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Synthesis of Oligomeric 4-(Glycosyloxy)benzoate Macrocyclic Glycosides

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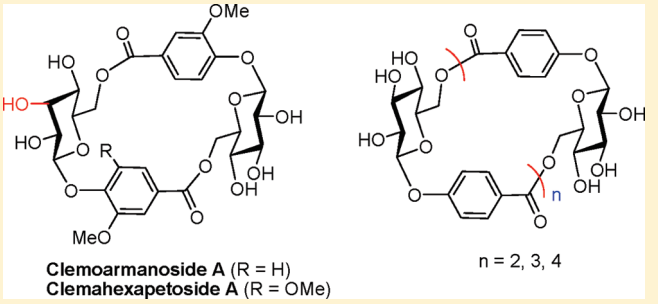
Supporting Information

ABSTRACT: Clemoarmanoside A and Clemahexapetoside A, two novel cyclic dimers of 4-(glycosyloxy)benzoates containing the unusual D-allopyranose as one of the sugar units, were synthesized for the first time. The convenient synthetic approach was adapted to the assembly of the symmetrical trimeric, tetrameric, and pentameric congeners. The synthesis clarified the discrepancy in the NMR data reported for the natural products. X-ray diffraction analysis of Clemahexapetoside A revealed that it adopted an armchair conformation with two carbohydrate rings as the arms and two aromatic rings as the back and seat, respectively.

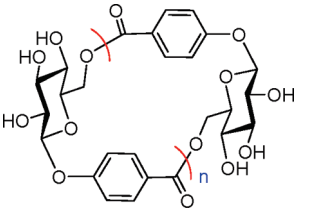


INTRODUCTION

Since 1992, eight cyclic dimers of 4-(glycosyloxy)benzoates have been identified from a variety of the folk medicinal plants (Table 1).[1−8] Compounds **1**, **2**, **5**, and **6** are homodimers, while compounds **3**, **4**, 7, and **8** consist of two slightly different monomers.

The cyclic structure of these natural metabolites is reminiscent of the artificial glycophanes,[9] which possess a chiral cavity with both hydrophilic and hydrophobic facets and thus could be utilized as a new type of host molecules. In addition, these scarce components of medicinal plants might possess various bioactivities. Thus, synthesis of these molecules and their congeners becomes an interesting subject. The homodimer **1** has been synthesized via cyclodimerization of 4-*O*-(2,3,4-tri-*O*-benzyl-*β*-D-glucopyranosyl) syringic acid.[10] Recently, compounds **1**−**3** were synthesized in a one-pot fashion via homo- and heterocyclodimerization of two types of the monomers using the fluorous mixture synthesis strategy.[11]

Different from other members, compounds 7 and **8**, named Clemoarmanoside A and Clemahexapetoside A, respectively, contain the unusual D-allopyranose as one of the sugar units. Their synthesis would require coupling of two disparate monomers prior to cyclization. The great discrepancy in the reported ^{1}H NMR data for Clemoarmanoside A (7) from two research groups was an additional impetus for us to embark on their synthesis.[5,6] Herein, we report the synthesis of these two novel cyclic glycosides, the X-ray diffraction analysis of Clemahexapetoside A (**8**), and the extension of the present synthetic approach to the preparation of trimeric, tetrameric, and pentameric congeners **9**−**11**.



9 (n=2), **10** (n=3), **11** (n=4)

RESULTS AND DISCUSSION

Synthesis of Clemoarmanoside A (7) and Clemahexapetoside A (8). To synthesize the cyclic heterodimers Clemoarmanoside A (7) and Clemahexapetoside A (**8**), three 4-(glycosyloxy) benzoate building blocks (i.e., **17**, **26**, and **27**) were designed, in that benzyl ethers were used as permanent protecting groups while trityl ether and allyl ester, which are selectively removable after ester condensation, were used as temporary protecting groups. The preparation of these 4-(glycosyloxy)benzoate derivatives were straightforward, as shown in Schemes 1 and 2.

Thus, glycosylation of methyl vanillate with peracetyl glucopyranosyl trifluoroacetimidate **12** under the action of $BF_3 \cdot Et_2O$ (0.1 equiv) in CH_2Cl_2 at 0 °C afforded the phenolic *β*-D-glucoside **13** (H-1, 5.07 ppm, J = 7.5 Hz) in a high 90% yield without detection of the corresponding α-anomer (Scheme 1).[12] Worth noting is that replacement of $BF_3 \cdot Et_2O$ with TMSOTf as the promoter in the present glycosylation reaction led to a complex mixture. Removal of the acetyl groups (K_2CO_3, MeOH,

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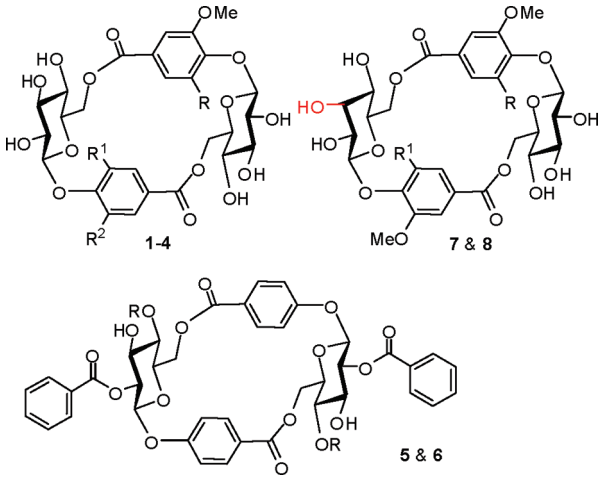
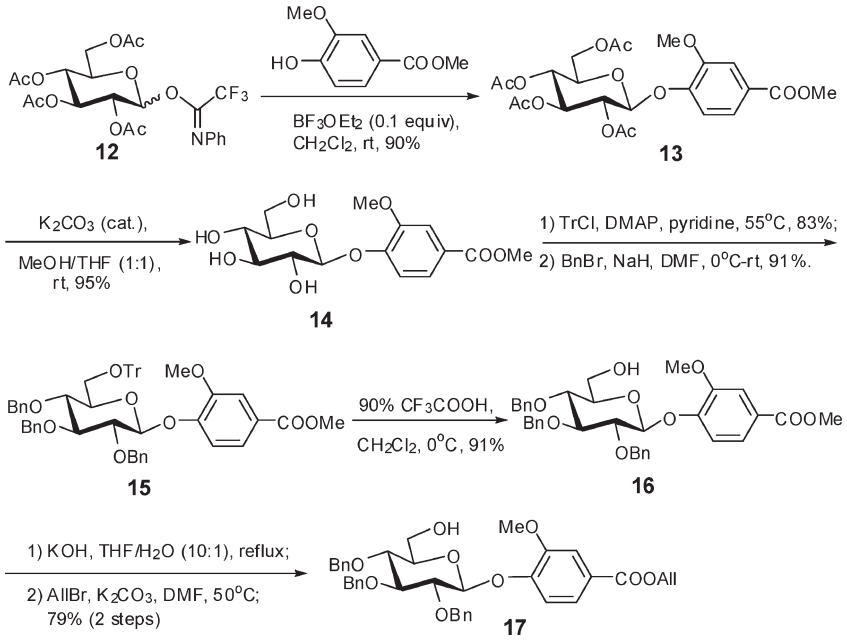
Table 1. Naturally Occurring Cyclic Dimers of 4-(Glycosyloxy)benzoates



compounds	plants and references
1 (Clemochinenoside A): R = R^1 = R^2 = OMe	*Clematis chinensis*,[1] *C. hexapetala*,[6] *C. hexapetala* (Ranunculaceae),[7] and *Capparis tenera* (Capparidaceae)[8]
2 (Berchemolide): R = R^1 = H, R^2 = OMe	*Berchemia racemosa* (Rhamnaceae)[2] and *Clematis armandii* (Ranunculaceae)[5]
3 (Clemochinenoside B): R = H, R^1 = R^2 = OMe	*Clematis chinensis*,[3] *C. armandii*,[5] *C. hexapetala* (Ranunculaceae),[7] and *Capparis tenera* (Capparidaceae)[8]
4 (Clemoarmanoside B): R = R^1 = R^2 = H	*Clematis armandii* (Ranunculaceae)[5]
5 (Pakistolide A): R = β-D-glucopyranosyl	*Berchemia pakistanica* (Rhamnaceae)[4]
6 (Pakistolide B): R = (4*Z*)-1,6-dioxohept-4-enyl	*Berchemia pakistanica* (Rhamnaceae)[4]
7 (Clemoarmanoside A): R = R^1 = H	*Clematis armandii*[5] and *C. hexapetala* (Ranunculaceae)[6]
8 (Clemahexapetoside A): R = H, R^1 = OMe	*Clematis hexapetala* (Ranunculaceae)[6]

Scheme 1. Preparation of 4-(Glucopyranosyloxy)benzoate Derivative 17



THF, rt, 95%) led to tetraol **14**,[11] which was subjected to selective protection of the primary 6-OH with trityl group (TrCl, pyridine, DMAP, 55 °C) followed by protection of the remaining 2,3,4-OHs with benzyl group to provide **15** (76% for two steps). The trityl group on **15** was removed with 90% CF_3COOH in CH_2Cl_2 at 0 °C to give **16** (91%).[13] Conversion of the methyl ester in **16** into allyl ester via hydrolysis (KOH, THF, H_2O, reflux) and subsequent allyl ester formation (AllBr, K_2CO_3, DMF, 50 °C, 79%)[14] furnished the desired 4-(glycosyloxy)benzoate building block **17**.

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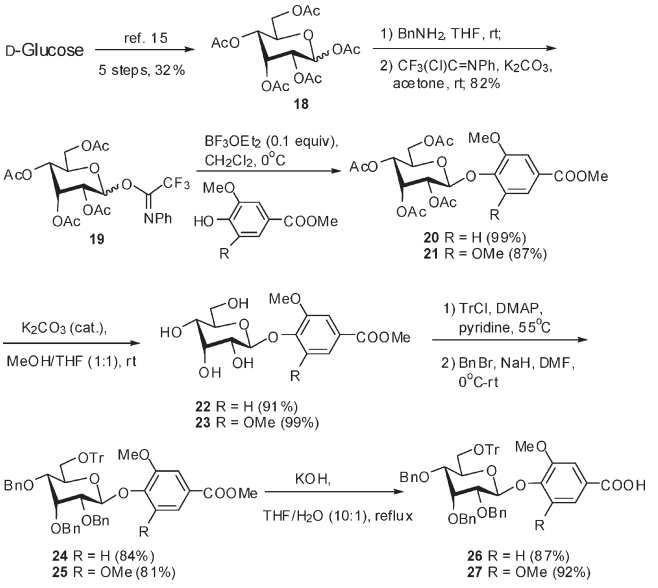
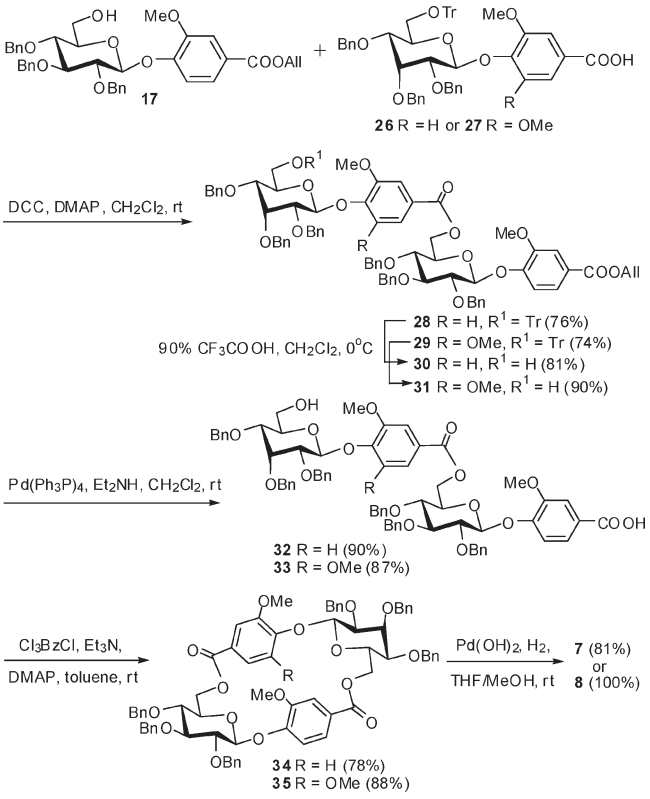
Scheme 2. Preparation of 4-(Allopyranosyloxy)benzoate Derivatives 26 and 27



Scheme 3. Assembly of the Macrocyclic Glycosides 7 and 8



1,2,3,4,6-Penta-*O*-acetyl-D-allopyranose **18** was prepared from D-glucose (5 steps, 32% overall yield) following a literature method (Scheme 2).[15] Selective removal of the anomeric acetyl group ($BnNH_2$, THF, rt) followed by trifluoroacetimidate formation ($CF_3(Cl)C{=}NPh$, K_2CO_3, acetone, rt; 82%)[12] provided allopyranosyl donor **19**. Glycosylation of methyl vanillate with **19** under the effect of $BF_3 \cdot Et_2O$ (0.1 equiv) in CH_2Cl_2 at 0 °C provided the desired β-D-allopyranoside **20** (H-1, 5.38 ppm, J = 8.4 Hz) nearly quantitatively. Similar conditions applied to the coupling of **19** with the stereohindered methyl syringate led to β-D-allopyranoside **21** (H-1, 5.32 ppm, J = 8.1 Hz) also in good yield (87%). Employing similar protecting group manipulations as that in the synthesis of glucoside **17** (Scheme 1), allosides **20** and **21** were readily converted into the desired 4-(allopyranosyloxy)benzoate building blocks **26** and **27** via four convenient steps, that is, deacetylation, selective tritylation, benzylation, and hydrolysis of methyl ester.

With building blocks **17**, **26**, and **27** in hand, the stage was set for final assembly of the target macrocyclic glycosides **7** and **8** (Scheme 3). Treatment with DCC and DMAP allowed alcohol **17** to be coupled with acid **26** or **27** to form ester **28** or **29** in ~75% yields. Removal of the 6-*O*-trityl group from **28** and **29** (90% CF_3COOH, CH_2Cl_2, 0 °C) followed by cleavage of the allyl ester ($Pd(PPh_3)_4$, Et_2NH, CH_2Cl_2, 0 °C)[16] afforded the key intermediates **32** and **33** in satisfactory yields. Intramolecular esterification of **32** and **33** proceeded sluggishly under the action of DCC and DMAP, leading to the desired cyclic esters **34** and **35** in <10% yields. Nevertheless, under the Yamaguchi conditions (2,4,6-trichlorobenzoyl chloride, Et_3N, DMAP)[17] in a diluted toluene solution (2.5×10^{-3} mol/L), **32** and **33** were converted into cyclic esters **34** and **35** in satisfactory yields (78 and 88%, respectively); polar byproducts were discerned on TLC, which were presumably derived from the intermolecular condensation. Finally, global removal of the benzyl groups on **34** and **35** was effected via hydrogenolysis over $Pd(OH)_2$, furnishing the target macrocyclic glycosides **7** and **8** in 81 and 100% yield, respectively.

The ^1H and ^{13}C NMR data of the synthetic compound **7** were identical to those of the natural product Clemoarmanoside A reported by Xu et al.[5] Identical ^{13}C NMR data were reported by Tu et al. for the same natural product; however, the ^1H NMR data Tu et al. provided were in great discrepancy.[6] The ^1H and ^{13}C NMR data of the natural compound Clemahexapetoside A reported by Tu et al. were also in apparent discrepancy with those of the synthetic compound **8**.[6] Fortunately, a single crystal of compound **8** was obtained, and the X-ray diffraction analysis confirmed the correctness of the synthetic structure.[18]

X-ray Diffraction Analysis of Clemahexapetoside A (8). Clemahexapetoside A (**8**) crystallized in the monoclinic crystal system with space group $P21$. Each unit cell of the crystal structure contained two identical macrocycles and five water molecules (Figures 1 and 2), with one water molecule disordered. The whole structure exhibited as an armchair with two carbohydrate rings as the arms and two aromatic rings (A, C8−C13; B, C22−C27) as the back and seat, respectively. The stability of the crystal structure resulted from dense networks of hydrogen bonds and hydrophobic interactions. The intramolecular hydrophobic interactions were observed between methyl group C29 and aromatic ring A. Intermolecular hydrophobic interactions mainly occurred between methyl C14 and aromatic ring B of the adjacent molecule. Hydroxyl groups of the two sugar units and H atoms of the five water molecules formed strong hydrogen bondings, which played a major role in the dense stacking of the crystal structure (see Supporting Information).

Synthesis of the Cyclic Trimer, Tetramer, and Pentamer 9−11. The above synthetic approach to natural cyclic dimers of 4-(glycosyloxy)benzoates was successfully adapted to the synthesis of larger cyclic congeners (i.e., **9**−**11**). Cyclic trimer **9**, which possesses a C_3 symmetry, was assembled starting from β-D-glucoside **36** (5 steps and 54% overall yield from D-glucose)[19]

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(Scheme 4). Thus, selective tritylation of the primary 6-OH on **36** followed by benzylation of the remaining OHs provided **37** (70% for 2 steps). Hydrolysis of the methyl ester on **37** gave acid **38** (91%). Removal of the trityl ether on **38** followed by chemoselective formation of the allyl ester furnished alcohol **40** (65% for 2 steps). Condensation of acid **38** and alcohol **40** under the action of EDCI and DMAP led to the dimer **41** in a satisfactory 87% yield. Under similar conditions, the corresponding alcohol resulting from **41** via removal of the trityl group was condensed with acid **38** to provide the linear trimer **42** in 61% yield (2 steps). The 90% CF_3COOH mediated detritylation of **42** led to **43** (85%). The allyl ester on **43** was cleaved smoothly with $Pd(PPh_3)_4$ (Et_2NH, CH_2Cl_2, 0 °C, 75%), and the resulting alcohol acid was subjected to the Yamaguchi conditions to afford the cyclic trimer **44** in a good 64% yield. Global cleavage of the benzyl groups via hydrogenolysis furnished the desired trimer **9** quantitatively.

Following a similar reaction sequence as in the trimer synthesis, tetramer **10** and pentamer **11** were successfully synthesized (Scheme 5). The intramolecular macrolactonization of the linear tetramer and pentamer under Yamaguchi conditions met with no problem, leading to the corresponding macrocyclic glycosides **47** and **50** in 60 and 50% yield, respectively. Interestingly, the final tetrameric cyclic glycoside **10** was hardly soluble in methanol, while the trimeric and pentameric congeners **9** and **11** were easily soluble. The ^{1}H NMR of the cyclic oligomers **9**−**11** showed only one set of the signals corresponding to the monomer 4-(glycosyloxy) benzoate, indicating that a symmetrical conformation was adopted by these macrocyclic glycosides in solution.

In summary, two natural cyclic dimers of 4-(glycosyloxy) benzoates containing the unusual D-allopyranose as one of the sugar units, Clemoarmanoside A (**7**) and Clemahexapetoside A (**8**), were synthesized for the first time. The synthesis clarified the discrepancy in the NMR data reported for these natural products. X-ray diffraction analysis of Clemahexapetoside A (**8**) revealed that it adopted an armchair conformation with two carbohydrate rings as the arms and two aromatic rings as the back and seat, respectively. The macrocyclic trimer, tetramer, and pentamer (**9**−**11**) were also assembled conveniently with the present synthetic approach. The inclusion properties of these macrocyclic glycosides as a new type of glycophanes will be studied, and the results will be reported in due course.

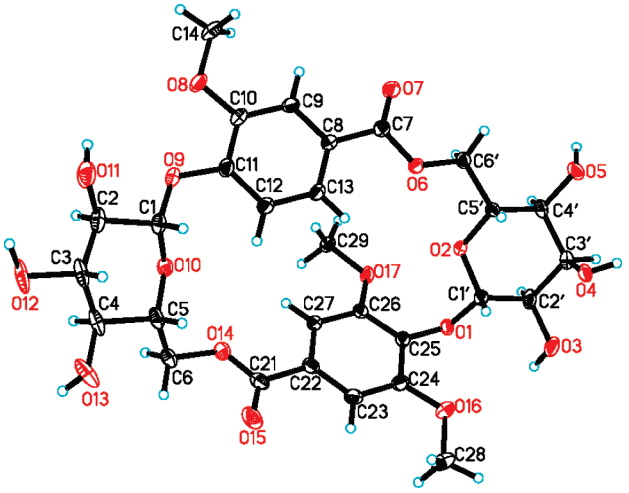

Figure 1. View of molecule **8** showing the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level for non-H atoms.

EXPERIMENTAL SECTION

Methyl 3-Methoxy-4-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-*β*-D-glucopyranosyloxy)benzoate (15). To a solution of glucoside **14** (1.7 g, 5.1 mmol) in pyridine (40 mL) were added TrCl (5.6 g, 20.0 mmol) and DMAP (62 mg, 0.5 mmol). After stirring at 55 °C for 5 h, the mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 40:1) to provide methyl 3-methoxy-4-(6′-*O*-trityl-*β*-D-glucopyranosyloxy)-benzoate (2.46 g, 83%) as a yellow solid.

The above solid was dissolved in dry DMF (40 mL), the solution was cooled to 0 °C, to which NaH (60%, 670 mg, 28.0 mmol) was added portionwise. After stirring at 0 °C for 15 min, BnBr (3.5 mL, 25.2 mmol) was added. The resulting mixture was stirred at room temperature for a further 3 h before MeOH (15 mL) was added to quench the reaction. Solvent removal gave a residue, which was purified by column chromatography on silica gel (petroleum ether/EtOAc, 6:1) to give **15** (3.59 g, 91%) as a white solid: $[\alpha]^{25}_D$ = −21.7 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.68−7.64 (m, 2 H), 7.48−7.19 (m, 30 H), 6.85 (m, 2 H), 5.30 (d, *J* = 10.8 Hz, 1 H), 5.08 (d, *J* = 7.8 Hz, 1 H), 4.98−4.80 (m, 3 H),

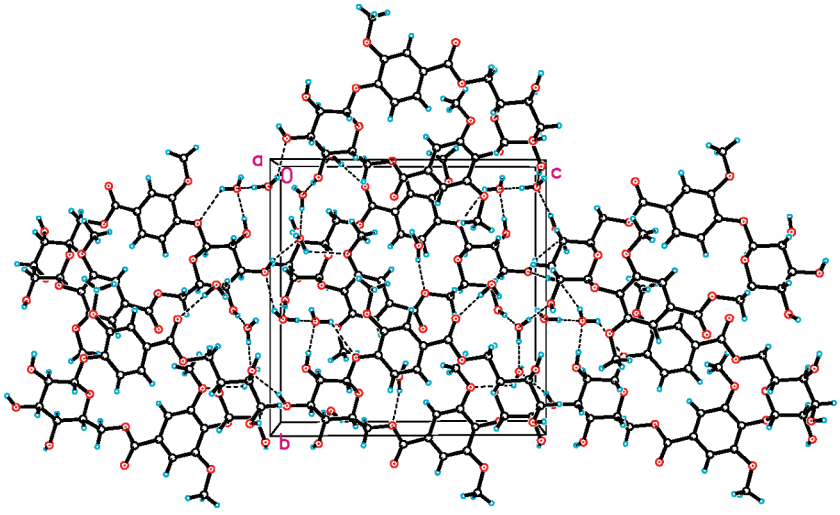

Figure 2. Molecular packing of macroglycoside **8** viewed along the *b* axis. Dashed lines indicate the hydrogen bonding interactions. Thermal ellipsoids are drawn on the 50% probability level.

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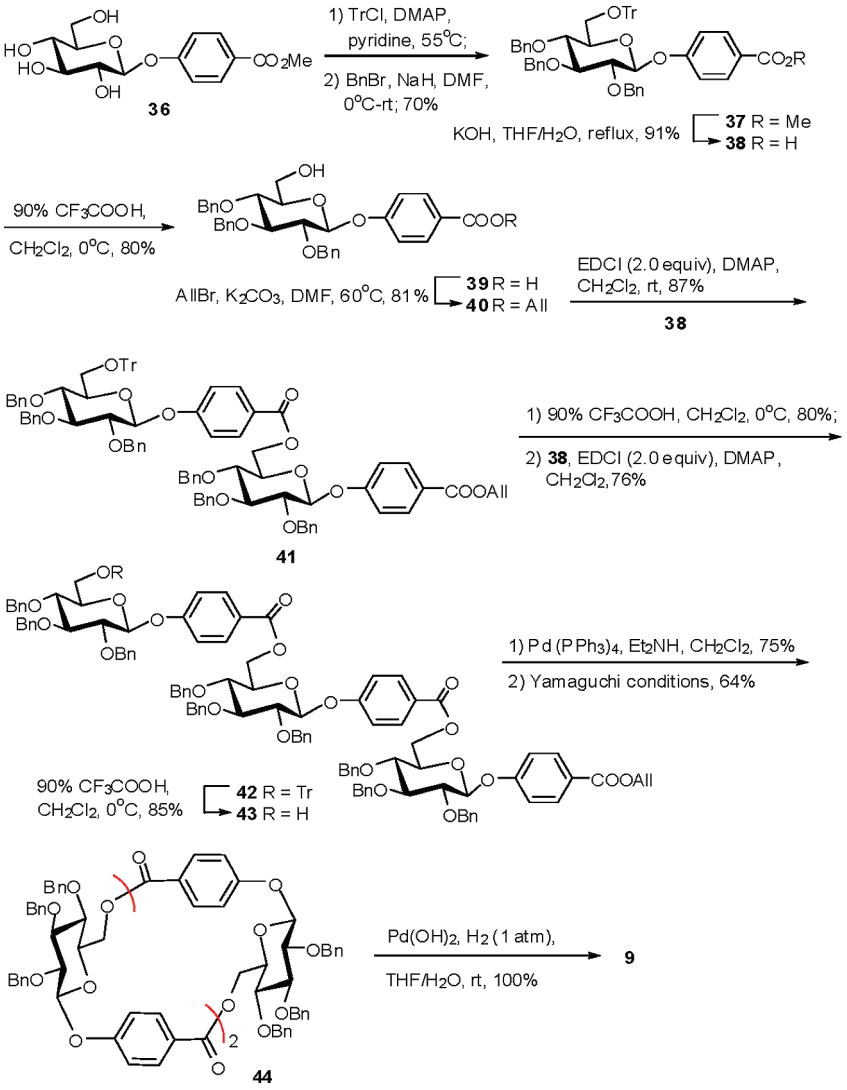
Scheme 4. Synthesis of the Cyclic Trimer of 4-(Glycosyloxy)benzoate 9



4.72 (d, J = 10.5 Hz, 1 H), 4.35 (d, J = 10.5 Hz, 1 H), 3.91−3.81 (m, 7 H), 3.78−3.58 (m, 4 H), 3.32 (dd, J = 4.8, 9.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 150.8, 149.4, 143.8, 138.5, 137.6, 128.8, 128.5, 128.4 (2 C), 128.3, 128.2, 128.0, 127.9, 127.8, 127.0, 124.7, 123.3, 116.0, 112.7, 102.2, 86.6, 84.4, 81.9, 77.8, 76.0, 75.2, 75.0, 74.9, 62.4, 55.9, 52.1; HRMS (MALDI) calcd for $C_{55}H_{52}O_9Na$ $[M + Na]^+$ 879.3504, found 879.3500.

Methyl 3-Methoxy-4-(2′,3′,4′-tri-*O*-benzyl-*β*-D-glucopyranosyloxy)benzoate (16). To a solution of trityl ether **15** (171 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added dropwise a 90% CF_3COOH solution (0.02 mL). After stirring at 0 °C for 30 min, the solution was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 4:1) to give **16** (123 mg, 91% yield) as a white solid: $[\alpha]^{25}_D$ = −23.9 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66−7.59 (m, 2 H), 7.34−7.26 (m, 15 H), 7.07 (d, J = 8.4 Hz, 1 H), 5.18 (d, J = 10.5 Hz, 1 H), 5.12−5.10 (m, 1 H), 5.01 (d, J = 11.1 Hz, 1 H), 4.91−4.81 (m, 3 H), 4.68 (d, J = 11.1 Hz, 1 H), 3.93−3.89 (m, 1 H), 3.91 (s, 3 H), 3.89 (s, 3 H), 3.79−3.63 (m, 4 H), 3.55−3.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 150.3, 149.3, 138.4, 138.2, 137.8, 128.5, 128.4, 128.3 (2 C), 128.0 (2 C), 127.8 (2 C), 127.7, 124.9, 123.1, 115.1, 112.8, 101.7, 84.2, 81.6, 77.1, 75.7, 75.5, 75.1, 74.8, 61.9, 55.9, 52.1; HRMS (MALDI) calcd for $C_{36}H_{38}O_9Na$ $[M + Na]^+$ 637.2408, found 637.2413.

Allyl 3-Methoxy-4-(2′,3′,4′-tri-*O*-benzyl-*β*-D-glucopyranosyloxy)benzoate (17). To a solution of methyl ester **16** (115 mg, 0.19 mmol) in THF (10 mL) was added dropwise a solution of KOH (319 mg, 5.70 mmol) in water (1 mL). The mixture was heated to 60 °C, and the stirring was continued for 10 h. HOAc was added dropwise to adjust the pH value of the reaction mixture to 7.0. The resulting mixture was extracted with ethyl acetate (100 mL × 3). The organic layers were combined, washed with saturated NaCl, dried over anhydrous Na_2SO_4, filtered, and then concentrated under vacuum to give a crude product.

The crude product was dissolved in DMF (15 mL), to which AllBr (0.1 mL, 1 mmol) and K_2CO_3 (2 mg, 0.01 mmol) were added. The resulting mixture was stirred for 5 h at 50 °C and was then concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 4:1) to give compound **17** (95 mg, 79% for two steps) as a white solid: $[\alpha]^{25}_D$ = −12.5 (c 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, J = 4.2, 8.1 Hz, 1 H), 7.62 (d, J = 1.5 Hz, 1 H), 7.34−7.28 (m, 15 H), 7.07 (d, J = 8.1 Hz, 1 H), 6.11−5.98 (m, 1 H), 5.44 (d, J = 14.4 Hz, 1 H), 5.31 (d, J = 10.2 Hz, 1 H), 5.18 (d, J = 11.1 Hz, 1 H), 5.12−5.10 (m, 1 H), 5.01 (d, J = 10.8 Hz, 1 H), 4.91−4.81 (m, 5 H), 4.68 (d, J = 10.8 Hz, 1 H), 3.93−3.92 (m, 1H), 3.89 (s, 3 H), 3.79−3.63 (m, 4 H), 3.56−3.51 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 150.4, 149.3, 138.4, 138.2, 137.8, 132.3, 128.5,

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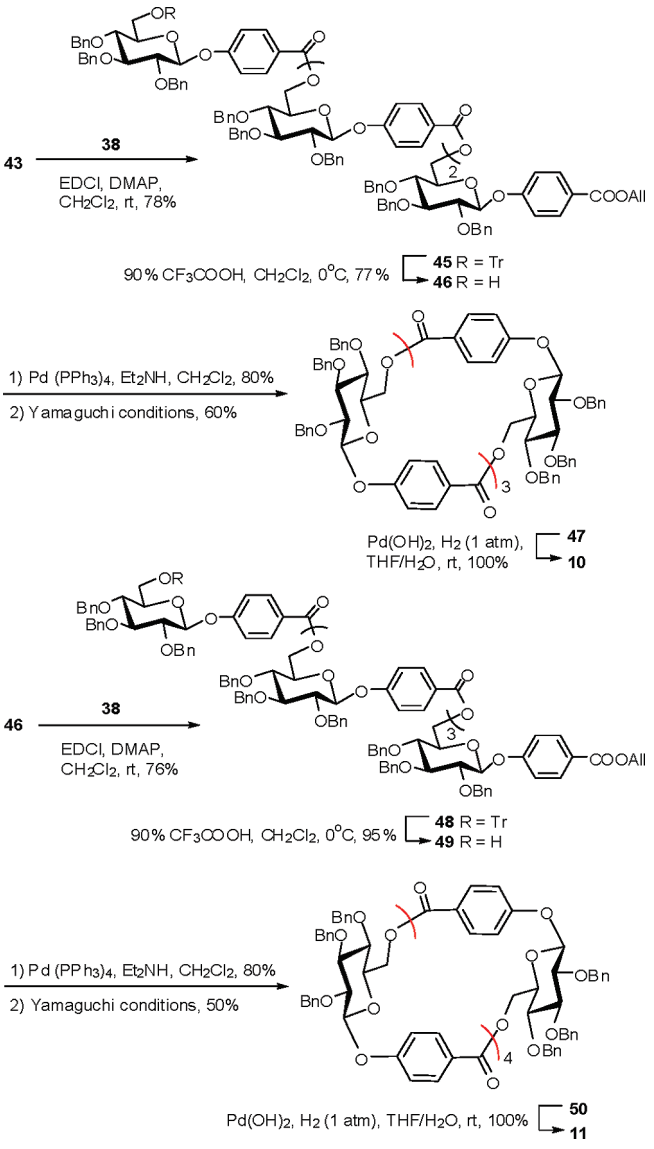
Scheme 5. Synthesis of the Cyclic Tetramer and Pentamer of 4-(Glycosyloxy)benzoates 10 and 11



128.4 (2 C), 128.3, 128.0 (2 C), 127.8 (2 C), 127.7, 124.8, 123.2, 118.2, 115.1, 112.9, 101.6, 84.2, 81.6, 77.1, 75.7, 75.5, 75.1, 74.8, 65.5, 61.9, 55.9; HRMS (MALDI) calcd for $C_{38}H_{40}O_9Na$ $[M + Na]^+$ 663.2565, found 663.2563.

2,3,4,6-Tetra-*O*-acetyl-D-allopyranosyl *N*-phenyltrifluoroacetimidate (19). To a solution of 2,3,4,6-tetra-*O*-acetyl-D-allopyranose (100 mg, 0.29 mmol) in acetone (5 mL) were added trifluoroacetimidoyl chloride (89 mg, 0.43 mmol) and K_2CO_3 (60 mg, 0.43 mmol). After being stirred at room temperature for 3 h, the solid was removed by filtration and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 2:1) to give **19** (119 mg, 82%) as a syrup. A small portion of the β isomer was isolated for characterization: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (t, J = 7.8 Hz, 2 H), 7.18 (t, J = 7.5 Hz, 1 H), 6.90 (d, J = 7.5 Hz, 1 H), 6.06 (s, 1 H), 5.73 (s, 1 H), 5.14−5.03 (m, 2 H), 4.22−4.11 (m, 3 H), 2.17 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 169.9, 169.2, 168.8, 142.9, 128.8, 124.6, 119.1, 94.5, 72.6, 72.4, 70.2, 67.7, 61.4, 20.4, 20.3, 20.2; HRMS (MALDI) calcd for $C_{22}H_{24}F_3NO_{10}Na$ $[M + Na]^+$ 542.1245, found 542.1238.

Methyl 3-Methoxy-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-allopyranosyloxy)benzoate (20). To a mixture of allosyl trifluoroacetimidate **19** (6.23 g, 12.63 mmol), methyl vanillate (1.93 g, 10.53 mmol), and 4 Å MS in dry CH_2Cl_2 (20 mL) was added $BF_3 \cdot Et_2O$ (0.14 mL, 1.30 mmol) dropwise at 0 °C. Stirring was continued for further 2 h at the same temperature. The MS was removed via filtration through a pad of Celite. The filtrate was concentrated under vacuum to give a residue, which was purified by column chromatography on silica gel (petroleum ether/EtOAc, 2.5:1) to afford **20** (5.34 g, 99%) as a white solid: $[\alpha]^{25}_D$ = −13.3 (c 1.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (dd, J = 1.5, 8.4 Hz, 1 H), 7.58 (d, J = 1.8 Hz, 1 H), 7.17 (d, J = 8.4 Hz, 1 H), 5.77 (t, J = 3.0 Hz, 1 H), 5.38 (d, J = 8.4 Hz, 1 H), 5.27 (dd, J = 3.0, 8.1 Hz, 1 H), 5.08−5.03 (m, 1 H), 4.26−4.22 (m, 3 H), 3.91 (s, 3 H), 3.88 (s, 3 H), 2.17 (s, 3 H), 2.09 (s, 3 H), 2.06 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 171.4, 170.8, 170.7, 168.2, 152.0, 151.6, 127.3, 124.7, 118.6, 115.2, 99.7, 72.4, 70.3, 70.2, 67.9, 64.0, 57.9, 53.8, 22.4 (2C), 22.2 (2 C); HRMS (MALDI) calcd for $C_{23}H_{28}O_{13}Na$ $[M + Na]^+$ 535.1422, found 535.1434.

Methyl 3,5-Dimethoxy-4-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-allopyranosyloxy)benzoate (21). Similar procedure as that used for the synthesis of alloside **20** (from **19**) was applied to provide **21** (800 mg, 87% from **19**) as a white solid: $[\alpha]^{25}_D$ = −7.1 (c 1.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 2 H), 5.65 (t, J = 3.0 Hz, 1 H), 5.32 (d, J = 8.1 Hz, 1 H), 5.17 (dd, J = 3.0, 8.1 Hz, 1 H), 5.04 (dd, J = 5.4, 9.6 Hz, 1 H), 4.17−4.15 (m, 2 H), 4.06−4.01 (m, 1 H), 3.84 (s, 3 H), 3.81 (s, 6 H), 2.07 (s, 3 H), 1.99 (s, 3 H), 1.94 (s, 3 H), 1.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 169.1, 169.0, 166.4, 152.6, 138.6, 126.2, 107.1, 99.5, 70.9, 69.6, 68.4, 66.2, 62.4, 56.4, 52.3, 21.0, 20.7 (2C), 20.5; HRMS (MALDI) calcd for $C_{24}H_{30}O_{14}Na$ $[M + Na]^+$ 565.1528, found 565.1525.

Methyl 3-Methoxy-4-(β-D-allopyranosyloxy)benzoate (22). To a solution of **20** (200 mg, 0.39 mmol) in THF/MeOH (10 mL, v/v = 1:1) was added K_2CO_3 (6 mg, 0.04 mmol). The resulting suspension was stirred at room temperature for 2 h and was then filtered through a pad of Celite. The filtrate was concentrated to give a residue, which was subjected to column chromatography on silica gel (CH_2Cl_2-MeOH, 10:1) to give **22** (122 mg, 91%) as a white solid: $[\alpha]^{25}_D$ = −33.7 (c 2.5, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.67 (dd, J = 2.1, 8.4 Hz, 1 H), 7.58 (d, J = 1.8 Hz, 1 H), 7.22 (d, J = 8.7 Hz, 1 H), 5.37 (d, J = 8.1 Hz, 1 H), 4.16 (t, J = 2.7 Hz, 1 H), 3.88 (s, 3 H), 3.87 (s, 3 H), 3.87−3.85 (m, 2 H), 3.70−3.58 (m, 3 H), 3.31 (d, J = 1.5 Hz, 1 H); ^{13}C NMR (100 MHz, CD_3OD) δ 166.8, 151.0, 148.9, 123.7, 123.1, 114.8, 112.6, 98.5, 74.4, 71.5, 70.4, 67.1, 61.3, 55.2, 51.1; HRMS (ESI) calcd for $C_{15}H_{20}O_9Na$ $[M + Na]^+$ 367.1000, found 367.1001.

Methyl 3,5-Dimethoxy-4-(β-D-allopyranosyloxy)benzoate (23). Similar procedure as that for **20**→**22** was used to convert **21** into **23** (60 mg, 99%) as a white solid: $[\alpha]^{25}_D$ = −15.8 (c 0.5, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 7.35 (s, 2 H), 5.38 (d, J = 5.7 Hz, 1 H), 4.14 (s, 1 H), 3.90 (s, 9 H), 3.78 (d, J = 7.2 Hz, 1H), 3.67−3.62 (m, 4 H), 3.31 (s, 1 H); ^{13}C NMR (100 MHz, CD_3OD) δ 168.1, 154.2, 140.7, 127.0, 108.4, 103.1, 76.4, 73.1, 72.4, 68.7, 63.0, 57.1, 52.8; HRMS (MALDI) calcd for $C_{16}H_{22}O_{10}Na$ $[M + Na]^+$ 397.1105, found 397.1106.

Methyl 3-Methoxy-4-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-β-D-allopyranosyloxy)benzoate (24). Similar procedure as that used for **14**→**15** was adopted to convert tetraol **22** into **24** (575 mg, 84%) as a white solid: $[\alpha]^{25}_D$ = −7.3 (c 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64−7.61 (m, 2 H), 7.48−7.18 (m, 29 H), 7.00−6.98 (m, 2 H), 5.60 (d, J = 7.8 Hz, 1 H), 5.14 (d, J = 12.0 Hz, 1 H), 4.89−4.79 (m, 3 H), 4.41 (d, J = 11.4 Hz, 1 H), 4.28−4.22 (m, 3 H), 3.93 (s, 3 H), 3.91 (s, 3 H), 3.91−3.88 (m, 1 H), 3.70−3.63 (m, 2 H), 3.58 (d, J = 9.6 Hz, 1 H), 3.23 (dd, J = 4.5, 10.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 150.1, 148.2, 137.8, 137.7 (2 C), 136.6, 127.8, 127.6, 127.3, 127.2, 127.1 (2 C), 126.7, 126.6, 126.5, 126.4, 125.9, 123.1, 122.4, 114.4, 111.6, 98.7, 85.4, 77.6, 76.2, 74.5, 74.1, 73.5, 72.1, 71.5, 70.8, 61.8, 55.0, 51.0; HRMS (MALDI) calcd for $C_{55}H_{52}O_9Na$ $[M + Na]^+$ 879.3504, found 879.3512.

Methyl 3,5-Dimethoxy-4-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-*β*-D-allopyranosyloxy)benzoate (25). Similar procedure as that used for **14**→**15** was adopted to convert tetraol **23** into **25** (29 mg, 81%) as a white solid: $[\alpha]^{25}_D = +38.0$ (*c* 3.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.31−7.10 (m, 30 H), 6.91 (d, *J* = 5.2 Hz, 2 H), 5.73 (d, *J* = 6.0 Hz, 1 H), 5.08 (d, *J* = 12.0 Hz, 1 H), 4.83 (d, *J* = 11.6 Hz, 1 H), 4.72−4.67 (m, 2 H), 4.29 (d, *J* = 11.6 Hz, 1 H), 4.13 (d, *J* = 11.2 Hz, 2 H), 3.95−3.93 (m, 1 H), 3.85 (s, 3 H), 3.73 (s, 6 H), 3.62 (d, *J* = 7.6 Hz, 1 H), 3.50 (d, *J* = 9.6 Hz, 1 H), 3.34 (d, *J* = 9.6 Hz, 1 H), 3.10−3.07 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 152.0, 143.0, 138.4, 138.2, 136.9, 127.8, 127.3, 127.2, 127.0, 126.8, 126.6, 126.5, 126.3, 126.2, 125.7, 124.4, 106.3, 100.7, 85.1, 78.9, 76.2, 74.8, 74.4, 73.3, 72.0, 71.6, 70.4, 61.4, 55.5, 51.2; HRMS (MALDI) calcd for $C_{56}H_{54}O_{10}Na$ $[M + Na]^+$ 909.3609, found 909.3623.

3-Methoxy-4-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-*β*-D-allopyranosyloxy)benzoic acid (26). To a solution of the methyl ester **24** (583 mg, 0.68 mmol) in THF (10 mL) was added dropwise a solution of KOH (1.14 g, 20.40 mmol) in H_2O (1 mL). The mixture was stirred at 70 °C for 10 h. HOAc was added to adjust the pH value of the reaction mixture to 7.0. The resulting mixture was extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 50:1) to give **26** (499 mg, 87%) as a white solid: $[\alpha]^{25}_D = -7.6$ (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 1.8, 8.4 Hz, 1 H), 7.67 (d, *J* = 2.1 Hz, 1 H), 7.49−7.18 (m, 29 H), 7.01−6.98 (m, 2 H), 5.63 (d, *J* = 7.5 Hz, 1 H), 5.14 (d, *J* = 12.3 Hz, 1 H), 4.90−4.80 (m, 3 H), 4.42 (d, *J* = 11.7 Hz, 1 H), 4.29−4.22 (m, 3 H), 3.95 (s, 3 H), 3.72−3.65 (m, 2 H), 3.61 (d, *J* = 9.6 Hz, 1 H), 3.24 (dd, *J* = 4.5, 10.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 151.8, 149.2, 143.9, 138.7, 137.6, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.4, 127.2, 127.0, 126.8, 124.3, 123.1, 115.3, 112.9, 99.7, 86.3, 78.6, 77.2, 75.5, 75.0, 74.4, 73.0, 72.5, 71.8, 62.7, 55.9; HRMS (MALDI) calcd for $C_{54}H_{50}O_9Na$ $[M + Na]^+$ 865.3347, found 865.3354.

3,5-Dimethoxy-4-(2′,3′,4′-tri-*O*-benzyl-6′-*O*-trityl-*β*-D-allopyranosyloxy)benzoic acid (27). Similar procedure as that used for **24**→**26** was adopted to convert methyl ester **25** into acid **27** (25 mg, 92%) as a white solid: $[\alpha]^{25}_D = +41.0$ (*c* 1.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.43−7.18 (m, 30 H), 6.99−6.96 (m, 2 H), 5.84 (d, *J* = 7.8 Hz, 1 H), 5.16 (d, *J* = 12.3 Hz, 1 H), 4.92 (d, *J* = 12.0 Hz, 1 H), 4.80 (dd, *J* = 4.5, 12.3 Hz, 2 H), 4.37 (d, *J* = 12.0 Hz, 1 H), 4.22 (d, *J* = 11.4 Hz, 2 H), 4.05−4.01 (m, 1 H), 3.82 (s, 6 H), 3.71 (d, *J* = 6.3 Hz, 1 H), 3.60 (d, *J* = 9.6 Hz, 1 H), 3.43 (d, *J* = 8.4 Hz, 1 H), 3.19 (dd, *J* = 5.1, 9.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 152.1, 143.0, 138.9, 138.3, 138.2, 136.8, 127.8, 127.7, 127.5 (2 C), 127.2, 127.0, 126.9, 126.8, 126.6, 126.5, 126.4, 126.2 (2 C), 125.8, 123.5, 106.8, 100.6, 85.1, 78.8, 74.8, 74.4, 73.3, 72.0, 71.6, 70.5, 61.4, 55.5; HRMS (MALDI) calcd for $C_{55}H_{52}O_{10}Na$ $[M + Na]^+$ 895.3453, found 895.3462.

Dimeric Ester 28. To a solution of alcohol **17** (320 mg, 0.50 mmol) and acid **26** (843 mg, 1.00 mmol) in dry CH_2Cl_2 (15 mL) were added DCC (206 mg, 1.00 mmol) and DMAP (61 mg, 0.5 mmol). After being stirred at room temperature for 24 h, the mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 7:1) to give **28** (619 mg, 76%) as a white solid: $[\alpha]^{25}_D = -14.5$ (*c* 0.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.65−6.98 (m, 51 H), 6.03−5.94 (m, 1 H), 5.62 (d, *J* = 7.8 Hz, 1 H), 5.36 (d, *J* = 16.8 Hz, 1 H), 5.24 (d, *J* = 10.5 Hz, 2 H), 5.14−5.01 (m, 3 H), 4.91−4.82 (m, 6 H), 4.75 (d, *J* = 5.4 Hz, 2 H), 4.67 (t, *J* = 11.7 Hz, 2 H), 4.50 (dd, *J* = 3.6, 12.0 Hz, 1 H), 4.42 (d, *J* = 11.4 Hz, 1 H), 4.30−4.23 (m, 3 H), 3.90 (s, 3 H), 3.85 (s, 3 H), 3.83−3.70 (m, 6 H), 3.63 (d, *J* = 10.2 Hz, 1 H), 3.23 (dd, *J* = 3.6, 10.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.5, 153.1, 152.2, 151.1, 151.0, 145.7, 140.5, 140.0 (2 C), 139.4, 139.2, 134.1, 130.5, 130.2 (2 C), 130.1 (2 C), 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.2, 129.1, 129.0, 128.6, 126.6, 125.4, 125.3, 124.9, 119.8, 117.4, 117.1, 114.6, 114.5, 103,7, 101.5, 88.0, 86.1, 83.3, 80.4, 79.1, 77.6, 77.2, 76.9, 76.8, 76.6, 76.2, 75.2, 74.8, 74.2, 73.6, 67.2, 64.9, 64.4, 57.8, 57.6; HRMS (MALDI) calcd for $C_{92}H_{88}O_{17}Na$ $[M + Na]^+$ 1487.5914, found 1487.5913.

Dimeric Ester 29. Similar procedure as that used for **17** + **26**→**28** was applied to condense **17** and **27** into **29** (95 mg, 74%) as a white solid: $[\alpha]^{25}_D = +9.3$ (*c* 1.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49−7.46 (m, 2 H), 7.33−7.03 (m, 46 H), 6.91−6.89 (m, 2 H), 5.93−5.86 (m, 1 H), 5.74 (d, *J* = 8.0 Hz, 1 H), 5.28 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.16 (dd, *J* = 3.6, 10.4 Hz, 2 H), 5.06 (d, *J* = 12.0 Hz, 1H), 5.01 (d, *J* = 7.6 Hz, 1 H), 4.94 (d, *J* = 11.2 Hz, 1 H), 4.84−4.55 (m, 10 H), 4.43 (dd, *J* = 5.6, 12.0 Hz, 1 H), 4.28 (d, *J* = 11.6 Hz, 1 H), 4.14 (dd, *J* = 1.6, 13.6 Hz, 2 H), 3.95−3.92 (m, 1 H), 3.75 (s, 3 H), 3.70 (s, 6 H), 3.75−3.70 (m, 3 H), 3.61−3.59 (m, 1 H), 3.52 (dd, *J* = 2.0, 11.6 Hz, 1 H), 3.34 (d, *J* = 8.8 Hz, 1 H), 3.09 (dd, *J* = 4.8, 10.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.8, 152.1, 149.6, 148.5, 143.0, 138.7, 138.4, 138.3, 137.3 (2 C), 136.9, 136.6, 131.3, 127.8, 127.6, 127.5, 127.4 (2 C), 127.2, 127.1 (2 C), 127.0 (3 C), 126.8, 126.7, 126.5, 126.4, 126.3, 126.2, 125.8, 124.0 (2 C), 122.2, 117.2, 114.6, 111.9, 106.8, 101.1, 100.7, 85.1, 83.4, 80.6, 79.0, 74.9, 74.8, 74.4, 74.2, 73.9, 73.4, 72.6, 72.0, 71.6, 70.5, 64.6, 62.7, 61.4, 55.8, 54.9; HRMS (MALDI) calcd for $C_{93}H_{90}O_{18}Na$ $[M + Na]^+$ 1517.6019, found 1517.6002.

Compound 30. Similar procedure as that used for **15**→**16** was applied to convert trityl ether **28** into alcohol **30** (502 mg, 81%) as a white solid: $[\alpha]^{25}_D = -5.8$ (*c* 1.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.48 (dd, *J* = 1.2, 6.4 Hz, 2 H), 7.43 (dd, *J* = 1.2, 8.4 Hz, 1 H), 7.32−7.16 (m, 30 H), 7.07 (dd, *J* = 8.8, 16.4 Hz, 2 H), 5.97−5.87 (m, 1 H), 5.56 (d, *J* = 8.0 Hz, 1 H), 5.30 (d, *J* = 17.2 Hz, 1 H), 5.18 (t, *J* = 12.0 Hz, 2 H), 4.97−4.92 (m, 3 H), 4.87−4.68 (m, 8 H), 4.56−4.46 (m, 3 H), 4.40−4.35 (m, 2 H), 4.14−4.09 (m, 2 H), 3.39 (dd, *J* = 1.5, 12.0 Hz, 1 H), 3.77 (s, 6 H), 3.66−3.60 (m, 4 H), 3.60−3.56 (m, 1 H), 3.46−3.35 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (2 C), 150.0, 149.5, 148.4, 148.3, 137.8, 137.5, 137.3 (2 C), 136.7, 136.6, 131.3, 127.5, 127.4, 127.3, 127.2, 127.1, 127.0, 126.9 (2 C), 126.8 (3 C), 126.6, 126.5, 123.9, 122.9, 122.3, 122.2, 117.1, 115.0, 113.8, 112.0, 111.8, 101.0, 98.4, 83.4, 80.6, 77.3, 76.6, 76.2, 74.8, 74.2, 74.1, 73.8, 73.7, 73.5, 72.5, 72.2, 72.0, 70.6, 64.6, 62.4, 60.9, 55.0, 54.9; HRMS (MALDI) calcd for $C_{73}H_{74}O_{17}Na$ $[M + Na]^+$ 1245.4818, found 1245.4802.

Compound 31. Similar procedure as that used for **15**→**16** was applied to convert trityl ether **29** into alcohol **31** (76 mg, 90%) as a white solid: $[\alpha]^{25}_D = -2.4$ (*c* 0.8, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.55 (d, *J* = 9.9 Hz, 1 H), 7.33−7.26 (m, 32 H), 7.10 (d, *J* = 8.7 Hz, 1 H), 6.01−5.96 (m, 1H), 5.62 (d, *J* = 7.2 Hz, 1 H), 5.39 (d, *J* = 17.1 Hz, 1 H), 5.27−5.19 (m, 2 H), 5.12−4.62 (m, 13 H), 4.57 (d, *J* = 11.4 Hz, 1 H), 4.46−4.40 (m, 2 H), 4.21 (s, 1 H), 3.97−3.93 (m, 1 H), 3.86 (s, 3 H), 3.80 (s, 6 H), 3.86−3.80 (m, 5 H), 3.67−3.52 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.9, 149.6, 148.4, 138.4, 138.1, 137.3, 137.2, 136.8, 136.5, 131.3, 127.5, 127.4 (3 C), 127.3, 127.2, 127.1 (2 C), 127.0, 126.8 (3 C), 126.3 (2 C), 124.5, 123.9, 122.1, 117.2, 114.6, 111.9, 106.3, 101.2, 101.0, 83.3, 80.5, 78.7, 76.5, 76.2, 74.8, 74.2 (2 C), 74.0, 73.8, 73.3, 72.6, 72.0, 70.5, 64.5, 62.7, 61.1, 55.4, 54.9; HRMS (MALDI) calcd for $C_{74}H_{76}O_{18}Na$ $[M + Na]^+$ 1275.4924, found 1275.4939.

Alcoholic Acid 32. To the solution of allyl ester **30** (104 mg, 0.09 mmol) in dry CH_2Cl_2 (8 mL) and Et_2NH (2 mL) was added $Pd(Ph_3P)_4$ (12 mg, 0.01 mmol). The solution was stirred at room temperature for 4 h. Evaporation to remove the solvent afforded a residue, which was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 50:1) to give acid **32** (90 mg, 89%) as a white solid: $[\alpha]^{25}_D = +3.1$ (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.6, 8.4 Hz, 1 H), 7.45 (dd, *J* = 1.6, 8.0 Hz, 2 H), 7.35−7.18 (m, 30 H), 7.08 (d, *J* = 8.8 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 5.59 (d, *J* = 7.6 Hz, 1 H), 5.14 (d, *J* = 10.8 Hz, 1 H), 4.96−4.69 (m, 9 H), 4.59−4.52 (m, 2 H), 4.46 (d, *J* = 11.2 Hz, 1 H), 4.36 (d, *J* = 11.6 Hz, 1 H), 4.21−3.11 (m, 3 H), 3.89 (dd, *J* = 2.4, 12.4 Hz, 1 H), 3.76 (s, 3 H), 3.75 (s, 3 H), 3.75−3.70 (m, 4 H), 3.52−3.43 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 150.2,

149.2, 148.4, 148.3, 137.4, 137.3, 137.2, 136.6, 136.5, 127.6, 127.5 (2 C), 127.4 (4 C), 127.2, 127.1, 127.0 (2 C), 126.9, 126.8 (3 C), 126.6, 124.1, 123.0, 122.5, 122.4, 115.3, 113.7, 112.0, 111.9, 100.8, 98.5, 83.5, 80.4, 77.1, 76.2, 74.8, 74.3, 74.1, 73.6, 73.4, 73.4, 72.3, 72.1, 72.0, 70.7, 62.7, 60.9, 55.0, 54.8; HRMS (MALDI) calcd for $C_{70}H_{70}O_{17}Na$ $[M + Na]^+$ 1205.4505, found 1205.4500.

Alcoholic Acid 33. Similar procedure as that for **30**→**32** was used to convert allyl ester **31** into **33** (42 mg, 87%) as a white solid: $[\alpha]^{25}_D = +2.8$ (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 1.6 Hz, 1 H), 7.33−7.16 (m, 33 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 5.57 (d, *J* = 8.0 Hz, 1 H), 5.14 (d, *J* = 10.8 Hz, 1 H), 5.02 (d, *J* = 11.6 Hz, 1 H), 5.96−4.75 (m, 7 H), 4.62 (d, *J* = 12.0 Hz, 1 H), 4.58 (d, *J* = 11.2 Hz, 1 H), 4.48 (d, *J* = 11.2 Hz, 1 H), 4.36 (m, 2 H), 4.16 (s, 1 H), 3.92−3.89 (m, 1 H), 3.80−3.74 (m, 3 H), 3.76 (s, 3 H), 3.68 (s, 6 H), 3.64 (dd, *J* = 4.8, 11.6 Hz, 1 H), 3.53−3.50 (m, 2 H), 3.40 (dd, *J* = 9.6, 18.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 151.8, 149.4, 148.4, 138.5, 138.0, 137.7, 137.3, 137.2, 136.6, 136.5, 127.6, 127.5, 127.4 (2 C), 127.2, 127.1, 127.0, 126.9 (2 C), 126.8 (2 C), 126.4, 126.3, 124.5, 122.6, 114.8, 112.0, 106.2, 101.4, 100.8, 83.4, 80.4, 78.5, 76.9, 76.2, 74.8, 74.2, 74.1, 73.8, 73.7, 73.3, 72.5, 72.2, 72.0, 70.5, 62.8, 61.0, 55.4, 54.8; HRMS (MALDI) calcd for $C_{71}H_{72}O_{18}Na$ $[M + Na]^+$ 1235.4611, found 1235.4609.

Cyclic Dimer 34. To a solution of **32** (13 mg, 0.01 mmol) and Et_3N (0.08 mL) in dry THF (1.00 mL) was added 2,4,6-trichlorobenzoyl chloride (0.05 mL, 0.3 mmol). The solution was stirred at room temperature for 3 h, and then a solution of DMAP (86 mg, 0.72 mmol) in toluene (40 mL) was added. The resulting mixture was stirred for another 4 h at the same temperature and was then diluted with ethyl acetate (300 mL). The resulting mixture was washed with saturated $NaHCO_3$, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (petroleum ether/EtOAc, 3:1) to give **34** (10 mg, 78%) as a white solid: $[\alpha]^{25}_D = +44.6$ (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.64 (m, 1 H), 7.48 (dd, *J* = 2.0, 5.2 Hz, 2 H), 7.39−7.17 (m, 32 H), 5.61 (d, *J* = 8.0 Hz, 1 H), 5.15 (d, *J* = 10.8 Hz, 1 H), 5.06−4.75 (m, 9 H), 4.61−4.43 (m, 5 H), 4.34 (d, *J* = 11.2 Hz, 1 H), 4.20 (t, *J* = 2.4 Hz, 1 H), 4.09 (t, *J* = 10.4 Hz, 1 H), 4.01 (t, *J* = 10.8 Hz, 1 H), 3.88 (dd, *J* = 1.6, 9.6 Hz, 1 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.83−3.74 (m, 2 H), 3.58 (dd, *J* = 2.4, 8.0 Hz, 1 H), 3.44−3.39 (m, 1 H), 3.31 (dd, *J* = 2.4, 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8 (2 C), 149.4, 149.2, 148.4, 148.3, 137.6, 137.4, 137.3, 137.2, 136.5, 136.1, 127.6, 127.5, 127.4, 127.2, 127.1, 127.0, 126.9 (2 C), 126.8 (2 C), 126.7, 126.6, 123.3, 122.7, 122.4, 122.2, 114.2, 114.0, 111.7, 100.1, 97.4, 83.7, 80.2, 77.4, 76.8, 76.2, 74.9, 74.2, 73.9, 73.7, 73.6, 72.3, 72.0, 70.4, 70.0, 64.2, 63.6, 55.0, 54.9; HRMS (MALDI) calcd for $C_{70}H_{68}O_{16}Na$ $[M + Na]^+$ 1187.4400, found 1187.4391.

Cyclic Dimer 35. Similar procedure as that for **32**→**34** was adopted to convert **33** into **35** (20 mg, 88%) as a white solid: $[\alpha]^{25}_D = -9.5$ (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 1.6 Hz, 1 H), 7.37−7.14 (m, 32 H), 6.82 (dd, *J* = 1.6, 8.4 Hz, 1 H), 6.76 (d, *J* = 8.4 Hz, 1 H), 5.46 (d, *J* = 8.0 Hz, 1H), 5.20 (d, *J* = 11.6 Hz, 1 H), 5.14 (d, *J* = 10.8 Hz, 1 H), 4.95 (dd, *J* = 4.4, 11.6 Hz, 3 H), 4.86−4.72 (m, 5 H), 4.69 (d, *J* = 11.6 Hz, 1 H), 4.59 (d, *J* = 11.2 Hz, 1 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.48 (dd, *J* = 3.6, 12.4 Hz, 1 H), 4.32 (d, *J* = 12.0 Hz, 1 H), 4.20 (t, *J* = 2.4 Hz, 1 H), 4.13−4.10 (m, 1 H), 3.97−3.87 (m, 2 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.77−3.72 (m, 3 H), 3.64 (dd, *J* = 2.4, 8.0 Hz, 1 H), 3.43 (s, 3 H), 3.41 (t, *J* = 8.8 Hz, 1 H), 3.33 (dd, *J* = 2.4, 9.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 165.4, 154.1, 152.9, 150.5, 149.1, 139.3, 139.2, 139.1, 138.3, 138.1, 137.6, 137.3, 128.6, 128.5 (2 C), 128.4, 128.2, 128.1, 128.0 (2 C), 127.9, 127.8, 127.4, 127.3, 125.7, 124.4, 123.5, 114.5, 112.4, 107.0, 106.8, 103.0, 101.5, 84.5, 81.1, 79.2, 78.6, 77.4, 76.3, 76.0, 75.3, 74.9, 74.8, 74.6, 73.3, 73.1, 71.1, 70.8, 65.3, 63.8, 56.2, 56.1, 55.9; HRMS (MALDI) calcd for $C_{71}H_{70}O_{17}Na$ $[M + Na]^+$ 1217.4505, found 1217.4520.

Clemoarmanoside A (7). To a solution of **34** (30 mg, 0.026 mmol) in THF/MeOH (5 mL, v/v = 3:2) was added $Pd(OH)_2$ (3 mg, 0.02 mmol). The reaction flask was evacuated and refilled with H_2. The mixture was stirred at room temperature for 3 h under H_2 atmosphere. Filtration through a pad of Celite and evaporation of the filtrate under vacuum gave a residue, which was purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 6:1) to give **7** (13 mg, 81%) as a white solid: $[\alpha]^{25}_D = +80.8$ (*c* 0.3, pyridine); ^1H NMR (500 MHz, CD_3SOCD_3) δ 7.79 (dd, *J* = 2.0, 7.0 Hz, 1 H), 7.77 (dd, *J* = 1.5, 6.0 Hz, 1 H), 7.42 (d, *J* = 2.5 Hz, 1 H), 7.41 (t, *J* = 3.0 Hz, 2 H), 7.38 (d, *J* = 9.0 Hz, 1 H), 7.33 (d, *J* = 9.5 Hz, 1 H), 5.52 (s, 1 H), 5.45 (d, *J* = 5.0 Hz, 1 H), 5.39 (d, *J* = 9.0 Hz, 1 H), 5.33 (d, *J* = 3.0 Hz, 1 H), 5.25 (d, *J* = 7.5 Hz, 2 H), 5.21 (d, *J* = 7.0 Hz, 1 H), 5.06 (d, *J* = 8.0 Hz, 1 H), 4.42 (d, *J* = 10.0 Hz, 1 H), 4.38 (d, *J* = 11.5 Hz, 1 H), 4.28−4.24 (m, 1 H), 4.13−4.07 (m, 2 H), 3.99−3.97 (m, 2 H), 3.79 (s, 6 H), 3.58 (m, 1 H), 3.45−3.39 (m, 3 H), 3.18−3.16 (m, 1 H); ^{13}C NMR (125 MHz, CD_3SOCD_3) δ 165.2, 165.1, 150.1, 149.8, 148.5, 148.4, 123.1, 123.0, 122.5, 122.4, 114.4, 114.3, 112.1, 98.3, 96.8, 76.9, 73.5, 72.8, 71.7, 71.2, 70.6, 69.8, 68.2, 65.4, 65.1, 55.5; HRMS (ESI) calcd for $C_{28}H_{32}O_{16}Na$ $[M + Na]^+$ 647.1588, found 647.1600.

Clemahexapetoside A (8). Similar procedure as that used for **34**→**7** was applied to convert **35** into Clemahexapetoside A (**8**) (20 mg, 100%) as a white solid: $[\alpha]^{25}_D = +81.1$ (*c* 0.2, pyridine); ^1H NMR (500 MHz, CD_3SOCD_3) δ 7.50 (d, *J* = 1.5 Hz, 1 H), 7.36 (d, *J* = 1.0 Hz, 1 H), 7.08 (d, *J* = 1.0 Hz, 1 H), 6.99 (d, *J* = 8.0 Hz, 1 H), 6.82 (dd, *J* = 1.5, 9.0 Hz, 1 H), 5.61 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 4.5 Hz, 1 H), 5.43 (d, *J* = 5.0 Hz, 1 H), 5.29 (d, *J* = 4.0 Hz, 1 H), 5.15 (d, *J* = 6.5 Hz, 1 H), 5.07 (d, *J* = 3.5 Hz, 1H), 5.05 (d, *J* = 7.0 Hz, 1 H), 4.87 (d, *J* = 7.5 Hz, 1 H), 4.51 (d, *J* = 10.5 Hz, 1 H), 4.44−4.39 (m, 1 H), 4.36 (d, *J* = 10.0 Hz, 1 H), 3.96 (s, 3 H), 3.94−3.83 (m, 4 H), 3.79 (s, 3 H), 3.59 (s, 3 H), 3.49−3.46 (m, 1 H), 3.40−3.37 (m, 3 H), 3.22−3.19 (m, 1 H); ^{13}C NMR (125 MHz, CD_3SOCD_3) δ 165.2, 164.8, 153.2, 152.0, 149.9, 148.4, 138.1, 124.5, 122.6, 122.3, 114.4, 111.9, 107.0, 106,9, 99.2, 99.0, 77.2, 73.9, 73.0, 71.7, 71.4, 71.0, 70.7, 68.6, 65.4, 64.3, 56.6, 55.9, 55.5; HRMS (ESI) calcd for $C_{29}H_{34}O_{17}Na$ $[M + Na]^+$ 677.1688, found 677.1707.

Methyl 4-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-trityl-β-D-glucopyranosyloxy)benzoate (37). Similar procedure as that used for **14**→**15** was applied to convert tetraol **36** into **37** (438 mg, 70% for two steps) as a white solid: $[\alpha]^{25}_D = -25.4$ (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2 H), 7.40−7.09 (m, 30 H), 6.81 (d, *J* = 6.8 Hz, 2 H), 5.05 (d, *J* = 7.6 Hz, 1 H), 4.99 (d, *J* = 10.8 Hz, 1 H), 4.86−4.74 (m, 3 H), 4.64 (d, *J* = 10.0 Hz, 1 H), 4.29 (d, *J* = 10.8 Hz, 1 H), 3.82 (s, 3 H), 3.78 (t, *J* = 8.4 Hz, 1 H), 3.71−3.61 (m, 2 H), 3.53−3.51 (m, 2 H), 3.21 (dd, *J* = 5.2, 10.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 159.9, 142.7, 137.3, 137.1, 136.6, 130.6, 127.7, 127.4, 127.3, 127.2, 127.0, 126.8 (2 C), 126.0, 123.4, 115.4, 100.0, 85.6, 83.6, 81.0, 76.7, 75.0, 74.2, 74.1, 74.0, 61.4, 51.0; HRMS (MALDI) calcd for $C_{54}H_{50}O_8Na$ $[M + Na]^+$ 849.3398, found 849.3409.

4-(2′,3′,4′-Tri-*O*-benzyl-6′-*O*-trityl-β-D-glucopyranosyloxy)-benzoic acid (38). Similar procedure as that used for **24**→**26** was applied to convert methyl ester **37** into acid **38** (348 mg, 91%) as a white solid: $[\alpha]^{25}_D = -25.6$ (*c* 1.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 9.2 Hz, 2 H), 7.39−7.10 (m, 30 H), 6.82−6.80 (m, 2 H), 5.08 (d, *J* = 7.6 Hz, 1 H), 5.00 (d, *J* = 11.2 Hz, 1 H), 4.87−4.75 (m, 3 H), 4.65 (d, *J* = 10.4 Hz, 1 H), 4.30 (d, *J* = 10.4 Hz, 1 H), 3.80 (t, *J* = 8.0 Hz, 1 H), 3.71−3.64 (m, 2 H), 3.55−3.53 (m, 2 H), 3.21−3.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 160.5, 142.7, 137.3, 137.1, 136.5, 131.3, 127.7, 127.4, 127.3, 127.2, 127.0, 126.9, 126.8, 126.0, 122.6, 115.4, 99.9, 85.6, 83.5, 81.0, 76.7, 75.0, 74.2, 74.1, 74.0, 61.3; HRMS (MALDI) calcd for $C_{53}H_{48}O_8Na$ $[M + Na]^+$ 835.3241, found 835.3251.

4-(2′,3′,4′-Tri-*O*-benzyl-β-D-glucopyranosyloxy)benzoic acid (39). Similar procedure as that used for **15**→**16** was applied to convert trityl ether **38** into **39** (354 mg, 80%) as a white solid: $[\alpha]^{25}_D = -20.5$ (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 2 H), 7.29−7.18 (m, 15 H), 6.98 (d, *J* = 8.8 Hz, 2 H), 5.10 (d, *J* = 7.2 Hz, 1 H), 4.91 (dd, *J* = 4.8, 10.8 Hz, 2 H), 4.83−4.74 (m, 3 H), 4.62 (d, *J* = 10.8 Hz, 1 H), 3.85−3.82 (m, 1 H), 3.72−3.57 (m, 4 H), 3.49−3.48 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 161.2,

138.3, 137.9, 137.8, 132.4, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9 (2 C), 127.8, 123.6, 115.9, 100.5, 84.3, 81.8, 75.8, 75.6, 75.2 (2 C), 61.8; HRMS (MALDI) calcd for $C_{34}H_{34}O_8Na$ $[M + Na]^+$ 593.2146, found 593.2150.

Allyl 4-(2′,3′,4′-Tri-*O*-benzyl-β-D-glucopyranosyloxy)benzoate (40). Similar procedure as that used for **16**→**17** was applied to convert acid **39** into allyl ester **40** (308 mg, 81%) as a white solid: $[\alpha]^{25}_D = -11.8$ (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2 H), 7.36−7.30 (m, 15 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.07−6.00 (m, 1 H), 5.43−5.38 (m, 1 H), 5.30−5.27 (m, 1 H), 5.16 (d, *J* = 7.6 Hz, 1 H), 4.99−4.80 (m, 7 H), 4.69 (d, *J* = 11.2 Hz, 1 H), 3.92 (dd, *J* = 2.4, 12.0 Hz, 1 H), 3.80−3.64 (m, 4 H), 3.56−3.53 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 159.6, 137.4, 136.9, 136.8, 131.4, 130.8, 127.6, 127.5, 127.2, 127.1 (2 C), 127.0, 126.9, 126.8, 123.6, 117.2, 114.9, 99.6, 83.4, 80.9, 74.8, 74.6, 74.3, 74.2, 64.5, 60.9; HRMS (MALDI) calcd for $C_{37}H_{38}O_8Na$ $[M + Na]^+$ 633.2459, found 633.2459.

Dimeric Ester 41. To a solution of alcohol **40** (400 mg, 0.65 mmol) and acid **38** (800 mg, 0.98 mmol) in dry CH_2Cl_2 (25 mL) were added EDCI (200 mg, 1.30 mmol) and DMAP (79 mg, 0.65 mmol). After being stirred at room temperature for 24 h, the mixture was concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc, 8:1) to provide **41** (800 mg, 87%) as a white solid: $[\alpha]^{25}_D = -27.2$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2 H), 7.90 (d, *J* = 8.8 Hz, 2 H), 7.37−7.10 (m, 45 H), 6.97 (d, *J* = 8.8 Hz, 2 H), 6.81 (d, *J* = 6.4 Hz, 2 H), 5.92−5.83 (m, 1 H), 5.27 (dd, *J* = 1.2, 16.8 Hz, 1 H), 5.15−4.74 (m, 12 H), 4.65−4.55 (m, 5 H), 4.33−4.27 (m, 2 H), 3.80−3.51 (m, 9 H), 3.20 (dd, *J* = 4.4, 10.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 160.2, 159.6, 142.7, 137.4, 137.2, 136.9, 136.7, 136.4, 131.3, 130.8, 130.6, 127.7, 127.5 (2 C), 127.4, 127.2 (2 C), 127.1, 127.0 (3 C), 126.9 (2 C), 126.8 (2 C), 126.7, 126.0, 123.6, 122.9, 117.0, 115.4, 115.1, 99.9, 99.8, 85.5, 83.6, 81.1, 80.8, 76.8, 75.0, 74.9, 74.2, 74.1 (2 C), 73.9, 72.6, 64.3, 62.1, 61.3; HRMS (MALDI) calcd for $C_{90}H_{84}O_{15}Na$ $[M + Na]^+$ 1427.5702, found 1427.5747.

Trimeric Ester 42. Similar procedure as that used for **40** + **38**→**41** was applied to condense acid **38** and the alcohol resulting from trityl ether **41** into **42** (275 mg, 76%) as a white solid: $[\alpha]^{25}_D = -40.5$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.86 (m, 6 H), 7.42−6.85 (m, 66 H), 6.02−5.87 (m, 1 H), 5.35−4.63 (m, 26 H), 4.38−4.31 (m, 3 H), 4.20 (dd, *J* = 8.8, 15.2 Hz, 1 H), 4.04−3.54 (m, 13 H), 3.29−3.24 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (2 C), 164.3, 160.1, 159.9, 159.4, 142.7, 142.6, 137.4, 137.2 (2 C), 137.0, 136.9, 136.6, 136.5, 131.3, 130.7, 130.6 (2 C), 130.5, 127.7, 127.5, 127.4 (2 C), 127.2 (4 C), 127.1, 127.0 (2 C), 126.9, 126.8 (2 C), 126.7, 126.5, 126.0, 123.4, 123.0, 122.7, 116.9, 115.4, 115.1, 115.0, 114.8, 99.8, 99.6, 99.5, 85.6, 83.7, 83.6, 83.5, 81.1, 80.8, 77.0, 76.9, 76.5, 75.1, 75.0, 74.8, 74.2 (2 C), 74.1, 73.7, 72.7, 72.4, 64.3, 62.2, 62.1, 61.3; HRMS (MALDI) calcd for $C_{124}H_{116}O_{22}Na$ $[M + Na]^+$ 1979.7850, found 1979.7825.

Trimer Derivative 43. Similar procedure as that used for **15**→**16** was applied to convert trityl ether **42** into alcohol **43** (33 mg, 85%) as a white solid: $[\alpha]^{25}_D = -29.8$ (*c* 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2 H), 7.78 (dd, *J* = 5.6, 8.4 Hz, 4 H), 7.29−7.13 (m, 45 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.80 (d, *J* = 8.8 Hz, 2 H), 5.92−5.80 (m, 1 H), 5.26 (dd, *J* = 1.2, 17.2 Hz, 1 H), 5.17−5.13 (m, 2 H), 5.05 (t, *J* = 8.0 Hz, 2 H), 4.98−4.56 (m, 21 H), 4.40 (d, *J* = 10.4 Hz, 1 H), 4.23−4.13 (m, 2 H), 3.96−3.92 (m, 1 H), 3.83−3.50 (m, 13 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.4, 160.0, 159.7, 159.4, 137.4, 137.2 (2 C), 137.0 (2 C), 136.9, 136.6, 136.4, 131.3, 130.6 (2 C), 130.5 (3 C), 127.5 (2 C), 127.4 (2 C), 127.2 (2 C), 127.1 (2 C), 127.0 (3 C), 126.9, 126.8 (2 C), 126.7 (2 C), 123.5, 123.0, 122.8, 116.9, 115.2, 114.8, 114.6, 99.6 (2 C), 99.5, 83.6, 81.0, 80.9, 80.8, 77.0, 76.9, 76.5, 74.9 (2 C), 74.6, 74.2, 74.1, 72.6, 72.2, 64.3, 62.6, 62.5, 60.7; HRMS (MALDI) calcd for $C_{105}H_{102}O_{22}Na$ $[M + Na]^+$ 1737.6755, found 1737.6759.

Cyclic Trimer 44. Similar procedure as that used for **30**→**32**→**34** was applied to convert **43** into **44** (12 mg, 48% for two steps) as a white solid: $[\alpha]^{25}_D = -24.4$ (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 6 H), 7.27−7.18 (m, 45 H), 6.97 (d, *J* = 8.8 Hz, 6 H), 5.10 (d, *J* = 6.8 Hz, 3 H), 4.91−4.87 (m, 9 H), 4.80−4.72 (m, 6 H), 4.66−4.57 (m, 6 H), 4.29 (dd, *J* = 5.2, 11.6 Hz, 3 H), 3.76−3.65 (m, 9 H), 3.55−3.51 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 159.4, 137.2, 136.9, 136.6, 130.6, 127.5 (2 C), 127.4, 127.2, 127.1, 126.9 (2 C), 126.8, 123.3, 115.8, 99.4, 83.4, 81.2, 76.4, 76.2, 74.8, 74.2, 74.0, 73.1, 62.2; HRMS (MALDI) calcd for $C_{102}H_{96}O_{21}Na$ $[M + Na]^+$ 1679.6336, found 1679.6372.

Cyclic Trimer 9. Similar procedure as that used for **34**→**7** was applied to convert **44** into **9** (12 mg, 100%) as a white solid: $[\alpha]^{25}_D = -33.0$ (*c* 2.3, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 8.4 Hz, 6 H), 7.03 (d, *J* = 8.8 Hz, 6 H), 4.99 (d, *J* = 6.8 Hz, 3 H), 4.75−4.70 (m, 3 H), 4.36 (dd, *J* = 5.6, 12.0 Hz, 3 H), 3.64−3.60 (m, 3 H), 3.41−3.29 (m, 9 H); ^{13}C NMR (100 MHz, CD_3OD) δ 167.4, 162.4, 132.4, 125.3, 117.9, 101.2, 77.6, 76.8, 75.1, 71.6, 64.6; HRMS (MALDI) calcd for $C_{39}H_{42}O_{21}Na$ $[M + Na]^+$ 869.2111, found 869.2145.

Tetramer 45. Similar procedure as that used for **40** + **38**→**41** was applied to condense acid **38** and alcohol **43** into **45** (110 mg, 78%) as a white solid: $[\alpha]^{25}_D = -71.6$ (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73−6.72 (m, 91 H), 5.85−5.75 (m, 1 H), 5.23−4.43 (m, 32 H), 4.20−3.18 (m, 24 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.3, 164.1 (2 C), 159.8, 159.6, 159.1, 142.6, 137.5 (2 C), 137.4 (2 C), 137.3, 137.2, 137.0, 136.9, 136.7, 136.5, 136.4 (2 C), 131.4, 130.4 (2 C), 130.3 (2 C), 127.6, 127.5, 127.4 (3 C), 127.3 (2 C), 127.2 (3 C), 127.0, 126.9 (2 C), 126.8 (2 C), 126.7,126.6, 125.9, 123.3, 123.0, 122.6, 122.4, 116.9, 114.8 (2 C), 114.5, 114.4, 99.5, 99.4, 99.1, 85.6, 83.9 (2 C), 83.7, 83.6, 81.1, 81.0, 77.5, 77.4, 77.3 (2 C), 75.2 (2 C), 74.8, 74.7, 74.6, 74.2, 74.1, 74.0, 73.8, 73.5, 73.0, 72.5, 72.2, 64.3, 62.6, 62.3, 62.2, 61.3; HRMS (MALDI) calcd for $C_{158}H_{148}O_{29}Na$ $[M + Na]^+$ 2531.9998, found 2532.0021.

Tetrameric Derivative 46. Similar procedure as that used for **15**→**16** was applied to convert trityl ether **45** into alcohol **46** (438 mg, 77%) as a white solid: $[\alpha]^{25}_D = -42.9$ (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69−7.59 (m, 8 H), 7.29−7.06 (m, 60 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 8.8 Hz, 2 H), 6.57 (d, *J* = 8.8 Hz, 2 H), 5.86−5.76 (m, 1 H), 5.24−4.44 (m, 33 H), 4.25−3.43 (m, 23 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (2 C), 164.3, 164.1, 159.8, 159.6, 159.4, 159.2, 137.4 (2 C), 137.2, 137.1, 137.0, 136.9 (2 C), 136.7, 136.5, 136.4, 131.3, 130.4, 130.3, 130.2, 127.6, 127.5 (2 C), 127.4 (3 C), 127.3, 127.2 (2 C), 127.1, 127.0 (3 C), 126.9, 126.8, 126.7 (3 C), 126.6, 123.4, 123.1, 122.7, 122.4, 116.9, 114.7, 114.5 (2 C), 114.3, 99.7, 99.4, 99.1, 83.9, 83.8, 83.7, 81.2 (2 C), 81.0, 77.7, 77.5, 76.7, 75.2, 75.0, 74.8 (2 C), 74.6, 74.3, 74.2, 74.1, 73.9, 72.9, 72.2, 71.9, 64.3, 62.9 (2 C), 62.4, 60.6; HRMS (MALDI) calcd for $C_{139}H_{134}O_{29}Na$ $[M + Na]^+$ 2289.8903, found 2289.8890.

Cyclic Tetramer 47. Similar procedure as that used for **30**→**32**→**34** was applied to convert **46** into **47** (24 mg, 48%) as a white solid: $[\alpha]^{25}_D = -24.8$ (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.8 Hz, 8 H), 7.29−7.16 (m, 60 H), 6.96 (d, *J* = 8.4 Hz, 8 H), 5.15 (d, *J* = 7.2 Hz, 4 H), 4.97−4.90 (m, 8 H), 4.80−4.76 (m, 16 H), 4.56 (d, *J* = 11.2 Hz, 4 H), 3.95−3.74 (m, 16 H), 3.56−3.51 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 159.8, 137.3, 137.0, 136.5, 137.5, 127.5 (2 C), 127.4, 127.3, 127.2, 127.1, 126.9, 126.8, 122.8, 114.8, 99.3, 83.7, 81.0, 76.6, 74.9, 74.2, 74.0, 72.2, 63.0; HRMS (MALDI) calcd for $C_{136}H_{128}O_{28}Na$ $[M + Na]^+$ 2231.8484, found 2231.8488.

Cyclic Tetramer 10. Similar procedure as that used for **34**→**7** was applied to convert **47** into **10** (8 mg, 100%) as a white solid: $[\alpha]^{25}_D = -24.1$ (*c* 0.4, DMF); ^1H NMR (400 MHz, CD_3SOCD_3) δ 7.78 (d, *J* = 6.8 Hz, 8 H), 7.06 (d, *J* = 8.4 Hz, 8 H), 5.21 (d, *J* = 6.4 Hz, 4 H), 5.09 (d, *J* = 10.8 Hz, 4 H), 4.01 (t, *J* = 10.0 Hz, 4 H), 3.86 (t, *J* = 9.6 Hz, 4 H), 3.45−3.28 (m, 12 H); ^{13}C NMR (100 MHz, CD_3SOCD_3) δ 165.1, 160.6, 130.8, 122.6, 115.6, 98.4, 76.4, 73.9, 73.1, 70.7, 64.2; HRMS (ESI) calcd for $C_{52}H_{56}O_{28}Na$ $[M + Na]^+$ 1151.2850, found 1151.2903.

Pentamer 48. Similar procedure as that used for **40** + **38**→**41** was applied to condense acid **38** with alcohol **46** into ester **48** (58 mg, 76%) as a white solid: $[\alpha]_D^{25} = -33.4$ (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.45 (m, 6 H), 7.36−6.82 (m, 94 H), 6.72 (d, *J* = 6.8 Hz, 2 H), 6.62−6.57 (m, 6 H), 6.51 (*J* = 8.8 Hz, 2 H), 5.82−5.71 (m, 1 H), 5.27 (d, *J* = 7.2, 1 H), 5.15−3.21 (m, 68 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.2, 164.1, 164.0 (2 C), 159.8 (2 C), 159.7, 159.5, 158.9, 142.6, 137.7, 137.6, 137.5, 137.4 (2 C), 137.3 (2 C), 137.1, 136.9, 136.8, 136.6, 136.5, 131.4, 130.3, 130.2 (2 C), 130.1, 129.9, 128.0, 127.9, 127.6, 127.5, 127.4 (2 C), 127.3 (3 C), 127.2 (2 C), 127.1 (3 C), 126.9 (3 C), 126.8, 126.7, 126.6 (2 C), 126.5, 126.4 (2 C), 126.1, 126.0, 125.8, 123.1, 123.0, 122.8, 122.5, 122.4, 122.2, 116.7, 114.7, 114.6, 114.5, 114.3, 99.8, 99.7, 99.5, 99.1, 85.8, 84.2 (2 C), 84.1, 84.0, 83.9, 83.8, 81.7, 81.6, 81.3, 78.7, 78.1, 77.9, 77.4, 75.4 (2 C), 75.2, 75.1, 75.0 (2 C), 74.9, 74.8, 74.7, 74.6, 74.5 (2 C), 74.3, 74.2 (2 C), 74.1, 74.0 (2 C), 73.8, 72.7, 72.3, 72.2, 72.0, 64.2, 63.0, 62.8, 62.6, 62.4, 61.3; HRMS (MALDI) calcd for $C_{192}H_{180}O_{36}Na$ $[M + Na]^+$ 3084.2147, found 3084.2136.

Pentameric Derivative 49. Similar procedure as that used for **15**→**16** was applied to convert trityl ether **48** into alcohol **49** (51 mg, 95%) as a white solid: $[\alpha]^{25}{}_D = -16.9$ (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2 H), 7.50 (t, *J* = 8.0 Hz, 4 H), 7.35−6.85 (m, 81 H), 6.63−6.60 (m, 4 H), 6.47 (d, *J* = 8.8 Hz, 2 H), 6.39 (d, *J* = 8.8 Hz, 2 H), 5.80−5.70 (m, 1 H), 5.29 (d, *J* = 7.2 Hz, 1 H), 5.15−3.32 (m, 68 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.4, 164.1 (2 C), 163.9, 159.8, 159.7, 159.4, 159.3, 158.9, 137.7, 137.5 (2 C), 137.3, 137.2, 137.1, 136.9, 136.8, 136.5 (2 C), 136.4, 131.4, 130.2, 130.1, 130.0, 129.8, 127.5, 127.4 (2 C), 127.3 (2 C), 127.2, 127.1 (2 C), 127.0, 126.9 (2 C), 126.8 (3 C), 126.7 (2 C), 126.6, 126.5, 126.1, 123.1, 123.0, 122.9, 122.6, 122.2, 116.8, 114.7, 114.6, 114.4, 114.2, 114.1, 99.7, 99.4, 99.1, 84.1, 84.0, 83.8, 81.8, 81.6, 81.3, 81.2, 81.1, 78.8, 78.3, 78.1, 77.8, 77.1, 75.2, 75.1, 75.0, 74.9, 74.8, 74.6, 74.4 (2 C), 74.3 (2 C), 74.2 (2 C), 74.1, 74.0, 72.6, 72.2, 71.8 (2 C), 64.1, 63.2, 63.1, 62.9, 62.5, 60.5; HRMS (MALDI) calcd for $C_{173}H_{166}O_{36}Na$ $[M + Na]^+$ 2842.1051, found 2842.1054.

Cyclic Pentamer 50. Similar procedure as that used for **30**→**32**→**34** was applied to convert **49** into **50** (15 mg, 40% for two steps) as a white solid: $[\alpha]^{25}{}_D = -16.9$ (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.8 Hz, 10 H), 7.27−7.13 (m, 80 H), 6.84 (d, *J* = 8.8 Hz, 10 H), 5.06 (d, *J* = 7.2 Hz, 5 H), 4.92 (d, *J* = 10.8 Hz, 10 H), 4.80−4.71 (m, 15 H), 4.58 (d, *J* = 10.8 Hz, 5 H), 4.51 (d, *J* = 11.2 Hz, 5 H), 4.17 (dd, *J* = 6.8, 12.0 Hz, 5 H), 3.78−3.67 (m, 15 H), 3.51−3.46 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 159.6, 137.3, 137.0, 136.7, 130.6, 127.6, 127.5 (2 C), 127.4, 127.3, 127.2, 127.0 (2 C), 126.9, 126.7, 123.0, 115.1, 99.4, 83.6, 80.8, 76.7, 74.9, 74.1, 72.7, 62.3; HRMS (MALDI) calcd for $C_{170}H_{160}O_{35}Na$ $[M + Na]^+$ 2784.0632, found 2784.0680.

Cyclic Pentamer 11. Similar procedure as that used for **34**→**7** was applied to convert **50** into **11** (11 mg, 100%) as a white solid: $[\alpha]^{25}{}_D = 13.9$ (*c* 0.3, MeOH); ^1H NMR (400 MHz, CD_3OD) δ 7.56 (d, *J* = 8.4 Hz, 10 H), 6.80 (d, *J* = 8.4 Hz, 10 H), 5.01 (d, *J* = 6.0 Hz, 5 H), 4.71−4.68 (d, *J* = 12.0 Hz, 5 H), 4.17(dd, *J* = 7.6, 11.6 Hz, 5 H), 3.75 (t, *J* = 8.0 Hz, 5 H), 3.48−3.47 (m, 10 H), 3.40−3.37 (m, 5 H); ^{13}C NMR (100 MHz, CD_3OD) δ 167.3, 162.3, 132.4, 124.8, 117.1, 100.6, 77.9, 76.1, 74.9, 72.0, 65.1 (2 C); HRMS (ESI) calcd for $C_{65}H_{70}O_{35}Na$ $[M + Na]^+$ 1433.3590, found 1433.3622.

■ ASSOCIATED CONTENT

Supporting Information. Additional experimental details, the ^1H and ^{13}C NMR spectra for all new compounds, and the crystallographic data for compound **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Full crystallographic details of compound **8** have been deposited with the Cambridge Crystallographic Data Centre (CCDC 814588). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.
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