Formal Synthesis of D-*myo*-Inositol 1,4,5-Tris(dihydrogen phosphate): Cyclization by an Unusual Ene Reaction and Use of the Bu_2SnCl_2/Bu_2SnH_2 Reagent for Generating an Equatorial Alcohol

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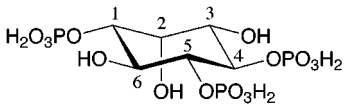
D-Glucose was converted into the propargyl silane aldehyde **5**, which, on treatment with camphorsulfonic acid, cyclized with retention of silicon. The allenic product (**7**) was elaborated via ketone **24** into **4**, which had previously been converted into D-*myo*-inositol 1,4,5-tris(dihydrogen phosphate). Selective reduction of the advanced intermediate **24** was accomplished with Bu_2SnCl_2/Bu_2SnH_2, a reagent mixture that shows a very strong preference for generating equatorial alcohols. The cyclization step leading to allene **7** was studied by examining a number of model compounds; the unusual retention of silicon appears to be limited to highly oxygenated substrates, such as **5** and its all-benzyl analogue (**27**).

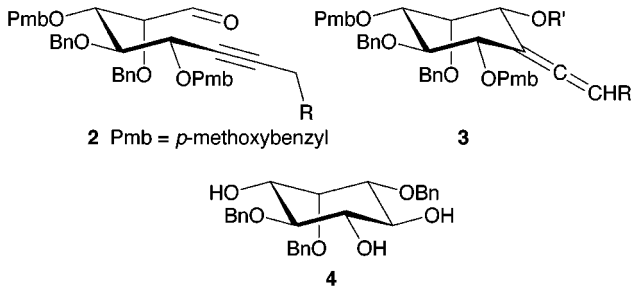
Introduction and Discussion

We report full details[1] of a formal synthesis of D-*myo*-inositol-1,4,5-tris(dihydrogen phosphate) (**1**) in optically pure form, starting from D-glucose. Our approach illustrates the use of the reagent system Bu_2SnCl_2/Bu_2SnH_2 for conversion of a cyclohexanone into the corresponding equatorial alcohol in circumstances where conventional reagents gave the axial isomer. The ketone that we reduce was itself made by an unusual ene reaction. We also describe a general survey of that ene reaction and conclude that it probably works only for highly oxygenated substrates.



1

Inositol phosphates play an essential role in the coupling of cell surface receptors to cellular responses, and the chemistry and biochemistry of these compounds have been reviewed extensively.[2] D-*myo*-Inositol 1,4,5-tris(dihydrogen phosphate) (**1**) is a very important messenger in the metabolism of calcium, and consequently, it has been the object of a great deal of synthetic work.[2,3] A resolution is usually employed in the synthesis of optically pure **1**,[2,4] but there are a few methods by which it has been obtained from compounds in the chiral pool; (−)-quinic acid,[5] D-pinnitol,[6] and D-glucose[7,8] have been used for this purpose. In the case of glucose, the pyranose ring was converted into the required carbocycle by Ferrier[9] rearrangement. Our synthesis is based on a type of ene[10,11] reaction for converting a linear chain into a carbocycle. The plan was to convert D-glucose into acetylenic aldehyde (**2**), where the group R is chosen so as to facilitate an ene reaction that would afford **3** (R′ = H or other atom). The latter seemed properly constituted for elaboration into **4**, which had been converted[12] by others into D-*myo*-inositol 1,4,5-tris(dihydrogen phosphate). However, compound **2** (R = H) did not behave in the required manner; little, if any, cyclization was observed under the conditions we tried,[13] and so we prepared the silicon-substituted analogue **5** (≡ **2**, R = $SiMe_3$), in the expectation that the ene pathway (Scheme 1) would be facili-



(1) Preliminary communication: Clive, D. L. J.; He, X.; Postema, M. H. D.; Mashimbye, M. J. *Tetrahedron Lett*. **1998**, *39*, 4231−4234.

(2) (a) Billington, D. C. *The Inositol Phosphates*; VCH: Weinheim, 1993. (b) Potter, B. V. L.; Lampe, D. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1933−1972.

(3) Tethered versions of inositol phosphates: Prestwich, G. D. *Acc. Chem. Res*. **1996**, *29*, 503−513.

(4) (a) For an example of an enzymatic resolution, see: Ling, L.; Ozaki, S. *Tetrahedron Lett*. **1993**, *34*, 2501−2504. (b) For an example of chemical resolution, see: Aguiló, A.; Martín-Lomas, M.; Penadés, S. *Tetrahedron Lett*. **1992**, *33*, 401−404.

(5) Falk, J. R.; Yadagiri, P. *J. Org. Chem*. **1989**, *54*, 5851−5852.

(6) Tegge, W.; Ballou, C. E. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 94−98.

(7) Sato, K.; Bokura, M.; Taniguchi, M. *Bull. Chem. Soc. Jpn*. **1994**, *67*, 1633−1640.

(8) Tethered versions of **1** have also been made from glucose: see ref 3.

(9) Ferrier, R. J.; Middleton, S. *Chem. Rev*. **1993**, *93*, 2779−2831.

(10) Review on ene reaction: Snider, B. B. In *Comprehensive Organic Synthesis: Selectivity, Strategy, and Efficiency in Modern Organic Chemistry*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, pp 1−27.

(11) For use of an intramolecular pinacol coupling in inositol synthesis, see: (a) Guidot, J. P.; Gall, T. Le; Mioskowski, C. *Tetrahedron Lett*. **1994**, *35*, 6671−6674. (b) Chiara, J. L.; Martín-Lomas, M. *Tetrahedron Lett*. **1994**, *35*, 2969−2972.

(12) (a) Racemic series: Yu, K.-L.; Fraser-Reid, B. *Tetrahedron Lett*. **1988**, *29*, 979−982. (b) Optically active series: Dreef, C. E.; Tuinman, R. J.; Elie, C. J. J.; van der Marel, G. A.; van Boom, J. H. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 395−397.

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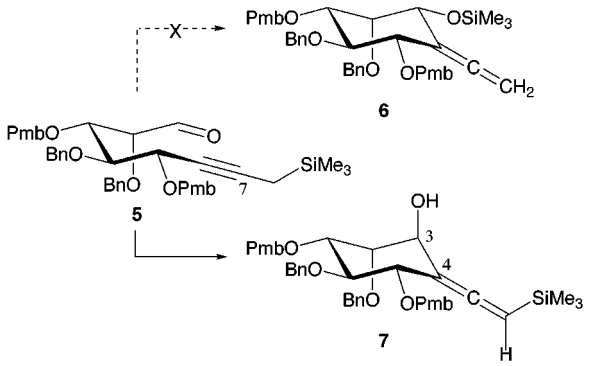
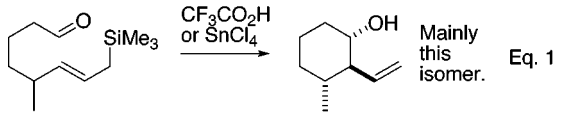
Scheme 1[a]



[a] Pmb = *p*-methoxybenzyl.

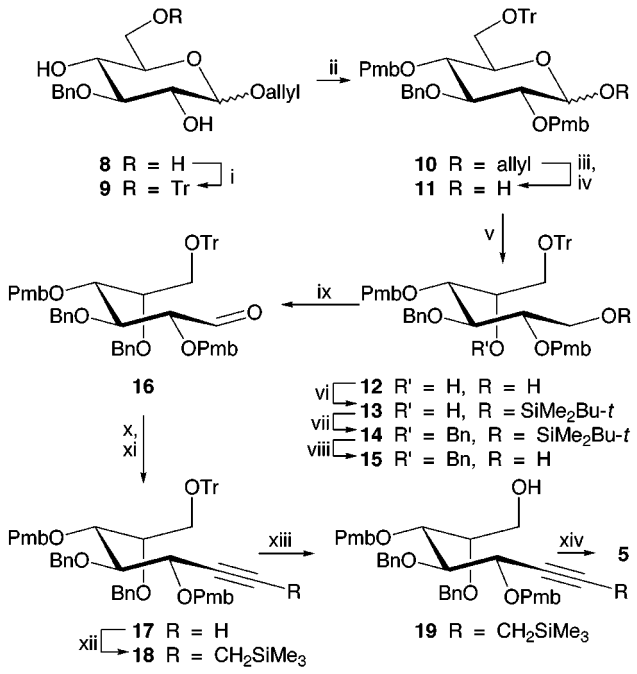
tated, either in the sense **5** → **6**[14] (with subsequent hydrolysis of the silyl ether) or with direct loss[15] of the silicon unit. This expectation was based on the fact that *allyl* silanes are known[18] to undergo cyclizations[19] (see eq 1[18a]) formally related to the process we wanted. In the



event, cyclization was now easily effected (in the presence of camphorsulfonic acid), but the silicon unit did not migrate, nor was it lost; instead, **5** was transformed stereoselectively into **7**.[20]

Aldehyde **5** was prepared as summarized in Scheme 2. D-Glucose was converted in three steps[21] (76% overall) into the allyl[22] glucopyranosides **8**. The C(6) primary hydroxyl was protected by tritylation (**8** → **9**; TrCl, pyridine, DMAP, 110 °C, 80%) and the remaining two hydroxyls by conversion into their *p*-methoxybenzyl ethers [**9** → **10**; *p*-$MeOC_6H_4CH_2Cl$ (PmbCl), NaH, THF,

Scheme 2[a]



[a] (i) TrCl, pyridine, DMAP, 110 °C, 8 h, 80%; (ii) NaH, PmbCl, 0 °C to room temperature, then reflux, 24 h, 91%; (iii) *t*-BuOK, DMSO, 100 °C, 1 h; (iv) $HgCl_2$, HgO, acetone−water, room temperature, 4 h, 88% from **10**; (v) $LiAlH_4$, THF, 0 °C to room temperature, 4 h, 93%; (vi) *t*-$BuMe_2SiCl$, Et_3N, DMAP, CH_2Cl_2, room temperature, 16 h, 99%; (vii) NaH, BnBr, 0 °C to room temperature, then reflux, 24 h, 96%; (viii) Bu_4NF, THF, room temperature, 4 h, 92%; (ix) Swern oxidation, 89%; (x) Ph_3P, CBr_4, CH_2Cl_2, −20 °C, then cool to −60 °C and add Et_3N, then warm to room temperature, 83%; (xi) *n*-BuLi, THF, −78 °C, 85%; (xii) *n*-BuLi, HMPA, THF, −78 °C, $Me_3SiCH_2OSO_2CF_3$, room temperature, overnight, 82%; (xiii) CSA, MeOH, CH_2Cl_2, room temperature, 36 h, 94%; (xiv) Swern oxidation, 92%.

reflux, 91%]. At that point deallylation could be effected by the two-step method of double-bond isomerization, using Wilkinson's catalyst,[23] or *t*-BuOK in hot (110 °C) DMSO,[24] followed by hydrolysis[25] of the resulting enol ethers, catalyzed by Hg^{2+} ($HgCl_2$, HgO, acetone−water, room temperature). Both procedures gave similar yields overall [92% with use of $(Ph_3P)_3RhCl$ and 88% with *t*-BuOK], but the base-induced isomerization was more economical. The resulting lactols (**11**) were reduced to the glucitol **12** ($LiAlH_4$, THF, 0 °C to room temperature, 93%), and the primary hydroxyl was silylated (**12** → **13**; *t*-$BuMe_2SiCl$, Et_3N, DMAP, CH_2Cl_2, room temperature, 99%) so that the remaining secondary hydroxyl could be benzylated (**13** → **14**; NaH, BnBr, THF, reflux, 96%). Next, removal of the silyl group (**14** → **15**; Bu_4NF, THF, room temperature, 92%) and Swern oxidation (**15** → **16**; 89%) brought us to the appropriate stage for construction of the ethynyl unit. This was initiated (**16** → **17**) by sequential treatment with $CBr_4/Ph_3P/Et_3N$ (−60 °C to room temperature, 83%) and *n*-BuLi (THF, −78 °C, 85%).[26] Deprotonation of **17** with *n*-BuLi, and reaction with $Me_3SiCH_2OSO_2CF_3$ (HMPA, THF, room temperature, 82%), then completed the required propargyl silane

(13) Thermolysis (140 °C, *p*-xylene): no cyclization. TFA in CH_2Cl_2 at 0 °C: decomposition. TFA in $CHCl_3$ at room temperature: decomposition. Camphorsulfonic acid in CH_2Cl_2 or $CHCl_3$ at room temperature: decomposition. Me_2AlCl, CH_2Cl_2, −78 °C: little, if any cyclization product.

(14) For related cyclizations involving allyl silanes (with loss of silicon), see: Schinzer, D. *Synthesis* **1988**, 263−273.

(15) α,β-Unsaturated ketones incorporating a suitably located propargyl silane unit undergo cyclization with loss of silicon (see ref 16). For a single example of cyclization onto a carbonyl, also with loss of silicon, see ref 17.

(16) (a) Schinzer, D.; Dettmer, G.; Ruppelt, M.; Sólyom, S.; Steffen, J. *J. Org. Chem*. **1988**, *53*, 3823−3828. (b) Schinzer, D.; Kabbara, J.; Ringe, K. *Tetrahedron Lett*. **1992**, *33*, 8017−8018. (c) Schinzer, D.; Ringe, K. *Synlett* **1994**, 463−464. (d) Schinzer, D.; Ruppelt, M. *Ber*. **1991**, *124*, 247−248.

(17) Schinzer, D.; Panke, G. *J. Org. Chem*. **1996**, *61*, 4496−4497.

(18) E.g., (a) Asao, K.; Iio, H.; Tokoroyama, T. *Tetrahedron Lett*. **1989**, *30*, 6397−6400. (b) Yamamoto, Y.; Asao, N. *Chem. Rev*. **1993**, *93*, 2207−2293.

(19) For *intermolecular* reactions of propargyl silanes with electrophiles, see: (a) Pornet, J.; Aubert, P.; Randrianoélina, B.; Miginiac, L. *Tetrahedron Lett*. **1984**, *25*, 651−654. (b) Pornet, J.; Randrianoélina, B.; Miginiac, L. *J. Organomet. Chem*. **1994**, *481*, 217−225.

(20) For cyclizations of allenyl silanes that occur with retention of silicon, and for which the presence of the silicon substituent is essential, see: (a) Jin, J.; Smith, D. T.; Weinreb, S. M. *J. Org. Chem*. **1995**, *60*, 5366−5367. (b) Weinreb, S. M.; Smith, D. T.; Jin, J. *Synthesis* **1998**, 509−521. (c) Cf. Esch, P. M.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett*. **1988**, *29*, 367−370.

(21) Fukase, K.; Matsumoto, T.; Ito, N.; Yoshimura, T.; Kotani, S.; Kusumoto, S. *Bull. Chem. Soc. Jpn*. **1992**, *65*, 2643−2654.

(22) Exploratory studies guided our choice of *allyl* glycosides, as we found indications that hydrolysis of *methyl* glycosides was not possible without loss of *p*-methoxybenzyl groups (which we wished to use for protection of two of the hydroxyls).

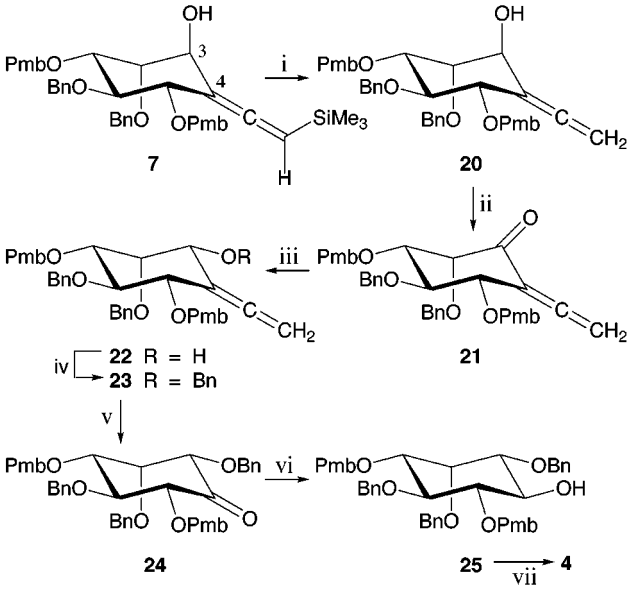
(23) Corey, E. J.; Suggs, J. W. *J. Org. Chem*. **1973**, *38*, 3224.

(24) Cunningham, J.; Gigg, R.; Warren, C. D. *Tetrahedron Lett*. **1964**, 1191−1196.

(25) Grigg, R.; Warren, C. D. *J. Chem. Soc. C* **1968**, 1903−1911.

(26) Grandjean, D.; Pale, P.; Chuche, J. *Tetrahedron Lett*. **1994**, *35*, 3529−3530.

Scheme 3[a]



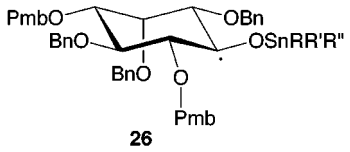
[a] (i) K_2CO_3, 3:1 MeOH−THF, reflux, 4 h, 86%; (ii) Dess−Martin periodinane, CH_2Cl_2, 30 min, 84%; (iii) $NaBH_4$, $CeCl_3 \cdot 7H_2O$, 1:10 THF−MeOH, −78 °C to 0 °C, 92%; (iv) NaH, BnBr, 0 °C to room temperature, then reflux, 24 h, 87%; (v) O_3 (<1 equiv), 1:6 pyridine−CH_2Cl_2, −78 °C, 80% after correction for recovered **23** (27%); (vi) 1:1 *n*-Bu_2SnCl_2/*n*-Bu_2SnH_2, PhMe, reflux, 24 h, 88%; (vii) DDQ, 1:20 water−CH_2Cl_2, room temperature, 4 h, 70%.

unit (**17** → **18**). Finally, detritylation (**18** → **19**; camphorsulfonic acid, MeOH, room temperature) was accomplished in 94% yield, with no loss of the silyl group, and Swern oxidation (92%) gave the key aldehyde **5** for ene cyclization.

Our first experiments, in which **5** was exposed to potentially suitable reagents ($TiCl_4$, $BF_3 \cdot Et_2O$, CF_3CO_2H, TBAF[27]), were unpromising.[28] Fortunately, however, a sample of **5** that had been stored for a few days in a mixture of CH_2Cl_2 and $CDCl_3$ was examined, and we found that the compound had been partially converted into a new substance, which was subsequently fully characterized as **7**. A small amount of the corresponding desilylated material (see **20** in Scheme 3) was also isolated. The conditions for the unusual ring closure with retention of silicon were optimized, it being found that use of CSA in PhMe gave **7** in 91% yield.

Conversion of **7** into **4** required a number of apparently simple operations: stereochemical inversion at C(3), benzylation of the resulting alcohol, oxidative cleavage of the exocyclic double bond at C(4), and reduction of the resulting carbonyl to an equatorial alcohol. These operations proved unexpectedly troublesome. However, each was eventually achieved in good yield—but only after considerable effort to establish the proper choice and sequence of reagents.

Our exploratory experiments suggested that the silyl group should be removed first, and this was done by treatment of **7** with K_2CO_3 in refluxing MeOH−THF (**7** → **20**, 86%). Oxidation, best[29] carried out with the Dess−Martin reagent in CH_2Cl_2, gave ketone **21** (84%), and then reduction, using the $NaBH_4$−$CeCl_3 \cdot 7H_2O$ system[30] in MeOH−THF at a low temperature (−78 to 0 °C), afforded (92%) the required equatorial alcohol **22**, which was easily benzylated (**22** → **23**; NaH, BnBr, THF, reflux, 87%). Ozonolysis of the allene required careful control, and our optimized procedure calls for a deficiency of O_3 in CH_2Cl_2−pyridine at −78 °C.[31] This procedure allows isolation of the ketone **24** in 80% yield [after correction for recovered **23** (27%)]. Reduction of **24** in the correct stereochemical sense (to the *equatorial* alcohol **25**) required a good deal of effort, as formation of the undesired *axial* alcohol was observed with all the conventional hydride reducing agents we tried.[32] Moreover, attempts[33] to invert the axial into the equatorial alcohol proved fruitless. We were eventually led to consider a stannane-based method for reduction, because we expected the intermediate radical[34] (see **26**) to abstract hydrogen from



26

the conformation shown (with the bulky $OSnR_3$ group equatorial). Examination of the literature on the stannane reduction of ketones brought to our attention the use of Bu_2SnHCl[35] for reduction of α-alkoxy cyclohexanones to equatorial alcohols. The reagent is generated in situ from Bu_2SnH_2 and Bu_2SnCl_2.[36] An equilibrium is, apparently, set up with Bu_2SnHCl.[37] When we used this reagent system in THF at room temperature, we obtained a 1:2 ratio of equatorial to axial alcohols. In refluxing THF, the ratio improved to 2:1 in favor of the desired equatorial alcohol, but in refluxing PhMe, only the equatorial alcohol was formed (**24** → **25**, 88%). The mechanism of reduction by Bu_2SnHCl has been sug-

(27) Cf. Pornet, J. *Tetrahedron Lett.* **1981**, *22*, 455−456.

(28) TFA, CH_2Cl_2, 0 °C: no reaction. $BF_3 \cdot Et_2O$, CH_2Cl_2, −78 °C: complex mixtures. TBAF, THF, 0 °C: complex mixtures. $TiCl_4$, CH_2Cl_2, −78 °C: some cyclization (<39%) probably occurred.

(29) We also tried MnO_2, PDC, PCC, Swern, TPAP−NMO.

(30) (a) Luche, J.-L. *J. Am. Chem. Soc.* **1978**, *100*, 2226−2227. (b) Luche, J.-L.; Rodriguez-Hahn, L.; Crabbé, P. *J. Chem. Soc., Chem. Commun.* **1978**, 601−602.

(31) Cf. (a) Slomp, G.; Jr.; Johnson, J. L. *J. Am. Chem. Soc.* **1958**, *80*, 915−921. (b) Boddy, I. K.; Boniface, P. J.; Cambie, R. C.; Craw, P. A.; Huang, Z.-D.; Larsen, D. S.; McDonald, H.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1984**, *37*, 1511−1529.

(32) E.g., various versions of the Meerwein−Ponndorf−Verley reduction [$Al(OPr\text{-}i)_3$-*i*-PrOH; $Sc(OSO_2CF_3)_3$-*i*-PrOH; $Ce(OPr\text{-}i)_3$-*i*-PrOH] and use of SmI_2 in *i*-PrOH or THF−H_2O gave complex mixtures; $Al(OPr\text{-}i)_2(OCOCF_3)$ or $BH_3 \cdot Me_2S$ did not react; DIBAL, DIBAL/methylaluminum bis(2,6-di-*tert*-butylphenoxide) [MAD], $NaBH_4$/MAD and Bu_4NBH_4/MAD gave the axial alcohol; $NaBH(OAc)_3$−AcOH apparently gave an epimer mixture containing a trace (^1H NMR) of the desired equatorial alcohol. For relevant examples of reduction to equatorial alcohols, see: (a) Evans, D. A.; Kaldor, S. W.; Jones, T. K.; Clardy, J.; Stout, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7001−7031. (b) Corey, E. J.; Hopkins, P. B.; Kim, S.; Yoo, S.-e.; Nambiar, K. P.; Falck, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7131−7134.

(33) Treatment of the derived triflate with AcOK in DMF; AcOCs in DMF; KOCHO, 18-crown-6 in DMF; CF_3COONa, 18-crown-6 in DMF gave none of the desired product. Use of AcOCs, 18-crown-6 in refluxing PhH or of KO_2 in DMSO−DMF (followed by treatment with Ph_3P) each gave a trace of the desired products. Use of KONO, 18-crown-6 in DMF, followed by water at reflux, gave the equatorial alcohol in about 40% yield. The system was prone to dehydration under Mitsunobu conditions.

(34) Radical stannane reduction of ketones has been reported, but is not an established synthetic method: Cf. (a) Kupchik, E. J. In *Organotin Compounds*; Sawyer, A. K., Ed.; Dekker: New York, , 1971; p 49. (b) Kuivila, H. G. *Synthesis* **1970**, 499−509.

(35) (a) Martin, S. F.; Josey, J. A.; Wong, Y.-L.; Dean, D. W. *J. Org. Chem.* **1994**, *59*, 4805−4820. (b) Shibata, I.; Yoshida, T.; Kawakami, T.; Baba, A.; Matsuda, H. *J. Org. Chem.* **1992**, *57*, 4049−4051.

(36) (a) Neumann, W. P.; Pedain, J. *Tetrahedron Lett.* **1964**, 2461−2465. (b) Sawyer, A. K.; Brown, J. E.; Hanson, E. L. *J. Organomet. Chem.* **1965**, *3*, 464−471.

(37) For the composition of the reagent, see: Davies, A. G.; Osei-Kissi, D. K. *J. Organomet. Chem.* **1994**, *474*, C8−C10.

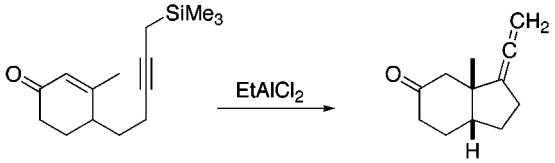
gested[38] to involve a radical process, but the reagent is known[39] to reduce α-(phenylseleno) ketones (albeit in very poor yield) with preservation of the phenylseleno group, and this behavior suggests that, at least in those reactions, a radical mechanism is not involved. In our case, the correlation between temperature and the axial/equatorial ratio may reflect the operation of competing ionic and radical mechanisms.

Finally, having reached **25**, oxidative removal of the *p*-methoxybenzyl groups (DDQ, water−CH_2Cl_2, room temperature, 70%) gave the target compound (**4**), which is convertible[12] by phosphorylation and deprotection into D-*myo*-inositol 1,4,5-tris(dihydrogen phosphate) (**1**).

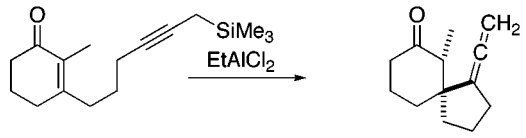
In principle, other inositol phosphates[40] may be accessible by the method described here, but we have not tested this possibility. The outcome of any such attempts would depend on the generality of both the ene cyclization for other oxygenated acetylenes and the stereochemical outcome of the stannane reduction. We have, however, made a number of observations on the ene process.

Observations on the Closure of Propargyl Silanes onto Aldehyde Groups

Several cases have been reported in which α,β-unsaturated ketones incorporating a suitably located propargyl silane unit undergo cyclization to afford allenes that contain a spiro-fused or linearly fused bicyclic structure, as illustrated in eqs 2[16a] and 3.[16a] The silicon

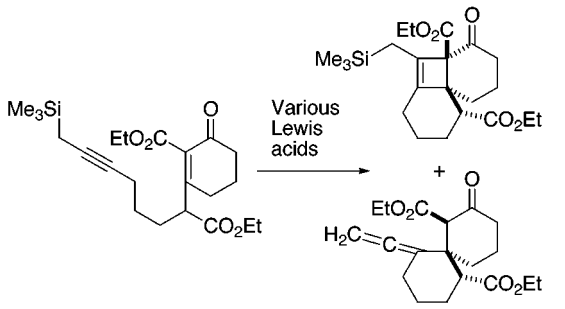


Eq. 2



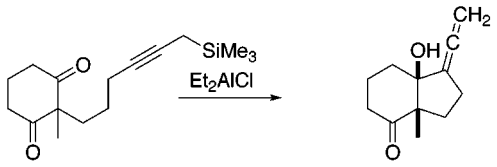
Eq.3

group is lost[41] during the cyclization, except in one case (eq 4),[42] where the expected product was accompanied by a substance arising formally by [2 + 2] cycloaddition.



Eq. 4

Reactions such as those given in eqs 2 and 3, and related processes,[43] have been examined in some detail[16] and used in natural product synthesis.[44] However, related cyclizations directly onto a carbonyl group have received little attention, and we know of only one prior example (see eq 5).[17]



Eq. 5

In view of the unexpected retention of silicon in the inositol work described above, we investigated the closure of propargyl silanes onto aldehyde carbonyls (see Table 1) and have also examined corresponding cyclizations with ketones and acetals.[45] The reaction is a general route to five- and six-membered carbocycles, but only in certain situations is the silicon group retained.[20]

The starting materials **27**−**34** (see Table 1) were prepared by standard reactions, as follows: **27** (Scheme 4), **28** (Scheme 5), **29** (Scheme 6), **30** (Scheme 7), **32** (Scheme 8), **34** (Scheme 9). Ketals **31** and **33** were made by ketalization of **29** and **32** (see Supporting Information), respectively.

In studying the ene reaction, we tried Lewis acids, as well as CF_3CO_2H, CSA, and TBAF. With the highly oxygenated substances **5** (Scheme 1) and **27** (Table 1, entry 1) and ketals **31** and **33** (Table 1, entries 6 and 8), the silicon unit is retained. The structure of **27a** was established by X-ray analysis, and the similarity of the ^{1}H NMR signal for the vinyl hydrogen with the corresponding signal for **7** suggested that **27a** and **7** have the same stereochemistry, and the fact that the hydroxyl in **7** is axial was subsequently confirmed by conversion of **7** into **4**. The preferred conformation of **28a** is tentatively assigned as shown, based on the observation of a coupling constant of >3 Hz for coupling[46] between the C**H**(OH) proton and the allene C**H**$_2$. An equatorial hydrogen would be associated with a *J* of 1.2 Hz.[46] The stereochemical assignments to **29a** and **29b** were made on the basis of

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(42) (a) Spence, J. D.; Lowrie, L. E.; Nantz, M. H. *Tetrahedron Lett*. **1995**, *36*, 5499−5502. (b) For the formation of (cyclobutylmethyl)silanes in intermolecular reactions of *allyl* silanes, see: House, H. O.; Gaa, P. C.; VanDerveer, D. *J. Org. Chem*. **1983**, *48*, 1661−1670, and references therein.

(43) (a) For use of propargyl silanes in biomimetic polyene cyclizations, see: Johnson, W. S.; Plummer, M. S.; Pulla Reddy, S.; Bartlett, W. R. *J. Am. Chem. Soc*. **1993**, *115*, 515−521. (b) For use of iminium ions in the cyclization of propargyl silanes, see: Fischer, M. J.; Overman, L. E. *J. Org. Chem*. **1990**, *55*, 1447−1459. Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett*. **1983**, *24*, 1407−1410. Hiemstra, H.; Fortgens, H. P.; Stegenga, S.; Speckamp, W. N. *Tetrahedron Lett*. **1985**, *26*, 3151−3154. Esch, P. M.; Hiemstra, H.; Klaver, W. J.; Speckamp, W. N. *Heterocycles* **1987**, *26*, 75−79. Klaver, W. J.; Moolenaar, M. J.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron* **1988**, *44*, 3805−3818.

(44) (a) Review: Langkopf, E.; Schinzer, D. *Chem. Rev*. **1995**, *95*, 1375−1408. (b) Schinzer, D.; Ringe, K.; Jones, P. G.; Döring, D. *Tetrahedron Lett*. **1995**, *36*, 4051−4054. (c) Solé, D.; Bonjoch, J.; García-Rubio, S.; Suriol, R.; Bosch, J. *Tetrahedron Lett*. **1996**, *37*, 5213−5216. (d) Klaver, W. J.; Hiemstra, H.; Speckamp, W. N. *J. Am. Chem. Soc*. **1989**, *111*, 2588−2595. (e) Hiemstra, H.; Klaver, W. J.; Speckamp, W. N. *Rec. Trav. Pays-Bas* **1986**, *105*, 299−306.

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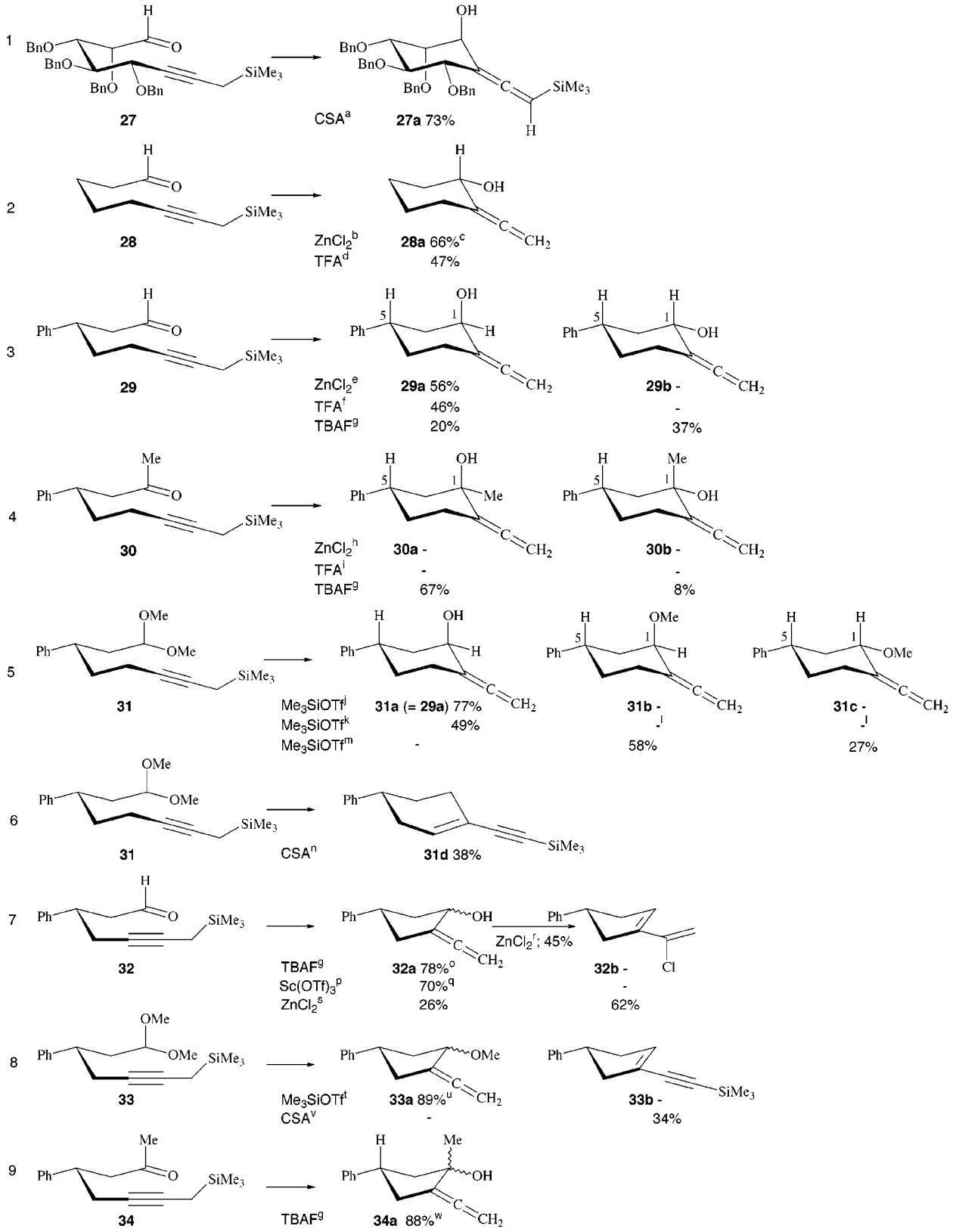
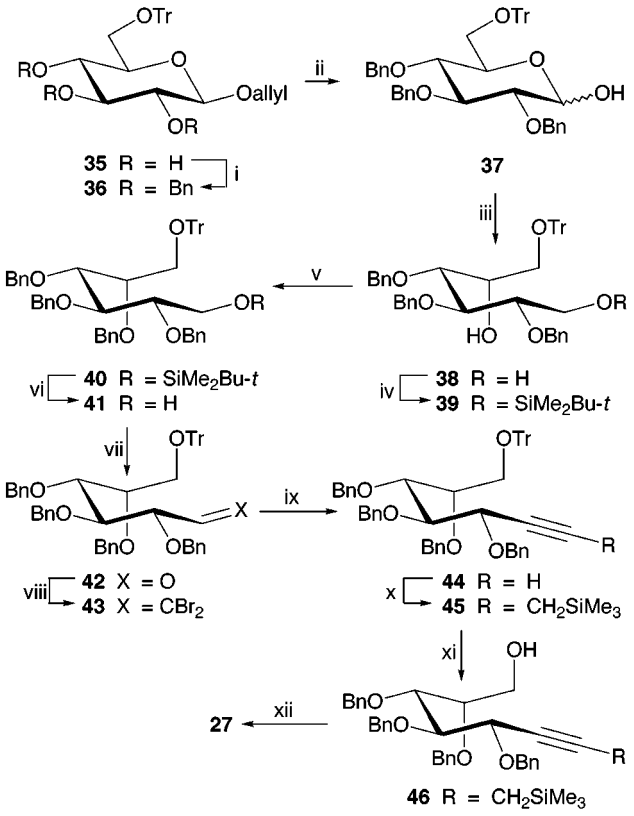
Table 1



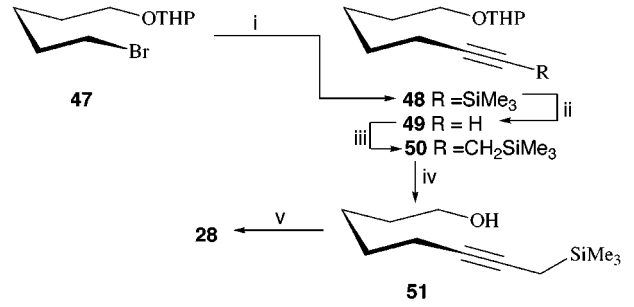
[a] CSA, PhMe, room temperature, 5 h. [b] $ZnCl_2$, CH_2Cl_2, 0 °C, 2.5 h. [c] Preferred conformation of **28a** is a tentative assignment. [d] TFA, CH_2Cl_2, −78 °C, 30 min. [e] $ZnCl_2$, CH_2Cl_2, 0 °C, 3 h. [f] TFA, CH_2Cl_2, −78 °C, 1 h. [g] TBAF, THF, 0 °C, 1 h. [h] $ZnCl_2$, CH_2Cl_2, 0 °C, 20 h; no reaction. [i] TFA, CH_2Cl_2, 0 °C, 12 h; no reaction. [j] $Me_3SiOSO_2CF_3$ (catalytic), CH_2Cl_2, −78 °C to room temperature, 11 h. [k] $Me_3SiOSO_2CF_3$ (catalytic), CH_2Cl_2, −78 °C, 3 h, yield corrected for recovered starting material. [l] A 1.2:1.0:1.3 mixture of **31** (corresponding to 13% recovery), **31b** (corresponding to 12% yield), and **31c** (corresponding to 16% yield). [m] $Me_3SiOSO_2CF_3$ (1 equiv), CH_2Cl_2, −78 °C, 3 h. [n] CSA, CH_2Cl_2, room temperature, 48 h. [o] Epimer mixture (55:45). [p] $Sc(OSO_2CF_3)_3$, $MeNO_2$, room temperature, 12 h. [q] Epimer mixture (1:1). [r] $ZnCl_2$, CH_2Cl_2, room temperature, 24 h. [s] $ZnCl_2$, CH_2Cl_2, 0 °C to room temperature, 14 h. [t] $Me_3SiOSO_2CF_3$ (1 equiv), CH_2Cl_2, −78 °C, 1.5 h. [u] Epimer mixture (3:2). [v] CSA, CH_2Cl_2, room temperature, 20 h. [w] Epimer mixture (1:7.2).

Scheme 4[a]



[a] (i) NaOH, BnCl, 120 °C, 36 h, 87%; (ii) DMSO, *t*-BuOK, 100 °C, 1 h; HgO, $HgCl_2$, acetone−water, 4 h, 88%; (iii) $LiAlH_4$, THF, 0 °C to room temperature, 4 h, 95%; (iv) *t*-$BuMe_2SiCl$, Et_3N, DMAP, CH_2Cl_2, room temperature, 16 h, 95%; (v) NaH, THF, BnBr, reflux, 14 h, 94%; (vi) TBAF, THF, room temperature, 4 h, 97%; (vii) Swern, 89%; (viii) Ph_3P, CBr_4, CH_2Cl_2, −20 °C, then cool to −60 °C and add Et_3N, then warm to room temperature, 30 min, 76%; (ix) *n*-BuLi, THF, −78 °C, 2 h, 78%; (x) *n*-BuLi, $Me_3SiCH_2OSO_2CF_3$, HMPA, THF, −78 °C to room temperature, 10 h, 78%; (xi) CSA, MeOH, room temperature, 24 h, 94%; (xii) Swern, 84%.

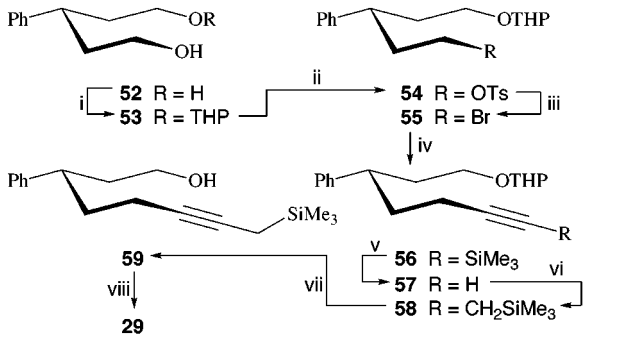
Scheme 5[a]



[a] (i) $Me_3SiC{\equiv}CH$, *n*-BuLi, THF, HMPA, −78 °C, then room temperature, 15 h, 94% after correction for recovered **47** (35%); (ii) K_2CO_3, MeOH, 0 °C, 5 h, then room temperature, 12 h, 94%; (iii) *n*-BuLi, THF, −78 °C, $Me_3SiCH_2OSO_2CF_3$, HMPA, room temperature, 18 h, 91% after correction for recovered **49** (18%); (iv) TsOH·H_2O, MeOH−water, reflux, 3 h, 93%; (v) Swern, 80%.

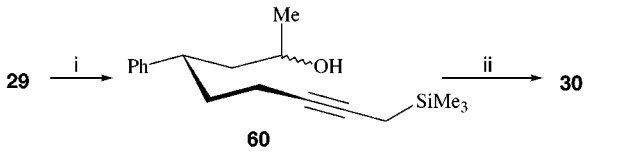
^{1}H NMR measurements: Compound **29a** has signals centered at δ 3.14 [C(5)H] and 4.57 [C(1)H], while the corresponding values for **29b** are δ 2.71 [C(5)H] and 4.15 [C(1)H]. The signal at δ 4.15 has larger *J* values than that at 4.57, as expected for an *axial* hydrogen. The acetate derived from **29a** has only small couplings (2.8 Hz) for the C(1)H signal, corresponding to an equatorial

Scheme 6[a]



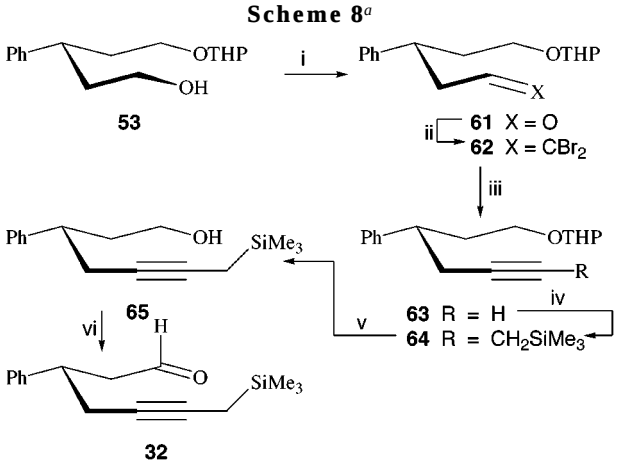
[a] (i) Dihydropyran, TsOH·H_2O, room temperature, 24 h, 66% after correction for recovered **52** (36%); (ii) TsCl, pyridine, DMAP, CH_2Cl_2, room temperature, 12 h, 63%; (iii) LiBr, acetone, reflux, 2 h, 95%; (iv) $Me_3SiC{\equiv}CH$, *n*-BuLi, THF, HMPA, −78 °C, then room temperature, 12 h, 81%; (v) K_2CO_3, MeOH−THF, 0 °C, 6 h, then room temperature, 12 h, 94%; (vi) *n*-BuLi, THF, −78 °C, $Me_3SiCH_2OSO_2CF_3$, HMPA, room temperature, 10 h, 92%; (vii) TsOH·H_2O, MeOH−water, reflux, 4 h, 89%; (viii) Swern, 90%.

Scheme 7[a]



[a] (i) MeMgBr, Et_2O, 0 °C to room temperature, 2 h, 90%; (ii) PCC, 3 Å molecular sieves, CH_2Cl_2, 25 min, 90%.

Scheme 8[a]

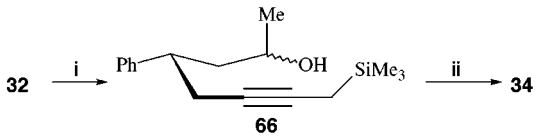


[a] (i) PCC, 3 Åmolecular sieves, CH_2Cl_2, 35 min, 82%; (ii) Ph_3P, CBr_4, CH_2Cl_2, −20 °C, then cool to −60 °C and add Et_3N, then warm to room temperature, 30 min, 76%; (iii) *n*-BuLi, THF, −78 °C, 2 h, then room temperature, 30 min, 94%; (iv) *n*-BuLi, THF, −78 °C, $Me_3SiCH_2OSO_2CF_3$, HMPA, room temperature, 10 h, 86%; (v) TsOH·H_2O, MeOH−water, reflux, 3.5 h, 98%; (vi) PCC, 3 Å molecular sieves, CH_2Cl_2, 30 min, 90%.

hydrogen [C**H**(OAc)]. The tentative stereochemical assignments to **30a** and **30b** were made on the basis that the signal for C(5)H in **30a** is at lower field than in **30b** (δ 3.14 versus 2.78). Similar arguments were used in the case of **31b** and **31c** to make the tentative assignments shown.[47] The epimers of **32a** and **33a** were not separated, and no stereochemical assignments were made for these

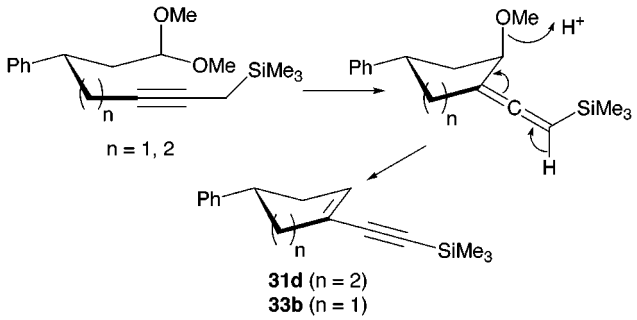
(47) The sensitivity of the ratio **31a**:**31b**:**31c** to changes in reaction conditions is difficult to understand. We did not monitor the purity of the $Me_3SiOSO_2CF_3$ in these experiments.

Scheme 9[a]



[a] (i) MeMgBr, Et_2O, 0 °C, 2 h, 90%; (ii) PCC, 3 Å molecular sieves, CH_2Cl_2, 30 min, 92%.

Scheme 10



compounds or for **34a**, which was also obtained as a chromatographically inseparable mixture.

We interpret the formation of **31d** and **33b** according to the process of Scheme 10, where the stereochemistry shown for the intermediate allenic silanes is arbitrary.

Our experiments with **5** (Scheme 1), **27** (Table 1), and **2** (R = H) show that the silicon unit is needed for the cyclization to occur. Possibly, the transition state has a partial positive charge on C(7) (see structure **5** for numbering), and this is stabilized by the silicon unit,[20] but it is not clear why in some cases (see Table 1) a proton is lost rather than the trimethylsilyl group. Likewise, the stereochemical outcome—OH and $SiMe_3$ *syn* and OH axial—for **5** and **27** is also difficult to interpret.

The loss of the silicon unit in those cases where best yields are obtained by use of TBAF (Table 1, entries 4, 7, and 9) is expected, as the process would be initiated by F^- attack on silicon.[27]

Although the mechanistic details are unclear, the cyclization of *ω*-formyl propargyl silanes represents a route to carbocycles that incorporate an allene[48] appendage; in favorable cases the yield is good and the reaction can be highly stereoselective.

Experimental Section

General Procedures. Unless stated to the contrary, the general procedures used previously[49] were followed. Optical rotations were measured at room temperature.

The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate zero, one, two, or three attached hydrogens, respectively. Where the number of ^{13}C NMR signals is less than expected, we assume that this is due to overlap of signals.

2-Propenyl 3-*O*-(Phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucopyranoside (9). Dry pyridine (130 mL) was added to a dry 250 mL round-bottomed flask charged with triol **8**[21,50] (10.32 g, 33.25 mmol), Ph_3CCl (13.91 g, 49.89 mmol), and DMAP (400 mg, 3.27 mmol). The mixture was heated at 110 °C for 8 h, cooled to room temperature, and evaporated. The residue was dissolved in CH_2Cl_2 (200 mL), washed sequentially with cold (4 °C) aqueous hydrochloric acid (0.5 M, 2 × 50 mL), saturated aqueous $NaHCO_3$ (1 × 50 mL), and brine (1 × 50 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (6 × 24 cm), using 2:8 EtOAc—hexane, gave diols **9** (14.62 g, 80%) as a pure (^1H NMR, 400 MHz), yellow solid, which was a mixture of epimers: mp 47—52 °C; $[\alpha]_D = 28.41$ (*c* 1.45, $CHCl_3$); FTIR ($CHCl_3$ cast) 3463 (br) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) *δ* 2.15 (d, *J* = 9.0 Hz, 0.64 H), 2.37 (d, *J* = 0.9 Hz, 0.64 H), 2.42 (d, *J* = 2.1 Hz, 0.36 H), 2.54 (d, *J* = 2.3 Hz, 0.36 H), 3.28—3.43 (m, 3 H), 3.50—3.80 (m, 3 H), 4.02—4.20 (m, 1 H), 4.22—4.40 (m, 1 H), 4.75—4.82 (m, 1 H), 4.89—4.95 (m, 2 H), 5.20—5.25 (m, 1 H), 5.28—5.35 (m, 1 H), 5.89—6.01 (m, 1 H), 7.18—7.55 (m, 20 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 63.8 (t′), 64.0 (t′), 68.3 (t′), 70.0 (t′), 70.4 (d′), 71.3 (d′), 71.4 (d′), 72.5 (d′), 74.1 (d′), 74.3 (d′), 74.7 (t′), 75.0 (t′), 82.9 (d′), 83.9 (d′), 86.8 (s′), 97.3 (d′), 101.6 (d′), 117.9 (t′), 127.0 (d′), 127.8 (d′), 127.9 (d′), 128.0 (d′), 128.5 (d′), 128.6 (d′), 133.7 (d′), 133.8 (d′), 138.6 (s′), 143.7 (s′), 143.8 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{35}H_{36}NaO_6$ (M + Na) 575.240959, found 575.241310. Anal. Calcd for $C_{35}H_{36}O_6$: C, 76.06; H, 6.57. Found: C, 75.82; H, 6.64.

2-Propenyl 2,4-Bis-*O*-[(4-methoxyphenyl)methyl]-3-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucopyranoside (10). NaH (80% dispersion in oil, 10.0 g, 333.0 mmol) was added portionwise to a stirred and cooled (0 °C) solution of diols **9** (30.02 g, 54.38 mmol) in THF (450 mL) over 5 min. The mixture was stirred (Ar atmosphere) for 30 min, and then *p*-methoxybenzyl chloride (45.0 mL, 333.0 mmol) was added neat in one portion by syringe. Stirring was continued at 0 °C for 15 min. The cold bath was removed, and the solution was allowed to warm to room temperature and then refluxed for 24 h. The mixture was cooled to 0 °C, and the excess of NaH was carefully decomposed by addition of MeOH (ca. 50 mL). The mixture was filtered through a pad (5 × 4 cm) of Celite which was rinsed with Et_2O (ca. 200 mL), and the solvent was evaporated. Flash chromatography of the residue over silica gel (6 × 35 cm), using 1.5:8.5 to 2:8 EtOAc—hexane, gave **10** (39.37 g, 91%) as a pure (^1H NMR, 400 MHz), off-white solid, which was a mixture of epimers: mp 41—43 °C; $[\alpha]_D = 8.8$ (*c* 2.07, $CHCl_3$); FTIR ($CHCl_3$ cast) unexceptional; ^1H NMR ($CDCl_3$, 400 MHz) *δ* 3.15—3.25 (m, 1 H), 3.35—3.50 (m, 1 H), 3.53—3.64 (m, 2 H), 3.73—3.87 (m, including singlets at *δ* 3.76, 3.77, 3.81 and 3.83, 7 H), 3.92—3.99 (m, 0.65 H), 4.05—4.12 (m, 0.65 H), 4.20—4.31 (m, 2.05 H), 4.46—4.56 (m, 0.65 H), 4.56—4.83 (m, 4 H), 4.86—4.98 (m, 2 H), 5.21—5.46 (m, 2 H), 5.92—6.13 (m, 1 H), 6.66—6.90 (m, 6 H), 7.21—7.41 (m, 16 H), 7.45—7.55 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) *δ* 55.2 (q′), 55.6 (q′), 62.5 (t′), 62.6 (t′), 68.0 (t′), 70.1 (t′), 70.5 (d′), 72.8 (t′), 74.6 (t′), 75.9 (t′), 77.6 (d′), 77.9 (d′), 79.9 (d′), 82.2 (d′), 82.3 (d′), 84.8 (d′), 86.3 (s′), 86.4 (s′), 95.3 (d′), 102.8 (d′), 113.6 (d′), 113.8 (d′), 117.3 (t′), 118.2 (t′), 126.8 (d′), 126.9 (d′), 127.5 (d′), 127.6 (d′), 127.8 (d′), 128.0 (d′), 128.1 (d′), 128.3 (d′), 128.4 (d′), 128.9 (d′), 129.2 (d′), 129.6 (d′), 129.8 (d′), 129.9 (d′), 130.1 (s′), 130.2 (s′), 130.5 (s′), 130.8 (s′), 133.9 (d′), 134.3 (d′), 138.7 (s′), 138.9 (s′), 144.0 (s′), 144.3 (s′), 159.2 (s′), 159.2 (s′), 159.3 (s′), 159.4 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{51}H_{52}NaO_8$ (M + Na) 815.355989, found 815.355280. Anal. Calcd for $C_{51}H_{52}O_8$: C, 77.25; H, 6.61. Found: C, 77.39; H, 6.56.

2,4-Bis-*O*-[(4-methoxyphenyl)methyl]-3-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucopyranose (11). (a) Use of *t*-BuOK. DMSO (45 mL) was added in one portion to a suspension of **10** (9.68 g, 12.2 mmol) and *t*-BuOK (2.73 g, 24.4 mmol). The mixture was stirred to dissolve the solids and then heated at 100 °C for 1 h. The solution was allowed to cool to room temperature and then poured into water (150 mL). The orange mixture was extracted with CH_2Cl_2 (4 × 50 mL), and the combined organic extracts were washed with water (1 × 40 mL) and brine (1 × 30 mL) and evaporated. The solid residue was dissolved in 8:1 acetone—water (40 mL), and HgO (3.96 g, 18.3 mmol) was added to the solution (stirring). A solution of $HgCl_2$ (4.97 g, 18.3 mmol) in 8:1 acetone—water (15 mL) was added dropwise, and stirring was continued for 4 h at room temperature. The mixture was filtered through a pad (5 × 4 cm) of Celite, and the pad was rinsed with acetone

(48) Chemistry of allenes. Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984.

(49) Clive, D. L. J.; Wickens, P. L.; Sgarbi, P. W. M. *J. Org. Chem.* **1996**, *61*, 7426—7437.

(50) Cf. Freudenberg, K.; Hochstetten, H. v.; Engels, H. *Ber.* **1925**, *58*, 666—671.

(50 mL). The combined filtrates were evaporated, and the residue was dissolved in CH_2Cl_2 (100 mL), washed with 20% aqueous NaI (1 × 100 mL) and brine (1 × 40 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (6 × 20 cm), using 1.5:8.5 EtOAc−hexane, gave **11** (8.07 g, 88%) as a pure (^{1}H NMR, 400 MHz), off-white solid, which was a mixture of epimers: mp 61−63 °C; $[\alpha]_D = 7.8$ (*c* 0.32, $CHCl_3$); FTIR ($CDCl_3$ cast) 3428 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.86 (d, $J = 2.1$ Hz, 0.27 H), 3.07 (d, $J = 5.3$ Hz, 0.64 H), δ 3.16−3.24 (m, 1 H), 3.40−3.47 (m, 1.35 H), 3.50−3.66 (m, 2 H), 3.67−3.81 (m, including singlets at δ 3.74, 3.78, 3.81, 7 H), 3.84−4.02 (m, 0.65 H), 4.25 (d, $J = 10.1$ Hz, 1 H), 4.57−4.63 (m, 1 H), 4.64−4.93 (m, 4.65 H), 5.30 (dd, $J = 2.8$, 2.8 Hz, 0.28 H), 6.65−6.75 (m, 4 H), 6.80−6.87 (m, 2 H), 7.18−7.39 (m, 16 H), 7.41−7.51 (m, 6 H); ^{13}C NMR (CD_3COCD_3, 75.5 MHz) δ 55.4 (q′), 63.7 (t′), 63.8 (t′), 70.9 (d′), 72.5 (t′), 74.5 (t′), 74.8 (t′), 74.8 (t′), 75.3 (d′), 75.8 (t′), 75.9 (t′), 78.6 (d′), 78.7 (d′), 81.5 (d′), 82.6 (d′), 84.3 (d′), 85.6 (d′), 86.9 (s′), 91.5 (s′), 98.6 (d′), 114.1 (d′), 114.3 (d′), 114.4 (d′), 127.7 (d′), 128.0 (d′), 128.4 (d′), 128.5 (d′), 128.9 (d′), 129.6 (d′), 130.1 (d′), 130.2 (d′), 130.3 (d′), 130.3 (d′), 131.3 (s′), 131.4 (s′), 131.8 (s′), 132.1 (s′), 140.1 (s′), 140.3 (s′), 145.0 (s′), 145.0 (s′), 159.9 (s′), 160.0 (s′), 160.1 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{48}H_{48}NaO_8$ (M + Na) 775.324689, found 775.324710. Anal. Calcd for $C_{48}H_{48}O_8$: C, 76.57; H, 6.42. Found: C, 76.18; H, 6.41.

(b) Use of Wilkinson's catalyst. $(Ph_3P)_3RhCl$ (800.0 mg, 0.8464 mmol) and DABCO (398.0 mg, 3.55 mmol) were added sequentially to a stirred solution of **10** (3.75 g, 4.73 mmol) in a mixture of PhH (45 mL), EtOH (105 mL, 98%) and water (15 mL). The mixture was stirred at room temperature for 1 h and then refluxed, open to the atmosphere, for 36 h. The resulting brown solution was evaporated, and the residue was dissolved in 9:1 acetone−water (150 mL). $HgCl_2$ (14.4 g, 53.04 mmol) and yellow HgO (40 mg, 0.185 mmol) were added, and the mixture was stirred at room temperature for 12 h, evaporated, diluted with CH_2Cl_2 (100 mL), and filtered through a pad (6 × 6 cm) of Celite. The pad was rinsed with CH_2Cl_2 (200 mL), and the combined filtrates were washed with 20% aqueous NaI (1 × 60 mL). The aqueous layer was extracted with CH_2Cl_2 (1 × 40 mL), and the combined organic extracts were washed with brine (1 × 20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (4 × 31 cm), using EtOAc−hexane mixtures (15% to 30% EtOAc), gave **11** (3.27 g, 92%) as a pure (^{1}H NMR, 400 MHz) solid, which was a mixture of epimers: mp 58−64 °C; $[\alpha]_D = 7.8$ (*c* 0.32, $CHCl_3$).

2,4-Bis-*O*-[(4-methoxyphenyl)methyl]-3-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (12). $LiAlH_4$ (1.41 g, 37.2 mmol) was added in five portions to a stirred and cooled (0 °C) solution of **11** (10.27 g, 13.65 mmol) in THF (200 mL). The cold bath was removed, and stirring was continued for 4 h. The solution was recooled to 0 °C, and water (1.4 mL), 15% aqueous NaOH (1.4 mL), and water (4.2 mL) were added sequentially. The cold bath was removed, and the solution was stirred for 30 min and then filtered through a pad (6 × 6 cm) of Celite. The pad was rinsed with Et_2O (500 mL), and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (6 × 20 cm), using 1:3 to 4:6 EtOAc−hexane, gave **12** (9.64 g, 93%) as a pure (^{1}H NMR, 400 MHz), white solid: mp 44−46 °C; $[\alpha]_D = -6.78$ (*c* 1.15, $CHCl_3$); FTIR ($CHCl_3$ cast) 3460 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.12 (t, $J = 6.5$ Hz, 1 H), 3.12 (d, $J = 5.1$ Hz, 1 H), 3.28 (dd, $J = 9.5$, 5.3 Hz, 1 H), 3.36 (dd, $J = 9.5$, 4.3 Hz, 1 H), 3.50−3.57 (m, 1 H), 3.65−3.72 (m, 1 H), 3.73−3.86 (m, including singlets at δ 3.78, 3.79, 9 H), 4.01−4.08 (m, 1 H), 4.33 (d, $J = 11.0$ Hz, 1 H), 4.35 (d, $J = 11.0$ Hz, 1 H), 4.48−4.60 (m, 3 H), 4.67 (d, $J = 11.3$ Hz, 1 H), 6.75−6.80 (m, 2 H), 6.81−6.85 (m, 2 H), 6.97−7.03 (m, 2 H), 7.17−7.34 (m, 16 H), 7.42−7.49 (m, 6 H); ^{13}C NMR (CD_3COCD_3, 75.5 MHz) δ 55.5 (q′), 62.5 (t′), 66.5 (t′), 71.8 (d′), 73.0 (t′), 73.3 (t′), 74.9 (t′), 79.1 (d′), 80.1 (d′), 81.0 (d′), 87.3 (s′), 114.2 (d′), 114.3 (d′), 127.7 (d′), 128.1 (d′), 128.5 (d′), 128.6 (d′), 129.0 (d′), 129.7 (d′), 130.2 (d′), 131.6 (s′), 132.0 (s′), 140.0 (s′), 145.3 (s′), 160.0 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{48}H_{50}NaO_8$ (M + Na) 777.340339, found 777.340650. Anal. Calcd for $C_{48}H_{50}O_8$: C, 76.37; H, 6.68. Found: C, 76.15; H, 6.83.

1-*O*-[(1,1-Dimethylethyl)dimethylsilyl]-2,4-bis-*O*-[(4-methoxyphenyl)methyl]-3-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (13). Et_3N (4.05 mL, 29.0 mmol) was added in one portion to a stirred solution of **12** (14.0 g, 18.6 mmol), DMAP (570 mg, 4.66 mmol), and *t*-$BuMe_2SiCl$ (4.18 g, 27.7 mmol) in CH_2Cl_2 (400 mL). Stirring was continued for 16 h, and the mixture was diluted with CH_2Cl_2 (200 mL) and washed with brine (2 × 200 mL). The organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (6 × 25 cm), using 1:10 EtOAc−hexane, gave **13** (16.0 g, 99%) as a pure (^{1}H NMR, 400 MHz), gummy solid: $[\alpha]_D = 3.93$ (*c* 1.5, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3510 (br) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.03 (s, 6 H), 0.88 (s, 9 H), 3.12 (d, $J = 4.8$ Hz, 1 H), 3.27 (dd, $J = 9.5$, 5.7 Hz, 1 H), 3.34 (dd, $J = 9.8$, 3.7 Hz, 1 H), 3.65−3.84 (m, including singlets at δ 3.78 and 3.79, 11 H), 3.95−4.04 (m, 1 H), 4.34 (d, $J = 11.0$ Hz, 1 H), 4.38 (d, $J = 11.0$ Hz, 1 H), 4.53 (d, $J = 11.4$ Hz, 1 H), 4.55 (d, $J = 11.2$, 1 H), 4.60 (d, $J = 11.4$ Hz, 1 H), 4.64 (d, $J = 11.2$ Hz, 1 H), 6.73−6.80 (m, 2 H), 6.82−6.87 (m, 2 H), 6.95−7.02 (m, 2 H), 7.21−7.35 (m, 16 H), 7.42−7.50 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ −5.4 (q′), 18.2 (s′), 26.0 (q′), 55.2 (q′), 63.1 (t′), 65.0 (t′), 71.2 (d′), 72.5 (t′), 72.8 (t′), 74.0 (t′), 76.7 (d′), 78.3 (d′), 79.4 (d′), 86.6 (s′), 113.6 (d′), 113.7 (d′), 127.0 (d′), 127.7 (d′), 127.8 (d′), 128.3 (d′), 128.4 (d′), 128.8 (d′), 129.6 (d′), 129.7 (d′), 130.3 (s′), 130.7 (s′), 138.2 (s′), 144.0 (s′), 159.1 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{54}H_{64}NaO_8Si$ (M + Na) 891.426818, found 891.426920. Anal. Calcd for $C_{54}H_{64}O_8Si$: C, 73.24; H, 7.42. Found: C, 73.32; H, 7.46.

1-*O*-[(1,1-Dimethylethyl)dimethylsilyl]-2,4-bis-*O*-[(4-methoxyphenyl)methyl]-3,5-bis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (14). NaH (80% dispersion in oil, 1.40 g, 46.0 mmol) was added in five portions to a stirred and cooled (0 °C) solution of **13** (16.0 g, 18.4 mmol) in THF (500 mL). The resulting mixture was stirred for 30 min, and then BnBr (5.50 mL, 46.0 mmol) was added neat in one portion by syringe. The cold bath was removed, and the mixture was stirred for 1 h and then refluxed for 24 h. The resulting mixture was cooled (0 °C), quenched with MeOH (50 mL), diluted with brine (200 mL), and extracted with Et_2O (3 × 300 mL). The combined organic extracts were washed with brine (1 × 200 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (6 × 35 cm), using 5:95 to 1:10 EtOAc−hexane, gave **14** (17.0 g, 96%) as a pure (^{1}H NMR, 400 MHz), thick syrup: $[\alpha]_D = 5.71$ (*c* 2.38, $CHCl_3$); FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 400 MHz) δ −0.02 (d, $J = 2.5$ Hz, 6 H), 0.86 (s, 9 H), 3.37 (dd, $J = 10.4$, 5.6 Hz, 1 H), 3.56 (dd, $J = 10.3$, 2.6 Hz, 1 H), 3.60−3.70 (m, 3 H), 3.71−3.80 (m, including singlets at δ 3.74 and 3.76, 8 H), 4.01 (dd, $J = 5.7$, 5.7 Hz, 1 H), 4.35 (d, $J = 11.6$ Hz, 1 H), 4.43−4.72 (m, 7 H), 6.68−6.76 (m, 4 H), 6.92−6.97 (m, 2 H), 7.16−7.32 (m, 21 H), 7.41−7.46 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ −5.4 (q′), 18.2 (s′), 26.0 (q′), 55.2 (q′), 63.2 (t′), 63.9 (t′), 72.2 (t′), 72.8 (t′), 73.5 (t′), 74.5 (t′), 78.3 (d′), 78.6 (d′), 79.7 (d′), 80.2 (d′), 86.8 (s′), 113.5 (d′), 113.7 (d′), 126.9 (d′), 127.3 (d′), 127.8 (d′), 128.1 (d′), 128.2 (d′), 128.9 (d′), 129.5 (d′), 129.7 (d′), 130.9 (s′), 131.1 (s′), 138.8 (s′), 138.9 (s′), 144.1 (s′), 158.9 (s′), 159.0 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{61}H_{70}NaO_8Si$ (M + Na) 981.473768 found 981.474400. Anal. Calcd for $C_{61}H_{70}O_8Si$: C, 76.38; H, 7.36. Found: C, 76.50; H, 7.51.

2,4-Bis-*O*-[(4-methoxyphenyl)methyl]-3,5-bis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucitol (15). TBAF (1 M in THF, 17.75 mL, 17.75 mmol) was added in one portion by syringe to a stirred solution of **14** (16.67 g, 17.40 mmol) in THF (340 mL). The mixture was stirred for 4 h at room temperature, diluted with Et_2O (150 mL), and washed with water (1 × 150 mL). The aqueous layer was extracted with Et_2O (2 × 90 mL), and the combined organic extracts were washed with brine (1 × 150 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (6 × 35 cm), using 2:8 to 3:7 EtOAc−hexane, gave **15** (13.50 g, 92%) as a pure (^{1}H NMR, 400 MHz), white solid: mp 41−43 °C; $[\alpha]_D = -11.90$ (*c* 2.66, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3476 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.12 (br s, 1 H), 3.41 (dd, $J = 11.3$, 3.8

Hz, 1 H), 3.51−3.61 (m, 2 H), 3.61−3.79 (m, including singlets at δ 3.74 and 3.77, 8 H), 3.79−3.88 (m, 2 H), 4.08 (dd, J = 4.4, 4.4 Hz, 1 H), 4.42 (d, J = 11.3 Hz, 1 H), 4.45−4.55 (m, 4 H), 4.61 (br s, 2 H), 4.75 (d, J = 11.3 Hz, 1 H), 6.75 (d, J = 8.0 Hz, 2 H), 6.80 (d, J = 8.0 Hz, 2 H), 7.00 (d, J = 8.5 Hz, 2 H), 7.16−7.35 (m, 21 H), 7.43−7.50 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 55.2 (q′), 61.9 (t′), 63.2 (t′), 72.2 (t′), 73.3 (t′), 74.4 (t′), 78.0 (d′), 78.8 (d′), 79.1 (d′), 79.3 (d′), 86.9 (s′), 113.5 (d′), 113.8 (d′), 127.0 (d′), 127.4 (d′), 127.6 (d′), 127.8 (d′), 128.2 (d′), 128.3 (d′), 128.8 (d′), 129.6 (d′), 129.7 (d′), 130.4 (s′), 130.5 (s′), 138.4 (s′), 138.7 (s′), 144.0 (s′), 159.1 (s′), 159.2 (s′); exact mass (HR electrospray) m/z calcd for $C_{55}H_{56}NaO_8$ (M + Na) 867.387289, found 867.387600. Anal. Calcd for $C_{55}H_{56}O_8$: C, 78.17; H 6.68. Found: C, 78.14; H, 6.74.

2,4-Bis-*O*-[(4-methoxyphenyl)methyl]-3,5-bis-*O*-(phenylmethyl)-6-*O*-(triphenylmethyl)-D-glucose (16). DMSO (0.91 mL, 12.8 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of $(COCl)_2$ (0.84 mL, 9.62 mmol) in CH_2Cl_2 (40 mL). After 20 min **15** (2.69 g, 3.19 mmol) in CH_2Cl_2 (7 mL plus 3 mL as a rinse) was added by syringe over 1 min. Stirring was continued for 30 min at −78 °C, and then Et_3N (3.65 mL, 26.2 mmol) was added dropwise over ca. 2 min. The cold bath was removed, and stirring was continued for 6 h. The mixture was diluted with water (2 mL) and CH_2Cl_2 (50 mL), washed with brine (1 × 20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (3 × 25 cm), using 1:9 to 2:8 EtOAc−hexane, gave **16** (2.39 g, 89%) as a pure (^{1}H NMR, 400 MHz), white solid: mp 46−48 °C; $[\alpha]_D$ = 0.600 (c 1.50, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1727 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.28 (dd, J = 10.3, 4.7 Hz, 1 H), 3.64 (dd, J = 10.3, 2.7 Hz, 1 H), 3.70−3.79 (m, including singlets at δ 3.72 and 3.74, 7 H), 3.82 (d, J = 5.2 Hz, 1 H), 4.02−4.10 (m, 2 H), 4.24 (d, J = 10.3 Hz, 1 H), 4.30−4.43 (m, 4 H), 4.49 (d, J = 11.6 Hz, 1 H), 4.71 (dd, J = 21.9, 11.6 Hz, 2 H), 6.62−6.65 (m, 2 H), 6.75−6.82 (m, 4 H), 7.04−7.10 (m, 2 H), 7.15−7.23 (m, 14 H), 7.23−7.36 (m, 5 H), 7.40−7.45 (m, 6 H), 9.64 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.2 (q′), 55.3 (q′), 62.7 (t′), 72.2 (t′), 72.8 (t′), 73.1 (t′), 74.0 (t′), 76.6 (d′), 78.8 (d′), 80.0 (d′), 80.8 (d′), 86.9 (s′), 113.4 (d′), 113.9 (d′), 127.0 (d′), 127.3 (d′), 127.5 (d′), 127.9 (d′), 128.1 (d′), 128.4 (d′), 128.9 (d′), 129.6 (s′), 129.7 (d′), 130.0 (s′), 130.2 (d′), 137.9 (s′), 138.6 (s′), 144.0 (s′), 159.0 (s′), 159.5 (s′), 201.1 (d′); exact mass (HR electrospray) m/z calcd for $C_{55}H_{54}NaO_8$ (M + Na) 865.371639, found 865.371920. Anal. Calcd for $C_{55}H_{54}O_8$: C, 78.36; H, 6.46. Found: C, 78.01; H, 6.52.

1,2-Dideoxy-3,5-bis-*O*-[(4-methoxyphenyl)methyl]-4,6-bis-*O*-(phenylmethyl)-7-*O*-(triphenylmethyl)-D-*gluco*-hept-1-ynitol (17). (a) 1,1-Dibromo-1,2-dideoxy-3,5-bis-*O*-[(4-methoxyphenyl)methyl]-4,6-bis-*O*-(phenylmethyl)-7-*O*-(triphenylmethyl)-D-*gluco*-hept-1-enitol. A solution of CBr_4 (1.36 g, 4.10 mmol) in CH_2Cl_2 (20 mL) was added at a fast dropwise rate to a stirred and cooled (−20 °C) solution of Ph_3P (1.07 g, 4.08 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred for 15 min at −20 °C, and then a solution of **16** (1.73 g, 2.05 mmol) and Et_3N (0.28 mL, 2.05 mmol) in CH_2Cl_2 (20 mL) was added dropwise at −60 °C. The cold bath was removed, and the solution was allowed to warm to room temperature. After 30 min, the mixture was filtered through a pad (3 × 3 cm) of flash chromatography silica gel which was rinsed with Et_2O (50 mL), and the combined filtrates were evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 1:9 EtOAc−hexane, gave the required dibromo alkene (1.70 g, 83%) as a pure (^{1}H NMR, 300 MHz), white solid: mp 39−41 °C; $[\alpha]_D$ = 17.1 (c 1.52, $CHCl_3$); FTIR ($CHCl_3$ cast) unexceptional; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.36−3.46 (m, 2 H), 3.65−3.75 (m, including singlet at δ 3.73, 5 H), 3.78 (s, 3 H), 4.07 (dd, J = 5.5, 5.5 Hz, 1 H), 4.22 (dd, J = 8.4, 4.6 Hz, 1 H), 4.31 (d, J = 11.4 Hz, 1 H), 4.41 (d, J = 11.7 Hz, 1 H), 4.51−4.64 (m, 5 H), 4.70 (d, J = 11.6 Hz, 1 H), 6.60 (d, J = 8.5 Hz, 1 H), 6.72 (d, J = 8.5 Hz, 2 H), 6.81 (d, J = 9.0 Hz, 2 H), 6.99 (d, J = 9.0 Hz, 2 H), 7.18−7.36 (m, 21 H), 7.40−7.50 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.2 (q′), 63.2 (t′), 70.9 (t′), 72.4 (t′), 73.9 (t′), 75.0 (t′), 78.6 (d′), 79.0 (d′), 79.6 (d′), 79.7 (d′), 86.7 (s′), 92.3 (s′), 113.5 (d′), 113.8 (d′), 126.9 (d′), 127.4 (d′), 127.6 (d′), 127.8 (d′), 128.2 (d′), 128.3 (d′), 128.9 (d′), 129.7 (s′), 129.7 (d′), 129.9 (d′), 130.8 (s′), 137.6 (d′), 138.3 (s′), 138.8 (s′), 144.1 (s′), 159.0 (s′), 159.4 (s′); exact mass (HR electrospray) m/z calcd for $C_{56}H_{54}{}^{79}Br^{81}BrNaO_7$ (M + Na) 1021.211350, found 1021.211970. Anal. Calcd for $C_{56}H_{54}O_7Br_2$: C, 67.34; H, 5.45. Found: C, 67.40; H, 5.41.

(b) 1,2-Dideoxy-3,5-bis-*O*-[(4-methoxyphenyl)methyl]-4,6-bis-*O*-(phenylmethyl)-7-*O*-(triphenylmethyl)-D-*gluco*-hept-1-ynitol (17). *n*-BuLi (2.5 M in hexane, 1.30 mL, 3.25 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of the above dibromo alkene (1.62 g, 1.62 mmol) in THF (40 mL). Stirring at −78 °C was continued for 2 h, and then water (2.0 mL) was added. The cold bath was removed, and stirring was continued for 30 min. The mixture was diluted with Et_2O (20 mL), washed with brine (2 × 10 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 2:8 EtOAc−hexane, gave **17** (1.15 g, 85%) as a pure (^{1}H NMR, 300 MHz), white solid: mp 43−45 °C; $[\alpha]_D$ = 23.4 (c 0.65, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3281 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.64 (d, J = 2.4 Hz, 1 H), 3.24 (dd, J = 10.2, 4.7 Hz, 1 H), 3.63 (dd, J = 10.2, 2.3 Hz, 1 H), 3.73−3.87 (m, including singlets at δ 3.77 and 3.78, 7 H), 4.04 (dd, J = 7.5, 3.2 Hz, 1 H), 4.26−4.42 (m, 3 H), 4.44−4.56 (m, 4 H), 4.72 (d, J = 11.6 Hz, 1 H), 4.79 (d, J = 11.2 Hz, 1 H), 4.89 (d, J = 11.6 Hz, 1 H), 6.65−6.75 (m, 2 H), 6.77−6.93 (m, 4 H), 7.14−7.38 (m, 21 H), 7.38−7.52 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 62.7 (t′), 71.0 (d′), 71.0 (t′), 71.9 (t′), 74.2 (t′), 74.8 (t′), 76.3 (s′), 78.4 (d′), 78.5 (d′), 81.0 (d′), 81.1 (s′), 86.7 (s′), 113.5 (d′), 113.8 (d′), 126.9 (d′), 127.3 (d′), 127.3 (d′), 127.8 (d′), 128.1 (d′), 128.3 (d′), 128.9 (d′), 129.6 (s′), 129.7 (d′), 129.9 (d′), 130.8 (s′), 138.7 (s′), 139.0 (s′), 144.1 (s′), 159.0 (s′), 159.3 (s′); exact mass (HR electrospray) m/z calcd for $C_{56}H_{54}NaO_7$ (M + Na) 861.376724, found 861.377150.

1,2,3-Trideoxy-4,6-bis-*O*-[(4-methoxyphenyl)methyl]-5,7-bis-*O*-(phenylmethyl)-1-(trimethylsilyl)-8-*O*-(triphenylmethyl)-D-*gluco*-oct-2-ynitol (18). *n*-BuLi (2.5 M in hexane, 0.61 mL, 1.53 mmol) was added over 30 s to a stirred and cooled (−78 °C) solution of **17** (1.15 g, 1.37 mmol) in THF (35 mL). Stirring at −78 °C was continued for 1 h, and then $Me_3SiCH_2OSO_2CF_3$ (0.35 mL, 1.75 mmol) and HMPA (1.0 mL, 5.75 mmol) were added, each in one portion. The cold bath was removed, and stirring was continued for 8 h. The mixture was diluted with Et_2O (40 mL) and washed with brine (1 × 20 mL). The aqueous layer was extracted with Et_2O (2 × 20 mL), and the combined organic extracts were dried and evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 1:9 EtOAc−hexane, gave **18** (1.04 g, 82%) as a pure (^{1}H NMR, 400 MHz), gummy solid: $[\alpha]_D$ = 19.4 (c 1.17, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 2212 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 9 H), 1.64 (dd, J = 3.2, 2.2 Hz, 2 H), 3.21 (dd, J = 10.3, 4.7 Hz, 1 H), 3.60 (dd, J = 10.3, 2.2 Hz, 1 H), 3.75 (s, 3 H), 3.76 (s, 3 H), 3.80−3.85 (m, 1 H), 3.98 (dd, J = 8.0, 2.9 Hz, 1 H), 4.26 (d, J = 11.5 Hz, 1 H), 4.29 (dd, J = 8.0, 2.9 Hz, 1 H), 4.35 (d, J = 10.5 Hz, 1 H), 4.45−4.52 (m, 4 H), 4.69 (d, J = 11.6 Hz, 1 H), 4.77 (d, J = 11.1 Hz, 1 H), 4.91 (d, J = 11.7 Hz, 1 H), 6.65−6.69 (m, 2 H), 6.75−6.81 (m, 2 H), 6.82−6.86 (m, 2 H), 7.13−7.32 (m, 21 H), 7.41−7.50 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ −1.8 (q′), 7.4 (t′), 55.2 (q′), 62.8 (t′), 70.6 (t′), 71.9 (s′), 71.9 (d′), 74.3 (t′), 74.7 (t′), 76.0 (t′), 78.5 (d′), 78.8 (d′), 81.7 (d′), 86.7 (s′), 86.8 (s′), 113.4 (d′), 113.7 (d′), 126.9 (d′), 127.1 (d′), 127.2 (d′), 127.2 (d′), 127.7 (d′), 128.0 (d′), 128.2 (d′), 128.9 (d′), 129.7 (d′), 129.8 (d′), 130.2 (s′), 130.9 (s′), 138.9 (s′), 139.4 (s′), 144.2 (s′), 158.9 (s′), 159.2 (s′); exact mass (HR electrospray) m/z calcd for $C_{60}H_{64}NaO_7Si$ (M + Na) 947.431903, found 947.432090. Anal. Calcd for $C_{60}H_{64}O_7Si$: C, 77.89; H, 6.97. Found: C, 77.81; H, 7.23.

1,2,3-Trideoxy-4,6-bis-*O*-[(4-methoxyphenyl)methyl]-5,7-bis-*O*-(phenylmethyl)-1-(trimethylsilyl)-D-*gluco*-oct-2-ynitol (19). CSA (40.0 mg, 0.172 mmol) in MeOH (5 mL) was added in one portion to a stirred solution of **18** (1.17 g, 1.27 mmol) in CH_2Cl_2 (50 mL). Stirring was continued for 36 h, Et_3N (1 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 × 25 cm), using 2:8 EtOAc−hexane, gave **19** (0.82 g, 94%) as a pure (^{1}H NMR, 400 MHz) oil: $[\alpha]_D$ = 37.59 (c 3.20, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3492, 2212 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ

0.13 (s, 9 H), 1.55 (d, J = 2.5 Hz, 2 H), 2.07 (dd, J = 7.5, 4.0 Hz, 1 H), 3.66−3.86 (m, including singlets at δ 3.78 and 3.79, 10 H), 4.15 (dd, J = 7.0, 4.0 Hz, 1 H), 4.28 (d, J = 11.7 Hz, 1 H), 4.43−4.49 (m, 3 H), 4.56 (d, J = 11.6 Hz, 1 H), 4.64 (s, 2 H), 4.77 (d, J = 11.2 Hz, 1 H), 4.93 (d, J = 11.3 Hz, 1 H), 6.78−6.84 (m, 4 H), 7.15−7.32 (m, 14 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ −1.9 (q′), 7.4 (t′), 55.2 (q′), 60.3 (t′), 70.5 (t′), 71.2 (t′), 71.6 (d′), 74.6 (t′), 74.9 (t′), 75.4 (s′), 79.0 (d′), 79.0 (d′), 81.5 (d′), 87.0 (s′), 113.6 (s′), 113.7 (s′), 127.3 (d′), 127.5 (d′), 127.6 (d′), 128.0 (d′), 128.1 (d′), 128.4 (d′), 129.7 (d′), 130.0 (s′), 130.6 (s′), 138.3 (s′), 138.9 (s′), 159.2 (s′); exact mass (HR electrospray) m/z calcd for $C_{41}H_{50}NaO_7Si$ (M + Na) 705.322353, found 705.321500.

6,7,8-Trideoxy-3,5-bis-*O*-[(4-methoxyphenyl)methyl]-2,4-bis-*O*-(phenylmethyl)-8-(trimethylsilyl)-L-*gulo*-oct-6-ynose (5). DMSO (0.43 mL, 6.06 mmol) was added dropwise to a stirred and cooled solution (−78 °C) of $(COCl)_2$ (0.40 mL, 4.58 mmol) in CH_2Cl_2 (30 mL). After 20 min **19** (1.02 g, 1.50 mmol) in CH_2Cl_2 (10 mL) was added by syringe over 1 min. Stirring was continued for 30 min at −78 °C, and then Et_3N (1.72 mL, 12.3 mmol) was added. After a further 30 min, the cold bath was removed and stirring was continued for 6 h. The mixture was diluted with water (5 mL) and CH_2Cl_2 (20 mL), washed with brine (20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 × 20 cm), using 1:10 to 2:8 EtOAc−hexane, gave **5** (0.94 g, 92%) as a pure (^{1}H NMR, 400 MHz) oil: $[\alpha]_D$ = 33.38 (c 1.33, $CHCl_3$); FTIR (CH_2Cl_2 cast) 2212, 1733 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.14 (s, 9 H), 1.56 (d, J = 2.5 Hz, 2 H), 3.77 (s, 3 H), 3.78 (s, 3 H), 3.82 (dd, J = 8.0, 4.5 Hz, 1 H), 4.02 (dd, J = 5.0, 2.0 Hz, 1 H), 4.22−4.27 (m, 2 H), 4.40−4.58 (m, 6 H), 4.76 (d, J = 11.7 Hz, 1 H), 4.90 (d, J = 11.5 Hz, 1 H), 6.77−6.86 (m, 4 H), 7.15 (d, J = 9.0 Hz, 2 H), 7.18−7.34 (m, 12 H), 9.64 (d, J = 2.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ −1.8 (q′), 7.3 (t′), 55.3 (q′), 70.6 (t′), 71.3 (d′), 72.3 (t′), 74.2 (t′), 75.0 (t′), 75.2 (s′), 80.4 (d′), 81.5 (d′), 83.9 (d′), 87.0 (s′), 113.7 (d′), 113.8 (d′), 127.6 (d′), 127.8 (d′), 127.8 (d′), 128.3 (d′), 128.4 (d′), 129.8 (d′), 129.9 (d′), 130.0 (s′), 130.1 (s′), 137.5 (s′), 138.5 (s′), 159.3 (s′), 201.3 (d′); exact mass (HR electrospray) m/z calcd for $C_{41}H_{48}NaO_7Si$ (M + Na) 703.306703, found 703.306590.

(R_a)-5-Deoxy-2,4-bis-*O*-[(4-methoxyphenyl)methyl]-1,3-bis-*O*-(phenylmethyl)-5-[(trimethylsilyl)ethenylidene]-L-*chiro*-inositol (7). CSA (64 mg, 0.28 mmol) was added to a stirred solution of **5** (0.90 g, 1.32 mmol) in PhMe (200 mL). Stirring was continued for 2.5 h, Et_3N (2 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 2:8 EtOAc−hexane, gave **7** (0.82 g, 91%) as a pure (^{1}H NMR, 300 MHz), gummy solid: $[\alpha]_D$ = −0.504 (c 4.96, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3441, 1947 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.16 (s, 9 H), 1.97 (br s, 1 H), 3.74 (dd, J = 6.6, 2.7 Hz, 1 H), 3.80 (s, 6 H), 3.89 (dd, J = 6.2, 2.9 Hz, 1 H), 3.97 (dd, J = 6.0, 6.0 Hz, 1 H), 4.23 (dd, J = 5.5, 2.6 Hz, 1 H), 4.46 (d, J = 11.2 Hz, 1 H), 4.52 (d, J = 11.5 Hz, 1 H), 4.54−4.76 (m, 7 H), 5.35 (dd, J = 2.7, 2.7 Hz, 1 H), 6.78−6.87 (m, 4 H), 7.21−7.40 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ −0.9 (q′), 55.2 (q′), 68.4 (d′), 71.3 (t′), 72.1 (t′), 72.2 (t′), 73.8 (t′), 77.2 (d′), 78.0 (d′), 79.4 (d′), 86.4 (d′), 95.5 (s′), 113.6 (d′), 127.5 (d′), 127.8 (d′), 128.2 (d′), 128.3 (d′), 129.3 (d′), 129.4 (d′), 130.8 (s′), 130.8 (s′), 138.6 (s′), 159.0 (s′), 206.5 (s′); exact mass (HR electrospray) m/z calcd for $C_{41}H_{48}NaOSi$ (M + Na) 703.306703, found 703.306710. Anal. Calcd for $C_{41}H_{48}OSi$: C, 72.32; H, 7.11. Found: C, 72.25; H, 7.11.

5-Deoxy-5-ethenylidene-2,4-bis-*O*-[(4-methoxyphenyl)-methyl]-1,3-bis-*O*-(phenylmethyl)-L-*chiro*-inositol (20). Powdered K_2CO_3 (~325 mesh, 0.880 g, 6.37 mmol) was added in one portion to a stirred solution of **7** (1.45 g, 2.13 mmol) in 3:1 MeOH−THF (280 mL), and the resulting mixture was refluxed for 4 h, cooled, diluted with Et_2O (50 mL), and filtered through a pad (2.5 × 2 cm) of flash chromatography silica gel, using Et_2O (50 mL) as a rinse. The combined filtrates were evaporated, and flash chromatography of the residue over silica gel (2 × 25 cm), using 3:7 EtOAc−hexane, gave **20** (1.12 g, 86%) as a pure (^{1}H NMR, 300 MHz) oil: $[\alpha]_D$ = 23.1 (c 1.06, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3440, 1959 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.14 (br s, 1 H), 3.76 (dd, J = 6.1, 2.9 Hz, 1 H), 3.80 (s, 6 H), 3.88 (dd, J = 6.9, 2.8 Hz, 1 H), 3.98 (dd, J = 6.6, 6.6 Hz 1 H), 4.25 (ddd, J = 6.2, 2.7, 2.7 Hz, 1 H), 4.49 (d, J = 10.7 Hz, 1 H), 4.52−4.78 (m, 8 H), 4.97−5.11 (m, 2 H), 6.78−6.87 (m, 4 H), 7.20−7.41 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.2 (q′), 68.9 (d′), 71.9 (t′), 72.3 (t′), 72.4 (t′), 74.3 (t′), 77.5 (d′), 78.5 (t′), 79.0 (d′), 80.0 (d′), 101.8 (s′), 113.7 (d′), 127.5 (d′), 127.7 (d′), 127.8 (d′), 128.3 (d′), 129.4 (d′), 129.5 (d′), 130.6 (s′), 130.8 (s′), 138.5 (s′), 138.8 (s′), 159.1 (s′), 205.8 (s′); exact mass (HR electrospray) m/z calcd for $C_{38}H_{40}NaO_7$ (M + Na) 631.267174, found 631.266900.

(3*S*,4*R*,5*S*,6*S*)-2-Ethenylidene-3,5-bis[(4-methoxyphenyl)methoxy]-4,6-bis(phenylmethoxy)cyclohexanone (21). A solution of **20** (296.7 mg, 0.488 mmol) in CH_2Cl_2 (6 mL) was added to a stirred suspension of Dess−Martin periodinane (289.6 mg, 0.693 mmol) in CH_2Cl_2 (12 mL). The mixture was stirred for 30 min, diluted with Et_2O (18 mL), and poured into saturated aqueous $NaHCO_3$ (18 mL) containing $Na_2S_2O_3$ (4.5 g). The mixture was stirred for 5 min. Et_2O (20 mL) was added, and the layers were separated. The Et_2O layer was washed with saturated aqueous $NaHCO_3$ (20 mL), water (20 mL), and brine (10 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1 × 25 cm), using 3:7 EtOAc−hexane, gave **21** (248.3 mg, 84%) as a pure (^{1}H NMR, 400 MHz), gummy solid: $[\alpha]_D$ = −13.7 (c 1.30, acetone); FTIR (CH_2Cl_2 cast) 1960, 1708 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 400 MHz) δ 3.77 (s, 3 H), 3.78 (s, 3 H), 3.87 (dd, J = 5.6, 2.3 Hz, 1 H), 3.98 (dd, J = 4.8, 4.8 Hz, 1 H), 4.27 (d, J = 2.5 Hz, 1 H), 4.38 (ddd, J = 5.6, 4.1, 4.1 Hz, 1 H), 4.45−4.57 (m, 6 H), 4.66 (d, J = 11.2 Hz, 1 H), 4.86 (d, J = 11.9 Hz, 1 H), 5.41 (dd, J = 14.9, 4.0 Hz, 1 H), 5.43 (dd, J = 14.9, 4.0 Hz, 1 H), 6.80−6.91 (m, 4 H), 7.17−7.41 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 72.0 (t′), 72.3 (t′), 72.6 (t′), 72.6 (t′), 76.7 (d′), 77.4 (d′), 81.2 (d′), 81.8 (d′), 82.1 (t′), 104.3 (s′), 113.7 (d′), 113.8 (d′), 127.8 (d′), 127.8 (d′), 127.9 (d′), 127.9 (d′), 128.4 (d′), 128.5 (d′), 129.6 (d′), 129.6 (d′), 129.9 (s′), 130.1 (s′), 137.8 (s′), 159.3 (s′), 159.4 (s′), 194.6 (s′), 211.2 (s′); exact mass (HR electrospray) m/z calcd for $C_{38}H_{38}NaO_7$ (M + Na) 629.251524, found 629.251915.

4-Deoxy-4-ethenylidene-1,5-bis-*O*-[(4-methoxyphenyl)-methyl]-2,6-bis-*O*-(phenylmethyl)-D-*myo*-inositol (22). $CeCl_3 \cdot 7H_2O$ (0.42 g, 1.13 mmol) was added in one portion to a stirred solution of **21** (0.63 g, 1.04 mmol) in 1:10 THF−MeOH (126 mL). After 10 min, the mixture was cooled to −78 °C, and $NaBH_4$ (42.8 mg, 1.13 mmol) was added. Stirring was continued at −78 °C for 1 h and then at 0 °C (ice bath) for 4 h. The reaction was quenched with saturated aqueous NH_4Cl (25 mL), and the mixture was diluted with water (25 mL), evaporated, and extracted with Et_2O (3 × 25 mL). The combined organic extracts were washed with brine (1 × 20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 3:7 EtOAc−hexane, gave **22** (0.58 g, 92%) as a pure (^{1}H NMR, 300 MHz), gummy solid: $[\alpha]_D$ = 56.3 (c 2.05, CH_2Cl_2); FTIR (CH_2Cl_2 cast) 3479, 1970 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.66 (d, J = 11.0 Hz, 1 H), 3.53 (dd, J = 8.2, 2.5 Hz, 1 H), 3.80 (s, 3 H), 3.81 (s, 3 H), 3.89−3.96 (m, 2 H), 4.00 (dd, J = 8.0, 8.0 Hz, 1 H), 4.06 (ddd, J = 10.8, 3.0, 3.0 Hz, 1 H), 4.49 (d, J = 10.9 Hz, 1 H), 4.57−4.80 (m, 5 H), 4.83 (d, J = 11.0 Hz, 1 H), 4.98 (d, J = 11.8 Hz, 1 H), 5.11−5.22 (m, 2 H), 6.78−6.86 (m, 4 H), 7.22−7.41 (m, 14 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 67.9 (d′), 72.4 (t′), 72.9 (t′), 73.8 (t′), 75.1 (t′), 77.4 (d′), 78.3 (d′), 79.8 (d′), 81.2 (d′), 81.6 (t′), 103.8 (s′), 113.7 (d′), 113.8 (d′), 127.5 (d′), 127.5 (d′), 127.5 (d′), 127.9 (d′), 128.3 (d′), 128.3 (d′), 129.4 (d′), 129.8 (d′), 130.3 (s′), 130.4 (s′), 138.8 (s′), 138.9 (s′), 159.2 (s′), 203.2 (s′); exact mass (HR electrospray) m/z calcd for $C_{38}H_{40}NaO_7$ (M + Na) 631.267174, found 631.267670.

4-Deoxy-4-ethenylidene-1,5-bis-*O*-[(4-methoxyphenyl)-methyl]-2,3,6-tris-*O*-(phenylmethyl)-D-*myo*-inositol (23). NaH (80% dispersion in oil, 34.2 mg, 1.14 mmol) was added in one portion to a stirred and cooled (0 °C) solution of **22** (0.580 g, 0.954 mmol) in THF (40 mL). After 30 min, BnBr (0.14 mL, 1.14 mmol) was added neat in one portion, the cold bath was removed, and the mixture was stirred for 1 h and then refluxed for 24 h. The resulting mixture was cooled (0 °C) and quenched with MeOH (5 mL), diluted with brine (10 mL), and extracted with Et_2O (3 × 20 mL). The combined

organic extracts were washed with brine (1 × 20 mL), dried, and evaporated. Flash chromatography of the residue over silica gel (2 × 25 cm), using 2:8 EtOAc−hexane, gave **23** (0.580 g, 87%) as a pure (^{1}H NMR, 300 MHz), white solid: mp 100−101 °C; $[\alpha]_D = 1.50$ (*c* 1.60, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1965 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.29 (dd, $J = 9.5$, 2.5 Hz, 1 H), 3.69−3.74 (m, 1 H), 3.75−3.84 (m, including singlets at δ 3.80 and 3.81, 7 H), 3.97−4.06 (m, 2 H), 4.44 (d, $J = 11.9$ Hz, 1 H), 4.50−4.59 (m, 3 H), 4.75−4.96 (m, 6 H), 5.14−5.30 (m, 2 H), 6.78−6.87 (m, 4 H), 7.18−7.43 (m, 19 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 71.9 (t′), 72.2 (t′), 73.1 (t′), 73.4 (t′), 75.9 (t′), 76.1 (d′), 76.5 (d′), 78.1 (d′), 80.1 (d′), 81.8 (t′), 83.1 (d′), 101.3 (s′), 113.8 (d′), 127.1 (d′), 127.4 (d′), 127.4 (d′), 127.6 (d′), 127.8 (d′), 128.0 (d′), 128.1 (d′), 128.3 (d′), 128.4 (d′), 129.3 (d′), 129.8 (d′), 130.5 (s′), 130.7 (s′), 138.3 (s′) 139.3 (s′), 139.4 (s′) 159.2 (s′), 159.3 (s′), 202.8 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{45}H_{46}NaO_7$ (M + Na) 721.314124, found 721.316612.

1,5-Bis-*O*-[(4-methoxyphenyl)methyl]-2,3,6-tris-*O*-(phenylmethyl)-D-*epi*-4-inososе (24). The apparatus described[51] by Rubin was used for this experiment. A cold (−78 °C), saturated solution of ozone in CH_2Cl_2 (21.5 mL) was transferred to a stirred and cooled (−78 °C) solution of **23** (188.1 mg, 0.269 mmol) and pyridine (3.2 mL) in CH_2Cl_2 (20 mL).[31] The mixture was stirred for 30 min and then evaporated. Flash chromatography of the residue over silica gel (1 × 20 cm), using 2:8 EtOAc−hexane, gave **24** [109.1 mg, 80% (after correction for recovered starting material (50.5 mg, 27%)] as a pure (^{1}H NMR, 400 MHz), white solid: mp 150−151 °C; $[\alpha]_D = 24.1$ (*c* 1.12, $CHCl_3$); FTIR (CH_2Cl_2 cast) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (dd, $J = 9.4$, 2.1 Hz, 1 H), 3.80 (s, 3 H), 3.82 (s, 3 H), 3.93−3.99 (m, 2 H), 4.10 (dd, $J = 2.1$, 2.1 Hz, 1 H), 4.19 (dd, $J = 9.4$, 9.4 Hz, 1 H), 4.47 (d, $J = 11.9$ Hz, 1 H), 4.50−4.59 (m, 3 H), 4.78−4.91 (m, 6 H), 6.81−6.88 (m, 4 H), 7.17−7.41 (m, 19 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 55.3 (q′), 72.2 (t′), 72.5 (t′), 73.2 (t′), 73.7 (t′), 75.8 (d′), 75.9 (t′), 79.8 (d′), 81.4 (d′), 82.6 (d′), 83.7 (d′), 113.8 (d′), 127.4 (d′), 127.6 (d′), 127.8 (d′), 128.0 (d′), 128.0 (d′), 128.1 (d′), 128.3 (d′), 128.5 (d′), 129.4 (d′), 129.8 (s′), 129.9 (d′), 130.1 (s′), 137.4 (s′), 138.3 (s′), 138.8 (s′), 159.3 (s′), 159.4 (s′), 201.7 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{43}H_{44}NaO_8$ (M + Na) 711.293389, found 711.293620.

1,5-Bis-*O*-[(4-methoxyphenyl)methyl]-2,3,6-tris-*O*-(phenylmethyl)-D-*myo*-inositol (25). A solution of *n*-Bu_2SnCl_2 (279 mg, 0.918 mmol) in PhMe (5 mL) was added to a stirred solution of *n*-Bu_2SnH_2 (216 mg, 0.918 mmol) in PhMe (5 mL), and the mixture was stirred at room temperature for 15 min. A solution of **24** (63.3 mg, 0.0920 mmol) in PhMe (6 mL) was added, and the resulting solution was refluxed for 24 h and then cooled to room temperature. MeOH (2 mL) was added, and the solvents were evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm), using 2:8 EtOAc−hexane, gave **25** (56.2 mg, 88%) as a pure (^{1}H NMR, 300 MHz), gummy solid: $[\alpha]_D = 8.00$ (*c* 2.26, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3473 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.40 (br s, 1 H), 3.17 (dd, $J = 9.8$, 2.2 Hz, 1 H), 3.35 (dd, $J = 9.0$, 9.0 Hz, 1 H), 3.36 (dd, $J = 9.0$, 2.4 Hz, 1 H), 3.79 (s, 3 H), 3.81 (s, 3 H), 4.00 (dd, $J = 2.2$, 2.2 Hz, 1 H), 4.02 (dd, $J = 9.6$, 9.6 Hz, 1 H), 4.15 (dd, $J = 9.6$, 9.6 Hz, 1 H), 4.52−4.63 (m, 4 H), 4.73−4.94 (m, 6 H), 6.80−6.90 (m, 4 H), 7.18−7.42 (m, 19 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 55.3 (q′), 72.3 (t′), 72.6 (t′), 73.0 (d′), 73.8 (d′), 74.1 (t′), 75.0 (t′), 75.8 (t′), 80.2 (d′), 80.9 (d′), 81.5 (d′), 83.3 (d′), 113.8 (d′), 113.9 (d′), 127.4 (d′), 127.5 (d′), 127.8 (d′), 127.9 (d′), 128.0 (d′), 128.2 (d′) 128.3 (d′), 128.5 (d′), 129.3 (d′), 129.6 (d′), 130.5 (s′), 131.1 (s′), 138.1 (s′), 139.0 (s′), 139.0 (s′), 159.2 (s′), 159.3 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{43}H_{46}NaO_8$ 713.309039, found 713.309230.

2,3,6-Tris-*O*-(phenylmethyl)-D-*myo*-inositol (4). DDQ (55.9 mg, 0.246 mmol) was added in one portion to a stirred solution of **25** (51.5 mg, 0.0746 mmol) in CH_2Cl_2 (20 mL) and water (1 mL). Stirring was continued for 4 h, and the solution was then washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL) and brine (10 mL), dried, evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 1:1 EtOAc−hexane, gave **4** (23.5 mg, 70%) as a pure (^{1}H NMR, 400 MHz), white solid: mp 122−123 °C; $[\alpha]_D = 10.3$ (*c* 1.73, $CHCl_3$); lit.[52] mp 117−119 °C; $[\alpha]^{16}_D = 15.5$ (*c* 1, $CHCl_3$); lit.[53] mp 117−119 °C; $[\alpha]_D = 12.4$ (*c* = 0.8, $CHCl_3$); lit.[54] mp 121−123 °C; $[\alpha]^{25}_D = 10$ (*c* 1, $CHCl_3$); FTIR (CH_2Cl_2 cast) 3439 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (br d, $J = 6.1$ Hz, 1 H), 2.68 (br s, 2 H), 3.27 (dd, $J = 9.8$, 2.4 Hz, 1 H), 3.47 (dd, $J = 9.1$, 9.1 Hz, 1 H), 3.52 (br d, $J = 9.0$ Hz, 1 H), 3.68 (dd, $J = 9.3$, 9.3 Hz, 1 H), 4.01 (dd, $J = 9.4$, 9.4 Hz, 1 H), 4.08 (dd, $J = 2.5$, 2.5 Hz, 1 H), 4.58 (d, $J = 11.6$ Hz, 1 H), 4.69 (d, $J = 11.6$ Hz, 1 H), 4.72 (d, $J = 11.4$ Hz, 1 H), 4.84 (d, $J = 11.3$ Hz, 1 H), 4.88 (d, $J = 11.3$ Hz, 1 H), 4.93 (d, $J = 11.4$ Hz, 1 H), 7.28−7.40 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75.5 Hz) δ 72.6 (t′), 72.6 (d′), 72.6 (d′), 74.8 (t′), 74.9 (d′) 75.1 (t′), 76.4 (d′), 80.3 (d′), 81.8 (d′), 127.8 (d′), 127.9 (d′), 127.9 (d′), 128.1 (d′), 128.5 (d′), 128.6 (d′), 128.6 (d′), 137.7 (s′), 138.5 (s′), 138.6 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{27}H_{30}NaO_6$ (M + Na) 473.194009, found 473.194360.

(R_a)-5-Deoxy-1,2,3,4-tetrakis-*O*-(phenylmethyl)-5-[(trimethylsilyl)ethenylidene]-L-*chiro*-inositol (27a). CSA (6.0 mg, 0.026 mmol) was added to a stirred solution of **27** (96.9 mg, 0.156 mmol) in PhMe (20 mL). Stirring was continued for 5 h, Et_3N (1 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 1:9 EtOAc−hexane, gave **27a** (70.8 mg, 73%) as a pure (^{1}H NMR, 360 MHz), white solid: FTIR (CH_2Cl_2 cast) 3386, 1948 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.08 (s, 9 H), 1.86 (br s, 1 H), 3.75 (dd, $J = 6.8$, 3.0 Hz, 1 H), 3.89 (dd, $J = 6.2$, 3.0 Hz, 1 H), 3.99 (dd, $J = 5.8$, 5.8 Hz, 1 H), 4.23 (dd, $J = 5.5$, 2.6 Hz, 1 H), 4.48−4.72 (m, 8 H), 4.78 (d, $J = 11.6$ Hz, 1 H), 5.33 (dd, $J = 2.8$, 2.8 Hz, 1 H), 7.20−7.40 (m, 20 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ −0.8 (q′), 68.3 (d′), 71.6 (t′), 72.3 (t′), 72.6 (t′), 73.8 (t′), 77.6 (d′), 78.4 (d′), 79.4 (d′), 79.6 (d′), 86.6 (d′), 95.4 (s′), 127.4 (d′), 127.5 (d′), 127.6 (d′), 127.7 (d′), 127.9 (d′), 128.3 (d′), 128.3 (d′), 128.4 (d′), 138.6 (s′), 138.6 (s′), 138.65 (s′), 138.70 (s′), 206.5 (s′); exact mass (HR electrospray) *m*/*z* calcd for $C_{39}H_{44}NaO_5Si$ (M + Na) 643.285573, found 643.286700. Crystal data: compound **27a** crystallizes in the monoclinic space group $P2_1$ (No. 4) with $a = 11.401$ (2) Å, $b = 12.219$ (2) Å, $c = 13.716$ (2) Å, $\beta = 108.353$ (10)°, $V = 1813.6$ (5) Å^3, $Z = 2$, $\rho_{calcd} = 1.137$ g cm^{-3}, $\mu = 0.105$ mm^{-1}. X-ray diffraction data were collected on a Siemens P4/RA instrument with Mo Kα radiation ($\lambda = 0.71073$ Å) at −60 °C. The final model, with 6315 unique data used and 407 parameters varied, converged to values of R_1 (F_o) = 0.0810 (for 3100 data with $F_o^2 > 2\sigma(F_o^2)$) and wR_2 (F_o^2) = 0.2366 (all data). The absolute stereochemistry of the molecule was not established from the structural results alone but was assigned on the basis of the known stereochemistry of its chemical precursors.

2-Ethenylidenecyclohexanol (28a).[55] (a) Use of $ZnCl_2$. A solution of **28** (40.0 mg, 0.204 mmol) in CH_2Cl_2 (10 mL) was added to a stirred and cooled (0 °C) suspension of $ZnCl_2$ (61.0 mg, 0.45 mmol) in CH_2Cl_2 (20 mL). Stirring was continued for 2.5 h, and water (10 mL) was then added. After 2 min, the organic phase was washed with saturated aqueous $NaHCO_3$ (10 mL), water (10 mL), and brine (10 mL), dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 2:8 EtOAc−hexane, gave **28a** (16.7 mg, 66%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3381, 1961 cm^{-1}; ^{1}H NMR (CD_2Cl_2, 300 MHz) δ 1.28−1.46 (m, 3 H), 1.58−1.72 (m, 1 H), 1.72−1.84 [m, 2 H, including doublet at δ 1.79 ($J = 4.5$ Hz, 1 H) which disappeared on exchange with D_2O)], 1.90−2.07 (m, 2 H), 2.30−2.42 (m, 1 H), 3.93−4.04 (m, 1 H), 4.76−4.88 (m, 2 H), [irradiation of the

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=C**H**$_2$ signal caused the width of the C**H**(OH) multiplet to decrease by 6.6 Hz.]; ^{13}C NMR (CD_2Cl_2, 75.5 MHz) δ 23.9 (t′), 26.8 (t′), 29.7 (t′), 36.2 (t′), 69.0 (d′), 78.2 (s′), 107.2 (s′), 201.1 (s′); exact mass *m*/*z* calcd for $C_8H_{12}O$ 124.08881, found 124.08886.

(b) Use of CF_3CO_2H. TFA (0.05 mL, 0.65 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **28** (50.0 mg, 0.255 mmol) in CH_2Cl_2 (40 mL). The mixture was stirred for 30 min, Et_3N (0.05 mL) was added, and stirring was continued for 10 min. Evaporation of the solvent and flash chromatography of the residue over silica gel (1.5 × 15 cm), using 2:8 EtOAc−hexane, gave **28a** (15.0 mg, 47%) as a pure (^{1}H NMR, 300 MHz), colorless oil, identical with material obtained in the previous experiment.

***trans*-2-Ethenylidene-5-phenylcyclohexanol (29a). (a) Use of $ZnCl_2$.** A solution of **29** (30.2 mg, 0.110 mmol) in CH_2Cl_2 (5 mL) was added to a stirred and cooled (0 °C) suspension of $ZnCl_2$ (20.0 mg, 0.147 mmol) in CH_2Cl_2 (15 mL). Stirring was continued for 3 h, and the mixture was filtered through a pad (4 × 2 cm) of flash chromatography silica gel which was rinsed with Et_2O (30 mL). Evaporation of the combined filtrates, and flash chromatography of the residue over silica (1.5 × 15 cm), using 2:8 EtOAc−hexane, gave **29a** (12.3 mg, 56%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 3216, 1958 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.56−1.74 (m, 2 H), 1.83 (br t, J = 13.0 Hz, 1 H), 1.99 (br d, J = 12.6 Hz, 1 H), 2.12 (br d, J = 13.0 Hz, 1 H), 2.30 (ddd, J = 13.0, 3.1, 3.1 Hz, 1 H), 2.51−2.68 (m, 1 H), 3.14 (dddd, J = 13.0, 13.0, 3.1, 3.1 Hz, 1 H), 4.57 (br s, 1 H), 4.71 (d, J = 4.5 Hz, 2 H), 7.13−7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.2 (t′), 33.9 (t′), 37.1 (d′), 40.8 (t′), 69.9 (d′), 74.5 (s′), 102.2 (t′), 126.2 (d′), 127.0 (d′), 128.5 (d′), 146.3 (s′), 203.9 (s′); exact mass *m*/*z* calcd for $C_{14}H_{16}O$ 200.12012, found 200.12035. The derived acetate (see Supporting Information) showed in its ^{1}H NMR spectrum (300 MHz, $CDCl_3$) a signal for C(1)H at δ 5.57 (dd, J = 2.8, 2.8 Hz), and we conclude, therefore, that the acetate is axial.

(b) Use of CF_3CO_2H. TFA (0.01 mL, 0.13 mmol, in 1.0 mL CH_2Cl_2) was added dropwise to a stirred and cooled (−78 °C) solution of **29** (31.7 mg, 0.116 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for 1 h, Et_3N (0.05 mL) was added, and stirring was continued for 10 min. Evaporation of the solvent, and flash chromatography of the residue over silica gel (1.5 × 12 cm), using 2:8 EtOAc−hexane, gave **29a** (10.8 mg, 46%) as a pure (^{1}H NMR, 300 MHz), colorless oil, identical with material obtained by use of $ZnCl_2$.

***trans*-2-Ethenylidene-5-phenylcyclohexanol (29a) and *cis*-2-Ethenylidene-5-phenylcyclohexanol (29b). Use of Bu_4NF.** TBAF (1 M in THF, 0.51 mL, 0.51 mmol) was added dropwise to a stirred and cooled (0 °C) mixture of **29** (93.0 mg, 0.342 mmol) in THF (40 mL) and powdered molecular sieves (4 Å, 2.50 g). The mixture was stirred at 0 °C for 1 h, diluted with Et_2O (20 mL), and filtered through a pad (2.5 × 2 cm) of flash chromatography silica gel, using Et_2O (50 mL) as a rinse. Evaporation of the solvent, and flash chromatography of the residue over silica gel (3 × 20 cm), using 1.5:8.5 EtOAc−hexane, gave **29a** (14.0 mg, 20%) as a pure (^{1}H NMR, 300 MHz), colorless oil, which was identified by comparison of its ^{1}H NMR spectrum with that of material obtained by use of $ZnCl_2$, and **29b** (25.5 mg, 37%) as a pure (^{1}H NMR, 300 MHz), colorless oil: FTIR (CH_2Cl_2, cast) 3396, 1962 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.47−1.66 (m, 2 H), 1.90−2.01 [(m, 2 H, including doublet at δ 1.96 (J = 4.9 Hz, 1 H)], 2.11−2.27 (m, 1 H), 2.35 (dddd, J = 11.9, 4.8, 2.8, 1.6 Hz, 1 H), 2.56 (ddd, J = 13.0, 5.1, 2.3 Hz, 1 H), 2.71 (dddd, J = 11.9, 11.9, 2.8, 2.8 Hz, 1 H), 4.09−4.21 (m, 1 H), 4.94−5.08 (m, 2 H), 7.18−7.35 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 29.8 (t′), 34.2 (t′), 42.6 (d′), 43.2 (t′), 68.3 (d′), 80.2 (t′), 106.7 (s′), 126.4 (d′), 126.8 (d′), 128.6 (d′), 145.4 (s′), 199.8 (s′); exact mass *m*/*z* calcd for $C_{14}H_{16}O$ 200.12012, found 200.12021.

***trans*-2-Ethenylidene-1-methyl-5-phenylcyclohexanol (30a) and *cis*-2-Ethenylidene-1-methyl-5-phenylcyclohexanol (30b). Use of Bu_4NF.** TBAF (1 M in THF, 0.31 mL, 0.31 mmol) was added dropwise to a stirred and cooled (0 °C) mixture of **30** (70.0 mg, 0.244 mmol) in THF (40 mL) and powdered molecular sieves (4 Å, 2.50 g). The mixture was stirred at 0 °C for 1 h, diluted with Et_2O (ca. 20 mL), and filtered through a pad (2.5 × 2 cm) of flash chromatography silica gel, using Et_2O (ca. 50 mL) as a rinse. Evaporation of the solvent, and flash chromatography of the residue over silica gel (2 × 15 cm), using 1.5:8.5 EtOAc−hexane, gave **30a** (35.0 mg, 67%) and **30b** (4.0 mg, 8%), each as a pure (^{1}H NMR, 300 MHz), colorless oil.

Alcohol **30a**: FTIR (CH_2Cl_2 cast) 3355, 1958 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.41 (s, 3 H), 1.46−1.70 [m, 3 H, including singlet at δ 1.51 (1 H)], 1.95−2.10 (m, 2 H), 2.34 (ddd, J = 13.8, 4.8, 2.4 Hz, 1 H), 2.55−2.71 (m, 1 H), 3.14 (dddd, J = 12.2, 12.2, 3.4, 3.4 Hz, 1 H), 4.75 (dd, J = 9.9, 4.5 Hz, 1 H), 4.79 (dd, 9.9, 4.0 Hz, 1 H), 7.15−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 28.0 (t′), 29.4 (q′), 33.9 (t′), 39.2 (d′), 47.5 (t′), 70.1 (s′), 76.0 (t′), 106.1 (s′), 126.1 (d′), 127.0 (d′), 128.5 (d′), 146.3 (s′), 202.8 (s′); exact mass *m*/*z* calcd for $C_{15}H_{18}O$ 214.13577, found 214.13574.

Alcohol **30b**: FTIR (CH_2Cl_2 cast) 3442, 1960 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.49 (s, 3 H), 1.58 (dddd, J = 12.7, 12.7, 12.7, 4.2 Hz, 1 H), 1.77 (br dd, J = 12.7, 12.7 Hz, 1 H), 1.94−2.11 [m, 3 H, including singlet at δ 2.07 (1 H)], 2.24−2.39 (m, 1 H), 2.50 (ddd, J = 12.7, 4.8, 2.2 Hz, 1 H), 2.78 (dddd, J = 12.7, 12.7, 3.4, 3.4 Hz, 1 H), 4.92 (dd, J = 9.9, 4.3 Hz, 1 H), 4.99 (dd, J = 9.9, 3.9 Hz, 1 H), 7.17−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 26.8 (q′), 29.3 (t′), 34.6 (t′), 42.0 (d′), 48.6 (t′), 70.1 (s′), 79.2 (t′), 109.9 (s′), 126.4 (d′), 126.9 (d′), 128.6 (d′), 145.5 (s′), 200.2 (s′); exact mass *m*/*z* calcd for $C_{15}H_{18}O$ 214.13577, found 214.13536.

***trans*-2-Ethenylidene-5-phenylcyclohexanol (31a) [≡ 29a]. Use of a Catalytic Amount of $Me_3SiOSO_2CF_3$ at −78 °C to Room Temperature.** $Me_3SiOSO_2CF_3$ (0.0062 M in CH_2Cl_2, 0.20 mL, 0.00124 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **31** (3.5 mg, 0.011 mmol) in CH_2Cl_2 (5 mL). Stirring was continued for 6 h, the cold bath was removed, and stirring was continued for another 5 h. The mixture was poured into saturated aqueous $NaHCO_3$ (ca. 3.0 mL) and extracted with Et_2O (2 × 5 mL). The combined organic extracts were washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 2:10 EtOAc−hexane, gave **31a** (1.7 mg, 77%) as a pure (^{1}H NMR, 300 MHz), colorless oil, identical with material (**29a**) obtained from **29**.

***trans*-1-Ethenylidene-2-methoxy-4-phenylcyclohexane (31b) and *cis*-1-Ethenylidene-2-methoxy-4-phenylcyclohexane (31c). Use of 1.1 equiv of $Me_3SiOSO_2CF_3$ at −78 °C.** $Me_3SiOSO_2CF_3$ (0.0517 M in CH_2Cl_2, 2.75 mL, 0.142 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **31** (39.4 mg, 0.124 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 3 h, saturated aqueous $NaHCO_3$ (10 mL) was added, the cold bath was removed, and stirring was continued for 30 min. The mixture was extracted with CH_2Cl_2 (2 × 10 mL), and the combined organic extracts were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 0.5:9.5 EtOAc−hexane, gave **31b** (15.3 mg, 58%) as a pure (^{1}H NMR, 300 MHz), colorless oil and **31c** (7.1 mg, 27%) as a pure (^{1}H NMR, 300 MHz), colorless oil.

Compound **31b**: FTIR (CH_2Cl_2 cast) 1960 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.64 (dddd, J = 12.6, 12.6, 12.6, 4.2 Hz, 1 H), 1.81 (ddd, J = 13.1, 13.1, 2.8 Hz, 1 H), 1.91−2.02 (m, 1 H), 2.13−2.23 (m, 1 H), 2.28 (br ddd, J = 13.1, 13.1, 3.4 Hz, 1 H), 2.33−2.48 (m, 1 H), 3.06 (dddd, J = 12.6, 12.6, 3.2, 3.2 Hz, 1 H), 3.33 (s, 3 H), 3.98 (dd, J = 2.8, 2.8 Hz, 1 H), 4.72 (d, J = 4.2 Hz, 2 H), 7.17−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.3 (t′), 34.0 (t′), 37.7 (d′), 39.9 (t′), 55.6 (d′), 73.6 (t′), 78.6 (q′), 98.7 (s′), 126.1 (d′), 127.0 (d′), 128.4 (d′), 146.5 (s′), 204.9 (s′); exact mass *m*/*z* calcd for $C_{15}H_{18}O$ 214.13577, found 214.13534.

Compound **31c**: FTIR (CH_2Cl_2 cast) 1962 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.51−1.72 (m, 2 H), 1.90−2.00 (m, 1 H), 2.08−2.22 (m, 1 H), 2.29−2.39 (m, 1 H), 2.49 (ddd, J = 13.2, 4.3, 2.3 Hz, 1 H), 2.69 (dddd, J = 12.3, 12.3, 2.8, 2.8 Hz, 1 H), 3.48 (s, 3 H), 3.69−3.79 (m, 1 H), 4.88 (ddd, 9.2, 4.2, 3.9 Hz, 1

H), 4.91 (ddd, 9.2, 3.2, 3.2 Hz, 1 H), 7.16−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 30.6 (t′), 34.6 (t′), 40.5 (t′), 43.0 (d′), 57.4 (d′), 77.1 (t′), 78.6 (q′), 103.5 (s′), 126.4 (d′), 126.8 (d′), 126.8 (d′), 128.5 (d′), 145.5 (s′), 201.5 (s′); exact mass *m*/*z* calcd for $C_{15}H_{18}O$ 241.13577, found 214.13551.

***trans*-2-Ethenylidene-5-phenylcyclohexanol (31a), *trans*-1-Ethenylidene-2-methoxy-4-phenylcyclohexane (31b), and *cis*-1-Ethenylidene-2-methoxy-4-phenylcyclohexane (31c). Use of a Catalytic Amount of $Me_3SiOSO_2CF_3$ at −78 °C.** $Me_3SiOSO_2CF_3$ (0.0062 M in CH_2Cl_2, 0.18 mL, 0.0011 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **31** (3.4 mg, 0.011 mmol) in CH_2Cl_2 (5 mL). Stirring was continued for 3 h, saturated aqueous $NaHCO_3$ (ca. 3.0 mL) was added, the cold bath was removed, and stirring was continued for ca. 30 min. The mixture was extracted with Et_2O (2 × 5 mL), and the combined organic extracts were washed with water (5 mL) and brine (5 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 10 cm), using 2:10 EtOAc−hexane, gave **31a** (0.9 mg, 48% based on conversion) as a pure (^{1}H NMR, 300 MHz), colorless oil, and a mixture (1.0 mg) of **31b**, **31c**, and unreacted **31** in a ratio of **31**:**31b**:**31c** = 1.2:1:1.3] as a colorless oil. Compounds **31b**, **31c**, and **31** were not further separated, identification being made through the ^{1}H NMR spectrum of the mixture.

Trimethyl[(4-phenyl-1-cyclohexen-1-yl)ethynyl]silane (31d). CSA (15.0 mg, 0.0645 mmol) was added in one portion to a stirred solution of **31** (20.0 mg, 0.0629 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 48 h, Et_3N (1 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 × 10 cm), using 1:20 EtOAc−hexane, gave **31d** (6.1 mg, 38%) as a pure (^{1}H NMR, 360 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2144 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 0.02 (s, 9 H), 1.70−1.82 (m, 1 H), 1.91−2.00 (m, 1 H), 2.17−2.46 (m, 4 H), 2.71−2.82 (m, 1 H), 6.24−6.29 (m, 1 H), 7.16−7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.1 (q′), 29.5 (t′), 29.8 (t′), 33.8 (t′), 39.1 (d′), 91.7 (s′), 106.8 (s′), 120.8 (s′), 126.3 (d′), 126.9 (d′), 128.5 (d′), 135.6 (d′), 146.4 (s′); exact mass *m*/*z* calcd for $C_{17}H_{22}Si$ 254.14908, found 254.14893.

***cis*- and *trans*-2-Ethenylidene-4-phenylcyclopentanol (32a). (a) Use of Bu_4NF.** TBAF (1 M in THF, 0.27 mL, 0.27 mmol) was added dropwise to a stirred and cooled (0 °C) mixture of **32** (46.5 mg, 0.18 mmol) in THF (60.0 mL) and powdered 3 Å molecular sieves (1.50 g). The mixture was stirred at 0 °C for 1 h, diluted with Et_2O (ca. 20 mL), and filtered through a pad (2.5 × 2 cm) of flash chromatography silica gel, which was rinsed with Et_2O (ca. 50 mL). Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (2 × 15 cm), using 2:8 EtOAc−hexane, gave **32a** (26.3 mg, 78%) as a colorless oil, which was a 55:45 mixture of epimers: FTIR (CH_2Cl_2 cast) 3356, 1959 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.73−2.00 (m, 2 H), 2.17−2.27 (m, 0.45 H), 2.45−2.60 (m, 1 H), 2.63−2.79 (m, 0.55 H), 2.79−2.92 (m, 0.55 H), 2.92−3.05 (m, 0.45 H), 3.05−3.19 (m, 0.55 H), 3.49−3.62 (m, 0.45 H), 4.78−5.04 (m, 3 H), 7.18−7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 37.1 (t′), 37.3 (t′), 41.6 (d′), 42.7 (d′), 43.1 (t′), 43.5 (t′), 73.9 (d′), 74.7 (d′), 77.8 (t′), 79.3 (t′), 106.8 (s′), 106.9 (s′), 126.4 (d′), 126.5 (d′), 127.0 (d′), 127.1 (d′), 128.5 (d′), 128.6 (d′), 143.4 (s′), 143.7 (s′), 202.4 (s′), 203.7 (s′); exact mass *m*/*z* calcd for $C_{13}H_{14}O$ 186.10446, found 186.10406.

(b) Use of $Sc(OSO_2CF_3)_3$. Aldehyde **32** (32.9 mg, 0.128 mmol) in $MeNO_2$ (5 mL) was added to a stirred solution of $Sc(OSO_2CF_3)_3$ in $MeNO_2$ (10 mL). Stirring was continued for 12 h, and the mixture was poured into brine (ca. 15 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 2:10 EtOAc−hexane, gave **32a** (16.8 mg, 70%) as a colorless oil, which was a 1:1 mixture of epimers. The structures were identified by examination of the ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of the mixture.

***cis*- and *trans*-2-Ethenylidene-4-phenylcyclopentanol (32a) and 1-(1-Chloroethenyl)-4-phenylcyclopentene (32b). Use of $ZnCl_2$.** A solution of **32** (50.9 mg, 0.197 mmol) in CH_2Cl_2 (5 mL) was added to a stirred and cooled (0 °C) suspension of $ZnCl_2$ (59.1 mg, 0.434 mmol) in CH_2Cl_2 (35 mL). The mixture was stirred for 2.5 h, the cold bath was removed, and stirring was continued for 12 h. The mixture was diluted with Et_2O (ca. 20 mL) and filtered through a pad (2 × 2 cm) of flash chromatography silica gel, using Et_2O (ca. 40 mL). Evaporation of the combined filtrates, and flash chromatography of the residue over silica gel (2 × 15 cm), using first hexane and then 2:8 EtOAc−hexane, gave **32a** (10.1 mg, 26%) as a colorless oil, which was a 55:45 mixture of epimers, identified by its ^{1}H NMR spectrum ($CDCl_3$, 360 MHz), and **32b** (25.0 mg, 62%) as a pure (^{1}H NMR, 360 MHz), colorless oil. Compound **32b**: FTIR (CH_2Cl_2 cast) unexceptional; ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.57−2.71 (m, 2 H), 2.93−3.06 (m, 2 H), 3.57−3.67 (m, 1 H), 5.25 (br s, 1 H), 5.35 (br s, 1 H), 6.22 (br s, 1 H), 7.18−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 41.3 (t′), 41.6 (t′), 44.2 (d′), 112.6 (t′), 126.2 (d′), 126.9 (d′), 128.6 (d′), 132.2 (d′), 136.3 (s′), 139.5 (s′), 146.4 (s′); exact mass *m*/*z* calcd for $C_{13}H_{13}{}^{37}Cl$ 206.06763, found 206.06751.

***trans*- and *cis*-1-Ethenylidene-2-methoxy-4-phenylcyclopentane (33a).** $Me_3SiOSO_2CF_3$ (0.0517 M in CH_2Cl_2, 4.34 mL, 0.224 mmol) was added dropwise to a stirred and cooled (−78 °C) solution of **33** (62.0 mg, 0.204 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 1.5 h, saturated aqueous $NaHCO_3$ (10 mL) was added, and the cold bath was removed. The mixture was stirred for 30 min and extracted with CH_2Cl_2 (2 × 15 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 20 cm), using 1:10 EtOAc−hexane, gave **33a** (36.4 mg, 89%) as a colorless oil, which was as a 3:2 mixture of epimers: FTIR (CH_2Cl_2 cast) 1958 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.76−1.96 (m, 1 H), 2.26 (br dd, J = 13.2, 6.0 Hz, 0.6 H), 2.43−2.80 (m, 1.8 H), 2.91−3.20 (m, 1 H), 3.38 (s, 1.8 H), 3.43 (s, 1.2 H), 3.45−3.57 (m, 0.6 H), 4.32 (br d, J = 5.1 Hz, 0.6 H), 4.41−4.48 (m, 0.4 H), 4.83−4.90 (m, 2 H), 7.17−7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 37.0 (t′), 38.0 (t′), 40.7 (t′), 42.0 (t′), 42.7 (d′), 42.9 (d′), 56.0 (q′), 56.8 (q′), 76.2 (t′), 76.9 (t′), 82.9 (d′), 84.0 (d′), 102.0 (s′), 103.0 (s′), 126.3 (d′), 126.4 (d′), 127.1 (d′), 128.5 (d′), 128.5 (d′), 143.7 (s′), 144.2 (s′), 203.9 (s′), 205.0 (s′); exact mass calcd for $C_{14}H_{16}O$ 200.12012, found 200.12014.

Trimethyl[(4-phenyl-1-cyclopenten-1-yl)ethynyl]silane (33b). A solution of **33** (31.7 mg, 0.104 mmol) in CH_2Cl_2 (ca. 2 mL) was added to a stirred solution of CSA (26.6 mg, 0.115 mmol) in CH_2Cl_2 (30 mL). Stirring was continued for 20 h, Et_3N (1 mL) was added, and the solution was evaporated. Flash chromatography of the residue over silica gel (1.5 × 15 cm), using 5:100 EtOAc−hexane, gave **33b** (8.6 mg, 34%) as a pure (^{1}H NMR, 360 MHz), colorless oil: FTIR (CH_2Cl_2 cast) 2146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.21 (s, 9 H), 2.42−2.62 (m, 2 H), 2.78−2.93 (m, 2 H), 3.46 (dddd, J = 8.4, 8.4, 8.4, 8.4 Hz, 1 H), 6.10−6.19 (m, 1 H), 7.15−7.34 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 0.1 (q′), 41.8 (t′), 43.5 (d′), 44.5 (t′), 95.6 (s′), 102.1 (s′), 123.9 (s′), 126.2 (d′), 126.9 (d′), 128.5 (d′), 138.0 (d′), 146.2 (s′); exact mass calcd for $C_{16}H_{20}Si$ 240.13342, found 240.13362.

***cis*-2-Ethenylidene-1-methyl-4-phenylcyclopentanol and *trans*-2-Ethenylidene-1-methyl-4-phenylcyclopentanol (34a).** TBAF (1 M in THF, 0.14 mL, 0.14 mmol) was added dropwise to a stirred and cooled (0 °C) mixture of **34** (31.2 mg, 0.114 mmol) in THF (40 mL) and powdered 3 Å molecular sieves (0.50 g). The mixture was stirred at 0 °C for 1 h. Saturated aqueous NH_4Cl (ca. 10 mL) was added, and after 5 min, the organic phase was washed with water (10 mL) and brine (10 mL), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1.5 × 12 cm), using 1.5:8.5 EtOAc−hexane, gave **34a** (20.2 mg, 88%) as a colorless oil, which was a 1:7.2 mixture of epimers: FTIR (CH_2Cl_2 cast) 3367, 1958 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (s, 3 H), 1.60 (br s, 0.12 H), 1.65 (br s, 0.88 H), 1.80 (dd, J = 12.7, 12.7 Hz, 0.88 H), 2.09 (dd, J = 12.2, 12.2 Hz, 0.12 H), 2.29 (ddd, J = 12.8, 6.2, 1.7 Hz, 1 H), 2.55−2.67 (m, 0.88 H), 2.73−2.92 (m, 0.24 H), 2.97−3.08 (m, 0.88 H), 3.16 (dddd, J = 11.5, 11.5,

7.0, 7.0 Hz, 0.12 H), 3.50−3.62 (m, 0.88 H), 4.88−5.01 [m, 2 H, including two sets of doublets at δ 4.93 (J = 3.4 Hz) and δ 4.94 (J = 3.4 Hz)], 7.18−7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 27.1 (q′), 28.9 (q′), 37.7 (t′), 37.8 (t′), 42.5 (d′), 49.3 (t′), 79.2 (t′), 79.6 (t′), 110.5 (s′), 126.3 (d′), 126.5 (d′), 127.0 (d), 127.1 (d′), 128.47 (d′), 128.54 (d′), 143.6 (s′), 143.7 (s′), 201.5 (s′), 202.1 (s′); exact mass calcd for $C_{14}H_{16}O$ 200.12012, found 200.12000.

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Supporting Information Available: Procedures for making **27**, **28**, **28a**−acetate, **29**−**32**, **32b**, **33**−**46**, **48**−**51**, and **53**−**66**, NMR spectra for compounds not analyzed, and X-ray data on **27a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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