, 6.18; N, 0.71%. And **6** (68 mg, 35%); $[\alpha]_D$ +73° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.79 (3H, s, Ac), 4.50 (d, J=7.5 Hz, $H1^A$), 5.04 (t, J=9.5 Hz, $H4^H$), 5.07 (d, J=3.5 Hz, $H1^H$), 5.18 (d, J=3.5 Hz, $H1^D$); 5.59, 5.61, 5.63, 5.66, 5.70 (d, J=3.5 Hz each, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR ($CDCl_3$) δ=64.4 ($C6^C$), 65.8 ($C6^G$), 70.4 ($C4^H$); 96.0, 96.0[6], 96.1[1], 96.2, 96.3 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$); 96.7 ($C1^D$), 97.1 ($C1^H$), 102.6 ($C1^A$); 20.8, 169.6 (Ac); 70.2, 117.2, 134.1 (AL).

Found: C, 74.24; H, 6.70%. Calcd for $C_{221}H_{232}O_{42}$: C, 74.56; H, 6.57%.

***O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (4).** Refluxing **6** (166.8 mg) with TRC (26 mg) in EBW (10 ml) overnight, followed by evaporation to dryness, gave an product mixture. Hydrolysis with hydrochloric acid (3.7%, 100 μl) in acetone (5.0 ml) and chromatography were carried out as described for the preparation of **16** to afford the unreacted **6** (28.7 mg, 17%) and **4** (88.5 mg, 54%); $[\alpha]_D$ +69° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ($\alpha:\beta=4:1$) δ=1.82 (3H, s, Ac), 5.07 (t, J=9.5 Hz, $H4^H$), 5.09 (d, J=3.5 Hz, $H1^H$), 5.21 (d, J=3.5 Hz, $H1^D$); 5.58, 5.64, 5.66, 5.68, 5.72 (d, J=3.5 Hz each, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR ($CDCl_3$) δ=64.4 ($C6^C$), 65.2 ($C6^G$), 70.4 ($C4^H$), 90.8 ($C1^A\alpha$); 96.0, 96.1 (2C), 96.2, 96.4 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$); 96.6 ($C1^D$), 97.0 ($C1^H$), 97.4 ($C1^A\beta$); 20.8, 169.6 (Ac).

Found: C, 74.02; H, 6.72%. Calcd for $C_{218}H_{228}O_{42}$: C, 74.38; H, 6.39%.

Allyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (5). Deacetylation of **6** (68.0 mg) with methanolic sodium methoxide (8%, 0.75 ml) in methanol (6.0 ml) containing acetone (6.0 ml), followed by processing and chromatography as in the above-described procedure for **14**, gave **5** (190.2 mg, 92%); $[\alpha]_D$ +75° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$), 5.08 (d, J=3.5 Hz, $H1^H$), 5.18 (d, J=3.5 Hz, $H1^D$); 5.60, 5.61, 5.62, 5.65, 5.70 (d, J=3.5 Hz each, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR ($CDCl_3$) δ=64.4 ($C6^C$), 65.1 ($C6^G$), 70.6 ($C4^H$); 96.1 (3C), 96.2, 96.3 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$); 96.7 ($C1^D$), 97.2 ($C1^H$), 102.6 ($C1^A$); 70.2, 117.2, 134.1 (AL).

Found: C, 74.59; H, 6.69%. Calcd for $C_{219}H_{230}O_{41}$: C, 74.76; H, 6.59%.

Allyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-tris[*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-](2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl β-D-glucopyranoside (20). A cross-coupling between donor **4** (60.2 mg) and acceptor **5** (63.7 mg) with NSC (40.2 mg), STF (46.6 mg), DMA (16.9 μl), and TEA (25.3 μl) in DCM (0.40 ml) afforded **allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (68)** (17.9 mg, 27%); $[\alpha]_D$ +84° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$), 4.89 (t, J=9.5 Hz, $H4^H$), 5.02 (d, J=3.5 Hz, $H1^H$), 5.17 (d, J=3.5 Hz, $H1^D$); 5.59, 5.60, 5.64, 5.65, 5.69 (d, J=3.5 Hz each, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR ($CDCl_3$) J=64.5 ($C6^C$), 65.5 ($C6^G$), 79.2 ($C4^H$); 95.9[7] (2C), 96.0[3], 96.1, 96.3 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$); 96.5 ($C1^D$), 96.7 ($C1^H$), 102.6 ($C1^A$); 70.2, 117.2, 134.1 (AL); 142.7, 150.0 (Ns). Found: C, 73.11; H, 6.43; N, 0.45%. Calcd for $C_{225}H_{233}NO_{45}S$: C, 72.97; H, 5.96; N, 0.38%. And **20** (42.4 mg, 35%); $[\alpha]_D$ +88° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.80 (3H, s, Ac), 4.50 (d, J=7.5 Hz, $H1^A$), 5.05 (t, J=9.5 Hz, $H4^P$), 5.08 (d,

J=3.5 Hz, $H1^P$), 5.19 (3H, d(br), $J\approx3$ Hz, $H1^D$, $H1^H$, $H1^L$); 5.61 (2H, br), 5.65 (6H, br), 5.71 (3H, br) ($H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$, $H1^I$, $H1^J$, $H1^K$, $H1^M$, $H1^N$, $H1^O$); ^{13}C NMR ($CDCl_3$) δ=64.4 (3C, $C6^C$, $C6^G$, $C6^K$), 65.2 ($C6^O$), 70.4 ($C4^P$), 96.0—96.2 (11C) ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$, $C1^I$, $C1^J$, $C1^K$, $C1^M$, $C1^N$, $C1^O$), 96.7 (3C, $C1^D$, $C1^H$, $C1^L$), 97.1 ($C1^P$), 102.6 ($C1^A$); 20.8, 169.6 (Ac); 70.2, 117.2, 134.2 (AL).

Found: C, 74.22; H, 6.73%. Calcd for $C_{437}H_{456}O_{82}$: C, 74.76; H, 6.55%.

Allyl *O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-tris[*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-]*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (21). Treatment of **20** (30.0 mg) with methanolic sodium methoxide (8%, 0.20 ml) in methanol (2.0 ml) containing acetone (3.0 ml) at room temp overnight, followed by quenching with acetic acid, evaporation to dryness and chromatography with TB system gave **21** (10.2 mg, 34%); $[\alpha]_D$ +92° (*c* 0.2, $CHCl_3$) ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, $H1^A$), 5.07 (d, J=3.5 Hz, $H1^P$), 5.17 (3H, d, J=3 Hz, $H1^D$, $H1^H$, $H1^L$); 5.61 (2H), 5.65 (6H), 5.71 (3H) ($H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$, $H1^I$, $H1^J$, $H1^K$, $H1^M$, $H1^N$, $H1^O$); ^{13}C NMR ($CDCl_3$) δ=64.4 (3C, $C6^C$, $C6^G$, $C6^K$), 65.1 ($C6^O$), 70.4 ($C4^P$), 96.0—96.3 (11C) ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$, $C1^I$, $C1^J$, $C1^K$, $C1^M$, $C1^N$, $C1^O$), 96.6—96.7 (3C) ($C1^D$, $C1^H$, $C1^L$), 97.2 ($C1^P$), 102.6 ($C1^A$); 70.2, 117.2, 134.1 (AL).

Found: C, 74.65; H, 6.59%. Calcd for $C_{435}H_{454}O_{81}$: C, 74.78; H, 6.54%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α- and β-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (26 and 69). Condensation of donor **24** (154.4 mg) and acceptor **25** (45.7 mg) using NSC (50.6 mg), STF (58.7 mg), DMA (42.5 μl), and TEA (31.9 μl) in DCM (0.46 ml) afforded **26** (52.0 mg, 32%); $[\alpha]_D$ +60° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.55 (d, J=7.5 Hz, $H1^A$), 5.19 (d, J=3.5 Hz, $H1^B$); 5.69, 5.73 (d, J=3.5 Hz each, $H1^C$, $H1^D$); ^{13}C NMR ($CDCl_3$) δ=65.6 ($C6^A$); 96.2, 96.7[7] ($C1^C$, $C1^D$); 96.8[3] ($C1^B$), 102.2 ($C1^A$). And **69** (35.9 mg, 22%); $[\alpha]_D$ +37° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.50 (d, J=7.5 Hz, $H1^A$), 4.56 (d, J=3.5 Hz, $H1^B$); 5.61, 5.72 (d, J=3.5 Hz each, $H1^C$, $H1^D$); ^{13}C NMR ($CDCl_3$) δ=68.6 ($C6^A$); 96.4, 96.9 ($C1^C$, $C1^D$); 102.6 ($C1^A$), 103.8 ($C1^B$).

Found: **26**: C, 75.94; H, 6.68% and **69**: C, 75.95; H, 6.67%. Calcd for $C_{122}H_{126}O_{21}$: C, 75.99; H, 6.59%.

***O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (70).** Refluxing **14** (976.9 mg) in EBW (60 ml) containing TRC (205 mg), followed by hydrolysis with hydrochloric acid (3.7%, 0.80 ml) in acetone (40 ml), as written for the preparation of **16**, produced **70** (753.3 mg, 79%); $[\alpha]_D$ +54° (*c* 0.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) (α:β=2:1) δ=5.07 (d, J=3.5 Hz, $H1^D$), 5.23 ($H1^A\alpha$), 5.53 (d, J=3.5 Hz, $H1^C$), 5.60 (d, J=3.5 Hz, $H1^B\beta$), 5.62 (d, J=3.5 Hz, $H1^B\alpha$); ^{13}C NMR ($CDCl_3$) δ=65.2 ($C6^C$), 90.9 ($C1^A\alpha$), 96.0 ($C1^B\alpha$), 96.2 ($C1^B\beta$), 96.5 ($C1^C$), 97.2 ($C1^D$), 97.4 ($C1^A\beta$).

Found: C, 74.01; H, 6.51%. Calcd for $C_{108}H_{114}O_{21}$: C, 74.21; H, 6.57%.

***O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (71).** Similarly, rearrangement of **5** (60.2 mg) with TRC (20 mg) in EBW (6.0 ml) under overnight refluxing and hydrolysis of the resulting product mixture with hydrochloric acid (3.7%, 0.15 ml) in acetone (6.0 ml) under stirring at 45 °C for 1.0 h afforded the unreacted **5** (19.6 mg, 29%) and **71** (32.8 mg, 49%); $[\alpha]_D$ +69° (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$) (α:β=7:3) δ=5.08 (d, J=3.5 Hz, $H1^H$), 5.18 (d, J=3.5 Hz, $H1^H$), 5.23 ($H1^A\alpha$); 5.56, 5.62 (2H), 5.64, 5.70 (d, J=3.5 Hz each, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR ($CDCl_3$) δ=64.3 ($C6^C$), 65.1 ($C6^G$), 70.5[6] ($C4^H$), 90.9 ($C1^A\alpha$); 95.9, 96.1 (3C), 96.4 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$), 96.6 ($C1^D$), 97.1 ($C1^H$), 97.4 ($C1^A\beta$).

Found: C, 74.50; H, 6.38%. Calcd for $C_{216}H_{226}O_{41}$: C, 74.59; H, 6.55%.

***O*-(2,3,6-Tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-tris[*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-]*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (22).** A mixture of **21** (8.7 mg), TRC (3.9 mg), and EBW (20 ml) was refluxed for 24 h. Evaporation to dryness afforded a residue, which was then stirred in acetone (2.1 ml) containing hydrochloric acid (3.7%, 20 μl). Evaporation to dryness, followed by chromatography using TB system, gave **22** (4.2 mg, 49%); $[\alpha]_D$ +90° (*c* 0.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) (α:β=1:1) δ=5.06 (d, J=3.5 Hz, $H1^P$), 5.17 (3H, $H1^D$, $H1^H$, $H1^L$), 5.23 ($H1^A\alpha$), 5.54 (d, J=3.5 Hz), 5.60—5.64 (7H), 5.67—5.70 (3H) ($H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$, $H1^I$, $H1^J$, $H1^K$, $H1^M$, $H1^N$, $H1^O$); ^{13}C NMR ($CDCl_3$, HMQC) δ=64.2 ($C6^C$, $C6^G$, $C6^K$), 64.6 ($C6^O$), 90.8 ($C1^A\alpha$), 96.0—96.2 ($C1^B$, $C1^C$, $C1^E$, $C1^F$, $C1^G$, $C1^I$, $C1^J$, $C1^K$, $C1^M$, $C1^N$, $C1^O$), 96.6 ($C1^D$, $C1^H$, $C1^L$), 97.0 ($C1^P$).

***O*-α-D-Glucopyranosyl-(1→6)-bis[*O*-α-D-glucopyranosyl-(1→4)-]D-glucopyranose (2).** Hydrogenolysis of **70** (38.4 mg) over Pd on C (10%, 20.0 mg) in acetic acid[38] (6.0 ml) containing H_2O (0.05 ml) under 350 kPa of H_2 at 20 °C overnight. After removal of catalyst through a glass filter and quick evaporation below 30 °C to dryness, the residue so obtained was again reduced over the catalyst (14.0 mg) in acetic acid (6.0 ml) containing H_2O (0.20 ml). Removal of the catalyst, evaporation, and subsequent chromatography (CM system) gave a glassy **2** (8.6 mg, 57%); $[\alpha]_D$ +158° (*c* 0.4, H_2O) (lit,[13] $[\alpha]_D^{25}$ +165° (*c* 0.8, H_2O)); ^{1}H NMR (D_2O) (α:β=45:55) δ=4.55 (d, J=8.0 Hz, $H1^A\beta$), 4.85 (d, J=3.5 Hz, $H1^D$), 5.12 (d, J=3.5 Hz, $H1^A\alpha$), 5.28 (d, J=3.5 Hz, $H1^C$), 5.30 (d, J=3.5 Hz, $H1^B$); ^{13}C NMR (D_2O) δ=63.1[6], 63.2[3] ($C6^B$, $C6^D$); 63.4 ($C6^A\beta$), 63.6 ($C6^A\alpha$), 68.6 ($C6^C$), 72.1, 72.2 ($C4^C$, $C4^D$); 72.6 ($C5^A\alpha$), 73.9 ($C5^C$), 73.9[9] ($C5^B\alpha$), 74.0[3] ($C5^B\beta$); 74.1 (2C), 74.4 ($C2^B$, $C2^C$, $C2^D$); 74.2 ($C2^A\alpha$), 74.5 ($C5^D$), 75.8 (2C), 75.9[2] ($C3^B$, $C3^C$, $C3^D$);

75.8[5] ($C3^A\alpha$), 76.7 ($C2^A\beta$), 77.2 ($C5^A\beta$), 78.8 ($C3^A\beta$), 79.8 ($C4^A\beta$), 79.9 ($C4^A\alpha$), 80.0 ($C4^B$), 94.6 ($C1^A\alpha$), 98.5 ($C1^A\beta$), 100.7 ($C1^D$), 102.1[6] ($C1^B\beta$), 102.2[3] ($C1^B\alpha$), 102.6 ($C1^C$).

Found: C, 42.21; H, 6.50%. Calcd for $C_{24}H_{42}O_{21}\cdot H_2O$: C, 42.11; H, 6.48%.

***O*-α-D-Glucopyranosyl-(1→6)-tris[*O*-α-D-glucopyranosyl-(1→4)-]*O*-α-D-glucopyranosyl-(1→6)-bis[*O*-α-D-glucopyranosyl-(1→4)-]D-glucopyranose (3).** Similarly repeated hydrogenolyses of **71** (45.3 mg) over Pd on C (10%, 30.0 mg) first in acetic acid (6.0 ml) containing H_2O (0.05 ml) and then in the acid (6.0 ml) containing H_2O (0.3 ml), followed by chromatogtaphy (CM system) yielded a colorless glass of **3** (10.3 mg, 56%); $[\alpha]_D$ +163° (*c* 0.2, H_2O); ^{1}H NMR (D_2O) ($\alpha:\beta=45:55$) δ=4.58 (d, J=8.0 Hz, $H1^A\beta$), 4.88—4.90 (2H, $H1^D$, $H1^H$), 5.16 (d, J=3.5 Hz, $H1^A\alpha$), 5.28—5.35 (5H, $H1^B$, $H1^C$, $H1^E$, $H1^F$, $H1^G$); ^{13}C NMR (D_2O) δ=63.1, 63.1[6], 63.1[9] (2C), 63.3, 63.4 ($C6^A$, $C6^B$, $C6^D$, $C6^E$, $C6^F$, $C6^H$); 68.7 ($C6^G$), 69.2 ($C6^C$); 72.1, 72.2 (2C) ($C4^H$, $C4^C$, $C4^G$); 72.7 ($C5^A\alpha$), 73.0 ($C5^D$), 74.5 ($C5^H$), 75.9 ($C3^A\alpha$), 76.7 ($C2^A\beta$), 77.3 ($C5^A\beta$), 78.9 ($C3^A\beta$), 79.7 ($C4^A\beta$), 79.9 ($C4^A\alpha$); 79.8, 80.0 (2C), 80.4 ($C4^B$, $C4^D$, $C4^E$, $C4^F$); 94.6 ($C1^A\alpha$), 98.5 ($C1^A\beta$), 100.7 ($C1^D$), 100.8 ($C1^H$), 102.2 ($C1^B\beta$), 102.3 ($C1^B\alpha$), 102.4 ($C1^E$), 102.5 ($C1^F$), 102.6 ($C1^G$), 102.8 ($C1^C$).

Found: C, 41.97; H, 6.55%. Calcd for $C_{48}H_{82}O_{41}\cdot 3H_2O$: C, 42.11; H, 6.48%.

Tris[*O*-α-D-Glucopyranosyl-(1→6)-tris[*O*-α-D-glucopyranosyl-(1→4)-]]*O*-α-D-glucopyranosyl-(1→6)-bis[*O*-α-D-glucopyranosyl-(1→4)-]D-glucopyranose (7). Analogously, a couple of hydrogenations of **22** (4.0 mg) over Pd on C (10%, 12.0 mg), first in acetic acid (6.0 ml) containing H_2O (0.05 ml) and then in aq acetic acid (50%, 6.0 ml), followed by chromatography on Bio Gel® P-2 (BIO-RAD Lab.) eluted with H_2O, lyophilization, and drying over P_2O_5, gave a glassy solid of **7** (1.0 mg, 66%); $[\alpha]_D$ +159° (*c* 0.1, H_2O); ^{1}H NMR (D_2O) ($\alpha:\beta=45:55$) δ=4.61 (d, J=8.0 Hz, $H1^A\beta$), 4.91—4.92 (4H, $H1^D$,$H1^H$,$H1^L$,$H1^P$), 5.19 (d, J=3.5 Hz, $H1^A\alpha$), 5.32—5.38 (11H, $H1^B$,$H1^C$,$H1^E$,$H1^F$, $H1^G$,$H1^I$,$H1^J$,$H1^K$,$H1^M$,$H1^N$,$H1^O$); ^{13}C NMR (D_2O, DEPT) δ=98.4 ($C1^A\beta$), 100.6 ($C1^D$, $C1^H$, $C1^L$), 100.7 ($C1^P$), 102.1 ($C1^B\beta$), 102.3 ($C1^E$, $C1^I$, $C1^M$), 102.4 ($C1^F$, $C1^J$); 102.5, 102.6 ($C1^N$, $C1^O$), 102.8 ($C1^C$, $C1^G$, $C1^K$).

Bis[*O*-α-D-glucopyranosyl-(1→4)-]*O*-α-D-glucopyranosyl-(1→6)-D-glucopyranose (23). Repeated hydrogenation of **26** (46.4 mg) over Pd on C (10%, 35 mg), first in acetic acid (6.0 ml) moistened with H_2O (0.05 ml) and then in the acid (6.0 ml) containing H_2O (0.75 ml), followed by chromatography (CM system), furnished glassy **23** (10.8 mg, 66%); $[\alpha]_D$ +156° (*c* 0.2, H_2O); ^{1}H NMR (D_2O) ($\alpha:\beta=2:3$) δ=4.58 (d, J=7.5 Hz, $H1^A\beta$), 4.86 (d, J=3.5 Hz, $H1^B\alpha$), 4.87 (d, J=3.5 Hz, $H1^B\beta$), 5.15 (d, J=3.5 Hz, $H1^A\alpha$), 5.30 (2H, d, J=3.5 Hz, $H1^C$, $H1^D$); ^{13}C NMR (D_2O) δ=63.1, 63.2 (2C) ($C6^B$, $C6^C$, $C6^D$); 68.5 ($C6^A\beta$), 70.6 ($C6^A\alpha$), 72.0 ($C4^D$), 72.1 ($C4^A\beta$), 72.2 ($C4^A\alpha$), 72.7 ($C5^A\alpha$), 72.9 ($C5^B\beta$), 73.0 ($C5^B$), 73.9 ($C5^C$); 74.0, 74.2, 74.4 ($C2^B$, $C2^C$, $C2^D$); 74.1 ($C2^A\alpha$), 75.6 ($C5^D$), 75.7 ($C3^A\alpha$); 75.4, 76.0, 76.1 ($C3^B$, $C3^C$, $C3^D$); 76.7 ($C2^A\beta$), 77.0 ($C5^A\beta$), 78.6 ($C3^A\beta$); 79.6, 79.8 ($C4^B$, $C4^C$); 94.9 ($C1^A\alpha$), 96.7 ($C1^A\beta$), 100.4[6] ($C1^B\beta$), 100.5[0] ($C1^B\alpha$); 102.2, 102.5 ($C1^C$, $C1^D$).

Found: C, 42.09; H, 6.77%. Calcd for $C_{24}H_{42}O_{21}\cdot H_2O$: C, 42.11; H, 6.48%.

Syntheses of Hexasaccharides. Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α- and β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranosides (30 and 72). (a) Condensation between donor **28** (283.3 mg) and acceptor **29** (206.7 mg) was conducted in the presence of NSC (124.1 mg), STF (143.9 mg), DMA (104.1 μl), and TEA (78.0 μl) in DCM (2.30 ml) yielded **allyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (73)** (47.6 mg, 19%); $[\alpha]_D$ +43° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (d, J=7.5 Hz, $H1^A$), 5.60 (d, J=3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ=68.8 ($C6^A$), 69.7 ($C6^B$), 95.7 ($C1^B$), 102.6 ($C1^A$); 70.2, 117.4, 134.0 (AL); 141.4, 150.5 (Ns). Found: C, 68.25; H, 6.00; N, 1.25%. Calcd for $C_{63}H_{65}NO_{15}S$: C, 68.28; H, 5.91; N, 1.26%. **30** (115.6 mg, 27%); $[\alpha]_D$ +63° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (d, J=7.5 Hz, $H1^A$); 4.97, 5.13 (d, J=3.5 Hz each, $H1^C$, $H1^D$); 5.64 ($C1^B$); ^{13}C NMR ($CDCl_3$) δ=65.4, 65.6 ($C6^B$, $C6^C$); 72.4 ($C4^A$), 96.2 ($C1^B$); 97.1, 97.3 ($C1^C$, $C1^D$); 102.6 ($C1^A$); 70.1, 117.1, 134.1 (AL). And **72** (57.1 mg, 14%); $[\alpha]_D$ +43° (*c* 1.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.22 (d, J=8.0 Hz, $H1^C$), 4.44 (d, J=7.5 Hz, $H1^A$), 5.14 (d, J=3.5 Hz, $H1^D$), 5.67 (d, J=3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ=65.5 ($C6^C$), 68.1 ($C6^B$), 72.5 ($C4^A$), 96.3 ($C1^B$), 97.3 ($C1^D$), 102.6 ($C1^A$), 103.8 ($C1^C$); 70.1, 117.0, 134.2 (AL).

Found: **30**: C, 75.04; H, 6.66% and **72**: C, 75.10; H, 6.57%. Calcd for $C_{118}H_{124}O_{21}$: C, 75.46; H, 6.65%.

After elution of the above compounds, **29** (32.7, 16%) and **28** (149.9 mg, 53%) were recovered.

(b) Condensation of donor **36** (77.9 mg) and acceptor **42** (20.9 mg) was carried out in the presence of NSC (37.8 mg), STF (43.9 mg), DMA (15.9 μl), and TEA (23.8 μl). This afforded **allyl 2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl-β-D-glucopyranoside (74)** (5.9 mg, 20%); $[\alpha]_D$ +15° (*c* 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (d, J=7.5 Hz, $H1^A$), 4.80 (t, J=9.0 Hz, $H4^A$); ^{13}C NMR ($CDCl_3$) δ=73.3 (C5), 68.7 (C6), 79.5 (C4), 80.8 (C2), 82.0 (C3), 102.4 (C1); 70.4, 117.7, 133.6 (AL); 142.4, 150.1 (Ns). Found: C, 63.99; H, 5.60; N, 2.10%. Calcd for $C_{36}H_{37}NO_{10}S$: C, 63.99; H, 5.52; N, 2.07%, and **30** (10.7 mg, 13%).

Compounds **42** (11.9 mg, 57%) and **36** (42.1, 54%) were recovered.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-D-glucopyranose (31).** Refluxing **30** (510.4 mg) in EBW (20 ml) in the presence of TRC (125.8 mg) overnight gave a preduct mixture. Treatment of this with hydrochloric acid (3.7%, 1.8 ml) in acetone (30 ml) at 45 °C for 3 h furnished **31** (430.6 mg, 86%); $[\alpha]_D$ +47° (*c* 2.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ($\alpha:\beta=2:1$) δ=4.95 (d, J=3.0 Hz, $H1^D$), 5.10 (d, J=3.5 Hz, $H1^C\alpha$), 5.11 (d, J=3.5 Hz, $H1^C\beta$), 5.20 (br, $H1^A\alpha$), 5.54 (d, J=3.5 Hz, $H1^B\alpha$), 5.57 (d, J=3.5 Hz, $H1^B\beta$); ^{13}C NMR ($CDCl_3$) δ=90.8 ($C1^A\alpha$), 96.3 ($C1^B\beta$), 96.6 ($C1^B\alpha$), 97.2 ($C1^C$), 97.3 ($C1^D$), 97.4 ($C1^A\beta$).

Found: C, 75.12; H, 6.66%. Calcd for $C_{115}H_{120}O_{21}$: C, 75.14; H, 6.58%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyra-

nosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl) -(1→4)-]2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (33). (a) Condensation of donor **31** (442.3 mg) and acceptor **32** (228.2 mg) with NSC (328.7 mg), STF (381.1 mg), DMA (138 μl), and TEA (207 μl) in DCM (2.50 ml) produced **allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (75)** (65.9 mg, 24%); $[\alpha]_D$ +29° (*c* 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, H1^A), 4.88 (t, J=9.5 Hz, H4^B), 5.69 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=79.2 (C4^B), 95.7 (C1^B), 102.5 (C1^A); 70.2, 117.4, 134.0 (AL); 142.4, 150.0 (Ns). Found: C, 68.27; H, 6.01; N, 1.24%. Calcd for $C_{63}H_{65}NO_{15}S$: C, 68.28; H, 5.91; N, 1.26%. And **33** (159.5 mg, 24%); $[\alpha]_D$ +72° (*c* 2.2, $CHCl_3$); ^{1} NMR ($CDCl_3$) δ=4.50 (d, J=7.5 Hz, H1^A), 5.01, 5.11 (d, J=3.5 Hz each, H1^E, H1^F); 5.57, 5.58, 5.63 (d, J=3.5 Hz each, H1^B, H1^C, H1^D); ^{13}C NMR ($CDCl_3$) δ=64.9, 65.3 (C6^D, C6^E); 68.5, 68.7, 68.8, 68.9 (C6^A, C6^B, C6^C,C6^F); 96.2[9], 96.3[3], 96.5 (C1^B, C1^C, C1^D); 97.1, 97.3 (C1^E, C1^F), 102.6 (C1^A); 70.2, 117.1, 134.1 (AL).

Found: C, 74.93; H, 6.61%. Calcd for $C_{172}H_{180}O_{31}$: C, 75.31; H, 6.61%.

(b) Condensation of donor **36** (158.6 mg) and acceptor **37** (104.7 mg) in the presence of NSC (94.2 mg), STF (109.3 mg), DMA (39.6 μl), and TEA (59.3 μl) in DCM (1.00 ml) gave **allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (76)** (17.3 mg, 15%); $[\alpha]_D$ +56° (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.49 (d, J=7.5 Hz, H1^A), 4.90 (t, J=9.5 Hz, H4^C); 5.59, 5.65 (d, J=3.5 Hz each, H1^B, H1^C); ^{13}C NMR ($CDCl_3$) δ=79.3 (C4^C); 95.9, 96.1 (C1^B, C1^C); 102.6 (C1^A); 70.2, 117.3, 134.1 (AL); 142.7, 150.0 (Ns). Found: C, 69.93; H, 6.26: N, 0.85%. Calcd for $C_{90}H_{93}NO_{20}S$: C, 70.16; H, 6.08; N, 0.91% and **33** (16.7 mg, 8%).

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α- and β-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranosides (39 and 77). Donor **8** (189.2 mg) and acceptor **38** (151.8 mg) were condensed using NSC (109.4 mg), STF (126.9 mg), DMA (91.9 μg), and TEA (68.9 μl) in DMA (1.50 ml). This afforded **allyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzenesulfonyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (78)** (56.0 mg, 31%); $[\alpha]_D$ +39° (*c* 2.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.46 (d, J=7.5 Hz, H1^A), 4.86 (d, J=3.5 Hz, H1^B); ^{13}C NMR ($CDCl_3$) δ=66.0 (C6^A), 69.9 (C6^B), 96.8 (C1^B), 102.6 (C1^A); 70.2, 117.1, 133.9 (AL); 141.7, 150.7 (Ns). Found: C, 68.51; H, 6.18; N, 1.15%. Calcd for $C_{63}H_{65}NO_{15}S$: C, 68.28; H, 5.91; N, 1.26%. **39** (148.5 mg, 48%); $[\alpha]_D$ +57° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (d, J=8.0 Hz, H1^A); 4.87, 5.14 (d, J=3.5 Hz each, H1^B, H1^C); 5.72 (d, J=3.5 Hz, H1^D); ^{13}C NMR ($CDCl_3$) δ=65.3, 65.7 (C6^A, C6^B); 68.2, 69.1 (C6^C, C6^D); 96.7[1] (C1^D); 96.6[6], 96.9 (C1^B, C1^C); 102.6 (C1^A); 70.2, 117.1, 134.0 (AL). And **77** (30.9 mg, 10%); $[\alpha]_D$ +42° (*c* 2.7, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.38 (d, J=8.0 Hz, H1^C), 4.43 (d, J=8.0 Hz, H1^A), 5.07 (d, J=3.5 Hz, H1^B), 5.68 (d, J=3.5 Hz, H1^D); ^{13}C NMR ($CDCl_3$) δ=65.5 (C6^A); 68.2, 68.4 (C6^B, C6^D); 69.1 (C6^C), 96.7 (C1^D), 96.9 (C1^B), 102.6 (C1^A), 103.7 (C1^C); 70.0, 117.1, 134.0 (AL).

Found: **39**: C, 75.30; H, 6.86% and **77**: C, 75.17; H, 6.86%. Calcd for $C_{118}H_{124}O_{21}$: C, 75.46; H, 6.65%.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-D-glucopyranose (40).** Rearrangement of **39** (187.4 mg) was performed by refluxing in EBW (15 ml) cotaining TRC (45 mg) overnight, followed by hydrolysis with hydrochloric acid (3.7%, 0.12 ml) in acetone (5.0 ml) at 45 °C for 5.5 h. This afforded **40** (145.1 mg, 79%); $[\alpha]_D$ +47° (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ($\alpha:\beta$=2:1) δ=4.65 (d, J=8.0 Hz, H1$^A\beta$); 4.98, 5.04 (d, J=3.5 Hz each, H1$^B\alpha$, H$^C\alpha$); 4.99, 5.06 (d, J=3.5 Hz each, H1$^B\beta$, H1$^C\beta$); 5.13 (d, J=3.0 Hz, H1$^A\alpha$), 5.66 (d, J=3.5 Hz, H1$^D\alpha$), 5.69 (d, J=3.5 Hz, H1$^D\beta$); ^{13}C NMR ($CDCl_3$) δ=65.2, 66.1 (C6$^A\alpha$, C6$^B\alpha$); 65.7, 66.7 (C6$^A\beta$, C6$^B\beta$); 91.1 (C1$^A\alpha$); 96.4, 97.1 (C1$^B\beta$, C1$^C\beta$); 96.6 (C1$^B\alpha$, C1$^D\beta$ or C1$^C\alpha$, C1$^D\beta$), 96.8 (C1$^D\alpha$), 96.9 (C1$^C\alpha$ or C1$^B\alpha$), 97.3 (C1$^A\beta$).

Found: C, 75.12; H, 6.66%. Calcd for $C_{115}H_{120}O_{21}$: C, 75.14; H, 6.48%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-bis[(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-](1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (41). Cross-condensation of donor **40** (109.8 mg) and acceptor **32** (63.0 mg) was conducted in the presence of NSC (105.9 mg), STF (122.9 mg), DMA (44.5 μl), and TEA (66.7 μl) in DCM (0.65 ml). This afforded sulfonate **75** (23.1 mg, 31%) and the fully-protected hexasaccharide **41** (5.6 mg, 3%); $[\alpha]_D$ +75° (*c* 0.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=4.48 (d, J=8.0 Hz, H1^A); 4.96, 5.16 (d, J=3.5 Hz each, H1^D, H1^E); 5.58, 5.63, 5.71 (d, J=3.5 Hz each, H1^B, H1^C, H^F); ^{13}C NMR ($CDCl_3$) δ=64.8, 65.0 (C6^C, C6^D); 68.2, 68.9, 69.1 (2C) (C6^A, C6^B, C6^E, C6^F); 96.2, 96.4, 96.7 (C1^B, C1^C, C1^F); 96.8, 97.1 (C1^D, C1^E), 102.5 (C1^A); 70.1, 117.2, 134.1 (AL).

Found: C, 75.43; H, 6.85%. Calcd for $C_{172}H_{180}O_{31}$: C, 75.31; H, 6.61%.

The donor **40** (104.9 mg, 96%) was recovered.

Two more experiments were carried out with the amount of NSDT increased to **40** and that of **32** also to **40** were carried out. The increased yield of the sulfonate **75** (>35%) and recovery of most of **40** (>90%) were observed, respectively.

***O*-(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-*O*-(2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-bis[*O*-(2,3,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-]2,3,6-tri-*O*-benzyl-D-glucopyranose (79).** Refluxing **33** (48.1 mg) in EBW (1.00 ml) containing TRC (8.0 mg) overnight, followed by treatment with hydrochloric acid (3.7%, 50 μl) in acetone (2.0 ml) at 45 °C for 2.0 h, gave **79** (31.8 mg, 67%); $[\alpha]_D$ +68° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) ($\alpha:\beta$=2:1) δ=5.02, 5.12 (d, J=3.5 Hz each, H1^E, H1^F); 5.25 (d, J=3.5 Hz, H1$^A\alpha$); 5.54, 5.69 (d, J=3.5 Hz each, H1^C, H1^D); 5.58 (d, J=3.5 Hz, H1$^B\beta$), 5.60 (d, J=3.5 Hz, H1$^B\alpha$); ^{13}C NMR ($CDCl_3$) δ=64.5, 65.2 (C6^D,

$C6^E$); 68.5, 68.7, 68.8 ($C6^B$, $C6^C$, $C6^F$); 68.9 ($C6^A\alpha$), 69.2 ($C6^A\beta$), 90.9 ($C1^A\alpha$), 96.2 ($C1^B\beta$), 96.3[3] ($C1^B\alpha$); 96.2[8], 96.7 ($C1^C$, $C1^D$); 97.1, 97.3 ($C1^E$, $C1^F$); 97.4 ($C1^A\beta$).

Found: C, 75.43; H, 6.85%. Calcd for $C_{169}H_{176}O_{31}$: C, 75.09; H, 6.56%.

Bis[*O*-α-D-glucopyranosyl-(1→6)-]*O*-α-D-glucopyranosyl-(1→4)-D-glucopyranose (34). Repeated hydrogenations similar to those in the case of preparing **2** from **70** were applied to **31** (31.3 mg) using Pd on C (10%, 20.0 mg) first in acetic acid (6.0 ml) moistened with H_2O (0.05 ml) and then in the acid (6.0 ml) containing H_2O (0.50 ml). Processing similar to that for **3** furnished **34** (7.7 mg, 64%); $[\alpha]_D$ +149° (*c* 0.2, H_2O); ^{1}H NMR (D_2O) (α:β=2:3) δ=4.58 (d, *J*=7.5 Hz, $H1^A\beta$); 4.88, 4.89 (d, *J*=3.5 Hz each, $H1^C$, $C1^D$); 5.15 (d, *J*=3.5 Hz, $H1^A\alpha$), 5.33 (d, *J*=3.5 Hz, $H1^B$); ^{13}C NMR (D_2O) δ=63.2 ($C6^D$), 63.4 ($C6^A\alpha$), 63.5 ($C6^A\beta$); 68.2, 68.7 ($C6^B$, $C6^C$); 72.1, 72.2, 72.3 ($C4^B$, $C4^C$, $C4^D$); 72.7 ($C5^A\alpha$), 72.9 ($C5^C$), 73.9 ($C2^B\beta$), 74.0 ($C2^B\alpha$); 74.1, 74.2 (>1C, $C2^B\alpha$) ($C2^C$, $C2^D$); 74.3 ($C2^B\beta$), 74.4 ($C2^A\alpha$), 74.5 ($C5^D$); 75.8 (2C), 76.1 ($C3^B$, $C3^C$, $C3^D$); 75.9 ($C3^A\alpha$), 76.7 ($C2^A\beta$), 77.3 ($C5^A\beta$), 78.9 ($C3^A\beta$), 79.9 ($C4^A\beta$), 80.1 ($C4^A\alpha$), 94.6 ($C1^A\alpha$), 98.5 ($C1^A\beta$); 100.4, 100.7 ($C1^C$, $C1^D$); 102.4 ($C1^B\beta$), 102.5 ($C1^B\alpha$).

Found: C, 40.80; H, 6.68%. Calcd for $C_{24}H_{42}O_{21}\cdot 2H_2O$: C, 41.03; H, 6.60%.

***O*-α-D-Glucopyranosyl-(1→4)-bis[*O*-α-D-glucopyranosyl-(1→6)-]D-glucopyranose (35).** Repeated hydrogenolyses of **40** (36.3 mg) over Pd on C (27.0 mg) was carried out in the same manner as described above to give **35** (8.6 mg, 60%); $[\alpha]_D$ +144° (*c* 0.2, H_2O); ^{1}H NMR (D_2O) (α:β=2:3) δ=4.58 (d, *J*=7.5 Hz, $H1^A\beta$), 4.86 (d, *J*=3.5 Hz, $H1^B\alpha$), 4.87 (d, *J*=3.5 Hz, $H1^B\beta$, $H1^C$), 5.15 (d, *J*=3.5 Hz, $H1^A\alpha$), 5.29 (d, *J*=3.5 Hz, $H1^D$); ^{13}C NMR (D_2O) δ=63.1, 63.2 ($C6^C$, $C6^D$); 68.3[6] ($C6^A\beta$), 68.4[3] ($C6^B$), 68.5 ($C6^A\alpha$); 72.0, 72.2 ($C4^B$, $C4^D$); 72.1 ($C4^A\beta$), 72.3 (C4α), 72.6 ($C5^A\alpha$), 72.9 ($C5^B\alpha$), 73.0 (>1C, $C5^B\beta$, $C5^C$); 73.9, 74.1 (>1C, $C2^A\alpha$), 74.4 ($C2^B$, $C2^C$, $C2^D$); 75.4 (2C, $C5^D$), 76.0, 76.1 ($C3^B$, $C3^C$, $C3^D$); 75.7 ($C3^A\alpha$), 76.7 ($C2^A\beta$), 76.9 ($C5^A\beta$), 78.7 ($C3^A\beta$), 79.8 ($C4^C$), 94.9 ($C1^A\alpha$), 98.7 ($C1^A\beta$), 100.2 ($C1^C$), 100.5[5] ($C1^B\beta$), 100.5[8] ($C1^B\alpha$), 102.4 ($C1^D$).

Found: C, 39.95; H, 6.85%. Calcd for $C_{24}H_{42}O_{21}\cdot 3H_2O$: C, 40.00; H, 6.71%.

Bis[*O*-α-D-glucopyranosyl-(1→6)-]tris[*O*-α-D-glucopyranosyl-(1→4)-]D-glucopyranose (27). Repeated hydrogenolyses of **79** (40.6 mg) with Pd on C (30.0 mg) first in acetic acid (6.0 ml) moistened with H_2O (0.05 ml) and then in aq acetic acid (37%, 6.0 ml), gave **27** (9.3 mg, 59%); $[\alpha]_D$ +152° (*c* 0.2, H_2O); ^{1}H NMR (D_2O) (α:β=2:3) δ=4.56 (d, *J*=7.5 Hz, $H1^A\beta$); 4.87, 4.88 (d, *J*=3.5 Hz, $H1^E$, $H1^F$), 5.13 (d, *J*=3.5 Hz, $H1^A\alpha$); 5.29, 5.30 (d, *J*=4.0 Hz, each), 5.32 (d, *J*=3.5 Hz) ($H1^B$, $H1^C$, $H1^D$); ^{13}C NMR (D_2O) δ=63.2 (>2C, $C6^A\alpha$), 63.3 ($C6^B$, $C6^C$, $C6^F$); 63.4 ($C6^A\beta$); 68.3, 68.7 ($C6^D$, $C6^E$); 72.1[7], 72.2[3], 72.3 ($C4^D$, $C4^E$, $C4^F$); 72.7 ($C5^A\alpha$); 72.9, 73.8[8], 73.9[2], 74.0 ($C5^B$, $C5^C$, $C5^D$, $C5^E$); 74.0, 74.1, 74.1[8] (2C), 74.2[4] ($C2^B$, $C2^C$, $C2^D$, $C2^E$, $C2^F$); 74.4 ($C2^A\alpha$), 74.5 ($C5^F$); 75.8 (2C), 76.0 (2C), 76.1 ($C3^B$, $C3^C$, $C3^D$, $C3^E$, $C3^F$), 75.9 ($C3^A\beta$), 76.7 ($C2^A\beta$), 77.3 ($C5^A\beta$), 78.9 ($C3^A\alpha$), 79.6 ($C4^A\alpha$); 79.7, 79.8 ($C4^B$, $C4^C$); 80.0 ($C4^A\beta$), 94.6 ($C1^A\alpha$), 98.5 ($C1^A\beta$); 100.4, 100.7 ($C1^E$, $C1^F$); 102.1 ($C1^B\alpha$), 102.2 ($C1^B\beta$); 102.4, 102.6 ($C1^C$, $C1^D$).

Found: C, 41.29; H, 6.43%. Calcd for $C_{36}H_{62}O_{31}\cdot 3H_2O$: C, 41.38; H, 6.56%.

Recycling Acceptors. (a) The sulfonate **15** (100.5 mg) was stirred in DMF (2.0 ml) containing sodium acetate (54 mg) at 80 °C for 3 h. Evaporation to dryness and chromatography using TB system afforded **80** (81.4 mg, 89%). Treatment of **80** (90.0 mg) with methanolic sodium methoxide (0.23%, 1.03 ml), followed by chromatography with the TB system, gave the acceptor **12** (75.1 mg, 86%). Similar conversions of compounds **73** and **78** gave **29** (68%) and **38** (77%) via **81** and **82**.

Allyl *O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (80). $[\alpha]_D$ +56° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.95 (s, 3H, Ac), 4.06 (dd, *J*=11.5, 2.0 Hz, $H6^Ca$), 4.18 (dd, *J*=3.5 Hz, $H6^Cb$), 4.49 (d, *J*=7.5 Hz, $H1^A$); 5.56, 5.58 (d, *J*=4.0 Hz each, $H1^B$, $H1^C$); ^{13}C NMR ($CDCl_3$) δ=63.0 ($C6^C$); 68.8, 69.1 ($C6^A$, $C6^B$); 96.3, 96.7 ($C1^B$, $C1^C$); 102.6 ($C1^A$); 20.8, 170.6 (Ac); 70.2, 117.2, 134.1 (AL).

Found: C, 73.51; H, 6.69%. Calcd for $C_{86}H_{92}O_{17}$: C, 73.90; H, 6.63%.

Allyl *O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (81). $[\alpha]_D$ +32° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=1.99 (s, 3H, Ac), 4.11 (dd, *J*=11.5, 2.0 Hz, $H6^Ba$), 4.21 (dd, *J*=4.0 Hz, $H6^Bb$), 4.50 (d, *J*=7.5 Hz, $H1^A$), 5.62 (d, *J*=3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ=63.1 ($C6^B$), 69.0 ($C6^A$), 96.5 ($C1^B$), 102.5 ($C1^A$); 20.8, 170.6 (Ac); 70.2, 117.3, 134.0 (AL).

Found: C, 73.42; H, 6.68%. Calcd for $C_{59}H_{64}O_{12}$: C, 73.42; H, 6.68%.

Allyl *O*-(6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (82). $[\alpha]_D$ +37° (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ=2.02 (s, 3H, Ac), 4.23 (dd, *J*=11.5, 2.0 Hz, $H6^Ba$), 4.26 (dd, *J*=4.0 Hz, $H6^Bb$), 4.45 (d, *J*=8.0 Hz, $H1^A$), 5.01 (d, *J*=3.5 Hz, $H1^B$); ^{13}C NMR ($CDCl_3$) δ=63.0 ($C6^B$), 65.8 ($C6^A$), 96.9 ($C1^B$), 102.6 ($C1^A$); 20.9, 170.6 (Ac); 70.1, 117.1, 134.0 (AL).

Found: C, 73.25; H, 6.71%. Calcd for $C_{59}H_{64}O_{12}$: C, 73.42; H, 6.68%.

(b) Stirring **15** (12.0 mg) in 1,4-dioxane (0.1 ml) containing aq tetrabutylammonium hydroxide (10%, 40 μl) at 80 °C for 3 h afforded **12** (5.7 mg, 54%) directly.

(c) Refluxing the sulfonate **18** (51.1 mg) in 1,2-dimethoxyethane (1.0 ml) containing $LiAlH_4$ (9.8 mg) for 30 min, with the usual processing and chromatography, yielded the unreacted **18** (6.4 mg, 13%) and the acceptor **14** (19.2 mg, 42%).

References

1) A. F. Bochkov and G. E. Zaikov, "Chemistry of the *O*-Glycosidic Bond: Formation and Cleavage," ed by C. Schuerch, Pergamon Press, New York (1979), Chap. 2; R. R. Schmidt, "Carbohydrates-Synthetic Methods and Applications in Medicinal Chemistry," ed by H. Ogura, A. Hasegawa, and T. Suami, Kodansha, Tokyo (1992), pp. 66—88; K. Toshima and K. Tatsuta, *Chem. Rev.*, **93**, 1503 (1993); G. Magnusson, A. Y. Chernyak, J. Kihlberg, and L. O. Kononov, "Neoglycoconjugates. Preparation and Appli-

cations," ed by Y. C. Lee and R. T. Lee, Academic Press, San Diego (1994), pp. 53—143.

2) Y. Matsuzaki, Y. Ito, Y. Nakahara, and T. Ogawa, *Tetrahedron Lett.*, **34**, 1061 (1993).

3) E. A. Kabat, *Adv. Chem. Ser.*, **117**, 334 (1973).

4) T. Mukaiyama and S. Suda, *Chem. Lett.*, **1990**, 1143; S. Suda and T. Mukaiyama, *Chem. Lett.*, **1991**, 431; T. Mukaiyama, K. Matsubara, and S. Suda, *Chem. Lett.*, **1991**, 981; J. Inanaga, Y. Yokoyama, and T. Hanamoto, *J. Chem. Soc., Chem. Commun.*, **1993**, 1090; N. Shimomura and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **67**, 2532 (1994); H. Susaki, *Chem. Pharm. Bull.*, **42**, 1917 (1994).

5) Y. Nishimura and S. Kondo, *Nat. Prod. Lett.*, **2**, 137 (1993).

6) S. Koto, N. Morishima, M. Owa, and S. Zen, *Carbohydr. Res.*, **130**, 73 (1984).

7) S. Koto, N. Morishima, S. Shichi, H. Haigoh, M. Hirooka, M. Okamoto, T. Higuchi, K. Shimizu, Y. Hashimoto, T. Irisawa, H. Kawasaki, Y. Takahashi, M. Yamazaki, Y. Mori, K. Kudo, T. Ikegaki, S. Suzuki, and S. Zen, *Bull. Chem. Soc. Jpn.*, **65**, 3257 (1992).

8) P. Hallgren, G. Hansson, K. G. Henriksson, A. Häger, A. Lundblad, and S. Svensson, *Eur. J. Clin. Invest.*, **4**, 429 (1974).

9) D. A. Zopf, R. E. Levinson, and A. Lundblad, *J. Immunol. Methods*, **48**, 109 (1982).

10) M. Kuriyama, R. Hiwatari, T. Ariga, Y. Sakano, J. Abe, M. Osame, and A. Igata, *J. Biochem.*, **98**, 1041 (1985).

11) G. Lennartson, A. Lundblad, J. Lundsten, S. Svensson, and A. Häger, *Eur. J. Biochem.*, **83**, 325 (1978).

12) S. Koto, N. Morishima, K. Takenaka, K. Kanemitsu, N. Shimoura, M. Kase, S. Kojiro, T. Nakamura, T. Kawase, and S. Zen, *Bull. Chem. Soc. Jpn.*, **62**, 3549 (1989).

13) J. Dahmén, T. Frejd, G. Magnusson, G. Noori, and A. -S. Carlström, *Carbohydr. Res.*, **127**, 27 (1984).

14) T. Tonozuka, H. Sakai, T. Ohta, and Y. Sakano, *Carbohydr. Res.*, **261**, 157 (1994).

15) R. E. Hoffman, J. C. Christofides, D. B. Davies, and C. J. Lawson, *Carbohydr. Res.*, **153**, 1 (1986).

16) A. Thompson and M. L. Wolfrom, *Methods Carbohydr. Chem.*, **2**, 215 (1963).

17) J. Gigg and R. Gigg, *J. Chem. Soc. C*, **1966**, 82.

18) E. Breitmaier and W. Voelter, "Carbon-13 NMR Spectroscopy: High Resolution Methods and Application in Organic Chemistry and Biochemistry," 3rd and completely revised ed, VCH, Weinheim (1987), Chap. 2, pp. 80—84.

19) S. Koto, T. Uchida, and S. Zen, *Bull. Chem. Soc. Jpn.*, **46**, 2520 (1973).

20) H. P. Wessel, B. Mayer, and G. Englert, *Carbohydr. Res.*, **242**, 141 (1993).

21) S. Koto, N. Morishima, T. Irisawa, Y. Hashimoto, M. Yamazaki, and S. Zen, *Nippon Kagaku Kaishi*, **1982**, 1651.

22) J. Kumlien, G. Grönberg, B. Nilsson, O. Månsson, D. Zopf, and A. Lundblad, *Arch. Biochem. Biophys.*, **269**, 678 (1989).

23) F. Sugawara, H. Nakayama, G. A. Strobel, and T. Ogawa, *Agric. Biol. Chem.*, **50**, 2251 (1986).

24) E. Zissis and H. G. Fletcher, Jr., *Carbohydr. Res.*, **12**, 361 (1970); P. Fügedi, A. Lipták, P. Nánási, and J. Szejtli, *Carbohydr. Res.*, **104**, 55 (1982).

25) A. L. Raymond, R. S. Tipson, and P. A. Levene, *J. Biol. Chem.*, **130**, 47 (1939).

26) L. V. Volkova, M. G. Luchinskaya, N. G. Morozova, N. B. Rozanova, and R. P. Evstigneeva, *Zh. Obshch. Khim.*, **42**, 2107 (1972).

27) N. Roy and C. P. J. Glaudemans, *Carbohydr. Res.*, **45**, 299 (1975).

28) S. Koto, N. Morishima, M. Uchino, M. Fukuda, M. Yamazaki, and S. Zen, *Bull. Chem. Soc. Jpn.*, **61**, 3943 (1988).

29) Y. Takahashi and T. Ogawa, *Carbohydr. Res.*, **164**, 277 (1987).

30) S. Koto, T. Yoshida, K. Takenaka, and S. Zen, *Bull. Chem. Soc. Jpn.*, **55**, 3667 (1982).

31) K. Takeo and T. Imai, *Carbohydr. Res.*, **165**, 123 (1987).

32) S. Koto, N. Morishima, T. Yoshida, M. Uchino, and S. Zen, *Bull. Chem. Soc. Jpn.*, **56**, 1171 (1983).

33) T. Ogawa and T. Horisaki, *Carbohydr. Res.*, **123**, C1 (1983).

34) A. Thompson and M. L. Wolfrom, *J. Am. Chem. Soc.*, **74**, 3612 (1952).

35) K. Takeo, K. Mine, and T. Kuge, *Carbohydr. Res.*, **48**, 197 (1976).

36) T. Ogawa, S. Nakabayashi, and T. Kitajima, *Carbohydr. Res.*, **114**, 225 (1983).

37) P. A. Gent and R. Gigg, *J. Chem. Soc., Perkin Trans. 1*, **1974**, 1835.

38) J. C. Jacquinet and P. Sinaÿ, *Tetrahedron*, **32**, 1693 (1976).