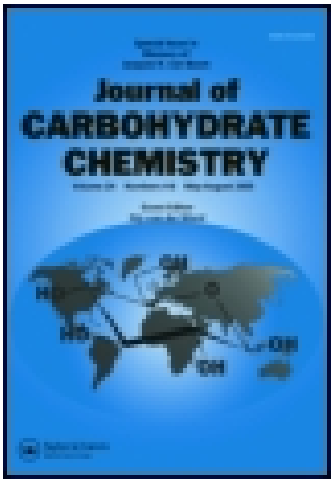

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Synthesis of Branched Tetrasaccharide Derivatives of Schizophyllan-like β-Glucan

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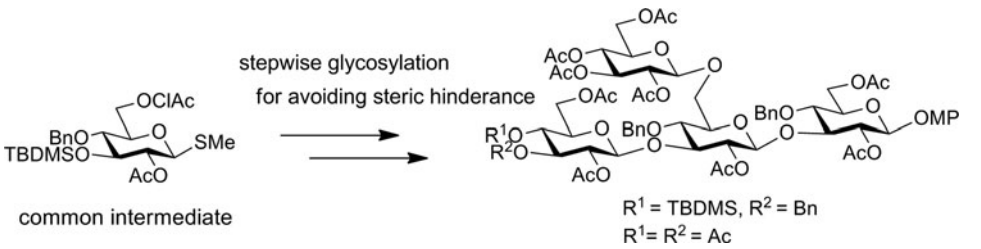
GRAPHICAL ABSTRACT



Branched tetrasaccharide derivatives as the repeating units of schizophyllan were synthesized using a common intermediate that had different protecting groups on the hydroxyl groups. Accordingly, β-1,3-disaccharide acceptors were efficiently glycosylated in a stepwise manner using monosaccharide donors to construct the branched tetrasaccharides. As a result, oligosaccharides with an internal branch rather than a branch on the terminal residue suitable for the synthesis of branched β-glucan were obtained.

Keywords β-Glucan; Glycosylation; Aglycon transfer; Schizophyllan

INTRODUCTION

Polysaccharides are very important biomolecules. They have unique biological functions, such as serving as structural components of cell walls and functioning in energy storage, cell recognition, regulation of signaling, and immune

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responses.[1–3] Consequently, polysaccharides have attracted considerable attention in the study of the mechanisms of biological events.[4,5] The structures of polysaccharides are highly diverse. It is difficult to obtain polysaccharides by purification from natural sources containing heterogeneous compounds, such as proteins and lipids, and structurally homogenous polysaccharides cannot be isolated from the polysaccharides of various structural isomers.[6–8] Therefore, it is difficult to evaluate the biological activity of polysaccharides quantitatively, and a method for the preparation of pure and structurally defined polysaccharides is an important undertaking.

Recently, Brown et al.[9] identified dectin-1 as a β-1,3-glucan receptor. Dectin-1 is expressed predominantly on myeloid tissue cells.[10] Dectin-1 mediates cellular responses to β-glucans as immune cell activators and induces the production of cytokines and chemokines.[11,12] Consequently, the use of β-glucan to elucidate this immune mechanism has been intensively investigated. Palma et al.[13] reported that dectin-1 did not recognize mammalian oligosaccharides linked on microarray, and when using oligosaccharides fractionated from curdlan hydrolysate, the minimum length required for detectable binding by dectin-1 was an 11-mer. Tanaka et al.[8] evaluated the binding activity of synthetic β-1,3-glucan 10−17-mer for dectin-1 and found that synthetic glucan ligands promoted the activation of NF-κB by binding to dectin-1.

When higher plants are attacked by pathogens, they initiate immune responses against penetration and infection.[14] The interaction and signaling between plants and pathogens have been investigated to identify binding molecules and receptors. Elicitor molecules induce synthesis and accumulation of antimicrobial compounds in plant cells.[15,16] It has been found that β-glucan fragments, characterized as an elicitor, from the cell wall of fungi and plants have the ability to elicit biosynthesis of phytoalexins, which act as natural antibiotics in plants.[17,18] The structure of the fragment with high elicitor activity was elucidated, and it was determined that the smallest active structure was a branched hepta-β-glucan. This result was achieved by analysis of phytoalexin accumulation activity using synthetic β-glucans.[19] However, the biological activities of β-glucans are not completely clear, and interesting challenges remain in the synthesis of branched β-glucans.

In 1982, Ogawa and Kaburagi[20] reported the first synthesis of tetra-β-glucan having β-1,6-branched glucose on the reducing end of the main chain. Takeo and Saimei[21] synthesized three types of repeating units of schizophyllan. In these reports, the syntheses of β-glucans were achieved in high yields and excellent stereoselectivity using glucosyl bromides as donors. However, the strong acidic and oxidative conditions involved in the preparation of glucosyl bromides were not suitable for continuous glycosylations, which need selective deprotection and activation. Some studies utilized thioglucosides and glucosyl

imidates as donors and found that these glycosylations formed β-1,3-linkages with anomalous stereoselectivity despite having an acyl group that assists β-selectivity by neighboring group participation at the 2-position on the glucosyl donor.[22–25] Therefore, a novel protecting group for β-1,3-glycosylation was developed by adding a steric hindering group, which provided β-selective glycosylation with thioglucosyl and glucosyl imidate donors.[25–27] However, NMR study showed that the synthesized intermediates of β-glucans, which were protected by the novel protecting group, showed a small coupling constant for $J_{1,2}$ and the peak of the C-1 appeared in a higher magnetic field like α-anomer.[26] Consequently, it was not easy to identify the anomeric configuration of the synthetic compounds, and deprotection was necessary to confirm the structure, indicating that a more practical method for the synthesis of β-glucans should be developed. Recently, Tanaka et al.[8,28] achieved the synthesis of hexadeca-β-glucan using a thioglucosyl donor and glucosyl acceptor protected with a benzylidene group. On the glucosyl acceptor, the benzylidene group is effective for less steric hindrance and the 2-free hydroxyl group enhances the reactivity of the 3-hydroxyl group for the glucosyl donor. However, it is difficult to synthesize branched β-glucan and to completely avoid 2-*O*-glycosylation using this method because the benzylidene group only protected the 4,6-*O*-positions. Branches are known to be important for β-glucans in terms of solubility, helix conformation, and biological activity and consequently have attracted the attention of researchers in both biology and medicine.[29–32] Therefore, a more reliable method to synthesize branched β-glucans is desirable. Herein, the synthesis of repeating units of schizophyllan with branches is reported. The results suggest a strategy for the introduction of branches in the construction of β-glucans.

RESULTS AND DISCUSSION

Synthesis of tetrasaccharide derivatives **1–3** (Fig. 1) of the repeating unit of schizophyllan was attempted by glycosylation using thioglucosides as glucosyl acceptors and glucosyl imidates as glucosyl donors. The acceptors and donors were derived from a common intermediate **12** that had *tert*-butyldimethylsilyl (TBDMS) and a chloroacetyl group (ClAc) at the 3- and 6-*O*-positions. An acetyl group with less steric hindrance at the 2-*O*-position was selected for β-selective glycosylation utilizing neighboring group participation. The intermediate was converted to glucosyl donors and glucosyl acceptors that were then utilized to prepare disaccharides as main chain units and branch units. Repeating units of schizophyllan were synthesized using these disaccharides to investigate a suitable route for the synthesis of β-glucans.

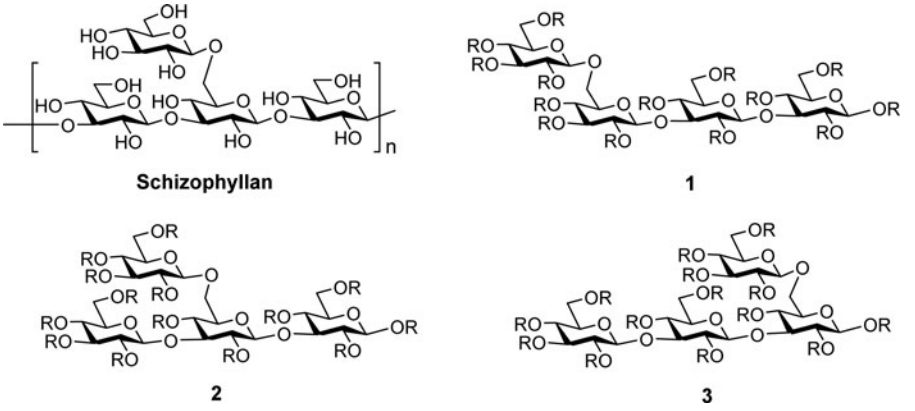
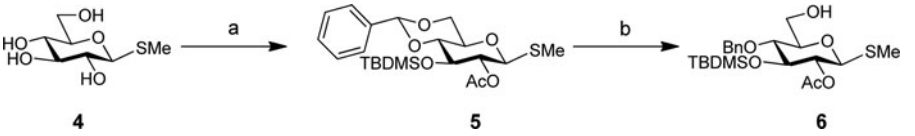


Figure 1: Branched tetrasaccharide derivatives **1–3** as repeating units of schizophyllan.

Methyl thioglucoside **4** was used as a starting material (Sch. 1). A benzylidene group was introduced to protect the 4,6-*O*-positions, followed by treatment with TBDMS chloride to protect the 3-*O*-position and then protection of the 2-*O*-position with the acetyl group to afford **5** in a 90% yield. Finally, the benzylidene group in **5** was selectively cleaved by $CoCl_2$ and BH_3[33] to give **6** in a 98% yield, which was used as the glucosyl acceptor for the introduction of a branch.



Scheme 1: Synthesis of thioglucoside acceptor 6. Reagents and conditions: (a) i. $C_6H_5CH(OCH_3)_2$, CSA, DMF, 60°C, 2.5 h, under reduced pressure; ii. TBDMSCl, imidazole, DMF, 0°C, 14.5 h, 90% (2 steps); iii. Ac_2O, pyridine, rt, 22 h, quant. (b) BH_3-THF, $CoCl_2$, rt, 22.5 h, quant.

Initially, we planned to directly use thioglycoside **6** as a glycosyl donor. However, when it reacted with glucosyl imidate **7**, instead of getting the desired disaccharide **8**, an aglycon transfer reaction[34–38] occurred to give only methyl thioglucoside **9** (Fig. 2).

Therefore, in the synthesis, the aglycon portion of the glucosyl acceptor **6** was changed to a *p*-methoxyphenyl (MP) group (Sch. 2).[34] The 6-hydroxyl group of **6** was chloroacetylated first, and then the methyl thioglucoside **10** was hydrolyzed with *N*-bromosuccinimide[38] and converted to glucosyl imidate **11** efficiently. The imidate was glycosidated with *p*-methoxyphenol to afford **12** in a 75% yield. The common intermediate **12** was treated with DABCO[39] to give glucosyl acceptor **13,** which had a free hydroxyl group at the 6-position.

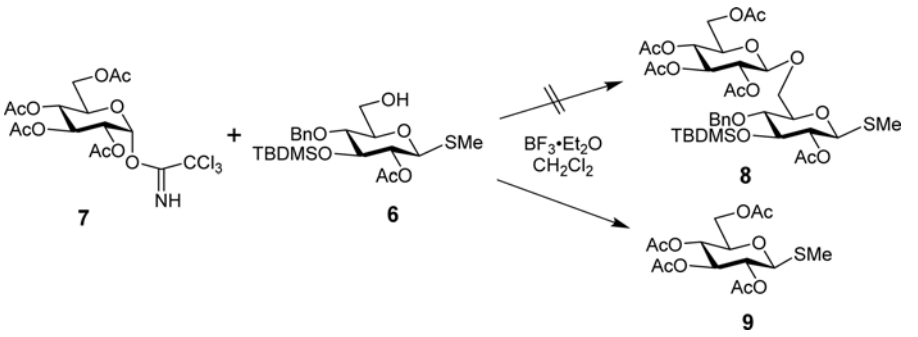
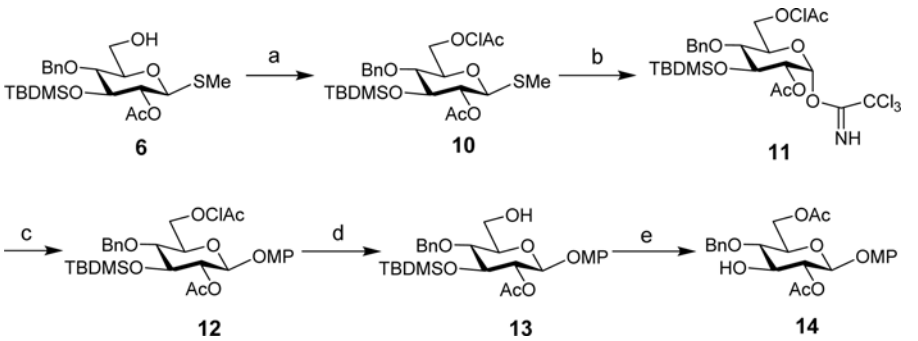


Figure 2: Aglycon transfer reaction of methyl thioglucoside **6**.

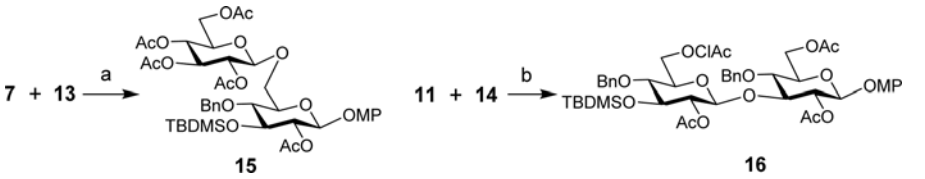


Scheme 2: Synthesis of glucosyl donor 11 and acceptors 13 and 14. Reagents and conditions: (a) $ClCH_2COCl$, pyridine, 0°C, 12 h, quant. (b) i. NBS, acetone, H_2O, rt, 10 min, 97%; ii. Cl_3CCN, DBU, CH_2Cl_2, rt, 12 h, 70%. (c) *p*-methoxyphenol, MeOTf, CH_2Cl_2, MS4Å, −20°C, 1 h, 0°C, 3.5 h, 75%. (d) DABCO, EtOH, 50°C, 30 min, 89%. (e) i. Ac_2O, pyridine, rt, 16.5 h, 96%; ii. $BF_3{\cdot}Et_2O$, CH_3CN, 0°C, 15 min, 71%.

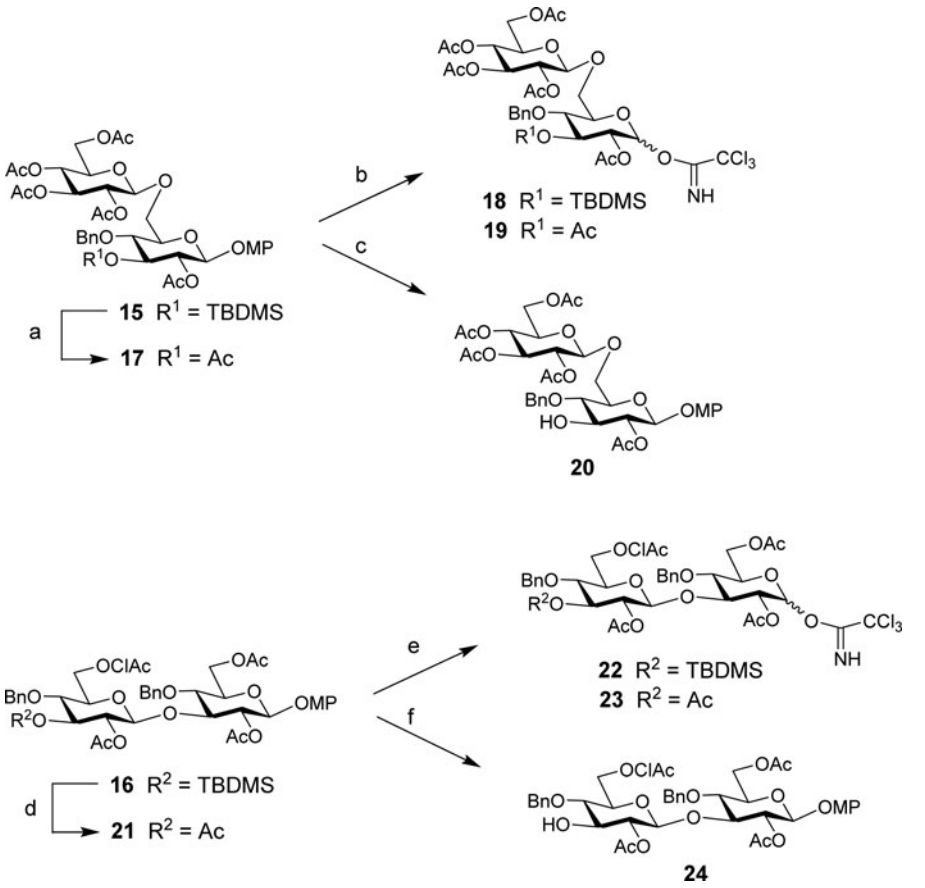
Subsequently, acetylation of **13** and subsequent removal of the TBDMS group using BF_3-Et_2O[40] provided glucosyl acceptor **14** with a free 3-hydroxyl group.

Acceptors **13** and **14** were utilized to construct the β-1,6-linked branch units and the β-1,3-linked main chain units, respectively (Sch. 3). The glycosylation of glucosyl acceptor **13** with glucosyl imidate **7** in the presence of BF_3-Et_2O as a catalytic promoter proceeded smoothly to afford only β-1,6-disaccharide **15** in an 87% yield. Glycosylation of **14** with **11** in an acceptor/donor ratio of 2/1 formed β-1,3-disaccharide **16** in a 68% yield with 65% recovery of the acceptor **14**.

Disaccharides **15** and **16** were converted to acceptors and donors (Sch. 4), respectively, to construct the repeating units of schizophyllan. Disaccharide **15** was treated with BF_3-Et_2O and was subsequently acetylated to give disaccharide **17** in an 80% yield. The MP group in **15** and **17** was selectively removed



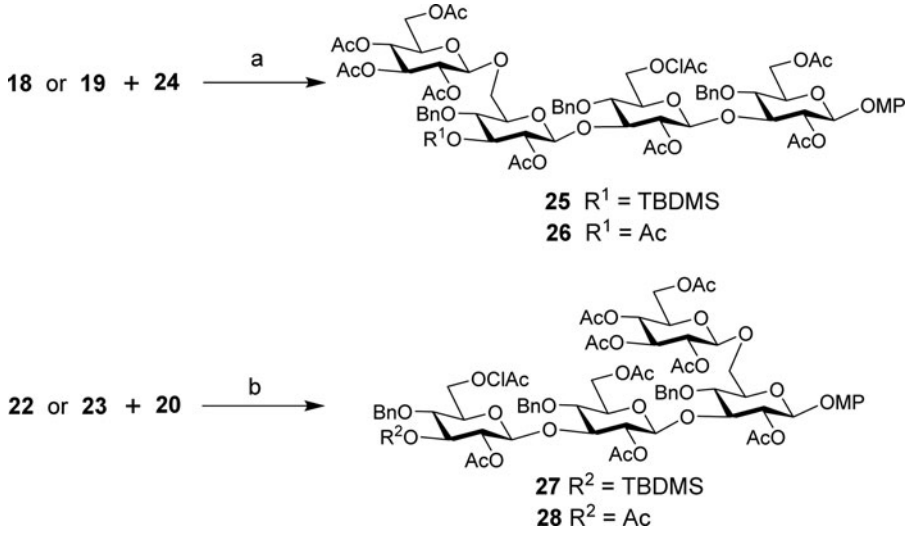
Scheme 3: Synthesis of disaccharides 15 and 16. Reagents and conditions: (a) BF_3-Et_2O, CH_2Cl_2, MS4Å, −40°C, 2 h, 87%. (b) BF_3-Et_2O, CH_2Cl_2, MS4Å, −40°C, 4.5 h, 68%.



Scheme 4: Synthesis of disaccharide donors 18, 19, 22, and 23 and acceptors 20 and 24. Reagents and conditions: (a) i. BF_3-Et_2O, CH_3CN, −20°C, 13 min, quant.; ii. Ac_2O, pyridine, rt, 16 h, 89%. (b) i. CAN, CH_3CN, H_2O, 0°C, 7 min, 92%; ii. Cl_3CCN, DBU, CH_2Cl_2, rt, 31 h, 75% (α only) for **18**; i. CAN, CH_3CN, H_2O, 0°C, 17 min, 94%; ii. Cl_3CCN, DBU, CH_2Cl_2, rt, 8.5 h, 94% (α:β = 10:1) for **19**. (c) BF_3-Et_2O, CH_3CN, −20°C, 17 min, 98%. (d) i. BF_3-Et_2O, CH_3CN, 0°C, 30 min, quant.; ii. Ac_2O, pyridine, rt, 17 h, 89%. (e) i. CAN, CH_3CN, H_2O, 0°C, 20 min, 98%; ii. Cl_3CCN, DBU, CH_2Cl_2, rt, 25 h, 74% (α only) for **22**; i. CAN, CH_3CN, H_2O, 0°C, 15 min, 85%; ii. Cl_3CCN, DBU, CH_2Cl_2, rt, 12.5 h, 84% (α:β = 25:1) for **23.** (f) BF_3-Et_2O, CH_3CN, 0°C, 30 min, 91%.

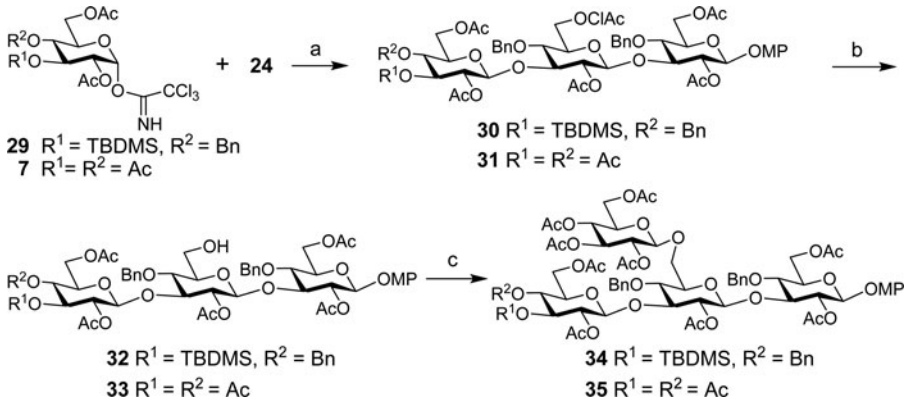
by oxidation and then treated with trichloroacetonitrile and DBU to afford disaccharide donors **18** and **19** in a 68% and 89% yield, respectively. On the other hand, **15** was treated with BF_3-Et_2O to give disaccharide acceptor **20** in a 91% yield. By similar procedures, disaccharide donors **22** and **23** and disaccharide acceptor **24** for the branch units were prepared efficiently from disaccharide **16**.

Next, an attempt was made to prepare tetrasaccharides with a branch at terminal positions (Sch. 5) by combining the donors and the acceptors obtained above. First, acceptor **24** was glycosylated with donor **18** protected with the TBDMS group to provide tetrasaccharide **25** in a 26% yield. Similarly, the glycosylation of acceptor **20** with donor **22** having the TBDMS protection gave tetrasaccharide **27** in a 27% yield. Glycosylation of acceptor **24** with donor **19** having an acetyl protection at the 3-*O*-position afforded a moderate yield (56%) of tetrasaccharide **26**. Glycosylation of acceptor **20** with donor **23** gave tetrasaccharide **28** in a 15% yield only. These results showed that the glycosylation of the glucose 3-OH using β-1,6-linked disaccharide donors was hampered by the steric hindrance at the 6-*O*-position. Therefore, tetrasaccharides having a branch at the reducing or nonreducing end were not suitable for use as the repeating unit toward the construction of β-glucans.



Scheme 5: Synthesis of branched tetrasaccharides 25–28 at the terminal position. Reagents and conditions: (a) BF_3-Et_2O, CH_2Cl_2, MS4Å, −40°C, 2 h, −20°C, 2 h, then TMSOTf, 0°C, 3 h, 26% for 25; BF_3-Et_2O, CH_2Cl_2, MS4Å, −40°C, 1 h, 0°C, 1.5 h, rt, 14 h, 56% for 26. (b) TMSOTf, CH_2Cl_2, MS4Å, −40°C, 0.5 h, rt, 5.5 h, 27% for 27; BF_3-Et_2O, CH_2Cl_2, MS4Å, −40°C, 1 h, rt, 45 min, 15% for 28.

Therefore, disaccharide acceptor **24** was sequentially glycosylated to introduce a main chain sugar unit and a branch to form tetrasaccharide repeating



Scheme 6: Synthesis of branched tetrasaccharides 34 and 35 at the central position. Reagents and conditions: (a) TMSOTf, CH_2Cl_2, MS4Å, −40°C, 50 min, 87% for **30**; $BF_3{\cdot}Et_2O$, CH_2Cl_2, MS4Å, −40°C, 2 h, rt, 15 h, then $BF_3{\cdot}Et_2O$, rt, 1 h, 60% for **31**. (b) DABCO, EtOH, 50°C, 7.5 h, quant. for **32**; DABCO, EtOH, 50°C, 13 h, quant. for **33**. (c) **7**, TMSOTf, CH_2Cl_2, MS4Å, −40°C, 3 h, 75% for **34**; **7**, TMSOTf, CH_2Cl_2, MS4Å, −40°C, 35 min, 83% for **35**.

units with a branch at the central sugar unit (Sch. 6). First, we attempted a procedure to remove the 6-*O*-ClAc group in **24** and glycosylate both the 3- and 6-*O*-positions with imidate **7** in one step to obtain tetrasaccharide **35**. However, only a trisaccharide was given, owing to the steric hindrance resulting from 6-*O*-glycosylation that proceeded first. Therefore, the tetrasaccharides were constructed by introducing two glucose units stepwise. Initially, **24** was glycosylated with glucosyl donor **29**, which was prepared readily from **6** by a procedure similar to that used to prepare **11** or with imidate **7** to afford the β-linked trisaccharide **30** or **31** in a 87% or 56% yield, respectively. The result that **29** gave better yields than **11** showed that the TBDMS and benzyl groups enhanced the reactivity of the glucosyl donor in glycosylation. Then, trisaccharides **30** and **31** were treated with DABCO to remove the ClAc group, and glycosylation of the resulting trisaccharide acceptors **32** and **33** with **7** provided tetrasaccharides **34** and **35** efficiently in 75% and 83% yields, respectively.

CONCLUSION

Branched tetrasaccharide derivatives as the repeating units of schizophyllan were synthesized, and in the process, the influence of a branch on β-1,3-glycosylation was investigated. The tetrasaccharide derivatives were synthesized using **12** as the common intermediate, and the intermediate was efficiently converted to glucosyl acceptors and donors by regioselective modifications of the hydroxyl groups. It is noteworthy that glucosyl donors with an

acetyl group at the 2-*O*-position provided exclusively β-glycosylation without orthoester formation. In the construction of tetrasaccharide derivatives, the benzyl group at the 4-*O*-position of disaccharide acceptors sterically hindered β-1,3-glycosylation. Furthermore, glycosylation of β-1,6-linked disaccharide acceptor **20** with donors **22** and **23** did not provide 3-*O*-glycosylation owing to the steric hindrance of the branch. Thus, unlike previous reports using glucosyl bromide,[20,21] the disaccharide imidates **22** and **23** cannot be used to achieve double glycosylation in a one-pot manner. On the other hand, stepwise glycosylation of 1,3-disacchride acceptor **24** with monosaccharide donors proceeded efficiently to afford tetrasaccharides **34** and **35** with a branch at the central sugar unit. The results suggest that the branch should be introduced as late as possible to avoid steric hindrance, and the repeating unit with a branch at the central position rather than at the terminal position is more suitable for continuous glycosylation, which may enable the construction of schizophyllan-like β-glucans to develop artificial immunological agents.

EXPERIMENTAL SECTION

General Methods

^{1}H NMR spectra were recorded at 400, 500, or 600 MHz using a Bruker AVANCE 400 Plus Nanobay, AVANCE 500US with a cryoprobe, or AVANCE 600 spectrometer in chloroform-*d*. ^{13}C NMR spectra were recorded at 101, 126, or 151 MHz with the same instruments. Chemical shifts are given in ppm (δ) and referenced to tetramethylsilane or to the internal solvent signal used as an internal standard. Assignments in the NMR spectra were made by first-order analysis of spectra and supported by correlation spectroscopy and heteronuclear chemical shift correlation. Matrix-assisted laser desorption ionization time-of-flight high-resolution mass spectrometry (MALDI-TOF HRMS) spectra were recorded on a Jeol JMS-S3000 using 2,5-dihydroxylbenzoic acid as matrix.

Unless otherwise stated, all commercially available solvents and reagents were used without further purification. Dry solvents were prepared by storage over molecular sieves, which were activated in vacuum at 200°C. Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F_{254} (layer thickness, 0.25 mm; E. Merk, Darmstadt, Germany). For detection of intermediates, TLC sheets were dipped in a solution of 85:10:5 (v/v/v) methanol–resorcinol–concentrated sulfuric acid and heated for a few minutes or irradiated with UV lamp.

Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-β-D- thioglucopyranoside (5)

To a solution of **4** (500 mg, 951 μmol) in DMF (2.4 mL) was added benzaldehyde dimethylacetal (213 μL, 1.43 mmol) and *para*-toluenesulfonic acid monohydrate (16.4 mg, 95.1 μmol), and the mixture was stirred under reduced pressure at 60°C for 2.5 h. The solution was cooled on an ice bath and triethylamine (26 μL, 190 μmol) added to neutralize. The solution was then evaporated under vacuum to give the mixture. The mixture was dissolved in DMF (951 μL) and cooled at 0°C. To the solution were added imidazole (97.2 mg, 1.43 mmol) and *tert*-butyldimethylsilyl chloride (172 mg, 1.14 mmol) and the solution was stirred for 14.5 h. Then, the mixture was diluted with dichloromethane and washed with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 25:1 (v/v) hexane–ethyl acetate to give 3-*O*-silylate (354 mg, 90%). The silylate (220 mg, 533 μmol) was subsequently stirred with pyridine (1.2 mL) and acetic anhydride (1.0 mL) at rt for 22 h and the mixture was coevaporated with toluene to give **5** (242 mg, quantitative) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.49–7.47 (m, 2 H, Ph), 7.36–7.35 (m, 3 H, Ph), 5.52 (s, 1 H, Ph-C*H*-O_2-), 5.02 (dd, 1 H, $J_{2,3}$ = 8.4 Hz, H-2), 4.38–4.34 (m, 1 H, H-6a), 4.36 (d, 1 H, $J_{1,2}$ = 9.6 Hz, H-1), 3.89 (t, 1 H, H-3), 3.75 (br-t, 1 H, H-6b), 3.56–3.47 (m, 2 H, H-4, 5), 2.16 (s, 3 H, S-C*H*$_3$), 2.11 (s, 3 H, Ac), 0.82 (s, 9 H, *t*-Bu), 0.03 (s, 3 H, Si-C*H*$_3$), 0.00 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,101 MHz): 169.6, 137.0, 129.1, 128.2, 126.2, 101.8 (C-1), 83.5 (C-4), 81.4 (C-3), 74.0 (C-2), 72.0 (C-5), 68.6 (C-6), 25.6, 21.2, 18.0, 11.2, −4.2, −5.0; MALDI-TOF HRMS (positive ion): calcd for ($C_{22}H_{34}O_6SSi$+Na^+): 477.1743; found m/z: 477.1708.

Methyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-thioglucopyranoside (6)

To the compound **5** were added 1M borane-tetrahydrofuran complex solution (22.3 mL, 22.3 mmol) and cobalt (II) chloride (2.90 g, 22.3 mmol) on an ice bath and the mixture was stirred at rt for 22.5 h. The suspension was filtered and diluted with dichloromethane and washed with water and brine. The solution was dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 10:1 (v/v) hexane–ethyl acetate to give **6** (3.34 g, 99%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.34–7.26 (m, 5 H, Ph), 5.02 (t, 1 H, $J_{2,3}$ = 9.4 Hz, H-2), 4.85 (d, 1 H, J = 11.4 Hz, Ph-C*H*-), 4.63 (d, 1 H, J = 11.6 Hz, Ph-C*H*-), 4.27 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 3.87–3.79 (m, 2 H, H-3, 6a), 3.67–3.61 (m, 1 H, H-6b), 3.48 (t, 1 H, $J_{3,4}$ = 9.2 Hz, H-4), 3.41–3.39 (m, 1 H, H-5), 2.14 (s, 3 H, S-C*H*$_3$), 2.11 (s, 3 H, Ac), 0.89 (s, 9 H, *t*-Bu), 0.07 (s, 6 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,101 MHz):

169.7, 137.8, 128.4, 127.7, 127.6, 83.1 (C-1), 79.7(C-5), 78.3(C-4), 75.1 (C-3), 71.8 (C-2), 61.9 (C-6), 25.7, 21.4, 17.8, 11.4, −4.1, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{22}H_{36}O_6SSi+Na^+$) 479.1900; found m/z: 479. 1921.

Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-thioglucopyranoside (9) from aglycon transfer reaction

To a solution of **6** (100 mg, 219 μmol) and **7** (162 mg, 329 μmol) in dichloromethane (2.0 mL) was added molecular sieves 4Å powder (200 mg), and the mixture was stirred at rt for 1 h and then cooled at –40°C. To the mixture was added trimethylsilyl trifluoromethansulfonate (6.0 mL, 21.9 mmol) and it was stirred at –40°C for 4.0 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 10:1 (v/v) hexane–ethyl acetate to give **9** (75.7 mg, 91%) as a syrup: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 5.24 (t, 1 H, $J_{3,4}$ = 9.4 Hz, H-3), 5.11–5.05 (m, 2 H, H-2, 4), 4.40 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.26 (dd, 1 H, $J_{5,6a}$ = 4.8 Hz, $J_{6a,6b}$ = 12.4 Hz, H-6a), 4.15 (dd, 1 H, $J_{5,6b}$ = 2.4 Hz, H-6b), 3.74 (ddd, 1 H, $J_{4,5}$ = 4.8 Hz, H-5), 2.17 (s, 3 H, S-C*H*$_3$), 2.09–2.02 (m, 12 H, Ac).

Methyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-chloroacetyl-β- D-thioglucopyranoside(10)

Compound **6** (811 mg, 1.78 mmol) was dissolved in dichloromethane (8.9 mL) and pyridine (0.72 mL, 8.90 mmol), and the solution was cooled on an ice bath. Then to the solution was added chloroacetyl chloride (170 μL, 2.14 mmol) dropwise and the mixture was stirred at rt for 12 h. The solution was diluted with dichloromethane and washed with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 10:1 (v/v) hexane–ethyl acetate to give **10** (994 mg, 100%) as a syrup: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.35–7.27 (m, 5 H, Ph), 4.92 (t, 1 H, $J_{2,3}$ = 9.4 Hz, H-2), 4.87 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.54 (d, 1 H, Ph-*CH*-), 4.23 (d, 1 H, $J_{1,2}$ = 10.0 Hz, H-1), 4.15–4.09 (m, 1 H, 6a), 3.98 (d, 2 H, J = 4.4 Hz, ClAc), 3.82 (t, 1 H, $J_{3,4}$ = 8.8 Hz, H-3), 3.58–3.54 (m, 1 H, H-5), 3.46 (t, 1 H, H-4), 2.12 (s, 3 H, S-C*H*$_3$), 2.11 (s, 3 H, Ac), 0.91 (s, 9 H, *t*-Bu), 0.09 (s, 6 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,101 MHz): 169.7, 166.9, 137.4, 128.7, 128.5, 128.3, 128.2, 128.0, 127.8, 82.9 (C-1), 77.9 (C-4), 76.7 (C-5), 76.6 (C-3), 75.2, 71.4 (C-2), 64.4 (C-6), 40.6, 25.7, 25.6, 21.4, 17.8, 11.1, −4.0, −4.3; MALDI-TOF HRMS

(positive ion): calcd for ($C_{24}H_{37}ClO_7SSi+Na^+$): 555.1615; found m/z: 555. 1641.

2-*O*-Acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-chloroacetyl-α-D- glucopyranosyl 2,2,2-trichloroacetimidate (11)

Compound **9** (822 mg, 1.54 mmol) was dissolved in acetone/water (36.7 mL, 4.8/1, v/v). To the solution was added *N*-bromosuccinimide (1.37 g, 7.70 mmol) and the mixture was stirred vigorously at rt for 10 min. The solution was diluted with dichloromethane and washed with aqueous sodium sulfite and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 10:1 to 4:1 (v/v) hexane–ethyl acetate to give an intermediate with a free 1-hydroxyl group (754 mg, 97%). The intermediate (710 mg, 1.41 mmol) was dissolved in dichloromethane (14.1 mL) and trichloroacetonitrile (713 μL, 7.05 mmol), and the solution was cooled on an ice bath. Then to the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (31.6 μL, 212 μmol) and the mixture was stirred at rt for 12.0 h. The solution was concentrated and the residue was purified by silica gel chromatography with 10:1 (v/v) hexane–ethyl acetate to give **11** (640 mg, 70%) as a syrup: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 8.57 (s, 1 H, N*H*), 7.37–7.31 (m, 5 H, Ph), 6.45 (d, 1 H, $J_{1,2} = 2.0$ Hz, H-1), 4.92–4.89 (m, 2 H, H-2, Ph-*CH*-), 4.58 (d, 1 H, $J = 11.6$ Hz, Ph-*CH*-), 4.40 (dd, 1 H, $J_{6a,6b} = 8.0$ Hz, H-6a), 4.26 (t, 1 H, $J_{3,4} = 6.2$ Hz, H-3), 4.17 (dd, 1 H, $J_{5,6b} = 2.8$ Hz, H-6b), 4.04–4.02 (m, 1 H, H-5), 3.95 (d, 2 H, $J = 10.0$ Hz, ClAc), 3.56 (t, 1 H, H-4), 2.05 (s, 3 H, Ac), 0.93 (s, 9 H, *t*-Bu), 0.15 (s, 3 H, Si-CH_3), 0.13 (s, 3 H, Si-CH_3); ^{13}C NMR ($CDCl_3$,151 MHz): 166.7, 160.9, 137.2, 128.5, 128.2, 128.1, 93.5 (C-1), 75.5, 72.7 (C-2), 72.0 (C-3), 71.4 (C-5), 63.8 (C-6), 40.5, 25.7, 20.8, 18.0, −4.0, −4.5.

para-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-chloroacetyl-β-D-glucopyranoside (12)

To a solution of compound **10** (550 mg, 1.03 mmol) and *para*-methoxy phenol (639 mg, 5.15 mmol) in dichloromethane (5.15 mL) was added molecular sieves 4Å powder (2.0 g) and it was stirred at rt for 1.5 h and cooled at –20°C. To the mixture was added methyl trifluoromethansulfonate (451 μL, 4.12 μmol) and it was stirred at –20°C for 1.0 h, and then at 0°C for 3.5 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 8:1 to 2:1 (v/v) hexane–ethyl acetate to give **12** (380 mg, 75%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz)

7.38–7.29 (m, 5 H, *Ph*-CH_2-), 6.93–6.89 (m, 2 H, Ph), 6.81–6.77 (m, 2 H, Ph), 5.11 (dd, 1 H, $J_{2,3} = 9.2$ Hz, H-2), 4.88 (d, 1 H, $J = 11.6$ Hz, Ph-*CH*-), 4.78 (d, 1 H, $J_{1,2} = 7.6$ Hz, H-1), 4.56 (d, 1 H, Ph-*CH*-), 4.44 (dd, 1 H, $J_{5,6a} = 2.4$ Hz, $J_{6a,6b} = 12.0$ Hz, H-6a), 4.15 (dd, 1 H, $J_{5,6b} = 5.2$ Hz, H-6b), 3.95 (d, 2 H, $J = 8.4$ Hz, ClAc), 3.86 (t, 1 H, $J_{3,4} = 9.2$ Hz, H-3), 3.75 (s, 3 H, O*CH*$_3$), 3.66–3.62 (m, 1 H, H-5), 3.54 (t, 1 H, $J_{4,5} = 9.6$ Hz, H-4), 2.12 (s, 3 H, Ac), 0.92 (s, 9 H, *t*-Bu), 0.10 (s, 6 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,151 MHz): 169.4, 166.8, 155.5, 151.28, 137.3, 128.5, 128.1, 127.9, 118.5, 114.5, 100.6 (C-1), 78.0 (C-4), 75.2 (Ph-*C*H_2-), 75.1 (C-3), 73.5 (C-2), 72.8 (C-5), 64.4 (C-6), 55.6, 40.6, 25.7, 21.2, 17.9, −4.1, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{30}H_{41}ClO_9Si$+Na^+): 631.2106; found m/z: 631.2126.

para-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D- glucopyranoside (13)

To a solution of **12** (50.0 mg, 82.1 μmol) in ethanol (4.0 mL) was added 1,4-diazabicyclo[2.2.2]octane (58 mg, 517 μmol), and the mixture was stirred at 50°C for 30 min. The solution was evaporated and the residue was purified by silica gel chromatography with 6:1 (v/v) hexane–ethyl acetate to give **13** (39.0 mg, 89%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.38–7.26 (m, 5 H, *Ph*-CH_2), 6.92–6.88 (m, 2 H, Ph), 6.83–6.77 (m, 2 H, Ph), 5.11 (dd, 1 H, $J_{2,3} = 9.2$ Hz, H-2), 4.87 (d, 1 H, $J = 11.6$ Hz, Ph-*CH*-), 4.84 (d, 1 H, $J_{1,2} = 8.0$ Hz, H-1), 4.65 (d, 1 H, Ph-*CH*-), 3.86 (m, 2 H, H-3, 6a), 3.70 (s, 3 H, O*CH*$_3$), 3.68 (dd, 1 H, $J_{5,6b} = 4.4$ Hz, $J_{6a,6b} = 12.4$ Hz, H-6b), 3.59 (t, 1 H, $J_{4,5} = 9.6$ Hz, H-4), 3.49–3.45 (m, 1 H, $J_{5,6a} = 2.8$ Hz, H-5), 2.11 (s, 3 H, Ac), 0.91 (s, 9 H, *t*-Bu), 0.08 (s, 6 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,101 MHz): 169.4, 155.4, 151.3, 137.8, 128.4, 127.8, 127.6, 118.1, 114.6, 100.5 (C-1), 78.2 (C-4), 75.6 (C-5), 75.1, 74.9 (C-3), 73.7 (C-2), 61.8 (C-6), 55.6, 25.7, 21.3, 17.9, −4.1, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{28}H_{40}O_8Si$+Na^+): 555.2390; found m/z: 555.2387.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside (14)

Compound **13** (5.10 g, 9.57 mmol) was dissolved in dichloromethane (19.1 mL), and pyridine (3.87 mL, 47.8 mmol) and acetic anhydride (2.71 mL, 28.7 mmol) were added. The mixture was stirred at rt for 16.5 h. The solution was evaporated and the residue was purified by silica gel chromatography with 100:1 (v/v) toluene–acetone to give acetate (5.25 g, 96%). The acetate (4.98g, 8.66 mmol) was dissolved in acetonitrile (155 mL) and cooled at –40°C. To the solution was added boron trifluoride–ethyl ether complex (2.18 mL, 17.4 mmol) diluted with acetonitrile (18.2 mL), and the mixture was stirred

at 0°C for 15 min. The solution was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 6:1 (v/v) toluene–ethyl acetate to give **14** (3.60 g, 71%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.38–7.26 (m, 5 H, *Ph*-CH_2), 6.96–6.92 (m, 2 H, Ph), 6.82–6.78 (m, 2 H, Ph), 5.11 (dd, 1 H, $J_{2,3}$ = 9.6 Hz, H-2), 4.87 (d, 1 H, J = 11.2 Hz, Ph-*CH*-), 4.84 (d, 1 H, $J_{1,2}$ = 7.6 Hz, H-1), 4.69 (d, 1 H, Ph-*CH*-), 4.38 (dd, 1 H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.25 (dd, 1 H, $J_{5,6b}$ = 5.0 Hz, H-6b), 3.86 (m, 1 H, $J_{3,4}$ = 9.6 Hz, H-3), 3.76 (s, 3 H, O*CH*$_3$), 3.64–3.55 (m, 2 H, H-4, 5), 2.86 (d, 1 H, $J_{3,OH}$ = 4.8 Hz, 3-OH), 2.14 (s, 3 H, Ac), 2.04 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,101 MHz): 170.9, 170.7, 155.6, 151.2, 137.6, 128.7, 128.3, 128.2, 118.6, 114.5, 100.1 (C-1), 77.7 (C-4), 76.1 (C-3), 74.9, 74.2 (C-2), 73.0 (C-5), 63.0 (C-6), 55.7, 20.9, 20.8; MALDI-TOF HRMS (positive ion): calcd for ($C_{24}H_{28}O_9$+Na^+): 483.1631; found m/z: 483.1632.

para-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-(2,3,4,6- tetra-*O*-acetyl-β-D-glucosyl)-β-D-glucopyranoside (15)

To a solution of **7** (60.1 mg, 122 μmol) and **13** (50.0 mg, 93.9 μmol) in dichloromethane (470 μL) was added molecular sieves 4Å powder (4.14 g), and the mixture was stirred at rt for 1.0 h and cooled at –40°C. To the mixture was added boron trifluoride–ethyl ether complex (3.1 μL, 24.6 μmol) and it was stirred at –40°C for 2.0 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 3:1 (v/v) hexane–ethyl acetate to give **15** (70.6 mg, 87%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.35–7.30 (m, 5 H, *Ph*-CH_2-), 6.93–6.92 (m, 2 H, Ph), 6.88–6.85 (m, 2 H, Ph), 5.16–5.05 (m, 3 H, H-2, 3′, 4′), 5.01 (t, 1 H, $J_{1,2}$ = 8.4 Hz, H-2′), 4.85 (d, 1 H, J = 11.2 Hz, Ph-*CH*-), 4.76 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1), 4.56 (d, 1 H, $J_{1,2}$ = 8.4 Hz, H-1′), 4.53 (d, 1 H, Ph-*CH*-), 4.22 (dd, 1 H, $J_{5',6a'}$ = 4.4 Hz, $J_{6a',6b'}$ = 12.4 Hz, H-6a′), 4.09 (dd, 1 H, $J_{5',6b'}$ = 2.4 Hz, H-6b′), 4.04 (br-d, 1 H, $J_{6a,6b}$ = 10.0 Hz, H-6a), 3.84 (t, 1 H, $J_{3,4}$ = 9.0 Hz, H-3), 3.78 (s, 3 H, O*CH*$_3$), 3.67–3.54 (m, 3 H, H-5, 5′, 6b), 3.35 (t, 1 H, H-4), 2.11 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.07 (s, 3 H, Si-C*H*$_3$), 0.06 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6, 170.2, 169.3, 169.3, 169.2, 155.4, 151.5, 137.5, 128.4, 128.3, 127.9, 127.7, 117.9, 114.7, 100.4 (C-1′), 100.4 (C-1), 78.8 (C-4), 75.5 (C-5), 75.2, 74.9 (C-3), 73.6 (C-2), 72.9 (C-3′), 71.8 (C-5′), 71.1 (C-2′), 68.3 (C-4′), 68.0 (C-6′), 61.9

(C-6), 55.6, 25.7, 21.2, 20.6, 20.6, 20.5, 20.5, 17.9, −4.1, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{42}H_{58}O_{17}Si+Na^+$): 885.3341; found *m*/*z*: 885.3364.

para-Methoxyphenyl 3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*- chloroacetyl-β-D-glucopyranosyl)-2,6-di-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside (16)

To a solution of **11** (1.05 g, 1.72 mmol) and **14** (1.70 g, 3.43 mmol) in dichloromethane (8.58 mL) was added molecular sieves 4Å powder (4.3 g), and the mixture was stirred at rt for 2.0 h and cooled at –40°C. To the mixture was added boron trifluoride–ethyl ether complex (86.8 μL, 860 μmol) diluted in dichloromethane (1.72 mL) and stirred at –40°C for 4.5 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 4:1 (v/v) hexane-ethyl acetate and reverse phase silica gel chromatography with 1:9 to 17:3 (v/v) acetonitrile–water to give **16** (1.10 g, 68%) and the recovery of acceptor **14** (1.11 g, 65%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.34–7.26 (m, 10 H, *Ph*-CH_2), 6.90–6.87 (m, 2 H, Ph), 6.80–6.78 (m, 2 H, Ph), 5.12 (dd, 1 H, $J_{1,2}$ = 7.6 Hz, H-2), 5.00–4.94 (m, 2 H, H-2′, Ph-*CH*-), 4.84 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.80 (d, 1 H, $J_{1,2}$ = 7.6 Hz, H-1), 4.62 (d, 1 H, $J_{1',2'}$ = 8.0 Hz, H-1′), 4.52 (d, 1 H, J = 11.2 Hz, Ph-CH_2-), 4.50 (d, 1 H, Ph-CH_2-), 4.36 (dd, 1 H, $J_{5',6a'}$ = 2.2 Hz, $J_{6a',6b'}$ = 11.6 Hz, H-6a′), 4.27 (br-d, 1 H, $J_{6a,6b}$ = 10.8 Hz, H-6a), 4.16–4.09 (m, 2 H, H-6b, 6b′), 4.01 (m, 1 H, H-3), 3.77 (m, 1 H, H-3′), 3.76 (s, 3 H, OCH_3), 3.66 (d, 2 H, J = 3.6 Hz, ClAc), 3.61–3.47 (m, 4 H, H-4, 4′, 5, 5′), 2.15 (s, 6 H, Ac), 1.93 (s, 3 H, Ac), 0.91 (s, 9 H, *t*-Bu), 0.09 (s, 6 H, Si-CH_3); ^{13}C NMR ($CDCl_3$,101 MHz): 170.6, 169.9, 168.9, 166.7, 155.4, 150.9, 137.9, 137.2, 128.5, 128.2, 128.0, 128.0, 127.8, 118.3, 114.4, 100.8 (C-1′), 99.6 (C-1), 80.5 (C-3), 78.1 (C-3′), 77.2 (C-4′), 75.3 (C-4), 75.1, 74.3, 74.2 (C-2′), 73.1 (C-2), 73.1 (C-5′), 72.9 (C-5), 72.6, 64.3 (C-6′), 62.6 (C-6), 55.6, 40.4, 25.6, 21.2, 20.9, 20.7, 17.8, −4.0, −4.5; MALDI-TOF HRMS (positive ion): calcd for ($C_{47}H_{61}ClO_{16}Si+Na^+$): 967.3315; found *m*/*z*: 967.3362.

para-Methoxyphenyl 2,3-di-*O*-acetyl-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D- glucosyl)-β-D-glucopyranoside (17)

Compound **15** (80 mg, 92.7 μmol) was dissolved in acetonitrile (1.60 mL), and the solution was cooled at –20°C. To the solution was added boron trifluoride–ethyl ether complex (23.3 μL, 185 μmol) diluted with acetonitrile (0.24 mL) and the mixture was stirred at –20°C for 13 min. The solution was

diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 5:1 to 1:1 (v/v) toluene–ethyl acetate to give **20** (69 mg, 100%). To a solution of **20** (20.0 mg, 26.7 μmol) in dichloromethane (350 μL) was added pyridine (108 μg, 1.34 mmol) and acetic anhydride (76 μg, 0.801 mmol), and the mixture was stirred at rt for 4.5 h. The solution was evaporated under vacuum to give **17** (39.0 mg, 89%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.34–7.25 (m, 5 H, *Ph*-CH_2), 6.95–6.93 (m, 2 H, Ph), 6.88–6.86 (m, 2 H, Ph), 5.30 (t, 1 H, $J_{2,3} = 9.6$ Hz, H-3), 5.17–5.07 (m, 3 H, H-2, 3′, 4′), 5.03 (br-t, 1 H, H-2′), 4.94 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1), 4.63 (d, 1 H, $J_{1',2'} = 8.0$ Hz, H-1′), 4.61 (d, 1 H, $J = 11.4$ Hz, Ph-CH_2-), 4.57 (d, 1 H, Ph-CH_2-), 4.22 (dd, 1 H, $J_{5',6a'} = 4.8$ Hz, $J_{6a',6b'} = 12.6$ Hz, H-6a′), 4.12 (dd, 1 H, $J_{5',6b'} = 2.4$ Hz, H-6b′), 4.09 (br-d, 1 H, $J_{6a,6b} = 10.8$ Hz, H-6a), 3.79 (s, 3 H, OCH_3), 3.79–3.70 (m, 2 H, H-5, 6b), 3.59 (t, 1 H, $J_{3,4} = 9.0$ Hz, H-4), 3.58–3.55 (m, 1 H, H-5′), 2.06 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.90 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 171.5, 170.6, 168.9, 166.9, 155.5, 151.0, 137.9, 137.4, 128.6, 128.3, 128.3, 128.2, 127.9, 127.8, 118.4, 114.5, 100.6 (C-1′), 99.9 (C-1), 81.1 (C-3), 77.2 (C-4′), 76.6 (C-3′), 74.8 (C-4), 74.7, 74.5, 74.0 (C-2′), 73.0 (C-2), 73.0 (C-5′), 72.5 (C-5), 64.3 (C-6′), 62.7 (C-6), 55.6, 40.4, 21.0, 20.7, 20.7; MALDI-TOF HRMS (positive ion): calcd for ($C_{38}H_{46}O_{18}$+Na^+): 813.2582; found m/z: 813.2546.

2-*O*-Acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D- glucosyl)-α-D-glucopyranosyl 2,2,2-trichloroacetimidate (18)

Compound **15** (150 mg, 174 μmol) was dissolved in acetonitrile/water (6.1 mL, 4.1/1, v/v), and the solution was cooled at 0°C. To the solution was added cerium (IV) ammonium nitrate (476 mg, 868 μmol) diluted with acetonitrile/water (2.5 mL, 4/1, v/v), and the mixture was stirred at 0°C for 7 min. The solution was poured into aqueous sodium hydrogen carbonate, extracted with dichloromethane, washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 3:1 (v/v) toluene–ethyl acetate to give an intermediate with a free 1-hydroxyl group (121 mg, 92%). The intermediate (120 mg, 159 μmol) dissolved in dichloromethane (1.6 mL) and trichloroacetonitrile (79.7 μL, 795 mmol) was cooled on an ice bath. Then to the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (3.6 μL, 23.9 μmol) and the mixture was stirred at rt for 31 h. The solution was concentrated and the residue was purified by silica gel chromatography with 10:1 to 3:1 (v/v) toluene–ethyl acetate to give **18** (107 mg, 75%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 8.55 (s, 1 H, N*H*α),

7.38–7.29 (m, 5 H, *Ph*-CH_2), 6.50 (d, 1 H, $J_{1,2} = 3.2$ Hz, H-1α), 5.19–5.02 (m, 3 H, H-2′, 3′, 4′), 4.88–4.85 (m, 2 H, H-2, Ph-*CH*-), 4.59–4.54 (m, 2 H, $J_{1',2'} = 8.0$ Hz, H-1′, Ph-*CH*-), 4.26–4.20 (m, 2 H, H-3, 6a′), 4.11 (dd, 1 H, $J_{5',6b'} = 2.4$ Hz, $J_{6a',6b'} = 10.4$ Hz, H-6b′), 4.06 (br-d, 1 H, $J_{5,6a} = 1.6$ Hz, $J_{6a,6b} = 11.2$ Hz, H-6a), 4.00 (m, 1 H, H-5), 3.76 (dd, 1 H, $J_{5,6b} = 4.4$ Hz, H-6b), 3.65 (m, 1 H, H-5′), 3.53 (t, 1 H, $J_{3,4} = 9.2$ Hz, H-4), 2.06 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.09 (s, 3 H, Si-C*H*$_3$), 0.08 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,101 MHz): 170.7, 170.3, 170.0, 169.3, 169.1, 161.0, 137.7, 128.5, 127.9, 127.5, 100.4 (C-1′), 93.8 (C-1), 78.1 (C-4), 75.2, 73.2 (C-2), 73.0 (C-5), 73.0 (C-3′), 71.9 (C-5′), 71.8 (C-3), 71.2 (C-4′), 68.3 (C-2′), 67.6 (C-6), 61.8 (C-6′), 25.7, 20.8, 20.7, 20.6, 20.6, 18.0, −4.1, −4.5.

2,3-Di-*O*-acetyl-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucosyl)-D- glucopyranosyl 2,2,2-trichloroacetimidate (19)

Compound **17** (1.10 g, 1.39 mmol) was dissolved in acetonitrile/water (27.5 mL, 4/1, v/v), and the solution was cooled at 0°C. To the solution was added cerium (IV) ammonium nitrate (3.81 g, 6.95 mmol) dissolved with acetonitrile/water (10.4 mL, 4.2/1, v/v), and the mixture was stirred at 0°C for 17 min. The solution was poured into aqueous sodium hydrogen carbonate, extracted with dichloromethane and washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 2:1 (v/v) toluene–ethyl acetate to give an intermediate with a free 1-hydroxyl group (896 mg, 94%). The intermediate (813 mg, 1.19 mmol) dissolved in dichloromethane (1.19 mL) and trichloroacetonitrile (597 μL, 5.95 mmol) was cooled on an ice bath. To the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (26.6 μL, 179 μmol) and the mixture was stirred at rt for 8.5 h. The solution was concentrated and the residue was purified by silica gel chromatography with 3:1 to 2:1 (v/v) toluene–ethyl acetate to give **19** (928 mg, 94%, α:β = 10:1) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 8.76 (s, 1 H, N*H*β), 8.63 (s, 1 H, N*H*α), 6.50 (d, 1 H, $J_{1\alpha,2} = 1.8$ Hz, H-1α), 5.84 (d, 1 H, $J_{1\beta,2} = 8.0$ Hz, H-1β), 5.63 (t, 1 H, $J_{3,4} = 9.0$ Hz, H-3), 5.20 (t, 1 H, $J_{3',4'} = 9.0$ Hz, H-3′), 5.11 (t, 1 H, H-4′), 5.08–5.03 (m, 2 H, H-2, 2′), 4.63 (d, 1 H, $J_{1',2'} = 7.2$ Hz, H-1′), 4.59 (s, 2 H, H-2, Ph-*CH*-), 4.26–4.18 (dd, 1 H, $J_{5',6a'} = 3.9$ Hz, $J_{6a',6b'} = 12.6$ Hz, H-6a′), 4.11 (br-d, 1 H, H-6b′), 4.09 (br-d, 2 H, H-5, 6a), 4.00 (m, 1 H, H-5), 3.86 (dd, 1 H, $J_{5,6b} = 3.3$ Hz, $J_{6a,6b} = 11.2$ Hz, H-6b), 3.77 (t, 1 H, H-4), 3.69 (m, 1 H, H-5′), 2.07 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.98 (br-s, 9 H, Ac); ^{13}C NMR ($CDCl_3$, 151 MHz): 170.6, 170.3, 170.0, 169.6, 169.3, 169.0, 161.0, 137.2, 129.0, 128.6, 128.2, 127.9, 125.2, 100.4 (C-1′), 93.3 (C-1α), 90.8 (C-1β), 75.6, 74.8, 72.9, 72.6, 71.9, 71.5, 71.3, 68.2, 67.3, 61.8, 20.8, 20.7, 20.5, 20.4.

para-Methoxyphenyl 2-*O*-acetyl-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-O-acetyl-β-D-glucosyl)- β-D-glucopyranoside (20)

Compound **15** (150 mg, 174 μmol) was dissolved in acetonitrile (3.00 mL) and cooled at –20°C. To the solution was added boron trifluoride–ethyl ether complex (43.7 μL, 358 μmol) diluted with acetonitrile (0.48 mL) and the mixture was stirred at –20°C for 17 min. The solution was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 5:1 to 1:1 (v/v) toluene–ethyl acetate to give **20** (127 mg, 98%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.34 (m, 5 H, *Ph*-CH_2), 6.95 (br-d, 2 H, Ph), 6.87 (br-d, 2 H, Ph), 5.17–4.99 (m, 4 H, H-2, 2′, 3′, 4′), 4.88 (d, 1 H, J = 12.0 Hz, Ph-*CH*-), 4.85 (d, 1 H, $J_{1,2}$ = 9.2 Hz, H-1), 4.67 (d, 1 H, Ph-*CH*-), 4.63 (d, 1 H, $J_{1,2}$ = 8.0 Hz, H-1′), 4.24–4.15 (m, 2 H, $J_{5',6a'}$ = 4.4 Hz, $J_{6a',6b'}$ = 12.4 Hz, H-6a′, 6b′), 4.10 (br-d, 1 H, $J_{6a,6b}$ = 11.2 Hz, H-6a), 3.86–3.79 (m, 2 H, H-3, 6b), 3.79 (s, 3 H, O*CH*$_3$), 3.64 (br-t, 1 H, H-5), 3.56 (m, 1 H, H-5′), 3.47 (br-t, 1 H, H-4), 2.14 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.90 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 170.8, 170.7, 170.2, 169.4, 169.2, 155.6, 151.2, 137.7, 128.6, 128.1, 128.1, 118.1, 114.7, 100.6 (C-1′), 99.8 (C-1), 78.1, 76.0, 75.3, 75.0, 74.1, 72.9, 71.8, 71.3, 68.3, 68.2, 61.7, 55.6, 20.9, 20.7, 20.6, 20.5; MALDI-TOF HRMS (positive ion): calcd for ($C_{36}H_{44}O_{17}$+Na^+): 771.2476; found m/z: 771.2467.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,3-di-*O*-acetyl-4-*O*-benzyl-6-*O*- chloroacethyl-β-D-glucopyranosyl)-β-D-glucopyranoside (21)

Compound **16** (1.60 g, 1.69 mmol) was dissolved in acetonitrile (30.4 mL) and the solution was cooled at –20°C. To the solution was added boron trifluoride–ethyl ether complex (425 μL, 3.38 mmol) diluted with acetonitrile (3.52 mL) and the mixture was stirred at 0°C for 30 min. The solution was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 3:1 to 1:1 (v/v) hexane–ethyl acetate to give **24** (1.40 g, 99%) as a white powder. To a solution of **24** (292 mg, 351 μmol) in dichloromethane (3.51 mL) was added pyridine (1.0 mL, 12.4 mmol) and acetic anhydride (1.0 mL, 10.6 mmol), and the mixture was stirred at rt for 17 h. The solution was diluted with dichloromethane and washed successively with aqueous 1M hydrochloric acid and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The

solution was concentrated and the residue was purified by silica gel chromatography with 6:1 to 3:1 (v/v) toluene–ethyl acetate to give **19** (274 mg, 89%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.37–7.22 (m, 10 H, *Ph*-CH_2), 6.89–6.87 (m, 2 H, Ph), 6.80–6.77 (m, 2 H, Ph), 5.25 (t, 1 H, $J_{3',4'}$ = 9.6 Hz, H-3′), 5.16 (dd, 1 H, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 9.0 Hz, H-2), 5.00 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 5.16 (dd, 1 H, $J_{1',2'}$ = 8.4 Hz, $J_{2',3'}$ = 9.6 Hz, H-2′), 4.77 (d, 2 H, H-1, H-1′), 4.60 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.51 (d, 1 H, Ph-*CH*-), 4.50 (d, 1 H, Ph-*CH*-), 4.36 (dd, 1 H, $J_{5',6a'}$ = 1.8 Hz, $J_{6a',6b'}$ = 12.0 Hz, H-6a′), 4.29–4.25 (m, 2 H, $J_{6a,6b}$ = 4.2 Hz, $J_{5,6a}$ = 6.6 Hz, H-6a, 6b′), 4.13 (m, 1 H, $J_{5,6b}$ = 1.8 Hz, H-6b), 4.02 (m, 1 H, H-3), 3.74 (s, 3 H, O*CH*$_3$), 3.68 (t, 1 H, H-4′), 3.62 (s, 1 H, ClAc), 3.58 (br-d, 1 H, H-4, 5), 2.17 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.95 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 151 MHz): 170.5, 170.1, 169.9, 169.0, 166.7, 155.5, 151.0, 137.9, 136.9, 128.6, 128.2, 128.1, 128.0, 127.7, 118.3, 114.4, 100.7 (C-1′), 99.8 (C-1), 81.2 (C-3), 77.2 (C-4′), 76.8 (C-3′), 75.1 (C-4), 74.8, 74.6, 74.4 (C-2′), 72.9 (C-2), 72.8 (C-5′), 72.5 (C-5), 71.5, 63.9 (C-6′), 62.6 (C-6), 55.5, 40.3, 20.9, 20.7, 20.6, 20.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{43}H_{49}ClO_{17}$+Na^+): 895.2556; found m/z: 895.2532.

3-*O*-(2-*O*-Acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-chloroacethyl-β-D- glucopyranosyl)-2,6-di-*O*-acetyl-4-*O*-benzyl-α-D-glucopyranosyl 2,2,2-trichloroacetimidate (22)

Compound **16** (1.10 g, 1.16 mmol) was dissolved in acetonitrile/water (29.0 mL, 4/1, v/v), and the solution was cooled at 0°C. To the solution was added cerium (IV) ammonium nitrate (3.18 g, 5.80 mmol) dissolved in acetonitrile/water (14.8 mL, 6/1, v/v), and the mixture was stirred at 0°C for 20 min. The solution was poured into aqueous sodium hydrogen carbonate, extracted with dichloromethane and washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 9:1 to 1:4 (v/v) hexane–ethyl acetate to give an intermediate with a free 1-hydroxyl group (958 mg, 98%). The intermediate (242 mg, 289 μmol) dissolved in dichloromethane (1.4 mL) and trichloroacetonitrile (146 μL, 1.45 mmol) was cooled on an ice bath. Then to the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (6.5 μL, 43.4 μmol) and the mixture was stirred at rt for 25 h. The solution was concentrated and the residue was purified by silica gel chromatography with 20:1 to 10:1 (v/v) toluene–ethyl acetate to give **22** (211 mg, 74%) as a syrup: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 8.62 (s, 1 H, N*H*α), 7.37–7.28 (m, 10 H, Ph), 6.39 (d, 1 H, $J_{1\alpha,2}$ = 3.6 Hz, H-1α), 5.00–4.93 (m, 3 H, H-2, 2′, Ph-*CH*-), 4.84 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.67 (d, 1 H, $J_{1'\beta,2'}$ = 8.4 Hz, H-1′β), 4.54 (d, 1 H, J = 11.2 Hz, Ph-*CH*-), 4.51 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.38 (dd, 1 H, $J_{5,6b}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.28–4.13 (m, 4 H, H-3, 6b, 6a′, 6b′), 3.99 (m, 4 H, H-5), 3.79

(t, 4 H, $J_{3',4'}$ = 9.0 Hz, H-3′), 3.71 (d, 2 H, J = 4.4 Hz, ClAcα), 3.59 (m, 2 H, H-4, 5′), 3.49 (t, 1 H, H-4′), 2.13 (s, 3 H, Ac), 2.13 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.08 (s, 3 H, Si-CH_3), 0.07 (s, 3 H, Si-CH_3); ^{13}C NMR ($CDCl_3$,101 MHz): 170.6, 169.8, 169.6, 166.8, 160.6, 137.7, 137.3, 128.5, 128.3, 128.0, 127.9, 127.7, 101.3 (C-1′), 93.3 (C-1), 90.8, 78.4, 78.2, 77.3, 75.3, 75.1, 74.6, 73.6, 73.4, 72.8, 72.6, 64.4, 62.1, 40.4, 25.6, 21.2, 20.8, 20.7, 17.8, −4.0, −4.4.

2,6-Di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,3-di-*O*-acetyl-4-*O*-benzyl-6-*O*-chloroacethyl-β-D-glucopyranosyl)-D-glucopyranosyl 2,2,2-trichloroacetimidate (23)

Compound **21** (380 mg, 435 μmol) was dissolved in acetonitrile/water (8.6 mL, 4.1/1, v/v), and the solution was cooled at 0°C. To the solution was added cerium (IV) ammonium nitrate (1.19 g, 2.18 mmol) dissolved in acetonitrile/water (3.6 mL, 4.2/1, v/v), and the mixture was stirred at 0°C for 15 min. The solution was poured into aqueous sodium hydrogen carbonate, extracted with dichloromethane and washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 2:1 to 1:1 (v/v) toluene–ethyl acetate to give an intermediate with a free 1-hydroxyl group (305 mg, 85%). The intermediate (290 mg, 378 μmol) dissolved in dichloromethane (1.9 mL) and trichloroacetonitrile (190 μL, 1.89 mmol) was cooled on an ice bath. Then to the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (8.5 μL, 56.9 μmol) and the mixture was stirred at rt for 12.5 h. The solution was concentrated and the residue was purified by silica gel chromatography with 6:1 to 3:1 (v/v) toluene–ethyl acetate to give **23** (343 mg, 99%; α:β = 25:1) as a syrup: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 8.64 (s, 1 H, N*H*), 7.35–7.23 (m, 10 H, Ph), 6.39 (d, 1 H, $J_{1\alpha,2}$ = 3.6 Hz, H-1α), 5.69 (d, 1 H, $J_{1\beta,2}$ = 7.2 Hz, H-1β), 5.25 (t, 1 H, $J_{2',3'}$ = 9.6 Hz, H-3′), 5.01–4.94 (m, 3 H, H-2, 2′, Ph-*CH*-), 4.84 (d, 1 H, $J_{1',2'}$ = 8.4 Hz, H-1′), 4.61 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.54 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.53 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.40 (br-d, 1 H, $J_{6a',6b'}$ = 12.0 Hz, H-6a′), 4.31–4.23 (m, 3 H, H-3, 6a, 6b′), 4.17 (dd, 1 H, $J_{5,6b}$ = 3.6 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6b), 4.00 (m, 1 H, H-5), 3.75 (s, 2 H, ClAc), 3.71–3.65 (m, 2 H, H-4′, 5′), 3.61 (t, 1 H, $J_{3,4}$ = 9.6 Hz, H-4), 2.15–1.95 (s, 12 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 170.5, 170.0, 169.9, 167.3, 166.8, 160.8, 137.7, 137.0, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 101.0 (C-1′), 93.3 (C-1), 90.8, 78.8, 78.15, 77.2, 75.3, 75.1, 74.7, 74.6, 74.1, 72.8, 72.2, 71.9, 71.2, 64.0, 62.1, 40.4, 20.8, 20.7, 20.5.

para-Methoxyphenyl 3-*O*-(2-*O*-acetyl-4-*O*-benzyl-6-*O*-chloroacethyl-β-D- glucopyranosyl)-2,6-di-*O*-acetyl-4-*O*-benzyl-β-D-glucopyranoside (24)

Compound **16** (200 mg, 212 μmol) was dissolved in acetonitrile (3.80 mL), and the solution was cooled at –20°C. To the solution was added boron trifluoride–ethyl ether complex (53.3 μL, 424 μmol) diluted with acetonitrile (0.44 mL) and the mixture was stirred at 0°C for 30 min. The solution was diluted with dichloromethane and washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 3:1 to 2:1 (v/v) toluene–ethyl acetate to give **24** (161 mg, 91%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.37–7.26 (m, 10 H, *Ph*-CH_2), 6.89 (d, 2 H, J = 9.0 Hz, Ph), 6.79 (d, 2 H, J = 9.0 Hz, Ph), 5.18 (t, 1 H, $J_{1,2}$ = 7.8 Hz, H-2), 5.00 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.85–4.82 (m, 2 H, H-2′, Ph-*CH*-), 4.78 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 4.70 (d, 1 H, J = 12.0 Hz, Ph-*CH*-), 4.69 (d, 2 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.49 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.36 (br-d, 1 H, $J_{6a',6b'}$ = 12.0 Hz, H-6a′), 4.30–4.78 (m, 2 H, H-6a, 6b′), 4.13 (m, 1 H, $J_{5,6b}$ = 3.0 Hz, $J_{6a,6b}$ = 11.4 Hz, H-6b), 4.02 (br-t, 1 H, $J_{3,4}$ = 8.4 Hz, H-3), 3.78 (m, 1 H, H-3′), 3.76 (s, 3 H, O*CH*$_3$), 3.68 (s, 2 H, ClAc), 3.60 (br-d, 2 H, H-4, 5), 3.57–3.50 (m, 2 H, H-4′, 5′), 2.55 (d, 1 H, J = 4.2 Hz, 3-OH), 2.19 (s, 3 H, Ac), 2.15 (s, 3 H, Ac), 1.96 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,101 MHz): 171.5, 170.6, 168.9, 166.9, 155.5, 151.0, 137.9, 137.5, 128.6, 128.4, 128.3, 128.2, 127.9, 127.8, 118.4, 114.5, 100.6 (C-1′), 99.9 (C-1), 81.1 (C-3), 77.2 (C-4′), 76.6 (C-3′), 74.8 (C-4), 74.7, 74.5, 74.0 (C-2′), 73.0 (C-2), 73.0 (C-5′), 72.5 (C-5), 64.3 (C-6′), 62.7 (C-6), 55.6, 40.4, 21.0, 20.7, 20.7; MALDI-TOF HRMS (positive ion): calcd for ($C_{41}H_{47}ClO_{16}$+Na^+): 853.2450; found m/z: 853.2463.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-((2- *O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D- glucopyranosyl)-6-*O*-chloroacetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl))-β-D-glucopyranoside (25)

To a solution of **18** (105 mg, 117 μmol) and **24** (80.0 mg, 97.1 μmol) in dichloromethane (900 μL) was added molecular sieves 4Å powder (100 mg), and the mixture was stirred for 30 min and cooled at –40°C. To the mixture was added boron trifluoride–ethyl ether complex (7.3 μL, 58.1 μmol) diluted in dichloromethane (70 μL) and stirred at –40°C for 2.0 h and then at –20°C for 2.0 h. To the mixture was added trimethylsilyl trifluoromethansulfonate (10.1 μL, 58.1 μmol) and it was stirred at 0°C for 3.0 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was

washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 6:1 (v/v) toluene–ethyl acetate and reverse-phase silica gel chromatography with 7:3 to 9:1 (v/v) methanol–water to give **25** (39.0 mg, 26%) as a white powder and the recovery of acceptor **14** (48.0 mg, 60%): ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.37–7.24 (m, 15 H, *Ph*-CH_2), 6.89–6.87 (m, 2 H, Ph), 6.80–6.79 (m, 2 H, Ph), 5.05–4.93 (m, 8 H, $J_{1'',2''} = 8.4$ Hz, H-1″, 2, 2′, 2″, 2‴, 3‴, 4‴, Ph-*CH*-), 4.89–4.83 (m, 3 H, H-1′, Ph-*CH*- ×2), 4.84 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1), 4.58–4.45 (m, 5 H, $J_{1''',2'''} = 7.8$ Hz, H-1‴, 6a, Ph-*CH*- ×3), 4.35 (dd, 1 H, $J_{5,6b} = 3.9$ Hz, $J_{6a,6b} = 12.0$ Hz, H-6b), 4.30 (dd, 1 H, $J_{5',6b'} = 1.2$ Hz, $J_{6a',6b'} = 12.0$ Hz, H-6a′), 4.15 (t, 1 H, $J_{3,4} = 9.0$ Hz, H-3), 4.10–4.06 (m, 2 H, H-3′, 6b′), 4.01 (m, 1 H, H-6a″), 3.91 (dd, 1 H, $J_{5''',6a'''} = 3.0$ Hz, $J_{6a''',6b'''} = 12.0$ Hz, H-6a‴), 3.86 (m, 1 H, H-5), 3.76 (m, 4 H, H-3, O*CH*$_3$), 3.71–3.68 (m, 3 H, H-4′, 5′, 6b‴), 3.60–3.56 (m, 3 H, H-4, ClAc), 3.54–3.50 (m, 2 H, H-5″, 6b″), 3.24 (t, 1 H, $J_{3'',4''} = 8.4$ Hz, H-4″), 2.83 (m, 1 H, H-5‴), 2.36 (s, 3 H, Ac), 2.17 (s, 3 H, Ac), 2.12 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.97 (s, 3 H, Ac), 1.86 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.08 (s, 3 H, Si-C*H*$_3$), 0.07 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6, 170.2, 170.0, 169.4, 169.1, 169.0, 169.0, 167.0, 155.4, 150.8, 138.0, 137.6, 137.1, 129.1, 129.0, 128.5, 128.3, 128.2, 127.9, 127.7, 118.0, 114.5, 101.1 (C-1″), 100.0 (C-1′), 99.8 (C-1), 98.8 (C-1‴), 80.1, 79.9, 79.1, 75.5, 75.4, 75.2, 74.9, 74.2, 73.7, 73.4, 73.2, 72.9, 72.7, 72.1, 71.8, 70.9, 68.0, 67.5, 64.1, 62.6, 61.5, 55.6, 40.5, 25.6, 22.7, 21.4, 21.3, 21.0, 20.8, 20.7, 20.6, 17.8, −4.0, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{76}H_{97}ClO_{31}Si$+Na^+): 1591.5369; found *m*/*z*: 1591.5359.

2,6-Di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-((4-*O*-benzyl-2,6-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-6-*O*-chloroacetyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl))-*β*-D-glucopyranoside (26)

To a solution of **19** (673 mg, 812 μmol) in dichloromethane (2.71 mL) was added molecular sieves 4Å powder (100 mg), and the mixture was stirred for 1 h and cooled at –40°C. To the solution was added boron trifluoride–ethyl ether complex (41 μL, 406 μmol), then added **24** (450 mg, 541 μmol) dissolved in dichloromethane (1.62 mL) dropwise, and the mixture was stirred at –40°C for 1.0 h, at 0°C for 1.5 h, and then at rt for 14 h. The mixture was diluted with dichloromethane and filtered through Celite. The filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by reverse-phase silica gel chromatography with 4:6 to 7:3 (v/v) acetonitrile–water to give **26** (450 mg, 56%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.37–7.23 (m, 15 H, *Ph*-CH_2), 6.89–6.88 (m, 2 H, Ph), 6.81–6.79 (m, 2 H, Ph),

5.25 (t, 1 H, $J_{3'',4''}$ = 9.3 Hz, H-3″), 5.08–4.93 (m, 9 H, $J_{1',2'}$ = 7.8 Hz, $J_{1'',2''}$ = 8.4 Hz, H-1′, 1″, 2, 2′, 2″, 2‴, 4‴, Ph-*CH*- ×2), 4.87 (t, 1 H, $J_{3''',4'''}$ = 9.0 Hz, H-3‴), 4.77 (d, 1 H, $J_{1,2}$ = 8.4 Hz, H-1), 4.70 (d, 1 H, $J_{1''',2'''}$ = 8.4 Hz, H-1‴), 4.61 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.56 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.52 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.51 (d, 1 H, J = 11.4 Hz, Ph-*CH*-), 4.47 (dd, 1 H, $J_{5'',6a''}$ = 1.8 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a″), 4.37 (dd, 1 H, $J_{5'',6b''}$ = 3.6 Hz, H-6b″), 4.30 (dd, 1 H, $J_{5',6a'}$ = 2.1 Hz, $J_{6a',6b'}$ = 11.7 Hz, H-6a′), 4.18 (t, 1 H, $J_{3,4}$ = 9.3 Hz, H-3), 4.10–4.07 (m, 3 H, H-3, 6a, 6b′), 3.92–3.88 (m, 2 H, H-5′, 6a‴), 3.76 (s, 3 H, O*CH*$_3$), 3.72–3.56 (m, 8 H, H-4, 4′, 5, 5″, 6b, 6b‴, ClAc), 3.45 (t, 1 H, H-4‴), 2.81 (m, 1 H, H-5‴), 2.14 (s, 3 H, Ac), 2.11 (s, 3 H, Ac ×3), 2.04 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.86 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6, 170.2, 170.0, 169.2, 169.1, 169.0, 169.0, 168.8, 167.0, 155.3, 150.7, 138.0, 137.4, 136.7, 129.0, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.8, 127.7, 117.9, 114.5, 100.7 (C-1″), 100.0 (C-1′), 99.7 (C-1), 98.7 (C-1‴), 80.5, 80.0, 79.1, 76.2, 75.7, 75.7, 75.1, 74.8, 74.8, 74.2, 73.4, 73.1, 72.8, 72.6, 71.9, 71.8, 71.7, 70.9, 67.8, 67.5, 64.0, 62.6, 61.3, 55.6, 40.4, 20.9, 20.9, 20.7, 20.6, 20.6, 20.5, 20.5; MALDI-TOF HRMS (positive ion): calcd for ($C_{72}H_{85}ClO_{32}$+Na^+): 1519.4610; found *m*/*z*: 1519.4638.

para-Methoxyphenyl2-*O*-acetyl-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D- glucopyranosyl)-3-*O*-(2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*- *tert*-butyldimethylsilyl-6-*O*-chloroacetyl-β-D-glucopyranosyl)-β-D- glucopyranosyl)-β-D-glucopyranoside (27)

To a solution of **20** (50 mg, 66.8 μmol) and **22** (197 mg, 200 μmol) in dichloromethane (628 μL) was added molecular sieves 4Å powder (200 mg), and the mixture was stirred for 30 min and cooled at –40°C. To the mixture was added trimethylsilyl trifluoromethansulfonate (3.6 μL, 20.0 μmol) diluted in dichloromethane (40 μL), and the mixture was stirred at –40°C for 0.5 h and then at rt for 5.5 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 5:1 to 4:1 (v/v) toluene–ethyl acetate to give **27** (34.2 mg, 27%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.40–7.17 (m, 15 H, *Ph*-CH_2), 6.91–6.84 (m, 4 H, Ph), 5.13–4.89 (m, 8 H, H-2, 2′, 2″, 2‴, 3‴, 4 ‴, Ph-*CH*- ×3), 4.84 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.58 (d, 1 H, $J_{1'',2''}$ = 8.0 Hz, H-1″), 4.56 (d, 1 H, $J_{1',2'}$ = 8.0 Hz, H-1′), 4.50 (d, 1 H, $J_{1''',2'''}$ = 7.6 Hz, H-1‴), 4.47 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.44 (d, 1 H, J = 11.6 Hz, Ph-*CH*-), 4.34 (dd, 1 H, $J_{5'',6a''}$ = 2.0 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a″), 4.22–3.99 (m, 7 H, H-3, 3″, 6a, 6a′, 6b″, 6a‴, 6b‴), 3.87 (t, 1 H, $J_{3',4'}$ = 8.0 Hz, H-3′), 3.78 (s, 3 H, O*CH*$_3$), 3.72 (m, 1 H, H-5″), 3.65–3.46 (m, 5 H, H-4″, 5, 6b, ClAc), 3.52–3.46

(m, 3 H, H-4′, 5′, 5‴), 3.39 (t, 1 H, $J_{3,4}$ = 8.6 Hz, H-4), 2.17 (s, 3 H, Ac), 2.15 (s, 6 H, Ac ×2), 2.05 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.99 (s, 3 H, Ac), 1.88 (s, 3 H, Ac), 1.63 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.09 (s, 3 H, Si-C*H*$_3$), 0.07 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6, 170.6, 170.2, 169.9, 169.3, 169.3, 169.2, 169.0, 167.7, 166.7, 155.5, 151.1, 138.0, 137.9, 137.3, 132.5, 130.9, 128.8, 128.5, 128.3, 128.3, 128.1, 128.0, 127.8, 127.8, 117.9, 114.7, 101.3 (C-1″), 100.6 (C-1‴), 100.4 (C-1′), 99.6 (C-1), 80.9, 80.3, 78.3, 75.5, 75.3, 75.2, 74.6, 74.5, 74.3, 73.3, 73.2, 73.1, 72.9, 72.6, 71.7, 71.3, 68.4, 68.2, 68.1, 64.4, 61.8, 60.4, 55.6, 40.4, 38.7, 30.4, 29.7, 28.9, 25.6, 23.7, 23.0, 21.3, 21.1, 20.9, 20.7, 20.6, 20.6, 20.5, 20.5, 17.8, 14.2, 14.0, 10.9, −4.0, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{76}H_{97}ClO_{31}Si$+Na^+): 1591.5369; found *m*/*z*: 1591.5344.

para-Methoxyphenyl *p*-Methoxy phenyl 2-*O*-acetyl-4-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*- acetyl-β-D-glucopyranosyl)-3-*O*-(2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(4-*O*-benzyl-2,3-di-*O*-acetyl-6-*O*-chloroacetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (28)

To a solution of **20** (279 mg, 373 μmol) in dichloromethane (1.86 mL) was added molecular sieves 4Å powder (1.0 g), and the mixture was stirred for 1 h and cooled at –40°C. To the mixture was added boron trifluoride–ethyl ether complex (18.8 μL, 186 μmol) and then **24** (340 mg, 373 μmol) dissolved in dichloromethane (1.24 mL) dropwise, and the mixture was stirred at –40°C for 1.0 h and at rt for 45 min. The mixture was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by reverse-phase silica gel chromatography with 4:6 to 3:1 (v/v) acetonitrile–water and silica gel chromatography with 9:1 to 17:3 (v/v) toluene–acetone to give **28** (82.2 mg, 15%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.34–7.22 (m, 15 H, *Ph*-CH_2 ×3), 6.90–6.85 (m, 4 H, Ph), 5.24 (t, 1 H, $J_{3',4'}$ = 9.3 Hz, H-3″), 5.11–4.93 (m, 8 H, H-2, 2′, 2″, 2‴, 3‴, 4‴, Ph-*CH*- ×2), 4.79 (d, 1 H, $J_{1,2}$ = 7.8 Hz, H-1), 4.71 (d, 1 H, $J_{1'',2''}$ = 7.8 Hz, H-1″), 4.60 (d, 1 H, *J* = 10.8 Hz, Ph-*CH*-), 4.51 (d, 1 H, *J* = 11.4 Hz, Ph-*CH*-), 4.50 (d, 1 H, $J_{1''',2'''}$ = 7.8 Hz, H-1‴), 4.45 (d, 1 H, *J* = 11.4 Hz, Ph-*CH*-), 4.44 (d, 1 H, *J* = 11.4 Hz, Ph-*CH*-), 4.35 (dd, 1 H, $J_{5'',6a''}$ = 2.4 Hz, $J_{6a'',6b''}$ = 12.0 Hz, H-6a″), 4.26 (dd, 1 H, $J_{5'',6b''}$ = 4.2 Hz, H-6b″), 4.21–4.18 (m, 2 H, H-6a′,6a‴), 4.11 (dd, 1 H, $J_{5',6b'}$ = 3.6 Hz, $J_{5',6b'}$ = 12.0 Hz, H-6b′), 4.07–4.01 (m, 3 H, H-3, 6b, 6b‴), 3.89 (t, 1 H, $J_{3',4'}$ = 9.0 Hz, H-3′), 3.77 (s, 3 H, O*CH*$_3$), 3.70–3.46 (m, 9 H, H-4′, 4″, 5′, 5′, 5″, 5‴, 6a), 2.19 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 2.08 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.99 (s, 3 H, Ac ×2), 1.87 (s, 3 H, Ac), 1.76 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6,

170.5, 170.1, 170.1, 169.8, 169.4, 169.3, 169.1, 169.0, 166.6, 155.4, 151.0, 138.0, 137.9, 136.9, 128.9, 128.8, 128.6, 128.5, 128.4, 128.2, 128.2, 128.1, 128.0, 127.9, 125.2, 117.8, 114.6, 100.9 (C-1″), 100.5 (C-1‴), 100.2 (C-1′), 99.4 (C-1), 81.5, 80.0, 75.5, 75.3, 75.1, 74.8, 74.5, 74.5, 74.4, 73.2, 72.9, 72.8, 72.8, 71.6, 71.5, 71.1, 68.3, 68.1, 63.9, 62.6, 61.7, 55.6, 40.3, 21.0, 20.9, 20.7, 20.6, 20.5, 20.5, 20.4, 20.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{72}H_{85}ClO_{32}$+Na^+): 1519.4610; found *m*/*z*: 1519.4663.

2,6-Di-*O*-Acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-α-D-glucopyranosyl 2,2,2-trichloroacetimidate (29)

Compound **6** (2.51 g, 5.50 mmol) was dissolved in dichloromethane (20.0 mL), pyridine (4.00 mL, 49.5 mmol), and acetic anhydride (3.00 mL, 27.2 mmol), and the mixture was stirred at rt for 23.5 h. Then, the mixture was coevaporated with toluene. The residue was dissolved in acetone/water (139 mL, 4/1, v/v). To the solution was added *N*-bromosuccinimide (4.93 g, 27.7 mmol) and the mixture was stirred vigorously at rt for 100 sec. The solution was diluted with ethyl acetate and washed with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was dissolved in dichloromethane (18.4 mL) and trichloroacetonitrile (2.77 mL, 27.6 mmol) cooled on an ice bath. Then to the solution was added 1,8-diazabicyclo[5.4.0]-7-undecene (165 μL, 1.11 mmol) and the mixture was stirred at rt for 17 h. The solution was concentrated and the residue was purified by silica gel chromatography with 9:1 (v/v) hexane–ethyl acetate to give **29** (2.32 g, 68%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 8.56 (s, 1 H, N*H*), 7.37–7.29 (m, 5H, Ph), 6.48 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H-1), 4.93–4.88 (m, 2 H, H-2, Ph-*CH*-), 4.56 (d, 1 H, *J* = 11.2 Hz, Ph-*CH*-), 4.34 (dd, 1 H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.0 Hz, H-6a), 4.26 (t, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.13 (dd, 1 H, $J_{5,6b}$ = 3.6 Hz, H-6b), 4.02 (br-d, 1 H, H-5), 3.58 (t, 1 H, H-4), 2.05 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 0.91 (s, 9 H, t-Bu), 0.13 (s, 3 H, CH_3), 0.11 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$,101 MHz): 170.5, 170.1, 161.0, 137.3, 128.6, 128.1, 127.9, 93.7 (C-1α), 77.7, 75.6, 72.9, 72.0, 71.8, 62.4, 25.7, 20.8, 20.8, 18.0, −4.0, −4.5.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,6-di-*O*-acetyl-4-*O*- benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-6-*O*-chloroacetyl-β-D- glucopyranosyl)-β-D-glucopyranoside (30)

To a solution of **29** (2.32 g, 3.78 mmol) and **24** (6.29 g, 7.57 mmol) in dichloromethane (34.2 mL) was added molecular sieves 4Å powder (8.6 g), and the mixture was stirred at rt for 1.0 h and cooled at –40°C for 30 min. To the mixture was added trimethylsilyl trifluoromethansulfonate (137 μL, 758 μmol)

diluted in dichloromethane (3.64 mL) and the mixture was stirred at –40°C for 50 min. Then the solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 19:1 to 12:1 (v/v) toluene–acetone to give **30** (4.23g, 87%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.35–7.24 (m, 15 H, *Ph*-CH_2), 6.89–6.87 (m, 2 H, Ph), 6.80–6.78 (m, 2 H Ph), 5.11 (d, 1 H, $J_{2,3} = 8.4$ Hz, H-2), 4.98–4.91 (m, 4 H, H-2′, 2″, Ph-*CH*- ×2), 4.89 (d, 1 H, $J = 11.4$ Hz, Ph-*CH*-), 4.84 (d, 1 H, $J = 12.0$ Hz, Ph-*CH*-), 4.80 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1), 4.61 (d, 1 H, $J_{1'',2''} = 7.8$ Hz, H-1″), 4.59 (d, 1 H, $J_{1',2'} = 7.8$ Hz, H-1′), 4.57 (d, 1 H, $J = 12.0$ Hz, Ph-*CH*-), 4.51 (d, 1 H, $J = 11.4$ Hz, Ph-*CH*-), 4.48 (d, 1 H, $J = 10.8$ Hz, Ph-*CH*-), 4.36 (br-d, 1 H, $J_{6a,6b} = 12.0$ Hz, H-6a), 4.26 (br-d, 1 H, H-6a″), 4.22 (dd, 1 H, $J_{5',6b'} = 2.4$ Hz, $J_{6a',6b'} = 12.0$ Hz, H-6a′), 4.17–4.11 (m, 3 H, H-6b, 6b′, 6b″), 3.99 (m, 1 H, H-3), 3.91 (dd, 1 H, $J_{2',3'} = 8.4$ Hz, $J_{3',4'} = 9.6$ Hz, H-3′), 3.77 (m, 1 H, H-3″), 3.75 (s, 3 H, O*CH*$_3$), 3.59–3.47 (m, 8 H, H-4, 4′, 4″, 5, 5′, 5″, ClAc), 2.17 (s, 3 H, Ac), 2.17 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 1.93 (s, 3 H, Ac), 1.84 (s, 3 H, Ac), 0.91 (s, 9 H, *t*-Bu), 0.09 (s, 3 H, Si-C*H*$_3$), 0.07 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,151 MHz): 170.6, 170.5, 170.0, 169.3, 169.1, 166.8, 155.5, 151.0, 137.8, 137.7, 137.4, 128.6, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 118.3, 114.5, 101.2 (C-1″), 100.4 (C-1′), 99.6 (C-1), 80.8, 80.7, 75.2, 74.7, 74.4, 74.1, 73.2, 73.2, 73.1, 72.9, 72.6, 64.2, 62.7, 62.6, 55.6, 40.4, 25.6, 21.3, 21.1, 20.9, 20.7, 20.6, 17.8, −4.0, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{64}H_{81}ClO_{23}Si$+Na^+): 1303.4524; found *m*/*z*: 1303.4525.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-6-*O*-chloroacetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-*β*-D-glucopyranosyl)-*β*-D-glucopyranoside (31)

To a solution of **7** (474 mg, 962 μmol) and **24** (400 mg, 481 μmol) in dichloromethane (1.6 mL) was added molecular sieves 4Å powder (1.6 g), and the mixture was stirred at rt for 30 min and cooled at –40°C for 30 min. To the mixture was added boron trifluoride–ethyl ether complex (60.4 μL, 481 μmol) diluted in dichloromethane (962 μL) and the mixture was stirred at –40°C for 2.0 h and then at rt for 15 h. Moreover, to the mixture was added boron trifluoride–ethyl ether complex (60.4 μL, 481 μmol) diluted in dichloromethane (962 μL), and it was stirred at rt for 1.0 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed successively with aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by

reverse-phase silica gel chromatography with 5:5 to 7:3 (v/v) acetonitrile–water to give **31** (336 mg, 60%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.31–7.25 (m, 10 H, *Ph*-CH_2), 6.89–6.88 (d, $J = 9.1$ Hz, 2 H, Ph), 6.80–6.79 (d, $J = 9.1$ Hz, 2 H Ph), 5.20–5.06 (m, 4 H, H-2, 2″, 3″, 4 ″), 5.01–4.95 (m, 4 H, H-2′, Ph-*CH*- ×2), 4.82 (d, 1 H, $J_{1,2} = 7.8$ Hz, H-1), 4.75 (d, 1 H, $J_{1'',2''} = 7.8$ Hz, H-1″), 4.61 (d, 1 H, $J_{1',2'} = 8.4$ Hz, H-1′), 4.52 (d, 1 H, $J = 11.6$ Hz, Ph-*CH*-), 4.49 (d, 1 H, $J = 11.2$ Hz, Ph-*CH*-), 4.33 (dd, 1 H, $J_{5'',6a''} = 3.9$ Hz, $J_{6a'',6b''} = 12.0$ Hz, H-6a″), 4.29–4.26 (m, 2 H, H-6a, 6a′), 4.21 (m, 1 H, H-6b), 4.10 (m, 2 H, H-6b′, 6b″), 4.01 (t, 1 H, $J_{3,4} = 8.2$ Hz, H-3), 3.94 (m, 1 H, H-3′), 3.76 (s, 3 H, O*CH*$_3$), 3.74 (m, 1 H, H-5″), 3.64–3.58 (m, 4 H, H-4, 5′, ClAc), 3.56–3.54 (m, 2 H, H-4′, 5), 2.20 (s, 3 H, Ac), 2.19 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.92 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,151 MHz): 170.5, 170.1, 169.7, 169.4, 169.3, 169.0, 166.8, 155.4, 150.8, 137.8, 137.5, 128.4, 128.2, 128.0, 127.9, 127.8, 118.2, 114.4, 101.0 (C-1″), 100.2 (C-1′), 99.4 (C-1), 81.6, 80.5, 74.6, 74.6, 74.3, 73.2, 72.8, 72.5, 71.7, 71.0, 68.2, 64.1, 62.6, 61.6, 55.6, 40.4, 21.1, 20.9, 20.6, 20.5, 20.5, 20.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{55}H_{65}ClO_{25}$+Na^+): 1183.3401; found m/z: 1183.3422.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (32)

To a solution of **30** (2.00 g, 1.56 mmol) in ethanol (78.0 ml) was added 1,4-diazabicyclo[2.2.2]octane (1.10 g, 9.81 mmol), and the mixture was stirred at 50°C for 7.5 h. The solution was diluted with dichloromethane and washed successively with aqueous 1M hydrochloric acid and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 9:1 to 5:1 (v/v) toluene–acetone to give **32** (1.88g, quantitative) as a white powder: ^{1}H NMR δ ($CDCl_3$, 500 MHz) 7.35–7.24 (m, 15 H, *Ph*-CH_2), 6.89 (d, $J = 8.5$ Hz, 2 H, Ph), 6.79 (d, $J = 9.1$ Hz, 2 H, Ph), 5.16 (t, 1 H, $J_{2'',3''} = 3.5$ Hz, H-2″), 5.01–4.89 (m, 4 H, H-2, 2′, Ph-*CH*- ×2), 4.83 (d, 1 H, $J = 11.5$ Hz, Ph-*CH*-), 4.78 (d, 1 H, $J_{1'',2''} = 8.0$ Hz, H-1″), 4.58 (d, 2 H, $J = 9.5$ Hz, H-1, Ph-*CH*-), 4.53 (d, 1 H, $J_{1',2'} = 8.0$ Hz, H-1′), 4.50–4.46 (d, 2 H, $J = 11.5$ Hz, Ph-*CH*- ×2), 4.36–4.30 (m, 2 H, H-6a, 6a″), 4.22–4.15 (m, 2 H, H-6b, 6b″), 3.96 (t, 1 H, $J_{2'',3''} = 8.3$ Hz, H-3″), 3.90 (t, 1 H, $J_{2',3'} = 9.0$ Hz, H-3′), 3.75 (m, 4 H, H-3, O*CH*$_3$), 3.64–3.60 (m, 3 H, H-4″, 5″, 6a′), 3.54–3.53 (m, 2 H, H-4, 5), 3.42 (t, 1 H, $J_{3',4'} = 8.8$ Hz, H-4′), 3.31–3.29 (m, 2 H, H-5′, 6b′), 2.18 (s, 3 H, Ac), 2.16 (s, 3 H, Ac), 2.15 (s, 3 H, Ac), 2.00 (s, 3 H, Ac), 1.80 (s, 3 H, Ac), 0.90 (s, 9 H, *t*-Bu), 0.08 (s, 3 H, Si-C*H*$_3$), 0.07 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,126 MHz): 170.6, 170.6, 170.0, 169.3, 169.1, 155.5, 151.0, 138.2, 137.9, 137.7, 129.0, 128.5, 128.5, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.7, 127.6,

125.3, 118.4, 114.5, 101.2 (C-1), 100.6 (C-1′), 99.9 (C-1″), 81.0, 80.7, 78.4, 75.7, 75.2, 75.2, 74.9, 74.7, 74.6, 73.4, 73.2, 73.1, 73.1, 73.0, 62.9, 62.6, 62.1, 55.6, 25.6, 21.3, 21.0, 20.9, 20.8, 20.6, 17.8, −4.0, −4.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{62}H_{80}O_{22}Si$ $+Na^+$): 1227.4808; found *m*/*z*: 1227.4826.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (33)

To a solution of **31** (280 mg, 241 μmol) in ethanol (12.0 mL) was added 1,4-diazabicyclo[2.2.2]octane (170 mg, 1.52 mmol), and the mixture was stirred at 50°C for 13 h. The solution was diluted with dichloromethane and washed successively with aqueous 1M hydrochloric acid and brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by silica gel chromatography with 3:1 to 1:1 (v/v) toluene–ethyl acetate to give **33** (258 mg, 99%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 400 MHz) 7.36–7.23 (m, 10 H, *Ph*-CH_2), 6.89 (d, J = 9.1 Hz, 2 H, Ph), 6.78 (d, J = 9.1 Hz, 2 H Ph), 5.20–4.89 (m, 7 H, H-2, 2′,2″, 3″, 4″, Ph-*CH*- ×2), 4.78 (d, 1 H, $J_{1',2'}$ = 7.8 Hz, H-1′), 4.74 (d, 1 H, $J_{1'',2''}$ = 8.0 Hz, H-1″), 4.58 (d, 1 H, J = 9.6 Hz, Ph-*CH*-), 4.55 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H-1), 4.47 (d, 1 H, J = 11.0 Hz, Ph-*CH*-), 4.33–4.28 (m, 2 H, H-6a′, 6a″), 4.18 (dd, 1 H, $J_{5',6a'}$ = 3.8 Hz, $J_{6a',6b'}$ = 11.8 Hz, H-6b′), 4.04-4.00 (m, 2 H, H-3′, 6b″), 3.92 (t, 1 H, $J_{2,3}$ = 9.0 Hz, H-3), 3.71 (s, 3 H, O*CH*$_3$), 3.71–3.54 (m, 4 H, H-4′, 5′, 5″, 6a), 3.46 (t, 1 H, $J_{3,4}$ = 9.0 Hz, H-4), 3.40–3.30 (m, 2 H, H-5, 6b), 2.21 (s, 3 H, Ac), 2.14 (s, 3 H, Ac), 2.09 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.98 (s, 3 H, Ac), 1.96 (s, 3 H, Ac), 1.92 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$,101 MHz): 170.3, 169.9, 169.5, 169.2, 169.0, 168.8, 155.3, 150.7, 137.8, 137.5, 137.4, 128.8, 128.6, 128.2, 128.2, 128.1, 128.0, 128.0, 127.8, 127.6, 127.6, 127.5, 127.1, 118.1, 114.3, 100.9 (C-1″), 100.2 (C-1′), 99.5 (C-1), 81.5, 80.0, 75.6, 75.2, 74.7, 74.5, 73.0, 72.8, 72.7, 72.6, 72.4, 70.9, 68.0, 62.3, 61.6, 61.5, 55.3, 21.2, 20.8, 20.7, 20.4, 20.3, 20.2, 20.2; MALDI-TOF HRMS (positive ion): calcd for ($C_{53}H_{64}O_{24}$+Na^+): 1107.3685; found: *m*/*z*: 1107.3624.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-*tert*-butyldimethylsilyl-β-D-glucopyranosyl)-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (34)

To a solution of **7** (1.56 g, 3.17 mmol) and **32** (1.85 g, 1.53 mmol) in dichloromethane (13.8 mL) was added molecular sieves 4Å powder (5.00 g), and the mixture was stirred at rt for 1.0 h and then at –40°C for 30 min. To the mixture was added trimethylsilyl trifluoromethansulfonate (166 μL,

919 μmol) diluted in dichloromethane (1.49 mL) and the mixture was stirred at –40°C for 3.0 h. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 15:1 (v/v) toluene–acetone to give **34** (1.76 g, 75%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 500 MHz) 7.36–7.25 (m, 15 H, *Ph*-CH_2), 6.97–6.94 (m, 2 H, Ph), 6.80–6.77 (m, 2 H, Ph), 5.24 (dd, 1 H, $J_{2'',3''} = 9.5$ Hz, H-2″), 5.04 (d, 1 H, $J = 11.0$ Hz, Ph-*CH*-), 5.00–4.92 (m, 7 H, H-1″, 1‴, 2, 2′, 2‴, 4‴, Ph-*CH*-), 4.85–4.81 (m, 2 H, H-3‴, Ph-*CH*-) 4.58 (d, 1 H, $J_{1,2} = 8.0$ Hz, H-1), 4.55–4.47 (m, 4H, H-1′, Ph-*CH*- ×3), 4.45–4.43 (dd, 1 H, $J_{5'',6a''} = 1.8$ Hz, $J_{6a'',6b''} = 12.3$ Hz, H-6a″), 4.40–4.37 (dd, 1 H, $J_{5'',6b''} = 3.8$ Hz, H-6b″), 4.33 (br-d, 1 H, $J_{6a,6b} = 11.0$ Hz, H-6a), 4.26 (t, 1 H, $J_{2'',3''} = 9.3$ Hz, H-3″), 4.17–4.12 (m, 4H, H-5″, 6b), 4.00 (br-d, 1 H, $J_{6a',6b'} = 12.5$ Hz, H-6a′), 3.93 (t, 1 H, $J_{2',3'} = 9.0$ Hz, H-3′), 3.83–3.80 (dd, 1 H, $J_{5''',6a'''} = 3.0$ Hz, $J_{6a''',6b'''} = 12.5$ Hz, H-6a‴), 3.75 (m, 4 H, H-3, O*CH*$_3$), 3.70 (t, 1 H, $J_{3'',4''} = 9.5$ Hz, H-4″), 3.58–3.44 (m, 5 H, H-4, 5, 5′, 6b′, 6b‴), 3.28–3.25 (dd, 1 H, $J_{3',4'} = 9.5$ Hz, $J_{4',5'} = 8.5$ Hz, H-4′), 2.62 (br-d, 1 H, $J_{4''',5'''} = 9.5$ Hz, H-5‴), 2.35 (s, 3 H, Ac), 2.19 (s, 3 H, Ac), 2.17 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.03 (s, 3 H, Ac), 2.01 (s, 6 H, Ac ×2), 1.95 (s, 3 H, Ac), 1.79 (s, 3 H, Ac), 0.91 (s, 9 H, *t*-Bu), 0.09 (s, 3 H, Si-C*H*$_3$), 0.07 (s, 3 H, Si-C*H*$_3$); ^{13}C NMR ($CDCl_3$,126 MHz): 170.6, 170.6, 170.4, 170.3, 170.0, 169.2, 169.1, 168.6, 168.6, 155.1, 151.0, 137.6, 137.4, 137.4, 129.3, 129.0, 128.4, 128.4, 128.1, 127.9, 127.8, 127.5, 117.2, 114.3, 101.3 (C-1), 100.5 (C-1′), 99.9 (C-1″), 98.4 (C-1‴), 80.9, 79.6, 78.2, 77.5, 76.0, 75.9, 75.5, 75.1, 74.7, 73.3, 73.2, 73.1, 73.1, 73.0, 72.3, 71.8, 70.7, 67.6, 67.4, 62.7, 62.3, 61.1, 55.6, 25.6, 21.4, 21.3, 20.9, 20.8, 20.6, 20.6, 20.6, 20.5, 20.5, 17.8, −4.0, −4.5; MALDI-TOF HRMS (positive ion): calcd for ($C_{76}H_{98}O_{31}Si$+Na^+): 1557.5759; found m/z: 1557.5762.

para-Methoxyphenyl 2,6-di-*O*-acetyl-4-*O*-benzyl-3-*O*-(2-*O*-acetyl-4-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-6-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl)-β-D-glucopyranoside (35)

To a solution of **7** (41.0 mg, 83.2 μmol) and **34** (45.0 mg, 41.5 μmol) in dichloromethane (900 μL) was added molecular sieves 4Å powder (100 mg), and the mixture was stirred at rt for 1.0 h and at –40°C for 30 min. To the mixture was added trimethylsilyl trifluoromethansulfonate (3.0 μL, 16.6 μmol) diluted in dichloromethane (100 μL), and the mixture was stirred at –40°C for 35 min. The solution was diluted with dichloromethane and filtered through Celite, and the filtrate was washed with brine, dried over anhydrous sodium sulfate, filtered, and evaporated. The residue was purified by flash silica gel chromatography with 17:3 (v/v) toluene–acetone to give **35** (49.2 mg, 83%) as a white powder: ^{1}H NMR δ ($CDCl_3$, 600 MHz) 7.39–7.29 (m, 10 H, *Ph*-CH_2),

6.97–6.94 (m, 2 H, Ph), 6.80–6.78 (d, 2 H Ph), 5.25 (dd, 1 H, $J_{2,3}$ = 9.0 Hz, H-2‴), 5.20–5.13 (m, 2 H, H-3, 4), 5.09–5.06 (m, 2 H, H-2, Ph-*CH*-), 5.02–4.94 (m, 6 H, $J_{1″,2″}$ = 8.4 Hz, $J_{1‴,2‴}$ = 8.4 Hz, H-1″, 1‴, 2′, 2″, 4″, Ph-*CH*-), 4.85 (t, 1 H, $J_{2″,3″}$ = 9.0 Hz, H-3″), 4.74 (d, 1 H, $J_{1,2}$ = 8.4 Hz, H-1), 4.53 (m, 2 H, J = 10.2 Hz, H-1′, Ph-*CH*-), 4.46 (m, 2 H, J = 10.8 Hz, H-6a‴, Ph-*CH*-), 4.39 (dd, 1 H, $J_{5‴,6b‴}$ = 3.9 Hz, $J_{6a‴,6b‴}$ = 11.7 Hz, H-6b‴), 4.33 (dd, 1 H, $J_{5,6a}$ = 3.3 Hz, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.28 (t, 1 H, $J_{3‴,4‴}$ = 9.3 Hz, H-3‴), 4.15 (m, 1 H, H-5‴), 4.04 (m, 2 H, H-6b, 6a′), 3.95 (t, 1 H, $J_{2′,3′}$ = 9.0 Hz, H-3′), 3.82 (dd, 1 H, $J_{5″,6a″}$ = 3.0 Hz, $J_{6a″,6b″}$ = 12.6 Hz, H-6a″), 3.76 (s, 3 H, O*CH*$_3$), 3.79–3.70 (m, 2 H, H-4‴, 5), 3.60–3.47 (m, 3 H, H-5′, 6b′, 6b″), 3.32 (t, 2 H, $J_{3′,4′}$ = 8.6 Hz, H-4′), 2.61 (m, 1 H, H-5″), 2.35 (s, 3 H, Ac), 2.22 (s, 3 H, Ac), 2.11 (s, 3 H, Ac), 2.10 (s, 3 H, Ac), 2.05 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.02 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 2.01 (s, 3 H, Ac), 1.95 (s, 3 H, Ac), 1.94 (s, 3 H, Ac); ^{13}C NMR ($CDCl_3$, 151 MHz): 170.6, 170.6, 170.5, 170.3, 170.2, 169.8, 169.3, 169.1, 168.6, 155.1, 151.0, 137.4, 137.4, 129.3, 128.5, 128.4, 128.1, 128.0, 117.2, 114.4, 101.2 (C-1), 100.4 (C-1′), 99.9 (C-1″), 98.5 (C-1‴), 81.7, 79.6, 77.4, 76.0, 75.9, 75.1, 73.2, 73.1, 73.1, 72.3, 71.8, 71.6, 71.0, 70.7, 68.2, 67.5, 67.4, 62.2, 61.6, 61.1, 55.6, 20.9, 20.9, 20.8, 20.6, 20.6, 20.5, 20.4; MALDI-TOF HRMS (positive ion): calcd for ($C_{67}H_{82}O_{33}$+Na^+): 1437.4636; found m/z: 1437.4611.

SUPPLEMENTARY DATA

Supplementary data for this article including copies of the ^{1}H and ^{13}C NMR spectra of **5**, **6**, and **10–35** are available from the corresponding authors.

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