JOC Article

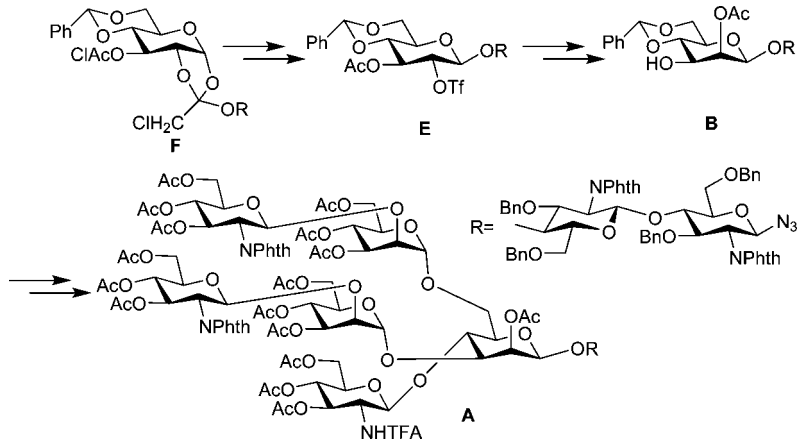
Convenient Synthesis of an *N*-Glycan Octasaccharide of the Bisecting Type

Guangfa Wang, Wei Zhang, Zhichao Lu, Peng Wang, Xiuli Zhang, and Yingxia Li*

Key Laboratory of Marine Drugs, The Ministry of Education of China, School of Medicine and Pharmacy, Ocean University of China, Qingdao 266003, China

liyx417@ouc.edu.cn

Received January 5, 2009



Convenient synthesis of an *N*-glycan octasaccharide (**A**) of the bisecting type was described. The stable and easily prepared orthoester **F**, 3″-*O*-chloroacetyl-4″,6″-*O*-benzylidene-α-D-glucopyranose 1″,2″-(chloromethyl 3′,6′-di-*O*-benzyl-2′-deoxy-2′-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide-4′-yl orthoacetate), was designed as the key intermediate with two advantages: (1) distinguishing OH-2″ from OH-3″ in β-D-glucopyranoside to construct the central β-D-mannopyranoside by inverting the configuration of OH-2″ in β-D-glucopyranoside and (2) distinguishing OH-4″ and OH-6″ from OH-3″ in the β-D-mannopyranoside to introduce the bisecting GlcNAc residue.

Introduction

Glycoproteins with *N*-glycans found on cell surfaces and in blood serum play important roles in many key biological events. It is widely recognized that the functions of glycoproteins are influenced by their *N*-glycans.[1] Among the great variety of their functions, tumor metastasis is a focal point in scientific research nowadays. β-1→6 GlcNAc branching, produced by GnT-V, plays a major role in cancer invasion and metastasis by stabilizing the proteases and angiogenic releasing factor.[2] While bisected *N*-glycans, which are the product of GnT-III, have unique function in terms of the suppression of cancer metastasis,[3] they also have been shown to be involved in cell development[4] and function of receptors.[5] Therefore, the bisected *N*-glycans are of great significance with regard to cancer therapy. Because of difficulties in obtaining homogeneous glycans from natural sources, we decided to synthesize octasaccharide **A**, which is a part of the structure of a bisected *N*-glycan and

(1) (a) Dwek, R. A. *Science* **1995**, *269*, 1234. (b) Dwek, R. A. *Chem. Rev.* **1996**, *96*, 683. (c) Van Dijk, W.; Van der Stelt, M. E.; Salera, A.; Dente, L. *Eur. J. Cell Biol.* **1991**, *55*, 143. (d) Shevinsky, L. H.; Knowles, B. B.; Damjanov, I.; Solter, D. *Cell* **1982**, *30*, 697. (e) Feizi, T. *Nature* **1985**, *314*, 53.

(2) (a) Dennis, J. W.; Laferte, S.; Waghorne, C.; Breitman, M. L.; Kerbel, R. S. *Science* **1987**, *236*, 582. (b) Zhao, Y.; Nakagawa, T.; Itoh, S.; Inamori, K.; Isaji, T.; Kariya, Y.; Kondo, A.; Miyoshi, E.; Miyazaki, K.; Kawasaki, N.; Taniguchi, N.; Gu, J. *J. Biol. Chem.* **2006**, *281*, 32122.

(3) (a) Narasimhan, S. *J. Biol. Chem.* **1982**, *257*, 10235. (b) Iijima, J.; Zhao, Y.; Isaji, T.; Kameyama, A.; Nakaya, S.; Wang, X. C.; Ihara, H.; Cheng, X.; Nakagawa, T.; Miyoshi, E.; Kondo, A.; Narimatsu, H.; Taniguchi, N.; Gu, J. *J. Biol. Chem.* **2006**, *281*, 13038. (c) Zhao, Y.; Sato, Y.; Isaji, T.; Fukuda, T.; Matsumoto, A.; Miyoshi, E.; Gu, J.; Taniguchi, N. *FEBS J.* **2008**, *275*, 1939.

(4) Yoshimura, M.; Ihara, Y.; Nishiura, T.; Okajima, Y.; Ogawa, M.; Yoshida, H.; Suzuki, M.; Yamamura, K. I.; Kanakura, Y.; Matsuzawa, Y.; Taniguchi, N. *Biochem. J.* **1998**, *331*, 733.

(5) Ihara, Y.; Sakamoto, Y.; Mihara, M.; Shimizu, K.; Taniguchi, N. *J. Biol. Chem.* **1997**, *272*, 9629.

10.1021/jo900016j CCC: $40.75
Published on Web 02/26/2009

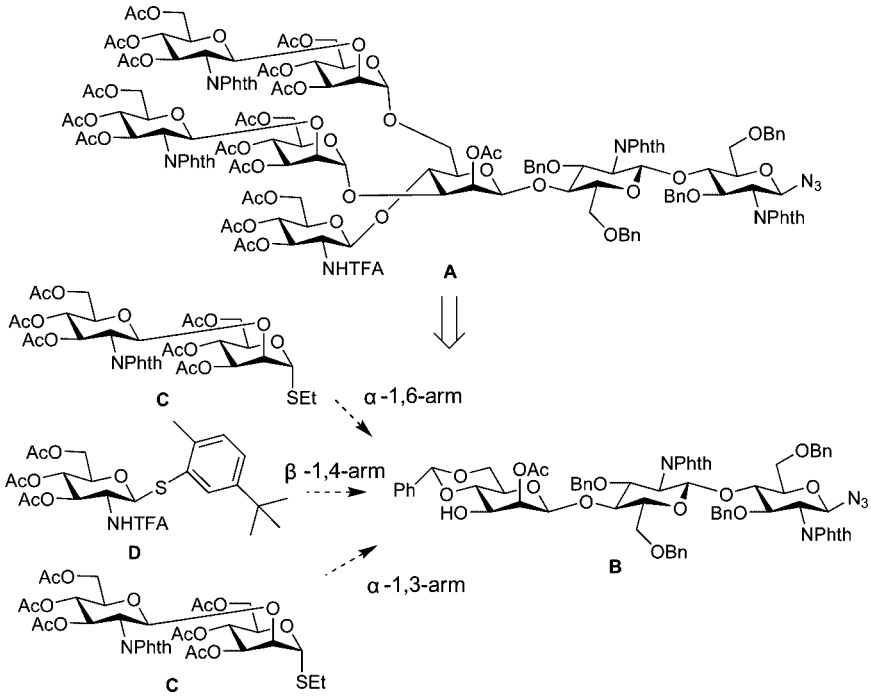


FIGURE 1. Retrosynthesis of octasaccharide **A**.

suitable for enzymatic elongation and coupling to proteins for function study.

However, the synthesis of bisected *N*-glycans is very difficult due to the sterically crowded β-mannosyl center. Only a few groups have developed synthetic approaches to this important class of compounds.[6] Among them, Unverzagt's strategy for introduction of the bisecting GlcNAc residue has been proven the most effective.[6] In fact, the construction of the central β-D-mannosidic linkage with proper protection is the other choke point for the synthesis of bisected *N*-glycans. As we know, methods for the construction of β-D-mannosidic linkage include the intramolecular aglycon delivery,[7] direct β-D-mannoside coupling protocol,[8] and epimerization of β-D-glucopyranosides at the C-2 position by S_N2 inversion[9] or by sequential oxidation/reduction routes.[10] Some of these methods have been applied to the synthesis of *N*-glycan oligosaccharides. However, the majority of these approaches need some precious glycosyl donors or tedious protection−deprotection manipulation. In this paper, we have described a convenient procedure to construct the central β-D-mannoside according to Ramström's new finding on the inversion of carbohydrate hydroxyl groups.[11] In the procedure, the designed protecting groups were exactly available for the formation of bisected *N*-glycans, and all the fragments involved were easily prepared. On the basis of this procedure, octasaccharide **A**, an *N*-glycan oligosaccharide of the bisecting type, was synthesized conveniently.

Results and Discussion

For retrosynthesis of octasaccharide **A** (Figure 1), it was disconnected to core trisaccharide **B**, disaccharide donor **C**, and monosaccharide donor **D** according to Unverzagt's strategy for introduction of the bisecting GlcNAc residue.[6] α1,3-Arm was first installed followed by the introduction of the bisecting GlcNAc residue, and α1,6-arm was installed in the final glycosylation step. To ensure the introduction sequence, the central β-mannoside in building block **B** was designed as depicted in Figure 1. The 4,6-*O*-benzylidene would be removed at a desired stage for the introduction of bisecting GlcNAc via regioselective protection of OH-6. The new structure **B** would permit good coupling to various building blocks for the synthesis of bisected *N*-glycans.

The retrosynthesis of fragment **B** is depicted in Figure 2. The intermediate **E** was designed to prepare **B** according to Ramström's new finding,[11] in which the OH-3″ was acetylated as the neighboring ester group to the triflate. The transformation from **E** into **B** was easily performed under the modified Lattrell−Dax reaction conditions by the inversion of OH-23. However, distinguishing OH-3″ from OH-2″ with two different ester groups in the β-D-glucopyranoside seemed to be a challenge. In fact, the regioselective protection of one of the two similar secondary 2,3-dihydroxyl groups of β-D-glucopyranoside was difficult to achieve in oligosaccharide synthesis.[12]

(6) (a) Eller, S.; Schuberth, R.; Gundel, G.; Seifert, J.; Unverzagt, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 4173. (b) Schuberth, R.; Unverzagt, C. *Tetrahedron Lett.* **2005**, *46*, 4201. (c) Weiss, H.; Unverzagt, C. *Angew. Chem., Int. Ed.* **2003**, *42*, 4261. (d) Unverzagt, C.; Seifert, J. *Tetrahedron Lett.* **2000**, *41*, 4549.

(7) (a) Barresi, F.; Hindsgaul, O. *Can. J. Chem.* **1994**, *72*, 1447. (b) Stork, G.; La Clair, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 247. (c) Ito, Y.; Ohnishi, Y.; Ogawa, T.; Nakahara, Y. *Synlett* **1998**, 1102.

(8) (a) Dudkin, V. Y.; Crich, D. *Tetrahedron Lett.* **2003**, *44*, 1787. (b) Dudkin, V. Y.; Miller, J. S.; Danishefsky, S. J. *Tetrahedron Lett.* **2003**, *44*, 1791. (c) Dudkin, V. Y.; Miller, J. S.; Danishefsky, S. J. *J. Am. Chem. Soc.* **2004**, *126*, 736. (d) Mandai, H.; Mukaiyama, T. *Chem. Lett.* **2005**, *34*, 702. (e) Tanaka, S.; Takashina, M.; Tokimoto, H.; Fujimoto, Y.; Tanaka, K.; Fukase, K. *Synlett* **2005**, *15*, 2325.

(9) (a) Matsuo, I.; Isomura, M.; Walton, R.; Ajisawa, K. *Tetrahedron Lett.* **1996**, *37*, 8795. (b) Li, B.; Zeng, Y.; Hauser, S.; Song, H.; Wang, L. X. *J. Am. Chem. Soc.* **2005**, *127*, 9692.

(10) (a) Shaban, M. A.; Jeanloz, R. W. *Carbohydr. Res.* **1976**, *52*, 115. (b) Warren, C. D.; Auge, C.; Laver, M. L.; Suzuki, S.; Power, D.; Jeanloz, R. W. *Carbohydr. Res.* **1980**, *82*, 71. (c) Kerekgyarto, J.; Van der Ven, J. G.; Kamerling, J. P.; Liptak, A.; Vliegenthart, J. F. *Carbohydr. Res.* **1993**, *238*, 135. (d) Hiro, S.; Usuki, Y.; Iio, H. *Carbohydr. Res.* **2006**, *341*, 1796.

(11) (a) Dong, H.; Pei, Z.; Angelin, M.; Bystroem, S.; Ramström, O. *J. Org. Chem.* **2007**, *72*, 3694. (b) Dong, H.; Pei, Z.; Ramström, O. *J. Org. Chem.* **2006**, *71*, 3306.

(12) Varki, A. *Glycobiology* **1993**, *3*, 97.

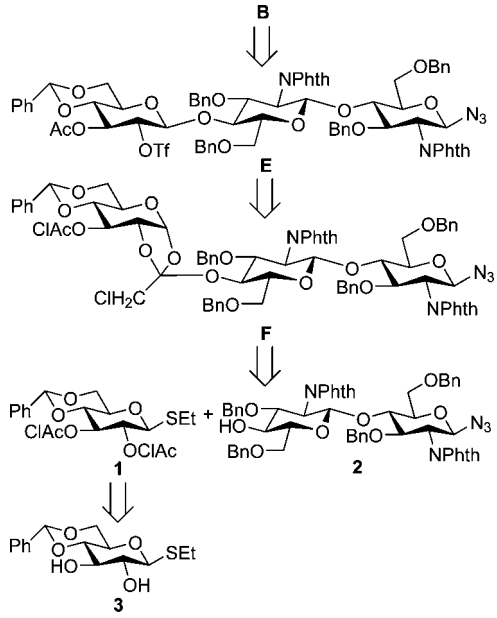
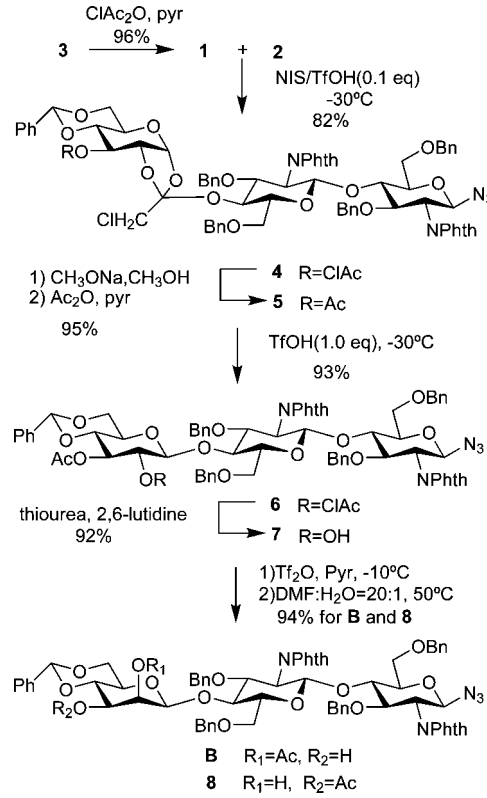


FIGURE 2. Retrosynthesis of trisaccharide **B**.

Herein, we explored a new strategy. The key intermediate orthoester **F**, 3″-*O*-chloroacetyl-4″,6″-*O*-benzylidene-α-D-glucopyranose 1″,2″-(chloromethyl 3′,6′-di-*O*-benzyl-2′-deoxy-2′-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide-4′-yl orthoacetate) was designed on the basis of the following considerations: (1) Distinguishing OH-3″ from OH-2″ with two different ester groups in the β-D-glucopyranoside could be easily achieved by switching chloroacetyl in **F** to the acetyl group before 1, 2-orthoester was transformed into the corresponding 3-*O*-acetyl-2-*O*-chloroacetyl-β-D-glucopyranoside.[13] (2) The cyclic 4″,6″-*O*-benzylidene protecting group was selected to distinguish OH-4″ and OH-6″ from OH-3″ for the introduction of three substituents to the β-mannosyl center. (3) The formation of orthoester **F** depended critically on the presence of the cyclic 4,6-*O*-benzylidene protecting groups which stabilized the intermediate oxycarbenium ion.[14] (4) The preparation of orthoester **F** could be conveniently carried out by designing ethyl 4,6-*O*-benzylidene-2,3-di-*O*-chloroacetyl-1-thio-β-D-glucopyranoside **1** as the glycosyl donor, which could be easily synthesized from the known compound **3**.[15]

The preparation of the core trisaccharide **B** started from compound **3**[15] according to the above retrosynthetic analysis (Scheme 1). The unmasked hydroxyls of compound **3** were protected with a chloroacetyl group to afford donor **1**, which was treated with disaccharide **2**[16] in the presence of NIS/TfOH (0.1 equiv), giving the desired orthoester **4** (key intermediate **F**) in 82% yield. The chloroacetyl ester of **4** was removed by using NaOMe, and then the unmasked hydroxyl was acetylated to afford orthoester **5** (95%). In the following attempt to transform orthoester **5** into the corresponding trisaccharide **6**, we found that 4,6-*O*-benzylidene-protected-orthoester **5** was very

SCHEME 1. Synthesis of Trisaccharide B



stable even in the presence of 0.5 equiv of TMSOTf at −30 °C. Then we tried TfOH as the promoter, as a result, part of the orthoester **5** was observed to be transformed into trisaccharide **6** in the presence of 0.5 equiv of TfOH at −30 °C after 1 h. When more TfOH was used (1.0 equiv), trisaccharide **6** was afforded in 93% yield. After selective removal of the chloroacetyl group in **6**,[17] the free hydroxyl group of **7** was inverted in a two-step procedure to afford the desired β-mannoside.[11] First, the 2″-OH of **7** was converted to a good leaving group using triflic anhydride−pyridine and then was substituted by an intramolecular nucleophilic attack of the neighboring acetyl moiety. The S_N2 reaction proceeded smoothly by warming the solution of the triflate intermediate in H_2O/DMF (1:20) to 50 °C, providing the key fragment **B** and isomer **8** as a mixture in a very satisfying yield (94%). The ratio of **B** and **8** was 12.7:1 (determined by ^{1}H NMR analysis), and pure **B** was obtained after careful column chromatography separation. The anomeric configuration of **B** was unequivocally deduced from the singlet at 4.85 ppm corresponding to the β-mannosyl anomeric proton and the $J_{C1'',H1''} = 161.8$ Hz which is a typical range for β-D-mannopyranoside. By the strategy of formation rearrangement 4,6-*O*-benzylidene-protected-1,2-orthoester, the core trisaccharide **B** was synthesized conveniently (62% for 7 steps).

The synthesis of disaccharide **C** is summarized in Scheme 2; the OH-6 of monosaccharide **9**[18] was selectively acetylated to afford **10** (82%). The latter was then treated with donor **11**[19] in the presence of TMSOTf to afford disaccharide **12** (85%).

(13) (a) Ogawa, T.; Beppu, K.; Nakabayashi, S. *Carbohydr. Res.* **1981**, *93*, C6. (b) Urban, F. J.; Moore, B. S.; Breitenbach, R. *Tetrahedron Lett.* **1990**, *31*, 4421. (c) Wang, W.; Kong, F. *J. Org. Chem.* **1998**, *63*, 5744.

(14) Yu, H.; Ensley, H. E. *Tetrahedron Lett.* **2003**, *44*, 9363.

(15) (a) Hou, S. J.; Xu, P.; Zhou, L.; Yu, De Q.; Lei, P. S.; Zou, C. C. *Chin. Chem. Lett.* **2006**, *17*, 183. (b) Ennis, S. C.; Gridley, J. J.; Osborn, H. M. I.; Spackman, D. G. *Synlett* **2000**, *11*, 1593.

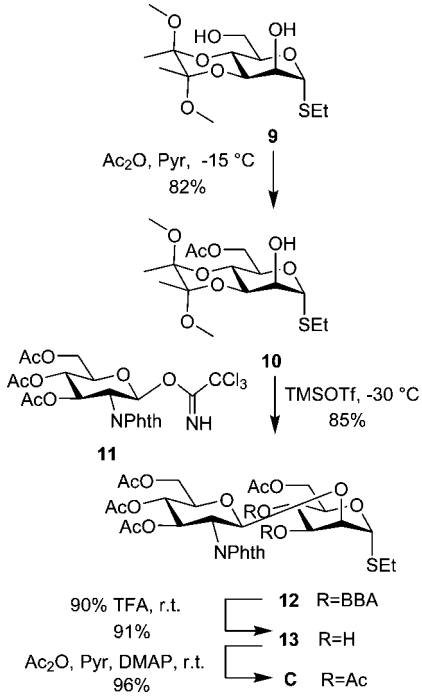
(16) (a) Unverzagt, C. *Chem. Eur. J.* **2003**, *9*, 1369. (b) Pratt, M. R.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2003**, *125*, 6149.

(17) Nicolaou, K. C.; Caulfield, T. J.; Kataoka, H.; Stylianides, N. A. *J. Am. Chem. Soc.* **1990**, *112*, 3693.

(18) Baeschlin, D. K.; Green, L. G.; Hahn, M. G.; Hinzen, B.; Ince, S. J.; Ley, S. V. *Tetrahedron: Asymmetry* **2000**, *11*, 173.

(19) (a) Macmillan, D.; Daines, A. M.; Bayrhuber, M.; Flitsch, S. L. *Org. Lett.* **2002**, *4*, 1467. (b) Grundler, G.; Schmidt, R. R. *Carbohydr. Res.* **1985**, *135*, 203.

SCHEME 2. Synthesis of Disaccharide Donor C



After cleavage of the biacetal function in **12** (91%), the unmasked hydroxyl was acetylated to afford disaccharide donor **C** in 96% yield.

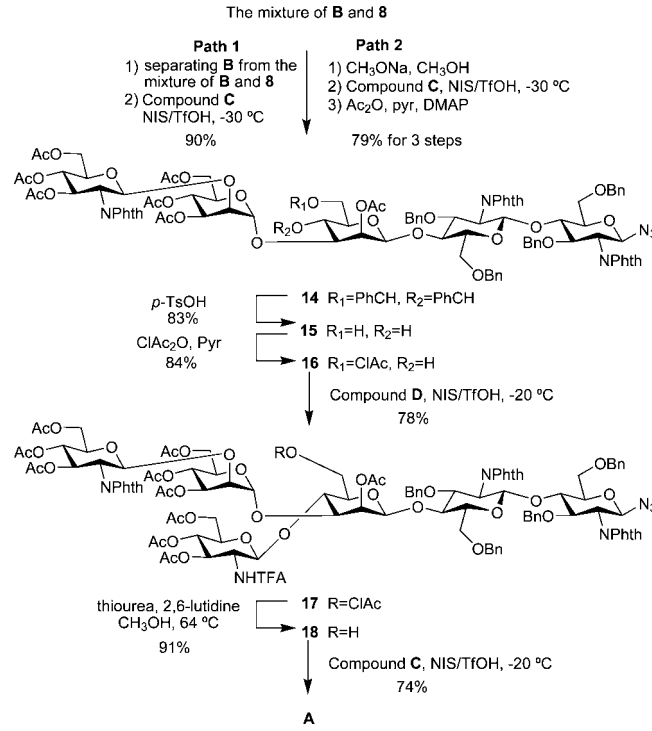
Monosaccharide **D** was prepared in five steps from commercially available glucosamine hydrochloride.[20]

With the core trisaccharide **B**, disaccharide donor **C** and donor **D** in hand, the synthesis of octasaccharide **A** was then carried out (Scheme 3).[6] Treating donor **C** with trisaccharide **B** was first performed to install the disaccharide residue on to the OH-3″of central β-mannoside in the presence of NIS/TfOH to afford pentasaccharide **14** in 90% yield (path 1). Compared with the corresponding glycosyl trichloroacetimidate donor,[21] thioglycoside donor **C** proved more effective in the glycosylation. While compound **B** was not easily separated from the mixture of **B** and **8**. We then tried another route (path 2): After cleaving the acetyl esters of **B** and **8**, the product was treated with disaccharide donor **C** in the presence of NIS/TfOH. To our delight, the glycosylation reaction preferred the equatorial OH-3″ of benzylidene protected β-mannoside to provide the only product α-(1→3)-linked pentasaccharide,[21] in which the OH-2″ of β-mannoside was then acetylated. Pentasaccharide **14** was also provided in 79% yield over 3 steps (Path 2). After cleavage of the benzylidene with TsOH in CH_3CN, the OH-6″ of the β-mannoside was selectively protected with the chloroacetyl group to afford **16**. Monosaccharide donor **D** was treated with **16** to introduce the bisecting residue in the presence of NIS/TfOH, providing **17** in 78% yield. After selective removal of the chloroacetyl group (91%), installation of the other disaccharide residue onto OH-6″ of central β-mannoside was finally carried out to provide the bisected *N*-glycan octasaccharide **A** in 74% yield. The structure of octasaccharide **A** was well characterized by 1D NMR and 2D NMR experiments (^{1}H NMR, ^{13}C NMR, COSY, TOCXY, HMQC, HMBC).

(20) (a) Myszka, H.; Bednarczyk, D.; Najder, M.; Kaca, W. *Carbohydr. Res.* **2003**, *338*, 133. (b) Silva, D. J.; Wang, H.; Allanson, N. M.; Jain, R. K.; Sofia, M. J. *J. Org. Chem.* **1999**, *64*, 5926.

(21) Seifert, J.; Unverzagt, C. *Tetrahedron Lett.* **1996**, *37*, 6527.

SCHEME 3. Synthesis of Octasaccharide A



Conclusions

In summary, we have developed a new and concise method for the synthesis of bisected *N*-glycan of the bisecting type based on the 4,6-*O*-benzylidene-protected-1,2-orthoesters strategy, which greatly simplified the procedure for introduction of the central β-mannoside and assured the sequence for three substituents. Notably, all the fragments involved were easily prepared. Owing to its simplicity and mild reaction conditions, the results of the present investigation will be widely used in the synthesis of *N*-glycans.

Experimental Section

3″-*O*-Chloroacetyl-4″,6″-*O*-benzylidene-α-D-glucopyranose 1″,2″-(Chloromethyl 3′,6′-Di-*O*-benzyl-2′-deoxy-2′-phthalimido-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide-4′-yl Orthoacetate) (4). After a mixture of **1** (8.28 g, 17.80 mmol), **2**[16] (8.78 g, 8.90 mmol), and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (100 mL) was stirred for 3 h at rt and then cooled to −30 °C, NIS (6.03 g, 26.70 mmol) was added. TfOH (79 μL, 0.89 mmol) was then added dropwise over a 1 min period. The reaction mixture was stirred for 30 min at −30 °C and then filtered through Celite. The filtrate was diluted with CH_2Cl_2 and washed with aqueousueous $NaHCO_3$, aqueous $Na_2S_2O_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (toluene/acetone = 50:1) to afford **4** (10.1 g, 82%) as a light yellow foam. $[\alpha]^{20}_D = +20.8$ (*c* 0.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88−6.75 (m, 33 H), 6.06 (d, 1 H, $J = 5.5$ Hz), 5.48 (s, 1 H), 5.44 (dd, 1 H, $J = 9.3$, 4.4 Hz), 5.28 (d, 1 H, $J = 8.2$ Hz), 5.14 (d, 1 H, $J = 9.9$ Hz), 4.86−4.81 (m, 2 H), 4.64 (d, 1 H, $J = 12.1$ Hz), 4.56−4.50 (m, 5 H), 4.41 (dd, 1 H, $J = 11.0$, 5.5 Hz), 4.31−4.23 (m, 3 H), 4.16−4.12 (m, 2 H), 4.08−4.03 (m, 2 H), 3.96−3.81 (m, 5 H,), 3.70−3.55 (m, 5 H), 3.43 (dd, 1 H, $J = 11.0$, 3.3 Hz), 3.37 (d, 1 H, $J = 9.9$ Hz), 3.26 (d, 1 H, $J = 9.4$ Hz). ^{13}C NMR (150 MHz, $^{13}C_3$): δ 166.0, 138.5, 138.3, 138.2, 138.1, 136.5, 129.2, 129.0, 128.3, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 127.5, 127.4,

127.2, 126.9, 126.1, 125.3, 123.2, 119.6, 101.4, 99.3, 96.6, 85.5, 78.5, 77.7, 76.5, 76.3, 75.4, 75.3, 75.1, 74.5, 74.5, 73.6, 73.1, 72.8, 68.5, 67.7, 67.5, 62.7, 56.5, 55.1, 46.8, 40.5. HRMS (ESI) *m/z*: calcd for $C_{73}H_{67}Cl_2N_5O_{19}Na$ $[M + Na]^+$ 1410.3705; found, 1410.3738.

3″-*O*-Acetyl-4″,6″-*O*-benzylidene-α-D-glucopyranose 1″,2″-(Chloromethyl 3′,6′-Di-*O*-benzyl-2′-deoxy-2′-phthalimido-*β*-D-glucopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide-4′-yl Orthoacetate) (5). To a solution of **4** (8.33 g, 6.00 mmol) in 1:3 CH_2Cl_2/CH_3OH (400 mL) was added a 1 M solution of NaOMe in MeOH until a pH of 10 was reached. The reaction was stirred for 1 h at rt. Then the solution was neutralized with ion-exchange resin, filtered, and concentrated. The residue was dissolved in CH_2Cl_2 (100 mL). Pyridine (5 mL), Ac_2O (1.2 mL, 12.00 mmol), and DMAP (100 mg) were added. The mixture was stirred for 5 h at rt. One milliliter of methanol was injected into the solution, and the solution was stirred for another 0.5 h at rt. The solution was diluted with CH_2Cl_2 and washed with aqueous 1 N HCl, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:2) to yield **5** (7.69 g, 95%) as a white foam. $[\alpha]^{20}_D = +22.5$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83−6.76 (m, 33 H), 6.02 (d, 1H, *J* = 5.5 Hz), 5.48 (s, 1 H), 5.34 (dd, 1 H, *J* = 9.7, 4.1 Hz), 5.27 (d, 1 H, *J* = 8.7 Hz), 5.13 (d, 1 H, *J* = 9.2 Hz), 4.86−4.83 (m, 2 H), 4.64 (d, 1 H, *J* = 11.9 Hz), 4.56−4.53 (m, 2 H), 4.51−4.48 (m, 3 H), 4.41 (dd, 1 H, *J* = 11.0, 5.5 Hz), 4.31−4.27 (m, 2 H), 4.23 (dd, 1 H, *J* = 9.6, 8.7 Hz), 4.15−4.12 (m, 2 H), 4.05−4.00 (m, 2 H), 3.87−3.81 (m, 3 H), 3.72−3.65 (m, 3 H), 3.62 (dd, 1 H, *J* = 9.5, 9.1 Hz), 3.55 (d, 1 H, *J* = 10.6 Hz), 3.42 (dd, 1 H, *J* = 11.5, 3.7 Hz), 3.37−3.35 (m, 1 H), 3.29−3.27 (m, 1 H), 1.98 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.5, 167.7, 138.5, 138.4, 138.3, 138.1, 137.9, 136.8, 134.0, 133.9, 133.7, 131.8, 131.5, 131.2, 129.2, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 127.1, 126.9, 126.1, 125.3, 123.6, 123.3, 119.5, 101.4, 99.2, 96.6, 85.5, 78.6, 78.2, 76.4, 75.5, 75.1, 74.6, 74.5, 73.6, 73.24, 73.1, 72.8, 68.6, 67.7, 67.6, 56.6, 55.2, 46.9, 20.9. HRMS (ESI) *m/z*: calcd for $C_{73}H_{68}ClN_5O_{19}Na$ $[M + Na]^+$ 1376.4095; found, 1376.4105.

***O*-(3-*O*-Acetyl-4,6-*O*-benzylidene-2-chloroacetyl-*β*-D-glucopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide (6).** After a mixture of **5** (1.25 g, 0.92 mmol) and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (100 mL) was stirred at rt for 3 h and then cooled to −30 °C, TfOH (82 μL, 0.92 mmol) was added dropwise over a 5 min period. The mixture was stirred for 1 h at −30 °C. The reaction mixture was neutralized with Et_3N and then filtered through Celite; the filtrate was concentrated and purified by column chromatography on silica gel (toluene/acetone = 50:1) to afford **6** (1.16 g, 93%) as a white foam. $[\alpha]^{20}_D = -15.6$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90−6.77 (m, 33 H), 5.38 (s, 1 H), 5.27 (d, 1 H, *J* = 8.2 Hz), 5.18 (t, 1 H, *J* = 9.6 Hz), 5.17 (d, 1 H, *J* = 9.2 Hz), 4.96 (dd, 1 H, *J* = 9.2, 8.2 Hz), 4.88 (d, 1 H, *J* = 12.8 Hz), 4.74 (d, 2 H, *J* = 7.7 Hz), 4.66 (d, 1 H, *J* = 11.9 Hz), 4.56−4.45 (m, 4 H), 4.39 (d, 1H, *J* = 11.9 Hz), 4.28−4.12 (m, 5 H), 4.05 (dd, 1 H, *J* = 10.1, 9.6 Hz), 3.93 (d, 1H, *J* = 14.7 Hz), 3.89 (d, 1H, *J* = 14.6 Hz), 3.65 (d, 1 H, *J* = 10.5 Hz), 3.59−3.55 (m, 3 H), 3.44−3.38 (m, 3 H), 3.25−3.20 (m, 3 H), 2.03 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.1, 166.2, 138.4, 138.1, 137.7, 128.7, 128.2, 128.1, 128.0, 127.9, 127.4, 101.5, 99.8, 96.8, 85.5, 78.3, 77.7, 76.4, 75.1, 74.6, 74.5, 73.4, 72.7, 71.8, 68.4, 67.7, 66.8, 66.0, 56.4, 55.2, 40.4, 20.7. HRMS (ESI) *m/z*: calcd for $C_{73}H_{68}ClN_5O_{19}Na$ $[M + Na]^+$ 1376.4095; found, 1376.4034.

***O*-(3-*O*-Acetyl-4,6-*O*-benzylidene-*β*-D-glucopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide (7).** To a solution of **6** (1.79 g, 1.32 mmol) in 80 mL of CH_2Cl_2/CH_3OH (1:3) was added 2,6-lutidine (0.77 mL, 6.60 mmol) and thiourea (502 mg, 6.60 mmol). After the reaction mixture was stirred for 10 h at rt, it was diluted with CH_2Cl_2 and washed with aqueous 1 N HCl, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:3) to afford **7** (1.55 g, 92%) as a white foam. $[\alpha]^{20}_D = +25.5$ (*c* 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84−7.55 (m, 8 H), 7.41−7.26 (m, 15 H), 7.02−6.89 (m, 7 H), 6.81−6.76 (m, 3 H), 5.38 (s, 1 H), 5.28 (d, 1 H, *J* = 8.4 Hz), 5.17 (d, 1 H, *J* = 9.4 Hz), 5.08 (t, 1 H, *J* = 9.5 Hz), 4.86 (d, 1 H, *J* = 12.7 Hz), 4.80 (d, 1 H, *J* = 12.2 Hz), 4.69 (d, 1 H, *J* = 7.7 Hz), 4.61 (d, 1 H, *J* = 12.1 Hz), 4.56−4.49 (m, 4 H), 4.41−4.37 (m, 2 H), 4.28 (dd, 1 H, *J* = 9.6, 9.2 Hz), 4.22 (dd, 1 H, *J* = 11.0, 8.7 Hz), 4.18−4.09 (m, 3 H), 4.06 (dd, 1 H, *J* = 10.6, 9.2 Hz), 3.82 (dd, 1 H, *J* = 11.5, 2.3 Hz), 3.66 (dd, 1 H, *J* = 11.5, 1.9 Hz), 3.58 (d, 1 H, *J* = 11.0 Hz), 3.52−3.37 (m, 6 H), 3.33−3.32 (m, 1 H), 3.23−3.19 (m, 1 H), 2.12 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 138.3, 138.1, 137.4, 136.9, 133.8, 131.5, 129.1, 128.6, 128.3, 128.2, 128.0, 127.9, 127.5, 127.3, 127.0, 126.2, 103.6, 101.4, 96.9, 85.6, 78.8, 78.4, 78.0, 76.7, 76.3, 74.9, 74.7, 74.5, 74.4, 74.3, 73.8, 73.3, 72.7, 68.5, 67.7, 67.2, 66.3, 56.5, 55.2, 21.0. HRMS (ESI) *m/z*: calcd for $C_{71}H_{67}N_5O_{18}Na$ $[M + Na]^+$ 1300.4379; found, 1300.4387.

***O*-(2-*O*-Acetyl-4,6-*O*-benzylidene-*β*-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide (B) and *O*-(3-*O*-Acetyl-4,6-*O*-benzylidene-*β*-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide (8).** To a solution of compound **7** (671 mg, 0.525 mmol) in distilled CH_2Cl_2 (10 mL) was added pyridine (170 μL, 0.787 mmol). The reaction was cooled to −15 °C. Tf_2O (133 μL, 0.788 mmol) was then added dropwise over a 2 min period, and the reaction mixture was stirred for 3 h. The reaction was concentrated under high vacuum. The crude mixture was dissolved in 20 mL of DMF, then 1 mL of H_2O was added, and the reaction mixture was stirred for 24 h at 50 °C. Then the reaction mixture was concentrated under high vacuum and purified by flash chromatography (EtOAc/petroleum ether = 1:3) to afford **B** and **8** (631 mg, 94%) as a white foam. The ratio of **B** and **8** was 12.7:1 (determined by NMR analysis). Pure **B** was obtained by column chromatography on silica gel (300−400 mesh, EtOAc/petroleum ether = 1:6) and pure **8** was obtained by HPLC (CH_3CN:H_2O).

Compound **B**. $[\alpha]^{20}_D = +0.6$ (*c* 0.2, $CHCl_3$). ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.95−6.75 (m, 33 H), 5.61 (s, 1 H), 5.44 (d, 1 H, *J* = 6.8 Hz), 5.33 (d, 1 H, *J* = 3.7 Hz), 5.30 (d, 1 H, *J* = 9.2 Hz), 5.25 (d, 1 H, *J* = 8.7 Hz), 4.85 (d, 1 H, *J* = 11.4 Hz), 4.85 (s, 1 H), 4.81 (d, 1 H, *J* = 12.4 Hz), 4.63 (d, 1 H, *J* = 12.4 Hz), 4.56 (d, 1 H, *J* = 12.4 Hz), 4.44 (d, 1 H, *J* = 11.9 Hz), 4.41 (d, 1 H, *J* = 11.9 Hz), 4.38 (d, 1 H, *J* = 12.4 Hz), 4.28 (d, 1 H, *J* = 12.4 Hz), 4.15−4.01 (m, 5 H), 3.97 (dd, 1 H, *J* = 10.6, 8.2 Hz), 3.83−3.74 (m, 3 H), 3.70−3.65 (m, 2 H) 3.63−3.59 (m, 2 H), 3.52 (d, 1 H, *J* = 10.5 Hz), 3.39 (dd, 1 H, *J* = 11.5, 3.7 Hz), 3.27−3.26 (m, 1 H), 3.20−3.16 (m, 1 H), 2.05 (s, 3 H). ^{13}C NMR (150 MHz, DMSO-d_6): δ 169.6, 168.1, 167.4, 167.2, 167.1, 138.4, 138.1, 138.0, 137.9, 137.7, 134.9, 134.8, 130.7, 130.6, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 127.2, 126.3, 123.4, 100.9, 98.3, 96.3, 84.9, 78.4, 77.2, 76.3, 76.2, 75.6, 74.9, 74.1, 73.9, 73.7, 72.0, 71.9, 71.8, 68.1, 67.7, 67.6, 66.6, 56.0, 54.6, 20.9. $J_{C1'',H1''} = 161.8$ Hz. HRMS (ESI) *m/z*: calcd for $C_{71}H_{67}N_5O_{18}Na$ $[M + Na]^+$ 1300.4379; found, 1300.4337.

Compound **8**. $[\alpha]^{20}_D = +5.3$ (*c* 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 (d, 1 H, *J* = 5.5 Hz), 7.79−7.56 (m, 7 H), 7.44−7.41 (m, 2 H), 7.38−7.27 (m, 13 H), 7.30 (d, 2 H, *J* = 7.3 Hz), 6.98−6.95 (m, 4 H), 6.93 (d, 1 H, *J* = 6.9 Hz), 6.81−6.76 (m, 3 H), 5.43 (s, 1 H), 5.29 (d, 1 H, *J* = 8.7 Hz), 5.18 (d, 1 H, *J* = 9.6 Hz), 4.92 (dd, 1 H, *J* = 10.1, 3.2 Hz), 4.86 (d, 1 H, *J* = 12.8 Hz), 4.82 (d, 1 H, *J* = 11.9 Hz), 4.79 (s, 1 H), 4.61 (d, 1 H, *J* = 11.9 Hz), 4.58−4.50 (m, 4 H), 4.41 (d, 1 H, *J* = 12.4 Hz), 4.38

(dd, 1 H, J = 8.7, 1.8 Hz), 4.29 (dd, 1 H, J = 9.6, 8.7 Hz), 4.25 (dd, 1 H, J = 10.5, 8.2 Hz), 4.19−4.10 (m, 4 H), 4.06 (dd, 1 H, J = 10.6, 9.6 Hz), 3.99 (dd, 1 H, J = 10.1, 9.6 Hz), 3.68 (d, 1 H, J = 10.1 Hz), 3.60−3.57 (m, 2 H), 3.53 (dd, 1 H, J = 10.5, 10.1 Hz), 3.44 (d, 1 H, J = 11.0, 3.2 Hz), 3.40 (dd, 1 H, J = 10.1, 2.3 Hz), 3.28 (d, 1 H, J = 9.6 Hz), 3.22−3.18 (m, 1 H), 2.14 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.2, 138.3, 138.2, 137.5, 137.1, 129.0, 128.6, 128.3, 128.2, 128.0, 127.9, 127.8, 127.5, 127.4, 127.3, 127.2, 127.0, 126.1, 101.7, 99.8, 96.8, 85.5, 78.3, 77.5, 76.3, 76.2, 75.2, 75.0, 74.6, 74.5, 74.4, 73.4, 72.7, 71.8, 69.3, 68.3, 67.7, 66.8, 56.4, 55.1, 21.0. HRMS (ESI) *m/z*: calcd for $C_{71}H_{67}N_5O_{18}Na$ [M + Na]$^+$ 1300.4379; found, 1300.4340.

(2′*S*,3′*S*)-Ethyl 3-*O*,4-*O*-[2′,3′-Dimethoxybutan-2′,3′-diyl]-6-*O*-acetyl-1-thio-α-D-mannopyranoside (10). To a solution of **9**[18] (13.54 g, 40.0 mmol) in CH_2Cl_2 (300 mL) was added pyridine (13 mL, 160.0 mmol), and the resulting mixture was cooled to −15 °C. Ac_2O (4.7 mL, 50 mmol) was added dropwise over 5 min. The reaction was stirred for 24 h. Subsequently, the solution was diluted with CH_2Cl_2 and washed with aqueous 1 N HCl, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:1) to afford **10** (12.42 g, 82%) as an oil. $[\alpha]^{20}_D$ = +287.5 (*c* 0.4, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.33 (s, 1 H), 4.35−4.31 (m, 2 H), 4.26 (dd, 1 H, J = 11.9, 5.9 Hz), 4.09 (t, 1 H, J = 10.1 Hz), 4.02 (dd, 1 H, J = 3.2, 1.4 Hz), 3.97 (dd, 1 H, J = 10.4, 2.8 Hz), 3.27 (s, 3 H), 3.22 (s, 3 H), 2.71−2.56 (m, 2 H), 2.07 (s, 3 H), 1.32 (s, 3 H), 1.30 (t, 3 H, J = 7.3 Hz), 1.28 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 100.4, 100.0, 84.5, 71.0, 68.8, 68.6, 63.5, 62.6, 48.0, 47.8, 25.1, 20.8, 17.7, 17.6, 14.9. HRMS (ESI) *m/z*: calcd for $C_{16}H_{28}O_8SNa$ [M + Na]$^+$ 403.1403; found, 403.1405.

(2′*S*,3′*S*)-Ethyl 3-*O*,4-*O*-[2′,3′-Dimethoxybutan-2′,3′-diyl]-6-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-thio-α-D-mannopyranoside (12). A solution of **11**[19] (3.57 g, 6.16 mmol), **10** (1.95 g, 5.13 mmol), and flame-activated 4 Å molecular sieves were stirred in freshly distilled CH_2Cl_2 (50 mL) under an Ar atmosphere for 0.5 h at rt. The reaction mixture was then cooled to −30 °C and stirred for 5 min, and then TMSOTf (134 μL, 0.77 mmol) was injected into the solution. The reaction mixture was stirred for 30 min at −30 °C; then the solution was quenched with triethylamine, stirred at rt for 0.5 h, and then filtered through Celite and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:1) to afford **12** (3.48 g, 85%) as a white foam. $[\alpha]^{20}_D$ = +45.2 (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (dd, 2 H, J = 5.0, 2.7 Hz), 7.70 (dd, 2 H, J = 5.5, 2.8 Hz), 5.83 (dd, 1 H, J = 10.6, 9.2 Hz), 5.55 (d, 1 H, J = 8.3 Hz), 5.23 (dd, 1 H, J = 10.1, 9.2 Hz), 5.12 (s, 1 H), 4.49 (dd, 1 H, J = 10.6, 8.2 Hz), 4.36 (dd, 1 H, J = 12.4, 4.1 Hz), 4.21 (dd, 1 H, J = 12.4, 2.3 Hz), 4.08−4.04 (m, 1 H), 4.03 (dd, 1 H, J = 2.8, 1.4 Hz), 3.99 (dd, 1 H, J = 11.9, 1.8 Hz), 3.87−3.84 (m, 2 H), 3.73 (t, 1 H, J = 10.1 Hz), 3.46 (dd, 1 H, J = 11.9, 7.3 Hz), 3.20 (s, 3 H), 3.12 (s, 3 H), 2.55−2.44 (m, 2 H), 2.12, 2.03, 1.94, 1.87 (s, 3 H each), 1.19 (t, 3 H, J = 3.2 Hz), 1.18, 1.14 (s, 3 H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.6, 170.2, 169.4, 134.1, 131.6, 129.0, 128.2, 125.3, 123.3, 100.2, 99.5, 96.0, 82.4, 76.3, 72.1, 70.6, 68.7, 67.4, 63.6, 63.0, 61.8, 54.0, 47.9, 47.6, 25.8, 21.4, 20.8, 20.7, 20.6, 20.5, 17.6, 17.4, 14.8. HRMS (ESI) *m/z*: calcd for $C_{36}H_{47}NO_{17}SNa$ [M + Na]$^+$ 820.2462; found, 820.2487.

Ethyl 6-*O*-Acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-thio-α-D-mannopyranoside (13). To a solution of **12** (3.48 g, 4.36 mmol) in CH_2Cl_2 (10 mL) were added 9 mL of TFA and 1 mL of H_2O. The reaction mixture was stirred at rt until the starting materials were consumed. Subsequently, the solution was diluted with CH_2Cl_2 and washed with H_2O, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (EtOAc/petroleum ether = 2:1) to afford **13** (2.70 g, 91%) as a white foam. $[\alpha]^{20}_D$ = +59.4 (*c* 0.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (dd, 2 H, J = 4.6, 3.7 Hz), 7.74 (dd, 2 H, J = 5.5, 2.7 Hz), 5.81 (dd, 1 H, J = 10.6, 9.2 Hz), 5.46 (d, 1 H, J = 8.7 Hz), 5.17 (t, 1 H, J = 9.6 Hz), 4.91 (s, 1 H), 4.36 (dd, 1 H, J = 11.0, 8.7 Hz), 4.31 (dd, 1 H, J = 12.4, 5.0 Hz), 4.19 (dd, 1 H, J = 12.4, 1.9 Hz), 4.05 (dd, 1 H, J = 2.3, 0.9 Hz), 4.01 (d, 1 H, J = 11.4 Hz), 3.93−3.90 (m, 2 H, H−5), 3.86 (dd, 1 H, J = 11.5, 6.0 Hz), 3.66 (dd, 1 H, J = 8.7, 6.4 Hz), 3.43 (t, 1 H, J = 9.6 Hz), 2.82 (d, 1 H, J = 9.7 Hz), 2.73 (s, 1 H), 2.48−2.40 (m, 2 H), 2.13, 2.05, 2.02, 1.88 (s, 3 H each), 1.14 (t, 3 H, J = 7.3 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.2, 170.7, 170.1, 169.4, 134.3, 131.3, 97.1, 82.0, 80.4, 72.3, 70.9, 70.4, 70.3, 68.7, 68.5, 63.5, 61.7, 60.4, 54.4, 25.3, 21.0, 20.7, 20.6, 20.4, 14.5, 14.2. HRMS (ESI) *m/z*: calcd for $C_{30}H_{37}NO_{15}SNa$ [M + Na]$^+$ 706.1782; found, 706.1792.

Ethyl 3,4,6-Tri-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-1-thio-α-D-mannopyranoside (C). Compound **13** (1.62 g, 2.37 mmol) and pyridine (1.9 mL, 23.70 mmol) were dissolved in CH_2Cl_2 (40 mL), and the solution was cooled to 0 °C. Ac_2O (1.1 mL, 11.85 mmol) and 100 mg of DMAP were added, and the reaction was stirred for 2 h at rt. Subsequently, the solution was diluted with CH_2Cl_2, washed with aqueous 1 N HCl, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, concentrated, and purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:1) to afford **C** (1.74 g, 96%) as a white foam. $[\alpha]^{20}_D$ = +23.3 (*c* 0.6, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (dd, 2 H, J = 5.5, 3.2 Hz), 7.72 (dd, 2 H, J = 5.5, 3.2 Hz), 5.80 (dd, 1 H, J = 10.6, 9.2 Hz), 5.40 (d, 1 H, J = 8.7 Hz), 5.16 (dd, 1 H, J = 10.1, 9.1 Hz), 5.12 (dd, 1 H, J = 11.0, 10.1 Hz), 4.95 (d, 1 H, J = 1.4 Hz), 4.89 (dd, 1 H, J = 10.1, 3.2 Hz), 4.43 (dd, 1 H, J = 10.6, 8.7 Hz), 4.31 (dd, 1 H, J = 12.4, 5.0 Hz), 4.27 (dd, 1 H, J = 3.2, 1.9 Hz), 4.09 (dd, 1 H, J = 11.9, 2.3 Hz), 4.07−4.04 (m, 1 H), 3.85−3.83 (m, 1 H), 3.76 (dd, 1 H, J = 12.4, 5.5 Hz), 3.64 (dd, 1 H, J = 11.9, 2.3 Hz), 2.52−2.42 (m, 2 H), 2.12, 2.04, 2.03, 2.00, 1.99, 1.89 (s, 3 H each), 1.19 (t, 3 H, J = 7.3 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.7, 170.6, 170.4, 170.2, 169.4, 169.2, 134.2, 131.5, 123.4, 96.5, 81.4, 75.9, 72.0, 70.5, 70.4, 68.8, 68.5, 65.9, 62.4, 61.9, 54.3, 25.4, 20.7, 20.6, 20.5, 14.5. HRMS (ESI) *m/z*: calcd for $C_{34}H_{41}NO_{17}SNa$ [M + Na]$^+$ 790.1993; found, 790.1978.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-(2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (14) Path 1:** After a mixture of **B** (311 mg, 0.243 mmol), **C** (280 mg, 0.365 mmol), and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (15 mL) was stirred at rt for 3.0 h and then cooled to −30 °C, NIS (110 mg, 0.486 mmol) was added. TfOH (4 μL, 0.049 mmol) was then added dropwise. The reaction mixture was stirred for 30 min at −30 °C. The reaction mixture was then filtered through Celite, and the filtrate was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$, aqueous $Na_2S_2O_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:1) to afford **14** (434 mg, 90%) as a white foam. $[\alpha]^{20}_D$ = +23.4 (*c* 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87−6.78 (m, 37 H), 5.46 (dd, 2 H, J = 10.3, 9.9 Hz), 5.26 (d, 1 H, J = 8.0 Hz), 5.20 (d, 1 H, J = 3.7 Hz), 5.16 (d, 1 H, J = 9.2 Hz), 5.02 (dd, 1 H, J = 10.3, 9.9 Hz), 4.97 (dd, 1 H, J = 9.9, 9.1 Hz), 4.94 (s, 1 H), 4.90−4.88 (m, 2 H), 4.84 (dd, 1 H, J = 10.3, 3.3 Hz), 4.82 (d, 1 H, J = 11.7 Hz), 4.66 (d, 1 H, J = 12.1 Hz), 4.53−4.47 (m, 4 H), 4.38 (d, 1 H, J = 12.1 Hz), 4.34 (d, 1 H, J = 12.1 Hz), 4.27−4.16 (m, 8 H), 4.04 (dd, 1 H, J = 10.6, 9.5 Hz), 4.01 (dd, 1 H, J = 3.3, 1.9 Hz), 3.95 (dd, 1 H, J = 12.5, 3.7 Hz), 3.85−3.82 (m, 1 H), 3.74 (t, 1 H, J = 9.5 Hz), 3.71−3.64 (m, 4 H), 3.61−3.55 (m 3 H), 3.49 (t, 1 H, J = 10.3 Hz), 3.42−3.39 (m, 2 H), 3.21−3.19 (m, 1 H), 3.04−2.99 (m, 1 H), 2.15, 2.05, 2.04, 2.00, 1.98, 1.87, 1.85 (s, 3 H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.6, 170.5, 170.2, 170.1, 169.4, 169.2, 168.5, 167.5, 138.6, 138.5, 138.1, 137.8, 137.3, 134.2, 134.1,

133.9, 133.8, 131.7, 131.5, 131.4, 130.2, 128.9, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.7, 127.6, 127.5, 127.2, 127.0, 126.9, 102.4, 98.4, 97.9, 97.1, 95.7, 85.5, 78.7, 78.1, 76.8, 76.6, 76.4, 75.3, 75.2, 74.6, 74.4, 74.3, 73.4, 72.9, 72.8, 71.1, 70.5, 70.4, 69.3, 68.8, 68.5, 68.4, 67.7, 67.4, 66.1, 65.4, 62.8, 61.0, 60.4, 56.4, 55.2, 54.0, 20.8, 20.7, 20.6, 20.5. HRMS (MALDI) *m/z*: calcd for $C_{103}H_{102}N_4O_{35}Na$ $[M - N_2 + Na]^+$ 1977.6217; found, 1977.6260.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (15).** To a solution of **14** (722 mg, 0.364 mmol) in CH_3CN (10 mL) was added $TsOH \cdot H_2O$ (346 mg, 1.820 mmol). The reaction mixture was stirred for 10 h at rt. Then the solution was neutralized with concentrated Et_3N. The crude mixture was diluted with CH_2Cl_2 and washed with brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 1:1) to afford **15** (574 mg, 83%) as a white foam. $[\alpha]^{20}_D = -1.7$ (*c* 0.5, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89−6.74 (m, 32 H), 5.73 (dd, 1 H, *J* = 10.6, 9.1 Hz), 5.37 (d, 1 H, *J* = 8.4 Hz), 5.27 (d, 1 H, *J* = 8.5 Hz), 5.16−5.13 (m, 4 H), 4.94 (d, 1 H, *J* = 1.8 Hz), 4.89−4.85 (m, 3 H), 4.61 (d, 1 H, *J* = 12.1 Hz), 4.54−4.48 (m, 4 H), 4.42−4.38 (m, 3 H), 4.29 (dd, 1 H, *J* = 12.5, 5.2 Hz), 4.25−4.09 (m, 7 H), 4.04 (dd, 1 H, *J* = 10.6, 9.5 Hz), 3.84−3.78 (m, 4 H), 3.74 (dd, 1 H, *J* = 9.9, 9.5 Hz), 3.71 (dd, 1 H, *J* = 11.7, 2.9 Hz), 3.63 (d, 1 H, *J* = 9.9 Hz), 3.57−3.53 (m, 3 H), 3.43−3.38 (m, 2 H), 3.35 (dd, 1 H, *J* = 9.2, 3.7 Hz), 3.23−3.21 (m, 1 H), 3.02−2.99 (m, 1 H), 2.11 (s, 6 H), 2.03, 2.02, 2.02, 1.98, 1.86 (s, 3 H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.7, 170.7, 170.2, 170.1, 169.4, 168.5, 167.6, 138.4, 138.1, 137.7, 134.4, 134.2, 134.0, 133.8, 131.7, 131.5, 131.3, 128.7, 128.4, 128.2, 128.1, 127.9, 127.6, 127.5, 127.4, 127.3, 127.0, 123.6, 123.4, 123.2, 98.4, 97.6, 97.1, 97.0, 85.5, 77.6, 77.4, 76.6, 75.4, 75.3, 74.7, 74.5, 74.4, 73.3, 72.9, 71.9, 70.6, 70.4, 69.9, 68.9, 68.3, 67.7, 67.2, 65.4, 62.4, 62.0, 56.4, 55.2, 54.4, 20.9, 20.8, 20.7, 20.6, 20.4. HRMS (MALDI) *m/z* calcd for $C_{96}H_{98}N_4O_{35}Na$ $[M - N_2 + Na]^+$ 1889.5904; found, 1889.5905.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-*O*-(2-*O*-acetyl-6-*O*-chloroacetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (16).** Compound **15** (512 mg, 0.270 mmol) and pyridine (0.12 mL, 1.35 mmol) were dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C. Chloroacetic anhydride (90%) (61 mg, 0.324 mmol) was added, and the reaction was stirred at 0 °C until compound **15** was consumed. Subsequently, 0.1 mL of methanol was injected into the solution and stirred for 0.5 h at rt. The solution was washed with aqueous 1 N HCl, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 2:3) to afford **16** (447 mg, 84%) as a white foam. $[\alpha]^{20}_D = -7.6$ (*c* 0.8, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85−6.74 (m, 32 H), 5.72 (dd, 1 H, *J* = 10.6, 9.2 Hz), 5.38 (d, 1 H, *J* = 8.4 Hz), 5.24 (d, 1 H, *J* = 8.0 Hz), 5.18−5.13 (m, 4 H), 4.93 (d, 1 H, *J* = 1.8 Hz), 4.87−4.84 (m, 3 H), 4.62 (d, 1 H, *J* = 12.1 Hz), 4.57−4.46 (m, 5 H), 4.42−4.39 (m, 2 H), 4.36 (d, 1 H, *J* = 12.5 Hz), 4.31 (dd, 1 H, *J* = 12.1, 4.4 Hz), 4.23−4.08 (m, 8 H), 4.03 (dd, 1 H, *J* = 10.6, 9.5 Hz), 3.99 (d, 1 H, *J* = 15.0 Hz), 3.96 (d, 1 H, *J* = 15.0 Hz), 3.84−3.79 (m, 4 H), 3.64−3.53 (m, 4 H), 3.41−3.34 (m, 3 H), 3.21−3.19 (m, 1 H), 3.15−3.12 (m, 1 H), 3.05 (brs, 1 H), 2.11, 2.10, 2.03, 2.02, 2.02, 1.97, 1.86 (s, 3H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.7, 170.2, 170.1, 169.4, 169.4, 168.3, 168.2, 167.6, 138.7, 138.4, 138.1, 137.8, 134.4, 134.0, 133.8, 131.7, 131.5, 131.3, 128.6, 128.3, 128.0, 127.9, 127.6, 127.5, 127.1, 127.0, 126.0, 123.6, 123.3, 123.2, 98.6, 98.1, 97.0, 96.9, 85.5, 78.0, 76.8, 76.7, 76.5, 75.1, 74.6, 74.4, 74.3, 73.5, 73.2, 72.8, 71.9, 70.6, 70.3, 69.8, 69.0, 68.8, 67.8, 67.7, 67.3, 65.4, 64.4, 62.4, 61.9, 60.4, 56.4, 55.2, 54.3, 40.6, 29.7, 20.8, 20.7, 20.6, 20.4. HRMS (MALDI) *m/z*: calcd for $C_{98}H_{99}ClN_4O_{36}Na$ $[M - N_2 + Na]^+$ 1965.5620; found, 1965.5612.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→4)]-*O*-(2-*O*-acetyl-6-*O*-chloroacetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (17).** After a mixture of **16** (118 mg, 0.060 mmol), **D** (135 mg, 0.239 mmol), and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (10 mL) was stirred at rt for 3 h and then cooled to −30 °C, NIS (68 mg, 0.299 mmol) was added. TfOH (27 μL, 0.299 mmol) was then added dropwise over 1 min. The reaction mixture was stirred for 2 h at −30 °C. The reaction mixture was then filtered through Celite, and the filtrate was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$, aqueous $Na_2S_2O_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 3:2) to afford **17** (110 mg, 78%) as a white foam. $[\alpha]^{20}_D = -22.9$ (*c* 0.9, $CHCl_3$).^{1}H NMR (600 MHz, $CDCl_3$): δ 8.03 (s, 1 H), 7.87−7.81 (m, 2 H), 7.73−7.66 (m, 7 H), 7.59 (d, 1 H, *J* = 7.3 Hz), 7.31−7.24 (m, 7 H), 7.18 (d, 2 H, *J* = 6.8 Hz), 7.13 (t, 2 H, *J* = 7.8 Hz), 6.94−6.92 (m, 5 H), 6.86−6.85 (m, 3 H), 6.78−6.73 (m, 3 H), 5.76 (dd, 1 H, *J* = 11.0, 9.2 Hz), 5.46 (d, 1 H, *J* = 8.3 Hz), 5.35 (dd, 1 H, *J* = 10.1, 9.6 Hz), 5.28−5.25 (m, 2 H), 5.22 (d, 1 H, *J* = 7.7 Hz), 5.13 (d, 1 H, *J* = 9.6 Hz), 5.06 (d, 1 H, *J* = 3.2 Hz), 4.85−4.79 (m, 3 H), 4.69 (s, 1 H), 4.59 (d, 1 H, *J* = 2.8 Hz), 4.57 (s, 1 H), 4.53 (dd, 1 H, *J* = 12.4, 3.2 Hz), 4.51−4.41 (m, 6 H), 4.33 (d, 1 H, *J* = 12.4 Hz), 4.29 (d, 1 H, *J* = 11.9 Hz), 4.27−4.06 (m, 12 H), 4.03−3.97 (m, 2 H), 3.95−3.79 (m, 6 H), 3.73−3.70 (m, 1 H), 3.60 (d, 1 H, *J* = 10.5 Hz), 3.53−3.48 (m, 2 H), 3.39−3.33 (m, 3 H), 3.18 (d, 1 H, *J* = 9.6 Hz), 3.05−3.04 (m, 1 H), 2.13, 2.09, 2.09, 2.08, 2.05, 2.05, 2.03, 2.01, 1.99, 1.87 (s, 3 H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.0, 170.9, 170.8, 170.5, 170.3, 170.0, 169.6, 169.5, 169.4, 167.3, 138.7, 138.3, 138.0, 137.5, 133.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.5, 127.4, 127.1, 127.0, 100.0, 98.7, 97.3, 97.2, 96.9, 85.5, 76.7, 76.5, 75.2, 74.6, 74.5, 74.3, 74.1, 74.0, 73.2, 72.9, 72.7, 72.5, 72.1, 71.4, 71.3, 70.7, 70.3, 69.4, 69.2, 69.0, 68.1, 67.6, 67.0, 65.5, 63.1, 62.4, 61.5, 56.3, 55.4, 55.1, 54.6, 40.5, 20.8, 20.7, 20.6, 20.5. HRMS (MALDI) *m/z*: calcd for $C_{112}H_{115}ClF_3N_5O_{44}Na$ $[M - N_2 + Na]^+$ 2348.6448; found, 2348.6418.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucopyranosyl)-(1→4)]-*O*-(2-*O*-acetyl-β-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosylazide (18).** To a solution of **17** (78 mg, 0.033 mmol) in methanol (10 mL) were added thiourea (50 mg, 0.66 mmol) and 2,6-lutidine (78 μL, 0.66 mmol). The reaction mixture was stirred for 6 h at 64 °C. Then the solution was concentrated and diluted with CH_2Cl_2, washed with aqueous 1 N HCl, aqueous $NaHCO_3$, and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 2:1) to afford **18** (68 mg, 91%) as a white foam. $[\alpha]^{20}_D = -23.3$ (*c* 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88−6.76 (33 H), 5.78 (dd, 1 H, *J* = 10.5, 9.1 Hz), 5.51 (d, 1 H, *J* = 8.7 Hz), 5.47 (t, 1 H, *J* = 10.1 Hz), 5.30−5.25 (m, 3 H), 5.19 (dd, 1 H, *J* = 9.7, 9.6 Hz), 5.15 (d, 1 H, *J* = 9.6 Hz), 5.01 (d, 1 H, *J* = 3.7 Hz), 4.88 (dd, 2 H, *J* = 12.4, 11.0 Hz), 4.81 (dd, 1 H, *J* = 10.1, 3.2 Hz), 4.75 (t, 1 H, *J* = 9.2 Hz), 4.72 (s, 1 H), 4.61−4.46 (m, 7 H), 4.38 (d, 1 H, *J* = 11.9 Hz), 4.34 (s, 1 H), 4.25−3.99 (m, 12 H), 3.85−3.73 (m, 5 H), 3.62 (dd, 2 H, *J* = 9.6, 9.2 Hz), 3.55−3.50 (m, 2 H), 3.43−3.38 (m, 3 H), 3.30 (dd, 1 H, *J* = 9.6, 3.2 Hz), 3.20 (d, 1 H, *J* = 10.1 Hz),

2.67 (d, 1 H, J = 9.6 Hz), 2.13, 2.12, 2.07, 2.06, 2.05, 2.01, 2.01, 1.99, 1.98, 1.87 (s, 3H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 172.4, 171.2, 171.0, 170.8, 170.4, 170.3, 169.8, 169.6, 169.5, 168.5, 167.6, 167.3, 157.2, 157.0, 138.6, 138.4, 138.1, 137.3, 134.2, 134.1, 133.8, 131.6, 131.5, 131.3, 128.6, 128.4, 128.3, 128.0, 127.9, 127.6, 127.5, 127.0, 126.4, 123.8, 123.4, 123.2, 116.8, 114.9, 101.0, 98.4, 97.1, 97.0, 96.9, 85.5, 76.8, 76.6, 76.5, 76.3, 75.4, 74.7, 74.5, 74.3, 74.2, 73.6, 73.4, 72.9, 72.5, 72.4, 72.0, 71.3, 71.0, 70.5, 21.0, 20.9, 20.7, 20.6, 20.5, 20.3. HRMS (MALDI) *m/z*: calcd for $C_{110}H_{114}F_3N_5O_{43}Na$ $[M - N_2 + Na]^+$ 2272.6732; found, 2272.6703.

***O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→3)-[*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-*β*-D-glucopyranosyl)-(1→4)]-[*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl)-(1→6)]-*O*-(2-*O*-acetyl-*β*-D-mannopyranosyl)-(1→4)-*O*-(3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-glucopyranosylazide (A).** After a mixture of **18** (80 mg, 0.035 mmol), **B** (54 mg, 0.070 mmol), and 4 Å molecular sieves in freshly distilled CH_2Cl_2 (10 mL) was stirred at rt for 3 h and then cooled to −30 °C, NIS (24 mg, 0.105 mmol) was added. TfOH (3 μL, 0.035 mmol) was then added. The reaction mixture was stirred for 1 h at −30 °C. The reaction mixture was then filtered through Celite, and the filtrate was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$, aqueous $Na_2S_2O_3$, and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude mixture was purified by column chromatography on silica gel (EtOAc/petroleum ether = 2:1) to afford **A** (78 mg, 74%) as a white foam. $[\alpha]^{20}_D$ = −13.3 (*c* 0.1, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (d, 1 H), 7.88−6.72 (m, 36 H), 5.79 (dd, 1 H, J = 10.5, 9.1 Hz), 5.50 (d, 1 H, J = 8.2 Hz), 5.42 (dd, 1 H, J = 10.6, 9.2 Hz), 5.35 (dd, 1 H, J = 10.1, 9.7 Hz), 5.30−5.25 (m, 2 H), 5.19 (d, 1 H, J = 8.2 Hz), 5.16 (dd, 1 H, J = 9.7, 9.6 Hz), 5.12 (dd, 1 H, J = 10.1, 9.6 Hz), 5.11 (d, 1 H, J = 9.6 Hz), 5.01 (d, 1 H, J = 3.2 Hz), 4.96−4.93 (m, 2 H), 4.89−4.84 (m, 3 H), 4.74 (s, 1 H), 4.61−4.53 (m, 6 H), 4.49 (dd, 1 H, J = 10.5, 8.2 Hz), 4.46 (s, 1 H), 4.44 (d, 1 H, J = 10.5, 8.2 Hz), 4.40 (d, 1 H, J = 12.8 Hz), 4.35 (d, 1 H, J = 12.4 Hz), 4.31 (s, 1 H), 4.26 (dd, 1 H, J = 10.6, 8.3 Hz), 4.21 (d, 1 H, J = 11.9 Hz), 4.16−4.09 (m, 9 H), 4.06−3.99 (m, 6 H), 3.92−3.86 (m, 3 H), 3.82−3.77 (m, 3 H), 3.74 (dd, 1 H, J = 12.4, 2.8 Hz), 3.67 (d, 1 H, J = 11.0 Hz), 3.57−3.55 (m, 2 H), 3.46−3.42 (m, 3 H), 3.34−3.26 (m, 3 H), 3.20 (d, 1 H, J = 10.1 Hz), 2.91 (dd, 1 H, J = 9.6, 2.8 Hz), 2.14, 2.14, 2.09, 2.08, 2.06, 2.05, 2.02, 2.02, 2.01, 2.00, 1.99, 1.88, 1.88, 1.87, 1.85 (s, 3 H each). ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.7, 170.9, 170.9, 170.8, 170.6, 170.3, 170.2, 169.9, 169.6, 169.4, 169.2, 169.2, 167.9, 167.3, 167.0, 138.5, 138.4, 138.0, 137.5, 134.3, 134.0, 133.8, 133.6, 131.8, 131.5, 131.3, 128.9, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.4, 127.0, 123.8, 123.5, 123.1, 100.5, 98.5, 98.0, 97.7, 97.0, 97.0, 96.5, 85.4, 78.3, 76.7, 75.5, 75.3, 74.5, 74.4, 74.2, 73.8, 73.5, 73.4, 73.2, 72.7, 72.2, 71.4, 71.2, 71.0, 70.8, 70.4, 70.3, 69.9, 69.8, 69.1, 68.9, 68.4, 68.2, 67.4, 67.3, 66.8, 66.6, 65.7, 63.8, 62.9, 62.5, 61.4, 61.4, 56.3, 55.1, 54.9, 54.7, 54.2, 20.9, 20.7, 20.6, 20.5, 20.4. HRMS (MALDI) *m/z*: calcd for $C_{142}H_{149}F_3N_6O_{60}Na$ $[M - N_2 + Na]^+$ 2977.8637; found, 2977.8623.

Acknowledgment. This work is supported by the National Basic Research Program of China (2003CB716403).

Supporting Information Available: General methods, the synthesis of compounds **1**, **D**, and **14** (path 2), ^{1}H NMR and ^{13}C NMR spectra for compounds **1**, **4**−**8**, **10**, **12**−**18**, and **A**−**D**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO900016J