

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

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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 methods¹⁾ has brought forth recent syntheses²⁾ 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.



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 IV₁ 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. ¹H and ¹³C NMR spectra of **2** matched well with the published data.^{13,14)} ¹³C NMR spectrum of **3** shows the presence

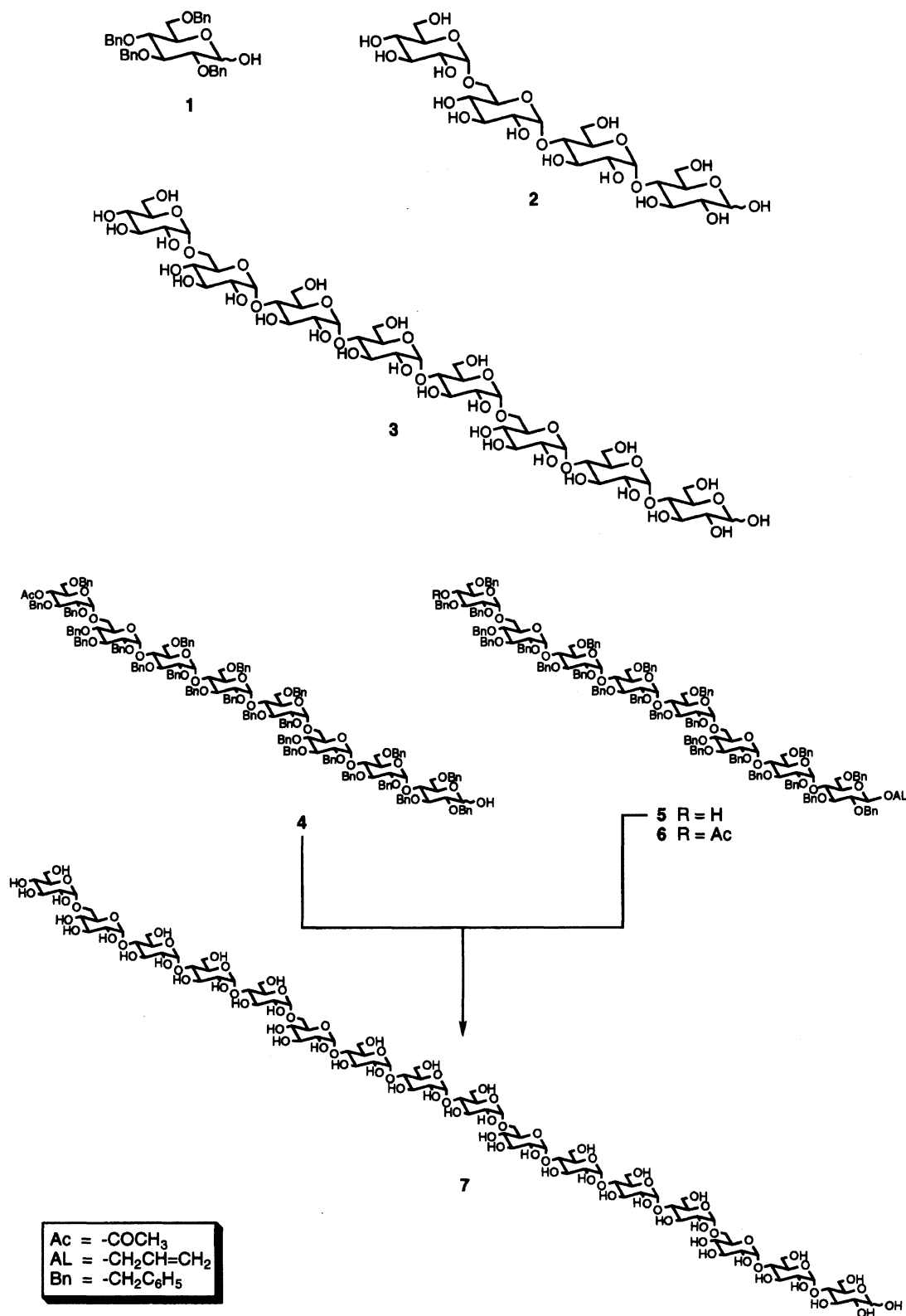


Chart 1.

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. ¹³C NMR

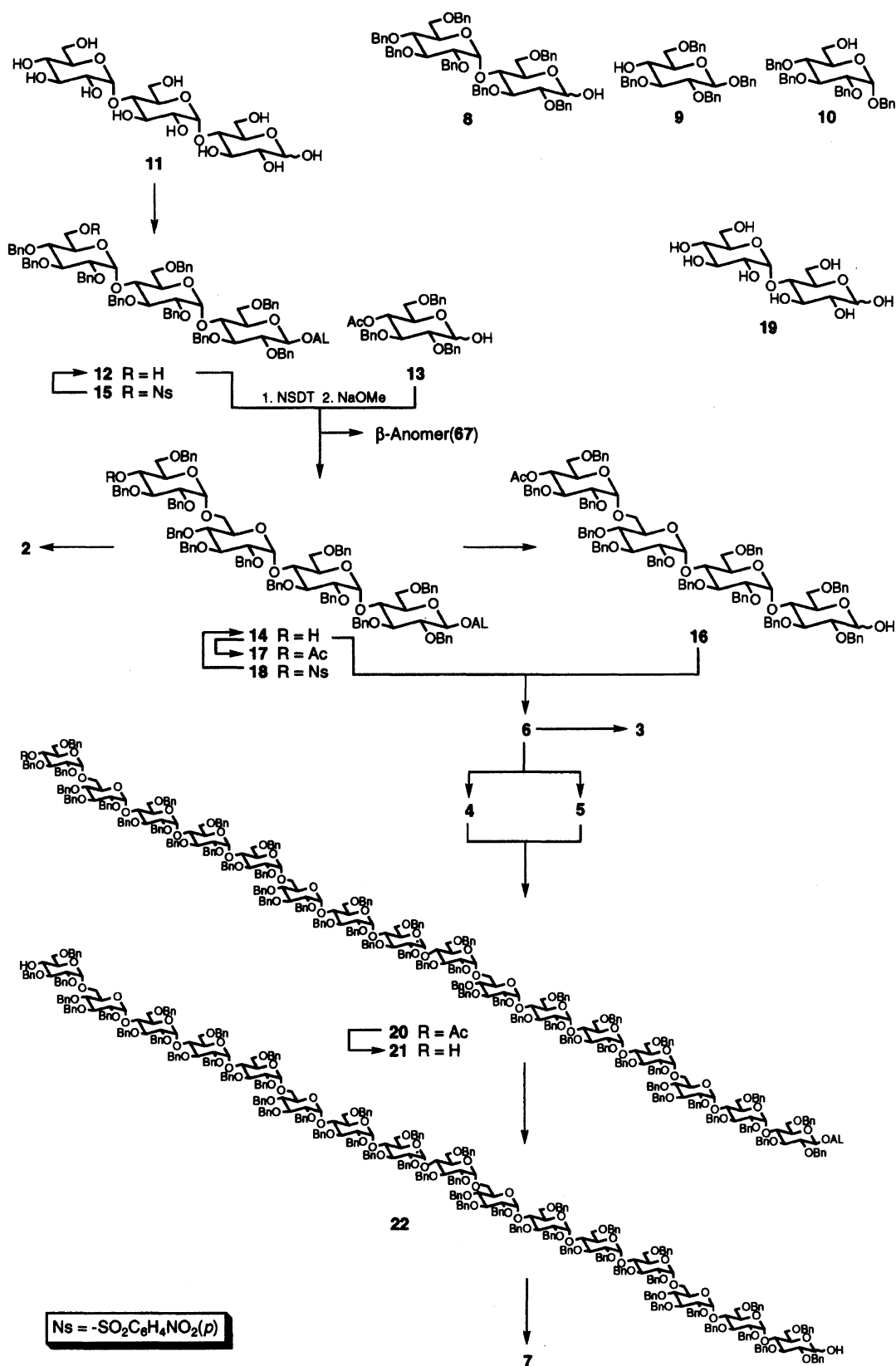


Chart 2.

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

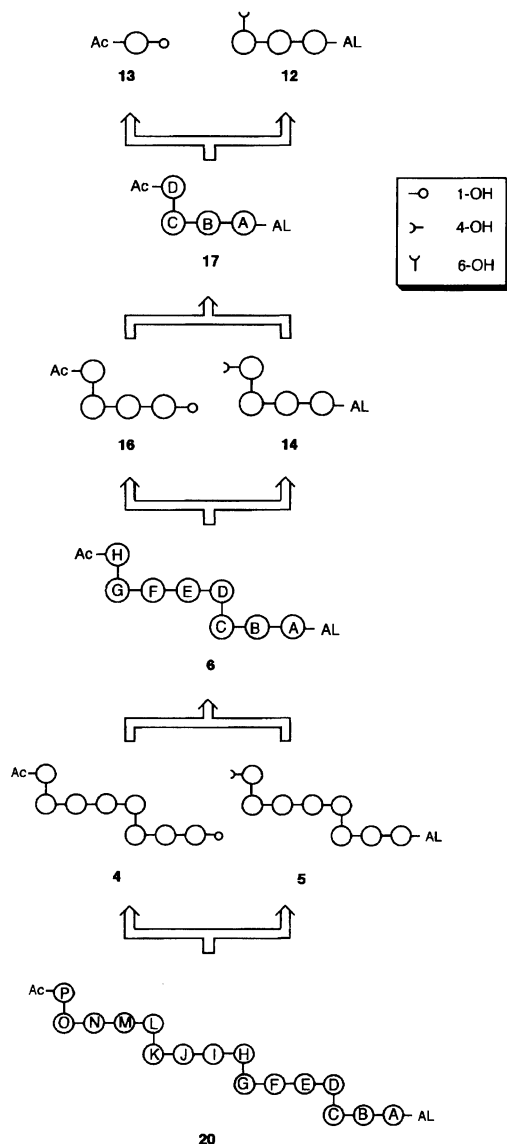


Fig. 1. A retro-synthetic scheme for the glucooctasaccharide **3** and the glucohexadecasaccharide **7**. A, B, ..., and P designate the sequential order of D-glucopyranosyl units from the reducing end to the nonreducing end. A horizontal line between large circles indicating α -D-Glcp(OBn)₃ or α -D-Glcp(OBn)₄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

terminal H-unit having α (1 $\rightarrow$ 6) linkage. In the spectrum of **20**, the signal at 96.7 ppm with increased intensity suggests the presence of three anomeric carbons of the inner D-, H-, and L-units with α (1 $\rightarrow$ 6) linkages. Unfortunately, the conventional deacetylation of **20** using sodium methoxide¹⁶⁾ encountered unexpected side reactions. Desired **21** was afforded only in a 34% yield. After mild deallylation¹⁷⁾ of **21**, the final hydrogenative debenzoylation of the intermediary diol **22** yielded the free glucohexadecaose **7**; the amount was enough to confirm its structure by its DEPT spectrum.¹⁸⁾ The ¹³C-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 $\rightarrow$ 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 ¹³C-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 unit¹⁹⁾ 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 route¹⁷⁾ 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**. ¹³CNMR shows the splitting of the signals of the anomeric carbon in B-unit¹⁵⁾ at δ 's of 102.26 and 102.30, as observed in the case of *O*- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-*O*- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-D-glucopyranose (isopanose).⁷⁾

The hexasaccharide **27**, which was once postulated^{11,22)} as component IV₂₁ 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. ¹³CNMR 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-unit¹⁵⁾ is present at δ 's of 102.1 and 102.2. Such a splitting is also present in the ¹³CNMR 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 IV₃^{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.

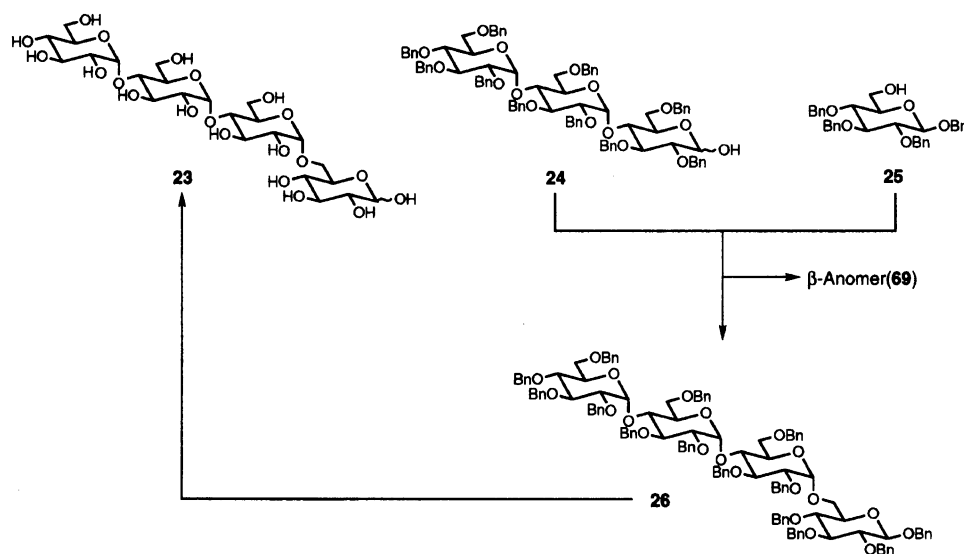


Chart 3.

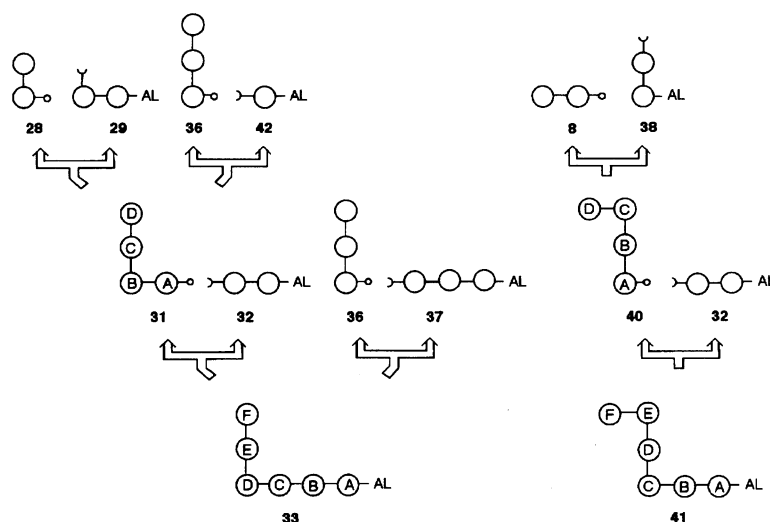


Fig. 2. A retro-synthetic scheme for glucohexasaccharides.

In conclusion, NSDT is capable of performing a dehydrative cross-condensation between both a donor and an acceptor of a linear glucosaccharide 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 F₂₅₄, 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-glucopyranoside²⁵⁾ via benzylation²⁶⁾ and detritylation of benzyl 6-*O*-trityl- β -D-glucopyranoside, $[\alpha]_D -73^\circ$ (*c* 0.2, CHCl₃) (lit,²⁷⁾ $[\alpha]_D -50^\circ$ (*c* 1.7, CHCl₃)). Found: C, 74.71; H, 6.39%. Calcd for C₃₂H₃₂O₆: 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 ¹³C 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 D₂O.

Synthetic Blocks. Allyl *O*-(2,3-Di-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (**47**). The synthetic route²⁹⁾ 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 $\rightarrow$ DOA)

No.	DOH ^{a)} mg	AOH ^{a)} mg	DOH/AOH mol/mol	NSC ^{a)} equiv ^{b)}	STF ^{a)} equiv ^{b)}	DMA ^{a)} equiv ^{b)}	TEA ^{a)} equiv ^{b)}	DCM ^{a)} ml	DOA %(α %)	AONs ^{a)} %
1	13 438.9	12 929.5	1.30	1.7	1.7	3.4	1.7	5.90	14^{c)}+67^{c)} 56 (65)	15 18
2	16 122.5	14 97.1	1.26	7.0	7.0	7.0	7.0	0.60	6 35 (100)	18 29
3	4 60.2	5 63.7	0.94	10.0	10.0	10.0	10.0	0.40	20 35 (100)	68 27
4	24 154.4	25 45.7	1.30	2.7	2.7	5.4	2.7	0.46	26+ 69 54 (60)	— ^{d)}
5	28 283.3	29 206.7	1.30	2.5	2.5	5.0	2.5	2.30	30+ 72 41 (67)	73 19
6	36 77.9	42 20.9	1.30	4.0	4.0	4.0	4.0	0.45	30 13 (100)	74 20
7	31 442.3	32 228.2	0.97	6.0	6.0	6.0	6.0	2.50	33 24 (100)	75 24
8	36 158.6	37 104.7	1.46	5.5	5.5	5.5	5.5	1.00	33 8 (100)	76 15
9	8 189.2	38 151.8	1.18	3.0	3.0	6.0	3.0	3.00	39+ 77 58 (83)	78 31
10	40 109.8	32 63.0	0.88	7.0	7.0	7.0	7.0	0.65	41 3 (100)	75 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%), $[\alpha]_D^{+73^\circ}$ (c 1.0, H₂O) (lit,³¹⁾ $[\alpha]_D^{+63^\circ}$ (c 3.3, H₂O)); ¹H NMR (D₂O) δ =4.48 (d, *J*=8.0 Hz, H1^A), # 5.36 (d, *J*=4.0 Hz, H1^B); ¹³C NMR (D₂O) 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 C₁₅H₂₆O₁₁·0.5H₂O: 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 $\rightarrow$ 4)- β -D-glucopyranoside (49)** (7.00 g, 78%); $[\alpha]_D^{+26^\circ}$ (c 2.0, CH₃OH); ¹H NMR (D₂O) δ =4.50 (d, *J*=8.0 Hz, H1^A), 5.44 (d, *J*=4.0 Hz, H1^B), 5.72 (s, Bd); ## ¹³C NMR (D₂O)

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 C₂₂H₃₀O₁₁: 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%); $[\alpha]_D^{+24^\circ}$ (c 1.4, CHCl₃) (lit,²⁹⁾ $[\alpha]_D^{+23.6^\circ}$ (CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₅₀H₅₆O₁₁: C, 72.10; H, 6.80%.

Allyl O- α -D-Glucopyranosyl-(1 $\rightarrow$ 4)-O- α -D-glucopyranosyl-(1 $\rightarrow$ 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%); $[\alpha]_D^{+99^\circ}$ (c 2.3, H₂O) (lit,²⁰⁾ $[\alpha]_D^{+111.5^\circ}$ (c H₂O); ¹H NMR (D₂O) δ =4.34 (d, *J*=8.0 Hz, H1^A), 5.22 (2H, d, *J*=3.5 Hz, H1^B, H1^C); ¹³C NMR (D₂O) δ =62.8

#D-Glucose units in the glucoooligosaccharides 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 H₂O (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.



Allyl *O*- α -D-Glucopyranosyl-(1 $\rightarrow$ 6)-*O*- α -D-glucopyranoside (52). Compound **44**⁷⁾ (2.65 g), obtained via the acetobromination³⁰⁾ 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%); [α]_D +35° (*c* 1.0, H₂O); ¹H NMR (D₂O) δ =4.46 (d, *J*=8.0 Hz, H1^A), 4.87 (d, *J*=3.5 Hz, H1^B); ¹³C NMR (D₂O) δ =63.0 (C6^B), 68.0 (C6^A); 71.9, 72.0 (C4^A, C4^B); 74.1 (C2^B), 74.4

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

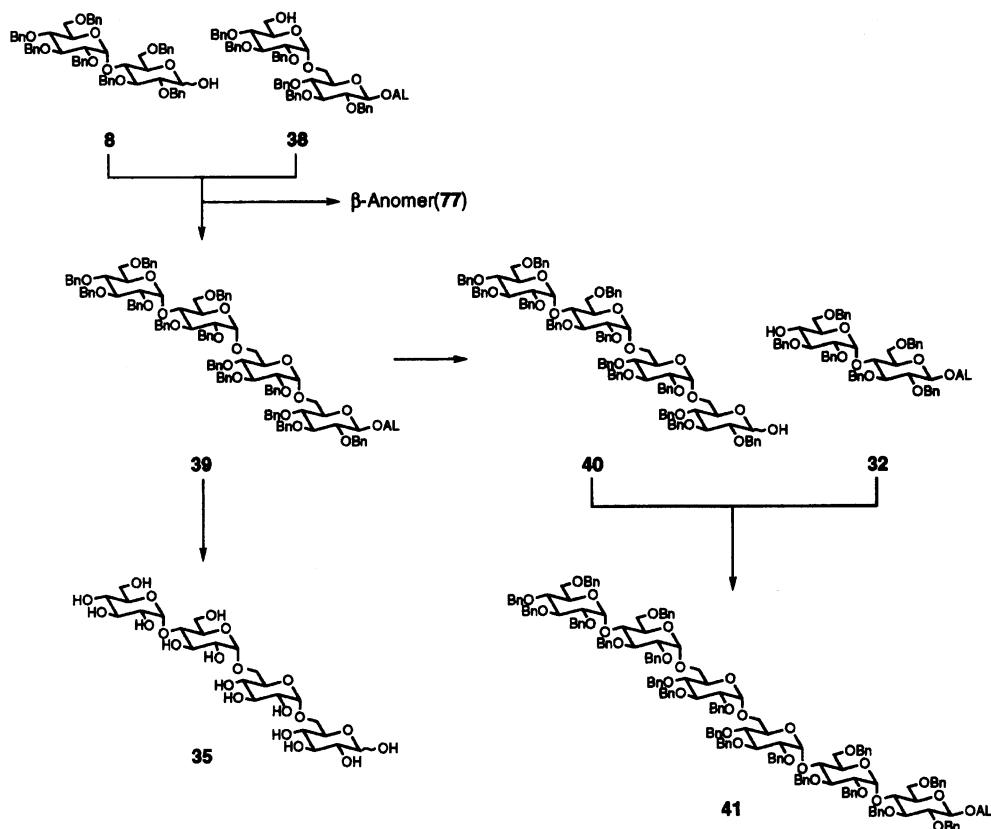


Chart 5.

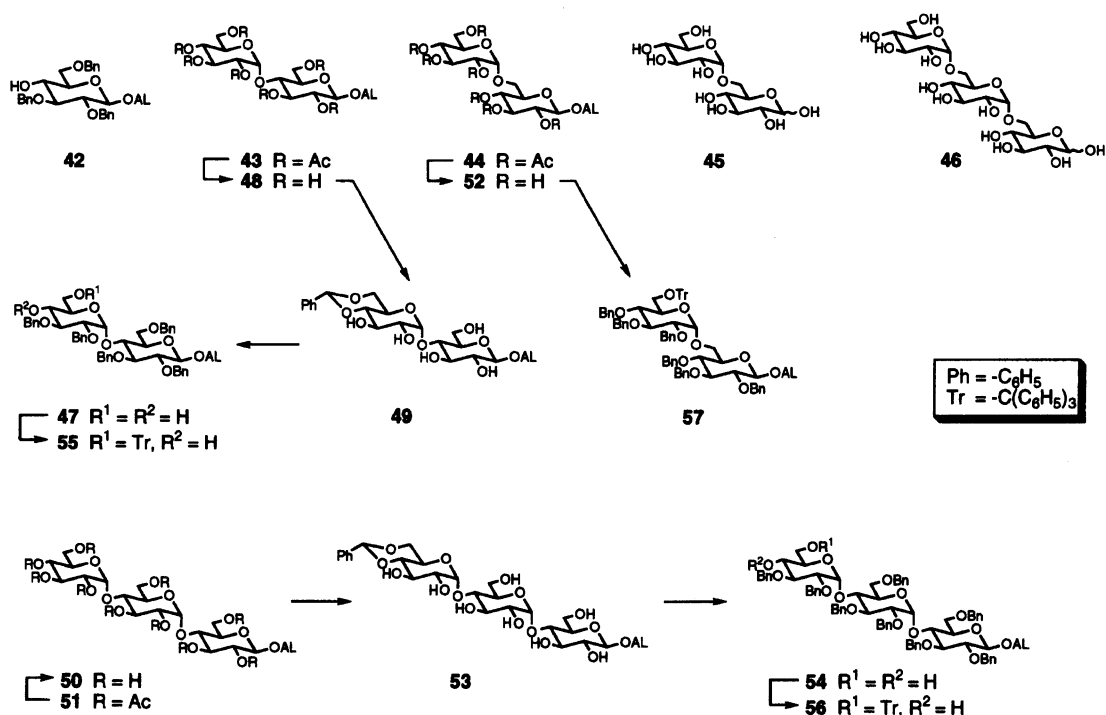


Chart 6.

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 $\rightarrow$ 4)- O -(2,3,6-tri- O -benzyl- α -D-glucopyranosyl)-

(1 $\rightarrow$ 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%); $[\alpha]_D +44^\circ$ (c 0.4, CHCl₃); ¹H NMR (D₂O) $\delta=4.48$ (d, $J=7.5$ Hz, H1^A); 5.61, 5.62 (d, $J=3.5$ Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) $\delta=96.2$, 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 C₇₇H₈₄O₁₆: 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 $\rightarrow$ 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 TEA³²⁾ (20 ml) and evaporation to dryness, chromatography (TE system) afforded **55** (8.53 g, 89%); $[\alpha]_D +21^\circ$ (c 1.7, CHCl₃); ¹H NMR (CDCl₃) $\delta=3.24$ (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); ¹³C NMR (CDCl₃) $\delta=63.5$ (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 C₆₉H₇₀O₁₁: C, 77.07; H, 6.56%.

Allyl O-(2,3-Di-O-benzyl-6-O-trityl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +41^\circ$ (c 1.9, CHCl₃); ¹H NMR (CDCl₃) $\delta=3.22$ (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); ¹³C NMR (CDCl₃) $\delta=63.2$ (C6^C); 96.2⁷, 96.3² (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 C₉₆H₉₈O₁₆: C, 76.74; H, 6.55%.

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

Allyl O-(6-O-Trityl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +23^\circ$ (c 0.4, CH₃OH-H₂O (1:1)); ¹H NMR (CD₃OD, $\delta_H=3.31$) $\delta=4.36$ (d, $J=7.5$ Hz, H1^A), 4.90 (d, $J=3.5$ Hz, H1^B); ¹³C NMR (CD₃OD, $\delta_C=49.0$), $\delta=65.0$ (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 C₃₄H₄₀O₁₁·2H₂O: C, 61.81; H, 6.51%.

Allyl O-(2,3,4-Tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +25^\circ$ (c 1.9, CHCl₃); ¹H NMR (CDCl₃) $\delta=4.50$ (d, $J=7.5$ Hz,

H1^A), 5.64 (d, $J=3.5$ Hz, H1^B); ¹³C NMR (CDCl₃) $\delta=96.4$ (C1^B), 102.5 (C1^A); 70.2, 117.3, 134.1 (AL).

Found: C, 73.89; H, 6.74%. Calcd for C₅₇H₆₂O₁₁: C, 74.16; H, 6.77%.

Allyl O-(2,3,4-Tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +44^\circ$ (c 1.7, CHCl₃); ¹H NMR (CDCl₃) $\delta=4.50$ (d, $J=7.5$ Hz, H1^A); 5.55, 5.60 (d, $J=3.5$ Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) $\delta=96.2$, 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 C₈₄H₉₀O₁₆: C, 74.42; H, 6.69%.

Allyl O-(2,3,4-Tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +35^\circ$ (c 1.2, CHCl₃) (lit,³³⁾ $[\alpha]_D^{25} +43.4^\circ$ (CHCl₃); ¹H NMR (CDCl₃) $\delta=4.46$ (d, $J=7.5$ Hz, H1^A), 4.98 (d, $J=3.5$ Hz, H1^B); ¹³C NMR (CDCl₃) $\delta=61.9$ (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 C₅₇H₆₂O₁₁: C, 74.16; H, 6.77%.

Allyl O-(2,3,6-Tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +23^\circ$ (c 0.9, CHCl₃) (lit,³¹⁾ $[\alpha]_D^{25} +21.6^\circ$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) $\delta=4.50$ (d, $J=8.0$ Hz, H1^A), 5.68 (d, $J=3.5$ Hz, H1^B); ¹³C NMR (CDCl₃) $\delta=70.6$ (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 C₅₇H₆₂O₁₁: 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 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D +41^\circ$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) $\delta=4.50$ (d, $J=7.5$ Hz, H1^A); 5.58, 5.67 (d, $J=3.5$ Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) $\delta=96.4$, 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 C₈₄H₉₀O₁₆: 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 $\rightarrow$ 4)-O-(2,3,6-tri-O-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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); $[\alpha]_D^{25} +88^\circ$ (*c* 1.5, CHCl₃) (lit.³⁴) $[\alpha]_D^{26} +89.5^\circ$ (*c* 2.9, CHCl₃); ¹H NMR (CDCl₃) δ =5.25, 5.39 (d, *J*=4.0 Hz each, H1^B, H1^C); 5.73 (d, *J*=7.5 Hz, H1); ¹³C NMR (CDCl₃) 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 C₄₀H₅₄O₂₇: C, 49.69; H, 5.63%, and **58** (30 mg); $[\alpha]_D^{25} +118^\circ$ (*c* 1.5, CHCl₃); ¹H NMR (CDCl₃) δ =5.30, 5.42 (d, *J*=4.0 Hz each, H1^B, C1^C); 6.24 (d, *J*=3.5 Hz, H1^A); ¹³C NMR (CDCl₃) 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 C₄₀H₅₄O₂₇: 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 H₂O (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 Ag₂CO₃ (9.69 g), the mixture was stirred at room temp overnight, followed by chromatography (TE system), to give **51** (6.59 g, 59%); $[\alpha]_D^{25} +74^\circ$ (*c* 1.5, CHCl₃) (lit.²⁰) $[\alpha]_D^{20} +75^\circ$ (*c* 0.5, dioxane); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₄₁H₅₆O₂₆: C, 51.04; H, 5.85%.

2-Methoxyethyl O-(2,3,4,6-Tetra-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 H₂O (0.42 ml) in chloroform (14.3 ml). The obtained bro-

mide was treated with 2-methoxyethanol (13.8 ml) in the presence of Ag₂CO₃ (4.40 g) to give **60** (3.63 g, 76%), mp 73–75 °C; $[\alpha]_D^{25} +78^\circ$ (*c* 2.5, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₄₁H₅₈O₂₇: C, 50.10; H, 5.95%.

Allyl O-(2,3,4,6-Tetra-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-acetyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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); $[\alpha]_D^{25} +94^\circ$ (*c* 0.3, CHCl₃); ¹H NMR (CDCl₃) δ =5.06, 5.10 (d, *J*=3.5 Hz each, H1^B, H1^C); 5.69 (d, *J*=8.5 Hz, H1^A); ¹³C NMR (CDCl₃) 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 C₄₀H₅₄O₂₇: C, 49.69; H, 5.63%. And **62** (33 mg); $[\alpha]_D^{25} +124^\circ$ (*c* 0.9, CHCl₃); ¹H NMR (CDCl₃) δ =5.06, 5.10 (d, *J*=3.5 Hz each, H1^B, H1^C); 6.32 (d, *J*=4.0 Hz, H1^A); ¹³C NMR (CDCl₃) 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 C₄₀H₅₄O₂₇: C, 49.69; H, 5.63%. A convenient bromination³⁰ of a mixture (1.60 g) of **62** and **63** described above with acetyl bromide (0.68 ml) and H₂O (0.12 ml) in chloroform (5.2 ml) likewise furnished the intermediate, which was then converted, with allyl alcohol (3.3 ml) and Ag₂CO₃ (0.46 g), into **61** (0.80 g, 50%); $[\alpha]_D^{25} +116^\circ$ (*c* 1.0, CHCl₃); ¹H NMR (CDCl₃) δ =4.56 (d, *J*=8.0 Hz, H1^A); 5.05, 5.13 (d, *J*=3.5 Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) δ =61.9 (C6^C); 66.0, 66.1 (C6^A,

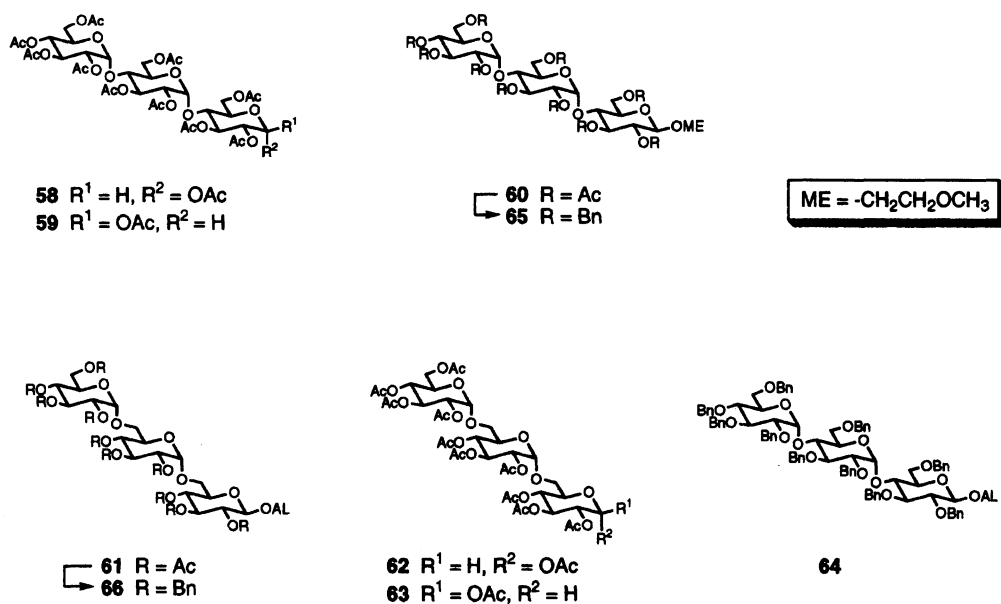


Chart 7.

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 C₄₁H₅₆O₂₆: C, 51.04; H, 5.85%.

Allyl O-(2,3,4,6-Tetra-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D^{20} +51^\circ$ (c 1.9, CHCl₃) (lit.²⁰) $[\alpha]_D^{20} +47.7^\circ$ (c 1, CHCl₃); ¹H NMR (CDCl₃) δ =4.49 (d, J =7.5 Hz, H1^A); 5.58, 5.67 (d, J =3.5 Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) 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 C₉₁H₉₆O₁₆: C, 75.60; H, 6.69%.

2-Methoxyethyl O-(2,3,4,6-Tetra-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (65). The decaacetate **60** (390.0 mg) was reacted with benzyl chloride (5.7 ml) and KOH (2.6 g), after chromatography (TB system), to afford **65** (385.9 mg, 66%); $[\alpha]_D^{20} +51^\circ$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) δ =4.49 (d, J =7.5 Hz, H1^A); 5.57, 5.65 (d, J =3.5 Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) 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 C₉₁H₉₈O₁₇: C, 74.67; H, 6.75%.

Allyl O-(2,3,4,6-Tetra-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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%); $[\alpha]_D^{20} +59^\circ$ (c 1.2, CHCl₃); ¹H NMR (CDCl₃) δ =4.42 (d, J =7.5 Hz, H1^A); 4.98, 5.04 (d, J =3.5 Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) 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 C₉₁H₉₆O₁₆: C, 75.60; H, 6.69%.

O-(2,3,4,6-Tetra-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (24). (a) A mixture of **64** (1.11 g), potassium *t*-butoxide¹⁷ (0.65 g), and dimethyl sulfoxide (1.99 ml) was stirred at 120 °C for 1 h under N₂. The processed syrupy reaction mixture was stirred in 1,4-dioxane (7.7 ml) containing aq H₂SO₄ (16%, 0.64 ml) at 100 °C for 1 h, followed by chromatography (HE system) to give **24** (0.91 g, 84%); $[\alpha]_D^{20} +53^\circ$ (c 0.8, CHCl₃); ¹H NMR (CDCl₃) (α : β =3:2) δ =5.24 (br, H1^A α), 5.52 (d, J =3.5 Hz, H1^C), 5.66 (d, J =3.5 Hz, H1^B β), 5.68 (d, J =3.5 Hz, H1^B α); ¹³C NMR (CDCl₃) δ =90.9 (C1^A α), 96.6 (C1^C), 96.8 (C1^B α), 96.9 (C1^B β), 97.4 (C1^A β).

Found: C, 75.25; H, 6.73%. Calcd for C₈₈H₉₂O₁₆: C, 75.19; H, 6.60%.

(b) Agitation of **64** (747.1 mg) in aq acetic acid (90%) in the presence of PdCl₂³⁶ (20 mg) and sodium acetate (20 mg) at 60 °C for 1 h, followed by processing and chromatography 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, TiCl₄¹² (6.2 μ l) was added. The resulting orange-colored solution was set aside for 5 min. After partition of the mixture between DCM and H₂O, the organic layer was washed with aq NaHCO₃ (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 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-O-benzyl- α -D-glucopyranose (36). Compound **66** (380.7 mg) was treated with PdCl₂³⁷ (25 mg) and sodium acetate (25 mg) in aq acetic acid to give **36** (258.9 mg, 70%); $[\alpha]_D^{20} +63^\circ$ (c 0.8, CHCl₃); ¹H NMR (CDCl₃) (α > β) δ =5.12 (d, J =3.5 Hz, H1 α); ¹³C NMR (CDCl₃) δ =91.1 (C1^A α), 96.8⁵ (C1^B β), 96.8⁹ (C1^B α), 97.2 (C1^B), 97.3 (C1 β).

Found: C, 75.30; H, 6.72%. Calcd for C₈₈H₉₂O₁₆: 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 P₂O₅) 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 quasi to perfectly homogeneous solution. To a mixture with stirring below -40 °C (bath temp), DMA^{##} (Wako Pure Chemical Industries, 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 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (240 μ l) in DCM (5.90 ml) afforded allyl **O-(2,3,4-tri-O-benzyl-6-O-*p*-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (15) (207.2 mg, 18%); $[\alpha]_D^{20} +56^\circ$ (c 2.2, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₉₀H₉₃NO₂₀S: C, 70.16; H, 6.08; N, 0.91%. And a condensate mixture, which**

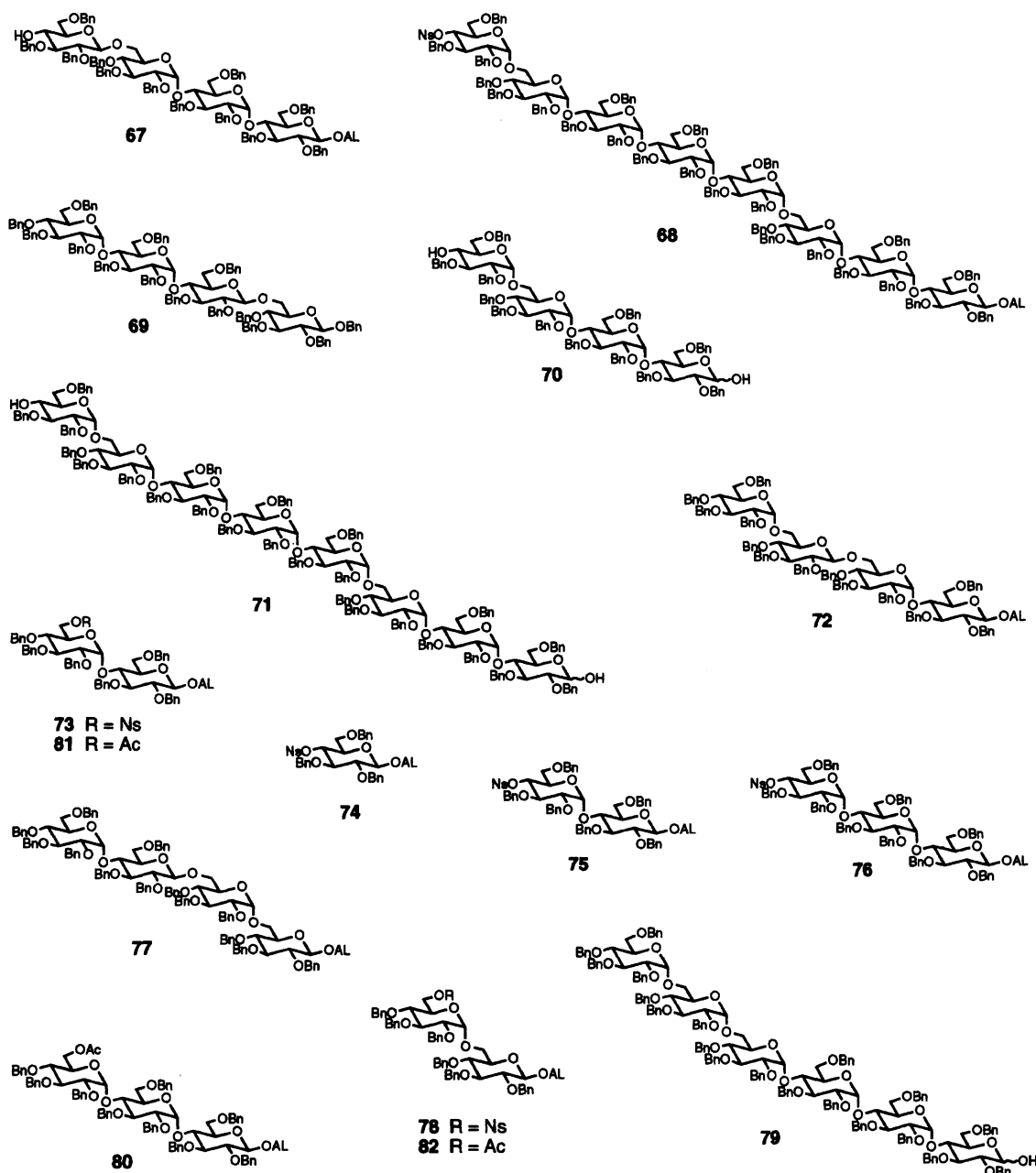


Chart 8.

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, chromatography with TB system gave **14** (441.8 mg, 36%); $[\alpha]_D +58^\circ$ (c 0.7, CHCl_3); $^1\text{H NMR}$ (CDCl_3) $\delta=4.52$ (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); $^{13}\text{C NMR}$ (CDCl_3) $\delta=65.2$ (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%); $[\alpha]_D +39^\circ$ (c 2.2, CHCl_3); $^1\text{H NMR}$ (CDCl_3) $\delta=4.21$ (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); $^{13}\text{C NMR}$ (CDCl_3) $\delta=68.2$ (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 $\text{C}_{111}\text{H}_{118}\text{O}_{21}$: C, 74.56; H, 6.65%.

Allyl *O*-(4-*O*-Acetyl-2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-*O*-(1 $\rightarrow$ 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%); $[\alpha]_D +67^\circ$ (c 0.8, CHCl_3); $^1\text{H NMR}$ (CDCl_3) $\delta=1.77$ (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); $^{13}\text{C NMR}$ (CDCl_3) $\delta=65.3$ (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 $\text{C}_{113}\text{H}_{120}\text{O}_{22}$: C,

74.16; H, 6.61%.

O-(4-O-Acetyl-2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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, CHCl₃); ¹H NMR (CDCl₃) (α : β =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 α), 5.57 (d, J =3.5 Hz, H¹_C), 5.64 (d, J =3.5 Hz, H¹_B β), 5.66 (d, J =3.5 Hz, H¹_B α); ¹³C NMR (CDCl₃) δ =65.2 (C⁶_C), 70.3 (C⁴_D), 90.8 (C¹_A α), 96.1 (C¹_B α), 96.2 (C¹_B β), 96.4 (C¹_C), 97.0 (C¹_D), 97.4 (C¹_A β); 20.8, 169.5 (Ac).

Found: C, 73.47; H, 6.46%. Calcd for C₁₁₀H₁₁₆O₂₂: C, 73.80; H, 6.53%.

Allyl O-(4-O-Acetyl-2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (53.0 μ l) in DCM (0.60 ml) furnished allyl **O-(2,3,6-tri-O-benzyl-4-O-p-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (18) (22.7 mg, 29%); $[\alpha]_D^{+71}$ (c 0.9, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁₇H₁₂₁NO₂₅S: C, 71.21; H, 6.18; N, 0.71%. And **6** (68 mg, 35%); $[\alpha]_D^{+73}$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ =64.4 (C⁶_C), 65.8 (C⁶_G), 70.4 (C⁴_H); 96.0, 96.0⁶, 96.1¹, 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 C₂₂₁H₂₃₂O₄₂: C, 74.56; H, 6.57%.

O-(4-O-Acetyl-2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (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 μ l) 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, CHCl₃); ¹H NMR (CDCl₃) (α : β =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); ¹³C NMR (CDCl₃) δ =64.4 (C⁶_C), 65.2 (C⁶_G), 70.4 (C⁴_H), 90.8 (C¹_A α); 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 β); 20.8, 169.6 (Ac).

Found: C, 74.02; H, 6.72%. Calcd for C₂₁₈H₂₂₈O₄₂: C, 74.38; H, 6.39%.

Allyl O-(2,3,6-Tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(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, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₂₁₉H₂₃₀O₄₁: C, 74.76; H, 6.59%.

Allyl O-(4-O-Acetyl-2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-tris[O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)]-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (25.3 μ l) in DCM (0.40 ml) afforded allyl **O-(2,3,6-tri-O-benzyl-4-O-p-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-O-(2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (68) (17.9 mg, 27%); $[\alpha]_D^{+84}$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ =64.5 (C⁶_C), 65.5 (C⁶_G), 79.2 (C⁴_H); 95.9⁷ (2C), 96.0³, 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 C₂₂₅H₂₃₃NO₄₅S: C, 72.97; H, 5.96; N, 0.38%.**

And **20** (42.4 mg, 35%); $[\alpha]_D^{+88}$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) 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), $J\approx 3$ 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) $\delta=64.4$ (3C , $\text{C}6^C$, $\text{C}6^G$, $\text{C}6^K$), 65.2 ($\text{C}6^O$), 70.4 ($\text{C}4^P$), 96.0–96.2 (11C) ($\text{C}1^B$, $\text{C}1^C$, $\text{C}1^E$, $\text{C}1^F$, $\text{C}1^G$, $\text{C}1^I$, $\text{C}1^J$, $\text{C}1^K$, $\text{C}1^M$, $\text{C}1^N$, $\text{C}1^O$), 96.7 (3C, $\text{C}1^D$, $\text{C}1^H$, $\text{C}1^L$), 97.1 ($\text{C}1^P$), 102.6 ($\text{C}1^A$); 20.8, 169.6 (Ac); 70.2, 117.2, 134.2 (AL).

Found: C, 74.22; H, 6.73%. Calcd for $\text{C}_{437}\text{H}_{456}\text{O}_{82}$: C, 74.76; H, 6.55%.

Allyl *O*-(2,3,6-Tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-tris[*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)]-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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) ^1H NMR (CDCl_3) $\delta=4.49$ (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) $\delta=64.4$ (3C , $\text{C}6^C$, $\text{C}6^G$, $\text{C}6^K$), 65.1 ($\text{C}6^O$), 70.4 ($\text{C}4^P$), 96.0–96.3 (11C) ($\text{C}1^B$, $\text{C}1^C$, $\text{C}1^E$, $\text{C}1^F$, $\text{C}1^G$, $\text{C}1^I$, $\text{C}1^J$, $\text{C}1^K$, $\text{C}1^M$, $\text{C}1^N$, $\text{C}1^O$), 96.6–96.7 (3C) ($\text{C}1^D$, $\text{C}1^H$, $\text{C}1^L$), 97.2 ($\text{C}1^P$), 102.6 ($\text{C}1^A$); 70.2, 117.2, 134.1 (AL).

Found: C, 74.65; H, 6.59%. Calcd for $\text{C}_{435}\text{H}_{454}\text{O}_{81}$: C, 74.78; H, 6.54%.

Benzyl *O*-(2,3,4,6-Tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α - and β -D-glucopyranosyl)-(1 $\rightarrow$ 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); ^1H NMR (CDCl_3) $\delta=4.55$ (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) $\delta=65.6$ ($\text{C}6^A$); 96.2, 96.7 ($\text{C}1^C$, $\text{C}1^D$); 96.8 ($\text{C}1^B$), 102.2 ($\text{C}1^A$). And **69** (35.9 mg, 22%); $[\alpha]_D^{+37}$ (c 0.8, CHCl_3); ^1H NMR (CDCl_3) $\delta=4.50$ (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) $\delta=68.6$ ($\text{C}6^A$); 96.4, 96.9 ($\text{C}1^C$, $\text{C}1^D$); 102.6 ($\text{C}1^A$), 103.8 ($\text{C}1^B$).

Found: **26**: C, 75.94; H, 6.68% and **69**: C, 75.95; H, 6.67%. Calcd for $\text{C}_{122}\text{H}_{126}\text{O}_{21}$: C, 75.99; H, 6.59%.

***O*-(2,3,6-Tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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); ^1H NMR (CDCl_3) ($\alpha:\beta=2:1$) $\delta=5.07$ (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) $\delta=65.2$ ($\text{C}6^C$), 90.9 ($\text{C}1^A\alpha$), 96.0 ($\text{C}1^B\alpha$), 96.2 ($\text{C}1^B\beta$), 96.5

($\text{C}1^C$), 97.2 ($\text{C}1^D$), 97.4 ($\text{C}1^A\beta$).

Found: C, 74.01; H, 6.51%. Calcd for $\text{C}_{108}\text{H}_{114}\text{O}_{21}$: C, 74.21; H, 6.57%.

***O*-(2,3,6-Tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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); ^1H NMR (CDCl_3) ($\alpha:\beta=7:3$) $\delta=5.08$ (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) $\delta=64.3$ ($\text{C}6^C$), 65.1 ($\text{C}6^G$), 70.5 ($\text{C}4^H$), 90.9 ($\text{C}1^A\alpha$); 95.9, 96.1 (3C), 96.4 ($\text{C}1^B$, $\text{C}1^C$, $\text{C}1^E$, $\text{C}1^F$, $\text{C}1^G$), 96.6 ($\text{C}1^D$), 97.1 ($\text{C}1^H$), 97.4 ($\text{C}1^A\beta$).

Found: C, 74.50; H, 6.38%. Calcd for $\text{C}_{216}\text{H}_{226}\text{O}_{41}$: C, 74.59; H, 6.55%.

***O*-(2,3,6-Tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-tris[*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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); ^1H NMR (CDCl_3) ($\alpha:\beta=1:1$) $\delta=5.06$ (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) $\delta=64.2$ ($\text{C}6^C$, $\text{C}6^G$, $\text{C}6^K$), 64.6 ($\text{C}6^O$), 90.8 ($\text{C}1^A\alpha$), 96.0–96.2 ($\text{C}1^B$, $\text{C}1^C$, $\text{C}1^E$, $\text{C}1^F$, $\text{C}1^G$, $\text{C}1^I$, $\text{C}1^J$, $\text{C}1^K$, $\text{C}1^M$, $\text{C}1^N$, $\text{C}1^O$), 96.6 ($\text{C}1^D$, $\text{C}1^H$, $\text{C}1^L$), 97.0 ($\text{C}1^P$).

***O*- α -D-Glucopyranosyl-(1 $\rightarrow$ 6)-bis[*O*- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-D-glucopyranose (2).** Hydrogenolysis of **70** (38.4 mg) over Pd on C (10%, 20.0 mg) in acetic acid³⁸⁾ (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⁾ $[\alpha]_D^{25}+165^\circ$ (c 0.8, H_2O)); ^1H NMR (D_2O) ($\alpha:\beta=45:55$) $\delta=4.55$ (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) $\delta=63.1^6$, 63.2 ($\text{C}6^B$, $\text{C}6^D$); 63.4 ($\text{C}6^A\beta$), 63.6 ($\text{C}6^A\alpha$), 68.6 ($\text{C}6^C$), 72.1, 72.2 ($\text{C}4^C$, $\text{C}4^D$); 72.6 ($\text{C}5^A\alpha$), 73.9 ($\text{C}5^C$), 73.9 ($\text{C}5^B\alpha$), 74.0 ($\text{C}5^B\beta$); 74.1 (2C), 74.4 ($\text{C}2^B$, $\text{C}2^C$, $\text{C}2^D$); 74.2 ($\text{C}2^A\alpha$), 74.5 ($\text{C}5^D$), 75.8 (2C), 75.9 ($\text{C}3^B$, $\text{C}3^C$, $\text{C}3^D$);

75.8⁵ (C3^A α), 76.7 (C2^A β), 77.2 (C5^A β), 78.8 (C3^A β), 79.8 (C4^A β), 79.9 (C4^A α), 80.0 (C4^B), 94.6 (C1^A α), 98.5 (C1^A β), 100.7 (C1^D), 102.1⁶ (C1^B β), 102.2³ (C1^B α), 102.6 (C1^C).

Found: C, 42.21; H, 6.50%. Calcd for C₂₄H₄₂O₂₁·H₂O: C, 42.11; H, 6.48%.

O- α -D-Glucopyranosyl-(1 $\rightarrow$ 6)-tris[O- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-]O- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-bis[O- α -D-glucopyranosyl-(1 $\rightarrow$ 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 H₂O (0.05 ml) and then in the acid (6.0 ml) containing H₂O (0.3 ml), followed by chromatography (CM system) yielded a colorless glass of **3** (10.3 mg, 56%); $[\alpha]_D +163^\circ$ (c 0.2, H₂O); ¹H NMR (D₂O) (α : β =45:55) δ =4.58 (d, J =8.0 Hz, H1^A β), 4.88–4.90 (2H, H1^D, H1^H), 5.16 (d, J =3.5 Hz, H1^A α), 5.28–5.35 (5H, H1^B, H1^C, H1^E, H1^F, H1^G); ¹³C NMR (D₂O) δ =63.1, 63.1⁶, 63.1⁹ (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 α), 73.0 (C5^D), 74.5 (C5^H), 75.9 (C3^A α), 76.7 (C2^A β), 77.3 (C5^A β), 78.9 (C3^A β), 79.7 (C4^A β), 79.9 (C4^A α); 79.8, 80.0 (2C), 80.4 (C4^B, C4^D, C4^E, C4^F); 94.6 (C1^A α), 98.5 (C1^A β), 100.7 (C1^D), 100.8 (C1^H), 102.2 (C1^B β), 102.3 (C1^B α), 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 C₄₈H₈₂O₄₁·3H₂O: C, 42.11; H, 6.48%.

Tris[O- α -D-Glucopyranosyl-(1 $\rightarrow$ 6)-tris[O- α -D-glucopyranosyl-(1 $\rightarrow$ 4)-]O- α -D-glucopyranosyl-(1 $\rightarrow$ 6)-bis[O- α -D-glucopyranosyl-(1 $\rightarrow$ 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 H₂O (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 H₂O, lyophilization, and drying over P₂O₅, gave a glassy solid of **7** (1.0 mg, 66%); $[\alpha]_D +159^\circ$ (c 0.1, H₂O); ¹H NMR (D₂O) (α : β =45:55) δ =4.61 (d, J =8.0 Hz, H1^A β), 4.91–4.92 (4H, H1^D, H1^H, H1^L, H1^P), 5.19 (d, J =3.5 Hz, H1^A α), 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); ¹³C NMR (D₂O, DEPT) δ =98.4 (C1^A β), 100.6 (C1^D, C1^H, C1^L), 100.7 (C1^P), 102.1 (C1^B β), 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 $\rightarrow$ 4)-]O- α -D-glucopyranosyl-(1 $\rightarrow$ 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 H₂O (0.05 ml) and then in the acid (6.0 ml) containing H₂O (0.75 ml), followed by chromatography (CM system), furnished glassy **23** (10.8 mg, 66%); $[\alpha]_D +156^\circ$ (c 0.2, H₂O); ¹H NMR (D₂O) (α : β =2:3) δ =4.58 (d, J =7.5 Hz, H1^A β), 4.86 (d, J =3.5 Hz, H1^B α), 4.87 (d, J =3.5 Hz, H1^B β), 5.15 (d, J =3.5 Hz, H1^A α), 5.30 (2H, d, J =3.5 Hz, H1^C, H1^D); ¹³C NMR (D₂O) δ =63.1, 63.2 (2C) (C6^B, C6^C, C6^D); 68.5 (C6^A β), 70.6 (C6^A α), 72.0 (C4^D), 72.1 (C4^A β), 72.2 (C4^A α), 72.7 (C5^A α), 72.9 (C5^B β), 73.0 (C5^B), 73.9 (C5^C); 74.0, 74.2, 74.4 (C2^B, C2^C, C2^D); 74.1 (C2^A α), 75.6 (C5^D), 75.7 (C3^A α); 75.4, 76.0, 76.1 (C3^B, C3^C, C3^D); 76.7 (C2^A β), 77.0 (C5^A β), 78.6 (C3^A β); 79.6, 79.8 (C4^B, C4^C); 94.9 (C1^A α), 96.7 (C1^A β), 100.4⁶ (C1^B β), 100.5⁹ (C1^B α); 102.2, 102.5 (C1^C, C1^D).

Found: C, 42.09; H, 6.77%. Calcd for C₂₄H₄₂O₂₁·H₂O:

C, 42.11; H, 6.48%.

Syntheses of Hexasaccharides. Allyl **O**-(2,3,4,6-Tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-**O**-(2,3,4-tri-*O*-benzyl- α - and β -D-glucopyranosyl)-(1 $\rightarrow$ 6)-**O**-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (78.0 μ l) in DCM (2.30 ml) yielded allyl **O**-(2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (**73**) (47.6 mg, 19%); $[\alpha]_D +43^\circ$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) δ =4.48 (d, J =7.5 Hz, H1^A), 5.60 (d, J =3.5 Hz, H1^B); ¹³C NMR (CDCl₃) 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 C₆₃H₆₅NO₁₅S: C, 68.28; H, 5.91; N, 1.26%. **30** (115.6 mg, 27%); $[\alpha]_D +63^\circ$ (c 1.1, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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%); $[\alpha]_D +43^\circ$ (c 1.4, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₁₈H₁₂₄O₂₁: 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 μ l), and TEA (23.8 μ l). This afforded allyl 2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl- β -D-glucopyranoside (**74**) (5.9 mg, 20%); $[\alpha]_D +15^\circ$ (c 1.5, CHCl₃); ¹H NMR (CDCl₃) δ =4.48 (d, J =7.5 Hz, H1^A), 4.80 (t, J =9.0 Hz, H4^A); ¹³C NMR (CDCl₃) 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 C₃₆H₃₇NO₁₀S: 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 $\rightarrow$ 6)-**O**-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-**O**-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 product 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%); $[\alpha]_D +47^\circ$ (c 2.8, CHCl₃); ¹H NMR (CDCl₃) (α : β =2:1) δ =4.95 (d, J =3.0 Hz, H1^D), 5.10 (d, J =3.5 Hz, H1^C α), 5.11 (d, J =3.5 Hz, H1^C β), 5.20 (br, H1^A α), 5.54 (d, J =3.5 Hz, H1^B α), 5.57 (d, J =3.5 Hz, H1^B β); ¹³C NMR (CDCl₃) δ =90.8 (C1^A α), 96.3 (C1^B β), 96.6 (C1^B α), 97.2 (C1^C), 97.3 (C1^D), 97.4 (C1^A β).

Found: C, 75.12; H, 6.66%. Calcd for C₁₁₅H₁₂₀O₂₁: C, 75.14; H, 6.58%.

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

nosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (207 μ l) in DCM (2.50 ml) produced allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (**75**) (65.9 mg, 24%); $[\alpha]_D^{+29}$ (c 1.3, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₆₃H₆₅NO₁₅S: C, 68.28; H, 5.91; N, 1.26%. And **33** (159.5 mg, 24%); $[\alpha]_D^{+72}$ (c 2.2, CHCl₃); ¹NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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); 96.2⁹, 96.3³, 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 C₁₇₂H₁₈₀O₃₁: 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 μ l), and TEA (59.3 μ l) in DCM (1.00 ml) gave allyl *O*-(2,3,6-tri-*O*-benzyl-4-*O*-*p*-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-2,3,6-tri-*O*-benzyl- β -D-glucopyranoside (**76**) (17.3 mg, 15%); $[\alpha]_D^{+56}$ (c 2.0, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₉₀H₉₃NO₂₀S: 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 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α - and β -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ g), and TEA (68.9 μ l) in DMA (1.50 ml). This afforded allyl *O*-(2,3,4-tri-*O*-benzyl-6-*O*-*p*-nitrobenzenesulfonyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- β -D-glucopyranoside (**78**) (56.0 mg, 31%); $[\alpha]_D^{+39}$ (c 2.4, CHCl₃); ¹H NMR (CDCl₃) δ =4.46 (d, *J*=7.5 Hz, H1^A), 4.86 (d, *J*=3.5 Hz, H1^B); ¹³C NMR (CDCl₃) 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 C₆₃H₆₅NO₁₅S: C, 68.28; H, 5.91; N, 1.26%. **39** (148.5 mg, 48%); $[\alpha]_D^{+57}$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) δ =65.3, 65.7 (C6^A, C6^B); 68.2, 69.1 (C6^C, C6^D); 96.7¹ (C1^D); 96.6⁶, 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, CHCl₃); ¹H NMR (CDCl₃) 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);

¹³C NMR (CDCl₃) 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 C₁₁₈H₁₂₄O₂₁: C, 75.46; H, 6.65%.

O-(2,3,4,6-Tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-*O*-benzyl- β -D-glucopyranose (**40**). Rearrangement of **39** (187.4 mg) was performed by refluxing in EBW (15 ml) containing 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, CHCl₃); ¹H NMR (CDCl₃) (α : β =2:1) δ =4.65 (d, *J*=8.0 Hz, H1^A β); 4.98, 5.04 (d, *J*=3.5 Hz each, H1^B α , H^C α); 4.99, 5.06 (d, *J*=3.5 Hz each, H1^B β , H1^C β); 5.13 (d, *J*=3.0 Hz, H1^A α), 5.66 (d, *J*=3.5 Hz, H1^D α), 5.69 (d, *J*=3.5 Hz, H1^D β); ¹³C NMR (CDCl₃) δ =65.2, 66.1 (C6^A α , C6^B α); 65.7, 66.7 (C6^A β , C6^B β); 91.1 (C1^A α); 96.4, 97.1 (C1^B β , C1^C β); 96.6 (C1^B α , C1^D β or C1^C α , C1^D β), 96.8 (C1^D α), 96.9 (C1^C α or C1^B α), 97.3 (C1^A β).

Found: C, 75.12; H, 6.66%. Calcd for C₁₁₅H₁₂₀O₂₁: C, 75.14; H, 6.48%.

Allyl *O*-(2,3,4,6-Tetra-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-bis[(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)]-(1 $\rightarrow$ 4)-*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 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 μ l), and TEA (66.7 μ l) 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, CHCl₃); ¹H NMR (CDCl₃) 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); ¹³C NMR (CDCl₃) 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 C₁₇₂H₁₈₀O₃₁: 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 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-*O*-(2,3,4-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-bis[*O*-(2,3,6-tri-*O*-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)]-2,3,6-tri-*O*-benzyl- β -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 μ l) in acetone (2.0 ml) at 45 °C for 2.0 h, gave **79** (31.8 mg, 67%); $[\alpha]_D^{+68}$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) (α : β =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 α); 5.54, 5.69 (d, *J*=3.5 Hz each, H1^C, H1^D); 5.58 (d, *J*=3.5 Hz, H1^B β), 5.60 (d, *J*=3.5 Hz, H1^B α); ¹³C NMR (CDCl₃) 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 α), 69.2 (C6^A β), 90.9 (C1^A α), 96.2 (C1^B β), 96.3³ (C1^B α); 96.2⁸, 96.7 (C1^C, C1^D); 97.1, 97.3 (C1^E, C1^F); 97.4 (C1^A β).

Found: C, 75.43; H, 6.85%. Calcd for C₁₆₉H₁₇₆O₃₁: C, 75.09; H, 6.56%.

Bis[O- α -D-glucopyranosyl-(1 $\rightarrow$ 6)]-O- α -D-glucopyranosyl-(1 $\rightarrow$ 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 H₂O (0.05 ml) and then in the acid (6.0 ml) containing H₂O (0.50 ml). Processing similar to that for **3** furnished **34** (7.7 mg, 64%); $[\alpha]_D^{+149}$ (c 0.2, H₂O); ¹H NMR (D₂O) (α : β =2:3) δ =4.58 (d, J =7.5 Hz, H1^A β); 4.88, 4.89 (d, J =3.5 Hz each, H1^C, C1^D); 5.15 (d, J =3.5 Hz, H1^A α), 5.33 (d, J =3.5 Hz, H1^B); ¹³C NMR (D₂O) δ =63.2 (C6^D), 63.4 (C6^A α), 63.5 (C6^A β); 68.2, 68.7 (C6^B, C6^C); 72.1, 72.2, 72.3 (C4^B, C4^C, C4^D); 72.7 (C5^A α), 72.9 (C5^C), 73.9 (C2^B β), 74.0 (C2^B α); 74.1, 74.2 (>1C, C2^B α) (C2^C, C2^D); 74.3 (C2^B β), 74.4 (C2^A α), 74.5 (C5^D); 75.8 (2C), 76.1 (C3^B, C3^C, C3^D); 75.9 (C3^A α), 76.7 (C2^A β), 77.3 (C5^A β), 78.9 (C3^A β), 79.9 (C4^A β), 80.1 (C4^A α), 94.6 (C1^A α), 98.5 (C1^A β); 100.4, 100.7 (C1^C, C1^D); 102.4 (C1^B β), 102.5 (C1^B α).

Found: C, 40.80; H, 6.68%. Calcd for C₂₄H₄₂O₂₁·2H₂O: C, 41.03; H, 6.60%.

O- α -D-Glucopyranosyl-(1 $\rightarrow$ 4)-bis[O- α -D-glucopyranosyl-(1 $\rightarrow$ 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, H₂O); ¹H NMR (D₂O) (α : β =2:3) δ =4.58 (d, J =7.5 Hz, H1^A β), 4.86 (d, J =3.5 Hz, H1^B α), 4.87 (d, J =3.5 Hz, H1^B β , H1^C), 5.15 (d, J =3.5 Hz, H1^A α), 5.29 (d, J =3.5 Hz, H1^D); ¹³C NMR (D₂O) δ =63.1, 63.2 (C6^C, C6^D); 68.3⁶ (C6^A β), 68.4³ (C6^B), 68.5 (C6^A α); 72.0, 72.2 (C4^B, C4^D); 72.1 (C4^A β), 72.3 (C4 α), 72.6 (C5^A α), 72.9 (C5^B α), 73.0 (>1C, C5^B β , C5^C); 73.9, 74.1 (>1C, C2^A α), 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 α), 76.7 (C2^A β), 76.9 (C5^A β), 78.7 (C3^A β), 79.8 (C4^C), 94.9 (C1^A α), 98.7 (C1^A β), 100.2 (C1^C), 100.5⁵ (C1^B β), 100.5⁸ (C1^B α), 102.4 (C1^D).

Found: C, 39.95; H, 6.85%. Calcd for C₂₄H₄₂O₂₁·3H₂O: C, 40.00; H, 6.71%.

Bis[O- α -D-glucopyranosyl-(1 $\rightarrow$ 6)]-tris[O- α -D-glucopyranosyl-(1 $\rightarrow$ 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 H₂O (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, H₂O); ¹H NMR (D₂O) (α : β =2:3) δ =4.56 (d, J =7.5 Hz, H1^A β); 4.87, 4.88 (d, J =3.5 Hz, H1^E, H1^F), 5.13 (d, J =3.5 Hz, H1^A α); 5.29, 5.30 (d, J =4.0 Hz, each), 5.32 (d, J =3.5 Hz) (H1^B, H1^C, H1^D); ¹³C NMR (D₂O) δ =63.2 (>2C, C6^A α), 63.3 (C6^B, C6^C, C6^F); 63.4 (C6^A β); 68.3, 68.7 (C6^D, C6^E); 72.1⁷, 72.2³, 72.3 (C4^D, C4^E, C4^F); 72.7 (C5^A α); 72.9, 73.8⁸, 73.9², 74.0 (C5^B, C5^C, C5^D, C5^E); 74.0, 74.1, 74.1⁸ (2C), 74.2⁴ (C2^B, C2^C, C2^D, C2^E, C2^F); 74.4 (C2^A α), 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 β), 76.7 (C2^A β), 77.3 (C5^A β), 78.9 (C3^A α), 79.6 (C4^A α); 79.7, 79.8 (C4^B, C4^C); 80.0 (C4^A β), 94.6 (C1^A α), 98.5 (C1^A β); 100.4, 100.7 (C1^E, C1^F); 102.1 (C1^B α), 102.2 (C1^B β); 102.4, 102.6 (C1^C, C1^D).

Found: C, 41.29; H, 6.43%. Calcd for C₃₆H₆₂O₃₁·3H₂O: 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 $\rightarrow$ 4)-O-(2,3,6-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (80). $[\alpha]_D^{+56}$ (c 0.9, CHCl₃); ¹H NMR (CDCl₃) δ =1.95 (s, 3H, Ac), 4.06 (dd, J =11.5, 2.0 Hz, H6^C α), 4.18 (dd, J =3.5 Hz, H6^C β), 4.49 (d, J =7.5 Hz, H1^A); 5.56, 5.58 (d, J =4.0 Hz each, H1^B, H1^C); ¹³C NMR (CDCl₃) 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 C₈₆H₉₂O₁₇: C, 73.90; H, 6.63%.

Allyl O-(6-O-Acetyl-2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranoside (81). $[\alpha]_D^{+32}$ (c 1.0, CHCl₃); ¹H NMR (CDCl₃) δ =1.99 (s, 3H, Ac), 4.11 (dd, J =11.5, 2.0 Hz, H6^B α), 4.21 (dd, J =4.0 Hz, H6^B β), 4.50 (d, J =7.5 Hz, H1^A), 5.62 (d, J =3.5 Hz, H1^B); ¹³C NMR (CDCl₃) 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 C₅₉H₆₄O₁₂: C, 73.42; H, 6.68%.

Allyl O-(6-O-Acetyl-2,3,4-tri-O-benzyl- α -D-glucopyranosyl)-(1 $\rightarrow$ 6)-2,3,4-tri-O-benzyl- β -D-glucopyranoside (82). $[\alpha]_D^{+37}$ (c 0.5, CHCl₃); ¹H NMR (CDCl₃) δ =2.02 (s, 3H, Ac), 4.23 (dd, J =11.5, 2.0 Hz, H6^B α), 4.26 (dd, J =4.0 Hz, H6^B β), 4.45 (d, J =8.0 Hz, H1^A), 5.01 (d, J =3.5 Hz, H1^B); ¹³C NMR (CDCl₃) 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 C₅₉H₆₄O₁₂: 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 μ l) 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 LiAlH₄ (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%).

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