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Preferred Conformation of C-Glycosides. 14. Synthesis and Conformational Analysis of Carbon Analogs of the Blood Group Determinant H-Type II

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The syntheses of *C*-trisaccharides **1**–**4**, carbon analogs of the human blood group determinant H-type II, have been achieved in a flexible and efficient manner. Vicinal coupling constants in the ^{1}H NMR spectrum provide experimental evidence that each of the four compounds **1**–**4** possesses a unique solution conformation, in accord with the predictions made on the basis of the preference of the *C*-glycosidic bond for the "exo-anomeric" conformation and the influence of 1,3-diaxial like interactions about the *C*-aglyconic bond.

Introduction

It has been demonstrated in previous studies that the overall conformations of *C*-disaccharides and *C*-trisaccharides can be predicted to the first degree of approximation solely on the basis of steric considerations.[1] In addition, the conformational similarities between *C*- and *O*-glycopyranosides have been experimentally established by ^{1}H NMR spectroscopy. Vicinal coupling constants verified experimentally that (1) the *C*-glycopyranosidic bond preferentially adopts the "exo-anomeric" conformation like its parent *O*-glycopyranosidic bond does, existing antiperiplanar to its respective C.1–C.2 bond, and (2) the *C*-aglyconic bond adopts a well-defined, staggered conformation in the absence of 1,3-diaxiallike steric interactions. The fruitfulness of these studies has encouraged an investigation of a substrate with significant biological relevance. We now wish to report the synthesis and conformational analysis of a carbon analog of the H-type II blood group determinant α-L-Fuc(1→2)-β-D-Gal(1→4)-β-D-GlcNAc-$(CH_2)_8CO_2Me$, a trisaccharide extensively studied by Lemieux and co-workers.[2]

The synthesis and conformational analysis of a *C*-trisaccharide resembling the H-type II antigen has already been accomplished, in which the C.2 acetamido group was replaced with a hydroxyl.[3] It was predicted, and experimentally proven, that rational structural modifications would induce the interglycosidic linkages to assume well-defined, staggered conformations, and that the conformations about the two linkages would be mutually independent. In this study, we demonstrate that the conformational preferences of the 2-deoxy-2-acetamido-*C*-trisaccharide **1** and its structurally modified analogs **2**–**4** are influenced in the same manner.

Results and Discussion

Synthesis. The synthesis of the aforementioned desacetamido-*C*-trisaccharide and its analogs proved to be an excellent paradigm for the route toward compounds **1**–**4**. Common intermediate **A** is transformed to methyl ketone **B**, with the optional excision of the hydroxymethyl group at C.5; aldol condensation with aldehyde **C**, followed by reductive tetrahydropyran formation, provides *C*-disaccharide ketone **D**. A second aldol condensation with aldehyde **E** and deoxygenation at C.α′ leads to *C*-trisaccharide **F**. The optional deoxygenation of O.3′, followed by several routine transformations, ultimately leads to desired compounds **1**–**4**.

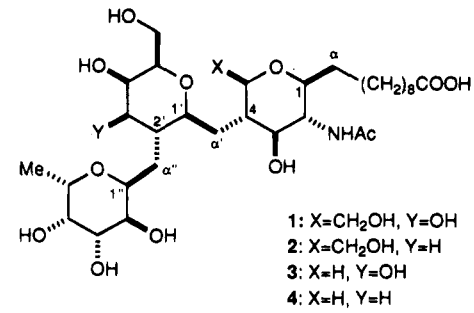

Figure 1.

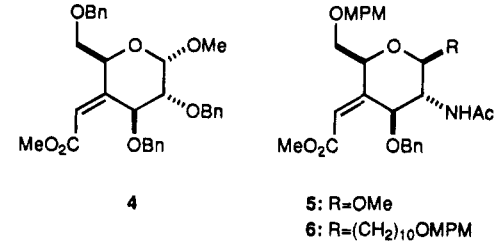

Figure 2.

To achieve an efficient synthesis of intermediate **A**, we initially had hoped to take advantage of some chemistry previously observed in this laboratory. It had been demonstrated that the hydrogenation of exocyclic enoate **4** in the presence of Pd on C produced the equatorial C.4 epimer as the sole product.[4] Attempts to hydrogenate β-methyl *N*-acetylglucosaminoside **5**, however, gave a 4:1 mixture of equatorial and axial products at best, and the hydrogenation of β-*C*-alkyl glucosamine derivative **6** gave only the axial stereoisomer. Other attempts to reduce the exocyclic alkene in a stereoselective fashion met with little success.

[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

(1) For Part 13 of this series, see: O'Leary, D. J.; Kishi, Y. *J. Org. Chem.* **1994**, *59*, 6629.

(2) (a) Hindsgaul, O.; Khare, D. P.; Bach, M.; Lemieux, R. U. *Can. J. Chem.* **1985**, *63*, 2653. (b) Spohr, U.; Paszkiewicz-Hnatiw, E.; Morishima, N.; Lemieux, R. U. *Can. J. Chem.* **1992**, *70*, 254. (c) Cromer, R.; Spohr, U.; Khare, D. P.; LePendu, J.; Lemieux, R. U. *Can. J. Chem.* **1992**, *70*, 1511.

(3) Haneda, T.; Goekjian, P. G.; Kim, S. H.; Kishi, Y. *J. Org. Chem.* **1992**, *57*, 490.

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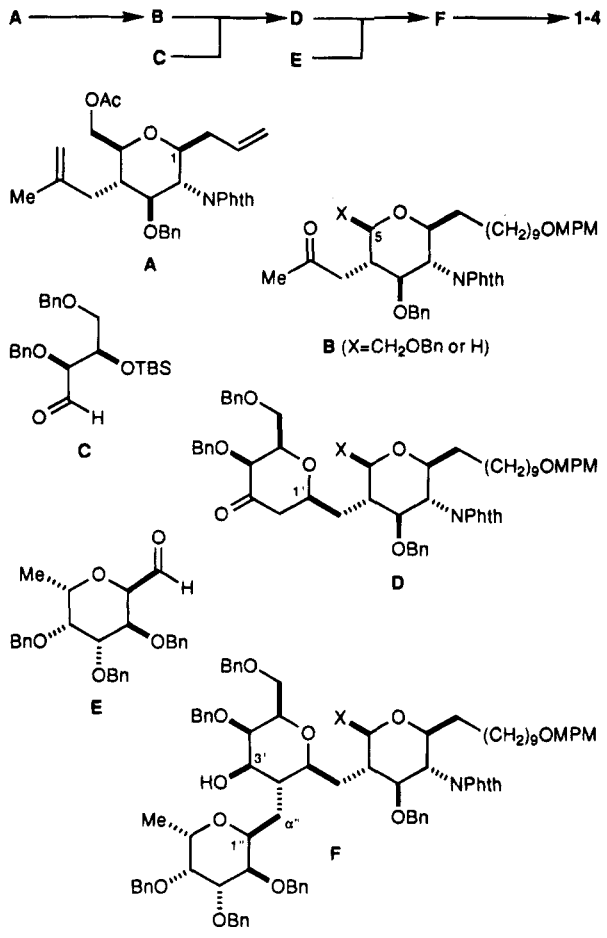
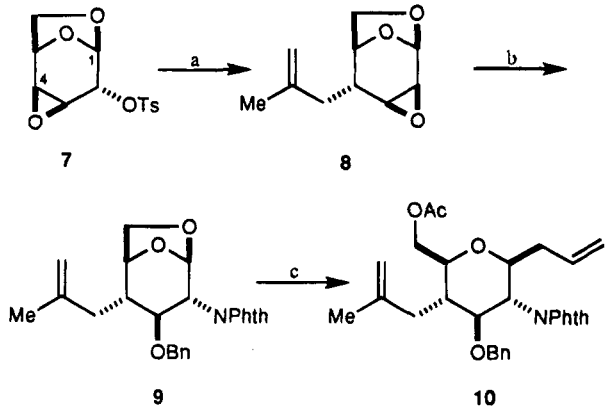


The difficulties encountered in stereocontrolled reduction encouraged us to find an alternate approach for installing the C.4 stereocenter, as shown in Scheme 1. A Cu(I)-catalyzed Grignard reaction at C.4 on known compound **7**, followed by base treatment, generated epoxide **8**.[5] Azide attack at C.2 and benzylation at O.3, followed by azide reduction and phthalimide formation, provided compound **9**. Opening of the anhydroglucose ring produced a 1,6-diacetate, which was then treated with allyltrimethylsilane in the presence of TMSOTf to yield *β-C*-allyl glycoside **10** as the sole product, as demonstrated by vicinal coupling constants in its ^{1}H NMR spectrum ($J_{1,2}$ = 10.2 Hz; C_6D_6, 500 MHz). The stereoselectivity of this reaction is remarkable and may be rationalized by neighboring-group assistance by the C.2 phthalimido group. However, it should be noted that *C*-allylation of activated glucosides possessing a C.2 *O*-acetate or *O*-benzoate has been observed to produce diastereomeric mixtures, with the α configuration as the predominant isomer.[6,7] Also noteworthy is the efficiency of this *C*-allylation in the presence of an acid-sensitive alkene; stronger Lewis acids catalyze its isomerization to the more stable trisubstituted olefin.

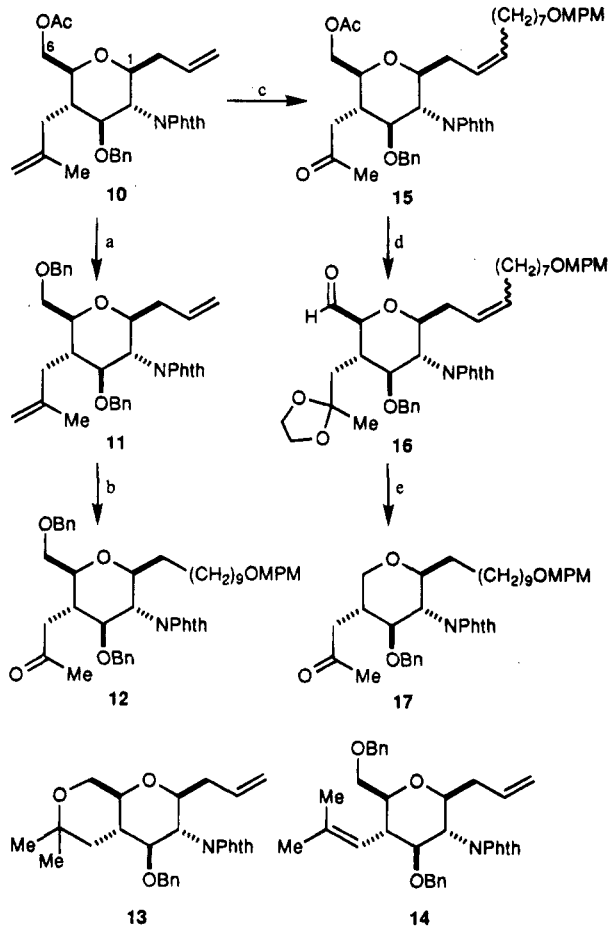
Both ketone **12** and C.5 deshydroxymethyl ketone **17** were generated from intermediate **10** (Scheme 2). Conversion of **10** to O.6 benzyl ether **11** was problematic due to the proximity of the reactive isobutenyl substituent at C.4, often producing **13** or **14** as major products. However, carefully controlled alkoxide generation at low

Scheme 1



[a] Reagents and conditions: (a) (i) CH_2=C(Me)CH_2MgCl, CuI, THF, (ii) NaH, $CHCl_3$:MeOH (1:1); (b) (i) NaN_3, TBAI, DME: $MeO(CH_2)_2OH:H_2O$ (3:2:1), (ii) BnBr, NaH, imidazole, TBAI, THF: DMF (1:1), (iii) H_2, Lindlar catalyst, MeOH, (iv) phthalic anhydride, pyridine, and then Ac_2O; (c) (i) Ac_2O, $BF_3{\cdot}Et_2O$, (ii) allyl-TMS, TMSOTf, CH_3CN.

Scheme 2



[a] Reagents and conditions: (a) (i) DBU, MeOH, (ii) BnBr, NaHMDS, DMF; (b) (i) O_3, MeOH:CH_2Cl_2 (2:1), and then Ph_3P, (ii) MPMO$(CH_2)_8PPh_3{}^+Br^-$, *n*-BuLi, THF, (iii) H_2, $(PPh_3)_3RhCl$, toluene:EtOH (1:1); (c) (i) O_3, MeOH:CH_2Cl_2 (2:1), and then Me_2S, (ii) MPMO$(CH_2)_8PPh_3{}^+Br^-$, *n*-BuLi, THF; (d) (i) HO$(CH_2)_2$OH, camphorsulfonic acid, $(EtO)_3CH$, benzene, (ii) DBU, MeOH, (iii) Dess–Martin periodinane, 4 Å mol sieves, CH_2Cl_2; (e) (i) $(PPh_3)_3RhCl$, xylenes, (ii) H_2, $(PPh_3)_3RhCl$, benzene:EtOH (1:1), (iii) *p*-TsOH, 95% aqueous acetone.

(4) Wang, Y.; Babirad, S. A.; Kishi, Y. *J. Org. Chem.* **1992**, *57*, 468.
(5) Carlson, L. J. *J. Org. Chem.* **1965**, *30*, 3953.
(6) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976.
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temperature allowed for an efficient reaction. Extension of the C.1 side chain was accomplished by ozonolysis and Wittig coupling; hydrogenation of the resulting alkene produced **12**.

Removal of the C.5 hydroxymethyl group was achieved by first appending the C.1 side chain to produce **15**, followed by protection of the ketone, unmasking of the O.6 alcohol, and oxidation to generate aldehyde **16**. A one-pot decarbonylation–hydrogenation was effected using Wilkinson's reagent;[8] it should be noted that alkene isomerization was not observed during decarbonylation.[9] Deketalization furnished ketone **17** in high overall yield.

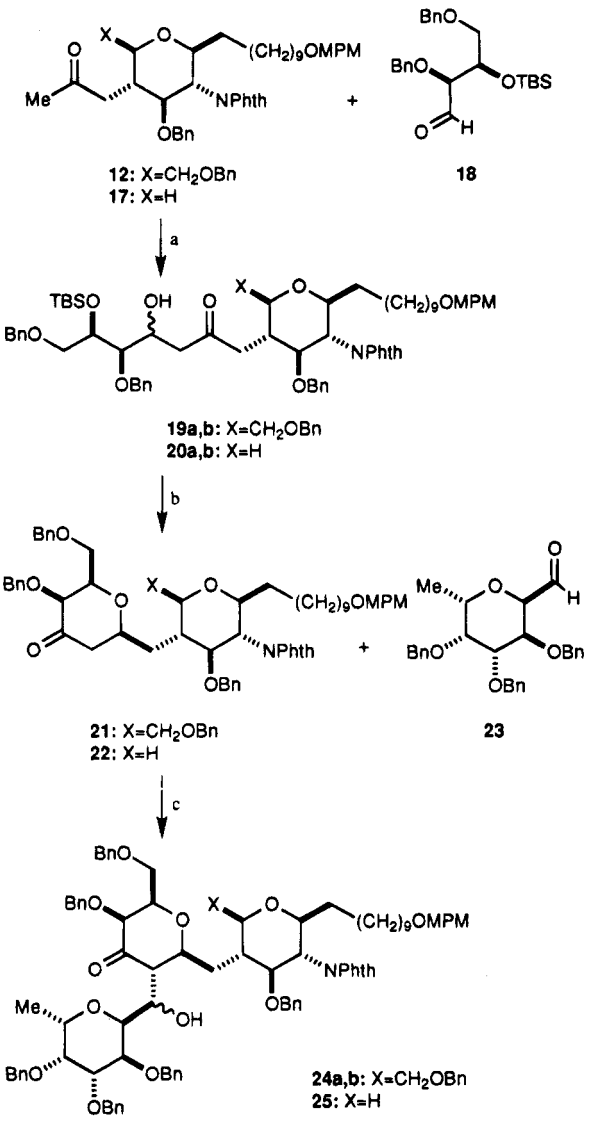
Methyl ketones **12** and **17** were subjected to aldol condensation with aldehyde **18** using lithium hexamethyldisilazane (LiHMDS) as base to produce a mixture of β-hydroxy ketones **19a,b** and **20a,b**, respectively (Scheme 3). The aldol products were efficiently converted to corresponding disaccharide ketones **21** and **22** by TBS deprotection, hemithioketal formation, reduction by Ph_3SnH,[10] and then oxidation.

The aldol condensation between the disaccharide ketones and aldehyde **23** proved to be more difficult. The synthesis of the previously reported *C*-trisaccharide[3] was optimized by using conditions which gave the thermodynamically controlled product (LiHMDS, TMEDA, $MgBr_2$, THF). However, the condensation of **21** or **22** with **23** under similar conditions gave only low yields primarily due to the retro-aldol process. This was effectively prevented by exchanging the solvent from toluene/THF to toluene/Et_2O. Thus, the lithium enolates of ketones **21** and **22** were generated using LiHMDS·TMEDA in toluene/Et_2O and were condensed at −78 °C with aldehyde **23** to produce in good yield (ca. 60%) trisaccharide aldol products **24a,b** and **25**, respectively, along with some double aldol-condensation products (ca. 3–10%). Additional **24** and **25** were generated from acid-catalyzed retro-aldol fragmentation of the bis-aldol-condensation products (p-TsOH·H_2O, CH_2Cl_2), producing the desired *C*-trisaccharide aldol products in 40–60% yield.

It is also noteworthy that only C.2′ equatorial product was observed in the aldol condensation. Kinetically controlled conditions in the synthesis of the previously reported *C*-trisaccharide[3] gave a mixture of axial and equatorial products at C.2′. This result can be rationalized by a tighter transition state, and greater sensitivity to steric effects, in a less polar solvent such as Et_2O.[11] Further support is provided by the fact that the reaction between ketone **22** and aldehyde **23** produced **25** as a single diastereomer.

Removal of the C.α″ hydroxyl group in aldol products **24** and **25** was accomplished by elimination of the corresponding mesylate to yield enones **26** and **27** as diastereomeric mixtures (Scheme 4). Conjugate reduction with Ph_3SnH, followed by ketone reduction with $NaBH_4$, produced exclusively C.3′ alcohols **28** and **30**. Bu_3SnH reduction of the corresponding methyl xanthate

Scheme 3



[a] Reagents and conditions: (a) LiHMDS, toluene:THF (4:1); (b) (i) TBAF, THF/H_2O (pH 5-6), (ii) MeSH, BF_3·Et_2O, CH_2Cl_2, (iii) Ph_3SnH, AIBN, toluene, (iv) Swern oxidation; (c) LiHMDS·TMEDA, Et_2O:toluene (1:1).

yielded C.3′ deoxy compounds **29** and **31**, thus giving rise to all four precursors to targets **1–4**.

Finally, hydrazinolysis of **28–31**, *N*-acetylation, MPM deprotection, and oxidation of the primary alcohol to the carboxylic acid led to compounds **32–35**. Debenzylation resulted in fully deprotected *C*-trisaccharides **1–4**.

NMR Analysis. *C*-Trisaccharides **1–4** and their partially protected forms **32–35** were analyzed by ^1H NMR spectroscopy. A solvent system was chosen for each compound such that (1) the *C*-trisaccharides did not exist as a mixture of slowly exchanging rotamers,[12] and (2) the ^1H NMR signals of the bridging methylene protons and their nearest-neighbor ring protons were sufficiently spread apart, thereby avoiding higher-order coupling effects. In all cases, the coupling constants around each pyranose ring demonstrated the expected chair conformations (Table 1).

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(9) For examples of Rh(I)-mediated olefin isomerization, see: (a) Birch, A. J.; SubbaRao, G. S. R. *Tetrahedron Lett.* **1968**, 3797. (b) Corey, E. J.; Suggs, J. W. *J. Org. Chem.* **1973**, *38*, 3224. (c) Andrieux, J.; Barton, D. H. R.; Patin, H. *J. Chem. Soc. Perkin 1* **1977**, 359.

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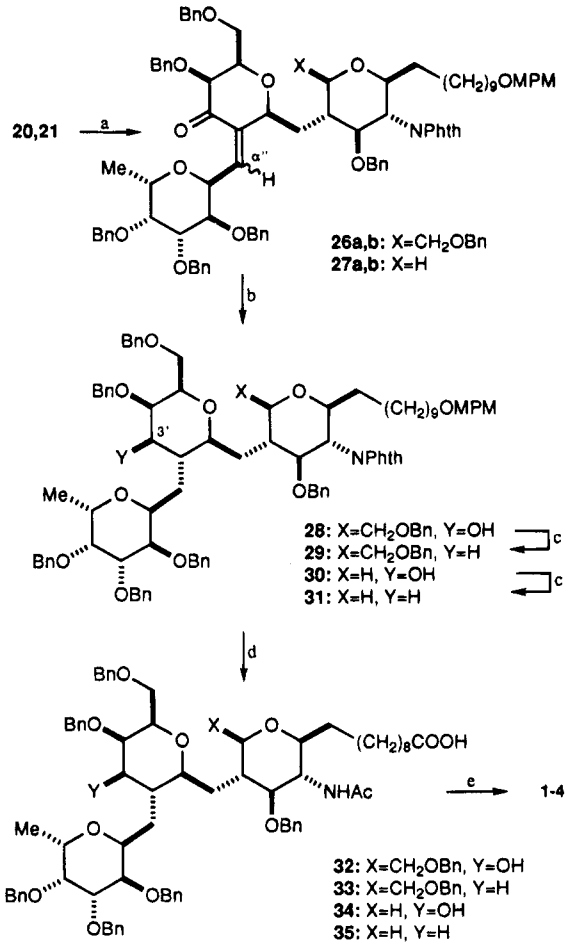
(11) For excellent reviews on the aldol reaction, see: (a) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J., Ed.; Academic Press: New York, 1984; Vol. 3, pp 111–212. (b) Evans, D. A. In *Topics in Stereochemistry*, Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; John Wiley and Sons: New York, 1982; Vol. 13, pp 1–116.

(12) We observed more than one set of ^1H NMR signals when using a nonpolar solvent such as $CDCl_3$ or C_6D_6. We attribute this to either a mixture of rotamers, one of which possibly is stabilized by hydrogen bonding between the C.2 *N*-acetate and the terminal carboxyl, or aggregation. When the solvent is sufficiently diluted with methanol-d_4 (approx. 25%), only one set of signals is observed.

Scheme 4



[a] Reagents and conditions: (a) (i) MsCl, 2,6-lutidine, CH_2Cl_2, and then $(i\text{-Pr})_2NEt$, (ii) NH_3, THF; (b) (i) Ph_3SnH, AIBN, toluene, (ii) $NaBH_4$, MeOH:CH_2Cl_2 (3:2); (c) (i) NaHMDS, CS_2, THF, then MeI, (ii) Bu_3SnH, AIBN, toluene; (d) (i) H_2NNH_2, *n*-BuOH, (ii) Ac_2O, Et_3N, CH_2Cl_2, (iii) DDQ, pH 7 buffer, CH_2Cl_2, (iv) $(Ph_3P)_3RuCl_2$, 3 Å mol sieves, benzene; (v) $NaClO_2$, NaH_2PO_4, *t*-BuOH:2-methyl-2-butene:H_2O (8:3:3); (e) (i) H_2, $Pd(OH)_2$, MeOH, (ii) 0.5 M LiOH.

The coupling constants about the interglycosidic linkages for each *C*-trisaccharide mirror those of the previously studied 2-hydroxy-2-desacetamido congeners (Table 2). Our observations can be summarized as follows. First, in all eight compounds, the three *C*-glycosidic bonds C.1−C.α, C.1′−C.α′, and C.1″−C.α″ preferentially adopt the "exo-anomeric" conformation. Second, for the *C*-trisaccharides in which X = CH_2OBn or CH_2OH (**1**, **2**, **32**, and **33**), the C.α′−C.4 aglyconic bond exists either in a conformation distorted away from a staggered position or as a mixture of staggered conformers. The same holds true for the C.α″−C.2′ aglyconic bond for those *C*-trisaccharides in which Y = OH (**1**, **3**, **32**, and **34**). Third, for the *C*-trisaccharides in which X = H (**3**, **4**, **34**, and **35**) or Y = H (**2**, **4**, **33**, and **35**), the corresponding *C*-aglyconic bond demonstrates a strong preference for a staggered conformation devoid of 1,3-diaxiallike interactions, without strongly affecting the apposing *C*-glycosidic conformation. Fourth, the presence of protecting groups has a minimal impact on conformation. Finally, the conformational preferences about the two interglycosidic linkages appear to be mutually independent. These last two observations confirm that long-range hydrogen bonding does not play an important role in the secondary solution structure of these *C*-trisaccharides.

Table 1.[a] Selected ^1H NMR Data for *C*-Trisaccharide 1 Methyl Ester

proton(s)	chemical shift(s)[b] (coupling constants = Hz)
H.α	1.72 (m), 1.96 (m)
H.1	3.55 (ddd, 2.6, 8.4, 9.5 Hz)
H.2	4.35 (t, 9.9 Hz)
H.3	4.01 (t, 10 Hz)
H.4	1.77 (m)
H.5	3.96 (ddd, 1.1, 5.5, 10.3 Hz)
H.6	4.08 (dd, 5.5, 11.8 Hz), 4.43 (1.2, 11.8 Hz)
H.α′	2.02 (ddd, 4.0, 9.6, 15.4 Hz), 2.82 (dd, 4.1, 15.1 Hz)
H.1′	3.89 (t, 10.3 Hz)
H.2′	2.50 (dq, 2.5, 10.3 Hz)
H.3′	4.06 (dd, 3.3, 10.3 Hz)
H.4′	4.24 (d, 3.3 Hz)
H.5′	3.79 (dd, 4.4, 7.3 Hz)
H.6′	4.38 (dd, 4.4, 11.4 Hz), 4.40 (dd, 7.1, 11.4 Hz)
H.α″	2.43 (ddd, 4.4, 5.9, 14.7 Hz), 2.57 (ddd, 2.6, 10.0, 14.7 Hz)
H.1″	5.00 (dt, 9.6, 4.8 Hz)
H.2″	4.70 (dd, 5.5, 8.8 Hz)
H.3″	4.36 (dd, 2.9, 9.2 Hz)
H.4″	4.18 (t, 3 Hz)
H.5″	4.48 (dq, 2.2, 6.6 Hz)
H.6″	1.58 (d, 6.6 Hz)

[a] The ^1H NMR spectrum was recorded on a Bruker AM-500 (500 MHz) spectrometer in 95:5 pyridine-d_5:methanol-d_4. [b] The chemical shifts are relative to the most downfield signal of C_5HD_4N at 295 K (8.71 ppm).

We wish to comment on some observations regarding the ring conformations of some *C*- and *O*-glycosides of *N*-acetylglucosamine. Based on the coupling constants of the ring protons, the simple monosaccharide β-methyl *N*-acetylglucosaminoside **36** possesses a chair conformation, as do other more complex *N*-acetylglucosamine derivatives which are functionalized at O.1 and O.4. However, when the *N*-acetylglucosamine ring is *C*-substituted at C.4, such as in compound **37**, ^1H NMR coupling constants reflect a half-chair or twist-boat conformation ($J_{1,2}$ = 1.8 Hz; $J_{2,3}$ = 4.4 Hz). If the *N*-acetylglucosaminoside is *C*-substituted at both C.1 and C.4, such as in compound **32**, the ring once again possesses the chair form. All other 1,4-di-*C*-substituted *N*-acetylglucosamine derivatives discussed in this paper also possess chair conformations.

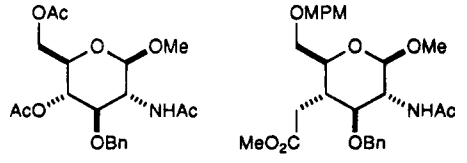
Our limited data may suggest that the forces involved in the conformation of the *N*-acetylglucosamine pyranose ring are primarily steric in nature. The substitution of oxygen with carbon at C.4 results in increased steric compression against the acetamido or phthalimido group at C.2, which is relieved by twisting the pyranoside into a half-chair conformation, with the C.1 substituent in a pseudoaxial position. However, replacement of oxygen with carbon at C.1 substantially raises the *A* value of this substituent and forces the pyranose ring back into a chair form, thereby negating any steric influence from the *C*-substituent at C.4. We are thus able to maintain our assumption that *C*- and *O*-glycosides are conformationally similar in the general sense.

Conclusions. In summary, the synthesis of *N*-acetylated *C*-trisaccharide **1**, the carbon analog of the H-type II blood group determinant, and three structurally modified analogs **2**−**4**, was achieved using a similar synthetic strategy as that developed for the 2-hydroxy-2-desacetamido analogs. We validated our expectations by ^1H NMR analysis that *C*-trisaccharides **1**−**4** would demonstrate identical conformational preferences to the previously studied desacetamido congeners, in which rational modifications in structure induced predictable conformational changes based on steric interactions. The superficially

Table 2. Selected ^{1}H NMR (500 MHz) Coupling Constants (Hz) for Compounds 1–4 and 32–35 at Room Temperature

compd	J(1',α')	J(4,α')	J(1'',α'')	J(2',α'')
1[a]	9.6	4.0	10.0	2.6
	(<1)	4.1	4.4	5.9
32[b]	10.4	1.9	10.4	2.7
	2.3	6.4	3.1	6.4
2[c]	9.2	3.7	12.1	2.6
	(<1)	4.8	3.3	11.0
33[c]	10.3	2.2	11.4	3.3
	1.5	6.2	3.3	11.8
3[d]	9.8	2.9	9.8	2.4
	2.0	11.5	4.2	5.4
34[c]	8.9	2.8	10.4	2.8
	2.4	10.7	3.0	6.7
4[e]	10.3	3.7	12.5	3.3
	1.9	9.2	3.0	11.4
35[f]	8.0	2.4	11.3	3.0
	2.4	10.4	2.4	11.6

The spectra were recorded in the following solvents: [a] 95:5 pyridine-d_5:methanol-d_4 (**1** methyl ester); [b] 50:50 methanol-d_4:acetone-d_6; [c] methanol-d_4; [d] 75:25 methanol-d_4:DMSO-d_6; [e] D_2O; [f] 80:20 methanol-d_4:acetone-d_6.



36 37

Figure 3.

trivial similarities in the conformations of the two *C*-trisaccharide systems are in fact quite significant; the substituents at C.1 and C.4 of the *N*-acetylglucosamine pyranose ring are influential in determining its conformation as chair or half-chair.

We are now in a position to examine the capacity of ground-state solution conformation of a biologically significant carbohydrate ligand to influence its binding affinity with macromolecules. Preliminary results demonstrate that (1) *C*-trisaccharides **1**–**4** are indeed biologically active, with compound **1** binding to the H-type-II-specific lectin from *Ulex europaeus* at micromolar concentrations, and (2) a gradient in binding affinity was observed, with compound **4** being the least active. These studies, and those of the parent *O*-trisaccharides, will be reported elsewhere.

Experimental Section

General Experimental Procedures. For the general experimental procedures, see Part 6 of this series. Only selected spectral data are presented. Photocopies of ^{1}H and ^{13}C NMR spectra are included in the supplementary material to demonstrate the purity of each compound.

2,3-Epoxide 8. A stirred suspension of CuI (0.41 g, 2.16 mmol) in anhydrous THF (5 mL) was treated at 0 °C with methallylmagnesium chloride (162 mL of a 2 M solution in THF). The mixture was stirred for 30 min at 0 °C, followed by addition via cannula of 2-tosyl-3,4-epoxy-1,6-anhydroglucose **7** (6.44 g, 21.6 mmol) in THF (75 mL). The reaction mixture was stirred for an additional 30 min at 0 °C and then quenched by slow addition of a saturated NH_4Cl solution. Aqueous workup (Et_2O/EtOAc) was followed by azeotropic removal of water with toluene.

A stirred solution of the crude tosylate alcohol in dry THF (250 mL) was treated at 0 °C with NaH (1.66 g of a 60% dispersion in mineral oil, 41.5 mmol) and imidazole (30 mg, 0.44 mmol). The reaction mixture was stirred for 30 min and then quenched with aqueous NH_4Cl. Aqueous workup (Et_2O) followed by silica gel chromatography (flash silica, 25% EtOAc/hexanes) yielded 2,3-epoxide **8** as a clear, colorless oil (2.84 g, 15.6 mmol, 72% yield over two steps). IR (neat): 2969, 2900, 1151, 1121 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.75 (3H, s), 2.12 (1H, m), 2.26 (2H, m), 2.92 (1H, d, J = 4.1 Hz), 3.34 (1H, t, J = 3.7 Hz), 3.71 (1H, t, J = 7 Hz), 3.74 (1H, dd, J = 2.2, 6.6 Hz), 4.20 (1H, br d, J = 6.3 Hz), 4.79 (1H, m), 4.88 (1H, br), 5.66 (1H, d, J = 3.3 Hz). ^{13}C NMR ($CDCl_3$): δ 22.16, 36.85, 38.87, 50.47, 53.80, 68.52, 70.97, 98.05, 113.47, 141.89. HRMS (EI): calcd for $C_{10}H_{14}O_3$ (M^+) 182.0943; found 182.0938. $[\alpha]_D$ −20.6° (*c* 1.40, $CHCl_3$).

Phthalimide 9. A solution of 2,3-epoxide **8** (2.00 g, 11.0 mmol) in a 3:2:1 mixture of DME:MeO(CH_2)$_2$OH:H_2O (40 mL) was treated with NaN_3 (4.71 g, 72.5 mmol) and *n*-tetrabutylammonium iodide (TBAI) (125 mg, 0.55 mmol). The reaction mixture was stirred at 120 °C for 3 days, concentrated, and subjected to silica gel purification (flash silica, 12–25% EtOAc/hexanes) to yield the corresponding 2-azido intermediate as a colorless oil.

A stirred solution of the azido alcohol in 4:1 THF:DMF (50 mL) was treated at 0 °C with NaH (0.53 g of a 60% dispersion in mineral oil, 13.2 mmol) and imidazole (37 mg, 0.55 mmol), followed by TBAI (250 mg, 1.1 mmol) and BnBr (2.1 mL, 17.7 mmol). The reaction mixture was stirred for 4 h at room temperature and then quenched with saturated NH_4Cl. Aqueous workup (Et_2O) followed by silica gel chromatography (12% EtOAc/hexanes) yielded the C.3 benzyl ether as a colorless oil (2.30 g, 7.3 mmol, 66% yield over two steps).

A stirred solution of the azide intermediate (3.75 g, 11.9 mmol) in EtOH (50 mL) was hydrogenated over Lindlar catalyst (10% Pd–Pb on $CaCO_3$, 800 mg) under 1 atm of H_2 at room temperature for 24 h. The reaction mixture was passed through filter paper (Whatman No. 42), concentrated, and dried.

The crude amine was redissolved in pyridine (12 mL) and treated with phthalic anhydride (5.25 g, 35.4 mmol). The reaction mixture was stirred at 90 °C for 1 h, treated with Ac_2O (12 mL), and then stirred at 90 °C for another 2 h. The reaction mixture was then concentrated and purified by recrystallization (hexanes/EtOAc) to yield phthalimide **9** as a white crystalline solid (3.64 g, 8.68 mmol, 73% yield over two steps). Mp 155–157 °C. IR (neat): 2924, 2849, 1712, 1385

cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.70 (3H, s), 1.87 (1H, dddd, J = 1.9, 4.1, 8.5, 11 Hz), 2.30 (1H, dd, J = 11, 14 Hz), 2.57 (1H, dd, J = 4, 14 Hz), 3.71 (1H, dd, J = 1.1, 7 Hz), 3.74 (1H, dd, J = 4.8, 7 Hz), 3.88 (1H, t, J = 8.5 Hz), 4.25 (1H, d, J = 8.8 Hz), 4.47 (1H, dt, J = 5.1, 1.4 Hz), 4.77 (1H, m), 4.86 (1H, m), 5.45 (1H, s), 6.92–7.07 (5H, m), 7.68 (2H, dd, J = 3.3, 5.5 Hz), 7.76 (2H, dd, J = 3.0, 5.5 Hz). ^{13}C NMR ($CDCl_3$): δ 22.30, 40.97, 43.82, 58.79, 70.32, 74.05, 74.18, 76.10, 102.47, 113.31, 123.35, 127.44, 127.83, 128.18, 131.61, 133.93, 137.70, 142.64, 167.70. HRMS (FAB, NaI): calcd for $C_{25}H_{25}NO_5$ (M + Na) 442.1630; found 442.1644. $[\alpha]_D$ −20.3° (c 1.49, $CHCl_3$).

***C*-Allyl Glycoside 10.** A stirred solution of phthalimide **9** (4.19 g, 10.0 mmol) in acetic anhydride (60 mL) was treated portionwise with BF_3·Et_2O (1 mL) diluted in acetic anhydride (10 mL) at room temperature over a period of 5 min. The reaction mixture was then quenched with solid $NaHCO_3$, stirred for 20 min, and then filtered over Celite with toluene. The crude reaction mixture was then concentrated and purified by flash silica gel chromatography (flash silica, 25% EtOAc/hexanes) to yield the corresponding 1,6-diacetate as a colorless oil (4.52 g, 8.68 mmol, 87% yield).

A stirred solution of the diacetate (3.33 g, 6.39 mmol) and allyltrimethylsilane (10.2 mL, 63.9 mmol) in dry acetonitrile (68 mL) was treated dropwise at −40 °C with TMSOTf (0.29 mL, 1.60 mmol). The reaction mixture was stirred at −20 °C for 8 h before being quenched with saturated $NaHCO_3$. Aqueous workup (Et_2O/EtOAc), followed by silica gel chromatography (flash silica, 12–30% EtOAc/hexanes), gave *C*-allyl-glycoside **10** as a clear, colorless oil (2.74 g, 5.44 mmol, 85% yield). IR (neat): 1787, 1753, 1711, 1387, 1243 cm^{-1}. ^{1}H NMR (C_6D_6): δ 1.60 (3H, s), 1.70 (3H, s), 1.82 (1H, dd, J = 7.4, 15.1 Hz), 2.12 (1H, ddt, J = 3.7, 7.7, 10.3 Hz), 2.26 (1H, br d, J = 15 Hz), 2.33 (2H, m), 3.30 (1H, ddd, J = 1.9, 5.5, 10.3 Hz), 4.16 (1H, dd, J = 5.9, 12.2 Hz), 4.39 (1H, ddd, J = 5.1, 6.6, 10 Hz), 4.46 (1H, dd, J = 1.8, 12.1 Hz), 4.71 (1H, br), 4.76 (1H, br), 4.82 (1H, dd, J = 10.3, 1.5 Hz), 4.89 (1H, dq, J = 17.3, 1.3 Hz), 5.87 (1H, m), 7.37-7.42 (5H, m). ^{13}C NMR ($CDCl_3$): δ 20.77, 22.43, 29.53, 36.67, 36.95, 41.71, 56.68, 64.78, 73.66, 74.39, 77.31, 78.84, 79.90, 112.14, 116.60, 123.04, 123.31, 167.84, 168.62, 170.67. HRMS (FAB, NaI): calcd for $C_{30}H_{33}NO_6$ (M + Na) 526.2206; found 526.2202. $[\alpha]_D$ +49.4° (c 1.08, $CHCl_3$).

O.6 Benzyl Ether 11. A stirred solution of *C*-allyl glycoside **10** (2.74 g, 5.44 mmol) in MeOH (250 mL) was treated with DBU (1.2 mL, 8.02 mmol). The reaction mixture was stirred for 10 h, neutralized with PPTS (1.85 g, 8.02 mmol), concentrated, and then purified by silica gel chromatography (12–30% EtOAc/hexanes), yielding the corresponding O.6 alcohol as a white crystalline solid (2.13 g, 4.62 mmol, 85% yield).

A stirred solution of the alcohol (2.11 g, 4.57 mmol) and benzyl bromide (5.25 mL, 44.2 mmol) in dry DMF (150 mL) was cooled to −60 °C and treated with NaHMDS (15.25 mL of a 0.6 M solution in toluene). The reaction mixture was stirred for 30 min at −60 °C and then quenched with saturated NH_4Cl. Aqueous workup (Et_2O) and silica gel chromatography (10–25% EtOAc/hexanes) yielded the O.6 benzyl ether **11** as a white solid (1.98 g, 3.59 mmol, 78% yield). Mp (hexanes/EtOAc) 104–106 °C. IR (neat): 1773, 1713 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.60 (3H, s), 1.97 (1H, dd, J = 7, 15 Hz), 2.01–2.17 (3H, m), 2.25 (1H, dd, J = 3, 15.2 Hz), 4.60 (2H, br s), 4.69 (1H, dd, J = 1.8, 10 Hz), 4.78 (1H, br d, J = 17 Hz), 5.65 (1H, m). ^{13}C NMR ($CDCl_3$): δ 22.69, 36.91, 37.31, 41.59, 56.75, 70.56, 73.10, 73.21, 74.44, 80.02, 80.86, 111.71, 116.61, 167.97, 168.74. HRMS (FAB, NaI): calcd for $C_{35}H_{37}O_5N$ (M + Na) 574.2569; found 574.2560. $[\alpha]_D$ +47.7° (c 1.18, $CHCl_3$).

Methyl Ketone 12. A stirred solution of O.6 benzyl ether **11** (2.57 g, 4.66 mmol) in 1:1 MeOH:CH_2Cl_2 (80 mL) was treated at −78 °C with O_3 at a rate of 1 L/min for 10 min and then purged with N_2 for 30 min. Ph_3P (3.15 g, 12 mmol) was added, and the reaction mixture was stirred at room temperature for 45 min, concentrated, and purified by silica gel chromatography (20–50% EtOAc/hexanes) to yield the desired keto aldehyde, which was dried by azeotropic removal of water with toluene.

A stirred solution of 8-[(*p*-methoxybenzyl)oxy]octyltriphenylphosphonium bromide (3.6 g, 6.26 mmol) in dry THF (22.5 mL) was treated dropwise at 0 °C under argon with *n*-BuLi (2.0 mL of a 2.7 M solution in hexanes). The reaction mixture was stirred for 20 min at 0 °C, followed by addition via cannula of the keto aldehyde in THF (2.4 mL). The reaction mixture was stirred for 5 min and then quenched with saturated NH_4-Cl. Aqueous workup (EtOAc) and silica gel chromatography (12–25% EtOAc/hexanes) yielded the corresponding disubstituted olefin as a colorless oil (1.73 g, 44% yield over two steps).

A stirred solution of the olefin (920 mg, 1.17 mmol) in 1:1 toluene:EtOH (16 mL) was hydrogenated over $(PPh_3)_3RhCl$ (100 mg, 0.11 mmol) under 1 atm of H_2 at room temperature for 1 day. The reaction mixture was concentrated and purified by silica gel chromatography (14–25% EtOAc/hexanes) to yield the desired methyl ketone **12** as a colorless oil (875 mg, 1.11 mmol, 95% yield). IR (neat): 1772, 1713 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.54 (2H, quint, J = 7 Hz), 1.92 (3H, s), 2.41–2.53 (3H, m), 3.39 (2H, t, J = 6.6 Hz), 3.78 (3H, s), 4.07 (1H, dt, J = 2.6, 8.5 Hz), 4.40 (2H, s). ^{13}C NMR ($CDCl_3$): 25.07, 26.18, 29.41, 29.45, 29.51, 29.75, 32.00, 41.53, 42.04, 55.25, 57.07, 70.25, 71.33, 72.47, 72.60, 73.32, 75.50, 78.64, 79.14, 113.79, 159.15, 168.03, 168.50, 206.91. HRMS (FAB, NaI): calcd for $C_{49}H_{59}O_8N$ (M + Na) 812.4138; found 812.4106. $[\alpha]_D$ +22.2° (c 1.30, $CHCl_3$).

Methyl Ketone 15. A stirred solution of the *C*-allyl glycoside **10** (5.0 g, 9.93 mmol) in 2:1 MeOH:CH_2Cl_2 (180 mL) was treated at −78 °C with O_3 at a rate of 2 L/min for 15 min and then purged with N_2. The reaction mixture was treated with Me_2S (14 mL), warmed to 0 °C, treated with saturated aqueous $NaHCO_3$ solution, and then stirred for an additional 30 min. Aqueous workup ($CHCl_3$) followed by silica gel chromatography (25–75% EtOAc/hexanes) yielded the desired keto aldehyde as a colorless oil, which was dried by azeotropic removal of water by toluene. The transformation of the keto aldehyde to methyl ketone **15** was performed according to the procedure described previously (cf. methyl ketone **12**) to yield a colorless oil (4.13 g, 5.58 mmol, 56% yield over two steps). IR (neat): 2930, 2855, 1774, 1740, 1712, 1612, 1513 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.51 (2H, quint, J = 7 Hz), 1.74 (2H, m), 2.03 (3H, s), 2.06 (3H, s), 2.21 (1H, m), 2.38 (1H, ddd, J = 4.9, 10.1, 15.5 Hz), 2.51 (2H, m), 3.38 (2H, t, J = 6.7 Hz), 3.65 (1H, ddd, J = 3.0, 4.9, 10.7 Hz), 3.76 (3H, s), 5.23 (2H, m), 6.84 (2H, d, J = 8.5 Hz), 7.23 (2H, d, J = 8.5 Hz). ^{13}C NMR ($CDCl_3$): δ 20.77, 25.98, 27.13, 28.71, 28.93, 29.02, 29.12, 29.17, 29.59, 29.69, 30.58, 32.05, 40.16, 41.80, 55.11, 56.55, 56.63, 64.53, 70.04, 72.35, 72.54, 72.63, 75.11, 77.20, 78.81, 113.60, 158.95, 167.75, 168.50, 170.70, 206.25. HRMS (FAB, NaI): calcd for $C_{44}H_{53}NO_9$ (M + Na) 762.3618; found 762.3651.

Aldehyde 16. A stirred solution of methyl ketone **15** (4.25 g, 5.76 mmol) and camphorsulfonic acid (33.4 mg, 0.144 mmol) in benzene (100 mL) and ethylene glycol (5 mL) under nitrogen was treated dropwise via syringe pump with triethyl orthoformate (10 mL, 60 mmol) over a period of 30 h. The reaction mixture was stirred at room temperature for 7 days, followed by aqueous workup (Et_2O) and silica gel chromatography (20–25% EtOAc/hexanes) to yield the desired ketal as a colorless oil (3.55 g, 4.53 mmol, 79% yield) plus recovered ketone (0.50 g, 0.68 mmol).

A stirred solution of the ketal (3.24 g, 4.13 mmol) in MeOH (280 mL) was treated with DBU (0.9 mL, 6.0 mmol). The reaction mixture was stirred at room temperature for 5 h, quenched with pyridinium *p*-toluenesulfonate (PPTS) (1.56 g, 6.2 mmol), concentrated, and passed through a short silica gel column (50% EtOAc/hexanes) to yield the desired O.6 alcohol as a colorless oil.

A stirred solution of the O.6 alcohol in dry methylene chloride (15 mL) was treated with powdered 4 Å molecular sieves (2.5 g) and Dess–Martin periodinane (2.55 g, 6.0 mmol). The reaction mixture was stirred at room temperature for 10 h, diluted with Et_2O, passed through Celite, and washed with 10% $Na_2S_2O_3$ in saturated $NaHCO_3$. Silica gel chromatography (20–40% EtOAc/hexanes) yielded the aldehyde **16** (2.05 g, 2.77 mmol, 67% yield over two steps) as a white solid. Mp (hexanes/EtOAc) 85–90 °C. IR (neat): 2852, 1766, 1730, 1706 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.22 (3H, s), 1.49 (2H, quint, J = 7 Hz), 1.75 (2H, m), 1.79 (1H, dd, J = 5.5, 15.5 Hz), 1.95 (1H, dd, J = 2.2, 15.5 Hz), 2.10 (1H, m), 2.18 (1H, dt, J = 15.4, 6.3

Hz), 2.25 (1H, ddd, J = 4.1, 7.4, 14.3 Hz), 3.35 (2H, J = 6.7 Hz), 3.67 (1H, dd, J = 3.3, 10.7 Hz), 3.70 (3H, s), 4.35 (2H, s), 5.17–5.28 (2H, m), 6.81 (2H, d, J = 8.5 Hz), 7.20 (2H, d, J = 8.5 Hz), 7.58 (2H, m), 7.66 (2H, m), 9.40 (1H, d, J = 3.3 Hz). ^{13}C NMR ($CDCl_3$): δ 24.46, 26.03, 27.17, 28.94, 29.05, 29.15, 29.21, 29.65, 30.59, 34.59, 39.63, 55.08, 56.62, 64.04, 64.40, 70.04, 72.37, 73.74, 75.37, 77.46, 79.47, 84.53, 109.43, 113.65, 159.01, 167.69, 168.52, 197.34. HRMS (FAB, NaI): calcd for $C_{44}H_{53}NO_9$ (M + Na) 762.3618; found 762.3590.

Methyl Ketone 17. A solution of aldehyde **16** (2.05 g, 2.77 mmol) in dry xylenes (20 mL) was treated with $(Ph_3P)_3RhCl$ (2.82 g, 3.05 mmol) and placed in a preheated (150 °C) oil bath. The reaction mixture was stirred at reflux under nitrogen for 45 min, cooled to room temperature, and then filtered from precipitated $Ph_3P(CO)RhCl$. The reaction mixture was concentrated, redissolved in 1:1 EtOH:benzene (20 mL), refiltered, and then stirred under 1 atm of H_2 at room temperature for 8 h. Silica gel chromatography (20–25% EtOAc/hexanes) yielded the decarbonylated product (1.81 g, 2.53 mmol) as a brown oil.

A stirred solution of the decarbonylated material (1.79 g, 2.51 mmol) in 95:5 acetone:H_2O (100 mL) was treated with p-TsOH·H_2O (45 mg, 0.225 mmol) and heated to reflux for 10 h. Aqueous workup (Et_2O) and silica gel chromatography (20–33% EtOAc/hexanes) yielded methyl ketone **17** as a colorless oil (1.65 g, 2.47 mmol, 90% yield over three steps). IR (neat): 1774, 1711, 1613 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.53 (2H, quint, J = 7 Hz), 2.07 (3H, s), 2.18 (1H, dd, J = 9.0, 16.8 Hz), 2.44 (1H, m), 2.65 (1H, dd, J = 4.4, 16.5 Hz), 3.22 (1H, t, J = 7.8 Hz), 3.39 (2H, t, J = 6.7 Hz), 3.77 (3H, s), 4.39 (2H, s). ^{13}C NMR ($CDCl_3$): δ 24.69, 25.96, 26.10, 29.20, 29.29, 29.49, 29.55, 29.69, 31.85, 39.75, 42.32, 55.01, 56.76, 69.71, 69.98, 72.25, 73.10, 76.07, 77.20, 79.24, 113.51, 158.85, 167.82, 168.36, 206.47. HRMS (FAB, NaI): calcd for $C_{41}H_{51}NO_7$ (M + Na) 692.3563; found 692.3558. $[\alpha]_D$ +25.1° (c 1.38, $CHCl_3$).

Monocyclic Aldol Products 19a,b and 20a,b. The aldehyde **18** (785 mg, 1.89 mmol) was oxidized by the usual Swern procedure from the corresponding alcohol. A stirred solution of HMDS (0.79 mL, 3.72 mmol) in THF (2.2 mL) was treated dropwise at 0 °C under argon with n-BuLi (0.62 mL of a 3.0 M solution in hexanes) and stirred for 20 min. The reaction mixture was cooled to −78 °C, and a solution of methyl ketone **12** (1.33 g, 1.68 mmol) in toluene (9.5 mL) was added dropwise via cannula. The reaction mixture was stirred for 30 min at −78 °C, and a solution of aldehyde in toluene (1.25 mL) was added via cannula. The reaction mixture was stirred for 10 min and quenched with saturated NH_4Cl. Aqueous workup (Et_2O/EtOAc) and silica gel chromatography (16–25% EtOAc/hexanes) followed by size-exclusion chromatography (JAI LC-908, $CHCl_3$) yielded as colorless oils major aldol product **19a** (1.26 g, 1.05 mmol, 63% yield), minor aldol product **19b** (315 mg, 0.26 mmol, 16% yield), and recovered methyl ketone **12** (109 mg, 0.14 mmol). Similar results were obtained using methyl ketone **17** (1.62 g, 2.42 mmol) and aldehyde **18** (1.12 g, 2.90 mmol), yielding aldol products **20a** and **20b** (1.74 g, 66% combined yield) and recovered methyl ketone **17** (216 mg, 0.32 mmol). **Erythro Diastereomer 19a.** IR (neat): 3470, 1772, 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.02 (3H, s), 0.03 (3H, s), 0.84 (9H, s), 1.54 (2H, m), 2.39 (1H, dd, J = 9.6, 15.8 Hz), 2.42 (1H, m), 2.58 (2H, m), 2.61 (1H, dd, J = 2.6, 15.8 Hz), 3.29 (1H, dd, J = 3.3, 7.4 Hz), 3.39 (2H, t, J = 6.6 Hz), 3.64 (1H, dt, J = 4, 9.9 Hz), 3.67 (1H, dd, J = 4, 9.5 Hz), 3.78 (3H, s), 4.36 (1H, t, J = 10.3 Hz), 4.41 (2H, s). ^{13}C NMR ($CDCl_3$): δ −5.04, −4.68, 17.95, 24.97, 25.74, 26.08, 29.08, 29.31, 29.36, 29.42, 29.67, 31.95, 40.90, 41.64, 46.35, 55.14, 56.92, 68.25, 70.13, 71.14, 71.30, 72.28, 72.38, 73.14, 73.27, 75.34, 78.49, 78.77, 80.79, 113.69, 159.05, 167.97, 168.34, 209.11. HRMS (FAB, NaI): calcd for $C_{73}H_{93}NO_{12}Si$ (M + Na) 1226.6364; found 1226.6345. $[\alpha]_D$ +28.1° (c 1.10, $CHCl_3$). **Threo Diastereomer 19b.** IR (neat): 3540, 1773, 1713 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.00 (3H, s), 0.01 (3H, s), 0.85 (9H, s), 2.19 (1H, dd, J = 3.3, 16.2 Hz), 2.37 (1H, dq, 15.1, 5.2 Hz), 2.46–2.57 (3H, m), 2.77 (1H, d, J = 5.6 Hz), 3.18 (1H, dd, J = 3.3, 5.5 Hz), 3.78 (3H, s), 3.99 (1H, m), 4.06 (1H, dt, J = 2.6, 10.3 Hz), 4.14 (1H, m), 4.40 (2H, s). ^{13}C NMR ($CDCl_3$): δ −4.81, −4.53, 18.04, 25.07, 25.66, 25.87, 26.17, 29.32, 29.41, 29.44, 29.47, 29.51, 29.67, 29.74, 32.02, 41.27, 42.05, 46.68, 55.26, 57.12, 66.93, 70.24, 71.13, 71.82, 72.15, 72.46, 72.72, 73.25, 73.44, 74.07, 75.43, 78.50, 79.07, 82.29, 113.77, 168.03, 168.44, 208.31. HRMS (FAB, NaI): calcd for $C_{73}H_{93}NO_{12}Si$ (M + Na) 1226.6364; found 1226.6327. $[\alpha]_D$ +17.4° (c 1.36, $CHCl_3$). **Erythro Diastereomer 20a.** IR (neat): 3460, 2854, 1773, 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.04 (3H, s), 0.05 (3H, s), 0.86 (9H, s), 1.55 (2H, dt, J = 6.6, 14.9 Hz), 2.20 (1H, dd, J = 8.8, 16.9 Hz), 2.43 (1H, m), 2.47 (1H, dd, J = 8.7, 16.0 Hz), 2.68 (1H, dd, J = 3.0, 16.0 Hz), 2.69 (1H, dd, J = 3.3, 16.9 Hz), 3.18 (1H, t, J = 11.4 Hz), 3.37 (1H, dd, J = 4.1, 6.3 Hz), 3.40 (2H, t, J = 6.6 Hz), 3.58 (1H, dd, J = 6.6, 9.9 Hz), 3.68 (1H, d, J = 2.6 Hz), 3.70 (1H, dd, J = 4.0, 9.5 Hz), 3.78 (3H, s), 4.19 (1H, m), 4.41 (2H, s). ^{13}C NMR ($CDCl_3$): δ −5.09, −4.69, 17.95, 24.82, 25.71, 26.07, 29.32, 29.41, 29.65, 32.00, 39.39, 42.24, 46.67, 55.25, 56.76, 68.49, 69.80, 70.11, 71.14, 72.37, 72.89, 73.22, 73.28, 76.14, 79.14, 80.62, 113.63, 158.97, 167.94, 168.45, 208.70. HRMS (FAB, NaI): calcd for $C_{65}H_{85}NO_{11}Si$ (M + Na) 1106.5789; found 1106.5747. $[\alpha]_D$ +28.5° (c 1.22, $CHCl_3$). **Threo Diastereomer 20b.** IR (neat): 3470, 2855, 1774, 1712 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.01 (3H, s), 0.02 (3H, s), 0.86 (9H, s), 2.10 (1H, dd, J = 8.6, 16.5 Hz), 2.32 (1H, dd, J = 4.0, 16.2 Hz), 2.39 (1H, m), 2.59 (1H, dd, J = 9.2, 16.2 Hz), 2.60 (1H, dd, J = 4.6, 16.5 Hz), 2.95 (1H, d, J = 5.0 Hz), 3.15 (1H, t, J = 11.3 Hz), 3.27 (1H, dd, J = 3.4, 5.5 Hz), 3.39 (2H, t, J = 6.75 Hz), 3.54 (1H, dd, J = 4.9, 10.1 Hz), 3.58 (1H, dd, J = 4.0, 10.1 Hz), 3.78 (3H, s). ^{13}C NMR ($CDCl_3$): δ −4.85, −4.58, 18.04, 24.92, 25.83, 26.15, 29.41, 29.50, 29.72, 32.07, 39.58, 42.36, 46.68, 55.24, 56.88, 66.59, 69.87, 70.20, 71.49, 71.89, 72.45, 73.12, 73.47, 73.97, 76.24, 77.21, 79.37, 81.87, 113.52, 159.05, 168.00, 168.55, 207.96. HRMS (FAB, NaI): calcd for $C_{65}H_{85}NO_{11}Si$ (M + Na) 1106.5789; found 1106.5763. $[\alpha]_D$ +20.1° (c 1.62, $CHCl_3$).

Disaccharide Ketones 21 and 22. A stirred solution of major aldol product **19a** (1.425 g, 1.18 mmol) in THF (15 mL) was treated with a solution of TBAF (12 mL of a 0.1 M solution in THF) acidified with 48% aqueous HF (0.4 mL). The reaction mixture was stirred for 1 day at room temperature and then passed through a short silica gel plug (THF). The filtrate was purified by silica gel chromatography (33% acetone/hexanes) to yield the corresponding hemiketal as a colorless oil (1.245 g, 1.14 mmol, 97% yield).

A stirred solution of the hemiketal (692 mg, 0.651 mmol) in CH_2Cl_2 (6 mL) was cooled to −78 °C, followed by condensation of MeSH (9 mL). The reaction mixture was treated with a 10% BF_3·Et_2O solution in CH_2Cl_2 (60 μL) at −78 °C, stirred for 5 min, warmed to 0 °C, stirred for an additional 15 min, and then quenched with saturated $NaHCO_3$. Aqueous workup (EtOAc) followed by column chromatography (10–33% EtOAc/hexanes) yielded as a colorless oil the desired hemithioketals as a 1:1 mixture of diastereomers (660 mg, 0.605 mmol, 95% yield).

A stirred solution of the hemithioketals (660 mg, 0.605 mmol) in toluene (12 mL) was treated with triphenyltin hydride (1.59 g, 4.53 mmol) and AIBN (25 mg, 0.151 mmol) and placed in an oil bath (preheated to 150 °C) for 15 min. The reaction mixture was subjected to silica gel chromatography (10–50% EtOAc/hexanes) to yield the desired 2-deoxy C-disaccharide as a colorless oil (609 mg, 0.581 mmol, 96% yield). The 2-deoxy C-disaccharide (680 mg, 0.651 μmol) was converted to the desired 2-deoxy disaccharide ketone **21** (colorless oil, 655 mg, 0.624 mmol, 96% yield) by the usual Swern procedure. The minor aldol product **19b** was converted to the disaccharide ketone **21** by the same procedure. Similarly, aldol products **20a** and **20b** (1.035 g, 0.954 mmol, a mixture of isomers) were converted to the corresponding disaccharide ketone **22** (826 mg, 0.868 mmol, 91% overall yield) by the same procedure. **Disaccharide Ketone 21.** IR (neat): 3280, 1716, 1645 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.37 (1H, m), 1.44 (1H, ddd, J = 4.8, 9.2, 14 Hz), 1.57 (2H, quint, J = 8.1 Hz), 1.64 (1H, dt, J = 14.1, 4.4 Hz), 1.96 (1H, ddd, J = 4.0, 8.8, 15.1 Hz), 2.18 (1H, br d, J = 12.8 Hz), 2.25 (1H, ddd, J = 5.1, 10.6, 14.3 Hz), 2.71 (1H, dd, J = 11.8, 13.6 Hz), 3.41 (2H, t, J = 6.6 Hz), 3.60 (1H, dt, J = 10.3, 2.9 Hz), 3.63 (1H, br), 3.67 (2H, m), 3.79 (3H, s), 4.08 (1H, m). ^{13}C NMR ($CDCl_3$): δ 25.06, 26.12, 29.37, 29.40, 29.47, 29.68, 32.03, 33.80, 40.07,

45.62, 55.17, 56.39, 68.34, 70.15, 70.56, 70.92, 71.86, 72.41, 73.29, 75.30, 75.87, 77.21, 78.58, 78.79, 79.59, 79.67, 113.67, 159.02, 168.10, 168.51, 206.48. HRMS (FAB, NaI): calcd for $C_{61}H_{77}O_{10}N$ (M + Na) 1006.5445; found 1006.5477. $[\alpha]_D$ +9.3° (*c* 0.88, $CHCl_3$). **Disaccharide Ketone 22.** IR (neat): 2854, 1773, 1710 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.34 (1H, m), 1.38 (1H, ddd, *J* = 3.3, 9.6, 14 Hz), 1.55 (2H, quint, *J* = 7.8 Hz), 2.08 (1H, ddd, *J* = 3.3, 8.4, 14.3 Hz), 2.19 (br d, *J* = 12.8 Hz), 2.27 (1H, m), 2.84 (1H, dd, *J* = 11.8, 13.6 Hz), 3.29 (1H, t, *J* = 11.4 Hz), 3.40 (2H, t, *J* = 6.6 Hz), 3.78 (3H, s), 4.01 (1H, ddd, *J* = 3.1, 8.5, 10.7 Hz), 4.41 (2H, s). ^{13}C NMR ($CDCl_3$): δ 24.89, 26.07, 29.33, 29.37, 29.41, 29.65, 32.14, 34.30, 39.41, 55.15, 56.79, 68.29, 70.02, 70.12, 71.86, 72.38, 72.77, 73.43, 75.27, 76.08, 77.19, 79.34, 79.57, 79.67, 113.64, 158.98, 168.02, 168.49, 206.72. HRMS (FAB, NaI): calcd for $C_{59}H_{69}O_{10}N$ (M + Na) 974.4819; found 974.4845. $[\alpha]_D$ +16.3° (*c* 1.42, $CHCl_3$).

Trisaccharide Aldol Products 24a,b and 25. The aldehyde **23** was obtained from the corresponding alcohol (475 mg, 1.06 mmol) by Dess–Martin periodinane oxidation and was passed through a short silica gel plug (25% EtOAc/hexanes) to yield a colorless oil (371 mg, 0.83 mmol, 78% yield). The aldehyde was azeotroped with toluene prior to use. A stirred solution of HMDS (217 μL, 1.03 mmol) in Et_2O (2.6 mL) was treated at 0 °C under argon with *n*-BuLi (230 μL of a 3 M solution in hexanes). After 20 min, the reaction mixture was treated with TMEDA (113 μL, 0.75 mmol) and cooled to −78 °C. A solution of disaccharide ketone **21** (655 mg, 0.63 mmol) in toluene (2.4 mL) was then added dropwise via cannula. The yellow reaction mixture was stirred for 45 min at −78 °C, followed by the dropwise addition of a solution of aldehyde in toluene (0.6 mL) via cannula. The reaction mixture was stirred at −78 °C for 30 min and then quenched with saturated NH_4Cl. Aqueous workup (Et_2O/EtOAc) followed by size-exclusion chromatography (JAI LC-908, $CHCl_3$) yielded as colorless oils aldol products **24a** and **24b** (2:1 mixture of diastereomers, 576 mg, 0.38 mmol, 61% yield), recovered ketone **21** (212 mg, 0.20 mmol), and a small amount of bis-aldol products (diastereomeric mixture, 33.6 mg, 0.02 mmol). The aldol products **24a** and **24b** were separable by silica gel chromatography (33% EtOAc/hexanes). A stirred solution of the bis-aldol product in CH_2Cl_2 (2 mL) was treated with *p*-TsOH·H_2O (5 mg). The reaction mixture was quenched with saturated $NaHCO_3$ after 2 h. Aqueous workup (CH_2Cl_2) and preparative thin-layer chromatography (0.5 mm, 5:95 acetone: benzene) yielded a mixture of trisaccharide aldol products **24a** and **24b** (15.2 mg, 10 μmol, 59% yield).

Similar results were obtained using disaccharide ketone **22** (730 mg, 0.77 mmol) and aldehyde **23** (432 mg, 0.97 mmol), yielding trisaccharide aldol product **25** (603 mg, 0.43 mmol, 56% yield), recovered ketone **22** (232 mg, 0.24 mmol), and bis-aldol products (144 mg, 0.08 mmol). **Major Diastereomer 24a.** IR (neat): 3500, 2855, 1772, 1711, 1612 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.30 (3H, d, *J* = 6.6 Hz), 1.37 (1H, m), 1.46 (1H, ddd, *J* = 4.4, 9.2, 14 Hz), 1.56 (2H, quint, *J* = 7 Hz), 1.86 (1H, dd, *J* = 7, 14 Hz), 2.04 (1H, dd, *J* = 10.7, 14.3 Hz), 2.52 (1H, m), 2.60 (1H, d, *J* = 11.4 Hz), 3.40 (1H, m), 3.41 (2H, t, *J* = 6.6 Hz), 3.57 (1H, ddd, *J* = 1.1, 3.3, 10.3 Hz), 3.79 (3H, s). ^{13}C NMR ($CDCl_3$): δ 13.31, 25.12, 26.12, 29.38, 29.43, 29.46, 29.50, 29.70, 30.43, 32.19, 39.07, 53.04, 55.19, 55.71, 67.07, 67.73, 68.12, 68.94, 70.16, 70.24, 70.40, 71.31, 71.72, 72.41, 73.04, 73.10, 73.18, 73.53, 73.92, 74.44, 74.76, 75.50, 77.18, 77.50, 79.56, 79.68, 80.60, 82.64, 113.69, 159.03, 168.21, 168.36, 213.79. MS (FAB, NaI): calcd for $C_{95}H_{107}NO_{16}$ (M + Na) 1540; found 1541. $[\alpha]_D$ −1.1° (*c* 1.25, $CHCl_3$). **Minor Diastereomer 24b.** IR (neat): 3450, 2855, 1772, 1712 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24 (3H, d, *J* = 6.6 Hz), 1.35 (1H, m), 1.44 (1H, ddd, *J* = 4.1, 8.9, 14.2 Hz), 1.55 (2H, quint, *J* = 7 Hz), 2.02 (1H, dd, *J* = 11, 14.6 Hz), 2.23 (1H, dd, *J* = 7.3, 13.8 Hz), 2.50 (1H, m), 3.07 (1H, br d, *J* = 3.3 Hz), 3.09 (1H, dd, *J* = 5.7, 9.3 Hz), 3.40 (2H, t, *J* = 6.6 Hz), 3.50 (1H, dt, *J* = 10.2, 2.9 Hz), 3.78 (3H, s), 3.87 (1H, dd, *J* = 2.9, 5.3 Hz), 4.04 (1H, t, *J* = 3.6 Hz), 4.06 (1H, dt, *J* = 2.4, 8.5 Hz), 4.16 (1H, m). ^{13}C NMR ($CDCl_3$): δ 14.37, 25.21, 26.18, 29.44, 29.53, 29.74, 32.32, 33.26, 38.86, 54.62, 55.25, 67.62, 68.25, 69.02, 70.23, 70.54, 71.97, 72.30, 72.47, 72.96, 73.04, 73.22, 74.58, 75.44, 75.53, 77.21, 77.48, 78.04, 78.57, 78.91, 80.85, 81.04, 113.74, 159.09, 168.34, 208.91. MS (FAB, NaI): calcd for $C_{95}H_{107}NO_{16}$ (M + Na) 1540; found 1540, 1541. $[\alpha]_D$ −10.6° (*c* 1.24, $CHCl_3$). **Aldol Product 25.** IR (neat): 3530, 2855, 1773, 1711, 1611 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.28 (3H, d, *J* = 6.6 Hz), 1.43 (1H, m), 1.54 (2H, quint, *J* = 7 Hz), 1.63 (1H, ddd, *J* = 2.6, 10.7, 14.3 Hz), 2.13 (1H, ddd, *J* = 2.6, 9.6, 14.3 Hz), 2.35 (1H, m), 2.57 (1H, d, *J* = 10.7 Hz), 3.28 (1H, t, *J* = 11.4 Hz), 3.39 (2H, t, *J* = 6.6 Hz), 3.40 (1H, dd, *J* = 1.8, 9.9 Hz), 3.78 (3H, s), 3.82 (1H, dt, *J* = 2.2, 10 Hz), 3.85 (1H, dd, *J* = 3.3, 5.5 Hz), 3.87 (1H, dd, *J* = 1.8, 4.4 Hz), 4.31 (1H, dd, *J* = 1.8, 9.2 Hz), 4.40 (2H, s). ^{13}C NMR ($CDCl_3$): δ 13.59, 25.00, 26.15, 29.41, 29.44, 29.73, 31.61, 32.30, 39.75, 52.46, 55.25, 56.80, 67.00, 67.82, 68.31, 70.02, 70.22, 70.42, 71.52, 71.75, 72.46, 72.69, 73.10, 73.50, 73.79, 74.09, 74.88, 76.19, 77.20, 78.63, 79.87, 80.22, 82.26, 113.73, 159.08, 168.13, 168.46, 213.48. MS (FAB, NaI): calcd for $C_{87}H_{99}NO_{15}$ (M + Na) 1420; found 1420. $[\alpha]_D$ +8.3° (*c* 1.67, $CHCl_3$).

Trisaccharide Enones 26a,b and 27a,b. A stirred solution of trisaccharide aldol products **24a,b** (317 mg, 0.21 mmol) in CH_2Cl_2 (5 mL) was treated at 0 °C with 2,6-lutidine (188 μL, 1.61 mmol) and MsCl (125 μL, 1.61 mmol). The reaction mixture was stirred for 45 min, then treated with (*i*-Pr)$_2$NEt (245 μL, 1.36 mmol), and stirred for an additional 30 min. Aqueous workup (Et_2O) yielded the crude mesylates, which were used without further purification.

A stirred solution of the mesylates in THF (20 mL) was cooled to −78 °C under argon. Ammonia (20 mL) was condensed into the flask, and the reaction mixture was stirred without external cooling for 30 min. The reaction mixture was flushed with nitrogen, followed by aqueous workup (Et_2O) and silica gel chromatography (20–33% EtOAc/hexanes) to yield as a colorless oil the trisaccharide enones **26a** and **26b** (mixture of isomers, 252 mg, 0.17 mmol, 80% yield over two steps). Similar results were obtained using the trisaccharide aldol product **25** (655 mg, 0.47 mmol) to yield as a colorless oil the trisaccharide enones **27a** and **27b** (mixture of isomers, 440 mg, 0.32 mmol, 68% yield over two steps). **Enone 26a (major isomer).** IR (neat): 2854, 1772, 1712, 1611 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.09 (3H, d, *J* = 6.6 Hz), 1.31 (1H, m), 1.41 (1H, m), 1.47 (1H, br), 1.54 (2H, quint, *J* = 6.6 Hz), 1.73 (1H, dd, *J* = 6.6, 14.7 Hz), 1.97 (1H, ddd, *J* = 1.8, 4.4, 14.7 Hz), 2.39 (1H, m), 3.39 (2H, t, *J* = 6.6 Hz), 3.50 (1H, dd, *J* = 2.9, 9.6 Hz), 3.77 (3H, s), 3.99 (1H, m), 4.36 (1H, dd, *J* = 1.8, 9.5 Hz), 4.40 (2H, s), 5.11 (1H, dd, *J* = 1.8, 9.9 Hz). ^{13}C NMR ($CDCl_3$): δ 16.84, 25.19, 26.17, 29.44, 29.50, 29.74, 31.49, 32.20, 39.47, 50.67, 55.25, 55.83, 68.39, 69.42, 70.22, 70.47, 71.67, 72.47, 73.09, 73.11, 73.26, 74.12, 74.67, 75.33, 75.43, 77.20, 77.52, 78.99, 79.88, 80.12, 80.44, 82.89, 101.67, 113.72, 154.06, 159.07, 168.28, 168.49. MS (FAB, NaI): calcd for $C_{95}H_{105}NO_{15}$ (M + Na) 1522; found 1523. $[\alpha]_D$ −25.7° (*c* 1.55, $CHCl_3$). **Enones 27a,b.** IR (neat): 2854, 1772, 1712, 1612 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.24 (d, *J* = 6.6 Hz), 1.31 (d, *J* = 6.6 Hz), 1.59 (quint, *J* = 7.7 Hz), 3.26 (t, *J* = 11.4 Hz), 3.31 (t, *J* = 11.4 Hz), 3.43 (t, *J* = 6.6 Hz), 3.79 (s), 3.95 (dt, *J* = 2.6, 5.9 Hz), 4.43 (s), 4.90 (dd, *J* = 2.2, 9.2 Hz), 5.25 (dd, *J* = 3.7, 8.1 Hz), 7.17 (dd, *J* = 1.4, 8.1 Hz). ^{13}C NMR ($CDCl_3$): δ 14.00, 14.74, 16.83, 24.87, 26.07, 29.33, 29.35, 29.41, 29.65, 30.48, 31.66, 32.16, 39.33, 55.13, 56.74, 56.89, 66.57, 68.61, 68.69, 69.88, 70.02, 70.11, 71.52, 72.37, 72.42, 72.45, 72.60, 72.84, 73.00, 73.09, 73.23, 73.50, 74.13, 74.34, 75.92, 76.06, 76.12, 77.09, 77.21, 79.31, 79.47, 113.64, 120.04, 158.99, 168.04, 168.38, 195.35, 197.30. MS (FAB, NaI): calcd for $C_{87}H_{97}NO_{14}$ (M + Na) 1402; found 1402.

Trisaccharide C.3′ Alcohols 28, 30. A solution of trisaccharide enones **26a,b** (139 mg, 94.4 μmol) in toluene (4 mL) was treated with Ph_3SnH (249 mg, 0.71 mmol) and AIBN (4 mg, 23.6 μmol) and placed in a preheated (140 °C) oil bath. The reaction mixture was stirred at reflux under argon for 30 min, cooled to room temperature, and subjected to silica gel chromatography (1–3% acetone/benzene) to yield the desired trisaccharide ketone as a colorless oil (104.5 mg, 69.6 μmol, 75% yield).

A stirred solution of the trisaccharide ketone (109.5 mg, 74.3 μmol) in 3:2 MeOH:CH_2Cl_2 (14 mL) was treated at −78 °C under argon with $NaBH_4$ (28 mg, 0.74 mmol). The reaction mixture was warmed to −30 °C over 2 h, quenched with

acetone (10 mL), warmed to 0 °C, and neutralized with saturated NH_4Cl. Aqueous workup (CH_2Cl_2) followed by silica gel chromatography (25–33% EtOAc/hexanes) yielded the C.3′ alcohol **28** as a colorless oil (99.5 mg, 66.2 μmol, 91% yield). Similar results were obtained using the trisaccharide enones **27a,b** (440 mg, 0.32 mmol) to yield the trisaccharide C.3′ alcohol **30** as a colorless oil (290 mg, 0.21 mmol, 66% yield over two steps). **C.3′ Alcohol 28.** IR (neat): 3450, 2855, 1772, 1712, 1611 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.16 (3H, d, J = 6.6 Hz), 1.39 (1H, m), 1.48 (1H, ddd, J = 4.8, 9.2, 14 Hz), 1.58 (2H, quint, J = 7 Hz), 1.68 (1H, dd, J = 6.2, 14.7 Hz), 1.73 (1H, m), 2.51 (1H, m), 2.65 (1H, d, J = 8.8 Hz), 3.27 (1H, t, J = 9.6 Hz), 3.43 (2H, t, J = 6.6 Hz), 3.51 (1H, m), 3.58 (2H, br s), 3.80 (3H, s), 3.88 (1H, m), 4.10 (1H, m), 4.30 (1H, dt, J = 4.4, 9 Hz), 4.43 (2H, s). ^{13}C NMR ($CDCl_3$): δ 15.84, 25.14, 26.05, 26.10, 28.88, 29.17, 29.36, 29.43, 29.67, 29.82, 32.20, 38.12, 41.54, 55.04, 55.15, 67.11, 68.13, 69.04, 70.13, 70.71, 72.39, 72.79, 73.09, 73.21, 73.59, 75.04, 75.13, 75.37, 76.40, 76.88, 77.17, 77.76, 80.40, 113.65, 159.00, 168.27. MS (FAB, NaI): calcd for $C_{95}H_{109}NO_{15}$ (M + Na) 1526; found 1526. $[\alpha]_D$ −21.1° (c 1.99, $CHCl_3$). **C.3′ Alcohol 30.** IR (neat): 3400, 2854, 1772, 1711, 1612 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.19 (3H, d, J = 6.6 Hz), 1.37 (1H, ddd, J = 2.2, 10.3, 15.1 Hz), 1.44 (1H, m), 1.54 (2H, quint, J = 7 Hz), 1.76–1.85 (2H, m), 1.91 (1H, ddd, J = 2.2, 9.6, 14.3 Hz), 2.32 (1H, ddq, J = 2.1, 4.4, 10.3 Hz), 2.53 (1H, d, J = 9.2 Hz), 3.14 (1H, t, J = 11.7 Hz), 3.15 (1H, dt, J = 2.2, 9.6 Hz), 3.39 (2H, t, J = 6.6 Hz), 3.78 (3H, s), 3.83 (1H, m), 3.98 (1H, ddd, J = 2.4, 8.4, 9.9 Hz), 4.11 (1H, dd, J = 4.8, 11.4 Hz), 4.26 (1H, dt, J = 4.1, 9.9 Hz), 4.40 (2H, s). ^{13}C NMR ($CDCl_3$): δ 15.77, 24.96, 26.09, 29.35, 29.39, 29.45, 29.67, 30.99, 32.26, 39.06, 40.33, 55.16, 56.56, 68.33, 69.15, 70.08, 70.13, 72.00, 72.39, 72.86, 73.19, 73.43, 73.53, 74.68, 74.95, 76.06, 76.10, 76.21, 76.29, 76.85, 77.20, 79.73, 113.66, 159.00, 168.11, 168.40. MS (FAB, NaI): calcd for $C_{87}H_{101}NO_{14}$ (M + Na) 1406; found 1406. $[\alpha]_D$ −0.71° (c 1.41, $CHCl_3$).

C.3′ Deoxy Trisaccharides 29, 31. A stirred solution of trisaccharide C.3′ alcohol **28** (77 mg, 52.2 μmol) in 1:1 CS_2:THF (6 mL) was treated at −78 °C under argon with a solution of NaHMDS (175 μL of a 0.6 M solution in toluene) and slowly warmed to 0 °C over 30 min. The reaction mixture was stirred at 0 °C for 20 min, treated with MeI (50 μL, 0.80 mmol), stirred for an additional 45 min, and then quenched with saturated NH_4Cl. Aqueous workup (Et_2O) and silica gel chromatography (20–25% EtOAc/hexanes) yielded the C.3′ methyl xanthate as a colorless oil.

A solution of methyl xanthate in toluene (1.8 mL) was treated with Bu_3SnH (250 μL, 0.93 mmol) and AIBN (3 mg, 18.3 μmol) and placed in a preheated (130 °C) oil bath. The reaction mixture was stirred at reflux for 45 min, cooled to room temperature, and subjected to column chromatography (20–25% EtOAc/hexanes) to yield the desired C.3′ deoxy trisaccharide **29** as a colorless oil (53.5 mg, 36 μmol, 70% yield over two steps). Similar results were obtained using the C.3′ alcohol **30** (111 mg, 80.4 μmol) to yield the C.3′ deoxy trisaccharide **31** as a colorless oil (58.3 mg, 42.6 μmol, 53% yield over two steps). **C.3′ Deoxy Trisaccharide 29.** IR (neat): 2853, 1772, 1711, 1610 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.96 (1H, dt, J = 2.6, 12.9 Hz), 0.99 (1H, m), 1.10 (3H, d, J = 6.6 Hz), 1.35 (1H, m), 1.43 (1H, ddd, J = 4.8, 9.9, 14.3 Hz), 1.55 (2H, quint, J = 7 Hz), 1.74 (1H, m), 1.86 (1H, dt, J = 3.7, 11 Hz), 2.38 (1H, dt, J = 13.6, 3 Hz), 2.43 (1H, m), 3.28 (1H, dt, J = 1.1, 9.9 Hz), 3.39 (2H, t, J = 6.6 Hz), 3.78 (3H, s), 3.91 (1H, m), 4.40 (2H, s). ^{13}C NMR ($CDCl_3$): δ 16.13, 25.19, 26.14, 29.41, 29.47, 29.53, 29.65, 29.71, 30.77, 31.68, 32.26, 38.91, 55.21, 55.57, 68.24, 70.09, 70.18, 70.20, 70.88, 71.00, 72.43, 72.94, 73.19, 73.26, 73.33, 75.31, 76.44, 76.79, 77.20, 77.79, 79.48, 80.10, 113.68, 159.02, 168.42. MS (FAB, NaI): calcd for $C_{95}H_{109}NO_{14}$ (M + Na) 1510; found 1510. $[\alpha]_D$ −30.4° (c 1.21, $CHCl_3$). **C.3′ Deoxy Trisaccharide 31.** IR (neat): 2854, 1773, 1711, 1611 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.97 (1H, q, J = 13.2 Hz), 1.22 (3H, d, J = 6.6 Hz), 1.49 (1H, ddd, J = 1.5, 9.9, 14.4 Hz), 1.56 (2H, quint, J = 7 Hz), 1.81–1.91 (2H, m), 1.96 (1H, ddd, J = 2.6, 9.2, 14.7 Hz), 2.34 (1H, m), 2.39 (1H, dt, J = 14, 2.9 Hz), 3.14 (1H, dt, J = 1.9, 9.2 Hz), 3.26 (1H, t, J = 11.4 Hz), 3.41 (2H, t, J = 6.6 Hz), 3.56 (1H, m), 3.69 (1H, dd, J = 2.6, 5.9 Hz), 3.76 (1H, m), 3.78 (3H, s), 3.93 (1H, br), 4.00 (1H, tt, J = 2.4, 7.7 Hz), 4.22 (1H, dd, J = 4.8, 11.8 Hz), 4.41 (2H, s). ^{13}C NMR ($CDCl_3$): δ 13.55, 15.93, 24.95, 26.10, 26.92, 28.67, 29.35, 29.38, 29.45, 29.67, 30.40, 30.70, 31.13, 32.27, 39.14, 55.18, 56.79, 67.85, 70.05, 70.15, 70.26, 70.36, 70.75, 72.30, 72.40, 72.94, 73.38, 73.47, 73.81, 76.06, 76.46, 76.91, 77.20, 78.61, 79.23, 80.00, 113.67, 159.02, 168.11, 168.50. MS (FAB, NaI): calcd for $C_{87}H_{101}NO_{13}$ (M + Na) 1390; found 1390. $[\alpha]_D$ −14.7° (c 1.17, $CHCl_3$).

***C*-Trisaccharide Carboxylic Acids 32–35.** A stirred solution of trisaccharide alcohol **28** (99.5 mg, 67.4 μmol) in n-BuOH (3 mL) was treated with H_2NNH_2 (95 μL, 0.98 mmol). The reaction mixture was stirred at reflux under argon for 12 h and then concentrated until all volatiles were removed. The crude amine was redissolved in CH_2Cl_2 (3 mL) and treated at 0 °C with Et_3N (95 μL, 0.68 mmol) and Ac_2O (63.5 μL, 0.67 mmol). The reaction mixture was stirred at 0 °C for 30 min and then quenched with saturated $NaHCO_3$. Aqueous workup (CH_2Cl_2) followed by silica gel chromatography (20–60% EtOAc/hexanes) yielded the corresponding N-acetyl trisaccharide as a colorless oil (77.3 mg, 53.5 μmol, 81% yield over two steps).

A stirred solution of the N-acetyl trisaccharide (77 mg, 53.3 μmol) in CH_2Cl_2 (4 mL) and pH 7 phosphate buffer (400 μL) was treated at 0 °C with DDQ (37 mg, 163 μmol) and stirred for 1 h. Aqueous workup ($CHCl_3$) and silica gel chromatography (33% acetone/hexanes) yielded the corresponding diol as a colorless oil (56 mg, 42.3 μmol, 80% yield).

A stirred solution of the diol (20 mg, 15.1 μmol) and 3 Å powdered molecular sieves (30 mg) in benzene (0.6 mL) was treated at room temperature with $(PPh_3)_3RuCl_2$ (14.5 mg, 15.1 μmol) and stirred for 1 h. The reaction mixture was subjected to silica gel chromatography (20–60% EtOAc/hexanes), followed by preparative thin-layer chromatography (0.5 mm, 50% EtOAc/hexanes) to yield the corresponding aldehyde as a light brown oil (12 mg, 9.1 μmol, 60% yield).

A stirred solution of the aldehyde (18.6 mg, 14 μmol) in 8:3 t-BuOH:2-methyl-2-butene (0.55 mL) was treated at room temperature with a 10% $NaClO_2$–10% $NaH_2PO_4{\cdot}H_2O$ aqueous solution (0.15 mL). The reaction mixture was stirred for 10 min and then diluted with H_2O (5 mL). Aqueous workup ($CHCl_3$) followed by preparative thin-layer chromatography (0.5 mm, 5% MeOH/CH_2Cl_2) yielded the desired C-trisaccharide carboxylic acid **32** as a colorless oil (16.7 mg, 12.5 μmol, 89% yield). Similar results were obtained using the C-trisaccharides **29** (53.5 mg, 36.7 μmol), **30** (44.3 mg, 32 μmol), and **31** (58 mg, 42.3 μmol) to yield the corresponding C-trisaccharide carboxylic acids **33** (24.8 mg, 19.2 μmol, 54% yield over five steps), **34** (18.3 mg, 15.4 μmol, 48% over five steps), and **35** (24.3 mg, 20.7 μmol, 49% yield over five steps). **Carboxylic Acid 32.** IR (neat): 3302, 2854, 1724, 1658, 1552 cm^{-1}. ^1H NMR (50:50 $(CD_3)_2CO$:CD_3OD): δ 1.15 (3H, d, J = 6.6 Hz), 1.39 (1H, m), 1.62 (1H, ddd, J = 3.1, 6.4, 15.2 Hz), 1.66 (1H, ddd, J = 1.9, 10.4, 15.2 Hz), 1.73 (1H, ddd, J = 2.7, 10.4, 15.1 Hz), 1.74 (1H, ddd, J = 2.3, 6.4, 15 Hz), 1.77 (1H, ddt, J = 2.7, 6.4, 9.8 Hz), 1.88 (3H, s), 2.20 (2H, t, J = 7.6 Hz), 2.27 (1H, ddt, J = 1.9, 6.4, 11 Hz), 3.12 (1H, dt, J = 2.5, 9.8 Hz), 3.31 (1H, dt, J = 2.4, 10.1 Hz), 3.43 (1H, dd, J = 9.2, 10.4 Hz), 3.59 (1H, dd, J = 2.4, 2.8 Hz), 3.81 (1H, dq, J = 2.7, 6.1 Hz), 3.95 (1H, t, J = 10.1 Hz), 4.28 (1H, ddd, J = 2.7, 4.9, 10.4 Hz). ^{13}C NMR (70:30 $CDCl_3$:CD_3OD): δ 15.41, 22.12, 24.48, 25.25, 28.64, 28.80, 28.96, 29.09, 29.16, 29.26, 31.69, 33.66, 36.80, 40.90, 51.87, 65.85, 67.87, 69.40, 70.44, 70.81, 72.45, 72.80, 72.90, 73.01, 73.47, 74.80, 75.14, 76.09, 76.26, 76.29, 76.35, 76.85, 77.54, 78.96, 79.78, 79.89, 171.04, 176.20. MS (FAB, NaI): calcd for $C_{81}H_{99}NO_{14}$ (M + Na) 1332; found 1332. $[\alpha]_D$ −33.2° (c 1.61, $CHCl_3$). **Carboxylic Acid 33.** IR (neat): 3302, 2855, 1727, 1649, 1552 cm^{-1}. ^1H NMR (CD_3OD): δ 0.99 (1H, ddd, J = 3.3, 11.4, 14 Hz), 1.05 (1H, ddd, J = 2.6, 12.1, 14 Hz), 1.17 (3H, d, J = 6.6 Hz), 1.44 (1H, q, J = 8.8 Hz), 1.63 (1H, ddd, J = 2.2, 10.3, 15.4 Hz), 1.70 (1H, q, J = 10.7 Hz), 1.87 (1H, m), 1.91 (3H, s), 2.24 (2H, t, J = 7.7 Hz), 2.27 (1H, ddt, J = 2.2, 6.2, 10.7 Hz), 2.34 (1H, dt, J = 14.3, 3.3 Hz), 3.16 (1H, dt, J = 1.8, 9 Hz), 3.27 (1H, dt, J = 1.5, 10.3 Hz), 3.48 (1H, t, J = 9.6 Hz), 3.64 (1H, ddd, J = 2.2, 10.3, 15.4 Hz), 3.84 (1H, dd, J = 4.8, 8.2 Hz), 3.95 (1H, t, J = 8.9 Hz), 4.06 (1H,

ddd, J = 3.3, 4.8, 11.8 Hz), 4.37 (2H, s). ^{13}C NMR (CD_3OD): δ 16.57, 22.96, 26.12, 26.61, 28.62, 30.24, 30.46, 30.54, 30.69, 32.30, 32.96, 33.24, 35.00, 39.89, 54.75, 69.34, 69.60, 71.73, 72.06, 72.14, 73.33, 73.87, 74.25, 74.36, 75.13, 77.94, 78.09, 79.21, 80.20, 80.67, 81.05, 81.77, 173.09, 177.70. MS (FAB, NaI): calcd for $C_{81}H_{99}NO_{13}$ (M + Na) 1316; found 1316. $[\alpha]_D$ −55.1° (c 1.24, $CHCl_3$). **Carboxylic Acid 34.** IR (neat): 3280, 2854, 1729, 1654, 1551 cm^{-1}. ^{1}H NMR (CD_3OD): δ 1.23 (3H, d, J = 6.6 Hz), 1.39 (1H, m), 1.43 (1H, ddd, J = 2.4, 10.7, 14.7 Hz), 1.61 (1H, ddd, J = 3.0, 6.7, 15.2 Hz), 1.80 (1H, ddd, J = 2.8, 10.7, 15.2 Hz), 1.88 (1H, m), 1.89 (3H, s), 1.95 (1H, ddd, J = 2.8, 8.9, 14.7 Hz), 2.20 (1H, ddq, J = 2.6, 4.4, 11 Hz), 2.25 (2H, t, J = 7.3 Hz), 3.04 (1H, t, J = 11.3 Hz), 3.12 (1H, br t, J = 9.2 Hz), 3.18 (1H, t, J = 10 Hz), 3.26 (1H, dt, J = 2.4, 9.8 Hz), 3.62 (1H, t, J = 2.9 Hz), 3.65 (1H, dd, J = 3.5, 10.5 Hz), 3.66 (1H, dd, J = 3.0, 7.9 Hz), 3.81 (1H, dd, J = 4.6, 7.9 Hz), 3.84 (1H, br t, J = 9.5 Hz), 3.93 (1H, dq, J = 2.7, 6.4 Hz), 4.14 (1H, dd, J = 4.5, 11.6 Hz), 4.33 (1H, ddd, J = 3.0, 4.6, 10.4 Hz). ^{13}C NMR (CD_3OD): δ 16.52, 22.92, 25.80, 26.11, 26.34, 30.22, 30.39, 30.48, 30.58, 30.64, 32.19, 33.17, 35.02, 39.43, 40.62, 55.88, 69.64, 71.29, 71.46, 71.96, 72.64, 73.75, 74.00, 74.40, 74.83, 76.18, 76.91, 77.77, 77.87, 78.36, 78.88, 80.87, 84.05, 173.12, 177.72. MS (FAB, NaI): calcd for $C_{73}H_{91}NO_{13}$ (M + Na) 1212; found 1212. $[\alpha]_D$ −30.8° (c 1.83, MeOH). **Carboxylic Acid 35.** IR (neat): 3278, 2855, 1727, 1650, 1552 cm^{-1}. ^{1}H NMR (80:20 CD_3OD:$(CD_3)_2CO$): δ 1.05 (1H, ddd, J = 2.4, 11.6, 15.2 Hz), 1.09 (1H, ddd, J = 2.4, 12.2, 14.3 Hz), 1.22 (3H, d, J = 6.4 Hz), 1.40 (1H, m), 1.45 (1H, ddd, J = 2.4, 10.4, 14.6 Hz), 1.88 (1H, ddd, J = 3, 11.9, 15 Hz), 1.90 (3H, s), 1.98 (1H, ddd, J = 2.4, 8.0, 14.6 Hz), 2.17 (1H, ddq, J = 2.4, 4.5, 10.7 Hz), 2.26 (2H, t, J = 7.4 Hz), 2.39 (1H, dt, J = 14, 3.3 Hz), 3.10 (1H, t, J = 11.6 Hz), 3.16 (1H, br t, J = 9.2 Hz), 3.24 (2H, br t, J = 10.1 Hz), 3.56 (1H, br t, J = 2.9 Hz), 3.64 (1H, dd, J = 3, 8.5 Hz), 3.66 (1H, dd, J = 2.5, 3 Hz), 3.84 (1H, dq, J = 2.4, 6.4 Hz), 3.89 (1H, dd, J = 5.2, 8.5 Hz), 4.09 (1H, ddd, J = 3, 4.9, 11.3 Hz), 4.23 (1H, dd, J = 4.6, 11.6 Hz). ^{13}C NMR (CD_3OD): δ 16.73, 22.95, 26.11, 26.30, 28.00, 30.21, 30.38, 30.48, 30.57, 30.64, 31.08, 31.91, 32.09, 33.15, 35.04, 39.66, 56.37, 69.23, 70.06, 71.46, 71.80, 71.93, 73.03, 73.73, 74.30, 74.43, 75.20, 77.96, 78.05, 79.74, 80.84, 84.46, 173.08, 177.73. MS (FAB, NaI): calcd for $C_{73}H_{91}NO_{12}$ (M + Na) 1196; found 1196. $[\alpha]_D$ −39.1° (c 1.28, MeOH).

***C*-Trisaccharide Polyols 1–4.** A stirred solution of the *C*-trisaccharide carboxylic acid **32** (12.6 mg, 9.4 μmol) in MeOH (0.75 mL) was hydrogenated over Pearlman's catalyst (20% $Pd(OH)_2$ on C, 10 mg) under 1 atm of H_2 at room temperature for 8 h. The reaction mixture was passed through filter paper (Whatman No. 42), concentrated, and then stirred in 0.5 M LiOH (1 mL) for 4 h. The reaction mixture was neutralized with 1 M HCl (0.5 mL) and purified by reverse-phase C_{18}-silica gel (0–20% MeOH) to yield the trisaccharide polyol **1** as a colorless oil (6.3 mg, 9.2 μmol, 98% yield over two steps). Similar results were obtained using the *C*-trisaccharides **33** (7.8 mg, 6.0 μmol), **34** (15 mg, 12.4 μmol), and **35** (9.6 mg, 8.1 μmol) to yield the *C*-trisaccharide polyols **2** (4.0 mg, 6.0 μmol, 100% yield over two steps), **3** (7.6 mg, 11.7 μmol, 94% yield over two steps), and **4** (4.8 mg, 7.6 μmol, 94% yield over two steps). ***C*-Trisaccharide Polyol 1.** ^{1}H NMR (methyl ester, 95:5 C_6D_5N:CD_3OD): δ 1.58 (3H, d, J = 6.6 Hz), 1.72 (1H, m), 1.77 (1H, m), 1.96 (1H, m), 2.02 (1H, ddd, J = 4, 9.6, 15.4 Hz), 2.12 (3H, s), 2.31 (2H, t, J = 7.3 Hz), 2.43 (1H, ddd, J = 4.4, 5.9, 14.7 Hz), 2.50 (1H, dq, J = 2.5, 10.3 Hz), 2.57 (1H, ddd, J = 2.6, 10, 14.7 Hz), 2.81 (1H, dd, J = 4.1, 15.1 Hz), 3.55 (1H, ddd, J = 2.6, 8.4, 9.5 Hz), 3.63 (3H, s), 3.79 (1H, dd, J = 4.4, 7.3 Hz), 3.89 (1H, t, J = 10.3 Hz), 3.96 (1H, ddd, J = 1.1, 5.5, 10.3 Hz), 4.00 (1H, t, J = 10 Hz), 4.05 (1H, dd, J = 3.3, 10.3 Hz), 4.08 (1H, dd, J = 5.5, 11.8 Hz), 4.15 (1H, dd, J = 4.7, 11.4 Hz), 4.18 (1H, t, J = 3 Hz), 4.23 (1H, d, J = 3.3 Hz), 4.36 (1H, dd, J = 2.9, 9.2 Hz), 4.38 (1H, dd, J = 4.4, 11.4 Hz), 4.43 (1H, dd, J = 1.2, 11.8 Hz), 4.48 (1H, dq, J = 2.2, 6.6 Hz), 4.69 (1H, dd, J = 5.5, 8.8 Hz), 5.00 (1H, dt, J = 9.6, 4.8 Hz). ^{13}C NMR (CD_3OD): δ 16.62, 22.98, 24.95, 26.22, 26.50, 30.26, 30.41, 30.54, 30.60, 30.75, 30.84, 33.35, 35.28, 40.76, 43.39, 58.40, 63.62, 64.56, 69.23, 69.99, 70.18, 71.97, 72.60, 74.65, 76.19, 78.25, 79.54, 80.19, 81.83, 173.68, 178.12. HRMS (FAB): calcd for $C_{32}H_{57}NO_{14}$ (M + H^+) 680.3857; found 680.3886. $[\alpha]_D$ −51.8° (c 0.63, MeOH). ***C*-Trisaccharide Polyol 2.** ^{1}H NMR (CD_3OD): δ 1.11 (1H, ddd, J = 3.3, 11, 14.7 Hz), 1.22 (3H, d, J = 6.6 Hz), 1.40 (1H, q, J = 8.8 Hz), 1.63 (1H, ddd, J = 3.7, 9.2, 15.4 Hz), 1.73 (1H, tt, J = 3.7, 10.3 Hz), 1.80 (1H, br q, J = 10.5 Hz), 1.93 (1H, ddd, J = 2.6, 12.1, 14.7 Hz), 1.98 (3H, s), 2.06 (1H, dd, J = 4.8, 14.7 Hz), 2.16 (1H, dt, J = 14, 3.7 Hz), 2.24 (2H, t, J = 7.4 Hz), 3.15 (1H, ddd, J = 1.8, 8, 9.9 Hz), 3.27 (1H, t, J = 9.2 Hz), 3.35 (1H, t, J = 10.1 Hz), 3.41 (1H, ddd, J = 1.8, 5.5, 10.7 Hz), 3.54 (1H, t, J = 9.9 Hz), 3.58 (1H, dd, J = 4, 11.8 Hz), 3.63 (1H, dd, J = 5.5, 11.8 Hz), 3.68 (1H, dd, J = 7.7, 11.8 Hz), 3.73 (1H, t, J = 3.3 Hz), 3.78 (1H, dq, J = 1.8, 6.6 Hz), 3.87 (1H, dd, J = 5.5, 8.8 Hz), 3.92 (1H, dd, J = 1.8, 11.8 Hz), 4.00 (1H, ddd, J = 2.9, 5.9, 12.1 Hz). ^{13}C NMR (CD_3OD): δ 16.65, 22.97, 26.40, 26.49, 27.44, 30.33, 30.43, 30.55, 30.61, 30.74, 31.00, 31.73, 33.35, 35.75, 37.57, 43.15, 58.40, 64.07, 64.61, 66.13, 68.78, 69.91, 72.04, 72.52, 72.84, 74.73, 79.49, 81.01, 81.46, 81.98, 173.90. HRMS (FAB): calcd for $C_{32}H_{57}NO_{13}$ (M + H^+) 664.3908; found 664.3900. $[\alpha]_D$ −64.2° (c 0.50, MeOH). ***C*-Trisaccharide Polyol 3.** ^{1}H NMR (75:25 CD_3OD:$(CD_3)_2SO$): δ 1.25 (3H, d, J = 6.6 Hz), 1.50 (1H, ddd, J = 2.0, 11.5, 14.4 Hz), 1.55 (1H, m), 1.70 (1H, ddd, J = 4.2, 5.4, 14.3 Hz), 1.74 (1H, m), 1.80 (1H, ddd, J = 2.4, 9.8, 14.6 Hz), 1.91 (1H, ddd, J = 2.9, 10, 14.7 Hz), 1.97 (1H, m), 1.98 (3H, s), 2.26 (2H, t, J = 7.3 Hz), 3.11 (1H, ddd, J = 2.4, 8.3, 10 Hz), 3.12 (1H, dd, J = 11.5, 12.7 Hz), 3.15 (2H, t, J = 10.2 Hz), 3.25 (1H, dt, J = 2.0, 9.8 Hz), 3.38 (1H, ddd, J = 1.0, 5.4, 6.9 Hz), 3.50 (1H, t, J = 9.8 Hz), 3.55 (1H, dd, J = 3.4, 10.5 Hz), 3.66 (1H, dd, J = 3.2, 8.3 Hz), 3.69 (2H, m), 3.84 (1H, dd, J = 5.3, 8.8 Hz), 3.94 (1H, dq, J = 2.2, 6.6 Hz), 4.03 (1H, dd, J = 4.6, 11.5 Hz), 4.15 (1H, dt, J = 9.5, 4.4 Hz). ^{13}C NMR (CD_3OD): δ 16.55, 22.92, 24.64, 26.21, 26.40, 30.25, 30.39, 30.48, 30.55, 30.61, 32.32, 33.31, 35.26, 40.70, 41.58, 58.31, 63.29, 69.43, 69.88, 70.32, 71.38, 72.04, 72.40, 75.67, 76.19, 77.91, 79.98, 80.77, 173.56. HRMS (FAB): calcd for $C_{31}H_{55}NO_{13}$ (M + H^+) 650.3751; found 650.3742. $[\alpha]_D$ −62.6° (c 0.76, MeOH). ***C*-Trisaccharide Polyol 4.** ^{1}H NMR (D_2O): δ 0.99 (1H, ddd, J = 3.3, 11.4, 14.7 Hz), 1.04 (3H, d, J = 6.6 Hz), 1.22 (1H, m), 1.28 (1H, ddd, J = 2.9, 12.5, 14 Hz), 1.40 (1H, m), 1.53 (1H, tq, J = 3.3, 11.4 Hz), 1.62 (1H, ddd, J = 3.7, 10.3, 14.7 Hz), 1.69 (1H, ddd, J = 3.3, 12.2, 14.3 Hz), 1.85 (3H, s), 1.85 (1H, m), 1.95 (1H, dt, J = 14, 3.7 Hz), 2.19 (2H, t, J = 7.3 Hz), 3.09 (1H, t, J = 11.4 Hz), 3.13 (1H, t, J = 9.9 Hz), 3.14 (1H, m), 3.37 (1H, t, J = 9.9 Hz), 3.38 (1H, ddd, J = 1.9, 6.4, 11.7 Hz), 3.69 (1H, dq, J = 1.0, 6.6 Hz), 3.72 (1H, t, J = 3.7 Hz), 3.79 (1H, ddd, J = 1.1, 4.4, 7.7 Hz), 3.87 (1H, dd, J = 4.8, 11.8 Hz), 3.94 (1H, ddd, J = 3, 6.2, 12.5 Hz). ^{13}C NMR (CD_3OD): δ 16.61, 23.10, 25.30, 25.49, 25.70, 29.22, 29.27, 29.33, 31.53, 31.63, 32.24, 35.24, 35.91, 40.37, 57.66, 63.19, 65.65, 68.11, 68.76, 70.56, 70.77, 72.70, 75.39, 79.91, 80.19, 80.67, 175.24. HRMS (FAB): calcd for $C_{31}H_{55}NO_{12}$ (M + H^+) 634.3802; found 634.3786. $[\alpha]_D$ −71.9° (c 0.64, MeOH).

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra are available for all compounds (62 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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