Alkynylation of Mixed Acetals with Organotin Acetylides

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Abstract: Reaction of halo acetals containing O, N, or S heteroatoms with tri-*n*-butyltin acetylides in the presence of $ZnCl_2$ in CCl_4 leads to the formation of α-alkynyl ethers, amines, and sulfides in good yields. The methodology is exemplified with the synthesis of amino acids and *C*-glycosides.

The utility of activated mixed acetals for the construction of carbon–carbon bonds has recently been receiving widespread attention[1-3] from various segments of the chemical community. In particular, efforts have been directed at constructing acetals (**1**) (Scheme I) with an appropriately activatable leaving group for coupling with specific carbon nucleophilic reagents. Furthermore, recent interest in the synthesis and reactions of propargylic ethers and alcohols (Nicholas reaction)[4] makes the development of new methods to prepare propargyl derivatives of this general type an attractive synthetic objective. In this paper, we report a new organometallic coupling reaction to more traditional mixed halo acetals based on organotin chemistry. We have found that a variety of O-, N-, and S-centered halo acetals undergo alkynylation with trialkyltin acetylides in the presence of $ZnCl_2$ under very mild conditions. The examples below serve to illustrate how this reaction methodology can be used to gain access to unusual amino acids and derivatives, homologated carbohydrate derivatives, and other functionalized alkynes.

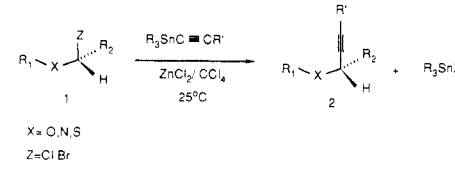
Results and Discussion

The bromoglycinate[5] **3** (Scheme II) when treated with 2 equiv of tri-*n*-butyltin acetylides **4** in the presence of $ZnCl_2$ (2 equiv) in CCl_4 at 25 °C afforded, after standard workup and silica gel chromatography, the crystalline alkynes **5a,b** in 55% and 53% yields after recrystallization, respectively.[6] This reaction proceeded with net *retention*[7] of stereochemistry as evidenced by the conversion of **5a,b** to the corresponding α-amino acids **6a,b** whose absolute configurations are known. A variety of other metalloalkynes were investigated to effect this coupling, including $R_3SnC{\equiv}CR/Pd^0$[8] and $RC{\equiv}CLi/ZnCl_2$,[9] which led to the decomposition of **3** and no detectable products **5**. It was also found that the solvent is crucial for this reaction, no reaction being observed in aprotic solvents such as toluene or THF;[10] CCl_4 has proven to be the best solvent for this coupling.

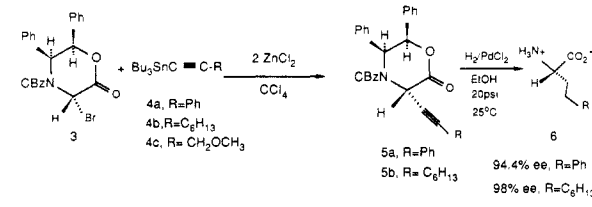
Synthetically useful C-glycosidation of 1-halo carbohydrates has been accomplished via this methodology as shown below in Scheme III and in Table I. In the glucopyranose series, the couplings displayed significant α selectivity (see Table I). The stereochemistry of the C-glycosylated products was not readily determined by examination of the spin–spin coupling constants for H_1 and H_2 in the ^1H NMR due to overlapping signals in the region δ 4–5.5, which precluded the assignment of the C-1 methine proton. However, Lindlar reduction of **8** followed by ozonolysis and reduction with $NaBH_4$ furnished the α-hydroxymethyl derivative **9**. Conservation of **9** to the optically active pentol **10** (H_2, 10% Pd/C, MeOH) and per-O-acetylation (**12**) or benzylation of **9** (furnishing **11**) firmly established the α stereochemistry. If the stereochemistry of **8** was β, the same series of transformations would have furnished optically inactive meso derivatives **10–12**.

Although a detailed mechanistic study has not been conducted on this reaction, the results are consistent with the hypothetical mechanism depicted in Scheme IV. Transmetalation with Zn^{2+} has been excluded,[9] so it seems reasonable that the acetylene π system attacks[11] the cationic species **14** generated from the halo acetal (**13**) and the Lewis acid ($ZnCl_2$). Development of positive charge on the β-acetylenic carbon can be stabilized by the adjacent

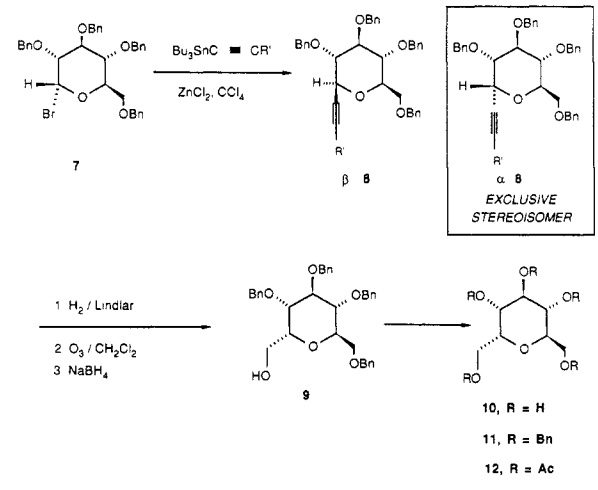
Scheme I



Scheme II



Scheme III



Scheme IV

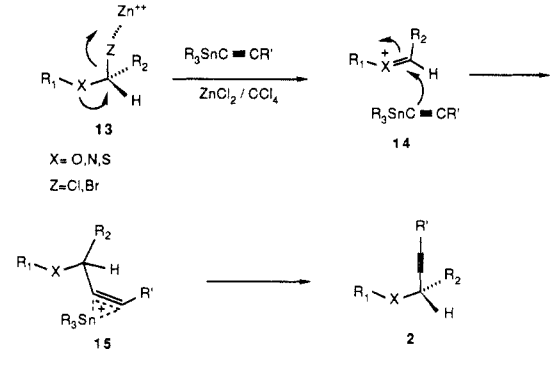


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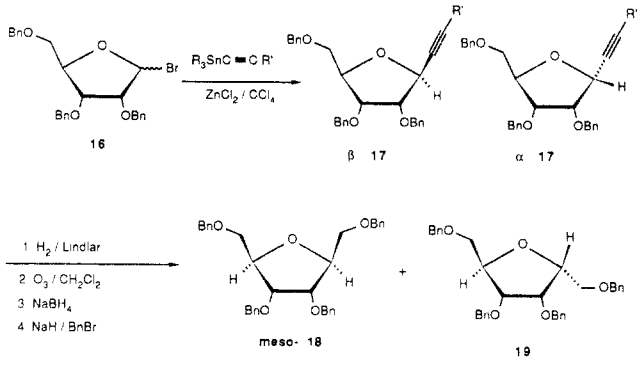
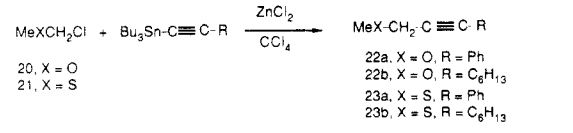
Table I. Alkynylation of Halo Acetals

substrate	R′	yield, %	α:β
7	n-C_6H_{13}	49	1:0
	C_6H_5	61	1:0
	H_3COCH_2	44	1:0
16	n-C_6H_{13}	45	1:0
	C_6H_5	55	1:2.8
	H_3COCH_2	66	1:1
20	C_6H_5	57	
	n-C_6H_{13}	62	
21	C_6H_5	50	
	n-C_6H_{13}	57	

Scheme V



Scheme VI



trialkyltin moiety (**15**)[11,12] that must suffer eventual capture by halide ion to generate the acetylene **2**. As with β-silyl carbocationic species, the β-stannyl carbocationic species **15** are stabilized through σ–π conjugation (hyperconjugation); Eaborn[13] and Traylor[14] have shown that these types of reactions involve stepwise cleavage of the Sn–C bond as depicted in Scheme IV.

Tri-*O*-benzyl-D-ribofuranosyl bromide[15] underwent coupling with the tin acetylides **4a–c** as shown in Table I and Scheme V. Unlike the glucose series, the stereoselectivity of the coupling seemed to be related to the nature of the R′ group on the tin acetylide. The *n*-hexyl derivative gave exclusively the α-stereoisomer; the phenyl derivative on the other hand gave an almost 3:1 ratio favoring the β-isomer, and the methoxymethyl derivative furnished a nearly 1:1 mixture. Here again, the assignment of stereochemistry to the adducts (**17**) was not straightforward and required a degradation of the alkyne functionality. Lindlar hydrogenolysis to the *Z* olefins, followed by ozonolysis, $NaBH_4$ reduction, and benzylation, furnished either *meso*-**18** or optically active **19** for the β and α stereoisomers, respectively.

In simpler systems, it was found that both chloromethyl methyl ether[18] (**20**) and chloromethyl methyl sulfide (**21**) underwent coupling with **4a** and **4b** to furnish the respective alkynes **22** and **23** in 50–62% isolated, purified yields (Scheme VI).

In summary, the methodologies described herein provide a mild and practical preparation of α-alkynyl amines, ethers, and sulfides from the corresponding mixed halo acetals. The recent isolation of ethynylglycine, which displays antibiotic activity and suicide enzyme inhibition toward alanine racemase, indicates that the coupling exemplified by **3** → **5** merits additional study. The potential for further functionalizing the alkyne of the *C*-glycosides is also an area of recent interest that is being pursued in these laboratories.

Experimental Section

Alkynylation of 3 with 4a (5a). To a stirred solution of bromide **3**[5] [(−)-5(*S*),6(*R*)] (0.806 mmol, 1.0 equiv) in dry CCl_4 (80 mL) was added $Bu_3SnC{\equiv}CPh$ (630.5 mg, 1.612 mmol, 2.0 equiv) and a solution of $ZnCl_2$ (0.8 M in THF, 2.0 mL, 1.612 mmol, 2.0 equiv). The mixture was refluxed for 40 min, cooled to 25 °C, and concentrated. The residue was separated by silica gel column chromatography (eluted with 3:1 hexanes/EtOAc) to yield **5a**, which was recrystallized from 50% benzene in hexanes: 218.3 mg (55.6%); mp 206.5–207.5 °C; $[\alpha]^{25}_D$ +31.2° (*c* 0.73, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ 4.92–5.38 (4 H, m), 5.98 ($^1/_2$ H, s), 6.11 ($^1/_2$ H, s), 6.45–7.53 (20 H, m); IR (NaCl, $CHCl_3$) 2390, 1770, 1705 cm^{-1}; MS (NH_3/CI) *m/z* 506 ($M^+ + NH_4$, 8.9), 505 (11.4), 489 ($M^+ + 1$, 15.5), 488 (M^+, 20.2), 106 (100). Anal. ($C_{32}H_{25}NO_4$) C, H, N.

L-Homophenylalanine from 5a (6a). A stirred solution of **5a** (87.3 mg, 0.18 mmol, 1.0 equiv) in THF (2 mL), EtOH (1 mL), and $PdCl_2$ (16 mg, 0.09 mmol, 0.5 equiv) in a pressure bottle was charged with H_2(g) to 30 psi and stirred for 40 h at room temperature. The pressure was reduced to 1 atm, purged with N_2, filtered through a small pad of Celite,

(1) For some selected examples of C-coupling to oxygen-centered mixed acetals, see: (a) Lewis, M. D.; Cha, J. K.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 4976. (b) Schmidt, R. R.; Hoffman, M. *Tetrahedron Lett.* **1982**, *23*, 409. (c) Hanessian, S.; Bacquet, C.; Lehong, N. *Carbohydr. Res.* **1980**, *80*, C17. (d) Posner, G. H.; Haines, S. R. *Tetrahedron Lett.* **1985**, *26*, 1823. (e) Murata, S.; Noyori, R. *Tetrahedron Lett.* **1982**, *23*, 2601. (f) Stewart, A. O.; Williams, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 4289. (g) Nicolaou, K. C.; Dolle, R. E.; Chucholowski, A.; Randall, J. L. *J. Chem. Soc. Chem. Comm.* **1984**, 1153.

(2) For selected examples of C-coupling to nitrogen-centered mixed acetals, see: (a) Keck, G. E.; Enholm, E. J. *Tetrahedron Lett* **1985**, *26*, 3311. (b) Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* **1983**, *24*, 1407. (c) Hiemstra, H.; Klaver, W. J.; Speckamp, W. N. *J. Org. Chem.* **1984**, *49*, 1149. (d) Hart, D. J.; Kanai, K. *J. Am. Chem. Soc.* **1983**, *105*, 1255. (e) Shono, T.; Matsumura, Y.; Uchida, K.; Tsubata, K.; Makino, A. *J. Org. Chem.* **1984**, *49*, 300. (f) Barrett, A. G. M.; Quayle, P. *J. Chem. Soc., Chem. Comm.* **1981**, 1076. (g) Martel, A.; Daris, J. P.; Bachand, C.; Menard, M.; Durst, T.; Belleau, B. *Can. J. Chem.* **1983**, *61*, 1899. (h) Williams, R. M.; Armstrong, R. W.; Maruyama, L. K.; Dung, J.-S.; Anderson, O. P. *J. Am. Chem. Soc.* **1985**, *107*, 3246. (i) Sinclair, P. J.; Zhai, D.; Reibenspies, J.; Williams, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 1103. (j) Kober, R.; Papadopoulos, K.; Miltz, W.; Enders, D.; Steglich, W.; Reuter, H.; Puff, H. *Tetrahedron* **1985**, *41*, 1693. (k) For a review, see: Zaugg, H. E. *Synthesis* **1984**, 85. (l) O'Donnell, M. J.; Falmagne, J. B. *Tetrahedron Lett.* **1985**, *26*, 699.

(3) For selected examples of C-coupling to sulfur-centered acetals, see: (a) Hosomi, A.; Sakata, Y.; Sakurai, H. *Chem. Lett.* **1983**, 405. (b) Trost, B. M.; Murayama, E. *J. Am. Chem. Soc.* **1981**, *103*, 6529 and references cited therein. (c) Miyazawa, S.; Ikeda, K.; Achiwa, K.; Seika, M. *Chem. Lett.* **1984**, 785. (d) Shimizu, M.; Akiyama, T.; Mukaiyama, T. *Chem. Lett.* **1984**, 1531. (e) Bates, H. A.; Rosenblum, S. B. *J. Org. Chem.* **1986**, *51*, 3447. (f) Paterson, I.; Fleming, I. *Tetrahedron Lett.* **1979**, 993 and 995.

(4) For leading references and a review, see: Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; Chapter 18. (b) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986** *108*, 3128. (c) Padmanabhan, S.; Nicholas, K. M. *Tetrahedron Lett.* **1982**, *23*, 2555, and references cited therein.

(5) Williams, R. M.; Zhai, D.; Sinclair, P. J. *J. Org. Chem.* **1986**, *51*, 5021, and ref 2h and 2i.

(6) Yields refer to quantities of analytically pure samples.

(7) The relative stereochemistry of the bromide **3** is known to be anti (depicted); the details of this determination shall be published separately.

(8) Crisp, G. T.; Scott, W. J.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7500.

(9) Various stoichiometries were examined to simulate $RC{\equiv}CZnCl$ and $(RC{\equiv}C)_2Zn$ species as potential intermediates in the coupling of the alkynyltin reagents via transmetalation; no reaction was observed in all cases.

(10) The $ZnCl_2$ is added to the reaction as a 1 M solution in THF and was chosen due to the solubility and anhydrous shelf life of $ZnCl_2$ in THF. The addition of THF in excess of the minimal amount required to dissolve the $ZnCl_2$ results in decreased yields.

(11) See: Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980; Vol. 1, Chapter 6.

(12) For a related observation of Sn stabilization of an electron-deficient β-reacting carbon, see: Nishiyama, H.; Matsumoto, M.; Arai, H.; Sakaguchi, H.; Itoh, K. *Tetrahedron Lett.* **1986**, *27*, 1599. (b) Himbert has extensively studied the amino ethynylation of acid chlorides with 1-(dialkylamino)-2-(trialkylstannyl)alkynes; see: Feustel, M.; Himbert, G. *Liebigs Ann. Chem.* **1982** 196. Himbert, G.; Schwickerath, W. *Ibid.* **1983** 1185 and references cited therein. (c) Pereyre, M.; Quintard, J. P.; Rahm, A. *Tin in Oganic Synthesis*; Butterworth: London, 1987.

(13) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43.

(14) (a) Hosomi, A.; Traylor, T. G. *J. Am. Chem. Soc.* **1975**, *97*, 3682. (b) Hartman, G. D.; Traylor, T. G. *Ibid.* **1975**, *97*, 6147.

(15) Hanessian, S.; Pernet, A. G. *Can. J. Chem.* **1974**, *52*, 1266.

(16) Barker, R.; Fletcher, H. G. *J. Org. Chem.* **1961**, *26*, 4605.

(17) α-Aminodecanoic acid (**6b**) is identical with decyline. See: Greenstein, J. P., Winitz, M. Eds. *Chemistry of the Amino Acids*; Robert E. Krieger Publishing: Malabar, FL, 1984; Vol. 3.

(18) *Caution*! Proper safety precautions should be employed when handling chloromethyl methyl ether, which is a cancer suspect agent.

evaporated, and triturated sequentially with CH_2Cl_2, THF, and Et_2O, leaving an insoluble, crystalline residue (22 mg, 57%), which was found to be identical with an authentic sample of L-homophenylalanine.[2i] The percent of asymmetric induction (ie., ee) was established by conversion to the corresponding MTPA amide as follows.

The crude amino acid obtained above (10 mg, 0.046 mmol) in HCl/EtOH (3 mL of a 1 M solution) was refluxed 2 h and evaporated to dryness. The resulting crude ethyl ester and (-)-MTPA-Cl (12 mg, 0.046 mmol, 1.0 equiv) were dissolved in CCl_4 (0.2 mL) and pyridine (0.2 mL), and the resultant mixture was allowed to stand for 12 h at room temperature. Water was added and the mixture thoroughly extracted with Et_2O. The ethereal extracts were washed with 1 N HCl, 10% Na_2CO_3, and H_2O and dried over anhydrous Na_2SO_4. Filtration, evaporation, and examination of the crude residue by ^1H NMR and ^{19}F NMR indicated an enantiomeric excess of 94.4%.

Alkynylation of 3 with 4b (5b). To a stirred solution of bromide **3**[4] [(-)-5(S),6(R)] (0.33 mmol, 1.0 equiv) in dry CCl_4 (80 mL) were added $Bu_3SnC{\equiv}CC_6H_{13}$ (198 mg, 0.49 mmol, 1.5 equiv) and a solution of $ZnCl_2$ (0.8 M in THF, 0.83 mL, 0.662 mmol, 2.0 equiv). The mixture was refluxed for 25 min, cooled to room temperature, and concentrated. The residue was separated by PTLC silica gel chromatography (eluted with 4:1 hexanes/EtOAc) to yield **5b**, which was recrystallized from hexanes: 87 mg (53.1%); mp 113.5–114 °C; $[\alpha]^{25}_D$ +6.87° (*c* 0.67, CH_2Cl_2); ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ-0.82 (3 H, m), 1.22–1.55 (8 H, m), 2.18–2.28 (2 H, m), 4.87–5.27 (4 H, m), 5.72 ($^1/_2$ H, s), 5.84 ($^1/_2$ H, s), 6.38–7.40 (15 H, m); IR (NaCl, $CHCl_3$) 2380, 1760, 1700 cm^{-1}; MS (NH_3/CI) *m/z* 513 ($M^+ + NH_4$, 50.2); 496 (33.3); 106 (100). Anal. ($C_{32}H_{33}NO_4$) C, H, N.

(*S*)-2-Aminodecanoic Acid from 5b (6b). A stirred solution of **5b** (45.9 mg, 0.093 mmol, 1.0 equiv) in THF (2.5 mL), EtOH (1.5 mL), and $PdCl_2$ (4.95 mg, 0.028 mmol, 0.3 equiv) in a pressure bottle was charged with H_2(g) to 30 psi and stirred for 40 h at room temperature. The pressure was reduced to 1 atm, purged with N_2, filtered through a small pad of Celite, evaporated, and triturated sequentially with CH_2Cl_2 and Et_2O, leaving an insoluble, crystalline residue **6b**[17] [14.1 mg (67.7%)]. The percent of asymmetric induction (ie., ee) was established by conversion to the corresponding MTPA amide as follows. The synthetic **6b** had spectroscopic properties identical with those reported in the literature.[17]

The crude amino acid obtained above (8.5 mg, 0.038 mmol, 1.0 equiv) in HCl/EtOH (2 mL of a 1 M solution) was refluxed for 2 h and evaporated to dryness. The resulting crude ethyl ester and (-)-MTPA-Cl (9.6 mg, 0.038 mmol, 1.0 equiv) were dissolved in CCl_4 (0.2 mL) and pyridine (0.2 mL), and the resultant mixture was allowed to stand for 72 h at room temperature. Water was added and the mixture thoroughly extracted with Et_2O. The ethereal extracts were washed with 1 N HCl, 10% Na_2CO_3, and H_2O and dried over anhydrous magnesium sulfate. Filtration, evaporation of the solvent, and examination of the crude residue by ^1H NMR (270 MHz, $CDCl_3$) indicated an enantiomeric excess of 98%. The corresponding racemic amino acid (prepared from racemic **3**) was coupled with (-)-MTPA-Cl to rigorously identify the NMR resonances of the antipodal amino acid.

1-Methoxy-2-nonyne (22b). To a stirred solution of chloromethyl methyl ether[18] (32 mg, 0.39 mmol, 1.0 equiv) in CCl_4 (30 mL) were added $Bu_3SnC{\equiv}CC_6H_{13}$ (159 mg, 0.39 mmol, 1.0 equiv) and a solution of $ZnCl_2$ (0.3 mL of a 0.7 M THF solution, 0.2 mmol, 0.5 equiv) at reflux temperature. The mixture was stirred at reflux for 30 min, cooled to 0 °C, and concentrated at reduced pressure at 0 °C. The residue was dissolved in a minimum volume of CH_2Cl_2, filtered, and separated by PTLC silica gel (eluted twice with hexanes and then with 2:1 hexanes/EtOAc) to afford 38 mg (62%) of 1-methoxy-2-nonyne as an oil: ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.86 (3 H, m), 1.22–1.58 (8 H, m), 2.16–2.26 (2 H, m), 3.36 (3 H, s), 4.08 (2 H, m); IR (NaCl neat) 2260 cm^{-1}; MS (NH_3/CI) *m/z* 172 ($M^+ + NH_4$, 100), 155 ($M^+ + 1$, 1.7), 140 (2.0), 123 (3.2). Anal. ($C_{10}H_{18}O$) C, H.

1-Phenyl-3-methoxy-1-propyne (22a). To a stirred solution of chloromethyl methyl ether[18] (32 mg, 0.39 mmol, 1.0 equiv) in CCl_4 (30 mL) were added $Bu_3SnC{\equiv}CPh$ (155 mg, 0.39 mmol, 1.0 equiv) and a solution of $ZnCl_2$ (0.3 mL of a 0.7 M THF solution, 0.2 mmol, 0.5 equiv) at reflux temperature. The mixture was stirred at reflux for 30 min, cooled to 0 °C, and concentrated at reduced pressure at 0 °C. The residue was dissolved in a minimum volume of CH_2Cl_2, filtered, and separated by PTLC silica gel (eluted twice with hexanes and then 2:1 hexanes/EtOAc) to afford 33 mg (57%) of 1-phenyl-3-methoxy-1-propyne as an oil: ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ-3.46 (3 H, s), 4.32 (2 H, s), 7.26–7.48 (5 H, m); IR (NaCl, neat) 2230, 1570 cm^{-1}; MS (NH_3/CI) *m/z* 164 ($M^+ + NH_4$, 100), 147 ($M^+ + 1$, 6.5), 146 (M^+, 3.9), 132 (43.9), 115 (23.3). Anal. ($C_{10}H_{10}O$) C, H.

1-(Methylthio)-2-nonyne (23b). To a stirred solution of chloromethyl methyl sulfide (34.6 mg, 0.36 mmol, 1.0 equiv) in CCl_4 (30 mL) were added $Bu_3SnC{\equiv}C_6H_{13}$ (214 mg, 0.54 mmol, 1.5 equiv) and a solution of $ZnCl_2$ (0.26 mL of a 0.7 M THF solution, 0.18 mmol, 0.5 equiv) at reflux temperature. The mixture was allowed to stir for 30 min at reflux, cooled to 0 °C, and concentrated at reduced pressure at 0 °C. The residue was dissolved in a minimum volume of CH_2Cl_2, filtered, and separated by PTLC silica gel (eluted twice with hexanes and then 3:1 hexanes/EtOAc) to afford 35 mg (58%) of 1-(methylthio)-2-nonyne as an oil: ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.86 (3 H, m), 1.22–1.58 (8 H, m), 2.20 (3 H, s), 2.16–2.26 (2 H, m), 3.22 (2 H, t, *J* = 2.1 Hz); IR (NaCl, neat) 2850, 2220, 1430, 720, 680 cm^{-1}; MS (NH_3/CI) *m/z* 188 ($M^+ + NH_4$, 10.8), 171 ($M^+ + 1$, 52.9), 170 (M^+, 6.2), 155 (24). Anal. ($C_{10}H_{18}S$) C, H, S.

1-Phenyl-3-(methylthio)-1-propyne (23a). To a stirred solution of chloromethyl methyl sulfide (34.6 mg, 0.36 mmol, 1.0 equiv) in CCl_4 (30 mL) were added $Bu_3SnC{\equiv}CPh$ (210 mg, 0.537 mmol, 1.5 equiv) and a solution of $ZnCl_2$ (0.26 mL of a 0.7 M THF solution, 0.18 mmol, 0.5 equiv) at reflux temperature. The mixture was stirred at reflux for 30 min, cooled to 0 °C, and concentrated at reduced pressure at 0 °C. The residue was dissolved in a minimum volume of CH_2Cl_2, filtered, and separated by PTLC silica gel (eluted twice with hexanes and then 2:1 hexanes/EtOAc) to afford 29 mg (50%) of 1-phenyl-3-(methylthio)-1-propyne as an oil. ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ 2.29 (3 H, s), 3.47 (2 H, s), 7.28–7.45 (5 H, m); IR (NaCl, neat) 2300, 1595, 1570, 1420, 730, 690 cm^{-1}; MS (NH_3/CI) *m/z* 180 ($M^+ + NH_4$, 10.6), 163 ($M^+ + 1$, 65.2), 162 (M^+, 26.0), 132 (46.1), 115 (100). Anal. ($C_{10}H_{10}S$) C, H, S.

General Procedure for Preparation of *C*-Acetylene Derivatives of Glucose (8) and Ribose (17). To a stirring solution of 2,3,4,6-tetra-*O*-benzyl-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose (1.0 equiv) or 2,3,5-tri-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-β-D-ribose (1.0 equiv) in anhydrous CH_2Cl_2 was bubbled anhydrous HBr for 3–5 min at room temperature. The precipitated *p*-nitrobenzoic acid was removed by filtration, and the filtrate was evaporated to dryness, affording a syrup, which was directly used for the next reaction without purification.[15,16]

The syrup was dissolved in anhydrous CCl_4. The solution was heated to reflux, to which the corresponding tri-*n*-butyltin acetylide ($Bu_3SnC{\equiv}$CR) (1.05 equiv) and a solution of $ZnCl_2$ in THF (0.5 equiv) were added. The resulting mixture was allowed to reflux for 20–30 min, cooled, evaporated, and separated on PTLC (silica gel, eluted with hexane/EtOAc (3:1)). Yields, physical data, and reaction scale are detailed below for each.

General Procedure for Selective Hydrogenation of *C*-Acetylene Derivatives of Glucose and Ribose To Form the Corresponding Olefins. To a solution of *C*-acetylene derivative of glucose or ribose (1.0 equiv) in absolute ethanol were added Lindlar catalyst (5% $Pd/CaCO_3$/Pb) (0.2 equiv) and quinoline (1.0 equiv, distilled over zinc before use). The reaction flask was evacuated and then flushed with H_2. The evacuation/H_2 flushing sequence was repeated four times, and the mixture was allowed to stir under 1 atm of H_2 for 12 h. The suspension was filtered through a plug of Celite. The filtrate was evaporated and separated on PTLC (silica gel, eluted with hexane/EtOAc (4:1)).

General Procedure for Ozonolysis and Reduction of *Z* Olefin Derivatives of Glucose (9–12) and Ribose (18, 19). The olefin derivative of glucose or ribose (1.0 equiv) was dissolved in anhydrous methylene chloride. To the solution was bubbled a stream of O_3 at −78 °C until no starting material was detected by TLC (usually 20–40 min). The O_3 dissolved in solution was purged with N_2. At the same temperature dimethyl sulfide (3.0 equiv) was added to the solution. The mixture was stirred at −78 °C for 1 h. The cooling bath was removed, and the stirring was continued for 2 h. $NaBH_4$ (excess) was added. The resulting mixture was stirred at room temperature for 2 h. Acidification, extraction, and separation of the crude product on PTLC (silica gel, eluted with hexane/EtOAC (2:1)) afforded the hydroxymethyl derivatives that were then derivatized as follows.

General Procedure for Benzylation of (2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)methanol (11) and (2,3,5-Tri-*O*-benzyl-α-D-ribosyl)- and (2,3,5-Tri-*O*-benzyl-β-D-ribosyl)methanols (18 and 19). To a solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosylmethanol (**19**) or 2,3,5-tri-*O*-benzyl-D-ribosylmethanol (1.0 equiv) in anhydrous tetrahydrofuran was added NaH (3.0 equiv). The resulting suspension was stirred at room temperature for 2 h, and benzyl bromide (1.3 equiv) was added. The mixture was allowed to stir at room temperature for 12 h. Workup was in the usual manner. The crude product was separated on PTLC (silica gel, eluted with hexane/EtOAc (3:1)).

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-1-octyne (8b). From 280 mg (0.406 mM) of 2,3,4,6-tetra-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose, 170 mg (0.427 mM) of (tri-*n*-butylstannyl)octyne, and 290 μL of a solution of zinc chloride in anhydrous THF (0.7 M solution, 0.203 mM), 125 mg (48.7%) of **8b** was obtained (oil): $[\alpha]^{25}_D$ +50.7° (*c* 0.21, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.86 (3 H, t, *J*

= 6.4 Hz), 1.25–1.55 (8 H, m), 2.25 (2 H, t, J = 6.8 Hz), 3.59–3.73 (4 H, m), 3.90–4.00 (2 H, m), 4.45–4.54 (8 H, m), 4.98 (2 H, d, J = 10.8 Hz), 7.12–7.3 (20 H, m); IR (NaCl, neat) 3030–3100, 2860–2920, 2220, 1600, 1585, 1500, 1455, 1360, 1205, 1120, 1080, 1040, 1025, 900, 725, 690 cm^{-1}; MS m/z 633 (M^+ + 1, 0.3), 615 (0.2), 541 (1.9), 107 (100), 91 (100).

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)phenylacetylene (8a). From 500 mg (0.726 mmol) of 2,3,4,6-tetra-*O*-benzoyl-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose and 298 mg (0.762 mM) of phenyl tributyltin acetylide, 274.5 mg of **8a** was obtained (60.6%): $[\alpha]^{25}_D$ +64.3° (c 0.255, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.63–3.79 (5 H, m), 3.97–4.07 (2 H, m), 4.46–4.66 (3 H, m), 4.74–5.09 (5 H, m), 7.22–7.49 (25 H, m); IR (NaCl, neat) 3040–3090, 2900, 2870, 2340, 1600, 1490, 1450, 1390, 1360, 1300, 1240, 1150, 1080, 1060, 1020, 995, 900, 740, 725, 685 cm^{-1}.

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)-3-methoxy-1-propyne (8c). From 500 mg (0.726 mM) of 2,3,4,6-tetra-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-α-D-glucopyranose and 274 mg (0.762 mM) of methoxy (tri-*n*-butylstannyl)propyne, 190 mg of **8c** was obtained: 44.2%; $[\alpha]^{25}_D$ +46.2° (c 0.225, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.38 (3 H, s), 3.62–3.7 (5 H, m), 3.86–3.95 (2 H, m), 4.18 (2 H, s), 4.45–4.95 (8 H, m), 7.26–7.34 (20 H, m); IR (NaCl neat) 3020–3080, 2860–2900, 2320, 1600, 1520, 1490, 1450, 1355, 1260, 1230, 1200, 1175, 1150, 1080, 1060, 1015, 895, 850, 735, 683 cm^{-1}; MS m/z 592 (M^+, 0.1), 591 (0.2), 501 (0.9), 107 (100). Anal. ($C_{38}H_{40}O_6$) C, H.

(2,3,5-Tri-*O*-benzyl-β-D-ribosyl)- and (2,3,5-Tri-*O*-benzyl-α-D-ribosyl)octyne (17b). From 500 mg (0.879 mM) of 2,3,5-tri-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-β-D-ribose and 368 mg (0.92 mM) of (tributylstannyl)octyne, 203 mg of **17b** was obtained: 45.1%; $[\alpha]^{25}_D$ + 36.7° (c 0.86, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.88 (3 H, t, J = 3.2 Hz), 1.22–1.47 (8 H, m), 2.14–2.25 (2 H, m), 3.50–3.65 (2 H, m), 3.92–4.02 (2 H, m), 4.41–4.77 (8 H, m), 7.25–7.46 (15 H, m); IR (NaCl, neat) 3038–3090, 2940, 2860, 2235, 1605, 1500, 1455, 1350, 1205, 1125, 1090, 1040, 1025, 900, 725, 690 cm^{-1}; MS m/z 512 (M^+, 4.0), 420 (7.3), 404 (5.5), 181 (60.2), 107 (100). Anal. ($C_{34}H_{40}O_4$)C, H.

(2,3,5-Tri-*O*-benzyl-β-D-ribosyl)- and (2,3,5-Tri-*O*-benzyl-α-D-ribosyl)phenylacetylene (17a). From 350 mg (0.615 mM) of 2,3,5-tri-*O*-benzoyl-*O*-(*p*-nitrobenzoyl)-β-D-ribose and 258 mg (0.66 mM) of phenyl(tri-*n*-butylstannyl)acetylene, 170 mg (54.9%) of **17a** was obtained; α:β = 1:2.8.

α-Anomer: $[\alpha]^{25}_D$ +79.55° (c 0.88, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.53–3.75 (2 H, m), 4.12 (2 H, d, J = 4.9 Hz), 4.33–5.00 (8 H, m), 7.28–7.30 (15 H, m), 7.41–7.45 (5 H, m); IR (NaCl, neat) 3030–3060, 2920, 2860, 2290, 2220, 1580, 1520, 1490, 1400, 1350, 1310, 1260, 1200, 1110, 1070, 1035, 1020, 900, 725, 685 cm^{-1}; MS m/z 505 (M^+ + 1, 0.4), 457 (0.2), 413 (0.8), 107 (56.3), 91 (100). Anal. ($C_{34}H_{32}O_4$) C, H.

β-Anomer: $[\alpha]^{25}_D$ 3.55° (c 0.62, $CHCl_3$) ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.61–3.64 (2 H, m), 4.09–4.13 (2 H, m), 4.20–4.25 (1 H, m), 4.50–4.67 (5 H, m), 4.73 (1 H, d, J = 8.3 Hz), 4.89 (1 H, d, J = 4.3 Hz), 7.25–7.39 (15 H, m), 7.40–7.44 (5 H, m); IR (NaCl, neat) 3020–3080, 2920, 2860, 2220, 1595, 1520, 1490, 1400, 1350, 1300, 1275, 1250, 1200, 1110, 1080, 1040, 1020, 900, 740, 720, 685 cm^{-1}; MS m/z 505 (M^+ + 1, 1.8), 413 (3.2), 107 (100), 91 (100).

(2,3,5-Tri-*O*-benzyl-β-D-ribosyl)- and (2,3,5-Tri-*O*-benzyl-α-D-ribosyl)-β-methoxy-1-propyne (17c). From 500 mg (0.88 mM) of 2,3,5-tri-*O*-benzyl-*O*-(*p*-nitrobenzoyl)-β-D-ribose and 331 mg (0.92 mM) of methoxy(tri-*n*-butylstannyl)propyne, 272 mg of **17c** (65.5%) was obtained; α:β = 1:1.

α-Anomer: $[\alpha]^{25}_D$ +68.3° (c 0.36, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$ vs TMS) δ 3.32 (3 H, s), 3.48–3.66 (2 H, m), 4.03 (2 H, s), 4.15–4.88 (10 H, m), 7.27–7.40 15 H, m); IR (NaCl, neat) 3030–3090, 2920, 2900, 2860, 2220, 1600, 1490, 1450, 1350, 1310, 1270, 1200, 1180, 1115, 1085, 1040, 1020, 900, 725, 690 cm^{-1}; MS m/z 455 (M^+ – 17, 0.1), 441 (0.3), 291 (0.5), 107 (93.4), 91 (100).

β-Anomer: $[\alpha]^{25}_D$ +6.03° (c 0.68, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.31 (3 H, s), 3.57–3.60 (2 H, m) 4.03 (2 H, d, J = 4.5 Hz), 4.07 (2 H, s), 4.15–4.20 (1 H, m), 4.47–4.72 (7 H, m), 7.29–7.34 (15 H, m); IR (NaCl, neat) 3030–3080, 2920, 2860, 2220, 1590, 1540, 1490, 1450, 1400, 1350, 1300, 1275, 1250, 1200, 1110, 1080, 1040, 1020, 900, 810, 740, 720, 685 cm^{-1}; MS m/z 455 (M^+ – 17; 0.2), 441 (0.2), 382 (0.2), 91 (100).

(2,3,4,6-Tetra-*O*-benzyl-α-D-glucopyranosyl)methanol (9). To a solution of **8b** (120 mg, 0.19 mM, 1.0 equiv) in anhydrous CH_2Cl_2 was bubbled O_3 at −78 °C until no starting material was detected by TLC. The reaction solution was purged with dry nitrogen, and Me_2S (38 μL, 0.513 mM, 2.7 equiv) was added. The resulting mixture was stirred at −78 °C for 1 h; the cooling bath was removed and stirring continued for 3 h. A solution of $NaBH_4$ (74.8 mg, 1.9 mM, 10.0 equiv) in ethanol was added into the reaction mixture and then stirred for 2 h. The mixture was diluted with CH_2Cl_2, and 2 mL of water was added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extract was dried over anhydrous Na_2SO_4, filtered, evaporated, and separated on PTLC (silica gel, eluted with hexane/EtOAc (2:1); 41 mg of **9** (39.1%) was obtained: $[\alpha]_D^{25}$ +13.5° (c 0.17, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.67–3.78 (4 H, m), 3.81–3.90 (4 H, m), 4.15 (1 H, s), 4.51–4.87 (9 H, m), 7.26–7.43 (20 H, m); IR (NaCl, neat) 3440 (br), 3030–3080, 2920, 2860, 1600, 1490, 1450, 1355, 1310, 1260, 1200, 1150, 1080, 1060, 1020, 800, 725, 685 cm^{-1}; MS m/z 555 (M^+ + 1, 0.6), 91 100).

1-(1(*Z*)-Octenyl)-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose. From 300 mg (0.474 mM) of **8b**, 204 mg of 5% Pd/$CaCO_3$/Pb, and 57 μL of quinoline, 271 mg (90.2%) of the Z olefin was obtained and directly subjected to the subsequent ozonolysis/reduction: $[\alpha]^{25}_D$ 49.15° (c 1.29, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.88 (3 H, t, J = 4.2 Hz), 1.15–1.39 (8 H, m), 2.15–2.18 (2 H, m), 3.60–3.80 (6 H, m), 4.42 (1 H, d, J = 4.5 Hz), 4.48 (1 H, d, J = 2.9 Hz), 4.60–4.66 (3 H, m), 4.78–5.00 (4 H, m), 5.76–5.81 (2 H, m), 7.25–7.38 (20 H, m); IR (NaCl, neat) 3030–3080, 2950, 2920, 2850, 1640, 1600, 1530, 1490, 1450, 1355, 1315, 1200, 1150, 1110, 1080, 1035, 1020, 720, 685 cm^{-1}. From 250 mg (0.396 mM) of the olefin obtained above, 87.4 μL of dimethyl sulfide, and 150 mg of sodium borohydride, 103.7 mg (47.3%) of **9** was obtained. This material was identical with that obtained from the direct ozonolysis of **8b**.

1-(1-Phenyl-2(*Z*)-ethylene)-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose. From 240 mg (0.385 mM) of **8a**, 164 mg of 5% Pd/$CaCO_3$/Pb, and 46 μL of quinoline, 239.2 mg (99%) of the Z olefin was obtained and directly carried on to **9**: $[\alpha]^{25}_D$ +82.4° (c 0.75, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.45–3.96 (6 H, m), 4.41–4.98 (9 H, m); IR (NaCl, neat) 3030–3090, 2920, 2900, 2860, 1630, 1605, 1575, 1500, 1455, 1360, 1300, 1235, 1200, 1150, 1110, 1080, 1055, 1020, 990, 900, 830, 800, 760, 725, 685 cm^{-1}. Anal. ($C_{42}H_{42}O_5$). From 220 mg (0.35 mM) of the Z olefin obtained above, 78 μL (1.054 mM) of dimethyl sulfide, and 132 mg (3.5 mM) of sodium borohydride, 88.3 mg of **9** was obtained.

1-(3-Methoxy-1′(*Z*)-propenyl)-2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranose. From 160 mg (0.27 mM) of **8c**, 115 mg of 5% Pd/$CaCO_3$/Pb, and 32 μL of quinoline, 150.5 mg (93.9%) of the Z olefin was obtained and directly carried on to **9**: $[\alpha]^{25}_D$ +56.0° (c 0.2, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) in δ 3.30 (3 H, s), 3.59–3.77 (6 H, m), 4.05–4.18 (3 H, m), 4.41–4.98 (8 H, m), 7.21–7.60 (20 H, m); IR (NaCl, neat) 3030–3090, 2860–2920, 1610, 1580, 1495, 1455, 1395, 1360, 1320, 1200, 1180, 1150, 1110, 1080, 1060, 1020, 990, 950, 900, 720, 685 cm^{-1}. From 145 mg (0.24 mM) of the Z olefin obtained above, 54 μL (0.732 mM) of dimethyl sulfide, and 93 mg (2.44 mM) of sodium borohydride, 12 mg of **9** was obtained (11%).

1,3,4,5,7-Penta-*O*-benzyl-2,6-anhydro-D-*glycero*-L-*gulo*-hepitol (11). From 80 mg (0.144 mM) of **9**, 8.4 mg (0.352 mM) of NaH, and 18 μL (0.152 mM) of benzylbromide, 82.6 mg of **11** (88.9%) was obtained: $[\alpha]^{25}_D$ + 19.5° (c 1.63, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.61–3.83 10 H, m), 4.45–4.65 (7 H, m), 4.72–4.89 (2 H, m), 7.21–7.41 (25 H, m); IR (NaCl, neat) 3010–3090, 2860–2900, 1600, 1585, 1498, 1455, 1390, 1360, 1310, 1270, 1210, 1150, 1110, 1090, 1060, 1025, 900, 810, 750, 730, 690 cm^{-1}; MS m/z 643 (M^+ – 1, 0.4), 553 (1.8), 537 (0.3), 179 (89.9), 107 (100). Anal. ($C_{42}H_{44}O_6$) C, H.

1,3,4,5,7-Penta-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*gulo*-hepitol (12). To a solution of **9** (100 mg, 0.181 mM) in ethanol was added 5% Pd on charcoal. The reaction flask was evacuated and flushed with H_2. The evacuation/H_2 flushing sequence was repeated four times, and the mixture was allowed to stir under 1 atm of H_2 for 12 h. The suspension was filtered through a plug of Celite. The filtrate was evaporated to a syrup. The syrup was dissolved in 3 mL of acetic anhydride. To the solution was added NaOAc (59 mg, 0.72 mM). The mixture was heated to reflux for 3 h and cooled. To the mixture was added a mixture of ice and aqueous $NaHCO_3$ solution, and the solution was stirred 5 h and extracted with CH_2Cl_2. The organic layer was dried over anhydrous Na_2SO_4, filtered, evaporated, and separated on PTLC (silica gel, eluted with hexane/EtOAc (3:1). A total of 37.7 mg (51.6%) of **12** was obtained: $[\alpha]^{25}_D$ +48.8° (c 0.7, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 2.01–2.21 (15 H, m), 4.06–4.13 (3 H, m), 4.25 (1 H, dd, J = 5.1 and 12.4 Hz), 4.43 (1 H, dd, J = 3.0 and 5.9 Hz), 4.67 (1 H, dd, J = 8.41 and 12.5 Hz), 5.02 (1 H, t, J = 8.9 Hz), 5.13–5.18 (1 H, m), 5.36 (1 H, t, J = 8.9 Hz); IR (NaCl, neat) 2950, 1750, 1370, 1220, 1090, 1020 cm^{-1}; MS m/z 405 (M^+ + 1, 1.5), 363 (2.9), 345 (100), 303 (17.5), 165 (20.3).

1-(2,3,5-Tri-*O*-benzyl-α-D-ribosyl)-1(*Z*)-octene. From 179 mg (0.35 mM) of α-**17b** and 149 mg of 5% Pd/$CaCO_3$/Pb, 21 mg (11.7%) of the Z olefin was obtained. As a byproduct, 140 mg (77.5%) of 1-(2,3,5-tri-*O*-benzyl-α-D-ribosyl)octane was obtained: $[\alpha]^{25}_D$ +32.9° (c 0.42, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 0.87 (3 H, t, J = 6.2 Hz), 1.17–1.44 (8 H, m), 2.05–2.13 (2 H, m), 3.56–3.74 (4 H, m), 4.07

(1 H, dd, J = 4.2 and 8.5 Hz), 4.32–4.80 (7 H, m), 5.48–5.57 (1 H, m), 5.70–5.78 (1 H, m), 7.25–7.48 (15 H, m); IR (NaCl, neat) 3030–3080, 2850–2920, 1660, 1600, 1580, 1495, 1455, 1360, 1300, 1200, 1080, 1060, 1020, 960, 900, 725, 685 cm^{-1} MS m/z 515 (M^+ + 1, 0.2), 423 (0.6), 89 (100).

(2,3,5-Tri-*O*-benzyl-α-D-ribosyl)methanol. From 20 mg (0.039 mM) of the Z olefin, 9 μL (0.117 mM) of dimethyl sulfide, and 15 mg (0.39 mM) of sodium borohydride, 6.9 mg of the α-hydroxymethyl derivative was obtained: 40.8%; $[\alpha]^{25}_D$ +7.19° (c 0.32, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$ vs TMS) δ 2.6 (1 H, br), 3.53 (2 H, dd, J = 3.8 and 7.2 Hz), 3.79–3.84 (2 H, m), 4.04 (1 H, m), 4.18–4.23 (2 H, m), 4.27–4.32 (1 H, m), 4.45–4.75 (6 H, m); IR (NaCl neat) 3460 (br), 3030–3080, 2860–2920, 1600, 1490, 1455, 1400, 1350, 1270, 1205, 1120, 1080, 1050, 1020, 910, 730, 690; MS m/z 435 (M^+ + 1, 1.5), 343 (2.6), 91 (100). From 20 mg (0.046 mM) of the alcohol obtained above, 3.3 mg (0.138 mM) of NaH, and 7 μL (0.06 mM) of benzyl bromide, 18 mg (74.7%) of **19** was obtained: $[\alpha]^{25}_D$ +32.1° (c 0.34, $CHCl_3$; ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.48–3.68 (2 H, m), 3.75 (2 H, t, J = 6.5 Hz), 4.02–4.12 (2 H, m), 4.19–4.29 (2 H, m), 4.42–4.74 (8 H, m), 7.25–7.50 (20 H, m); IR (NaCl, neat) 3030–3080, 2860–2920, 1600, 1500, 1360, 1350, 1260, 1200, 1150, 1085, 1020, 725, 690 cm^{-1}; MS m/z 525 (M^+ + 1, 2.5), 433 (1.6), 341 (1.9), 91 (100). Anal. ($C_{34}H_{36}O_5$) C, H.

1-(1-Phenyl-2(*Z*)-ethylene)-2,3,5-tri-*O*-benzyl-β-D-ribose. From 120 mg (0.238 mM) of **17a** (β anomer), 101 mg of 5% Pd/$CaCO_3$/Pb, and 20 μL of quinoline, 114.5 mg (95%) of the Z olefin was obtained: $[\alpha]^{25}_D$ +61.43° (c 0.28, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.53 (2 H, s), 3.81 (1 H, d, J = 5.9 Hz), 3.97–3.99 (1 H, m), 4.19 (1 H, d, J = 3.8 Hz), 4.46–4.68 (6 H, m), 4.97 (1 H, m), 5.61 (1 H, t, J = 8.7 Hz), 6.69 (1 H, d, J = 11.6 Hz), 7.18–7.42 (20 H, m); IR (NaCl, neat) 3030–3090, 2900, 2860, 1600, 1580, 1496, 1455, 1360, 1305, 1250, 1205, 1120, 1080, 1045, 1020, 900, 800, 770, 730, 690 cm^{-1}. From 25 mg (0.049 mM) of the Z olefin obtained above, 10.9 μL (0.148 mM) of dimethyl sulfide, and 18.5 mg (0.49 mM) of sodium borohydride, 9.1 mg (42.8%) of the hydroxymethyl derivative was obtained: $[\alpha]^{25}_D$ +23.03° (c 0.89, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 2.7 (1 H, br), 3.48 (2 H, d, J = 10.6 Hz), 3.73 (2 H, dd, J = 11.8 and 25.1 Hz), 4.02–4.17 (2 H, m), 4.59–4.61 (6 H, m); IR (NaCl, neat) 3430 (br), 3040–3090, 2870–2920, 1600, 1580, 1500, 1455, 1420, 1395, 1360, 1310, 1265, 1200, 1115, 1085, 1040, 1020, 935, 900, 890, 730, 690 cm^{-1}. From 35 mg (0.081 mM) of the β-hydroxymethyl derivative obtained above, 5.8 mg (0.242 mM) of NaH, and 13 μL (0.105 mM) of benzyl bromide, 25 mg (59%) of **18** was obtained: $[\alpha]^{25}_D$ 0; ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.52–3.55 (4 H, m), 3.88 (2 H, d, J = 3.8 Hz), 4.22 (2 H, d, J = 3.96 Hz), 4.47–4.58 (8 H, m), 7.29 (20 H, s); IR (NaCl, neat) 3030–3090, 2860–2920, 1500, 1450, 1360, 1270, 1200, 1110, 1090, 1020, 725, 690 cm^{-1}; MS m/z 523 (M^+ − 1, 0.1), 433 (1.2), 341 (1.6), 271 (2.5), 107 (84.4). Anal. ($C_{34}H_{36}O_5$) C, H.

1-(3-Methoxy-1′(*Z*)-propenyl)-2,3,5-tri-*O*-benzyl-β-D-ribose. From 250 mg (0.53 mM) of **β-17c**, 225 mg of 5% Pd/$CaCO_3$/Pb, and 63 μL of quinoline, 190 mg (75.6%) of the Z olefin was obtained: $[\alpha]^{25}_D$ +25.12° (c 0.605, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.30 (3 H, s), 3.49 (2 H, d, J = 4.2 Hz), 3.65 (1 H, dd, J = 5.6 and 6.7 Hz), 3.91 (1 H, dd, J = 3.8 and 5.1 Hz), 4.05–4.11 (1 H, m), 4.17–4.23 (1 H, m), 4.44–4.62 (7 H, m), 4.75 (1 H, t, J = 7.7 Hz), 5.52–5.57 (1 H, m), 5.70–5.75 (1 H, m), 7.24–7.31 (15 H, m); IR (NaCl, neat) 3040–3100, 2870–2920, 1605, 1590, 1500, 1460, 1400, 1360, 1325, 1305, 1250, 1210, 1190, 1110, 1085, 1050, 1028, 950, 910, 810, 730, 692 cm^{-1}. From 180 mg (0.28 mM) of the Z olefin obtained above, 84 μL (1.14 mM) of diemthyl sulfide, and 144 mg (3.8 mM) of sodium borohydride, 92.1 mg (55.8%) of the β-hydroxymethyl derivative was obtained. This material was identical with that obtained from **β-17a** and could be converted similarly to *meso*-**18**.

1-(1-Phenyl-2(*Z*)-ethylene)-2,3,5-tri-*O*-benzyl-α-D-ribose. From 40 mg (0.079 mM) of **α-17a**, 34 mg of 5% Pd/$CaCO_3$/Pb, and 10 μL of quinoline, 26.1 mg (66.1%) of the Z olefin was obtained: $[\alpha]^{25}_D$ +28.37° (c 0.5, $CHCl_3$); ^{1}H NMR (270 MHz, $CDCl_3$, vs TMS) δ 3.52 (1 H, $^1/_2$ AB q, J = 10.5 Hz), 3.65 (1 H, $^1/_2$ AB q, J = 10.5 Hz), 4.04–4.11 (2 H, m), 4.31–4.70 (7 H, m), 4.87 (1 H, dd, J = 3.8 and 9.2 Hz), 6.12 (1 H, t, J = 10.5 Hz), 6.76 (1 H, d, J = 11.6 Hz), 7.18–7.35 (20 H, m); IR (NaCl, neat) 3030–3080, 2860–2920, 1605, 1585, 1495, 1350, 1310, 1260, 1200, 1140, 1110, 1080, 1040, 1025, 910, 800, 725, 690 cm^{-1}. From 35 mg (0.069 mM) of the Z olefin obtained above, 15.3 μL (0.21 mM) of dimethyl sulfide, and 26 mg (0.69 mM) of sodium borohydride, 11.6 mg (38.9%) of the α-hydroxymethyl derivative was obtained. This material was identical with that obtained from **α-17b** and was converted into **19**.

α-1-(3-Methoxy-1(*Z*)-propenyl)-2,3,5-tri-*O*-benzyl-α-D-ribose. From 130 mg (0.275 mM) of **α-17c** (α-anomer), 118 mg of 5% Pd/$CaCO_3$/Pb, and 32 μL of quinoline, 89.7 mg (68.8%) of the Z olefin was obtained; $[\alpha]^{25}_D$ +18.7° (c 1.42, $CHCl_3$). This material was directly subjected to the ozonolysis/reduction/alkylation to **19**. From 60 mg (0.127 mM) of the Z olefin obtained above, 28 μL (0.38 mM) of dimethylsulfide, and 48 mg (1.27 mM) of sodium borohydride, 25 mg (45.4%) of the α-hydroxymethyl derivative was obtained. This material was identical with that obtained from **α-17b** and could be converted into **19**.

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