Multivalent Templated Saccharides: Convenient Syntheses of Spacer-Linked 1,1′-Bis -and 1,1′,1″-Tris-*β*-glycosides by the Glycal Epoxide Glycosidation Method

Raymond J. Patch,* Hang Chen, and Chennagiri R. Pandit

Department of Rational Drug Design, Procept, Inc., 840 Memorial Drive, Cambridge, Massachusetts 02139

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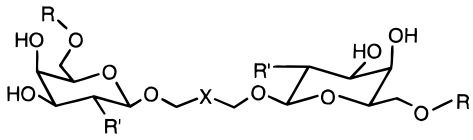
The importance of carbohydrates in mediating a host of biological responses has become increasingly appreciated in recent years. Cellular adhesion events rely on carbohydrate−protein interactions and have implications in a variety of disease states such as those involving cellular proliferation, cellular differentiation, inflammatory responses, pathogenic invasions, and tumor metastasis.[1] Furthermore, carbohydrates are believed to affect protein folding[2] and additionally may provide conformational stability to glycoprotein tertiary structure.[3]

Advances in synthetic methodology have allowed researchers to prepare complex oligosaccharides as tools for examining the binding modes of various protein−carbohydrate interactions. In some cases, such studies have given rise to important structure−function relationships for oligosaccharide binding to target proteins.[4] While advances continue to be made in the development of synthetic methodologies for preparing complex oligosaccharides, such molecules still pose formidable synthetic challenges and, as such, are not widely viewed as feasible candidates for drug development. However, oligosaccharide mimics may offer reasonable alternatives for therapeutic intervention.[5]

Along these lines, we recently required a series of molecules **1a**, wherein two carbohydrate moieties, benzylated at the 6-hydroxyl position, were to be connected via *β*-glycosidic linkages to an aliphatic spacer (X).



1 a R = CH_2Ar; R′ = OH

1 b R = H; R′ = $NHCOCH_3$

Similar molecules have been reported by Lehmann's group,[6,7] wherein a homologous series of spacer-modified disaccharides, **1b**, were prepared to study the mechanism of galactosylation by *β*-D-galactosyltransferase. In those studies, *N*-phthalimidoglucosamine peracetate residues were coupled to primary aliphatic diols (C_6−C_{12}) using tin(IV) chloride as the coupling agent to provide bis-*β*-glycosides in good yields.

We anticipated using similar methodology for our constructs and began our investigation by attempting the glycosidation of 1,6-hexanediol with 6-benzyl-*β*-D-galactose 1,2,3,4-tetra-*O*-acetate.[8] In this case, bis-coupling took place; however, the product was a mixed α,*β*-bis-glycoside. With lower order diols (C_5, C_4, C_2) no glycosidic products were obtained; moreover, debenzylation of the glycosyl donor was observed. In model studies with *β*-D-glucose pentaacetate, coupling gave rise to α,α-bis-glycosides in modest yields (ca. <25%) with none of the desired *β*,*β*-bis-glycosides being observed. Operating at lower temperatures (<5 °C), as suggested by Honma et al.,[9] did not affect the stereochemical outcome of the reaction. Clearly, the trans-directing ability of the 2-phthalimido group[10] does not extend to the 2-acetate group under these reaction conditions. The use of trimethylsilyl triflate, under conditions described for *β*-glycosylation with a primary alcohol by Ogawa,[11] also failed to provide the desired *β*,*β*-bis-glycoside. While Helferich-catalyzed glycosylation in toluene and toluene/nitromethane solvent mixtures[12] and modified Koenigs−Knorr glycosylations[13] provided the desired *β*,*β*-bis-glycosides in model reactions with α-D-acetobromoglucose and 1,6-hexanediol, yields were again quite modest. Thus, we turned our attention to alternative glycosidation methods that would be compatible with the somewhat labile 6-benzylic ether functionality.

Danishefsky's elegant glycal epoxide glycosidation methodology seemed well suited to our needs for providing *β*-glycosides in a highly stereoselective fashion under mild conditions.[14] To our knowledge, application of this method has been limited to monoglycosidation reactions. In certain cases where primary and secondary hydroxyl groups are present in the glycosyl acceptor, reactivity differences between the two may be sufficient to favor exclusive primary glycoside formation, thus obviating the need for secondary alcohol protection.[15] By contrast, in at least one instance it has been postulated that the presence of two hydroxyl groups may have "interfered with the ability of zinc chloride to orchestrate glycosidation".[16] Thus, the effectiveness of this methodology with glycosyl acceptors containing more than one reactive alcohol functionality has not been clearly established. Herein, we report that the utility of this method does in fact extend to *single-step* homologous bis- and even tris-glycosidations through reaction with reactive diols and triols affording bis- and tris-*β*-glycosides, respectively, in good yields.

Scheme 1 outlines the general synthesis of our target bis-glycosides. Benzyl galactal carbonate **3** was prepared in two steps (61%) from known silyl galactal carbonate

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(2) Helenius, A. *Mol. Biol. Cell* **1994**, *5*, 253−265.
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(6) Lehmann, J.; Petry, S. *Carbohydr. Res.* **1990**, *204*, 141−144.
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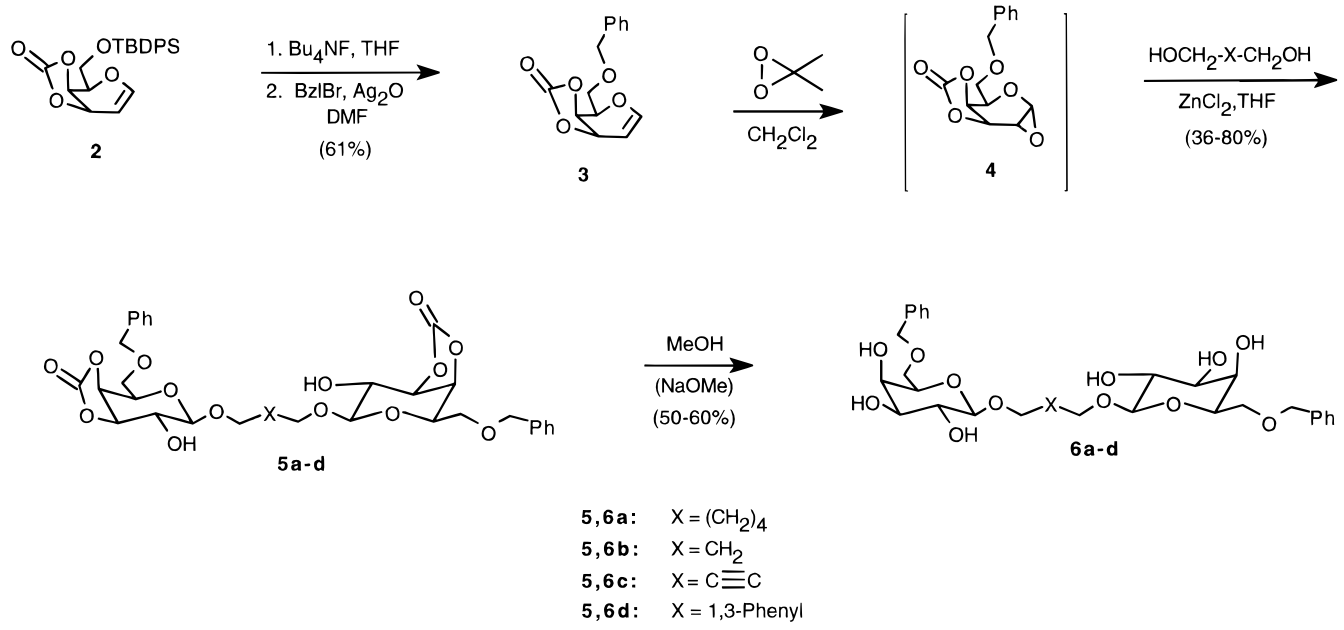
Scheme 1



2.[17] Using the standard conditions described by Danishefsky, modified to include 3 Å molecular sieves, a highly stereoselective α-epoxidation with 3,3-dimethyldioxirane[18] was realized. Subsequent treatment with diols (0.45 equiv) and zinc chloride afforded the symmetrical bis-β,β'-glycosides **5** in yields ranging from 36 to 80% (unoptimized). Deprotection of the cyclic carbonates was accomplished by methanolysis to provide target bis-glycosides **6** in satisfactory overall yield.

Anomeric configurations of cyclic carbonates **5** are readily assigned by inspection of H_1 and H_2 resonances in their ^{1}H NMR spectra. With the exception of **5c**, the anomeric proton signals lie between δ 4.4−4.5 ppm with the expected coupling ($J_{1,2} \approx 6-6.5$ Hz).[17] Interestingly, the anomeric proton of butyne analog **5c** is significantly deshielded. Its resonance signal is shifted downfield to δ 4.98 ppm and exhibits an apparent reduced coupling to H_2 ($J_{1,2} \approx 4.5$ Hz) due to broadening of the signal. However, examination of the H_2 resonance signal of **5c** (δ 4.19 ppm) reveals the true coupling between these protons (J = 6.3 Hz), confirming the assignment of β-configuration to this bis-glycoside.

Encouraged by these results, we next explored the possibility of extending the methodology to single-step tris-glycosidation reactions. In this case, galactal epoxide **4** (3.3 equiv based on galactal precursor **3**) was reacted with 1,3,5-benzenetrimethanol[19] to afford the tris-β-galactoside **7** in 25% yield along with bis-β-galactoside **8** (46%) (Scheme 2). Use of 4.8 equiv of galactal **3** led to an increased yield (66%) of tris-galactoside **7**. No α-galactoside-containing products were isolated from the reaction, again due to the high stereoselectivity of the reaction process. Methanolysis as before afforded **9** in 59% isolated yield.

The relative ease with which bis-glycosides **5**, **6**, and **8** and tris-glycosides **7** and **9** can be assembled is particularly noteworthy. As oligosaccharide mimetics, such molecules, in and of themselves or with minor modifications, may find biological utility as "cluster-type ligands"[20] and additionally may help to elucidate binding specificity of carbohydrate−protein interactions. Clustering effects have been observed with a number of lectin systems; multivalent compounds such as those above may prove useful as functional ligands for these systems.[21] Finally, differentially protected molecules similar to model compounds **5**, **7**, and **8** may be further elaborated selectively into oligosaccharide mimetics of increased complexity including, for example, carbohydrate-based dendrimers.[22,23] Results from such studies will be reported in due course.

Experimental Section

General Procedures. All reactions were carried out in flame-dried vessels under an inert argon atmosphere. Molecular sieves were flame-dried under vacuum immediately prior to use. Anhydrous THF and dichloromethane were used as supplied by Aldrich. Flash chromatography was performed with silica gel 60 (EM, 0.040−0.063 mm). Radial chromatography was performed on a chromatotron (Harrison Research Co.) using precoated silica gel rotors (Analtech). ^{1}H NMR (250 MHz, Bruker) spectra were obtained as solutions in $CDCl_3$ with chemical shifts reported in parts per million (ppm, δ) downfield from internal Me_4Si (TMS) or in DMSO-d_6, referencing DMSO at 2.49 ppm. ^{13}C NMR spectra were obtained as solutions in DMSO-d_6, referencing the solvent at 39.50 ppm. Infrared spectra were recorded on a Perkin-Elmer 1605 series FTIR spectrophotometer. Negative ion FAB MS spectra were obtained at the Harvard University Chemistry department[24] on samples dissolved in methanol using an SX102A mass spectrometer (JEOL Ltd.) with a glycerol matrix-coated probe. Elemental analyses were carried out by Atlantic Microlab Inc. Melting points are uncorrected.

6-*O*-Benzyl-3,4-(oxomethylene)-D-galactal (3). To an ice-cooled solution of 6-O-tert-butyldiphenylsilyl-3,4-(oxomethylene)-

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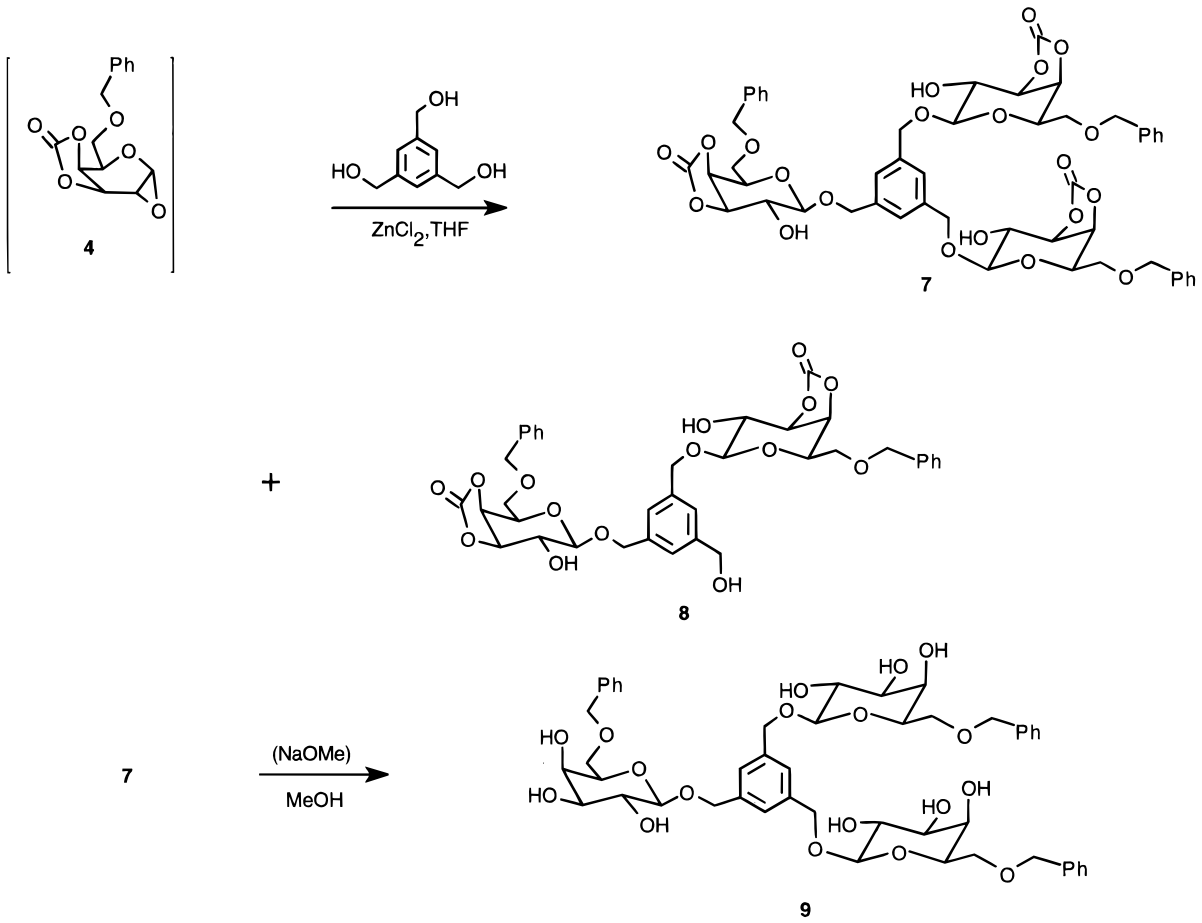
(24) We acknowledge Dr. Andrew Tyler for obtaining mass spectral data. The Harvard University Chemistry Department Mass Spectrometry Facility is supported by grants from NSF (CHE-9020043) and NIH (S10-RR06716).

Scheme 2



D-galactal **2**[17] (3.30 g; 8.0 mmol) in THF (40 mL) was added 1 M tetrabutylammonium fluoride in THF (8.2 mL; 8.2 mmol), and the resulting solution was stirred for 0.5 h. The solution was then concentrated, and the residue was purified by flash chromatography eluting with chloroform and then chloroform/methanol (25:1) to afford 3,4-(oxomethylene)-D-galactal (1.18 g; 85%) as a colorless syrup. A solution of this syrup in DMF (10ml) was treated with silver(I) oxide (4 g) and benzyl bromide (2 mL), and the resulting mixture was stirred at room temperature. After 3 days, the mixture was diluted with toluene (15 mL), filtered through Celite, and concentrated. Purification of the residue by flash chromatography eluting with hexane/ethyl acetate (4:1) afforded 6-*O*-benzyl-3,4-(oxomethylene)-D-galactal (**3**) (1.10g; 61%) as a colorless syrup: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 5H), 6.70 (d, J = 6.2 Hz, 1H), 5.18 (dd, J = 8.0, 3.2 Hz, 1H), 5.0−4.9 (m, 2H), 4.60 (s, 2H), 4.15−4.05 (m, 1H), 3.82 (q, J = 9.6 Hz, 1H), 3.78 (q, J = 9.6 Hz, 1H).

1,6-Bis[[6-*O*-benzyl-3,4-(oxomethylene)-*β*-D-galactopyranosyl]oxy]hexane (5a). To an ice-cooled solution of galactal **3** (147 mg; 0.56 mmol) and 3 Å molecular sieves (0.25 g) in dichloromethane (12 mL) was added a solution of 3,3-dimethyldioxirane[18] (6 mL; >0.6 mmol) in a steady, dropwise fashion. Upon complete addition, the ice bath was removed and stirring was continued at room temperature. After 1 h, the reaction was concentrated and briefly dried in vacuo. The residue was taken up in anhydrous THF (4 mL) and treated with 1,6-hexanediol (30 mg; 0.25 mmol) and additional sieves (0.25 g), and the resulting mixture was stirred at room temperature. After 15 min, the mixture was cooled to −78 °C, 1 M $ZnCl_2$ in ether (0.67mL) was added, and the reaction was maintained at this temperature for 2 h and then overnight at room temperature. Ethyl acetate (10 mL) was added, the mixture was filtered through Celite and the filtrate was quenched with saturated aqueous $KHCO_3$. The organic phase was separated and concentrated under reduced pressure, and the residue was purified by radial chromatography eluting with chloroform and then chloroform/methanol (25:1) to afford bis-galactoside **5a** (136 mg; 80%) as a white foam: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10H), 4.81 (dd, J = 7.7, 2.0 Hz, 2H), 4.67 (dd, J = 7.9, 6.1 Hz, 2H), 4.58 (s, 4H), 4.39 (d, J = 6.6 Hz, 2H), 4.02 (td, J = 6.6, 2.0 Hz, 2H), 3.90 (dt, J = 9.9, 6.0 Hz, 2H), 3.80−3.65 (m, 6H), 3.50 (dt, J = 9.9, 6.0 Hz, 2H), 3.05 (br d, J = 3.3 Hz, 2H), 1.70−1.50 (m, 4H), 1.50−1.30 (m, 4H).

1,3-Bis[[6-*O*-benzyl-3,4-(oxomethylene)-*β*-D-galactopyranosyloxy)propane (5b). According to the above procedure described for **5a**, galactal **3** (220 mg; 0.84 mmol) was converted to epoxide **4** and subsequently reacted with 1,3-propanediol (24 uL; 0.33 mmol) to afford after purification by radial chromatography [chloroform; chloroform/methanol (25:1)] bis-galactoside **5b** (75mg; 36%) as a white foam: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10H), 4.81 (dd, J = 7.7, 2.0 Hz, 2H), 4.67 (dd, J = 7.7, 5.5 Hz, 2H), 4.58 (s, 4H), 4.45 (d, J = 6.4 Hz, 2H), 4.04 (td, J = 6.4, 2.0 Hz, 2H), 3.93 (dt, J = 9.9, 5.5 Hz, 2H), 3.80−3.60 (m, 8H), 3.07 (br d, J = 3.3 Hz, 2H), 1.90 (quint, J = 7.2 Hz, 2H).

1,4-Bis-[[6-*O*-benzyl-3,4-(oxomethylene)-*β*-D-galactopyranosyl]oxy]but-2-yne (5c). According to the above procedure described for **5a**, galactal **3** (220 mg; 0.84 mmol) was converted to epoxide **4** and subsequently reacted with 1,4-butynediol (28 mg; 0.33 mmol) to afford after purification by radial chromatography [chloroform; chloroform/methanol (25:1)] bis-galactoside **5c** (89 mg; 42%) as a white foam: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 10H), 4.98 (br d, J = 4.5 Hz, 2H), 4.76 (dd, J = 8.1, 1.8 Hz, 2H), 4.66 (dd, J = 8.1, 3.8 Hz, 2H), 4.58 (s, 4H), 4.38 (s, 4H), 4.18 (td, J = 6.3, 1.8 Hz, 2H), 3.8−3.6 (m, 8H).

1,3-Bis-(6-*O*-benzyl-3,4-(oxomethylene)-*β*-D-galactopyranosyl]oxy]methyl]benzene (5d). According to the above procedure described for **5a**, galactal **3** (190 mg; 0.73 mmol) was converted to epoxide **4** and subsequently reacted with 1,3-benzenedimethanol (45.5 mg; 0.33 mmol) to afford after purification by radial chromatography [chloroform; chloroform/methanol (25:1)] bis-galactoside **5d** (121 mg; 53%) as a white foam: ^{1}H NMR ($CDCl_3$) δ 7.5−7.1 (m, 14H), 4.88 (d, J = 12.1 Hz , 2H), 4.81 (dd, J = 7.7, 2.0 Hz , 2H), 4.62 (dd, J = 7.7, 5.5 Hz , 2H), 4.60 (s, 4H), 4.58 (d, J = 12.1 Hz , 2H), 4.51 (d, J = 5.7 Hz , 2H),

4.04 (td, J = 6.1, 2.0 Hz , 2H), 3.90−3.70 (m, 6H), 3.05 (br d, J = 3.5 Hz , 2H).

1,6-Bis[6-*O*-benzyl-*β*-D-galactopyranosyl)oxy]hexane (6a). To a solution of bis-galactoside **5a** (136 mg; 0.20 mmol) in anhydrous methanol (5 mL) was added a pinch of sodium methoxide, and the resulting mixture was stirred at room temperature. After 2 h, the product, which formed as a white precipitate, was filtered and dried under vacuum to provide pure **6a** (67 mg; 54%): mp 174.5−176 °C; FTIR (KBr) 3513, 3446, 3260 (br), 2935, 2866, 1377, 1152, 1091, 1076, 1057, 1022, 948, 921, 908, 857, 786, 739, 699 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.5−7.2 (m, 10H), 4.84 (br d, J = 4.0 Hz , 2H), 4.72 (br d, J = 4.5 Hz , 2H), 4.49 (s, 4H), 4.46 (d, J = 5.0 Hz , 2H), 4.07 (br d, J = 7.0 Hz , 2H), 3.75−3.15 (m, 16H), 1.60−1.40 (m, 4H), 1.40−1.20 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 138.60, 128.16, 127.32, 127.30, 103.36, 73.31, 73.24, 72.13, 70.41, 69.53, 68.66, 68.50, 29.32, 25.39; MS (FAB (M$^-$)) m/e 621 [M − H], 531 [M − CH_2Ph], 439, 369 [M − (6-benzyl-1-deoxygalactose)]. Anal. Calcd for $C_{32}H_{46}O_{12}$: C, 61.72; H, 7.45. Found: C, 61.62; H, 7.49.

1,3-Bis[6-*O*-benzyl-*β*-D-galactopyranosyl)oxy]propane (6b). To a solution of bis-galactoside **5b** (91 mg; 0.14 mmol) in anhydrous methanol (5 mL) was added a pinch of sodium methoxide and the resulting mixture was stirred at room temperature. After 2 h, the solvent was evaporated and the residue was purified by flash chromatography, eluting with chloroform/methanol (4:1) to afford **6b** (41 mg; 49%) as a white solid: mp 118.5−120 °C; FTIR (KBr) 3497, 3426 (br), 2923, 2869, 1452, 1376, 1144, 1097, 1072, 1058, 949, 923, 851, 742, 697 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.5−7.2 (m, 10H), 4.86 (br d, J = 4.4 Hz , 2H), 4.72 (br d, J = 5.0 Hz , 2H), 4.49 (s, 4H), 4.47 (d, J = 5.5 Hz , 2H), 4.09 (br d, J = 7.1 Hz , 2H), 3.77 (dt, J = 9.9, 6.6 Hz), 3.65−3.40 (m, 10H), 3.30−3.20 (m, 4H), 1.80 (quint, J = 7.2 Hz , 2H); ^{13}C NMR (DMSO-d_6) δ 138.56, 128.17, 127.35, 127.29, 103.52, 73.26, 73.21, 72.13, 70.42, 69.45, 68.62, 65.82, 29.92; MS (FAB (M$^-$)) m/e 579 [M − H], 489 [M − CH_2Ph], 397, 327 [M − (6-benzyl-1-deoxygalactose)]. Anal. Calcd for $C_{29}H_{40}O_{12}$: C, 59.99; H, 6.94. Found: C, 59.77; H, 6.88.

1,4-Bis-(6-*O*-benzyl-*β*-D-galactopyranosyl)oxy]but-2-yne (6c). To a solution of bis-galactoside **5c** (89 mg; 0.14 mmol) in anhydrous methanol (5 mL) was added a pinch of sodium methoxide, and the resulting mixture was stirred at room temperature. After 2 h, the solvent was evaporated and the residue was treated with water (2 mL). The white crystalline product that resulted was filtered and dried under vacuum, affording pure **6c** (43 mg; 53%): mp 160−161.5 °C; FTIR (KBr) 3481, 3436, 3344, 3251, 2908, 2862, 1453, 1343, 1272, 1206, 1100, 1055, 1008, 923, 905, 888, 782, 753, 734, 697 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.5−7.2 (m, 10H), 5.02 (br d, J = 3.8 Hz , 2H), 4.75 (br d, J = 4.4 Hz , 2H), 4.55−4.45 (m, 6H), 4.40 (d, J = 13.6 Hz , 2H), 4.28 (d, J = 13.6 Hz , 2H), 4.23 (br d, J = 7.0 Hz , 2H), 3.65−3.40 (m, 8H), 3.40−3.20 (m, 4H); ^{13}C NMR (DMSO-d_6) δ 138.54, 128.19, 127.39, 127.32, 101.41, 82.18, 73.48, 73.08, 72.18, 70.23, 69.40, 68.54, 55.00; MS (FAB (M$^-$)) m/e 589 [M − H], 499 [M − CH_2Ph], 337 [M − (6-benzyl-1-deoxygalactose)]. Anal. Calcd for $C_{30}H_{38}O_{12}$: C, 61.01; H, 6.49. Found: C, 60.81; H, 6.46.

1,3-Bis-[[6-*O*-benzyl-*β*-D-galactopyranosyl)oxy]methyl)-benzene (6d). To a solution of bis-galactoside **5d** (121 mg; 0.17 mmol) in anhydrous methanol (5 mL) was added a pinch of sodium methoxide, and the resulting mixture was stirred at room temperature. After 2 h, the solvent was evaporated, and the residue was purified by flash chromatography, eluting with chloroform/methanol (20:3) to afford **6d** (65 mg; 58%) as a white solid: mp 132−149 °C (gradual melting); FTIR (KBr) 3405 (br), 2919, 2870, 1498, 1453, 1368, 1070, 908, 782, 736, 696 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.5−7.2 (m, 14H), 4.76 (d, J = 12.15 Hz , 2H), 4.7−4.4 (m, 8H), 4.22 (d, J = 7.0 Hz , 2H), 3.8−3.5 (m, 10H), 3.5−3.1 (m, 6H); ^{13}C NMR (DMSO-d_6) δ 138.59, 137.92, 128.18, 127.93, 127.35, 127.31, 126.89, 126.71, 102.73, 73.45, 73.16, 72.16, 70.46, 69.53, 69.50, 68.64; MS (FAB (M$^-$)) m/e 641 [M − H], 651 [M − CH_2Ph], 389 [M − (6-benzyl-1-deoxygalactose)]. Anal. Calcd for $C_{34}H_{42}O_{12}$·0.5 H_2O: C, 62.66; H, 6.65. Found: C, 62.62; H, 6.68.

1,3,5-Tris-[[[6-*O*-benzyl-3,4-(oxomethylene)-*β*-D-galacto-pyranosyl]oxy]methyl]benzene (7). According to the above procedure described for **5a**, galactal **3** (220 mg; 0.84 mmol) was converted to epoxide **4** and subsequently reacted with 1,3,5-benzenetrimethanol[19] (38 mg; 0.23 mmol) to afford after purification by radial chromatography [chloroform/methanol (15:1)] tris-galactoside **7** (52 mg; 25%) and bis-galactoside **8** (65 mg; 43%), each as a white foam. When the reaction was performed using 4.8 equivalents of galactal **3**, tris-galactoside **7** was isolated in 66% yield: ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 18H), 4.81 (d, J = 12.0 Hz , 3H), 4.72 (dd, J = 7.8, 2.0 Hz , 2H), 4.62−4.52 (m, 3H), 4.58 (s,6H), 4.48 (d, J = 5.5 Hz , 2H), 4.44 (d, J = 12.0 Hz , 2H), 4.05 (br td, J = 6.0, 2.0 Hz , 2H), 3.9−3.8 (br hump, 3H, exch), 3.8−3.6 (m, 9H).

Bis-galactoside (8): ^{1}H NMR ($CDCl_3$) δ 7.5−7.2 (m, 13H), 4.84 (d, J = 12.0 Hz , 2H), 4.77 (dd, J = 7.8, 2.0 Hz , 2H), 4.65-4.55 (m, 8H), 4.53 (d, J = 5.5 Hz , 2H), 4.49 (s, 2H), 4.05 (br td, J = 6.0, 2.0 Hz , 2H), 3.85−3.65 (m, 6H), 3.65−3.45 (br, 3H, exch). ^{13}C NMR ($CDCl_3$) δ 154.60, 141.41, 137.48, 137.26, 128.54, 128.02, 127.92, 127.34, 126.73, 99.44, 77.20, 77.10, 74.58, 73.75, 70.33, 69.65, 68.57, 64.48; MS (FAB (M$^+$)) m/e 747 [M + Na]; HRMS (FAB (M$^-$)) calcd for $C_{37}H_{40}O_{15}$ 723.2289 [M − H], found 723.2293.

1,3,5-[[Tris-(6-*O*-benzyl-*β*-D-galactopyranosyl]oxy]methyl]benzene (9). To a solution of tris-galactoside **7** (98 mg; 0.098 mmol) in anhydrous methanol (5 mL) was added a pinch of sodium methoxide, and the resulting mixture was stirred overnight at room temperature. The solvent was evaporated, and the residue was crystallized from water/EtOH, affording pure **9** (53 mg; 59%) as a tan amorphous powder: mp > 150 °C, dec; FTIR (KBr) 3406 (br), 2913, 2868, 1604, 1497, 1454, 1368, 1074, 908, 858, 785, 737, 697 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 7.5−7.2 (m, 18H), 5.15−5.0 (br hump, 3H), 4.95−4.75 (br hump, 3H), 4.79 (d, J = 12.4 Hz , 3H), 4.65−4.40 (m, 12H), 4.24 (d, J = 7.0 Hz , 3H), 3.7−3.5 (m, 12H), 3.5−3.2 (m, 6H); ^{13}C NMR (DMSO-d_6) δ 138.59, 137.86, 128.22, 127.39, 127.35, 126.15, 102.85, 73.48, 73.21, 72.19, 70.49, 69.63, 69.48, 68.66; MS (FAB (M$^-$)) m/e 923 [M − H], 833 [M − CH_2Ph], 671 [M − (6-benzyl-1-deoxygalactose)]; HRMS (FAB) calcd for $C_{48}H_{60}O_{18}$ 923.3701 [M − H], found 923.3731.

Supporting Information Available: Copies of the ^{1}H NMR spectra for compounds **3**, **5a**−**d**, and **7**−**9** (15 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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