(m, 2 H, $J_{1-3}$ = 16.4 Hz, $J_{3-4}$ = 1.8 Hz, $J_{2-4}$ = 1.8 Hz, $J_{1-2}$ = 10.8 Hz, $=CH_2$), 4.25 (m, 2 H, $J_{1-4}$ = 5.3 Hz, $J_{2-4}$ = $J_{3-4}$ = 1.8 Hz, $CH_2$) ppm; IR (KBr) 1710, 1430, 1390, 1310 $cm^{-1}$.

***N*-(1-Allyl-1*H*-pyrrol-2-yl)phthalimide (6b)**: 63% yield; mp 120–121 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 7.87 (m, 4 H), 6.75 (m, 1 H, $J_{3-5}$ = 2.0 Hz, $J_{4-5}$ = 2.9 Hz, C5H), 6.24 (m, 2 H, $J_{3-5}$ = 2.0 Hz, $J_{4-5}$ = 2.9 Hz, $J_{3-4}$ = 3.8 Hz, C4H and C3H); allyl group 5.83 (m, 1 H, =CH), 5.01 (m, 2 H, $=CH_2$), 4.35 (m, 2 H, $CH_2$) ppm; coupling constants same as in **6a**; IR (KBr) 1720, 1580, 1440, 1390, 1310 $cm^{-1}$.

***N*-(1-Allyl-1*H*-pyrrol-2-yl)maleimide (6c)**: yield 50%; mp 75–76 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 6.70 (s, 2 H), 6.65 (m, 1 H, $J_{4-5}$ = 3.3 Hz, $J_{3-5}$ = 2.1 Hz, C5H), 6.23 (m, 2 H, $J_{4-5}$ = 3.3 Hz, $J_{3-5}$ = 2.1 Hz, $J_{3-4}$ = 4.2 Hz, C4H and C3H); allyl group 5.75 (m, 1 H, =CH), 5.00 (m, 2 H, $=CH_2$), 4.30 (m, 2 H, $CH_2$) ppm; coupling constants same as in **6a**; IR (KBr) 1710, 1440, 1390, 1320 $cm^{-1}$.

**Registry No.** 1, 109-97-7; 2, 96-54-8; **2a**, 116625-45-7; **2b**, 116625-46-8; **2c**, 122845-00-5; 3, 635-90-5; **3a**, 122845-01-6; **3b**, 122845-02-7; **3c**, 122845-03-8; 4, 2051-97-0; **4a**, 122845-04-9; **4b**, 122845-05-0; **4c**, 122845-06-1; 5, 24764-40-7; **5a**, 122845-07-2; **5b**, 122845-08-3; **5c**, 122845-09-4; 6, 7435-07-6; **6a**, 122845-10-7; **6b**, 122845-11-8; **6c**, 122845-12-9; 7, 609-41-6; 8, 85684-89-5; NCP, 3481-09-2; NCS, 45514-70-3; NCM, 45514-70-3; 2-chloro-1-tritylpyrrole, 122845-13-0; 3-chloro-1-tritylpyrrole, 122845-14-1; chloropyrrole, 122845-15-2; 1-acetylchloropyrrole, 122845-16-3.

# Serial Radical Cyclization of Branched Carbohydrates. 1. Simple Pyranoside Diquinanes[1]

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The 2-deoxy-3-ketopyranoside **5** is converted efficiently into two multiply branched derivatives containing functionalized alkyl substituents at C2 and geminally at C3. For substrates bearing a 2-iodoethyl group at C2 and, at C3, axial vinyl and equatorial cyanomethyl groups, reaction with tri-*n*-butyltin hydride causes deiodination, and the resulting carbon-centered radical adds serially to the vinyl group and thence to the nitrile. A diquinane fused to the pyranoside ring thereby results. If aldehydo and amido groups are used instead of nitrile, the reaction takes a different course.

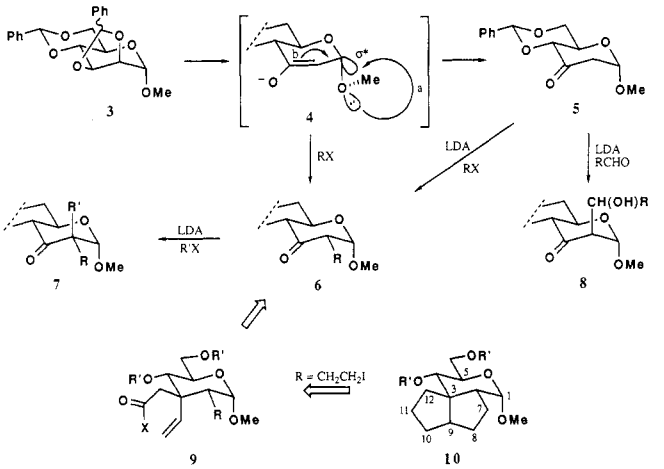
## Introduction

The use of carbohydrate derivatives in the synthesis of carbocycles has been a theme of interest in this laboratory for several years.[3,4] That the target products are furnished in optically active forms is an obvious outcome of this strategy. Therefore our attention has been focused on developing synthetic strategies that exploit the stereocontrolling properties of carbohydrates and also utilize the wide panoply of functional groups, actual or latent, that they possess. For example, in the case of annulated pyranosides, such as 1 (Scheme I), we suggested that, because of the anomeric effect, the conformational preference of the system should be dominated by the pyranoside moiety.[5] This expectation formed the basis for our synthetic work on actinobolin, where functionalization of the carbocyclic annulus relied on that stereocontrolling principle,[6] and for our earlier enantiodivergent synthesis of chrysanthemic acid enantiomers.[7] Structure **2** symbolizes a bis-annulated pyranoside, used in construction of the trichothecane ring system,[8] which demonstrated the range of functional groups that can be elaborated and utilized. In this and the accompanying[9] paper, we report the preparation of some bis-annulated pyranosides,[10] different from **2**, that have been prepared as potential precursors for a wide variety of naturally occurring polyquinanes.[11]

**Scheme I**


1 2

**Scheme II**




3 4 5 6 7 8 9 10

## Serial Radical Cyclizations

For some time, we have been intrigued by the keto sugar methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*erythro*-hexo-

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0022-3263/89/1954-5350$01.50/0 

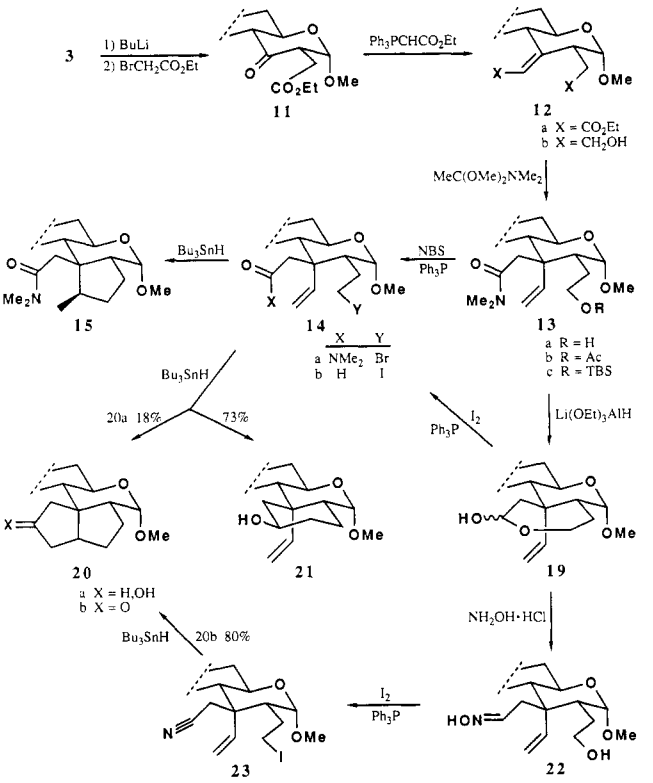
pyranosid-3-ulose (**5**) which is readily obtained by Horton and Weckerle's[12] modification of Klemer and Rodemeyer's[13] procedure (Scheme II). The value of the activated methylene of **5** became evident when our laboratory[14] and Chapleur's[15] found that alkylation could be carried out directly (**5** → **6**) or in situ (**4** → **6**). The surprising stability of the glycosidic methoxyl group toward β-elimination is further exemplified by the fact that (a) a second alkylation is possible to give **7** and (b) aldol condensations can be carried out smoothly to give **8**.[16,17] With respect to the C2 configurations of these products, we have found that **8** can be epimerized to the equatorial isomer upon treatment with base.[16,17] On these grounds, we assume that **6** arises by epimerization of an initially formed axial alkylation product.

Our rationalization for the unusual stability of enolate **4** invokes the exo anomeric effect,[18,19] i.e., the n–σ* interaction[20] depicted as "a" in **4**. This perturbation confers some double-bond character, which strengthens the pendant C1–O bond and, hence, opposes the electron flow required for β-elimination (depicted as "b"). In this connection, it may be noted that β-pyranosides, which have an even stronger exo anomeric effect,[19] are also smoothly alkylated.[21]

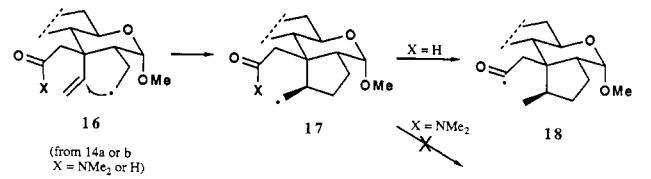
The foregoing advantages relating to the α-methylene group of **5** are complemented by the opportunities available to the carbonyl group, since we had earlier explored the value of carbonyl groups for creating geminally functionalized centers in sugars.[22] Thus, derivatives such as **9** were available by C3 Claisen rearrangements (vide infra), which usually yielded the axially oriented vinyl group. This strategy exemplifies an ideal protocol, where destruction of stereocenters at C2 and C3 of the original sugar (**3** → **4** → **5**) was well rewarded by formation of a much more complex synthon, **9**, with complete stereoselectivity, and yet retaining the carbon framework of the original sugar with its valuable functional groups, for future manipulations.

Compounds with a C3-axial vinyl group, as in **9**, show NOE enhancement of H5, upon irradiation of H10, which indicates that the vinyl group extends from beneath the pyranoside ring, as indicated in Scheme II. Epoxidation of analogues had earlier provided chemical proof that the molecule reacted preferentially from this rotamer.[23] Therefore, it followed that if the carbonyl moiety of **9** were a suitable radical trap with a 2-ethyl radical being present at C2 (R = $CH_2CH_2^{\bullet}$), serial cyclization[24,25] would afford a diquinane, such as **10**. This possibility was therefore

**Scheme III**




**Scheme IV**




tested, and the results are reported in this paper.

Methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside (**3**) was treated with *n*-butyllithium,[12,13] and the intermediate enolate **4** was trapped in situ with ethyl bromoacetate to give keto ester **11** (Scheme III). Following our typical strategy,[22] Wittig reaction gave diester **12a** and reduction gave the diol **12b**. Eschenmoser–Claisen rearrangement[26] led to a mixture of the alcohol **13a** and its acetate, **13b**, and the former was converted into the bromide **14a**.

Treatment of **14a** with tri-*n*-butyltin hydride led to the cyclopentane **15**. Evidently, the 5-hexenyl radical **16** (Scheme IV) cyclized as expected, but the amide group of the resulting cyclopentylmethyl radical **17** (X = $NMe_2$) was not a good enough radical trap for the second step. This was not entirely surprising, given Giese's ranking of radical acceptors.[27] On the other hand, nitriles are excellent radical traps,[28] and hence processing of the amido group of **13** was undertaken, the first step being a modified lithium aluminum hydride reduction to the aldehydo level.[29]

Radical cyclization of aldehydes to give cycloalkanols had been examined by Flies et al.[30] and had not met with

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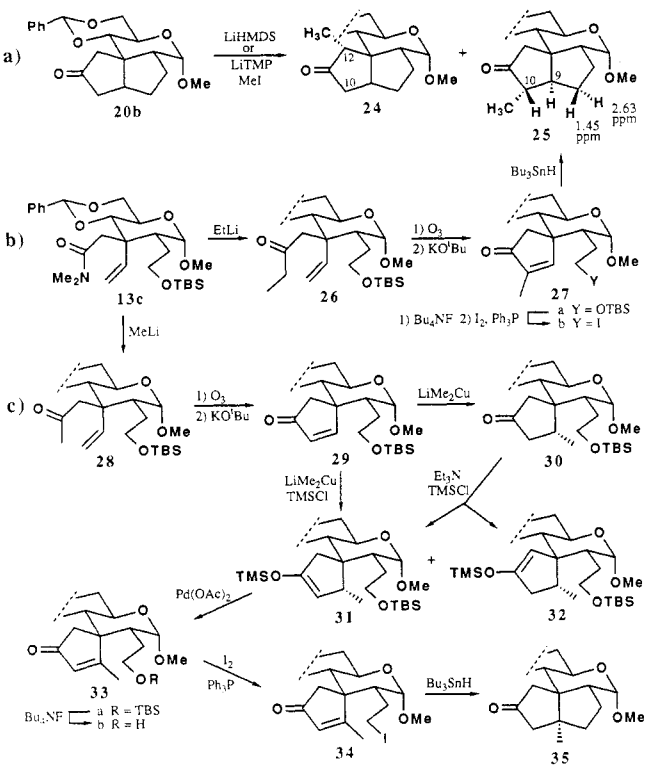
**Scheme V**



great success, owing to multiple side reactions.[31] In the case at hand, even if the favored first step (**16** → **17**; X = H) should go, hydrogen transfer to give the acyl radical **18** was a worrisome possibility.[32] Nevertheless, since the aldehyde was in hand (as its hemiacetal **19**) the corresponding iodide, **14b**, was prepared. Upon exposure to tri-*n*-butyltin hydride, the diquinane **20a** was indeed produced, but the major product was the cyclohexanol **21**. The latter observation prompted us to examine other instances of cycloalkanol formation by radical aldehyde cyclizations, and preliminary accounts of this work have been reported.[33]

In view of the poor yield of **20a**, hemiacetal **19** was converted into oxime **22**, but instead of the standard dehydrative procedure for obtaining the nitrile,[34] compound **22** was treated with triphenylphosphine and iodine. This caused simultaneous iodinolysis and dehydroiodination leading to **23** in virtually quantitative yield. This substrate then underwent smooth serial cyclization to give ketone **20b** in 80% yield, identical with the material obtained by oxidation of previously obtained **20a**.

With the formation of **20b**, a basic plan for obtaining key diquinanes of type **10** had been realized. However, a survey of the triquinane family[11] made it clear that methyl groups are frequently located at several sites. One option for installing a C10* or C12 methyl group was by alkylation of ketone **20b** (Scheme V, part a). (For the sake of consistency, carbohydrate numbering is used throughout.) However, this process, though stereoselective, proved to be nonregiospecific, affording inseparable mixtures of **24** and **25**.

An alternative based on radical conjugate addition (Scheme V, part b) was therefore examined, which made different use of the readily available precursor **13c**. Reaction with ethyllithium gave ketone **26**, which after ozonolysis followed by in situ aldolization afforded the methylcyclopentenone **27a**. Desilylation and iodinolysis gave the corresponding iodide, **27b**, which reacted with tri-*n*-butyltin hydride to give the diquinane **25** as the only isomer. The C10 orientation was established by irradiation of the $CH_3$ group, which caused NOE enhancement of the syn H9. Conversely, irradiation of H10 caused NOE enhancement of the endo H8′ at 1.45 ppm.

The radical conjugate addition protocol proved to be even more valuable for structures with an angular C9–$CH_3$ (Scheme V, part c). Thus, a comparable series of transformations on the methyl ketone **28** led to the spirocyclopentenone **29**. Reaction with lithium dimethylcuprate gave the *R* adduct **30**. The enol silane **31** was now required, but as with the simpler analogue **20b**, enolization was nonregiospecific, giving equal amounts of the isomers **31** and **32**. However, this problem was readily avoided by in situ trapping of the conjugate addition product, which then gave the crystalline enol silane **31**.

The Saegusa reaction[35] was then applied to obtain the desired α-enone **33**, which was processed in the usual way to give the corresponding iodide **34**. Cyclization then yielded diquinane **35** in 94% yield, there being no evidence of the reductive deiodination product.

The results reported above show that C2/C3 alkylated pyranosides of the general type **9** (R = $CH_2CH_2I$) undergo efficient serial radical cyclization, particularly where the radical trap is a nitrile. However, further substitution of the resulting keto diquinanes, for example, is nonregioselective, and hence other strategies are required for obtaining highly alkylated diquinanes. Some developments in this regard are reported in the accompanying paper.

## Experimental Section

**General Procedures.** Melting points were determined in capillary tubes and are uncorrected. The $^1H$ NMR coupling constants were verified by homonuclear decoupling experiments. The progress of all reactions was monitored by thin-layer chromatography (TLC), which was performed on aluminum plates precoated with silica gel HF-254 (0.2-mm layers) containing a fluorescent indicator (Merck, 5539). Detection was by UV (254 nm), followed by charring with sulfuric acid spray, or with a solution of ammonium molybdate(VI) tetrahydrate (12.5 g), and cerium sulfate hydrate (5.0 g) in 10% aqueous sulfuric acid (500 mL). Flash chromatography was performed by using Kieselgel 60 (230–400 mesh, Merck) silica gel, and petroleum ether/ethyl acetate mixtures as eluent.

**Standard Procedure for in Situ Alkylation of 4.** A solution of methyl 2,3:4,6-di-*O*-benzylidene-α-D-mannopyranoside (**3**)[12,13] (0.122 mol) in tetrahydrofuran (1000 mL) under argon was cooled to −40 °C in a dry ice/acetonitrile bath. *n*-Butyllithium (0.268 mol) was added dropwise to the stirred solution over 1 h. The resultant deep red solution was allowed to warm to −30 °C over 30 min to ensure complete formation of **4** and then cooled to −35 °C. A mixture of hexamethylphosphoramide (0.49 mol) and the alkyl halide (0.37 mol) was added dropwise over 1 h, and the resultant orange solution was maintained at −35 to −30 °C until alkylation was complete as judged by TLC. The reaction was quenched by addition of saturated aqueous ammonium chloride solution (300 mL), followed by addition of water (100 mL) and diethyl ether (1 L). The aqueous layer was extracted with diethyl ether (2 × 300 mL), and the ether extracts were combined, washed with brine (3 × 500 mL), dried ($Na_2SO_4$), and concentrated in vacuo. To the resultant orange syrup was added diethyl ether (100 mL), and the crude reaction mixture was placed in the freezer

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overnight. The solid mass obtained was filtered, washed with petroleum ether (100 mL) and diethyl ether (100 mL), and dried in a vacuum oven to give the desired alkylated ketone.

**Standard Procedure for Olefination of Keto Sugars. (a) Horner–Emmons Reaction.**[36] A suspension of hexane-washed sodium hydride (2.85 mmol) in tetrahydrofuran (5 mL) was cooled to 0 °C under argon, and triethyl phosphonoacetate or triethyl 2-phosphonopropionate (2.85 mmol) was added. After stirring for 0.5 h, a solution of the keto sugar (1.9 mmol) in tetrahydrofuran (30 mL) was added at 0 °C. The reaction mixture was then allowed to warm to room temperature, and the course of the reaction was monitored by TLC. Upon completion, the reaction mixture was washed with saturated aqueous ammonium chloride solution (3 × 10 mL) and water (10 mL), dried ($Na_2SO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.

**(b) Wittig Reaction.**[37] To a solution of the keto sugar (1.0 mmol) in acetonitrile (25 mL) was added the phosphorane (1.5–3.0 mmol). The reaction mixture was maintained at reflux until the reaction was complete (TLC), and then the mixture was concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.

**Standard Procedure for Diisobutylaluminum Hydride (DIBAL) Reduction.** To a solution of the ester or ketone (26.9 mmol) in toluene or dichloromethane (250 mL) under argon was added diisobutylaluminum hydride (80.6 mmol) slowly. When the reaction was complete (TLC), ethyl acetate (1 mL) was added to destroy any unreacted DIBAL, followed by addition of concentrated aqueous sodium/potassium tartrate solution (2 mL). After stirring for 0.5 h, the reaction mixture was filtered, and the aluminum salts collected were subjected to Soxhlet extraction overnight using ethyl acetate or acetonitrile as solvent. The combined filtrate and extract were concentrated in vacuo, and the crude product was purified by flash chromatography on silica gel.

**Standard Procedure for Claisen Rearrangements. (a) Eschenmoser Variation.**[26] To a mixture of the allylic alcohol (49.7 mmol) in toluene (500 mL) under argon was added *N,N*-dimethylacetamide dimethyl acetal (249 mmol). The reaction mixture was maintained at reflux with continuous removal of methanol by a molecular sieve (4 Å) trap until the reaction was complete (TLC), cooled to room temperature, and concentrated in vacuo. The resultant syrup was purified by flash chromatography on silica gel.

**(b) Johnson–Faulkner Variation.**[38] To a solution of the allylic alcohol (0.89 mmol) in xylene (7 mL) was added triethyl orthoacetate or triethyl orthopropionate (7.12 mmol) and propionic acid (0.089 mmol). The reaction mixture was maintained at reflux with continuous removal of ethanol by a molecular sieve (4 Å) trap until the reaction was complete (TLC), cooled to room temperature, and concentrated in vacuo. The resultant syrup was purified by flash chromatography on silica gel.

**(c) "Classical" Procedure via Allyl Vinyl Ethers.** A solution of the allylic alcohol (2.41 mmol) in ethyl vinyl ether (20 mL) was stirred at room temperature under argon with a catalytic amount of mercuric trifluoroacetate until the reaction was complete (TLC). The reaction mixture was washed with aqueous 10% potassium hydroxide solution (2 × 5 mL), dried ($Na_2SO_4$), and concentrated in vacuo to give the crude vinyl ether. A solution of the vinyl ether in xylene (20 mL) was maintained at reflux under argon until the reaction was complete (TLC), cooled to room temperature, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel.

**Standard Procedure for Modified Lithium Aluminum Hydride Reductions.** To a suspension of lithium aluminum hydride (63 mmol) in tetrahydrofuran (50 mL) at 0 °C under argon was added anhydrous ethanol (189 mmol) or 1-methylpiperazine (126 mmol) dropwise. The reaction mixture was stirred at 0 °C for 2 h, at which time the amide (21 mmol) in tetrahydrofuran (100 mL) was added slowly. The reaction mixture was stirred at 0 °C until the reaction was complete (TLC), followed by slow addition of ethyl acetate (30 mL) and dropwise addition of saturated aqueous ammonium chloride solution (10 mL). Several portions of anhydrous magnesium sulfate were added, and the reaction mixture was allowed to form a gel. The resultant gel was filtered through Celite and washed with ethyl acetate (200 mL). The aluminum salts collected were subjected to Soxhlet extraction overnight using ethyl acetate as solvent. The combined filtrate and extract were concentrated in vacuo, and the crude product was purified by flash chromatography on silica gel.

**Standard Procedure for Conversion of Aldehydes to Nitriles.**[34] To a solution of the aldehyde (0.89 mmol) in pyridine (5 mL) was added hydroxylamine hydrochloride (2.67 mmol). The reaction mixture was maintained at the indicated temperature until the reaction was complete (TLC). The reaction mixture was diluted with diethyl ether (10 mL), washed with brine (3 × 5 mL), dried ($Na_2SO_4$), and concentrated to give the corresponding mixture of oximes. For epimerizable aldehydes, hydroxylamine hydrochloride (2.67 mmol) and acetic acid/sodium acetate buffer (pH = 5) (2.67 mmol) were added to a solution of the aldehyde (0.89 mmol) in ethanol (10 mL). The reaction mixture was maintained at ~70 °C. Upon completion (TLC), the organic solvent was evaporated and the remaining aqueous layer was extracted with ethyl acetate, dried ($Na_2SO_4$), and evaporated to give the corresponding oximes. Without further purification, the oximes were dissolved in methylene chloride (5 mL), and pyridine (5.34 mmol) and trifluoroacetic anhydride (2.67 mmol) were added at room temperature. The reaction mixture was maintained at the indicated temperature under argon until the reaction was complete (TLC), concentrated, and azeotroped with toluene (5 mL). Flash chromatography of the resultant material on silica gel yielded the corresponding nitrile.

**Standard Procedure for Iodination or Bromination of Alcohols.**[39] To a mixture of the alcohol (10.0 mmol), triphenylphosphine (20.0 mmol), and pyridine (40.0 mmol) in dichloromethane (50 mL) cooled in an ice bath was added iodine or *N*-bromosuccinimide (20.0 mmol) in several portions. The reaction mixture was stirred at 0 °C until the reaction was complete (TLC), followed by addition of saturated aqueous sodium bisulfite (10 mL). The aqueous layer was removed and the organic layer washed with saturated sodium bicarbonate solution (2 × 15 mL) and brine (15 mL) and dried ($Na_2SO_4$). Evaporation of the solvent, followed by flash chromatography, gave the iodide or bromide.

**Standard Procedure for Free-Radical Cyclizations.** A mixture of the iodide (15 mmol) or alkyne (15 mmol), tri-*n*-butyltin hydride (16 mmol), and AIBN (0.3 mmol) in dry benzene (500 mL) under argon was maintained at reflux until the reaction was complete (TLC). The reaction mixture was cooled to room temperature, 10% aqueous ammonium hydroxide solution (300 mL) was added, and the mixture was stirred vigorously overnight. The organic layer was washed with brine (3 × 100 mL), dried ($Na_2SO_4$), and concentrated in vacuo. (In the case of an alkyne, the crude vinylstannane product was treated with silica gel in dichloromethane until protodestannylation was complete, filtered, and concentrated.) The crude product was purified by flash chromatography on silica gel.

**Methyl 4,6-*O*-Benzylidene-2-deoxy-2-*C*-((ethoxycarbonyl)methyl)-α-D-*ribo*-hexopyranosid-3-ulose (11).** Compound **3** (45.0 g, 0.122 mol) was fragmented and then alkylated in situ with ethyl bromoacetate, according to the standard procedure. Compound **11** (16.2 g, 38%) was obtained as a white solid: mp 157–158 °C (lit.[15] mp 163–165 °C); $R_f$ 0.23 (30% EtOAc/petroleum ether); $[\alpha]^{21}_D$ +98.0° (*c* 0.100, $CHCl_3$) (lit.[15] $[\alpha]_D$ +109° (*c* 0.1, $CHCl_3$)); IR (Nujol) 1725 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.50–7.31 (m, 5 H, aromatic), 5.55 (s, 1 H, PhC*H*), 5.10 (d, 1 H, $J_{1,2}$ = 4.2 Hz, H1), 4.36–4.31 (m, 2 H, H4, H6(eq)), 4.17–4.05 (m, 3 H, H5, $CH_3CH_2$), 3.90 (dd, 1 H, $J_{5,6(ax)}$ = 10.2 Hz, $J_{6(eq),6(ax)}$ = 10.2 Hz, H6(ax)), 3.36–3.28 (m, 4 H, H2, O*Me*), 2.89 (dd, 1 H, $J_{7,7'}$ = 17.5 Hz, $J_{2,7}$ = 7.0 Hz, H7), 2.36 (dd, 1 H, $J_{7,7'}$ = 17.5 Hz, $J_{2,7'}$ = 6.7 Hz, H7'), 1.23 (t, 3 H, *J* = 7.2 Hz, $CH_3CH_2$). Anal. Calcd for $C_{18}H_{22}O_7$: C, 61.71; H, 6.33. Found: C, 61.61; H, 6.14.

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**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-((ethoxycarbonyl)methyl)-3-*C*-((*Z*)-(ethoxycarbonyl)methylene)-α-D-*ribo*-hexopyranoside (12a).** The standard procedure for Wittig reaction of 11 (46.7 g, 0.133 mol) with 3 equiv of (carbethoxymethylene)triphenylphosphorane for 72 h gave **12a** (54.9 g, 98%) as a yellow oil: $R_f$ 0.42 (30% EtOAc/petroleum ether); $[\alpha]^{21}_D$ +139° (*c* 0.248, $CHCl_3$); IR (neat) 1725 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.50–7.34 (m, 5 H, aromatic), 6.16 (dd, 1 H, $J_{2,9}$ = 1.7 Hz, $J_{4,9}$ = 1.7 Hz, H9), 5.60 (s, 1 H, PhC*H*), 4.75 (d, 1 H, $J_{1,2}$ = 3.2 Hz, H1), 4.30–4.25 (m, 1 H, H6(eq)), 4.20–4.05 (m, 5 H, 2 × $CH_3CH_2$, H4), 3.88–3.75 (m, 2 H, H5, H6(ax)), 3.36 (s, 3 H, O*Me*), 3.25–3.17 (m, 1 H, H2), 3.00 (dd, 1 H, $J_{2,7}$ = 5.6 Hz, $J_{7,7'}$ = 16.9 Hz, H7), 2.69 (dd, 1 H, $J_{2,7'}$ = 8.9 Hz, $J_{7,7'}$ = 16.9 Hz, H7′), 1.28–1.22 (m, 6 H, 2 × $CH_3CH_2$). Anal. Calcd for $C_{22}H_{28}O_8$: C, 62.85; H, 6.71. Found: C, 62.71; H, 6.61.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-2-*C*-(2-hydroxyethyl)-*C*-((*Z*)-2-hydroxyethylidene)-α-D-*ribo*-hexopyranoside (12b).** Compound **12a** (16.1 g, 38.3 mmol) in dichloromethane was reduced with DIBAL, according to the standard procedure, to give **12b** (9.2 g, 71%) as a white solid: mp 144 °C; $R_f$ 0.22 (EtOAc); $[\alpha]^{20}_D$ +143° (*c* 1.04, EtOH); IR (Nujol) 3200 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.52–7.33 (m, 5 H, aromatic), 6.96–6.04 (m, 1 H, H9), 5.61 (s, 1 H, PhC*H*), 4.73 (d, 1 H, $J_{1,2}$ = 2.9 Hz, H1), 4.40–4.13 (m, 3 H, H10, H10′, H6(eq)), 3.96 (br d, 1 H, $J_{4,5}$ = 8.3 Hz, H4), 3.77–3.64 (m, 4 H, H6(ax), H5, H8, H8′), 3.37 (s, 3 H, O*Me*), 2.82–2.73 (m, 1 H, H2), 2.21–2.09 (m, 1 H, H7), 2.05–1.92 (m, 1 H, H-7′), 1.62 (br s, 1 H, O*H*). Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.27; H, 7.19. Found: C, 64.37; H, 7.08.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-((*N*,*N*-dimethylcarbamoyl)methyl)-2-*C*-(2-hydroxyethyl)-3-*C*-vinyl-α-D-allopyranoside (13a).** Claisen rearrangement of compound **12b** (16.7 g, 49.7 mmol) by the Eschenmoser variation was complete in 10 h to give a mixture of **13a** (13.6 g, 68%) and **13b** (6.08 g, 27%). The acetate in **13b** was cleaved with $MeOH/H_2O/Et_3N$ (5:4:1) to give **13a** quantitatively. **13a**: white foam; $R_f$ 0.26 (EtOAc); $[\alpha]^{22}_D$ +2.7° (*c* 1.1, $CHCl_3$); IR (neat) 3400, 1620 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5 H, aromatic), 6.46 (dd, 1 H, $J_{9,10(cis)}$ = 11.5 Hz, $J_{9,10(trans)}$ = 17.6 Hz, H9), 5.42 (s, 1 H, PhC*H*), 5.22 (d, 1 H, $J_{9,10(cis)}$ = 11.5 Hz, H10(cis)), 5.04 (d, 1 H, $J_{9,10(trans)}$ = 17.6 Hz, H10(trans)), 4.64 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H1), 4.25 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.2 Hz, H6(eq)), 4.15 (br s, 1 H, O*H*), 4.07 (ddd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 10.2 Hz, $J_{4,5}$ = 9.6 Hz, H5), 3.73–3.54 (m, 3 H, H6(ax), H8, H8′), 3.48 (d, 1 H, $J_{4,5}$ = 9.6 Hz, H4), 3.34 (s, 3 H, O*Me*), 3.00 (d, 1 H, $J_{12,12'}$ = 13.9 Hz, H12), 2.97 (s, 3 H, N*Me*), 2.96 (s, 1 H, N*Me*′), 2.75–2.69 (m, 1 H, H2), 2.41 (d, 1 H, $J_{12,12'}$ = 13.9 Hz, H12′), 1.80–1.59 (m, 2 H, H7, H7′). Anal. Calcd for $C_{22}H_{31}NO_6$: C, 65.17; H, 7.71. Found: C, 64.85; H, 7.81.

**Methyl 4,6-*O*-Benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-3-*C*-((*N*,*N*-dimethylcarbamoyl)methyl)-3-*C*-vinyl-α-D-allopyranoside (13c).** A mixture of amide **13a** (650 mg, 1.60 mmol), imidazole (218 mg, 3.20 mmol), and *tert*-butyldimethylsilyl chloride (291 mg, 1.93 mmol) in tetrahydrofuran (10 mL) was stirred at room temperature for 1 h and then concentrated in vacuo. Ethyl acetate (30 mL) and water (5 mL) were added, and the organic layer was washed with saturated aqueous sodium bicarbonate solution (10 mL) and brine (10 mL) and dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (25% EtOAc/petroleum ether) gave **13c** (670 mg, 81%) as a colorless oil: $R_f$ 0.72 (EtOAc); $[\alpha]^{19}_D$ +21.4° (*c* 3.32, $CHCl_3$); IR (neat) 1640 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.45–7.29 (m, 5 H, aromatic), 6.52 (dd, 1 H, $J_{9,10(cis)}$ = 11.5 Hz, $J_{9,10(trans)}$ = 17.7 Hz, H9), 5.49 (s, 1 H, PhC*H*), 5.21 (d, 1 H, $J_{9,10(cis)}$ = 11.5 Hz, H10(cis)), 5.04 (d, 1 H, $J_{9,10(trans)}$ = 17.7 Hz, H10(trans)), 4.68 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H1), 4.23 (dd, 1 H, $J_{5,6(eq)}$ = 4.9 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 4.11 (d, 1 H, $J_{4,5}$ = 9.8 Hz, H4), 4.01 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6(eq)}$ = 4.9 Hz, $J_{5,6(ax)}$ = 9.8 Hz, H5), 3.74–3.61 (m, 3 H, H6(ax), H8, H8′), 3.34 (s, 3 H, O*Me*), 2.97 (s, 3 H, N*Me*), 2.92 (s, 3 H, N*Me*′), 2.82 (d, 1 H, $J_{12,12'}$ = 15.4 Hz, H12), 2.80–2.72 (m, 1 H, H2), 2.41 (d, 1 H, $J_{12,12'}$ = 15.4 Hz, H12′), 1.73–1.46 (m, 2 H, H7, H7′), 0.87 (s, 9 H, Si$^t$*Bu*), 0.03 (s, 6 H, Si$Me_2$). Anal. Calcd for $C_{28}H_{45}NO_6Si$: C, 64.71; H, 8.73. Found: C, 64.98; H, 8.72.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-((*N*,*N*-dimethylcarbamoyl)methyl)-α-D-allopyranosido[3,2-*b*]-(*R*)-methylcyclopentane (15).** The alcohol **13a** (45 mg, 0.11 mmol) was brominated by the standard procedure to give 50 mg (94% yield) of **14a** as a white solid, which exhibited an $R_f$ of 0.7 ($Et_2O$). The bromide **14a** was treated with tri-*n*-butyltin hydride by standard procedure to give 41 mg (98% yield) of **15** as a syrup, which exhibited the following characteristics: $R_f$ 0.5 ($Et_2O$); $[\alpha]^{20}_D$ −60° (*c* 1.5, $CHCl_3$); $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.50–7.30 (m, 5 H, aromatic), 5.46 (s, 1 H, PhC*H*), 4.53 (d, 1 H, $J_{1,2}$ = 4.5 Hz, H1), 4.23 (dd, 1 H, $J_{5,6(eq)}$ = 4 Hz, $J_{6(ax),6(eq)}$ = 10 Hz, H6(eq)), 4.10–3.97 (m, 2 H, H4, H5), 3.70 (t, 1 H, $J_{5,6(ax)}$ = 10 Hz, H6(ax)), 3.30 (s, 3 H, O*Me*), 3.02 (s, 3 H, N*Me*), 2.95 (s, 3 H, N*Me*′), 2.91–2.70 (m, 3 H, H2, H12, H9), 2.02 (m, 1 H, H8), 1.96 (d, 1 H, $J_{12,12'}$ = 14 Hz, H12′), 1.79 (m, 1 H, H7), 1.58 (m, 1 H, H7′), 1.28 (m, 1 H, H8′), 1.01 (d, 3 H, $J_{9,10}$ = 7 Hz, H10). Anal. Calcd for $C_{22}H_{31}NO_5$: C, 67.84; H, 8.02. Found: C, 67.01; H, 7.98.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-(formylmethyl)-2-*C*-(2-hydroxyethyl)-3-*C*-vinyl-α-D-allopyranoside Hemiacetal (19).** Compound **13a** (8.3 g, 21 mmol) was reduced with $LiAl(OEt)_3H$, according to the standard procedure, to give **19** (5.2 g, 70%) as an anomeric mixture of lactols. Major anomer: white foam; $R_f$ 0.53 (EtOAc); IR (neat) 3420, 1735 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.47–7.30 (m, 5 H, aromatic), 6.39 (dd, 1 H, $J_{9,10(cis)}$ = 11.5 Hz, $J_{9,10(trans)}$ = 18.1 Hz, H9), 5.48 (s, 1 H, PhC*H*), 5.39–5.27 (m, 2 H, H10(trans), H10(cis)), 5.19–5.07 (m, 1 H, H11), 4.46 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H1), 4.23 (dd, 1 H, $J_{5,6(eq)}$ = 5.2 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 3.91–3.83 (m, 2 H, H8, H5), 3.72–3.53 (m, 2 H, H8′, H6(ax)), 3.32 (s, 3 H, O*Me*), 3.28 (d, 1 H, $J_{4,5}$ = 8.1 Hz, H4), 2.86 (dd, 1 H, $J_{11,12}$ = 4.6 Hz, $J_{12,12'}$ = 14.9 Hz, H12), 2.10–1.94 (m, 1 H, H7), 1.82–1.75 (m, 1 H, H2), 1.56–1.38 (m, 2 H, H7′, H12′). Anal. Calcd for $C_{20}H_{26}O_6$: C, 66.28; H, 7.23. Found: C, 66.12; H, 7.41.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-α-D-allopyranosido[3,2-*c*]bicyclo[3.3.0]octanone (20b).** The nitrile **23** (7.0 g, 15 mmol) was cyclized by the standard procedure over 1 h to give **20b** (4.1 g, 80%) as a white solid: mp 139–140 °C; $R_f$ 0.31 (30% EtOAc/petroleum ether); $[\alpha]^{20}_D$ −11° (*c* 2.3, $CHCl_3$); IR (Nujol) 1740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5 H, aromatic), 5.51 (s, 1 H, PhC*H*), 4.56 (d, 1 H, $J_{1,2}$ = 5.1 Hz, H1), 4.28 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.4 Hz, H6(eq)), 4.00 (ddd, 1 H, $J_{4,5}$ = 9.9 Hz, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 9.9 Hz, H5), 3.75–3.68 (m, 2 H, H4, H6(ax)), 3.33 (s, 3 H, O*Me*), 3.04–2.94 (m, 1 H, H9), 2.64 (ddd, 1 H, $J_{8',10}$ = 1.2 Hz, $J_{9,10}$ = 8.0 Hz, $J_{10,10'}$ = 18.5 Hz, H10), 2.48–2.30 (m, 3 H, H8, H2, H12), 2.22 (d, 1 H, $J_{12,12'}$ = 18.8 Hz, H12′), 2.09 (d, 1 H, $J_{10,10'}$ = 18.5 Hz, H10′), 1.92–1.78 (m, 1 H, H7), 1.71–1.60 (m, 1 H, H7′), 1.33–1.20 (m, 1 H, H8′). Anal. Calcd for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.65; H, 7.06.

**Alkylation of 20b.** To a solution of lithium hexamethyldisilazide (0.17 mL, 1.0 M in tetrahydrofuran, 0.17 mmol) in tetrahydrofuran (0.5 mL) at −78 °C under argon was added a solution of ketone **20b** (51 mg, 0.15 mmol) in tetrahydrofuran (0.5 mL). The reaction mixture was allowed to warm to 0 °C over 1 h, at which time methyl iodide (90 μL, 1.5 mmol) was added. The reaction mixture was stirred at 0 °C for 1 h, followed by addition of saturated aqueous ammonium chloride solution (0.5 mL). Ethyl acetate (10 mL) was added, and the organic layer was washed with water (2 mL) and brine (2 × 2 mL) and dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (20% EtOAc/petroleum ether) gave an inseparable mixture of **24** and **25** (38 mg, 71%) in a 2.5:1 ratio as determined by $^1H$ NMR. When lithium 2,2,6,6-tetramethylpiperidide (prepared from addition of *n*-butyllithium to the amine in tetrahydrofuran at 0 °C) was used as the base, a 5:1 ratio of **24**:**25** was obtained. For **24** (major isomer): crystalline solid; mp 146–162 °C; $R_f$ 0.41 (30% EtOAc/petroleum ether); IR (Nujol) 1730 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5 H, aromatic), 5.45 (s, 1 H, PhC*H*), 4.58 (d, 1 H, $J_{1,2}$ = 5.3 Hz, H1), 4.30 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.2 Hz, H6(eq)), 4.02 (ddd, 1 H, $J_{4,5}$ = 9.5 Hz, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 9.8 Hz, H5), 3.77 (d, 1 H, $J_{4,5}$ = 9.5 Hz, H4), 3.72 (dd, 1 H, $J_{5,6(ax)}$ = 9.8 Hz, $J_{6(eq),6(ax)}$ = 10.2 Hz, H6(ax)), 3.34 (s, 3 H, O*Me*), 3.06–2.94 (m, 1 H, H9), 2.60–2.28 (m, 3 H, H10, H8, H2), 2.16–2.06 (m, 2 H, H12, H10′), 1.94–1.80 (m, 1 H, H7), 1.74–1.62 (m, 1 H, H7′), 1.41–1.28 (m, 1 H, H8′), 1.10 (d, 3 H, $J_{12,13}$ = 7.0 Hz, H13's); HRMS (EI) 358.1780 $M^+$, calcd for $C_{21}H_{22}O_5$ 358.1776.

For **25**: crystalline solid; mp 120–123 °C; $R_f$ 0.41 (30% EtOAc/petroleum ether); $[\alpha]^{19}_D$ +37.5° (*c* 1.77, $CHCl_3$); IR (Nujol) 1740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.38–7.27 (m, 5 H, aromatic), 5.52 (s, 1 H, PhC*H*), 4.61 (d, 1 H, $J_{1,2}$ = 5.3 Hz, H1), 4.30 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 3.91 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 10.0 Hz, H5), 3.72–3.63 (m, 2 H, H6(eq), H4), 3.33 (s, 3 H, O*Me*), 2.69–2.50 (m, 3 H, H8, H9, H12), 2.40–2.25 (m, 2 H, H2, H12′), 2.18–2.08 (m, 1 H, H10), 2.00–1.85 (m, 1 H, H7), 1.74–1.58 (m, 1 H, H7′), 1.50–1.40 (m, 1 H, H8′), 1.02 (d, 3 H, $J_{10,13}$ = 7.4 Hz, H13's). Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.55; H, 7.37.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-3-*C*-vinyl-α-D-allopyranosido[3,2-*c*]-(*R*)-cyclohexanol (21).** The hemiacetal **19** (24 mg, 0.07 mmol) was iodinated by the standard procedure to give 30 mg (95% yield) of **14b** as a clear syrup, which exhibited an $R_f$ of 0.8 ($Et_2O$). The iodide **14b** was treated with tri-*n*-butyltin hydride by standard procedure to give 4 mg (18% yield) of **20a** and 16 mg (73% yield) of **21** as clear syrups. Alcohol **20a** was oxidized and characterized as ketone **20b** described above. For **21**: $R_f$ 0.53 ($Et_2O$); $[\alpha]^{20}_D$ +21.6° (*c* 2.16, $CHCl_3$); $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.50–7.30 (m, 5 H, aromatic), 6.45 (dd, 1 H, $J_{9,10}$ = 19 Hz, $J_{9,10}$ = 11 Hz, H9), 5.50 (s, 1 H, PhC*H*), 5.41–5.30 (m, 2 H, H10, H10′), 4.53 (d, 1 H, $J_{1,2}$ = 4.0 Hz, H1), 3.20 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(ax),6(eq)}$ = 10 Hz, H6(eq)), 3.90–3.76 (m, 2 H, H9, H5), 3.63 (t, 1 H, $J_{5,6(ax)}$ = 10 Hz, H6(ax)), 3.35 (d, 1 H, $J_{4,5}$ = 10 Hz, H4), 3.32 (s, 3 H, O*Me*), 2.65 (dd, 1 H, $J_{11,12(eq)}$ = 3.5 Hz, $J_{12(ax),12(eq)}$ = 11 Hz, H12(eq)), 2.06 (m, 1 H, H8), 1.62–1.50 (m, 2 H, H7, H7′), 1.04 (t, 1 H, $J_{11,12(ax)}$ = 11 Hz, H12(ax)). Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 68.77; H, 7.35.

**Methyl 4,6-*O*-Benzylidene-3-*C*-(cyanomethyl)-2,3-dideoxy-2-*C*-(2-iodoethyl)-3-*C*-vinyl-α-D-allopyranoside (23).** A solution of hemiacetals **19** (2.45 g, 6.77 mmol) and hydroxylamine hydrochloride (2.33 g, 33.8 mmol) in pyridine (50 mL) was maintained at reflux for 1 h. The reaction mixture was cooled to room temperature, and the solvent was removed in vacuo. The resultant mixture was partitioned between ethyl acetate (50 mL) and water (30 mL), and the aqueous layer was extracted with ethyl acetate (2 × 10 mL). The organic extracts were combined, washed with brine (3 × 15 mL), and dried ($Na_2SO_4$). Evaporation of the solvent gave a 1:1 mixture of oximes **22** as a colorless oil. To the crude oxime mixture in dichloromethane (50 mL) under argon were added triphenylphosphine (4.03 g, 15.4 mmol) and pyridine (2.2 mL, 27 mmol). The reaction mixture was cooled to 0 °C, and iodine (3.78 g, 14.9 mmol) was added in several portions. The reaction mixture was stirred at 0 °C for 45 min, followed by addition of saturated aqueous sodium bisulfite (10 mL). The aqueous layer was removed, and the organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 15 mL) and brine (15 mL) and dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (15–30% EtOAc/petroleum ether) gave **23** (2.89 g, 91%) as a white solid: mp 143–145 °C; $R_f$ 0.60 (30% EtOAc/petroleum ether); $[\alpha]^{21}_D$ +43.0° (*c* 0.314, $CHCl_3$); IR (Nujol) 2330 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.44–7.31 (m, 5 H, aromatic), 6.41 (dd, 1 H, $J_{9,10(cis)}$ = 17.8 Hz, $J_{9,10(trans)}$ = 11.2 Hz, H9), 5.57 (s, 1 H, PhC*H*), 5.27 (d, 1 H, $J_{9,10(cis)}$ = 17.8 Hz, H10(cis)), 4.93 (d, 1 H, $J_{9,10(trans)}$ = 11.2 Hz, H10(trans)), 4.72 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H1), 4.29 (dd, 1 H, $J_{5,6(eq)}$ = 4.9 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 3.98 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6(eq)}$ = 4.9 Hz, $J_{5,6(ax)}$ = 10.3 Hz, H5), 3.76 (d, 1 H, $J_{4,5}$ = 9.7 Hz, H4), 3.73 (dd, 1 H, $J_{5,6(ax)}$ = 10.3 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(ax)), 3.38 (s, 3 H, O*Me*), 3.31–3.24 (m, 1 H, H8), 3.08–2.99 (m, 1 H, H8′), 2.95 (d, 1 H, $J_{12,12'}$ = 17.1 Hz, H12), 2.56 (d, 1 H, $J_{12,12'}$ = 17.1 Hz, H12′), 2.35–2.28 (m, 1 H, H2), 2.07–1.93 (m, 1 H, H7), 1.78–1.64 (m, 1 H, H7′). Anal. Calcd for $C_{20}H_{24}INO_4$: C, 51.18; H, 5.15. Found: C, 51.17; H, 5.32.

**Methyl 4,6-*O*-Benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-3-*C*-(2-oxobutyl)-3-*C*-vinyl-α-D-allopyranoside (26).** To a solution of amide **13c** (341 mg, 0.657 mmol) in anhydrous diethyl ether (5 mL) at −78 °C under argon was added ethyllithium (1.4 mL, 0.5 M in diethyl ether, 0.72 mmol) dropwise. The reaction mixture was stirred for 10 min, quenched with saturated aqueous ammonium chloride solution (1 mL), and allowed to warm to room temperature. Diethyl ether (10 mL) and water (2 mL) were added, and the organic layer was washed with saturated aqueous ammonium chloride solution (3 mL) and brine (3 mL) and then dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (5–10% EtOAc/petroleum ether) gave **26** (230 mg, 69%) as a colorless oil: $R_f$ 0.59 (20% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +27.9° (*c* 3.00, $CHCl_3$); IR (neat) 1710 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.44–7.29 (m, 5 H, aromatic), 6.44 (dd, 1 H, $J_{9,10(cis)}$ = 11.3 Hz, $J_{9,10(trans)}$ = 17.6 Hz, H9), 5.48 (s, 1 H, PhC*H*), 5.21 (d, 1 H, $J_{9,10(cis)}$ = 11.3 Hz, H10(cis)), 5.06 (d, 1 H, $J_{9,10(trans)}$ = 17.6 Hz, H10(trans)), 4.64 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H1), 4.24 (dd, 1 H, $J_{5,6(eq)}$ = 4.8 Hz, $J_{6(eq),6(ax)}$ = 10.1 Hz, H6(eq)), 4.07 (d, 1 H, $J_{4,5}$ = 9.7 Hz, H4), 3.99 (ddd, 1 H, $J_{4,5}$ = 9.7 Hz, $J_{5,6(eq)}$ = 4.8 Hz, $J_{5,6(ax)}$ = 9.6 Hz, H5), 3.68 (dd, 1 H, $J_{5,6(ax)}$ = 9.6 Hz, $J_{6(eq),6(ax)}$ = 10.1 Hz, H6(ax)), 3.66–3.49 (m, 2 H, H8, H8′), 3.33 (s, 3 H, O*Me*), 2.90 (d, 1 H, $J_{12,12'}$ = 15.6 Hz, H12), 2.54 (d, 1 H, $J_{12,12'}$ = 15.6 Hz, H12′), 2.50–2.36 (m, 3 H, H2, C$H_2$CH$_3$), 1.70–1.56 (m, 1 H, H7), 1.53–1.41 (m, 1 H, H7′), 0.94 (t, 3 H, *J* = 7.2 Hz, CH$_2$C$H_3$), 0.87 (s, 9 H, Si*t*-*Bu*), 0.02 (s, 6 H, Si*Me*$_2$). Anal. Calcd for $C_{28}H_{44}O_6Si$: C, 66.63; H, 8.79. Found: C, 66.74; H, 8.70.

**Spiro[(methyl 4,6-*O*-benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-α-D-allopyranoside)-3,4-(2-methyl-2-cyclopenten-1-one)] (27a).** A solution of ketone **26** (96 mg, 0.19 mmol) in methanol/dichloromethane (1:1, 2 mL) was cooled to −78 °C, and ozone was bubbled through until the solution turned faint blue (~5 min). Dimethyl sulfide (0.5 mL) was added, and the reaction mixture was allowed to warm to room temperature, concentrated in vacuo, and azeotroped with toluene (2 mL) to give the crude aldehyde as a colorless oil. To a solution of the crude aldehyde in tetrahydrofuran (4 mL) under argon was added a potassium *tert*-butoxide/*tert*-butyl alcohol solution (0.36 mL, 0.53 M, 0.19 mmol) dropwise. The yellow reaction mixture was stirred at room temperature for 15 min, quenched by addition of saturated aqueous ammonium chloride solution (1 mL), and then concentrated in vacuo. Ethyl acetate (10 mL) was added, and the organic layer was washed with saturated aqueous ammonium chloride solution (2 × 2 mL) and brine (2 mL) and dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (10% EtOAc/petroleum ether) gave **27a** (66 mg, 71%) as a clear glass: $R_f$ 0.48 (20% EtOAc/petroleum ether; $[\alpha]^{22}_D$ +15° (*c* 0.36, $CHCl_3$); IR (neat) 1700 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.48 (d, 1 H, $J_{9,13}$ = 1.4 Hz, H9), 7.36–7.27 (m, 5 H, aromatic), 5.51 (s, 1 H, PhC*H*), 4.75 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H1), 4.30 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 4.03 (ddd, 1 H, $J_{4,5}$ = 9.8 Hz, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 9.9 Hz, H5), 3.72 (dd, 1 H, $J_{5,6(ax)}$ = 9.9 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(ax)), 3.63 (d, 1 H, $J_{4,5}$ = 9.8 Hz, H4), 3.62–3.48 (m, 2 H, H8, H8′), 3.40 (s, 3 H, O*Me*), 2.58 (d, 1 H, $J_{12,12'}$ = 18.3 Hz, H12), 2.25–2.15 (m, 1 H, H2), 2.20 (d, 1 H, $J_{12,12'}$ = 18.3 Hz, H12′), 1.77 (d, 3 H, $J_{9,13}$ = 1.4 Hz, H13's), 1.50–1.37 (m, 1 H, H7), 1.25–1.13 (m, 1 H, H7′), 0.87 (s, 9 H, Si*t*-*Bu*), 0.02 (s, 6 H, Si*Me*$_2$). Anal. Calcd for $C_{27}H_{40}O_6Si$: C, 66.36; H, 8.25. Found: C, 66.60; H, 8.55.

**Spiro[(methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-(2-iodoethyl)-α-D-allopyranoside)-3,4-(2-methyl-2-cyclopenten-1-one)] (27b).** A mixture of enone **27a** (97 mg, 0.20 mmol) and tetrabutylammonium fluoride (0.20 mL, 1.1 M, in tetrahydrofuran, 0.22 mmol) in tetrahydrofuran (1 mL) was stirred at room temperature for 20 min, concentrated in vacuo, and passed through a short column of silica gel (80% EtOAc/petroleum ether) to give the alcohol as a colorless oil. To a mixture of the alcohol, triphenylphosphine (105 mg, 0.40 mmol), and imidazole (54 mg, 0.80 mmol) in benzene (2 mL) under argon was added iodine (102 mg, 0.40 mmol) in three portions. The reaction mixture was stirred at room temperature for 5 min, followed by the addition of saturated aqueous sodium bisulfite (1 mL). After all solids had dissolved, ethyl acetate (10 mL) was added, and the organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 3 mL) and brine (3 mL) and then dried ($Na_2SO_4$). Evaporation of the solvent followed by flash chromatography (20% EtOAc/petroleum ether) gave **27b** (73 mg, 75%) as a white solid: mp 157–160 °C; $R_f$ 0.41 (30% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +15° (*c* 0.37, $CHCl_3$); IR (neat) 1705 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.43 (d, 1 H, $J_{9,13}$ = 1.0 Hz, H9), 7.36–7.28 (m, 5 H, aromatic) 5.51 (s, 1 H, PhC*H*), 4.70 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H1), 4.31 (dd, 1 H, $J_{5,6(eq)}$ = 5.0 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(eq)), 4.01 (ddd, 1 H, $J_{4,5}$ = 9.6 Hz, $J_{5,6(eq)}$ = 5.0 Hz, $J_{5,6(ax)}$ = 9.9 Hz, H5), 3.72 (dd, 1 H, $J_{5,6(ax)}$ = 9.9 Hz, $J_{6(eq),6(ax)}$ = 10.3 Hz, H6(ax)), 3.65 (d, 1 H, $J_{4,5}$ = 9.6 Hz, H4), 3.41 (s, 3 H, O*Me*), 3.32–3.23 (m, 1 H, H8), 3.03–2.92 (m, 1 H, H8′), 2.61 (d, 1 H, $J_{12,12'}$ = 18.5 Hz, H12), 2.26–2.17 (m, 1 H, H2), 2.21 (d, 1 H, $J_{12,12'}$ = 18.5 Hz, H12′),

1.81–1.67 (m, 1 H, H7), 1.77 (d, 3 H, $J_{9,13}$ = 1.0 Hz, H13's), 1.52–1.39 (m, 1 H, H7'); HRMS (EI) 484.0747 $M^+$, calcd for $C_{21}H_{25}IO_5$ 484.0743.

**Methyl 4,6-*O*-Benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-3-*C*-(2-oxopropyl)-3-*C*-vinyl-α-D-allopyranoside (28).** This compound was prepared exactly as described above for the analogue **26** by using MeLi in place of EtLi: yield 89%; $R_f$ 0.36 (7% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +32.9° (*c* 1.07, $CHCl_3$); IR (neat) 1715, 1640 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5 H, aromatic), 6.45 (dd, 1 H, $J_{9,10'}$ = 17.6 Hz, $J_{9,10}$ = 11.3 Hz, H9), 5.49 (s, 1 H, PhC*H*), 5.23 (dd, 1 H, $J_{10,9}$ = 11.3 Hz, $J_{10,10'}$ = 1.0 Hz, H10), 5.09 (dd, 1 H, $J_{10',9}$ = 17.6 Hz, $J_{10',10}$ = 1.0 Hz, H10'), 4.67 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H1), 4.26 (dd, 1 H, $J_{6(eq),6(ax)}$ = 10.0 Hz, $J_{6(eq),5}$ = 4.6 Hz, H6(eq)), 4.05 (dd, 1 H, $J_{6(eq),6(ax)} = J_{6(ax),5}$ = 10.0 Hz, H6(ax)), 4.02 (ddd, 1 H, $J_{6(ax),5} = J_{4,5}$ = 10.0 Hz, $J_{6(eq),5}$ = 4.6 Hz, H5), 3.72 (d, 1 H, $J_{4,5}$ = 10.0 Hz, H4), 3.70–3.52 (m, 2 H, H8), 3.34 (s, 3 H, O*Me*), 2.95 (d, 1 H, $J_{12,12'}$ = 15.6 Hz, H12), 2.56 (d, 1 H, $J_{12,12'}$ = 15.6 Hz, H12'), 2.48 (ddd, $J_{1,2}$ = 3.9 Hz, $J_{2,7}$ = 3.9 Hz, $J_{2,7'}$ = 10.7 Hz, H2), 2.15 (s, 3 H, C$H_3$CO), 1.71–1.43 (m, 2 H, H7), 0.88 (s, 9 H, Si*t*-*Bu*), 0.03 (s, 6 H, Si$Me_2$). Anal. Calcd for $C_{27}H_{42}O_6Si$: C, 66.09; H, 8.63. Found: C, 66.13; H, 8.69.

**Spiro[(methyl 4,6-*O*-benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-α-D-allopyranoside)-3,4-(2-cyclopenten-1-one)] (29).** This compound was prepared as described above for **27a**: yield 89%; $R_f$ 0.28 (10% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +4.1° (*c* 1.0, $CHCl_3$); IR (neat) 1720, 1680, 1595 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 1 H, $J_{9,10}$ = 5.8 Hz, H9), 7.35–7.30 (m, 5 H, aromatic), 6.22 (d, 1 H, $J_{9,10}$ = 5.8 Hz, H10), 5.55 (s, 1 H, PhC*H*), 4.78 (d, 1 H, $J_{1,2}$ = 3.4 Hz, H1), 4.33 (dd, 1 H, $J_{6(eq),6(ax)}$ = 10.3 Hz, $J_{6(eq),5}$ = 5.0 Hz, H6(eq)), 4.07 (ddd, 1 H, $J_{5,6(ax)} = J_{5,4}$ = 10.0 Hz, $J_{5,6(eq)}$ = 5.0 Hz, H5), 3.75 (dd, $J_{6(ax),6(eq)} = J_{6(ax),5}$ = 10.2 Hz, H6(ax)), 3.68 (d, 1 H, $J_{4,5}$ = 10.0 Hz, H4), 3.65–3.51 (m, 2 H, H8), 3.24 (s, 3 H, O*Me*), 2.58 (d, 1 H, $J_{12,12'}$ = 18.3 Hz, H12), 2.27 (ddd, $J_{1,2} = J_{2,7}$ = 3.4 Hz, $J_{2,7'}$ = 10.5 Hz, H2), 2.21 (d, 1 H, $J_{12,12'}$ = 18.3 Hz, H12'), 1.53–1.19 (m, 2 H, H7), 0.89 (s, 9 H, Si*t*-*Bu*), 0.03 (s, 6 H, Si$Me_2$). Anal. Calcd for $C_{26}H_{38}O_8Si$: C, 65.79; H, 8.07. Found: C, 65.71; H, 8.14.

**Spiro[(methyl 4,6-*O*-benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-α-D-allopyranoside)-3,3-(4-(*R*)-methylcyclopentanone)] (30).** To a suspension of 0.3 g of copper(I) iodide (1.58 mmol) in 10 mL of dry diethyl ether at 0 °C under argon was added dropwise 2.26 mL of a 1.4 M solution of methyllithium in ether (3.16 mmol). To the resultant slurry was added the enone **29** (250 mg, 0.527 mmol) dissolved in ether (5 mL). After 5 min, the reaction was quenched by addition of a pH = 8 solution of $NH_4OH/NH_4Cl$ and stirred for 30 min. The aqueous phase was washed with ether, and the combined organic extracts were dried over $Na_2SO_4$. Evaporation of the solvent, followed by flash chromatography (10% EtOAc/petroleum ether), afforded 250 mg (97%) of β-methyl ketone **30** as a colorless oil: $R_f$ 0.28 (10% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +19.3° (*c* 0.55, $CHCl_3$); IR (neat) 1750 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.40–7.30 (m, 5 H, aromatic), 5.46 (s, 1 H, PhC*H*), 4.65 (d, 1 H, $J_{1,2}$ = 3.9 Hz, H1), 4.34–4.18 (m, 2 H, H6(eq), H5), 3.74–3.54 (m, 4 H, H6(ax), H4, H8), 3.93 (s, 3 H, O*Me*), 2.55–2.45 (m, 2 H, H12, H9), 2.39–2.23 (m, 3 H, H12', H9, H9'), 2.09 (ddd, 1 H, $J_{1,2}$ = 3.9 Hz, $J_{2,7}$ = 2.5 Hz, $J_{2,7'}$ = 11.0 Hz, H2), 1.86–1.51 (m, 2 H, H7), 1.47 (d, 3 H, $J_{Me,9}$ = 6.9 Hz, C$H_3$), 0.88 (s, 9 H, Si*t*-*Bu*), 0.03 (s, 6 H, Si$Me_2$). Anal. Calcd for $C_{27}H_{42}O_6Si$: C, 66.09; H, 8.63. Found: C, 66.14; H, 8.72.

**Spiro[(methyl 4,6-*O*-benzylidene-2-*C*-(2-(*tert*-butyldimethylsiloxy)ethyl)-2,3-dideoxy-α-D-allopyranoside)-3,4-(3-methyl-2-cyclopenten-1-one)] (33a).** Enone **29** (1.5 g, 3.16 mmol) was treated with $Me_2CuLi$ as indicated for the preparation of **30**, except that after 5 min at 0 °C, the reaction mixture was treated with 4.4 mL of dry triethylamine and 4 mL of trimethylchlorosilane and the suspension stirred for an additional 5 min. The reaction was then quenched by successive addition of a solution of 3:1 saturated sodium bicarbonate and ice and a pH = 8 solution of $NH_4OH/NH_4Cl$. The mixture was exposed to air and stirred until all copper salts had dissolved in the resulting blue solution. The aqueous phase was washed with ether. The combined organic extracts were dried ($Na_2SO_4$) and evaporated to yield 1.8 g of silyl enol ether **31** as a white solid, which was dissolved into dry acetonitrile (150 mL) and stirred with 1.42 g (6.32 mmol) of palladium acetate for 8 h. The reaction mixture was filtered to remove the Pd(0) and evaporated to give, after flash chromatography (10% EtOAc/petroleum ether), 1.49 g (97%) of enone **33a** as a white solid: mp 110–111 °C; $R_f$ 0.15 (10% EtOAc/petroleum ether); $[\alpha]^{20}_D$ −35.9° (*c* 1.05, $CHCl_3$); IR (Nujol) 1745, 1700, 1615 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.39–7.31 (m, 5 H, aromatic), 6.01 (br s, 1 H, H10), 5.53 (s, 1 H, PhC*H*), 4.72 (d, 1 H, $J_{1,2}$ = 4.2 Hz, H1), 4.32 (dd, 1 H, $J_{6(ax),6(eq)}$ = 10.3 Hz, $J_{6(eq),5}$ = 4.9 Hz, H6(eq)), 4.19 (ddd, 1 H, $J_{5,6(ax)} = J_{5,4}$ = 10.0 Hz, $J_{5,6(eq)}$ = 5.1 Hz, H5), 3.73–3.65 (m, 2 H, H6(ax), H4), 3.65–3.48 (m, 2 H, H8), 3.41 (s, 3 H, O*Me*), 2.76 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12), 2.44 (d, 3 H, $J_{Me,10}$ = 1 Hz, C$H_3$), 2.37 (ddd, $J_{1,2} = J_{2,7}$ = 3.9 Hz, $J_{2,7'}$ = 11.2 Hz, H2), 2.28 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12'), 1.47–1.20 (m, 2 H, H7), 0.88 (s, 9 H, Si*t*-*Bu*), 0.03 (s, 6 H, Si$Me_2$). Anal. Calcd for $C_{27}H_{40}O_6Si$: C, 66.36; H, 8.25. Found: C, 66.47; H, 8.45.

**Spiro[(methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-(2-hydroxyethyl)-α-D-allopyranoside)-3,4-(3-methyl-2-cyclopenten-1-one)] (33b).** A mixture of enone **33a** (220 mg, 0.5 mmol) and tetrabutylammonium fluoride (0.45 mL, 1.1 M in tetrahydrofuran, 0.49 mmol) in tetrahydrofuran (5 mL) was stirred at room temperature for 20 min, concentrated in vacuo, and passed through a short column of silica gel (80% EtOAc/petroleum ether) to give the alcohol as a white solid in quantitative yield: mp 62–63 °C; $R_f$ 0.28 (80% EtOAc/petroleum ether); $[\alpha]^{20}_D$ −44.6° (*c* 1.1, $CHCl_3$); IR ($CHCl_3$) 3450, 1695, 1610 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5 H, aromatic), 6.02 (br s, 1 H, H10), 5.52 (s, 1 H, PhC*H*), 4.76 (d, 1 H, *J* = 4.3 Hz, H1), 4.33 (dd, 1 H, $J_{6(eq),6(ax)}$ = 10.3 Hz, $J_{6(eq),5}$ = 5.0 Hz, H6(eq)), 4.19 (ddd, 1 H, $J_{5,6(ax)} = J_{5,4}$ = 9.9 Hz, $J_{5,6(eq)}$ = 5.1 Hz, H5), 3.69 (d, 1 H, $J_{5,4}$ = 9.8 Hz, H4), 3.67 (dd, 1 H, $J_{6(ax),6(eq)} = J_{6(ax),5}$ = 10.1 Hz, H6(ax)), 3.73–3.52 (m, 2 H, H8), 3.40 (s, 3 H, O*Me*), 2.79 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12), 2.45 (d, 3 H, $J_{Me,10}$ = 12 Hz, C$H_3$), 2.38 (ddd, $J_{1,2} = J_{2,7}$ = 4.3 Hz, $J_{2,7'}$ = 11.7 Hz, H2), 2.29 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12'), 1.61 (br s, 1 H, OH), 1.55–1.25 (m, 2 H, H7). Anal. Calcd for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found: C, 67.44; H, 7.25.

**Spiro[(methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-*C*-(2-iodoethyl)-α-D-allopyranoside)-3,4-(3-methyl-2-cyclopenten-1-one)] (34).** A mixture of the alcohol **33b** (70 mg, 0.19 mmol), triphenylphosphine (196 mg, 0.75 mmol), and imidazole (51 mg, 0.75 mmol) in toluene (5 mL) under argon was treated with iodine (142 mg, 0.56 mmol) in three portions. The reaction mixture was stirred at room temperature for 5 min, followed by addition of saturated aqueous sodium bisulfite (2 mL). After all solids had dissolved, ethyl acetate (10 mL) was added, and the organic layer was washed with saturated aqueous sodium bicarbonate solution (2 × 3 mL) and brine (3 mL) and then dried ($Na_2SO_4$). Evaporation of the solvent, followed by flash chromatography (20% EtOAc/petroleum ether), gave **34** as a yellow pale solid (84 mg, 93%): mp 156–157 °C dec; $R_f$ 0.30 (20% EtOAc/petroleum ether); $[\alpha]^{20}_D$ −26.4° (*c* 0.8, $CHCl_3$); IR ($CHCl_3$) 1700, 1620 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.37–7.30 (m, 5 H, aromatic), 6.02 (m, 1 H, H10), 5.53 (s, 1 H, PhC*H*), 4.67 (d, 1 H, $J_{1,2}$ = 4.3 Hz, H1), 4.34 (dd, 1 H, $J_{6(eq),6(ax)}$ = 10.3 Hz, $J_{6(eq),5}$ = 5.1 Hz, H6(eq)), 4.18 (ddd, 1 H, $J_{6(ax),5} = J_{5,4}$ = 9.9 Hz, $J_{5,6(eq)}$ = 5.1 Hz, H5), 3.73 (d, 1 H, $J_{4,5}$ = 9.9 Hz, H4), 3.68 (dd, 1 H, $J_{6(ax),6(eq)} = J_{6(ax),5}$ = 10.2 Hz, H6(ax)), 3.43 (s, 3 H, O*Me*), 3.35–3.29 (m, 1 H, H8), 2.98 (ddd, 1 H, $J_{8,8'} = J_{8',7}$ = 10.8 Hz, $J_{8',7'}$ = 5.4 Hz, H8'), 2.79 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12), 2.44 (d, 1 H, $J_{Me,10}$ = 1.1 Hz, C$H_3$), 2.40–2.32 (m, 1 H, H2), 2.31 (d, 1 H, $J_{12,12'}$ = 17.9 Hz, H12'), 1.74–1.41 (m, 2 H, H7). Anal. Calcd for $C_{21}H_{25}IO_5$: C, 52.08; H, 5.20. Found: C, 52.19; H, 5.20.

**Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-α-D-allopyranosido[3,2-*c*]-3-methylbicyclo[3.3.0]octanone (35).** Compound **34** was cyclized as described above for **27b**: yield 94%; mp 88–89 °C; $R_f$ 0.33 (20% EtOAc/petroleum ether); $[\alpha]^{20}_D$ +8.1° (*c* 1.05, $CHCl_3$); IR ($CHCl_3$) 1740 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$), δ 7.42–7.31 (m, 5 H, aromatic), 5.49 (s, 1 H, PhC*H*), 4.59 (d, 1 H, $J_{1,2}$ = 5.6 Hz, H1), 4.31 (dd, 1 H, $J_{6(ax),6(eq)}$ = 10.1 Hz, $J_{6(eq),5}$ = 5.1 Hz, H6(eq)), 4.17 (ddd, $J_{6(ax),5} = J_{5,4}$ = 10.0 Hz, $J_{5,6(eq)}$ = 5.1 Hz, H5), 3.77 (d, 1 H, $J_{4,5}$ = 10.0 Hz, H4), 3.63 (dd, 1 H, $J_{6(ax),5} = J_{6(ax),6(eq)}$ = 10.0 Hz, H6(ax)), 3.38 (s, 3 H, O*Me*), 2.65–2.21 (m, 5 H, H12, H10, H2), 2.04–1.63 (m, 4 H, H7, H8), 1.61 (s, 3 H, C$H_3$). Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.29; H, 7.52.