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Stereoselective Construction of all-*anti* Polypropionate Modules: Synthesis of the C5−C10 Fragment of Streptovaricin U

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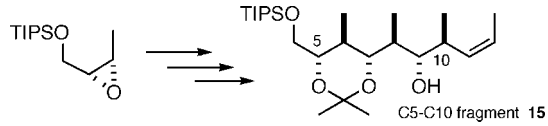

A concise nonaldol approach for the stereoselective construction of all-*anti* polypropionate fragments was developed. The iterative epoxide-based methodology consists of the *syn*-selective epoxidation of cis homoallylic alcohols with use of the $VO(acac)_2$-catalyzed conditions followed by epoxide cleavage with a propynyl aluminum reagent as key steps. The methodology was applied to the synthesis of the all-*anti* C6−C10 fragment of streptovaricin U.

Introduction

Polypropionate chains are structural motifs consisting of alternating methyl and hydroxy groups within an aliphatic framework. These structures are found in many natural products having a wide range of biological and medicinal activity.[1] Their synthesis has attracted great interest among synthetic chemists due to the challenge represented by the stereoselective assembly of the contiguous stereogenic centers.[2] Among the diverse approaches that have been developed for the synthesis of polypropionates, aldol and aldol-related strategies are most prevalent, since these processes are well understood and their intricacies are well documented.[3] Interestingly, the *anti*,*anti*,*anti*-stereotetrad **1** (Figures 1 and 2), found in many important natural products such as ionomycin, zincophorin, the streptovaricins, and others, has been the most difficult to construct when employing enantioselective aldol or crotylmetalation strategies.[4]

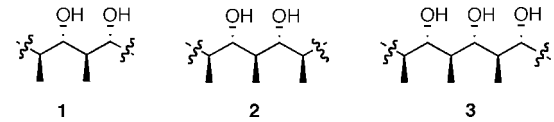

FIGURE 1. The all-*anti* stereotetrad **1**, stereopentad **2**, and stereohexad **3**.

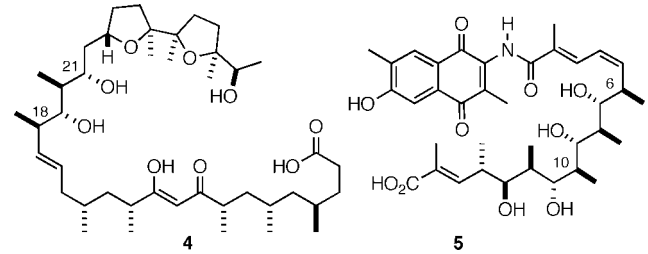

FIGURE 2. Ionomycin (**4**) and streptovaricin U (**5**) and their all-*anti*,*anti* C18−C21 and C6−C10 stereotetrad and stereopentad.

This is because the *anti*,*anti* relationship must arise from disfavored *anti*-Felkin transition states.[5] This challenge has produced a number of ingenious *anti* selective aldol and crotylmetal strategies that have been very useful in polyketide synthesis.[6,7]

While the alternative approaches present high diastereo- and enantioselectivities, efforts to develop efficient stereoselective nonaldol methods for the construction of *anti*,*anti* polypropionate subunits continue.[8] These efforts become more evident when longer all-*anti* stereotetrad (**1**) or stereopentad (**2**) subunits (such

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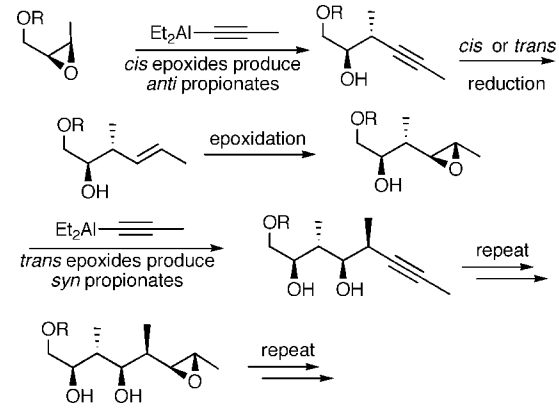
as the C18−C21 and the C6−C10 segments of ionomycin[9] and streptovaricin U,[10] respectively) need to be elaborated.

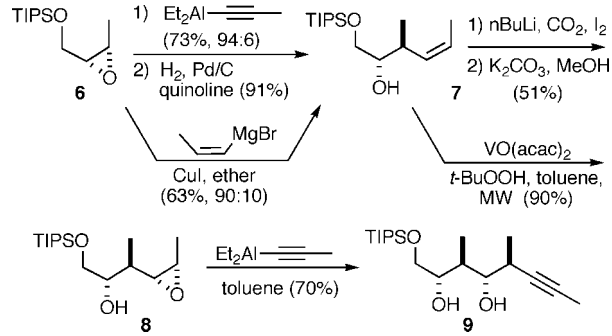
Epoxide-based approaches have also been used for the synthesis of polypropionates, albeit to a lesser extent. These versatile intermediates, which can be prepared stereoselectively by several methods,[11] were first considered for polypropionate synthesis by Kishi,[12] Corey,[13] and Bartlett,[14] in studies related to the synthesis of the rifamycin S ansa chain. During the mid-eighties, Lipshutz developed a reiterative route for the preparation of all-*syn*-1,3-polyols and polyketides, reacting optically active epoxides with higher order *cis*- or *trans*-propenyl cuprates.[15] Later, Miyashita and co-workers developed a reiterative entry to polypropionates by means of a regio- and stereoselective methylation of γ,δ-epoxy acrylates with trimethylalane.[16]

Recently, we reported an epoxide-based methodology for the stereoselective construction of polypropionates (Scheme 1).[17] Our reiterative approach includes a sequence of three reactions: stereoselective epoxidation of unsaturated alcohols, regioselective alkynyl alane cleavage of the epoxide, and cis or trans reduction of the incorporated alkyne to produce a new homoallylic alcohol. Each sequence incorporates a propionate fragment into the growing chain. The propionate unit formed during the epoxide cleavage step will have a *syn* relationship if the epoxide

SCHEME 1. General Reiterative Epoxide-Based Approach for Polypropionate Synthesis



SCHEME 2. Preparation of the *anti*,*anti*,*anti* Stereotetrad 9



geometry is trans or an *anti* arrangement if a cis epoxide is used. The configuration of the resulting hydroxy groups is determined by the absolute configuration of the epoxide precursor, which results from a diastereoselective epoxidation of the alkenol precursor.[18]

The application of our method to the preparation and cleavage of a series of diastereomeric 3,4-epoxy alcohols produced the corresponding stereotetrads with different degrees of regioselectivity and yield. Remarkably, the "arduously accessible"[19] all-*anti* stereotetrad **9** was readily attained using this approach (Scheme 2). For this, the TIPS protected cis epoxy alcohol **6** was regioselectively cleaved with diethyl propynyl alane to yield the first *anti* unit. Hydrogenation of the incorporated alkyne produced alkenol **7** in good yield. An alternative copper-catalyzed *cis*-propenylmagnesium bromide cleavage of epoxide **6** produced **7** in similar yield and regioselectivity with the convenient exclusion of the alkyne reduction step.[20] Alkenol **7** was converted to epoxide **8** by using the $VO(acac)_2$-catalyzed epoxidation under microwave irradiation, which produced exclusively the desired *syn* epoxy alcohol in higher yield than the established iodocarbonation/methanolysis method.[11b,c,18a] Finally, the propynyl alane cleavage of epoxide **8** produced the *anti*,*anti*,*anti* alkynyl diol **9** as the only regioisomer. These results prompted us to further elaborate on this approach with the intent to develop an effective methodology for the elaboration of all-*anti* polypropionate fragments, which could be incorporated as synthetic modules for the preparation of longer

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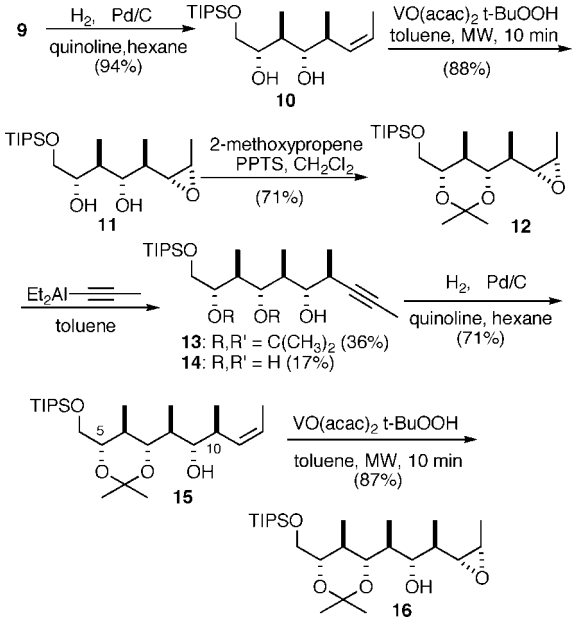
SCHEME 3. Synthesis of the all-*anti* Stereohexads 13, 14 and the Streptovaricin U C5−C10 Fragment 15



polypropionate chains. Herein, we report a highly stereo- and regioselective epoxide-based methodology for the synthesis of all-*anti* polypropionate units and its application to the synthesis of the all-*anti* C5−C10 segments of streptovaricin U.

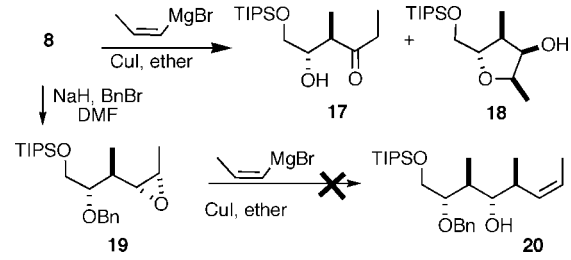
Results and Discussion

For the elaboration of longer all-*anti* polypropionate fragments, we envisaged a linear progression that comprises a reiteration of our three-step reaction cycles (or a two-step sequence if the Grignard method is used) starting from alkynediol **9**. An advantage of employing epoxide chemistry in this fashion is the inherent S_N2 behavior of epoxides toward nucleophilic attack, providing stereodefined products. In addition, contrary to the generally more efficient convergent methodologies, a linear approach circumvents the setbacks associated with the coupling of advanced fragments that already contain stereogenic centers and are prone to mismatched interactions.[21]

In this regard, alkyne **9** was reduced to the *cis*-alkenediol **10** and subjected to an epoxidation by using the microwave-assisted $VO(acac)_2$ conditions, producing epoxide **11** as a single diastereomer in 88% yield (Scheme 3). Epoxy diol **11** was protected as the acetonide **12** and reacted with the propynylalane reagent to produce the all-*anti*,*cis* epoxide **12**.

To evaluate the alternate epoxide cleavage manifold, epoxide **8** was subjected to the copper-catalyzed *cis*-propenyl Grignard reaction conditions, with the expectation that diol **10** could be produced in one step. Instead of the alkenol product, a 1:1 mixture of ethyl ketone **17** and furan **18** was obtained as the major product (Scheme 4). The formation of ketone **17** is consistent with a $MgBr_2$-promoted epoxide to ketone rearrangement under the Grignard reaction conditions (Schlenk equilibrium).[22] Furan **18** results from the intramolecular attack of the magnesium alkoxide to the external epoxide carbon. Both reactions occur because of the low reactivity of disubstituted epoxide **8** under the copper-catalyzed Grignard reaction conditions. To test this assumption and suppress the formation of these side products, epoxy alcohol **9** was protected as the benzyl ether **19**. Although this strategy did curtail the formation of the unwanted products, only the starting benzyl ether **19** was recovered. The epoxidation of alkenediol **10** was also evaluated by using the complementary iodocarbonation/methanolysis sequence. While the iodocarbonation reaction proceeded as expected, the methanolysis step produced epoxide **11**, together with a mixture of methyl carbonate products. The results establish the vanadium-catalyzed epoxidation and the propynyl alane-mediated epoxide cleavage as the preferred reactions for the elaboration of *anti* propionate units.

SCHEME 4. Epoxide Cleavage Attempts with Use of the Copper-Catalyzed *cis*-Propenylmagnesium Bromide Conditions



To further extend the all-*anti* polypropionate fragment, another iteration was implemented. The reaction of epoxide **12** with diethylpropynylalane provided exclusively the desired external cleavage product in a 53% yield; however, a 2:1 mixture of acetonide **13** with the deprotected triol **14** was obtained. Thus, to complete the reaction sequence, compounds **13** and **14** were easily separated by chromatography and acetonide **13** was hydrogenated to produce alkenol **15**. Compounds **13** and **14** represent termini-differentiated all-*anti* stereohexad elaborated in a straightforward and highly stereoselective fashion. The all-*anti* stereohexad **15** corresponds to the C5−C10 fragment of streptovaricin U containing the five chiral centers (C6−C10) with the correct relative configuration, a homoallylic alkene for further epoxidation (an *anti* epoxidation is required at this point), and a masked aldehyde at C5.

With alkenol **15** on hand, it was further *syn* epoxidized under the microwave-assisted $VO(acac)_2$-catalyzed conditions to efficiently furnish the more advanced epoxide **16**. The resulting polypropionate chain has seven consecutive all-*anti* stereogenic centers assembled in a simple and highly stereoselective iterative fashion. In principle, another *anti* subunit could be further generated by cleavage of the epoxide moiety. Therefore, this epoxidation/cleavage sequence can be successfully applied for the preparation of advanced all-*anti* polypropionate fragments, which could be used as modules for chain elongation allowing further manipulations in both directions.

The regioselectivity of the epoxide cleavage reactions to produce the 1,3-diols resulting from the attack at the external epoxide carbon (C4) was confirmed by ^{13}C NMR. For example, compound **13** showed diagnostic peaks at 38.9 ppm for the C2 methine and 30.1 ppm for the C4 propargyl carbon, compared

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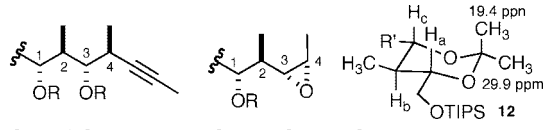

FIGURE 3. Selected ^{13}C NMR data for the regio- and stereoselectivity determination.

to the 1,4-diols peaks at 34−37 and 41−46 ppm for the C2 and C3 carbon atoms, respectively (Figure 3). This was corroborated by the COSY spectra of **13** and **14**, showing cross peaks between the C4 methyl protons and the propargylic methines.

The *syn* 1,3-diol relationship in **11** was confirmed by its conversion to the corresponding 1,3-acetonide **12**, where the ^{13}C NMR revealed peaks at 19.4 and 29.9 ppm for the *gem*-dimethyl carbon atoms.[17,23] In addition, **12** showed coupling constants of J_{ab} = 10.3 Hz and J_{bc} = 10.5 Hz for the 6-membered-ring vicinal protons corresponding to an axial−axial relationship, confirming the *anti*,*anti* stereotriad.[24] The *syn*/*anti* stereoselectivity of the epoxidation reaction was again established by ^{13}C NMR by using the diagnostic C2 methine and C3,C4 epoxide carbons. As previously reported,[18] when an *anti* 2-methyl-3-epoxy relationship is present, the epoxide C3 and C4 carbons show signals near 52 and 58 ppm, respectively, while a *syn* relationship displays higher values between 54 and 60 ppm. This tendency holds for the *cis*-2-methyl-3,4-epoxy alcohols **11**, **12**, and **16**, thus establishing the required *syn* hydroxy-epoxide selectivity (Figure 3).

Conclusion

In summary, we have successfully devised a concise method for the stereo- and regioselective construction of all-*anti* termini-differentiated polypropionate modules. The microwave-assisted $VO(acac)_2$-catalyzed epoxidation of the *cis*-homoallylic alcohol precursors produced better yields than the iodocarbonation sequence and excellent *syn* diastereoselectivity. The diethylpropynylalane cleavage of the *anti*,*anti*,*cis*-3,4-epoxy alcohol systems was shown to be more reliable than the copper-catalyzed *cis*-propenyl Grignard conditions for the more advance all-*anti* systems. The simplicity of the chemical transformations and iterativity of the reaction sequence make this method advantageous and practical. The methodology was applied to the synthesis of the all-*anti* C6−C10 fragment (**15**) of streptovaricin U.

Experimental Section

(±)-(2*S,3*S**,4*S**,5*S**,*Z*)-3,5-Dimethyl-1-[(triisopropylsilyl)-oxy]-6-octene-2,4-diol (10).** The alkyne diol **9** (3.0 g, 8.9 mmol) was hydrogenated[18a] with use of 0.59 mL of freshly distilled dry quinoline, 0.58 g of Pd/C catalyst (10% Pd, 0.066 g/mmol), and 18.8 mL of dry hexane. After workup and solvent evaporation, 2.88 g (94%) of neat crude was obtained. The alkenediol **10** was used for the next step without further purification. ^1H NMR δ 5.52 (dd, J = 10.5, 5.0 Hz, 1H), 5.50 (dd, J = 10.5, 7.1 Hz, 1H), 3.84 (dd, J = 9.7, 3.4 Hz, 1H), 3.70 (ddd, J = 7.8, 7.8, 3.4 Hz, 1H), 3.57 (dd, J = 9.7, 7.8 Hz, 1H), 3.47 (dd, J = 8.1, 3.6 Hz, 1H), 2.72 (ddq, J = 7.1, 6.6, 3.6 Hz, 1H), 1.66 (ddq, J = 8.1, 7.8, 6.9 Hz, 1H), 1.62 (d, J = 5.0 Hz, 3H), 1.06 (m, 21H), 1.06 (d, J = 6.6 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H). ^{13}C NMR δ 131.4, 124.1, 79.4, 76.2, 65.9, 38.6, 34.2, 18.1, 17.9, 13.0, 13.0, 12.1.

(±)-(2*S,3*S**,4*R**,5*R**,6*R**,7*S**)-6,7-Epoxy-3,5-dimethyl-1-[(triisopropylsilyl)oxy]-2,4-octanediol (11).** The alkene diol **10** (5.37 g, 15.60 mmol) was subjected to the vanadium-catalyzed epoxidation under MW irradiation condition[18b] with use of 0.058 g (0.014 equiv) of $VO(acac)_2$, 60 mL of toluene, and 4.1 mL of *tert*-butyl hydroperoxide (4.24 M in toluene, 1.1 equiv). After workup and solvent evaporation, 5.63 g (100%) of epoxide **11** was obtained. The crude was used without further purification. ^1H NMR δ 4.61 (s, 1H), 3.87 (dd, J = 9.6, 3.3 Hz, 1H), 3.68 (ddd, J = 8.3, 5.1, 3.3 Hz, 1H), 3.61 (dd, J = 8.3, 3.1 Hz, 1H), 3.57 (dd, J = 9.6, 8.3 Hz, 1H), 3.30 (s, 1H), 3.10 (dd, J = 9.2, 4.5 Hz, 1H), 2.99 (dq, J = 5.6, 4.5 Hz, 1H), 1.95 (ddq, J = 8.3, 6.8, 5.1 Hz, 1H), 1.70 (ddq, J = 9.3, 7.0, 3.1 Hz, 1H), 1.29 (d, J = 5.6 Hz, 3H), 1.06 (m, 21H), 1.06 (d, J = 7.0 Hz, 3H), 0.95 (d, J = 6.8 Hz, 3H). ^{13}C NMR δ 80.0, 76.7, 66.0, 57.1, 50.6, 38.6, 34.3, 17.9, 14.3, 13.4, 13.3, 11.8. Anal. Calcd for $C_{19}H_{40}O_4Si$: C, 63.28; H, 11.18. Found: C, 63.49; H, 11.32.

(±)-(4*R,5*S**,6*S**)-4-[(1*R**,2*R**,3*S**)-(2,3-Epoxy-1-methylbutyl)]-2,2,5-trimethyl-6-[(triisopropylsilyloxy)methyl]-1,3-dioxane (12).** The crude epoxy diol **11** (2.0 g, 5.55 mmol) was converted to the acetonide by adding 0.083 g of PPTS and 0.266 mL of 2-methoxypropene in 52.0 mL of CH_2Cl_2 at 0 °C. Workup, solvent evaporation, and column chromatography (100:1 hexane/ether) yielded 1.31 g (59% for the three-step sequence) of the expected product **12**. ^1H NMR δ 3.82 (dd, J = 10.8, 3.5 Hz, 1H), 3.71 (dd, J = 10.8, 5.1 Hz, 1H), 3.52 (ddd, J = 10.3, 5.3, 3.5 Hz, 1H), 3.48 (dd, J = 10.5, 2.1 Hz, 1H), 3.09 (dd, J = 9.2, 4.5 Hz, 1H), 2.93 (dq, J = 5.5, 4.5 Hz, 1H), 1.86 (ddq, J = 10.5, 10.3, 6.5 Hz, 1H), 1.70 (ddq, J = 9.2, 7.1, 2.1 Hz, 1H), 1.41 (s, 3H), 1.36 (s, 3H), 1.27 (d, J = 5.5 Hz, 3H), 1.08 (m, 21H), 0.96 (d, J = 7.1 Hz, 3H), 0.85 (d, J = 6.5 Hz, 3H). ^{13}C NMR δ 97.8, 77.4, 76.1, 66.3, 56.4, 50.3, 33.6, 33.0 29.9, 19.4, 17.9, 13.9, 13.4, 12.1, 12.0. Anal. Calcd for $C_{22}H_{44}O_4Si$: C, 65.95; H, 11.07. Found: C, 65.87; H, 11.14.

(±)-(4*S,5*S**,6*S**)-4-[(1*S**,2*S**,3*S**)-1,3-Dimethyl-2-hydroxy-4-hexynyl]-6-[(triisopropylsilyloxy)methyl]-2,2,5-trimethyl-1,3-dioxane (13).** Epoxide **12** (0.50 g, 1.25 mmol) was subjected to the propynylalane cleavage procedure[11] with use of 9.6 mL of dry toluene (0.13 M), 2.8 mL (6.2 mmol, 5 equiv) of *n*-BuLi (2.27 M in hexane), an excess of propyne gas, and 3.4 mL (6.2 mmol, 5 equiv) of diethylaluminum chloride (1.8 M in toluene). Workup, solvent evaporation, and flash chromatography (12:1 Hex/EtOAc), yielded 0.195 g (35%) of pure product **13** and 0.089 g (18%) of the expected product **14** without the acetonide moiety. ^1H NMR δ 3.79 (dd, J = 10.8, 3.5 Hz, 1H), 3.72 (dd, J = 10.8, 5.1 Hz, 1H), 3.55 (dd, J = 10.6, 1.7 Hz, 1H), 3.52 (ddd, J = 10.3, 5.1, 3.5 Hz, 1H), 3.43 (ddd, J = 8.5, 6.0, 2.4 Hz, 1H), 2.72 (d, J = 6.0 Hz, 1H), 2.67 (dqq, J = 7.0, 2.4, 2.4 Hz, 1H), 2.06 (ddq, J = 8.5, 7.0, 1.7 Hz, 1H), 1.94 (ddq, J = 10.6, 10.3, 6.5 Hz, 1H), 1.82 (d, J = 2.4, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.25 (d, J = 7.0 Hz, 3H), 1.06 (m, 21H), 0.96 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H). ^{13}C NMR δ 98.0, 79.6, 78.8, 78.1, 76.4, 76.3, 66.1, 38.9, 34.4, 30.4, 30.1, 19.2, 18.9, 18.0, 16.2, 12.5, 12.0, 3.7. Anal. Calcd for $C_{25}H_{48}O_4Si$: C, 68.13; H, 10.98. Found: C, 67.94; H, 11.08.

(±)-(3*S,4*S**,5*S**,6*S**,7*S**,8*S**,*Z*)-3,5,7-Trimethyl-1-[(triisopropylsilyl)oxy]-dec-8-ene-2,4,6-triol (14).** ^1H NMR δ 3.86 (dd, J = 9.6, 3.8 Hz, 1H), 3.76 (ddd, J = 8.3, 7.4, 3.8 Hz, 1H), 3.86 (dd, J = 9.6, 3.6 Hz, 1H), 3.58 (dd, J = 5.4, 5.4 Hz, 1H), 3.41 (dd, J = 8.4 2.2 Hz, 1H), 2.72 (dqq, J = 7.8, 2.2, 1.8 Hz, 1H), 2.08 (ddq, J = 8.4, 6.9, 5.4 Hz, 1H), 2.05 (ddq, J = 7.4, 6.9. 5.4 Hz, 1H), 1.81 (d, J = 1.8, 3H), 1.23 (d, J = 7.8 Hz, 3H), 1.06 (m, 21H), 0.95 (d, J = 6.9 Hz, 3H) and (d, J = 6.9 Hz, 3H). ^{13}C NMR δ 81.6, 79.1, 78.6, 78.5, 75.2, 65.8, 40.3, 39.2, 30.4, 18.7, 17.9, 15.5, 14.3, 11.9, 3.6.

(±)-(4*S,5*S**,6*S**)-4-[(1*S**,2*S**,3*S**,*Z*)-1,3-Dimethyl-2-hydroxy-4-hexenyl]-6-[(triisopropylsilyloxy)methyl]-2,2,5-trimethyl-1,3-**

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dioxane (15). Alkynol **13** (0.34 g, 0.77 mmol) was hydrogenated[18a] with use of 0.05 mL of freshly distilled dry quinoline, 0.05 g of Pd/C catalyst (10% Pd, 0.066 g/mmol), and dry hexane. After workup and solvent evaporation, column chromatography (50:1 HexEtAc) yielded 0.24 g (71%) of pure product **15**. ^{1}H NMR δ 5.52 (dq, J = 11.0, 5.0 Hz, 1 H), 5.49 (dd, J = 11.0, 8.9 Hz, 1H), 3.77 (dd, J = 10.9, 3.2 Hz, 1H), 3.72 (dd, J = 10.9, 5.0 Hz, 1H), 3.49 (ddd, J = 10.5, 5.0, 3.2 Hz, 1H), 3.49 (dd, J = 8.3, 3.4 Hz, 1H), 3.48 (dd, J = 10.5, 1.7 Hz, 1H), 3.10 (br s, 1H), 2.70 (ddq, J = 8.9, 6.8, 3.4 Hz, 1H), 1.93 (ddq, J = 10.5, 10.5, 6.5 Hz, 1H), 1.83 (ddq, J = 8.3, 7.1, 1.7 Hz, 1H), 1.62 (d, J = 5.0, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.06 (m, 21H), 1.05 (d, J = 6.8 Hz, 3H), 0.94 (d, J = 7.1 Hz, 3H), 0.86 (d, J = 6.5 Hz, 3H). ^{13}C NMR δ 132.1, 123.7, 98.1, 80.0, 78.7, 76.4, 65.9, 36.9, 34.6, 34.2, 30.2, 19.1, 18.4, 18.0, 13.0, 12.6, 12.0. Anal. Calcd. for $C_{25}H_{50}O_4Si$: C, 67.82; H, 11.38. Found: C, 67.55; H, 11.42.

(±)-(4*S,5*S**,6*S**)-4-[(1*S**,2*S**,3*R**,4*R**,5*S**)-1,3-Dimethyl-2-hydroxy-4,5-epoxyhexyl]-6-[(triisopropylsilyloxy)methyl]-2,2,5-trimethyl-1,3-dioxane (16).** Alkenol **15** (0.21 g, 0.47 mmol) was subjected to the vanadium-catalyzed epoxidation under MW irradiation conditions[18b] with use of 0.0017 g (0.014 equiv) of $VO(acac)_2$, 10 mL of toluene, and 0.13 mL of *tert*-butyl hydroperoxide (3.85 M in toluene, 1.1 equiv). After column chromatography (9:1 hexane/ethyl acetate), 0.176 g (87%) of the epoxide **16** was obtained. ^{1}H NMR δ 3.77 (dd, J = 10.9, 3.3 Hz, 1H), 3.71 (dd, J = 10.9, 5.1 Hz, 1H), 3.60 (ddd, J = 6.3, 2.6, 2.7 Hz, 1H), 3.51 (ddd, J = 10.3, 5.1, 3.3 Hz, 1H), 3.48 (dd, J = 10.8, 1.0 Hz, 1H), 3.38 (d, J = 2.7 H, 1H), 3.11 (dd, J = 9.2, 4.6 Hz, 1H), 2.98 (dq, J = 5.4, 4.6 Hz, 1H), 2.28 (ddq, J = 7.0, 6.3, 1.0 Hz, 1H), 1.95 (ddq, J = 10.8, 10.3, 6.5 Hz, 1H), 1.61 (ddq, J = 9.2, 6.9, 2.6 Hz, 1H), 1.42 (s, 3H), 1.39 (s, 3H), 1.28 (d, J = 5.4 Hz, 3H), 1.05 (m, 24H), 0.96 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H). ^{13}C NMR δ 98.1, 80.2, 78.3, 76.5, 65.8, 56.9, 50.3, 36.6, 35.1, 34.5, 30.2, 19.0, 18.2, 17.9, 14.7, 13.4, 12.6, 12.0. Anal. Calcd for $C_{25}H_{50}O_5Si$: C, 65.45; H, 10.99. Found: C, 65.72; H, 11.22.

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Supporting Information Available: . NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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