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Synthesis of β-(1→6)-Branched β-(1→3) Glucohexaose and Its Analogues Containing an α-(1→3) Linked Bond with Antitumor Activity

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Abstract—A β-(1→6)-branched β-(1→3)-glucohexaose, present in many biologically active polysaccharides from traditionally herbal medicines such as *Ganoderma lucidum*, *Schizophyllum commune* and *Lentinus edodes*, was synthesized as its lauryl glycoside **32**, and its analogues **18**, **20** and **33** containing an α-(1→3) linked bond were synthesized. It is interesting to find that coupling of a 3,6-branched acylated trisaccharide trichloroacetimidate donor **9** with 3,6-branched acceptors **13** and **16** with 3′-OH gave the α-(1→ 3)-linked hexasaccharides **17** and **19**, respectively, in spite of the presence of C-2 ester capable of neighboring group participation. However, coupling of **9** with 4-methoxyphenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**27**) selectively gave β-(1→3)-linked tetrasaccharide **28**. Simple chemical transformation of the tetrasaccharide **28** gave acylated tetrasaccharide trichloroacetimidate **29**. Coupling of **29** with lauryl (1→6)-linked disaccharide **26** with 3-OH gave β-(1→3)-linked hexasaccharide **30** as the major product. Bioassay showed that in combination with the chemotherapeutic agent cyclophospamide (CPA), the hexaose **18** at a dose of 0.5–1 mg/kg substantially increased the inhibition of S_{180} for CPA, but decreased the toxicity caused by CPA. Some of these oligosaccharides also inhibited U_{14} noumenal tumor in mice effectively.

Introduction

β-(1→6)-Branched β-(1→3) gluco-oligosaccharides are the common structure characteristic of many biologically active polysaccharides from traditionally herbal medicines such as *Ganoderma lucidum*, *Schizophyllum commune* and *Lentinus edodes*.[1] Of them, polysaccharides from *Lentinus edodes* called lentinan have the most strong antitumor effect, particularly, for Sarcoma-180 in mice, and have been used as an antitumor and immune reinforce medicine in Japan and China for many years. Clinically, lentinan has proved effective with chemotherapeutic agents for patients with recurrent gastric and colorectal cancer.[2] Some physicochemical and immunopharmacological investigations showed that the antitumor activity of these glucans may be closely related to the triplet-helix structures of the β-(1→3)-linked backbone chains[3a,b] and some biological aspects of β-glucans were reported.[3c,d,e] It was also reported that only higher molecular-weight fractions (MW >16,000) obtained from partial hydrolysis of lentinan with formic acid showed antitumor activity.[4] We hypothesize that the activity of lentinan is dependent upon its basic structure-oligosaccharide unit rather than its macroscopical morphology. It was reported that the β-(1→3)-branched β-(1→6) polysaccharides (MW $\sim 10^6$) of mycelial walls of the fungus *Phytophthora megasperma* f. sp. *Glycinea* can induce the formation of phytoalexins in soybean, and the heptasaccharide β-D-Glc*p*-(1→6)-[β-D-Glc*p*-(1→3)-]β-D-Glc*p*-(1→6)-β-D-Glc*p*-(1→6)-[β-D-Glc*p*-(1→3)-]β-D-Glc*p*-(1→6)-D-Glc*p* and the hexasaccharide β-D-Glc*p*-(1→6)-[β-D-Glc*p*-(1→3)-]β-D-Glc*p*-(1→6)-β-D-Glc*p*-(1→6)-[β-D-Glc*p*-(1→3)-]D-Glc*p* present in the polysaccharides have even more strong activity than the polysaccharides themselves.[5] Therefore, we deduce that the fragment of lentinan β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)-]β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)-]β-D-Glc*p*-(1→3)-D-Glc*p* or β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)-]β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)-]D-Glc*p* may have similar or better biological activities compared to lentinan itself.

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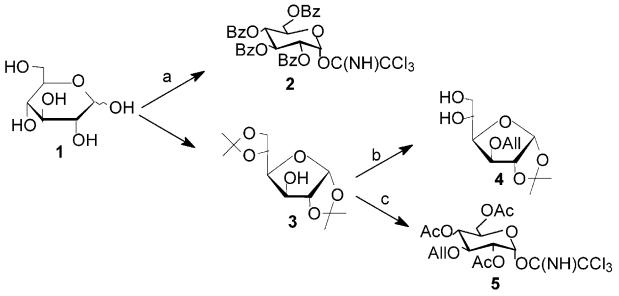
Here we would like to disclose the synthesis and biological activity of lentinan hexasaccharide and its analogues with an α-linkage in the backbone.

Results and Discussion

Preparation of oligosaccharides is more difficult and complex compared to the synthesis of other biopolymers such as peptides and nucleic acids. Most glycosylation methods are extremely sensitive to structural variations in the glycosyl donor-acceptor pairs.[6] Reaction conditions that provide excellent yields with one donor–acceptor pair may give virtually no product for another donor–acceptor pair. Furthermore, the stereochemical outcome is often difficult to predict. Our synthesis of the β-(1→6)-branched β-(1→3) glucohexaose again showed complexity of the oligosaccharide synthesis as described below.

More than 3 years ago we invented an efficient method for the synthesis of 3,6-branched β-linked gluco-oligosaccharids using 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose as the starting glycosyl acceptor.[7] The synthesis of β-(1→3)-branched β-(1→6)-linked glucohexaose phytoalexin elicitor on a 100 g scale was achieved in our laboratory and higher oligosaccharides of the elicitor including the hepta-, nona-, dodeca- and tetradecasaccharids were also readily synthesized by the developed strategy.[8] However, when the same strategy was used to prepare the β-(1→6)-branched β-(1→3)-linked glucohexaoses from a trisaccharide donor and a trisaccharide acceptor, the desired β-linked target was not obtained, but α-(1→3)-linked analogue was the product.[9,10]

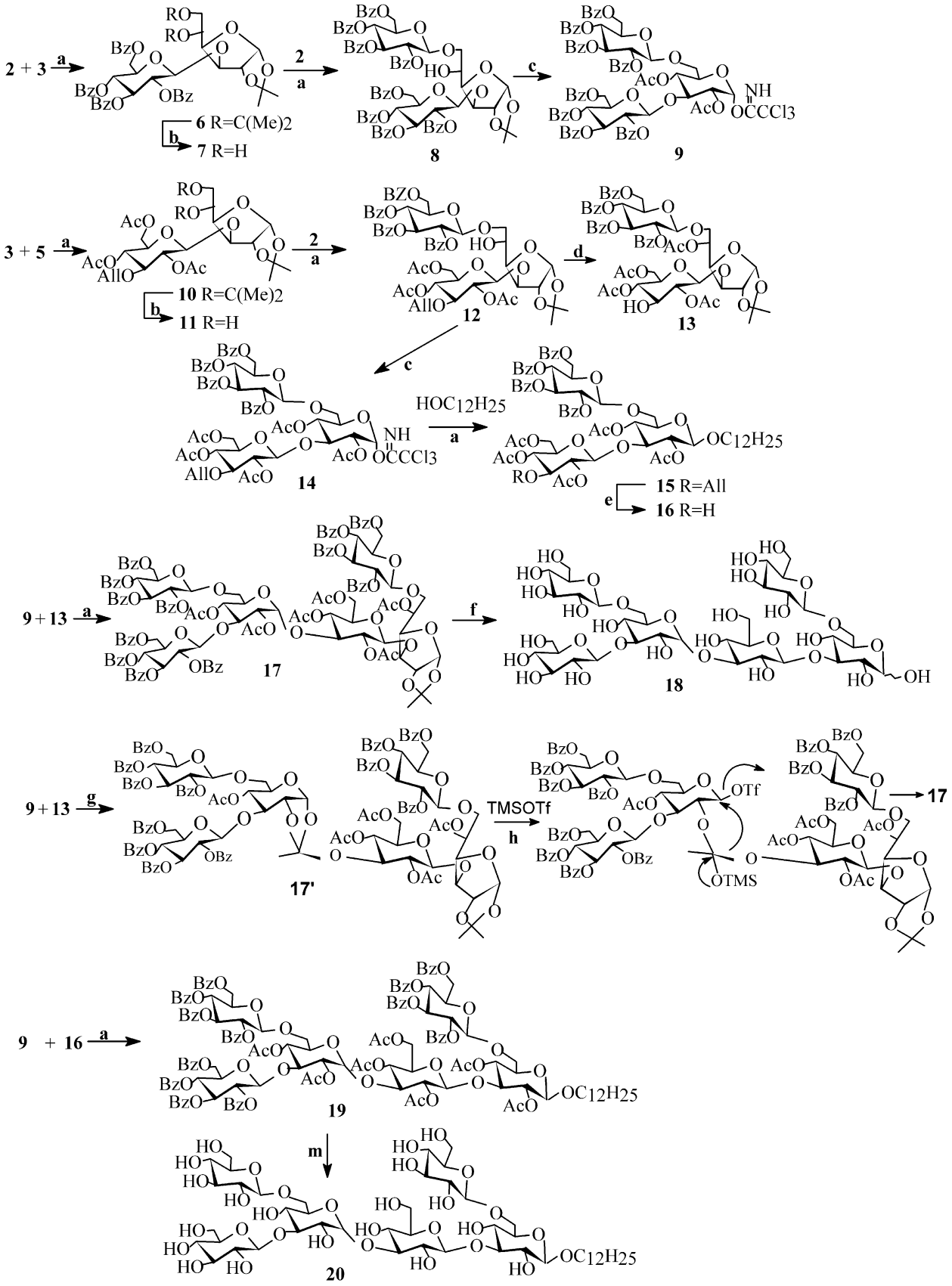
In our synthesis, 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate **2**, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **3**, 3-*O*-allyl-1,2-*O*-isopropylidene-α-D-glucofuranose **4** and 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl trichloroacetimidate **5** were the starting materials and the trisaccharides **8**, **12** and the disaccharide **21** were the key intermediates. Compound **2** was prepared as fine crystals via benzoylation of D-glucose followed by 1-*O*-debenzoylation with ammonia in THF–CH_3OH and trichloroacetimidation (Scheme 1). Compound **3** was readily obtained by diacetonation of D-glucose according the standard method. Compound **4** was prepared from allylation of **3** followed by selective removal of 5,6-*O*-isopropylidation with 90% HOAc. Compound **5** was obtained as white crystals from the allylation of **3** followed by deisopropylidenation, acetylation, 1-*O*-deacetylation and trichloroacetimidation. The coupling of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **3** with perbenzoyl glucosyl trichloroacetimidate **2** in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as the catalyst, followed by selective 5,6-*O*-deacetonation afforded β-(1→3)-linked disaccharide **7** as crystals in high yield (81% over the two steps, Scheme 2).



Scheme 1. Keys: (a) (i) PhCOCl, pyridine and toluene, 70 °C, 8 h; (ii) 3:1 (v/v) THF–CH_3OH, 1.5 N NH_3, rt, 12 h; (iii) CH_2Cl_2, CCl_3CN and K_2CO_3, rt, 24 h. (b) (i) AllBr, NaH and DMF, rt, 2 h; (ii) 90% HOAc, 40 °C, 24 h. (c) (i) AllBr, NaH and DMF, rt, 2 h; (ii) 80% HOAc, reflux, 4 h; (iii) Ac_2O–Pyridine, rt, 2 h; (iv) 3:1 (v/v) THF–CH_3OH, 1.5 N NH_3, rt, 3 h; (v) CH_2Cl_2, CCl_3CN and K_2CO_3, rt, 24 h.

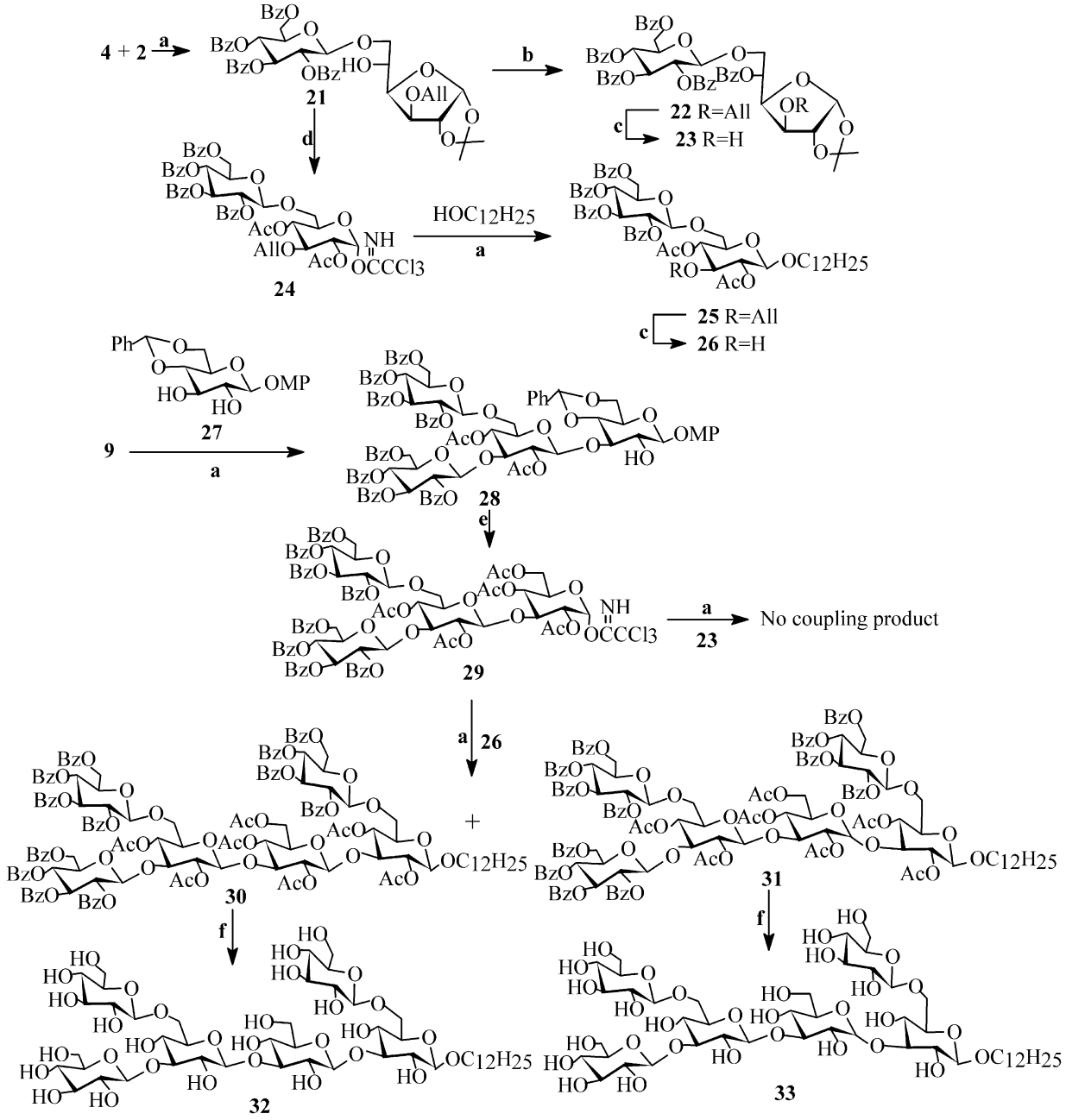
Condensation of **7** with **2** catalyzed by TMSOTf, regio- and stereoselectively gave one of the key intermediates: the 3,6-branched trisaccharides **8** in excellent yield (90%). Removal of the 1,2-*O*-isopropylidene of **8** in 80% HOAc followed by acetylation with acetic anhydride in pyridine, selective 1-*O*-deacetylation with ammonia in THF–CH_3OH, and subsequent treatment with trichloroacetonitrile in the presence of K_2CO_3 afforded the trisaccharide glycosyl donor **9** in good yield (71% over the four steps). Using the same procedure as described for the preparation of **8**, another key trisaccharide **12** was obtained from compounds **5**, **3**, and **2**. Acetylation of **12** with acetic anhydride in pyridine followed by deallylation with $PdCl_2$ in CH_3OH–CH_2Cl_2 afforded the trisaccharide glycosyl acceptor **13** in high yield (85%). Under the same conditions as described for the synthesis of **9** from **8**, compound **14** was obtained in good yield (71% over the four steps) from **12**. Coupling of **14** with $C_{12}H_{25}OH$ followed by deallylation afforded another trisaccharide glycosyl acceptor **16** in good yield (67% over the two steps). Coupling of the trisaccharide glycosyl donor **9** with either trisaccharide glycosyl acceptor **13** or **16**, catalyzed by TMSOTf in CH_2Cl_2, did not afford the expected β-linked haxasaccharides, but gave the pure α-linked haxasaccharides **17** and **19**, respectively, in excellent yields (86% for **17**, 84% for **19**). In the synthesis, the coupling of **9** with **13** gave an orthoester intermediate **17′** that was isolated and well identified, and could be transformed to **17** in the presence of catalytic TMSOTf. Deisopropylidenation of **17** in 80% HOAc, followed by deacylation in an ammonia-saturated solution in 1:1 CH_2Cl_2–CH_3OH, furnished the free hexasaccharide **18** as an amorphous white solid in 92% yield (over the two steps), and deacylation of **19** gave **20** as an amorphous white solid in 95% yield.

During our research, we found that the stereo-selectivity for the formation of (1→3) linked glucosyl bonds from the donor with C2 ester capable of neighboring group participation is influenced by the structure of both the glycosyl acceptors and glycosyl donors and some of these research results have been published recently.[11] For the synthesis of fully β-linked oligosaccharides, 4,6-*O*-benzylidene-β-D-glucopyranose was used as the acceptor since its derivatives often give the β-(1→3) linked glucosyl bonds exclusively as reported.[12] Thus condensation of **2** with **4**, catalyzed by TMSOTf, regioselectively gave the key disaccharide **21** in excellent yield



Scheme 2. Keys: (a) TMSOTf, 4 Å MS. CH_2Cl_2, rt, 3 h. (b) 90% HOAc, 40 °C, 24 h. (c) (i) 80% HOAc, reflux, 5 h; (ii) Ac_2O–Pyridine, rt, 2 h; (iii) THF–CH_3OH, 1.5 N NH_3, rt, 3 h; (iv) CH_2Cl_2, CCl_3CN and K_2CO_3, rt, 24 h. (d) (i) Ac_2O–Pyridine, rt, 2 h; (ii) $PdCl_2$, CH_2Cl_2–CH_3OH, rt, 5 h. (e) $PdCl_2$ in CH_2Cl_2–CH_3OH, rt, 5 h. (f) (i) 80% HOAc, reflux, 6 h; (ii) CH_2Cl_2–CH_3OH saturated with ammonia, rt, 24 h. (g) TMSOTf, 4 Å MS, CH_2Cl_2, rt, 20 min. (h) TMSOTf, 4 Å MS, CH_2Cl_2, rt, 3 h. (m) CH_2Cl_2–CH_3OH saturated with ammonia, rt, 24 h.

(84%) (Scheme 3). The disaccharide glycosyl acceptor **23** was subsequently obtained by 5-*O*-benzoylation of **21** followed by 3-*O*-deallylation in 78% yield. Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-β-D-glucopyranoside (**26**) as another disaccharide glycosyl acceptor was prepared from condensation of **24** with lauryl alcohol followed by deallylation. Regio- and stereoselective coupling of **9** with 4-methoxyphenyl 4,6-*O*-benzylidene-β-D-glucopyranoside (**27**)[13] afforded the desired tetrasaccharide **28** (77% yield) which was then converted to the tetrasaccharide glycosyl donor **29** by removal of the 4,6-*O*-benzylidene of **28** in 90% HOAc followed by acetylation, demethoxyphenylation with $(NH_4)_2Ce(NO_3)_6$ in CH_3CN-H_2O,[14] and subsequent trichloroacetimidation in 71% yield (over the four steps). However, coupling of **29** with **23**, catalyzed by TMSOTf in CH_2Cl_2, gave nothing except the decomposed product of glycosyl donor **29** and the unchanged glycosyl acceptor **23**. Condensation of **29** with **26** afforded a mixture of the β-(1→6)-branched β-(1→3)-linked glucohexatose **30** (38% yield) and its isomer containing an α-(1→3) linked bond **31** (16% yield). At the initial stage of the coupling, an orthoester intermediate **30′** was obtained and could be isolated. With addition of the extra catalyst TMSOTf or elongation of the reaction time, **30′** was transformed to a mixture of **30**



Scheme 3. Keys: (a) TMSOTf, 4 Å MS, CH_2Cl_2, rt, 3 h. (b) PhCOCl, pyridine, rt, 2 h. (c) $PdCl_2$ in CH_2Cl_2–CH_3OH, rt, 3 h. (d) (i) 80% HOAc, reflux, 5 h; (ii) Ac_2O–Pyridine, rt, 2 h; (iii) THF–CH_3OH, 1.5 N NH_3, rt, 3 h; (iv) CH_2Cl_2, CCl_3CN and K_2CO_3, rt, 24 h. (e) (i) 90% HOAc, 40 °C, 24 h; (ii) Ac_2O–Pyridine, rt, 2 h; (iii) $(NH_4)_2Ce(NO_3)_6$ in CH_3CN–H_2O, rt, 0.5 h; (iv) CH_2Cl_2, CCl_3CN and K_2CO_3, rt, 24 h. (f) CH_2Cl_2–CH_3OH saturated with ammonia, rt, 24 h.

and **31**. It seemed that transformation of the orthoester **30′** to the corresponding oligosaccharides **31** and **32** went through two different paths as indicated in Scheme 4. Path 1 (→**30**) was the normal rearrangement leading to trans glycosylation, while path 2 (→**31**) was the unusual one caused by C1-O1 breaking of the orthoester.[11] Finally, compounds **32** and **33** were obtained by deprotection of **30** and **31**, respectively.

Bioassay showed that in combination with the chemotherapeutic agent cyclophospamide (CPA), the hexaose **18** at a dose of 0.5–1 mg/kg subatantially increased the inhibition of CPA to S_{180}, but decreased the toxicity caused by CPA as indicated from the amount of nucleated cell in bone marrow (Table 1).

Inhibition of U_{14} noumenal tumor by the synthetic olgosaccharides was also investigated indicating that the allyl heptaoside, a fully β-linked lentinan repeating unit,[13] and lauryl hexaoside **20** were potential therapeutic agents for cancer treatment (Table 2).

Now in our laboratory, a lot of derivatives of the (1→6)-branched (1→3)-linked glucohexaoses are in preparation, and interesting results about the structure–activity relationship of the newly discovered biologically active oligosaccharides including **32** and **33** will be reported in due course.

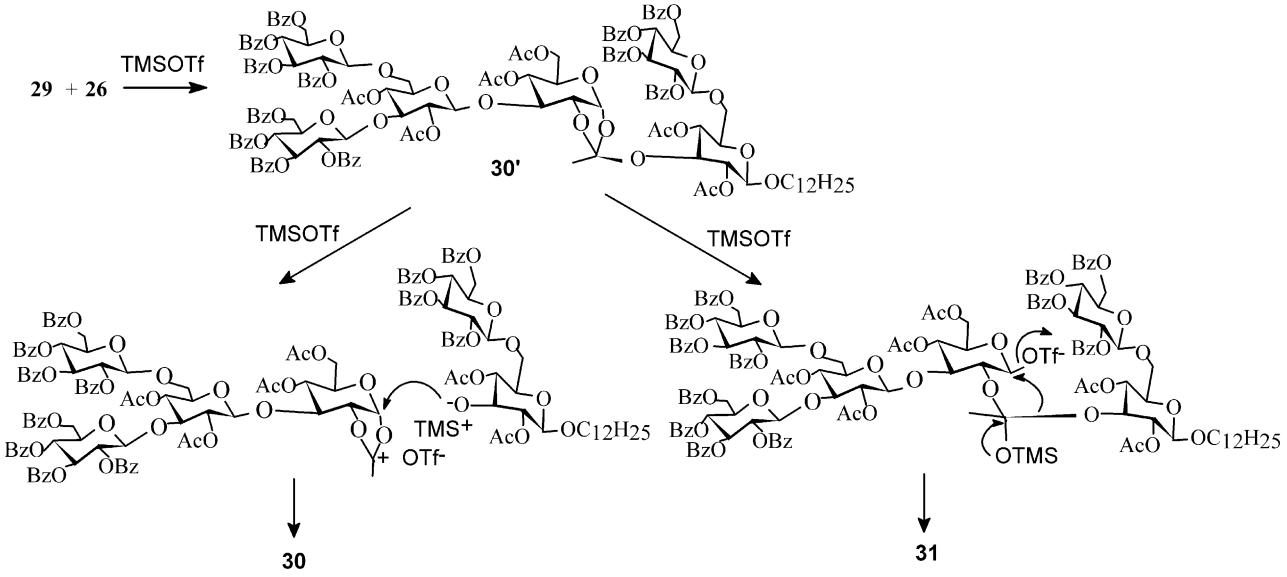
Table 2. Inhibition of U_{14} tumor by **18**, **20**, allyl heptaoside, and CPA

Groups	Weight (g)	Quotient of noumenal tumor (%)	Inhibition (%)
U_{14} cell line group	29.33±1.65	4.21±1.91	
Group 1: treatment with **18** (10 mg/kg)	27.40±1.90	2.63±0.90	29.41
Group 2: treatment with **20** (5 mg/kg)	27.45±2.67	1.54±0.56**	58.43
Group 3: treatment with allyl heptaoside (5 mg/kg)	28.10±1.79	1.51±0.41**	58.43
Group 4: treatment with CPA (70 mg/kg)	28.00±1.78	1.86±0.73*	39.22

Compared to U_{14} cell line group, *$p<0.05$ **$p<0.01$.

Experimental

Melting points were determined with a 'Mel-Temp' apparatus. Optical rotations were determined at 25 °C with digital polarimeter. The NMR spectra were recorded in $CDCl_3$ with TMS internal standard or D_2O with ethanol as standard on ARX 400 MHz. Mass spectra were recorded on an autospec mass spectrometer using ESI technique to introduce the sample. Elemental analyses were done on elemental analyzer model 1108 EA. Thin-layer chromatography (TLC) was performed on silica gel HF_{254} with detection by charring with 30% (v/



Scheme 4.

Table 1. Inhibition of S_{180} and effect on nucleated cell in bone marrow for the hexaose **18** and **18** + CPA

Groups	Weight (g)	Amount of nucleated cell (× 10^7)	Amount of tumor cell (× 10^7)
Control group	22.29±0.95	7.45±2.35###	
S_{180} Cell line group	22.00±1.00	7.65±3.05	2.94±0.54
Group 1: treatment with **18** (1 mg/kg)	21.86±0.90	6.70±1.95###∧	2.01±0.56*
Group 2: treatment with **18** (1 mg/kg) + CPA (50 mg/kg)	22.00±1.00	3.60±1.15#	1.53±0.85***
Group 3: treatment with **18** (0.5 mg/kg)	21.71±0.95	6.80±2.00###∧	2.38±0.61*
Group 4: treatment with **18** (0.5 mg/kg) + CPA (50 mg/kg)	22.00±0.82	3.55±1.55##	1.57±0.62**
Group 5 treatment with CPA (50 mg/kg)	21.86±0.69	1.50±0.45##	2.01±0.53*

Compared to group 5, #$p<0.05$. ##$p<0.01$. ###$p<0.001$. Comparison of a kind of drug to the combined two, ∧$p<0.05$. *Compared to the S_{180} cell line group, $p<0.05$. **$p<0.01$. ***$p<0.001$.

v) H_2SO_4 in MeOH or in some cases by a UV detector. Column chromatography was conducted by elution of a column (10×240 mm, 18×300 mm, 35×400 mm) of silica gel (100–200 mesh) with EtOAc–petroleum ether (60–90 °C) as the eluent. Solutions were concentrated at <60 °C under diminished pressure. Dry solvents were distilled over CaH_2 and stored over molecular sieves.

Bioassay for inhibition of S_{180}

Cyclophosphamide was purchased from Shanghai Hualian Pharmaceutical Co. Ltd. (permission No. Hu Medicines 95-012034). Animals: 50 Kunming male mice (weight 20±2 g, grade II) were obtained from the Experimental Animal Center, the Chinese Academy of Medicines. S_{180} cell line was provided by the Department of Tumorology, Institute of Pharmacy, the Chinese Academy of Medicines. The mice were randomly divided into seven groups according to weight, and into each of them was planted S_{180} cell line of ascites cancer 0.2 mL (amount of cell 7.9×10^6) in their euterocelia by intraperitoneal except for the control group mice. At 24 h after the planting, the mice were treated with the synthetic oligosaccharides or cyclophosphamide. The oligosaccharide was dissolved in saline at 0.1 mg/mL, given with a dose of 0.5 or 1 mg/kg/day to the mice within three consecutive days. Cyclophosphamide was dissolved in saline at 4 mg/mL, and given to the mice at a dose of 20 mg/kg by intraperitoneal at 24 h after the planting, and 30 mg/kg at 48 h after the planting. For inhibition of U_{14}, the same mice were used and divided into seven groups. Into each of the mice was planted U_{14} cell line 0.2 mL (amount of cell 4×10^6) by intraperitoneal. At 24 h after the planting, the mice were treated with the synthetic oligosaccharides or cyclophosphamide. The oligosaccharides **18** and **20** were dissolved in saline at 1 mg/mL, given with a dose of 10 mg/kg/d to the mice within ten consecutive days (0.2 mL/day, ip). Allyl heptaoside was dissolved in saline at 1 mg/mL, given with a dose of 5 mg/kg/day to the mice within ten consecutive days (0.1 mL/day ip). Cyclophosphamide was dissolved in saline at 6 mg/mL, and given to the mice at a dose of 30 mg/kg by intraperitoneal at 24 h after the planting, and 20 mg/kg at 72 h and 120 h after the planting, respectively.

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (2). BzCl (68 mL, 583 mmol) was added to a solution of D-glucose (**1**) (20 g, 111 mmol) in toluene (250 mL) and pyridine (47.3 mL, 585 mmol) over 1 h and the temperature was kept at 70 °C, and then the mixture was stirred at 70 °C for further 7 h. Filtration of pyridinum hydrochloride salt and concentration of the filtrate gave a residue which was directly dissolved in a 1.5 N solution of NH_3 in THF (350 mL) and CH_3OH (210 mL). The solution was kept at room temperature for 12 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under reduced pressure, and the residue was dissolved in a solution of CH_2Cl_2 (100 mL) and CCl_3CN (12 mL, 120 mmol) containing K_2CO_3 (30 g, 217 mmol). The reaction mixture was stirred for 24 h at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtrated, the solution was concentrated under reduced pressure, and the residue was decolorized by passing through a short silica-gel column with 3:1 petroleum ether–EtOAc as the eluent and 2,3,4,6-tetra-*O*-benzyol-α-D-glucopyranosyl trichloroacetimidate (**2**) (46 g, 56% for three steps) was crystallized from 3:1 petroleum ether–EtOAc as white crystals.[15]

3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-glucopyranose (4). To a solution of **3** (10.0 g, 38.4 mmol) in dry DMF (50 mL), AllBr (3.7 mL, 42.2 mmol) and NaH (3.0 g, 49% in oil, 61.4 mmol) were added under cooling with an ice bath. The mixture was stirred for 2 h at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was poured to water and extracted with CH_2Cl_2. The organic phase was concentrated, and the resulting residue was directly dissolved in 90% acetic acid solution (80 mL). The mixture was kept at 40 °C for 24 h and then concentrated to a residue under reduced pressure. The residue was purified by flash chromatography (2:1 petroleum ether–EtOAc) to give **4** (7.1 g, 71% for two steps) as syrup. $[\alpha]_D$ +14° (*c* 1.2, $CHCl_3$); ^{1}HNMR(400 MHz, $CDCl_3$) δ 5.92 (d, 1H, *J* = 3.8 Hz), 5.90 (m, 1H), 5.32 (dd, 1H, *J* = 1.3, 17.1 Hz), 5.23 (dd, 1H, *J* = 1.3 Hz, 10.4 Hz), 4.58 (d, 1H, *J* = 3.8 Hz), 4.22–4.03 (m, 5H), 3.84 (dd, 1H, *J* = 3.4, 11.4 Hz), 3.74 (dd, 1H, *J* = 5.5, 11.4 Hz). Anal. calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.81; H, 7.80.

3-*O*-Allyl-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (5). To a solution of **3** (50.0 g, 192 mmol) in dry DMF (160 mL), AllBr (18.6 mL, 211 mmol) and NaH (15.0 g, 49% in oil, 307 mmol) were added under cooling with an ice bath. The mixture was stirred for 2 h at rt, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was poured to water and extracted with CH_2Cl_2. The organic phase was concentrated, and the resulting residue was directly dissolved in 80% aqueous acetic acid solution (300 mL), and the mixture was heated under reflux for 4 h. The mixture was concentrated, and the residue was treated with acetic anhydride (250 mL) in pyridine (280 mL) for 2 h at rt. The acetylated sugar was dissolved in a 1.5 N solution of NH_3 in 3:1 THF–CH_3OH (300 mL), and the solution was kept at rt for 3 h, at the end of which time TLC (3:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was concentrated under reduced pressure, and the residue was dissolved in a solution of CH_2Cl_2 (200 mL) and CCl_3CN (39 mL, 384 mmol) containing K_2CO_3 (50 g, 362 mmol). The reaction mixture was stirred for 24 h at rt. After filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **5** (38.4 g, 54% for four steps) as a white crystals. Mp 71–73 °C; $[\alpha]_D$ +0.15° (*c* 1.5, $CHCl_3$); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 6.52 (d, 1H, *J* = 3.6 Hz), 5.80 (m, 1H), 5.24 (dd, 1H, *J* = 1.3, 17.1 Hz), 5.18–5.13 (m, 2H), 5.03 (dd, *J* = 3.6, 13.6 Hz), 4.24–4.18 (m, 2H), 4.13–4.08

(m, 3H), 3.97 (t, 1H, $J=9.6$ Hz), 2.10, 2.08, 2.07 (3 s, 9H). Anal. calcd for $C_{17}H_{22}NO_9Cl_3$: C, 55.13; H, 5.99. Found: C, 55.62; H, 5.90.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-1,2-*O*-isopropylidene-α-D-glucofuranose (7). To a stirred solution of **3** (10 g, 38 mmol) and **2** (26 g, 35 mmol) in CH_2Cl_2 (100 mL) was added TMSOTf (30 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the resulting residue was directly dissolved in 90% aqueous acetic acid solution (200 mL). The mixture was kept at 40 °C for 24 h and then concentrated to a residue under reduced pressure. The resulting residue was subjected to a short silica-gel column to give compound **7** (22.6 g, 81% for two steps). Mp 120–123 °C; $[\alpha]_D$ +14° (*c* 2.5, $CHCl_3$). ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.11–7.28 (m, 20H), 5.94 (t, 1H, $J=9.7$ Hz), 5.72 (t, 1H, $J=9.7$ Hz), 5.54 (dd, 1H, $J=7.9$, 9.7 Hz), 5.53 (d, 1H, $J=3.6$ Hz), 5.03 (d, 1H, $J=7.9$ Hz), 4.84 (dd, 1H, $J=3.6$, 11.9 Hz), 4.42 (dd, 1H, $J=4.3$, 11.9 Hz), 4.41(d, 1H, $J=2.6$ Hz), 4.24–4.23 (m, 2H), 4.16 (dd, 1H, $J=2.6$, 8.8 Hz), 4.02 (m, 1H), 3.83 (dd, 1H, $J=3.2$, 11.4 Hz), 3.67 (dd, 1H, $J=6.0$, 11.4 Hz), 1.44, 1.09 (2 s, 6H). Anal. calcd for $C_{43}H_{42}O_{15}$: C, 64.66; H, 5.30. Found: C, 64.94; H, 5.25.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-1,2-*O*-isopropylidene-α-D-glucofuranose (8). To a stirred solution of **7** (8 g, 10 mmol) and **2** (8 g, 10.8 mmol) in CH_2Cl_2 (60 mL) was added TMSOTf (30 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 1.5:1 petroleum ether–ethyl acetate as the eluent to give **8** (12.4 g, 90%). $[\alpha]_D$ +19.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06–7.28 (m, 40H), 5.88 (t, 1H, $J=9.7$ Hz), 5.87 (t, 1H, $J=9.7$ Hz), 5.69 (t, 1H, $J=9.7$ Hz), 5.64 (t, 1H, $J=9.7$ Hz), 5.53 (dd, 1H, $J=7.9$, 9.7 Hz), 5.43 (dd, 1H, $J=7.9$, 9.7 Hz), 5.41 (d, 1H, $J=3.5$ Hz), 4.96 (d, 1H, $J=7.9$ Hz), 4.93 (d, 1H, $J=7.9$ Hz), 4.71–4.67 (m, 2H), 4.48 (dd, 1H, $J=4.9$, 12.2 Hz), 4.35 (dd, 1H, $J=4.9$, 12.2 Hz), 4.34–3.65 (m, 8H), 1.26, 1.03 (2 s, 6H). Anal. calcd for $C_{77}H_{68}O_{24}$: C, 67.15; H, 4.98. Found: C, 66.89; H, 5.09.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (9). Compound **8** (10 g, 7.2 mmol) was added to 80% aqueous acetic acid solution (100 mL) and the mixture was heated under reflux for 5 h. The mixture was concentrated, and the residue was acetylated with acetic anhydride (20 mL) in pyridine (20 mL) for 2 h at rt. The resultant trisaccharide was dissolved in a 1.5 N solution of NH_3 in 3:1 THF–CH_3OH (100 mL), and the solution was kept at rt for 3 h. The solution was concentrated, the residue was dissolved in CH_2Cl_2 (50 mL). To the solution were added K_2CO_3 (2 g, 14.5 mmol) and CCl_3CN (1.4 mL, 14.4 mmol), and the mixture was stirred at rt for 24 h. Filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography to give **9** (8.0 g, 71% for four steps). $[\alpha]_D$ +23.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.07–7.19 (m, 40H), 6.21 (d, 1H, $J=3.6$), 5.91 (t, 1H, $J=9.6$ Hz), 5.85 (t, 1H, $J=9.6$ Hz), 5.62 (t, 1H, $J=9.6$ Hz), 5.61 (t, 1H, $J=9.6$ Hz), 5.46 (dd, 1H, $J=7.9$, 9.6 Hz), 5.42 (dd, 1H, $J=7.9$, 9.6 Hz), 4.97 (d, 1H, $J=7.9$ Hz), 4.96 (d, 1H, $J=7.9$ Hz), 4.85 (t, 1H, $J=9.5$ Hz), 4.67–4.59 (m, 3H), 4.50–4.37 (m, 2H), 4.19–4.02 (m, 4H), 3.91(dd, 1H), 3.69 (dd, 1H), 1.94, 1.78 (2 s, 6H). Anal. calcd for $C_{80}H_{68}NO_{26}Cl_3$: C, 61.37; H, 4.38. Found: C, 61.93; H, 4.51.

3-*O*-Allyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-1,2-*O*-isopropylidene-α-D-glucofuranose (11). To a stirred solution of **3** (10 g, 38.5 mmol) and **5** (14.1 g, 38.0 mmol) in CH_2Cl_2 (100 mL) was added TMSOTf (35 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the resulting residue was directly dissolved in 90% aqueous acetic acid solution (150 mL). The mixture was kept at 40 °C for 24 h and then concentrated to a residue under reduced pressure. The resulting residue was subjected to a short silica-gel column to give compound **11** (15 g, 72% for two steps) as a white crystals. Mp 91–93 °C; $[\alpha]_D$ +42 (*c* 1.8, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (d, 1H, $J=3.6$ Hz), 5.71 (m, 1H), 5.14 (dd, 1H), 5.08 (dd, 1H), 4.96 (t, 1H, $J=9.6$ Hz), 4.90 (dd, 1H, $J=7.9$, 9.4 Hz), 4.53 (d, 1H, $J=7.9$ Hz), 4.30 (d, 1H), 4.22 (d, 1H), 4.12–4.00 (m, 5H), 3.87 (m, 1H), 3.77 (dd, 1H), 3.60–3.58 (m, 2H), 3.54 (t, 1H, $J=9.4$ Hz), 2.05, 2.03, 2.02 (3 s, 9H), 1.42, 1.25 (2 s, 6H). Anal. calcd for $C_{24}H_{36}O_{14}$: C, 52.55; H, 6.61. Found: C, 52.81; H, 6.52.

3-*O*-Allyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-1,2-*O*-isopropylidene-α-D-glucofuranose (12). To a stirred solution of **11** (20 g, 36.5 mmol) and **2** (27.4 g, 37 mmol) in CH_2Cl_2 (150 mL) was added TMSOTf (40 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 1.5:1 petroleum ether–ethyl acetate as the eluent to give the trisaccharide **12** (37.0 g, 90%). $[\alpha]_D$ +16.1 (*c* 1.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02–7.27 (m, 20H), 5.89 (t, 1H, $J=9.6$ Hz), 5.76 (d, 1H, $J=3.7$ Hz), 5.75 (m, 1H), 5.69 (t, 1H, $J=9.6$ Hz), 5.55 (dd, 1H, $J=7.9$, 9.6 Hz), 5.20 (dd, 1H), 5.14 (dd, 1H), 5.01 (d, 1H, $J=7.9$ Hz), 5.00 (t, 1H, $J=9.7$ Hz), 4.89 (dd, 1H, $J=7.9$, 9.3 Hz), 4.67 (dd, 1H), 4.52 (d, 1H, $J=7.9$ Hz), 4.48 (dd, 1H), 4.33 (d, 1H), 4.23 (d, 1H), 4.17–4.01 (m, 8H), 3.80 (m, 1H), 3.60–3.54 (m, 2H), 2.08, 2.07, 2.02 (3 s, 9H), 1.32, 1.26 (2 s, 6H). Anal. calcd for $C_{58}H_{62}O_{23}$: C, 61.81; H, 5.54. Found: C, 61.46; H, 5.61.

2,4,6-Tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-5-*O*-acetyl-1,2-*O*-isopropylidene-α-D-glucofuranose (13). The compound **12** (25 g, 22.2 mmol) was acetylated with acetic anhydride (20 mL) in pyridine (20 mL) at rt for 2 h. The mixture was diluted with dichloromethane, washed with M HCl, water, and satd aq sodium bicarbonate subsequently.

The organic layer was combined, dried, and concentrated. The residue was dissolved in a solution of CH_3OH (250 mL) containing $PdCl_2$ (100 mg). The mixture was stirred for 5 h at rt, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated, and the residue was passed a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give **13** (21.3 g, 85%). $[\alpha]_D$ +26.6 (*c* 2.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07–7.27 (m, 20H), 5.87 (t, 1H, *J* = 9.5 Hz), 5.74 (t, 1H, *J* = 9.7 Hz), 5.73 (d, 1H, *J* = 3.5 Hz), 5.54 (dd, 1H, *J* = 7.9, 9.5 Hz), 5.16 (m, 1H), 4.99 (t, 1H, *J* = 9.6 Hz), 4.87 (d, 1H, *J* = 7.9 Hz), 4.81 (dd, 1H, *J* = 7.8, 9.3 Hz), 4.50 (d, 1H, *J* = 7.8 Hz), 4.43–4.39 (m, 2H), 4.30–4.27 (m, 2H), 4.22–4.06 (m, 5H), 3.81 (m, 1H), 3.67 (t, 1H, *J* = 9.6 Hz), 3.57 (m, 1H), 2.09, 2.08, 2.03, 1.73 (4 s, 12H), 1.37, 1.28 (2 s, 6H). Anal. calcd for $C_{57}H_{60}O_{24}$: C, 60.64; H, 5.36. Found: C, 60.98; H, 5.28.

3-*O*-Allyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (14). Compound **12** (14 g, 12.4 mmol) was added to 80% acetic acid solution (150 mL) and the mixture was heated under reflux for 5 h. The mixture was concentrated, and the residue was acetylated with acetic anhydride (20 mL) in pyridine (20 mL) for 2 h at rt. The mixture was diluted with dichloromethane, washed with M HCl, water, and satd aq sodium bicarbonate subsequently. The organic layer was combined, dried, and concentrated. The trisaccharide residue was dissolved in a 1.5 N solution of NH_3 in 3:1 THF–CH_3OH (150 mL), and the solution was kept at rt. After 3 h, the solution was concentrated, and the residue was dissolved in CH_2Cl_2 (80 mL). To the solution were added K_2CO_3 (5 g, 36.2 mmol) and CCl_3CN (2.0 mL, 20 mmol), and the mixture was stirred at rt for 24 h. Filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography to give the trisaccharide donor **14** (11.6 g, 71% for four steps). $[\alpha]_D$ +62.0 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.04–7.26 (m, 20H), 6.22 (d, 1H, *J* = 3.5 Hz), 5.86 (t, 1H, *J* = 9.6 Hz), 5.71 (m, 1H), 5.64 (t, 1H, *J* = 9.6 Hz), 5.47 (dd, 1H, *J* = 7.8, 9.6 Hz), 5.18 (dd, 1H), 5.06 (dd, 1H), 5.00 (t, 1H, *J* = 9.6 Hz), 4.94 (d, 1H, *J* = 7.8 Hz), 4.87 (t, 1H, *J* = 9.7 Hz), 4.86(t, 1H, *J* = 9.6 Hz), 4.80(dd, 1H, *J* = 7.9, 9.6 Hz), 4.62 (dd, 1H), 4.49 (d, 1H, *J* = 7.9 Hz), 4.48 (dd, 1H), 4.22 (dd, 1H), 4.15–4.01 (m, 6H), 3.93 (d, 1H), 3.69–3.51 (m, 3H), 2.06, 2.05, 2.04, 2.01, 1.99 (5 s, 15H). Anal. calcd for $C_{61}H_{62}NO_{25}Cl_3$: C, 55.69; H, 4.75. Found: C, 55.19; H, 4.58.

Lauryl 3-*O*-allyl-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (15). To a solution of **14** (4.5 g, 3.42 mmol) and lauryl alcohol (0.93 g, 5.0 mmol) in CH_2Cl_2 (50 mL) was added TMSOTf (30 μL) at rt. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated under reduced pressure to dryness. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **15** (3.66 g, 80%) as a syrup: $[\alpha]_D$ +32.1° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–7.27 (m, 20H), 5.88 (t, 1H, *J* = 9.8 Hz), 5.71 (m, 1H), 5.67 (t, 1H, *J* = 9.2 Hz), 5.50 (dd, 1H, *J* = 8.0, 9.6 Hz), 5.16 (dd, 1H), 5.11 (dd, 1H), 4,99 (t, 1H, *J* = 9.2 Hz), 4.94 (d, 1H, *J* = 8.0 Hz), 4.85 (d, 1H, *J* = 8.0 Hz), 4.84 (d, 1H, *J* = 8.0 Hz), 4.64 (m, 1H), 4.46 (m, 2H), 4.25 (dd, 1H, *J* = 12.4, 3.2 Hz), 4.15–3.43 (m, 11H), 3.01 (m, 1H), 2.07, 2.06, 2.05, 2.04, 1.95 (5 s, 15H), 1.30–1.18 (m, 20H), 0.88 (t, 3H). Anal. calcd for $C_{71}H_{86}O_{25}$: C, 63.67; H, 6.47. Found: C, 64.01; H, 6.20.

Lauryl 2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (16). Compound **15** (3.4 g, 2.54 mmol) was dissolved in a solution of CH_3OH (70 mL) and CH_2Cl_2 (10 mL). To the solution was added $PdCl_2$ (25 mg), and the mixture was stirred for 5 h at rt, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated, and the residue was passed through a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give **16** (2.77 g, 84%). $[\alpha]_D$ +19.3 (*c* 2.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.03–7.27 (m, 20H), 5.88 (t, 1H, *J* = 9.7 Hz), 5.67 (t, 1H, *J* = 9.6 Hz), 5.50 (dd, 1H, *J* = 7.9, 9.6 Hz), 4.93 (d, 1H, *J* = 7.9 Hz), 4.89 (t, 1H, *J* = 9.6 Hz), 4.87 (t, 1H, *J* = 9.7 Hz), 4.70–4.62 (m, 2H), 4.47 (dd, 1H), 4.45 (d, 1H, *J* = 7.9 Hz), 4.32 (dd, 1H), 4.16–4.14 (m, 2H), 4.03 (dd, 1H), 3.94 (d, 1H), 3.75 (t, 1H), 3.67–3.57 (m, 3H), 3.45 (m, 1H), 3.00 (m, 1H), 2.09, 2.08, 2.07, 2.06, 1.96 (5 s, 15H), 1.35–1.07 (m, 20H), 0.89 (t, 3H). Anal. calcd for $C_{68}H_{82}O_{25}$: C, 62.86; H, 6.36. Found: C, 62.41; H, 6.49.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-5-*O*-acetyl-1,2-*O*-isopropylidine-α-D-glucopyranoside (17). To a stirred solution of **9** (7.30 g, 4.66 mmol) and **13** (5.1 g, 4.5 mmol) in CH_2Cl_2 (60 mL) was added TMSOTf (30 μL) at rt. After 3 h, the mixture was neutralized with triethylamine and concentrated. The residue was purified on a silica gel column with 1.5:1 petroleum ether–EtOAc as the eluent to give **17** (9.8 g, 86%). $[\alpha]_D$ +18.7 (*c* 1.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.27 (m, 60H), 5.88, 5.87, 5.82, 5.75 (4 t, 4H, *J* = 9.5 Hz), 5.72 (d, 1H, *J* = 3.5 Hz), 5.68, 5.63 (2 t, 2H, *J* = 9.5 Hz,), 5.59, 5.45, 5.38 (3 dd, 3H, *J* = 7.9, 9.5 Hz,), 5.05 (m, 1H), 4.97, 4.92 (2 d, 2H, *J* = 7.9 Hz), 4.90 (d, 1H, *J* = 3.6 Hz), 4.84, 4.53 (2 d, 2H, *J* = 7.9 Hz), 2.00, 1.97, 1.84, 1.83, 1.82, 1.77 (6 s, 18H), 1.37, 1.35 (2 s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.01, 169.81, 169.22, 168.93, 168.78, 168.31, 165.70, 165.62, 165.52, 165.40, 165.32, 165.17, 165.02, 164.75, 164.61, 164.54, 111.92, 104.74 (C-1 for α bond, $J_{C\text{-}H}$ = 182.4 Hz), 100.69, 100.62, 100.48, 97.76 (4 C-1 for β bonds, $J_{C\text{-}H}$ = 161.3–163.7 Hz), 93.62 (C-1 for α bond, $J_{C\text{-}H}$ = 174.8 Hz), 81.60, 78.53, 74.48, 26.43, 25.93, 20.34, 20.21, 20.21, 20.21, 20.00, 20.00. Anal.

calcd for $C_{135}H_{126}O_{49}$: C, 64.03; H, 5.01. Found: C, 64.51; H, 4.93.

Orthoester 17′;. To a stirred solution of **9** (3.6 g, 2.3 mmol) and **13** (2.5 g, 2.2 mmol) in CH_2Cl_2 (80 mL) was added TMSOTf (20 μL) at rt. After 20 min the mixture was neutralized with triethylamine and concentrated. The residue was purified on a silica gel column with 1.5:1 petroleum ether–EtOAc as the eluent to give the product **17′** (4.2 g, 76%). $[\alpha]_D$ +25.9 (*c* 1.0, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.08, 169.65, 168.73, 168.50, 168.38, 121.77, 112.09, 104.62 (C-1 for glucofuranose α bond, $J_{C\text{-}H}$ = 182.4 Hz), 101.12, 100.59, 100.56, 98.00 (4 C-1 for β bonds, $J_{C\text{-}H}$ = 161.3–163.7 Hz), 96.32 (C-1 for α bond, $J_{C\text{-}H}$ = 174.8 Hz), 81.89, 78.75, 20.41, 20.22, 20.19, 20.11, 19.98. Anal. calcd for $C_{135}H_{126}O_{49}$: C, 64.03; H, 5.01. Found: C, 63.57; H, 4.87.

β-D-Glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-D-glucopyranose (18). Compound **17** (10 g, 3.95 mmol) was dissolved in 80% acetic acid solution (150 mL) and the mixture was heated under reflux for 5 h. The solution was concentrated, the residue was purified by chromatography with 1.5:1 petroleum ether–EtOAc as the eluent, and then the product was treated with a saturated solution of ammonia in CH_2Cl_2 (10 mL) and CH_3OH (120 mL) at rt. After 24 h, the reaction mixture was concentrated, and the residue was washed four times with CH_2Cl_2 to afford **18** as white solid (3.6 g, 92%). $[\alpha]_D$ −19.8 (*c* 0.1, H_2O); ^1H NMR (400 MHz, D_2O): δ 5.27 (d, 1H, *J* = 3.1 Hz), 4.74 (d, 1H, *J* = 6.8 Hz), 4.65 (d, 1H, *J* = 6.8 Hz), 4.64 (d, 1H, *J* = 6.8 Hz),4.44 (d, 1H, *J* = 6.8 Hz),4.43 (d, 1H, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, D_2O): δ 102.69, 102.69, 102.6, 102.60, 102.60 (5 C-1, $J_{C\text{-}H}$ = 163.9 Hz), 98.92 (C-1, $J_{C\text{-}H}$ = 173.9 Hz), 85.34, 84.87, 82.9, 81.96. Anal. calcd for $C_{36}H_{62}O_{31}$: C, 43.64; H, 6.30. Found: C, 42.92; H, 6.89. ESMS for $C_{36}H_{62}O_{31}$ (990.86): 989.84 $[M\text{-}1]^+$.

Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-α-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (19). To a stirred solution of **9** (2.30 g, 1.47 mmol) and **16** (1.75 g, 1.35 mmol) in CH_2Cl_2 (60 mL) was added TMSOTf (30 μL) at rt. After 3 h, the mixture was neutralized with triethylamine and concentrated. The residue was purified on a silica gel column with 1.5:1 petroleum ether–EtOAc as the eluent to give **19** (3.1 g, 84%). $[\alpha]_D$ +48.5 (*c* 1.7, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.47, 170.10, 169.62, 169.51, 169.50, 169.38, 168.76, 101.40, 101.28, 101.13, 100.65, 100.40, 93.16, 31.88–21.24, 20.75, 20.69, 20.65, 20.58, 20.48, 20.42, 14.09. Anal. calcd for $C_{146}H_{148}O_{50}$: C, 64.88; H, 5.52. Found: C, 64.43; H, 5.58.

Lauryl β-D-Glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-α-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (20). Compound **19** (1.6 g, 0.59 mmol) was dissolved in a saturated solution of ammonia in CH_2Cl_2 (10 mL) and CH_3OH (100 mL) at rt. After 24 h, the reaction mixture was concentrated, and the residue was washed four times with CH_2Cl_2 to afford **20** as white solid (650 mg, 95%).$[\alpha]_D$ −13.6 (*c* 0.1, H_2O); ^1H NMR (400 MHz, D_2O): δ 5.33 (d, 1H, *J* = 3.2 Hz), 4.73, 4.50, 4.46, 4.41, 4.21 (5 d, 5H, *J* = 7.5 Hz); 4.20–3.36 (m, 38H), 1.67 (m, 2H), 1.45–1.21 (m, 18H), 0.92 (t, 3H); ^{13}C NMR (100 MHz, D_2O): δ 105.22, 105.06, 105.06, 104.95, 104.66, 101.23, 86.51, 85.55, 84.31. Anal. calcd for $C_{48}H_{86}O_{31}$: C, 49.74; H, 7.48. Found: C, 49.02; H, 7.89. ESMS for $C_{48}H_{86}O_{31}$ (1159.18): 1158.17 $[M\text{-}1]^+$.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-3-*O*-allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (21). To a stirred solution of **2** (3.02 g, 4.1 mmol) and **4** (1.04 g, 4.0 mmol) in CH_2Cl_2 (50 mL) was added TMSOTf (20 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 3:1 petroleum ether–EtOAc as the eluent to give **21** (2.82 g, 84%) as a syrup: $[\alpha]_D$ +29.1° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07–7.27 (m, 20H), 5.92 (t, 1H, *J* = 9.8 Hz), 5.88 (m, 1H), 5.84 (d, 1H, *J* = 3.0 Hz), 5.69 (t, 1H, *J* = 9.8 Hz), 5.54 (dd, 1H, *J* = 8.0, 9.6 Hz), 5.28 (dd, 1H), 5.17 (dd, 1H), 4.94 (d, 1H, *J* = 8.0 Hz), 4.67 (dd, 1H, *J* = 12.4, 3.2 Hz), 4.50 (d, 1H, *J* = 3.0 Hz), 4.48 (dd, 1H, *J* = 12.4, 3.2 Hz), 4.12–3.86 (m, 8H), 1.39, 1.28 (2 s, 6H). Anal. calcd for $C_{46}H_{46}O_{15}$: C, 65.86; H, 5.53. Found: C, 65.39; H, 5.41.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-5-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (23). To a solution of **21** (4.8 g, 5.72 mmol) in pyridine (50 mL) was added BzCl (1.2 mL, 10 mmol) at rt. After 2 h, the mixture was poured to water and extracted with CH_2Cl_2. The organic phase was concentrated, and the resulting residue was treated with CH_3OH (100 mL) and $PdCl_2$ (15 mg) at rt for 4 h, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, and the filtrate was concentrated. The residue was passed a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give **23** (4.0 g, 78%) as a syrup; $[\alpha]_D$ +34.3° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.25 (m, 25H), 5.91 (d, 1H, *J* = 3.0 Hz), 5.87 (t, 1H, *J* = 9.8 Hz), 5.68 (t, 1H, *J* = 9.8 Hz), 5.56 (dd, 1H, *J* = 8.1, 9.6 Hz), 5.31 (m, 1H), 5.05 (d, 1H, *J* = 8.1 Hz), 4.62 (dd, 1H, *J* = 12.1, 3.3 Hz), 4.55 (d, 1H, *J* = 3.0 Hz), 4.46 (dd, 1H, *J* = 12.4, 3.3 Hz), 4.36–3.99 (m, 5H), 1.50, 1.31 (2 s, 6H). Anal. calcd for $C_{50}H_{46}O_{16}$: C, 66.51; H, 5.13. Found: C, 66.11; H, 5.07.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl trichloroacetimidate (24). Compound **21** (12 g, 14.3 mmol) was added to 80% aqueous acetic acid solution (150 mL) and the mixture was heated under reflux for 5 h. The mixture was concentrated and the residue was acetylated with acetic anhydride (20 mL) in pyridine (20 mL) for 2 h at rt. The resultant trisaccharide was dissolved in a 1.5 N

solution of NH_3 in 3:1 THF-CH_3OH (100 mL), and the solution was kept at rt. After 3 h, the solution was concentrated, and the residue was dissolved in CH_2Cl_2 (80 mL). To the solution were added K_2CO_3 (3,4 g, 25 mmol) and CCl_3CN (2 mL, 20 mmol), and the mixture was stirred at rt for 24 h. Filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography to give **24** (11 g, 75%) as a syrup: $[\alpha]_D$ +42.4° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.35 (s, 1H), 8.04–7.26 (m, 20H), 6.32 (d, 1H, *J* = 3.2 Hz), 5.86 (t, 1H, *J* = 9.6 Hz), 5.75 (m, 1H), 5.64 (t, 1H, *J* = 9.8 Hz), 5.48 (dd, 1H, *J* = 8.0, 9.6 Hz), 5.16 (dd, 1H), 5.10 (dd, 1H), 4.96 (d, 1H, *J* = 8.0 Hz), 4.86 (t, 1H, *J* = 9.8 Hz), 4.84 (dd, 1H, *J* = 10.4, 3.0 Hz), 4.61 (dd, 1H, *J* = 10.4, 3.2 Hz), 4.49 (dd, 1H, *J* = 9.6, 3.2 Hz), 4.17–3.90(m, 5H), 3.86 (t, 1H), 3.71 (dd, 1H), 2.04, 2.00 (2 s, 6H). Anal. calcd for $C_{49}H_{46}NO_{17}Cl_3$: C, 57.29; H, 4.51. Found: C, 57.71; H, 4.35.

Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-3-*O*-allyl-β-D-glucopyranoside (25). To a solution of **24** (2.5 g, 2.43 mmol) and lauryl alcohol (744 mg, 4.0 mmol) in CH_2Cl_2 (50 mL) was added TMSOTf (30 μL) at rt. The reaction mixture was stirred for 3 h, at the end of which time TLC indicated that the reaction was complete. Then the mixture was neutralized with triethylamine and concentrated under reduced pressure to dryness. Purification by column chromatography (3:1 petroleum ether–EtOAc) gave **25** as a syrup (2.35 g, 92%):$[\alpha]_D$ +33.7′ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.04–7.27 (m, 20H), 5.88 (t, 1H, *J* = 9.7 Hz), 5.71 (m, 1H), 5.66 (t, 1H, *J* = 9.6 Hz), 5.51 (dd, 1H, *J* = 8.0, 9.6 Hz), 5.16 (dd, 1H), 5.10 (dd, 1H), 4.95 (d, 1H, *J* = 8.0 Hz), 4.85 (t, 1H, *J* = 9.8 Hz), 4.78 (t, 1H, *J* = 9.8 Hz), 4.63 (dd, 1H, *J* = 10.4, 2.0 Hz), 4.47 (dd, 1H, *J* = 10.4, 3.2 Hz), 4.19 (d, 1H, *J* = 9.4 Hz), 4.15 (m, 1H), 4.01 (d, 2H), 3.88 (d, 1H), 3.65 (t, 1H), 3.60–3.40 (m, 3H), 3.05 (m, 1H), 2.04, 2.00 (2 s, 6H), 1.33–1.12 (m, 20H), 0.88 (t, 3H). Anal. calcd for $C_{59}H_{70}O_{17}$: C, 67.41; H, 6.71. Found: C, 67.02; H, 6.59.

Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-2,4-di-*O*-acetyl-β-D-glucopyranoside (26). To a solution of **25** (3.4 g, 3.23 mmol) in CH_3OH (50 mL) was added $PdCl_2$ (20 mg), and the mixture was stirred for 4 h at rt, at the end of which time TLC (2:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was filtered, the filtrate was concentrated, and the residue was passed a silica-gel column with 2:1 petroleum ether–EtOAc as the eluent to give **26** as a syrup (2.71 g, 83%): $[\alpha]_D$ +14.9° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.05–7.25 (m, 20H), 5.89 (t, 1H, *J* = 9.6 Hz), 5.68 (t, 1H, *J* = 9.6 Hz), 5.52 (dd, 1H, *J* = 7.8, 9.6 Hz), 4.95 (d, 1H, *J* = 7.8 Hz), 4.75–4.67 (m, 3H), 4.47 (dd, 1H, *J* = 4.9, 12.1 Hz), 4.24 (d, 1H, *J* = 7.8 Hz), 4.15 (m, 1H), 3.92 (dd, 1H), 3.72–3.50 (m, 4H), 3.12 (m, 1H), 2.07, 2.02 (2 s, 6H), 1.38–1.11 (m, 20H), 0.88 (t, 3H, *J* = 6.6 Hz). Anal. calcd for $C_{56}H_{66}O_{17}$: C, 66.52; H, 6.58. Found: C, 66.05; H, 6.74.

4-Methoxyphenyl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyransyl-(1→3)-4,6-*O*-benzylidene-β-D-glucopyranoside (28). To a stirred solution of **9** (3.6 g, 2.3 mmol) and **27**[13] (865 mg, 2.3 mmol) in CH_2Cl_2 (30 mL) was added TMSOTf (30 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 1.5:1 petroleum ether–EtOAc as the eluent to give **28** (3.15 g, 77%): $[\alpha]_D$ −10.3° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03–7.22 (m, 45H), 7.10, 6.83 (2 d, 4H, *J* = 9.1 Hz), 5.89 (t, 1H, *J* = 9.7 Hz), 5.73 (t, 1H, *J* = 9.4 Hz), 5.68–5.62 (m, 2H), 5.43–5.36 (m, 2H), 5.38 (s, 1H), 5.00 (t, 1H, *J* = 8.7 Hz), 4.89 (d, 1H, *J* = 7.6 Hz), 4.87 (dd, 1H, *J* = 7.8 Hz), 4.74 (d, 1H, *J* = 7.9 Hz), 4.60 (dd, 1H), 4.45 (m, 2H), 4.25–4.05 (m, 3H), 3.76 (s, 3H), 1.94, 1.91 (2 s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.88, 168.96, 166.15-164.80, 155.60, 151.26, 117.82, 114.68, 101.70, 101.10, 100.70, 100.38. Anal. calcd for $C_{98}H_{88}O_{32}$: C, 66.21; H, 4.99. Found: C, 66.64; H, 4.89.

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)-]2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (29). A solution of **28** (5 g, 2.81 mmol) in 90% acetic acid (80 mL) was kept at 40 °C for 24 h and then concentrated to a residue under reduced pressure. The residue was treated with pyridine (10 mL) and Ac_2O (10 mL) at rt for 2 h. This mixture was added to water and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4, and concentrated, the residue was dissolved in 4:1 CH_3CN–H_2O (40 mL). To this solution was added $(NH_4)_2Ce(NO_3)_6$ (2.72 g, 5.0 mmol), and the mixture was stirred for 30 min at rt, at the end of which time TLC (1:1 petroleum ether–EtOAc) indicated that the reaction was complete. The mixture was extracted with CH_2Cl_2, and washed with satd aq $NaHCO_3$. The organic layer was concentrated, the residue was dissolved in dichloromethane. To the solution were added K_2CO_3 (1.4 g, 10 mmol) and CCl_3CN (0.5 mL, 5 mmol), and the mixture was stirred at rt for 24 h. Filtering the mixture, the filtration and washings were concentrated, and the residue was subjected to column chromatography (1.5:1 petroleum ether–EtOAc) to give **29** (3.7 g, 71%): $[\alpha]_D$ +4.0° (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.15–7.24 (m, 40H), 6.38 (d, 1H, *J* = 3.5 Hz), 5.88 (t, 1H, *J* = 9.4 Hz), 5.87 (t, 1H, *J* = 9.4 Hz), 5.66 (t, 1H, *J* = 9.4 Hz), 5.64 (t, 1H, *J* = 9.3 Hz), 5.50 (dd, 1H, *J* = 7.8, 9.0 Hz), 5.37 (dd, 1H, *J* = 7.8, 9.0 Hz), 4.92–4.83 (m, 4H), 4.74–4.63 (m, 3H), 4.60–4.45 (m, 3H), 4.40 (d, 1H, *J* = 8.1 Hz), 4.16–3.56 (m, 10H), 2.08, 2.02, 1.86, 1.81, 1.74 (5 s, 15H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.77, 169.73, 169.71, 169.01, 168.09, 160.99, 101.32, 100.79, 100.66, 93.23, 20.72, 20.68, 20.60, 20.50, 20.32. Anal. calcd for $C_{92}H_{84}NO_{34}Cl_3$: C, 59.60; H, 4.57. Found: C, 59.09; H, 4.63.

Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-

benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (30) and Lauryl 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranosyl-(1→3)-2,4,6-tri-*O*-acetyl-α-D-glucopyranosyl-(1→3)-[2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-*O*-acetyl-β-D-glucopyranoside (31). To a stirred solution of **29** (3.6 g, 1.94 mmol) and **26** (1.82 g, 1.8 mmol) in CH_2Cl_2 (30 mL) was added TMSOTf (20 μL) at room temperature. After 3 h, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 1:1 petroleum ether–EtOAc as the eluent to give **30** (1.85 mg, 38%) and **31** (838 mg, 16%): For **30**: $[\alpha]_D$ +38° (*c* 1.0, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.35, 169.52, 169.38, 168.82, 168.63, 168.63, 168.28, 101.18, 100.18, 100.28, 100.28, 100.19, 100.19 (6 C-1, $J_{C\text{-}H}$ = 163.2-163.3 Hz), 78.45, 77.96, 77.94, 20.71, 20.65, 20.55, 20.47, 20.38, 20.30, 20.25. Anal. calcd for $C_{146}H_{148}O_{50}$: C, 64.88; H, 5.52. Found: C, 64.40; H, 5.65; For **31**: $[\alpha]_D$ +8.5° (*c* 1.0, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.52, 170.27, 169.67, 169.29, 169.06, 168.87, 167.88, 101.15, 101.08, 100.84, 100.54, 100.54, 95.19, 20.91, 20.80, 20.79, 20.65, 20.48, 40.30, 20.30. Anal. calcd for $C_{146}H_{148}O_{50}$: C, 64.88; H, 5.52. Found: C, 64.56; H, 5.47.

Orthoester 30′. To a stirred solution of **29** (1.30 g, 0.7 mmol) and **26** (0.71 g, 0.7 mmol) in CH_2Cl_2 (20 mL) was added TMSOTf (10 μL) at room temperature. After 20 min, triethylamine was added to the solution to quench the reaction. The solution was concentrated, the residue was subjected to column chromatography with 1.5:1 petroleum ether–EtOAc as the eluent to give **30′** (1.32 g, 71%): $[\alpha]_D$ +17.6° (*c* 1.0, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.53, 169.57, 169.46, 169.46, 169.08, 167.92, 121.90, 101.20, 101.04, 100.49, 100.38, 100.28, 96.60. Anal. calcd for $C_{146}H_{148}O_{50}$: C, 64.88; H, 5.52. Found: C, 65.22; H, 5.67.

Lauryl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl(1→6)]-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (32). Compound **30** (1.2 g, 0.44 mmol) was dissolved in a saturated solution of NH_3 in CH_2Cl_2 (5 mL) and CH_3OH (50 mL) at rt. After 24 h, the reaction mixture was concentrated, and the residue was washed four times with CH_2Cl_2 to afford **32** as white solid (470 mg, 92%): $[\alpha]_D$ −8.4° (*c* 1.0, H_2O); ^1H NMR (400 MHz, D_2O): δ 4.39–3.98 (m, 6H), 3.85–3.09 (m, 38H), 1.51 (m, 2H), 1.22–1.12 (m, 18H,), 0.76 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 105.52, 105.33, 105.23, 105.18, 105.14, 104.94 (6 C-1), 88.16, 87.42, 86.81. Anal. calcd for $C_{48}H_{86}O_{31}$: C, 49.74; H, 7.48. Found: C, 49.07; H, 7.76. ESMS for $C_{48}H_{86}O_{31}$ (1159.18): 1158.16 $[M\text{-}1]^+$.

Lauryl β-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl (1→6)]-β-D-glucopyranosyl-(1→3)-α-D-glucopyranosyl-(1→3)-[β-D-glucopyranosyl-(1→6)]-β-D-glucopyranoside (33). Compound **31** (470 mg, 0.17 mmol) was dissolved in a solution of CH_2Cl_2 (5 mL) and CH_3OH (50 mL) saturated with NH_3 at rt. After 24 h, the reaction mixture was concentrated, and the residue was washed four times with CH_2Cl_2 to afford **33** as white solid (183 mg, 93%). $[\alpha]_D$ −12.1° (*c* 1.0, H_2O); ^{13}C NMR (100 MHz, $CDCl_3$): δ 102.70, 102.68, 102.68, 102.65, 102.65 (5 C-1, $J_{C\text{-}H}$ = 164.2-164.9 Hz), 99.15 (C-1, $J_{C\text{-}H}$ = 175.44 Hz), 84.24, 83.47, 82.23. Anal. calcd for $C_{48}H_{86}O_{31}$: C, 49.74; H, 7.48. Found: C, 49.17; H, 7.89. ESMS for $C_{48}H_{86}O_{31}$ (1159.18): 1158.17 $[M\text{-}1]^+$.

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