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De Novo Synthesis of Sugar-Aza-Crown Ethers via a Domino Staudinger Aza-Wittig Reaction

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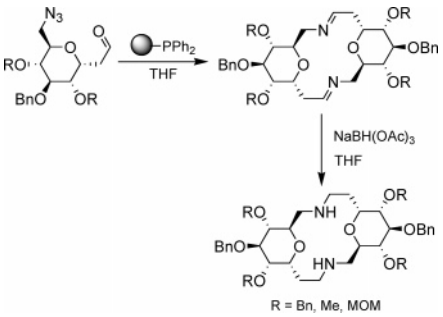
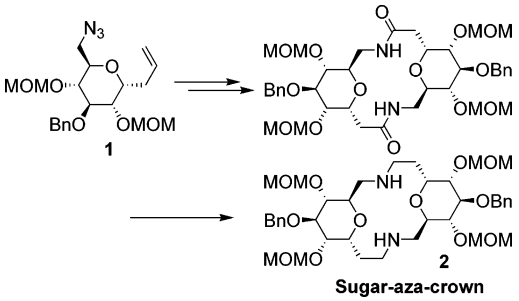


A short and highly efficient route to sugar-aza-crown (SAC) ethers has been developed. The key step of the transformation is a one-pot cyclodimerization of *C*-glycosyl azido aldehydes via a domino Staudinger aza-Wittig reaction. This process allows the preparation of various orthogonally protected SAC ethers, from both α- and *β*-*C*-glycosyl azido aldehydes.

Like cyclodextrins and calixarenes, crown ethers, aza-crown ethers, and cyclams are important molecular receptors for molecular or ionic recognition studies. They are currently used in analytical chemistry and biological model systems, as well as nuclear medicine.[1,2] Sugars are chiral entities that are very suitable for the design of chiral receptors and ligands for asymmetric synthesis or chemosensors. Chiral crown ethers containing various carbohydrate moieties have received much attention in recent years as a result of their ability to selectively complex with guest compounds and to control enantioselective reactions.[3] Very recently, we have realized the first synthesis of amine-linked sugar macrocycles (Scheme 1), which we would like to name as sugar-aza-crowns (SACs), by straightforward

SCHEME 1. Previous Synthesis of SAC 2 in 14 % Total Yields from 1[4]



reduction of the amide bonds in the cyclic oligomers of sugar amino acids.[4] These new receptors may lead to exquisite specificity of recognition and catalyst. Further functionalization would be possible by connecting either to the sugar hydroxyl groups or to the nitrogen atoms. To make an impact on supramolecular chemistry, we envisioned exploring intermolecular macrocyclization as a more convergent synthetic approach to SACs. Template-directed macrolactonization,[5] Schiff-base cyclocondensation strategies,[6] cyclooligomerization of saccharid-derived carbamate,[7] macrocyclization of amino acids derivatives,[8] and [3+2] Huisgen cyclization[9] have been recently employed to prepare medium-sized macrocycles. However, to the best of our knowledge, one-pot reductive amination or Staudinger/aza-Wittig reaction[10] of azido aldehydes has never been reported for macrocyclization. Herein, we describe the exploration of these two strategies.

The discovery of a new regioselective BCl_3-mediated debenzylation reaction toward *C*-glycosides allowed us to start the synthesis with a variety of orthogonally protected *C*-allyl glycosides.[11] The ozonolysis, first tested on the perbenzylated α-*C*-allyl glucoside **3**,[12] seemed to be inappropriate in our case. This reaction led to a complex mixture of sugar aldehydes with partial oxidation of the benzyl group as well as partial epimerization of the anomeric carbon. Therefore, we decided

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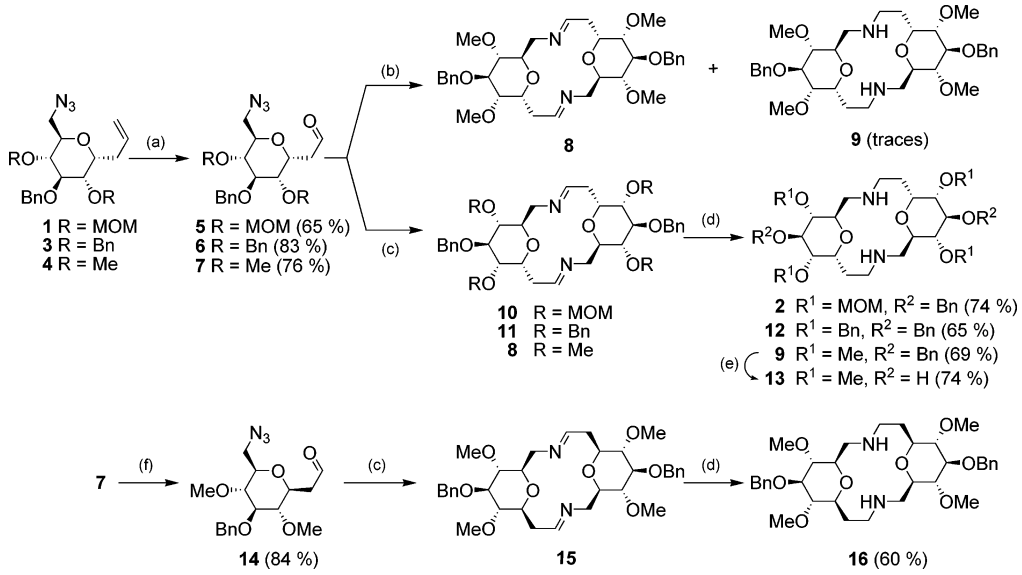
SCHEME 2. Preparation of *C*-Glucosyl Aldehydes and SAC Ethers[a]



[a] Reaction conditions: (a) OsO_4 cat., $NaIO_4$, 2,6-lutidine, dioxane/H_2O (3/1), rt, 30 min.; (b) H_2, 10% Pd/C, MeOH, rt, 24 h; (c) polymer-bound diphenylphosphine (3 equiv), THF, Ar, rt, 20 h; (d) (1) $NaBH(OAc)_3$ (5 equiv), THF, rt, 20 h; (2) 10% Pd/C, MeOH, rt, 24 h; (e) (1) Boc_2O, Et_3N, CH_2Cl_2, 2 h; (2) H_2, Pd black, AcOH; (3) AcCl, MeOH, 2 h; (f) $Zn(OAc)_2$ (5 equiv), 0.6 M NaOMe in MeOH, rt, 3 days.

to apply the well-known OsO_4-NaIO_4 protocol. In this case, the oxidative cleavage of the double bond occurred without epimerization, but the aldehyde **6** was isolated in poor yield (42%), accompanied by a α-hydroxy ketone that resulted from the over oxidation of the diol intermediate. Recently, an improved procedure was developed in which the addition of 2,6-lutidine inhibited the formation of side products, accelerated the reaction, and improved the yields of the desired aldehydes.[13] Oxidation of compounds **1**, **3**, and **4** under these conditions led to good yields of the corresponding aldehydes (65, 83, and 76%, respectively) without the formation of any detectable byproducts (Scheme 2).

As we have shown in a previous paper, the 3-*O*-benzyl group of the orthogonally protected *C*-glucosides is highly resistant under usual hydrogenation conditions,[4] therefore, azido aldehyde **7** was chosen to study the reductive amination strategy for macrocyclization. Treatment of **7** under hydrogenation conditions (10% Pd/C in methanol) led quantitatively to a mixture of imine intermediate **8** and a trace amount of amine macrocycle **9**. In fact, the azide group was totally reduced and converted quantitatively into the imine **8**. However, further reduction to amine **9** was held up, probably as a result of catalyst poisoning by the once-formed amine. Use of other catalysts such as Pd-$(OH)_2$, PtO_2, or Raney Ni did not improve the transformation.

Encouraged by these preliminary results and to identify the imine intermediate, we then decided to investigate a tandem Staudinger/aza-Wittig reaction, which proved to be successful in intramolecular cyclization.[10] Treatment of azido aldehyde **7** with PPh_3 (1.1 equiv) in anhydrous THF (0.1 M) led efficiently to the cyclic imine dimer **8**. The monitoring of experiments conducted at different concentrations was carried out without observing any dilution effect: the cyclic dimer was the only product, and no polymer was detected during the reaction. To better understand this macrocyclization, we decided to follow this reaction by ^{13}C NMR in $CDCl_3$. As shown in Figure 1, the

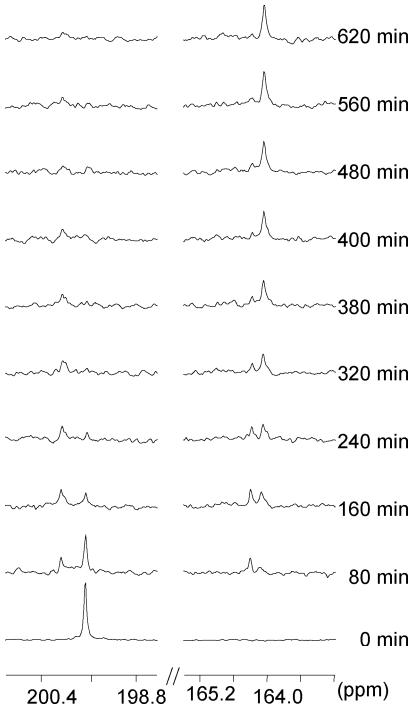


FIGURE 1. ^{13}C NMR kinetic study of the macrocyclization of compound **7** in $CDCl_3$ at 298 K.

chemical shift of the aldehyde function of **7** at 199.4 ppm diminished simultaneously with the appearance of an imine carbon at 164.1 ppm, and a new aldehyde carbon at 199.8 ppm, which could correspond to the linear intermediate **A** (Scheme 3), appeared after an 80 min reaction in $CDCl_3$. The cyclodimeric imine carbon at 163.9 ppm became visible after 160 min. Signals at 164.1 and 199.8 ppm lowered progressively along with the increase of the signal at 163.9 ppm. These results suggested that after the Staudinger reaction, two aza-Wittig reactions (formation of the linear dimer **A** and cyclization) were taking place successively (Scheme 3). The linear dimer would

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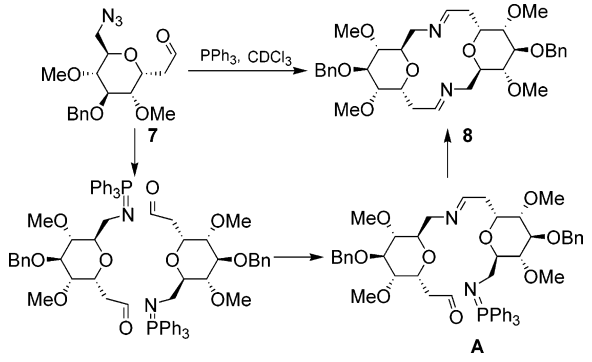
SCHEME 3. Proposed Reaction Pathway for the Staudinger/Aza-Wittig Macrocyclization



be in an adequate conformation to favor the macrocyclization without further polymerization.

An attempt at purification of the cyclic imine **8** over silica gel led to degradation. This difficulty was circumvented by the use of the polymer-bound diphenylphosphine (3 equiv), thus affording the corresponding cyclic imines in good yields (Scheme 2). Because the catalytic hydrogenation was inefficient for imine reduction, we decided to use classical reductive reagents like $NaBH_4$, which was totally inert toward the reduction. Use of $NaBH_3CN$, $NaBH_3CN$/AcOH, BH_3·THF, and $NaBH_4$/AcOH led to complex mixtures. Finally, reduction of the imines was achieved using the commercially available $NaBH(OAc)_3$ (5 equiv). Nevertheless, mass spectrometric analysis showed the presence of boron−amine adducts on each dimer. Attempts to cleave these adducts in acidic media (aqueous HCl 10%) led to the desired amines **2**, **9**, and **12** in moderate yields. Fortunately, a milder method described in a recent paper allowed us to cleave the N−B bonds using Pd/C in methanol.[14] Up to one gram of cyclic dimers can be prepared in this way. However, the 3-*O*-debenzylation of compound **9** by Pd-black-catalyzed hydrogenolysis in the presence of AcOH appeared to be unsuccessful.[4] We then decided to protect first the amine function with Boc_2O. In this case, the 3-*O*-benzyl group was removed after repeated hydrogenolysis, and the desired debenzylated compound **13** was obtained after acidic hydrolysis of the N−Boc protecting group in 74% total yield (Scheme 2).

To verify if this cyclodimerization was dependent on the anomeric configuration, the α-*C*-glucosyl aldehyde **7** was first epimerized to the corresponding *β*-anomer **14** using $Zn(OAc)_2$ in 0.6 M MeONa/MeOH[15] and then submitted to the optimized one-pot Staudinger/aza-Witting reaction (Scheme 2). As the α-anomer, compound **14** gave the corresponding cyclodimer **16** in a 60% yield after reduction.

In conclusion, we have presented an efficient domino Staudinger aza-Wittig reaction for cyclodimerization of *C*-glycosyl azido aldehydes. This reaction is compatible with a large number of protecting groups and more versatile than the reductive amination reaction. The resulting SAC ethers represent a new class of molecular receptors. These compounds are currently tested as ligands for metal complexation, polyfunctional building blocks in the synthesis of more complex structures for host−guest recognition studies, or as catalysts for asymmetric synthesis.

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Experimental Section

General Process for Cyclodimerization. To a solution of sugar azido aldehyde (1 equiv) in freshly distilled THF (0.1 M) under an argon atmosphere was added polymer-bound diphenylphosphine (3 equiv), and the reaction was stirred overnight at room temperature. Then the mixture was diluted in EtOAc, filtered over a Celite pad, and evaporated to give the corresponding cyclic imine dimer, which was used further without any purification.

Cyclic Imine 8: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.44 (dd, J = 2.2, 14.5 Hz, 2H), 2.68 (ddd, J = 14.5, 12.7, 8.2 Hz, 2H), 2.86 (t, J = 9.4 Hz, 2H), 3.01 (dd, J = 10.9, 9.4 Hz, 2H), 3.38−3.50 (m, 2H), 3.47 (s, 6H, OMe), 3.52 (s, 6H), 3.59 (t, J = 9.4 Hz, 2H), 3.76 (t, J = 9.4 Hz, 2H), 4.04 (d, J = 10.9 Hz, 2H), 4.35 (ddd, J = 5.9, 12.7, 2.2 Hz, 2H), 4.77 (d, J = 10.8, 2H), 4.85 (d, J = 10.8, 2H), 7.22−7.42 (m, 10H), 7.47 (d, J = 8.2 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 32.0, 59.0, 60.8, 62.6, 70.4, 70.5, 75.3, 81.8, 82.2, 82.8, 127.6, 127.9, 128.4, 138.8, 164.0.

Cyclic Imine 10: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.54 (dd, J = 2.2, 14.4 Hz, 2H), 2.77 (ddd, J = 14.4, 8.3, 12.6 Hz, 2H), 3.02 (dd, J = 11.6, 9.4 Hz, 2H), 3.24 (dd, J = 8.6, 9.4 Hz, 2H), 3.38 (s, 6H), 3.34 (s, 6H), 3.64 (dd, J = 9.9, 8.6 Hz, 2H), 3.77 (dd, J = 5.9, 9.9 Hz, 2H), 3.87 (t, J = 9.4 Hz, 2H), 4.15 (d, J = 11.6 Hz, 2H), 2.77 (ddd, J = 2.2, 12.6, 5.9 Hz, 2H), 4.61 (d, J = 6.5 Hz, 2H), 4.64 (d, J = 6.5 Hz, 2H), 4.72 (d, J = 11.1 Hz, 2H), 4.78 (d, J = 6.5 Hz, 2H), 4.82 (d, J = 11.1 Hz, 2H), 4.91 (d, J = 6.5 Hz, 2H), 7.20−7.39 (m, 10H), 7.47 (d, J = 8.3 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 32.4, 55.9, 56.5, 62.7, 70.0, 72.1, 75.6, 78.3, 79.5, 82.1, 97.8, 98.6, 127.5, 128.8, 138.5, 164.4.

Cyclic Imine 11: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.47−2.59 (m, 2H), 2.74 (ddd, J = 14.6, 8.3, 12.9 Hz, 2H), 2.91 (dd, J = 11.0, 9.7 Hz, 2H), 3.16 (dd, J = 8.5, 9.7 Hz, 2H), 3.70 (dd, J = 5.7, 9.4 Hz, 2H), 3.78 (dd, J = 9.4, 8.5 Hz, 2H), 3.87 (t, J = 9.7 Hz, 2H), 4.06 (d, J = 11.1 Hz, 2H), 4.20 (ddd, J = 5.7, 2.5, 12.9 Hz, 2H), 4.60 (d, J = 11.1 Hz, 2H), 4.62 (d, J = 11.7 Hz, 2H), 4.75 (d, J = 12.0 Hz, 2H), 4.80 (d, J = 11.1 Hz, 2H), 4.60 (d, J = 10.8 Hz, 4H), 7.20−7.41 (m, 32H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 32.3, 62.8, 70.5, 71.3, 73.5, 75.1, 75.8, 79.9, 80.9, 82.7, 127.7, 127.9, 128.1, 128.5, 128.6, 138.4, 138.7, 164.0.

Cyclic Imine 15: ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.44 (dt, J = 14.8, 6.1 Hz, 2H), 2.66 (dt, J = 14.8, 3.8 Hz, 2H), 2.83−3.00 (m, 2H), 3.07 (t, J = 9.3 Hz, 2H), 3.22 (t, J = 8.9 Hz, 2H), 3.33−3.64 (m, 6H), 3.55 (s, 6H), 3.60 (s, 6H), 3.64−3.78 (m, 2H), 4.75−4.94 (m, 4H), 7.20−7.48 (m, 10H), 7.62 (t, J = 4.8 Hz, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 37.4, 60.7, 61.5, 75.2, 75.8, 77.2, 81.6, 82.9, 86.7, 127.5, 127.7, 128.3, 138.7, 164.3.

General Procedure for the Reduction of Imine to Amine. To a solution of imine cyclodimer (1 equiv) in freshly distilled THF (0.1 M) under an argon atmosphere was added $NaBH(OAc)_3$ (5 equiv), and the reaction was stirred overnight at room temperature. Then the mixture was partitioned in EtOAc/H_2O, extracted three times with EtOAc, washed with brine, dried over $MgSO_4$, and evaporated. The residue was diluted in MeOH, and Pd/C (10% w/w) was added. After stirring for 24 h, the mixture was filtered over a Celite pad, washed with MeOH, evaporated, and purified over silica gel to give the corresponding SAC ethers.

Sugar-Aza-Crown 9: R_f 0.55 (6:4, EtOAc/cyclohexane, saturated with NH_3 gas), mp 128 °C, $[\alpha]_D$ +69.4 (*c* 1, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.71−1.87 (m, 2H), 1.87−2.07 (m, 2H), 2.34 (s, 2H, NH), 2.53−2.72 (m, 4H), 2.83 (t, J = 9.3 Hz, 2H), 2.90−3.09 (m, 4H), 3.37 (dd, J = 6.4, 9.3 Hz, 2H), 3.44 (s, 6H), 3.50 (s, 6H), 3.57 (t, J = 9.3 Hz, 2H), 3.65−3.78 (m, 2H), 4.12−4.26 (m, 2H), 4.75 (d, J = 10.8 Hz, 2H), 4.85 (d, J = 10.8 Hz, 2H), 7.22−7.43 (m, 10H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 23.5, 48.1, 52.1, 58.9, 60.6, 70.2, 74.6, 75.3, 81.8, 82.1, 82.7, 127.6, 128.0, 128.4, 138.8. MS (MALDI): *m*/*z* 615.40 $[M + H]^+$, 637.36 $[M + Na]^+$. HRMS (FAB^+) *m*/*z* $[M + H]^+$ calcd for $C_{34}H_{51}N_2O_8$, 615.3640; found, 615.3638.

Sugar-Aza-Crown 12: R_f 0.57 (9:1, EtOAc/EtOH), mp 177 °C, $[\alpha]_D$ +49.1 (*c* 1, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.76−2.16 (m, 4H), 2.44−2.71 (m, 4H), 2.91−3.09 (m, 4H), 3.15 (t, J = 9.2 Hz, 2H), 3.66 (dd, J = 6.0, 9.2 Hz, 2H), 3.78 (t, J = 9.2 Hz, 2H), 3.77−3.92 (m, 2H), 4.04−4.20 (m, 2H), 4.50−4.99 (m, 12H), 7.09−7.44 (m, 30H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 24.1, 47.4, 52.6, 70.6, 73.1, 74.7, 75.1, 75.7, 80.4, 81.3, 82.5, 127.8, 127.9, 128.0, 128.5, 138.3, 138.4, 138.8. MS (MALDI): *m*/*z* 919.48 [M + H]$^+$, 941.47 [M + Na]$^+$. HRMS (FAB$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{58}H_{67}N_2O_8$, 919.4892; found, 919.4888.

Sugar-Aza-Crown 13: To a solution of SAC **9** (60 mg, 0.0977 mmol) in CH_2Cl_2 (6 mL) was added Boc_2O (45 mg, 0.2062 mmol) and Et_3N (135 μL, 0.975 mmol), and the mixture was stirred for 2 h at room temperature. After evaporation, the crude product was purified over silica gel (3:7, EtOAc/cyclohexane) to give the desired $(Boc)_2$SAC (white solid, 77 mg, 0.0946 mmol, 97%), which was dissolved in acetic acid (2 mL) and hydrogenated under a H_2 atmosphere overnight in the presence of Pd black (23 mg, 30% w/w). Then the mixture was filtered over a Celite pad and rinsed with acetic acid, and the hydrogenation was repeated a second time. The filtered solution was finally coevaporated with toluene and purified over silica gel (8:2, EtOAc/cyclohexane) to give the fully debenzylated intermediate (46 mg, 0.0726 mmol, 77%). Finally, the debenzylated $(Boc)_2$SAC was dissolved in a solution of AcCl (320 μL, 4.5 mmol) in MeOH (3 mL), and the reaction was stirred for 2 h at room temperature. After evaporation, the crude product was dissolved in distilled water, neutralized with NaOH (2.9 mg, 0.0726 mmol), filtered over glass cotton, and evaporated under vacuum to give the desired deprotected compound **13** (32 mg, 0.0726 mmol, 74% overall yield) as a white solid: mp 214 °C, $[\alpha]_D$ +77.2 (*c* 1, D_2O). ^{1}H NMR (250 MHz, D_2O with 20% CD_3OD) δ 1.57−1.91 (m, 4H), 2.52−2.70 (m, 4H), 2.73−2.97 (m, 6H), 3.25−3.40 (m, 2H), 3.36 (s, 6H), 3.46 (s, 6H), 3.48−3.60 (m, 2H), 3.63 (t, J = 9.40 Hz, 2H), 4.19−4.35 (m, 2H).^{13}C NMR (62.9 MHz, D_2O with 20% CD_3OD) δ 23.7, 46.1, 51.6, 58.7, 61.2, 70.8, 73.0, 73.7, 81.6, 83.8. HRMS (FAB$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{39}N_2O_8$, 435.2701; found, 435.2700.

Sugar-Aza-Crown 16: R_f 0.55 (6:4, EtOAc/cyclohexane, saturated with NH_3 gas), mp 68 °C, $[\alpha]_D$ +9.4 (*c* 1, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.62−1.83 (m, 2H), 1.98−2.15 (m, 2H), 2.64−2.91 (m, 8H), 2.96 (t, J = 9.3 Hz, 2H), 3.10 (t, J = 9.4 Hz, 2H), 3.26−3.40 (m, 2H), 3.44 (dd, J = 8.8, 4.8 Hz, 2H), 3.47−3.58 (m, 2H), 3.52 (s, 6H), 3.54 (s, 6H), 4.83 (s, 4H), 7.27−7.43 (m, 10H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 30.3, 47.9, 50.6, 60.9, 61.1, 75.4, 77.6, 81.0, 82.0, 83.7, 86.6, 127.8, 128.0, 128.5, 138.8. MS (MALDI): *m*/*z* 615.29 [M + H]$^+$. HRMS (FAB$^+$) *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{51}N_2O_8$, 615.3640; found, 615.3634.

Supporting Information Available: General methods, syntheses of *C*-glycosyl azido aldehydes, ^{1}H and ^{13}C NMR spectra of all the products. This material is available free of charge via the Internet at http://pubs.acs.org

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