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Synthesis of Allenic Diols by Samarium Diiodide-Promoted Coupling Between Alkynyloxiranes and Ketones

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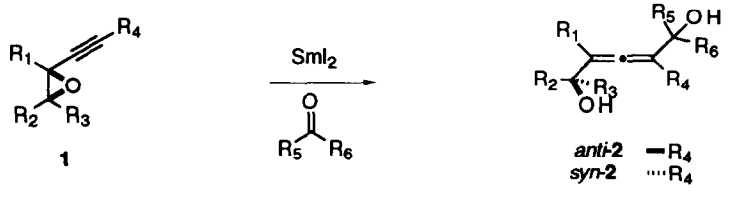
Abstract: The SmI_2-mediated reductive coupling between alkynyloxiranes and ketones provides a new route to 2,3-pentadiene-1,5-diols. The preferred stereochemistry observed in the coupling products is the result of the new C-C bond forming *anti* with respect to the opening epoxide ring. Yields and diastereoselectivities are dependent on the alkynyloxirane substitution pattern.

INTRODUCTION

The emergence of the one-electron reducing agent samarium diiodide (SmI_2) in the synthetic field has provided useful methodology for the formation of C-C bonds in processes involving radical and/or organometallic intermediates.[1]

Particularly valuable are those reactions that preserve the unsaturation present in the starting materials, as the products can be further elaborated within a synthetic scheme. Thus, SmI_2 promotes the coupling of carbonyl compounds with allylic derivatives[2] and vinyloxiranes[3] where these substrates behave, in a formal sense, as nucleophilic allylating agents. Similarly, a number of propargylic derivatives[2b,4] behave as synthetic equivalents of the propargyl-allenyl anion synthon when treated with SmI_2 in the presence of ketones. By analogy, alkynyloxiranes, under the same reductive conditions, should provide an entry into alkoxy propargyl-allenyl anion synthons, thus significantly expanding the synthetic utility of those substrates, which are normally employed as electrophiles in C-C bond-forming processes.[5]

Therefore, it became of interest to study the possibility of using SmI_2 to effect the coupling of simple alkynyloxiranes **1** with carbonyl compounds (Scheme 1). This paper reports the stereoselective synthesis of allenic diols **2** in this fashion.[6]



Scheme 1

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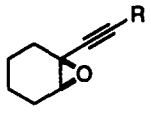
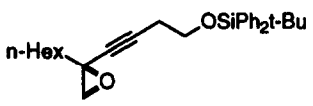
RESULTS AND DISCUSSION

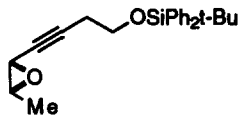
Representative alkynyloxiranes **1a-j** were selected for this study. They were obtained by epoxidation of commercial or readily available enynes that were prepared using conventional procedures.



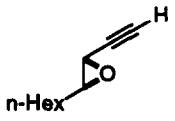
1a R = H
1b R = Me
1c R = Ph



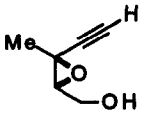
1d



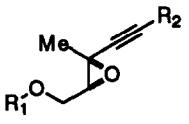
1e



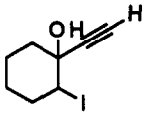
1f



1g



1h R_1 = Bn, R_2 = H
1i R_1 = $SiPh_2t$-Bu, R_2 = H
1j R_1 = $SiPh_2t$-Bu, R_2 = Me



3a

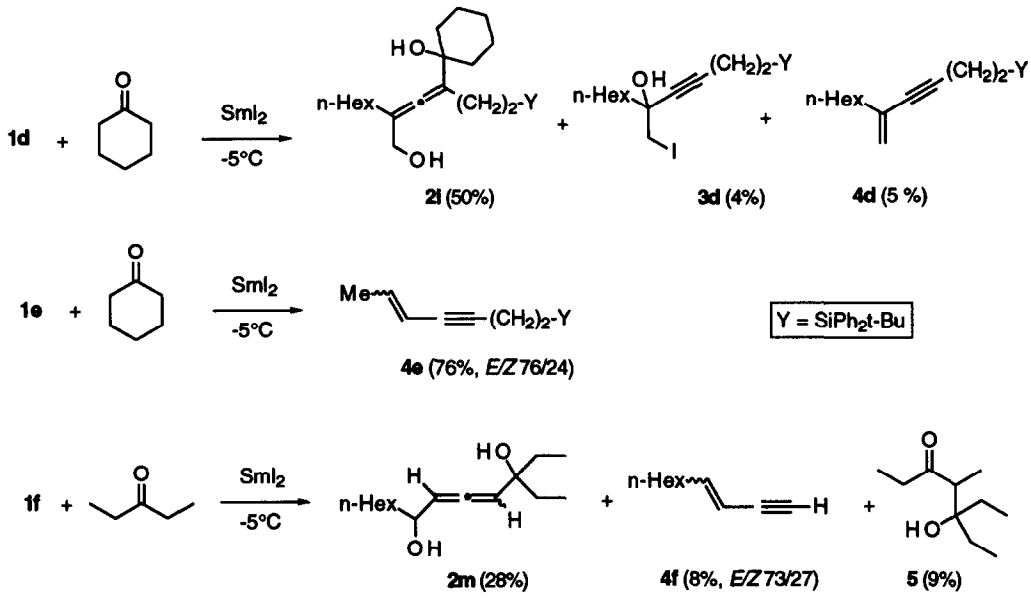
The addition of a mixture of a carbonyl compound and an alkynyloxirane **1a-j** to SmI_2 in THF gave in general good yields of coupling products **2** (Scheme 1, Table 1) and also provided clean reaction mixtures, as well as a simple procedure since the end of the reaction was easily visualized by the turning of the SmI_2 characteristic blue solutions into a yellow-green suspension. A reaction temperature in the range 0-(-5°C) was found optimal. Reversing the order of addition or adding the carbonyl compound after reaction between the alkynyloxirane and SmI_2 was complete gave inferior results. In the latter case the addition of a solution of **1a** to two equivalents of SmI_2 at 0°C resulted in a rapid (< 20 min) decoloration of the SmI_2 characteristic blue color but, after addition of 3-pentanone, only a 2 % yield of the allenic diol product **2e** was obtained. Unreacted starting **1a** and unidentified side products accounted for the remaining of the reaction mixture. The use of HMPA, that is known to facilitate many SmI_2-mediated reactions,[7] led with the same epoxide to intractable mixtures where substantial amounts of unreacted **1a** were detected by ^{1}H-NMR. In contrast to the related intermolecular reactions between propargylic esters and ketones, where products resulting from coupling at both the propargylic and allenic positions are observed,[4a] only allenic products were found in this case. Small amounts of 1-ethynyl-2-iodocyclohexanol (**3a**), the result of epoxide ring opening on unreacted epoxide by iodide anion,[8] usually accompanied the formation of allenes **2** derived from **1a**.

Table 1 reveals that, while both terminal and substituted alkynes can be employed successfully, the degree of substitution at the epoxide ring appears to be crucial for the outcome of the reaction. Thus, yields from alkynyloxiranes further substituted at both epoxide termini were uniformly high, with the exception of the Ph-substituted alkyne **1c** (entry 11). However, the absence of substitution at any of those positions resulted in much lower yields of coupling products and the competing reduction of the epoxide[9] with formation of the enynes **4** (Scheme 2); in one case (entry 14), the aldol product **5** (Scheme 2) was also obtained.[10]

Table 1. Reductive Coupling between Alkynyloxiranes and Ketones[a].

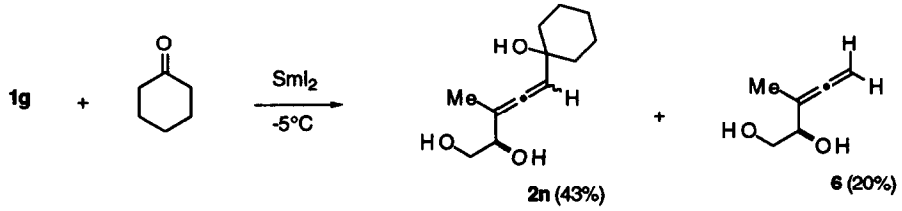
Entry	Epoxide	R_5	R_6	T (°C)	t (min)	Product	Yield (%)	*anti* / *syn*[b]
1	**1a**		$(CH_2)_5$	-5	150	**2a**	74	4.9 : 1
2	**1a**		$(CH_2)_6$	0	90	**2b**	77[c]	2.3 : 1
3	**1a**		$(CH_2)_4$	0	45	**2c**	56[c]	3.3 : 1
4	**1a**	Me	Me	-5	180	**2d**	81	5.7 : 1
5	**1a**	Et	Et	0	120	**2e**	73[c]	7.3 : 1
6	**1a**	Me	$Ph(CH_2)_2$	-5	60	**2f**	84	3.0:1
7	**1a**	Me	$(CH_2)_2CH{=}CH_2$	0	120	**2g**	64[c]	d
8	**1a**	Me	$(CH_2)_3CN$	0	80	**2h**	64[c]	d
9	**1a**	n-Hex	$(CH_2)_{10}CO_2Me$	0	90	**2i**	67[c]	4.5 : 1
10	**1b**		$(CH_2)_5$	-5	90	**2j**	77	> 50 : 1[e]
11	**1c**		$(CH_2)_5$	-5	45	**2k**	38	2.2 : 1
12[f]	**1d**		$(CH_2)_5$	-5	5	**2l**	50[g]	
13	**1e**		$(CH_2)_5$	-5	<1	**4e**	76[h]	
14	**1f**	Et	Et	-5	270	**2m**	28[i]	1.3 : 1
15	**1g**		$(CH_2)_5$	-5	90	**2n**	43[j]	1.2 : 1
16	**1h**		$(CH_2)_5$	-5	60	**2o**	96	1.2 : 1
17	**1i**		$(CH_2)_5$	-5	120	**2p**	89	3.3 : 1
18[k]	**1j**		$(CH_2)_5$	-5	210	**2q**	74[l]	4.5 : 1[m]

[a] Unless otherwise specified, the General Procedure was used. See Experimental. [b] Values obtained from ^1H NMR or HPLC (entries 17,18) data taken on the purified products. [c] Also isolated was **3a** in 3-7% yield. [d] Precise ratio could not be determined. [e] A single isomer to the limit of detection of NMR and GC. [f] Reaction run with three equivalents of SmI_2. [g] Also isolated were **1d** (5%), **3d** (4%) and **4d** (5%) (Scheme 2). [h] See Scheme 2. [i] Also isolated were **1f** (21%), **4f** (8%) and **5** (9%) (Scheme 2). [j] Also isolated was **6** (20%) (Scheme 3). [k] Reaction run with five equivalents of cyclohexanone. [l] Combined yield of **2q** and **8** (see Scheme 4). [m] Diastereomeric ratio is the result of assuming that diol **8** comes exclusively from ***anti*-2q**.



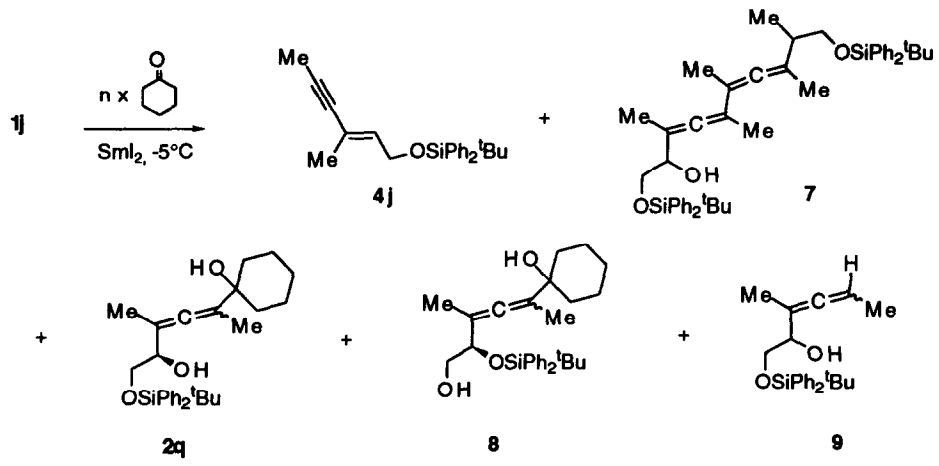
Scheme 2

The coupling reaction is tolerant of some useful functionality, both in the carbonyl substrate (entries 7-9) and in the alkynyloxirane (entries 12, 16-18). One exception is the hydroxyl group of substrate **1g** (entry 15; Scheme 3) which interferes with the coupling presumably by protonation of an organosamarium derived from the alkynyloxirane (*vide infra*). In marked contrast to ketones, aldehydes perform poorly in the coupling reaction. As previously noted,[11] the aldehyde carbonyl is comparatively very reactive towards SmI_2 and side reactions often preclude effective couplings.[4a,d] Thus, the coupling between **1a** and 3-phenylpropanal proceeded in very low yield and no other aldehyde was tested.



Scheme 3

The reaction of the silyl ether **1j** with cyclohexanone has some mechanistic interest. When performed under the standard conditions, with equimolar amounts of **1j** and ketone, a low yield of coupling product **2q** was obtained, being the dimer **7** the major product of the reaction (Scheme 4; Table 2). Also isolated were the enyne **4j** and some unreacted **1j** (4%). The formation of the dimer was dependent on the **1j**/cyclohexanone ratio and could be totally suppressed by increasing the amount of cyclohexanone to at least 4 equivalents relative to the oxirane **1j** (entries 3,4; Table 2). In these cases, small amounts of the uncoupled allene **9** and the diol **8** (the result of the migration of the silyl group to the adjacent hydroxyl group)[12] were also formed.



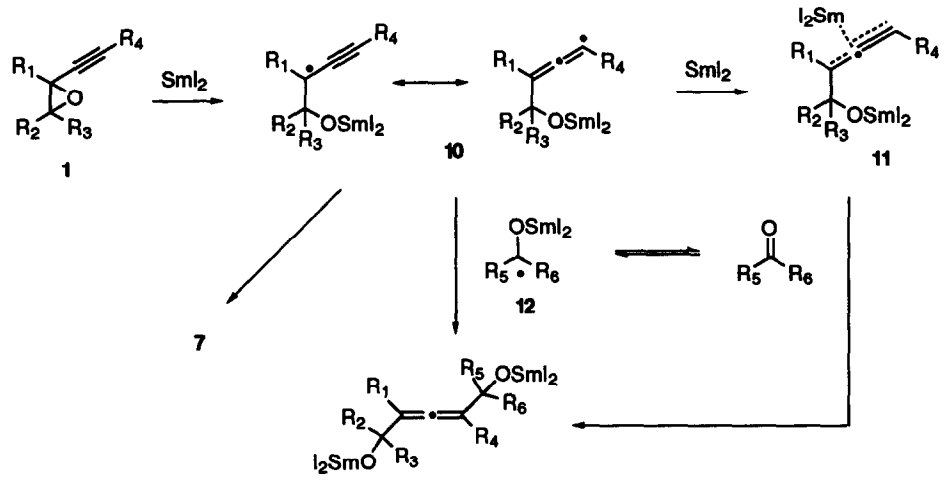
Scheme 4

Table 2. Reductive Coupling of 1j. Effect of the Relative Amount of Cyclohexanone

Entry	n[a]	4j (%)	7 (%)	2q (%)	9 (%)
1	1	10	32	27	-
2	2	26	21	42	-
3	4	<7	-	69[b]	10
4	5	-	-	74[b]	-

[a] n = Molar ratio of cyclohexanone to **1j**. [b] Combined yield **2q+8**.

The formation of the dimer **7** and its suppression in the presence of excess cyclohexanone are interpreted as an indication that resonance-stabilized radicals **10** (Scheme 5), produced in the one-electron transfer from SmI_2 to the starting alkynyloxirane,[13] are involved in the coupling. Thus, for substrate **1j**, the formation of product **2q** must proceed, at least partially, by coupling between a ketyl radical anion **12** and **10**. In this scenario, dimerization of **10** leading to **7** is the dominant pathway unless sufficient amounts of the ketyl **12** are present. However, these results do not necessarily rule out an alternative pathway involving carbonyl addition of an organosamarium **11** derived from **10**. The formation of **6** in the reaction of the hydroxy-substituted substrate **1g** (Scheme 3) indicates that, to some extent, organosamarium species are also involved.[14] Given these overall results and literature precedence in SmI_2-mediated couplings involving ketones,[15] it is likely that both mechanisms could be operative in general.



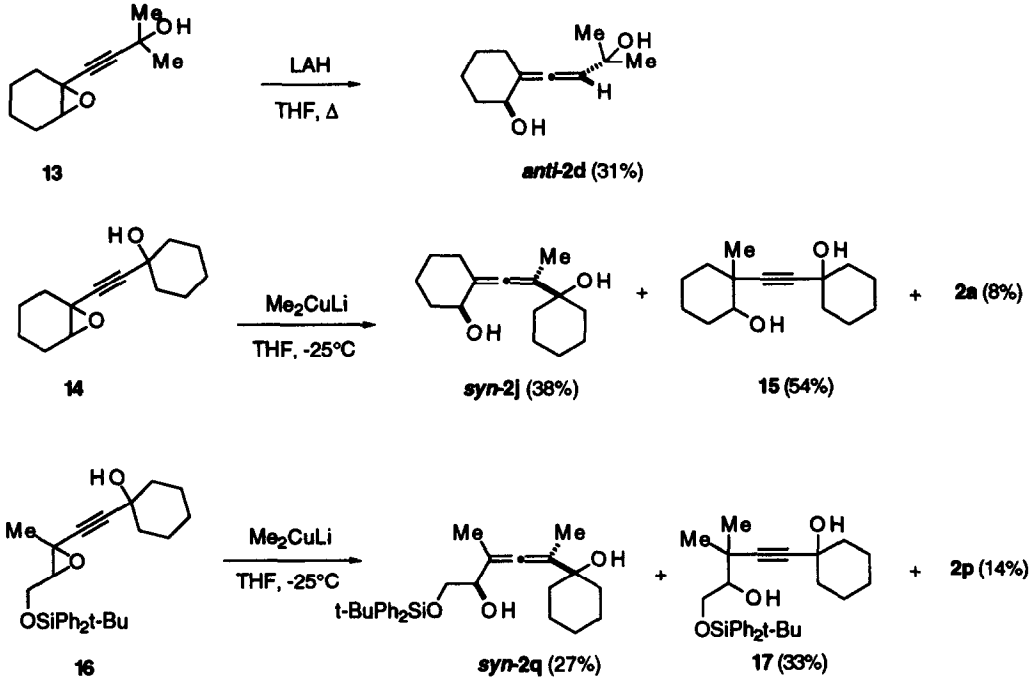
Scheme 5

Stereochemistry of the Coupling.

In general, the SmI_2-promoted between alkynyloxiranes and ketones took place with low to moderate diastereoselectivity. Monocyclic substrates without bulky substituents gave coupling products with low diastereoselectivity (see entries 14-16 in Table 1) probably as a result of the conformational flexibility of the presumed intermediates **10** or **11** (Scheme 5). The rigidity imposed by the added ring in bicyclic substrates **1a-c** results in moderate axial diastereoselectivities. Bicyclic substrate **1b**, with a methyl substituent at the alkynyl terminus (entry 10, Table 1) was exceptional in that a single isomer, as judged by NMR and capillary GC, was obtained. With substrates **1g-j** (entries 15-18, Table 1) the nature of the hydroxyl protecting group was also found to exert a significant effect on diastereoselectivity. Thus, no selectivity was found with hydroxy or benzyloxy substituents whereas the reactions of substrates with a bulkier sililoxy substituent were moderately selective. The couplings using a prochiral ketone (entries 6-9, Table 1) produced all the four possible isomers, with two of them predominating over the others in a ratio within the range of related couplings. This indicates that the carbonyl addition proceeds with no facial selectivity.

The stereochemistry of the major product is the result of the new C-C bond forming *anti* to the opening epoxide. Therefore, the formation of allenic diols with this new SmI_2-promoted coupling is stereochemically complementary to the alternative organocuprate S_N2' displacements on alkynyloxiranes bearing a propargylic hydroxyl group.[5e] Stereochemical assignments followed from chemical correlations of the coupling products **2d, j, q** with the corresponding diols obtained by stereochemically well defined literature procedures. The rest of diols were given stereochemical assignments by analogy with these cases. Thus, the major product obtained in the LAH reduction of the epoxypropargyl alcohol **13** (Scheme 6) was identical to the diol **2d** predominating in the SmI_2-promoted coupling reaction. Since the LAH reduction of propargyl alcohols related to **13** has been reported to lead to products resulting from overall *syn* hydride attack,[16] our major product is the result of the new group entering *anti* with respect to the opening epoxide. The methyl-substituted allenes **2j** and **2q** were similarly correlated with the products obtained by the cuprate S_N2' displacements on propargyl alcohols **14** and **16**. This known *anti* process[5e] afforded the minor (*syn*) diastereomers of **2j** (not obtained in the SmI_2-

promoted coupling) and **2q**, respectively, thus confirming the preferred *anti* stereocourse of the coupling.[17] Also obtained in the cuprate reactions of **14** and **16** were the alkynyl diols **15** and **17**, respectively, derived from direct cuprate addition to the epoxide, as well as the allenic diols **2a** and **2p** (diastereomeric mixtures), the result of alkynyloxirane reduction under the reaction conditions.[5e]



Scheme 6

In conclusion, the SmI_2-promoted reductive coupling between alkynyloxiranes and ketones provides a new strategy for the synthesis of penta-2,3-diene-1,5-diols with moderate *anti* diastereoselectivity. This stereochemical preference is complementary to that observed using alternative literature methodology. In general, effective couplings are realized when the alkynyloxirane substitution pattern favors electron transfer over iodide-promoted ring-opening.

Experimental.

General. All reactions involving air- and moisture-sensitive materials were conducted under an atmosphere of dry Ar. THF was freshly distilled from sodium/benzophenone and, for reactions with SmI_2, it was deoxygenated prior to use. Dichloromethane, and DMF were distilled from CaH_2 and stored over 4 Å molecular sieves. The carbonyl reagents used in the coupling reactions were distilled immediately prior to use. Organic extracts were dried over Na_2SO_4, filtered and evaporated under reduced pressure. Flash column chromatography[20] was performed on silica gel (230-400 mesh). HPLC purifications were carried out with either LiChrosorb Si60 (7μm, 25 x 2.5 cm) (column 1) or μPorasil (10μm, 19 x 1.5 cm) (column 2) columns. ^1H and ^{13}C RMN spectra were obtained in $CDCl_3$ at 250 MHz and 62.9 MHz, respectively. IR data include only characteristic absorptions. Mass spectra were obtained at 70 eV. GC-MS analysis were performed at 70-

280 °C (20 °C/min) with a stationary phase of methylphenylsilicone (0.25 μm, 30 m x 0.25 mm).

Epoxides **1a-c** were prepared according to literature procedures.[5a,21]

General Epoxidation Procedure. In a typical experiment, to a solution of the appropriate enyne (47.0 mmol) in CH_2Cl_2 (182 mL) at 0°C was added MCPBA (70.5 mmol). The solution was stirred for 30 min, allowed to warm to room temperature and further stirred for 13 h. 1M NaOH (100 mL) was added and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (50 mL) and the combined organic extracts washed with 1M NaOH (2 x 50 mL). The residue after evaporation was purified as indicated for the individual cases.

4-(tert-Butyldiphenylsilyloxy)but-1-yne. Tert-Butyldiphenylsilyl chloride (4.31 g, 15.0 mmol) was added dropwise at room temperature to a solution of but-3-yn-1-ol (1.00 g, 14.0 mmol) and imidazole (2.13 g, 31.0 mmol) in DMF (8.4 mL) under Ar. After stirring the solution for 30 min water (10 mL) was added, the mixture was stirred further 20 min, diluted with CH_2Cl_2 (10 mL) and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were extracted with H_2O (5 x 5 mL). The crude after evaporation was purified by flash chromatography (5:95 EtOAc/hexanes) to yield the title compound (4.40 g, 100%) as a colorless oil: ^{1}H NMR δ 1.10 (s, 9H, $(CH_3)_3$-C), 1.97 (t, J = 2.5 Hz, 1H, H-1), 2.50 (td, J = 7.0, 2.5 Hz, 2H, H-3), 3.82 (t, J = 7.0 Hz, 2H, H-4), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 19.2, 22.6, 26.7, 62.3, 69.3, 81.4, 127.6, 129.7, 133.5, 135.5; IR (neat) ν 3300, 2110, 1115 cm^{-1}; HRMS calcd for $C_{20}H_{24}OSi$ 308.159644, found 308.159181.

6-(tert-butyldiphenylsilyloxy)-2-hexylhex-1-en-3-yne (**4d**). Cacchi's procedure[22] was followed: $Pd(PPh_3)_2(OAc)_2$ (65 mg, 0.08 mmol) was added to a solution of 4-(*tert*-butyldiphenylsilyloxy)but-1-yne (1.75 g, 5.7 mmol) and oct-1-en-2-yl triflate[23] (93%, 1.00 g, 4.1 mmol) in DMF (14 mL) and tributylamine (20 mL) at 70°C under Ar and the solution was maintained at the same temperature for 1 h. After cooling to room temperature, H_2O (30 mL) was added and the resulting mixture was stirred for 20 min and the layers separated. The organic layer was washed with H_2O (5 x 10 mL). The residue after evaporation was purified by flash chromatography (2.5:97.5 EtOAc/hexanes) to yield **4d** (1.83 g, 59%) as an oil: ^{1}H NMR δ 0.89 (t, J = 6.5 Hz, 3H, CH_3), 1.08 (s, 9H, $(CH_3)_3$-C), 1.3 (m, 6H), 1.4-1.5 (m, 2H), 2.12 (t, J = 7.4 Hz, 2H, C_2-CH_2), 2.61 (t, J = 6.9 Hz, 2H, H-5), 3.81 (t, J = 6.9 Hz, 2H, H-6), 5.15 (t, J = 0.96 Hz, 1H, H-1), 5.23 (d, J = 1.7 Hz, 1H, H-1), 7.3-7.4 (m, 6H), 7.7-7.8 (m, 4H); ^{13}C NMR δ 14.1, 19.2, 22.6, 23.5, 26.7, 28.0, 28.6, 31.6, 37.4, 62.5, 82.1, 86.7, 119.8, 127.6, 129.6, 132.2, 133.6, 135.5; IR ($CHCl_3$) ν 2210, 1610, 1110 cm^{-1}. Anal. Calcd for $C_{28}H_{38}OSi$: C, 80.33; H, 9.16. Found: C, 80.08; H, 9.17.

6-(tert-Butyldiphenylsilyloxy)-1,2-epoxy-2-hexylhex-3-yne (**1d**). Enyne **4d** (0.80 g, 1.91 mmol) was subjected to the General Epoxidation conditions to afford, after flash chromatography (5:95 EtOAc/hexanes) and HPLC (Column 1, 9 mL/min, 5:95 EtOAc/hexanes, t_R = 16 min) the epoxide **1d** (0.65 g, 78%) as an oil: ^{1}H NMR δ 0.90 (distorted t, 3H, CH_3), 1.06 (s, 9H, $(CH_3)_3$-C), 1.3 (m, 6H), 1.5-1.7 (m, 4H), 2.48 (t, J = 6.9 Hz, 2H, H-5), 2.70 (d, J = 5.5 Hz, 1H, H-1), 2.93 (d, J = 5.5 Hz, 1H, H-1), 3.76 (t, J = 6.9 Hz, 2H, H-6), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 14.0, 19.2, 22.5, 22.8, 25.5, 26.7, 29.0, 31.7, 36.5, 51.1, 54.6, 62.2, 79.7, 80.8, 127.7, 129.7, 133.5, 135.5; IR (neat) ν 1115 cm^{-1}. Anal. Calcd for $C_{28}H_{38}O_2Si$: C, 77.37; H, 8.82. Found: C, 77.46; H, 8.97.

(Z)-7-(tert-butyldiphenylsilyloxy)hept-2-en-4-yne (**Z-4e**). A solution of 4-(*tert*-butyldiphenylsilyloxy)but-1-yne (1.80 g, 6.50 mmol) in Et_2NH (7 mL) was added to a solution of (*Z*)-1-bromopropene (0.94 g, 7.8 mmol), $Pd(PPh_3)_2Cl_2$ (0.11 g, 1.62 mmol) and CuI (0.12 g, 6.50 mmol) in Et_2NH (20 mL) at room temperature. The resulting solution was stirred for 15 h. Diethyl ether (15 mL) and saturated

NH_4Cl (10 mL) were added, the mixture was stirred for 20 min and the layers separated. The aqueous layer was extracted with diethyl ether (10 mL). The residue after evaporation was purified by flash chromatography (2.5:97.5 EtOAc/hexanes) to give a 86:14 *Z/E* mixture of (**4e**) (1.40 g, 70%) as a colorless oil. A second chromatographic separation (1:99 EtOAc/hexanes) afforded a sample (0.70 g) enriched in the *Z*-isomer (93:7): ^{1}H NMR δ 1.06 (s, 9H, $(CH_3)_3$-C), 1.83 (dd, *J* = 6.8, 1.7 Hz, 3H, H-1), 2.62 (td, *J* = 7.0, 2.0 Hz, 2H, H-6), 3.81 (t, *J* = 7.0 Hz, 2H, H-7), 5.4-5.5 (m, 1H, H-3), 5.90 (dq, *J* = 10.6, 6.8 Hz, 1H, H-2), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 15.7, 19.2, 23.7, 26.7, 62.7, 78.2, 91.5, 110.2, 127.6, 129.6, 133.6, 135.5, 137.3; IR ($CHCl_3$) ν 2200 1665, 1110 cm^{-1}.

(5S,6R*)-1-(tert-Butyldiphenylsilyloxy)-5,6-epoxyhept-3-yne* (**1e**). Enyne **4e** (93% *Z*, 600 mg, 1.72 mmol) was epoxidized according to the General Procedure to afford, after flash chromatography (5:95 EtOAc/hexanes), the epoxide **1e** (401 mg, 64%) as a colorless oil: ^{1}H NMR δ 1.06 (s, 9H, $(CH_3)_3$-C), 1.38 (d, *J* = 5.2 Hz, 3H, H-7), 2.50 (td, *J* = 6.9, 1.6 Hz, 2H, H-2), 3.11 (dq, *J* = 5.2, 4.0 Hz, 1H, H-6), 3.39 (dt, *J* = 4.0, 1.6 Hz, 1H, H-5), 3.76 (t, *J* = 6.9 Hz, 2H, H-1), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 14.6, 19.2, 22.9, 26.7, 45.7, 53.9, 62.2, 76.0, 83.5, 127.7, 129.7, 133.5, 135.5; IR (neat) ν 2230, 1110 cm^{-1}; HRMS calcd for $C_{19}H_{28}O_2Si$ (M-^{t}Bu) 307.11543, found 307.11399.

(E)-Dec-3-en-1-yne (***E*-4f**). Potassium *tert*-butoxide (4.70 g, 41.0 mmol) was added to a suspension of iodomethyltriphenylphosphonium iodide[24] (11.00 g, 20.0 mmol) in THF (300 mL) at room temperature. The resulting solution was cooled to -78°C and (*E*)-non-2-enal (2.90 g, 20.0 mmol) in THF (43 mL) was added. The mixture was stirred at the same temperature for 2 h and then allowed to warm to room temperature over 90 min. After adding hexanes (50 mL) the mixture was extracted with brine (2 x 20 mL) and water (10 mL). The residue after evaporation was purified by flash chromatography in hexanes to afford the enyne ***E*-4f** (1.10 g, 41%) as a volatile yellowish oil: ^{1}H NMR δ 0.8-0.9 (m, 3H, H-10), 1.3-1.4 (m, 8H), 2.1 (m, 2H, H-5), 2.76 (d, *J* = 2.0 Hz, 1H, H-1), 5.4 (dm, *J* = 16.0 Hz, 1H, H-3), 6.24 (dt, *J* = 15.9 Hz, 7.0 Hz, 1H, H-4); ^{13}C NMR δ 14.0, 22.5, 28.5, 28.7, 31.6, 33.0, 75.5, 82.6, 108.4, 147.0; IR ($CHCl_3$) ν 3300, 2100 cm^{-1}.

(3S,4S*)-3,4-Epoxydec-1-yne* (**1f**).[5a] Enyne ***E*-4f** (0.40 g, 2.94 mmol) was epoxidized according to the General Procedure to afford, after flash chromatography in hexanes, the epoxide **1f**[5a] (0.17 g, 39%) as a volatile colorless oil.

(2R,3S*)-2,3-Epoxy-3-methylpent-4-yn-1-ol* (**1g**).[25] The General Epoxidation Procedure was applied to (*Z*)-3-methylpent-2-en-4-yn-1-ol (1.00 g, 10.4 mmol). Flash chromatography (25:75 EtOAc/hexanes) of the crude product afforded the epoxide **1g** (0.72 g, 62%) as a colorless solid: mp 40-41°C.

(3S,4S*)-5-Benzyloxy-3,4-epoxy-3-methylpent-1-yne* (**1h**). (*E*)-3-Methylpent-2-en-4-yn-1-ol (10 g, 0.1 mol) was added to NaH (3.74 g, 0.15 mol) in THF (210 mL) at 0°C and the mixture was stirred for 2 h with occasional cooling while hydrogen was evolved. Benzyl bromide (23.13 g, 0.13 mol) was added, stirring continued for 48 h and the whole poured over ice/water (~ 30 g). The mixture was extracted with diethyl ether (4 x 30 mL),the combined organic extracts washed with brine (3 x 20 mL) and dried (Na_2SO_4). The residue after evaporation of the solvents was partially purified by flash chromatography (5:95 EtOAc/hexanes) to yield **(*E*)-benzyloxy-3-methyl-3-penten-1-yne** (17.2 g) which contained ~ 14% of benzyl bromide: ^{1}H NMR δ 1.56 (s, 3H, CH_3), 2.87 (s, 1H, acetylenic), 4.1 (d, *J* = 6.5 Hz, 2H, CH_2-C=C), 4.52 (s, 2H, CH_2-Ph), 6.1 (m, 1H, *H*-C=C), 7.2-7.4 (m, 5H). Without further purification this material (2.1 g) was subjected to the General Epoxidation conditions to afford, after flash chromatography (10:90 EtOAc/hexanes) the epoxide **1h** (1.45 g, 60% over two steps) as an oil: ^{1}H NMR δ 1.50 (s, 3H, CH_3), 2.32 (s, 1H, H-1), 3.42 (apparent t, *J* = 5.2 Hz, 1H, H-4), 3.56 (dd, *J* = 11.3, 5.5 Hz, 1H, H-5), 3.67 (dd, *J* = 11.3, 5.0 Hz, 1H, H-5), 4.53 (d, *J* =

11.8 Hz, 1H, C*H*-Ph), 4.63 (d, *J* = 11.8 Hz, 1H, C*H*-Ph), 7.3-7.4 (m, 5H); ^{13}C NMR δ 18.3, 49.8, 62.1, 67.5, 70.3, 73.2, 83.6, 127.7, 127.8, 128.4, 137.5; IR (neat) ν 3290, 2110 cm^{-1}; HRMS calcd for $C_{13}H_{14}O_2$ 202.09942, found 202.09860.

(3S,4S*)-5-(tert-Butyldiphenylsilyloxi)-3,4-epoxy-3-methylpent-1-yne* (**1i**). The silylation procedure described above was applied to (*E*)-methylpent-2-en-4-yn-1-ol (2.50 g, 26.0 mmol). The crude after evaporation was purified by flash chromatography (3:97 EtOAc/hexanes) to yield **(*E*)-5-(*tert*-butyldiphenylsilyloxy)-3-methylpent-3-en-1-yne** (8.02 g, 92%) as a yellowish oil: ^{1}H NMR δ 1.08 (s, 9H, (C*H*$_3$)$_3$-C), 1.65 (d, *J* = 1.1 Hz, 3H, C$_3$-C*H*$_3$), 2.81 (s, 1H, H-1), 4.29 (d, *J* = 6.2 Hz, 2H, H-5), 6.14 (td, *J* = 6.2, 1.3 Hz, 1H, H-4), 7.4-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 17.4, 19.1, 26.7, 60.6, 74.6, 86.1, 117.8, 127.7, 129.7, 133.4, 135.5, 138.1; IR (neat) ν 3280, 1110 cm^{-1}. This enyne (1.00 g, 3.0 mmol) was epoxidized according to the General Procedure and the epoxide **1i** (0.90 g, 86%) was obtained after flash chromatography (5:95 EtOAc/hexanes) as a yellowish oil. The analytical sample was obtained after HPLC purification (Column 1, 8 mL/min, 5:95 EtOAc/hexanes, t_R = 23 min): ^{1}H NMR δ 1.07 (s, 9H, (C*H*$_3$)$_3$-C), 1.35 (s, 3H, C$_3$-C*H*$_3$), 2.31 (s, 1H, H-1), 3.41 (t, *J* = 5.3 Hz, 1H, H-4), 3.71 (dd, *J* = 11.7, 5.3 Hz, 1H, H-5), 3.79 (dd, *J* = 11.7, 5.3 Hz, 1H, H-5), 7.4-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 18.2, 19.2, 26.7, 50.3, 61.8, 63.8, 70.2, 83.8, 127.8, 129.5, 129.8, 132.9, 133.1, 135.5; IR (neat) ν 3280, 2090, 1110 cm^{-1}; HRMS calcd for $C_{22}H_{26}O_2Si$ 350.170209, found 350.170229. Anal. Calcd for $C_{22}H_{26}O_2Si$: C, 75.40; H, 7.47. Found: C, 74.94; H, 7.43.

(E)-6-(tert-Butyldiphenylsilyloxy)-4-methylhex-4-en-2-yne (**4j**). n-BuLi (1.3 M in hexanes, 6.9 mL, 9.0 mmol) was added dropwise to a solution of (*E*)-5-(*tert*-butyldiphenylsilyloxy)-3-methylpent-3-en-1-yne (2.50 g, 7.5 mmol) in THF (26 mL) at -78°C and, after stirring the solution for 45 min, MeI (2.65 g, 18.7 mmol) in THF (8 mL) was added. The solution was stirred at the same temperature for 30 min and allowed to reach room temperature over 2 h. Water (10 mL) was added, the aqueous layer was extracted with ether (3 x 10 mL) and the combined organic layers were washed with brine (5 mL). The crude product was purified by flash chromatography (5:95 EtOAc/hexanes) to yield enyne **4j** (2.40 g, 92%) as an oil: ^{1}H NMR δ 1.06 (s, 9H, (C*H*$_3$)$_3$-C), 1.61 (s, 3H, C$_4$-C*H*$_3$), 1.95 (s, 3H, H-1), 4.26 (d, *J* = 6.2 Hz, 2H, H-6), 5.95 (t, *J* = 6.2 Hz, 1H, H-5), 7.3-7.4 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 4.1, 17.8, 19.1, 26.7, 60.7, 82.2, 83.2, 119.3, 127.6, 129.6, 133.6, 134.9, 135.5; IR ($CHCl_3$) ν 2240, 1725, 1115 cm^{-1}; HRMS calcd for $C_{23}H_{28}OSi$ 348.19094, found 348.19092.

(4S,5S*)-6-(tert-Butyldiphenylsilyloxy)-4,5-epoxy-4-methylhex-2-yne* (**1j**). The General Epoxidation Procedure was followed with enyne **4j** (2.25 g, 6.90 mmol). Purification by flash chromatography (5:95 EtOAc/hexanes) afforded the epoxide **1j** (1.80 g, 77%) as a colorless oil. The analytical sample was obtained after HPLC purification (Column 1, 8 mL/min, 5:95 EtOAc/hexanes, t_R = 20.5 min): ^{1}H NMR δ 1.06 (s, 9H, (C*H*$_3$)$_3$-C), 1.31 (s, 3H, C$_4$-C*H*$_3$), 1.83 (s, 3H, H-1), 3.35 (t, *J* = 5.3 Hz, 1H, H-5), 3.70 (dd, *J* = 11.6, 5.3 Hz, 1H, H-6), 3.78 (dd, *J* = 11.6, 5.3 Hz, 1H, H-6), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 3.5, 18.7, 19.2, 26.7, 51.1, 62.0, 64.1, 78.5, 79.5, 127.7, 129.8, 133.0, 133.2, 135.5; IR ($CHCl_3$) ν 2240, 1115 cm^{-1}. Anal. Calcd for $C_{23}H_{28}O_2Si$: C, 75.78; H, 7.75. Found: C, 75.79; H, 7.76.

SmI_2-Mediated Coupling between Alkynyloxiranes and Ketones. General Procedure. SmI_2 (*ca.* 0.1M in THF) was prepared[26] as reported from diiodoethane,[27] diiodomethane[1b] or iodine[1b]. In a typical experiment the mixture of **1** (1.14 mmol) and a ketone (1.14 mmol) in THF (6 mL) was added dropwise under Ar to SmI_2 (*ca.* 0.1M in THF, 2.56 mmol) at the temperature indicated in Table 1. The mixture was stirred until disappearance of the epoxide as judged by TLC or until the blue solution turned yellow-green (Table 1). The reaction mixture was poured over saturated K_2CO_3 (10 mL) and the aqueous layer was extracted with EtOAc (3 x 25 mL). The

crude product after evaporation was purified by flash chromatography as specified for the individual cases listed below.

2-[2-(1-Hydroxycyclohexyl)ethenylidene]cyclohexanol (**2a**). Eluent: 40:60 EtOAc/hexanes. Colorless solid: mp 105-107°C; ^{1}H NMR δ 1.3-1.8 (m, 15H), 1.9-2.0 (m, 2H), 2.36 (br d, J = 12.7 Hz, 1H), 3.1 (br s, 2H, O*H*), 4.0 (m, 1H, H-1), 5.36 (t, J = 2.9 Hz, 1H, *H*-C=C=C, *syn*-isomer), 5.41 (t, J = 2.7 Hz, 1H, *H*-C=C=C, *anti*-isomer); ^{13}C NMR δ 22.5, 22.6, 22.8, 23.8, 23.9, 25.5, 25.6, 26.5, 26.8, 30.1, 30.2, 35.9, 36.0, 37.4, 37.7, 38.6, 69.0, 69.2, 70.9, 71.1, 103.2, 103.4, 110.9, 111.1, 193.7, 193.9; IR ($CHCl_3$) ν 3350, 1975 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.98. Found: C, 75.49; H, 10.17.

2-[2-(1-Hydroxycycloheptyl)ethenylidene]cyclohexanol (**2b**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (6%). Further elution with 25:75 EtOAct/hexanes afforded the diastereomeric mixture of **2b** as a yellowish oil. The diastereomers were separated by HPLC (Column 1, 10 mL/min, 35:65 EtOAc/hexanes). **(1*S**,1'*S**)-Isomer** (***anti*-2b**): t_R = 43 min; colorless solid; mp 98-99°C; ^{1}H NMR δ 1.2-2.1 (m, 19H), 2.4 (br d, J = 12.9 Hz, 1H, H-3), 3.0 (br s, $W_{1/2}$ = 43.8 Hz, 2H, O*H*), 4.0 (m, 1H, H-1), 5.45 (t, J = 2.8 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 22.0, 22.3, 23.8, 26.5, 29.3, 30.2, 35.9, 41.1, 41.7, 69.1, 74.9, 104.5, 111.1, 192.8; IR (neat, diastereomeric mixture) ν 3650-3100, 1970 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.23; H, 10.23. Found: C, 75.92; H, 10.37. **(1*S**,1'*R**)-Isomer** (***syn*-2b**): t_R = 52 min; oil; ^{1}H NMR δ 1.3-2.1 (m, 19H), 2.4 (br d, J = 13.5 Hz, 1H, H-3), 2.5 (br s, 2H, O*H*), 4.0 (m, 1H, H-1), 5.46 (t, J = 3.3 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 22.2, 22.5, 23.9, 27.0, 29.4, 30.2, 36.2, 41.3, 41.7, 69.2, 74.9, 105.2, 111.5, 192.6; HRMS calcd for $C_{15}H_{24}O_2$ 236.17763, found 236.17818. Data for **1-ethynyl-2-iodocyclohexanol** (**3a**).: ^{1}H NMR δ 1.2-1.4 (m, 1H), 1.5-1.9 (m, 4H), 2.1-2.4 (m, 3H), 2.61 (s, 1H), 2.74 (s, 1H), 4.17 (dd, J = 12.3, 4.3 Hz, 1H, H-2); ^{13}C NMR δ 23.3, 28.1, 37.5, 37.9, 45.4, 72.6, 74.4, 84.7; IR (neat) ν 3420, 3280, 2100 cm^{-1}; MS (EI) *m/z* (%) 250 (9, M), 207 (10), 128 (15), 127 (85), 123 (base, M-I), 105 (22), 103 (13), 95 (77), 94 (14), 93 (19), 91 (13), 81 (60), 79 (36), 78 (12), 77 (36), 69 (18), 68 (14), 67 (78), 66 (19), 65 (17), 63 (11), 55 (68), 54 (12), 53 (76), 51 (28).

2-[2-(1-Hydroxycyclopentyl)ethenylidene]cyclohexanol (**2c**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (3%). Further elution with 25:75 EtOAc/hexanes afforded the diastereomeric mixture of **2c** as a yellowish oil. The diastereomers were separated by HPLC (Column 1, 10 mL/min, 75:25 EtOAc/hexanes). **(1*S**,1'*S**)-Isomer** (***anti*-2c**): t_R = 43 min; pale yellow solid; mp 95-96°C; ^{1}H NMR δ 1.2-1.5 (m, 3H), 1.6-2.0 (m, 10H), 2.0-2.1 (m, 2H), 2.4 (br d, J = 13.0 Hz, 1H, H-3), 2.7 (br s, $W_{1/2}$ = 34.3 Hz, 2H, O*H*), 4.0-4.1 (m, 1H, H-1), 5.55 (t, J = 3.0 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 23.5, 23.6, 23.9, 26.6, 30.3, 36.0, 40.0, 40.5, 69.2, 80.4, 103.0, 111.4, 192.6; IR (neat, diastereomeric mixture) ν 3500-3200, 1970 cm^{-1}; HRMS calcd for $C_{13}H_{20}O_2$ 208.14633, found 208.14605. **(1*S**,1'*R**)-Isomer** (***syn*-2c**): t_R = 51 min, oil; ^{1}H NMR δ 1.3-1.5 (m, 3H), 1.7-2.0 (m, 10H), 2.0-2.1 (m, 2H), 2.4 (br d, J = 13.3 Hz, 3H, O*H*, H-3), 4.0-4.1 (m, 1H, H-1), 5.55 (t, J = 3.3 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 23.5, 23.6, 23.8, 26.7, 27.0, 30.1, 36.1, 39.9, 40.4, 40.5, 69.1, 80.2, 103.1, 103.1, 111.5, 192.6; HRMS calcd for $C_{13}H_{20}O_2$ 208.14633, found 208.14649.

2-(3-Hydroxy-3-methylbut-1-enylidene)cyclohexanol (**2d**). Elution with 15:85 EtOAc/hexanes provided iodide **3a** (3%). Further elution with 60:40 EtOAc/hexanes afforded the diastereomeric mixture of **2d** as a solid. The analytical sample was obtained by HPLC (Column 2, 6 mL/min, 65:35 EtOAc/hexanes, t_R = 20.74 min): mp 53-54°C; ^{1}H NMR δ 1.1-1.3 (m, 9H), 1.23 (s, C*H*$_3$, overlapped with mult. at 1.1-1.3, *anti*-isomer), 1.25 (s, C*H*$_3$, overlapped with mult. at 1.1-1.3, *anti*-isomer), 1.29 (s, C*H*$_3$, overlapped with mult. at 1.1-1.3, *syn*-isomer), 1.32 (s, C*H*$_3$, overlapped with mult. at 1.1-1.3, *syn*-isomer), 1.6-1.7 (m, 2H), 1.9-2.0 (m, 2H), 2.28 (br d, J = 13.7 Hz, 1H), 3.73 (s, 2H, O*H*), 3.9 (m, 1H, C*H*-OH), 5.42 (t, J = 2.9 Hz, 1H, *H*-C=C=C, *anti*-

isomer), 5.47 (t, J = 2.8 Hz, 1H, *H*-C=C=C, *syn*-isomer); ^{13}C NMR δ 23.7, 23.9, 26.4, 28.9, 29.1, 30.1, 30.2, 35.7, 35.9, 69.0, 69.2, 69.4, 69.7, 103.7, 104.0, 110.5, 110.8, 192.7, 193.1; IR ($CHCl_3$) ν 3300, 1960, 1160 cm^{-1}; HRMS calcd for $C_{11}H_{18}O_2$ 182.13068, found 182.12888. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.47; H, 9.96. Found: C, 72.06; H, 10.04.

2-(3-Ethyl-3-hydroxypent-1-enylidene)cyclohexanol (**2e**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (7%). Further elution with 25:75 EtOAc/hexanes afforded the diastereomeric mixture of **2f** as a yellowish oil. The diastereomers were separated by HPLC (Column 1, 10 mL/min, 65:35 EtOAc/hexanes). **(1*S**,1'*S**)-Isomer (*anti*-2e)**: t_R = 31 min; colorless solid; mp 80-81°C; ^{1}H NMR δ 0.8-1.0 (m, 6H, C*H*$_3$), 1.3-2.3 (m, 11H), 2.4 (br d, J = 12.3 Hz, 1H, H-3), 2.6 (br s, 2H, O*H*), 4.0-4.1 (m, 1H, H-1), 5.31 (t, J = 3.0 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 7.9, 8.0, 23.7, 26.6, 30.3, 32.4, 32.8, 35.9, 69.0, 74.3, 102.1, 111.8, 193.1; IR (neat, diastereomeric mixture) ν 3600-3100, 1970 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.04; H, 10.58. **(1*S**,1'*R**)-Isomer (*syn*-2e)**: t_R = 36 min; oil; ^{1}H NMR δ 0.9-1.0 (m, 6H, C*H*$_3$), 1.4-2.4 (m, 14H), 4.0-4.1 (m, 1H, H-1), 5.3-5.35 (m, 1H, *H*-C=C=); ^{13}C NMR δ 7.9, 8.0, 8.1, 23.5, 23.7, 26.7, 26.9, 30.0, 30.2, 32.6, 32.7, 32.8, 32.9, 36.0, 36.1, 69.0, 74.1, 74.3, 102.3, 102.4, 112.1, 192.9, 193.1; HRMS calcd for $C_{13}H_{22}O_2$ 210.16198, found 210.16203.

2-(3-Hydroxy-3-methyl-5-phenylpent-1-enylidene)cyclohexanol (**2f**). Eluent: 40/60 EtOAc/hexanes. Oil: ^{1}H NMR δ 1.3-1.4 (m, 6H), 1.35, 1.38 and 1.42 (s, C*H*$_3$, overlapped with mult. at 1.3-1.4), 1.7-1.8 (m, 1H), 1.8-2.0 (m, 3H), 2.0-2.1 (m, 2H), 2.41 (br d, J = 13.8 Hz, 1H), 2.6-2.7 (m, 2H), 3.31 (br s, 1H, O*H*), 4.1 (m, 1H, H-1), 5.4-5.5 (m, 1H, *H*-C=C=C), 7.1-7.3 (m, 5H); ^{13}C NMR δ 23.6, 23.9, 26.5, 26.5, 26.9, 27.2, 28.4, 30.1, 30.4, 30.5, 30.7, 36.0, 36.0, 44.1, 44.6, 69.2, 69.3, 71.7, 71.8, 71.9, 102.8, 103.3, 103.3, 111.4, 111.9, 125.6, 128.3, 142.4, 142.5, 192.9, 193.3, 193.7; IR (neat) ν 3300, 1975 cm^{-1}; HRMS calcd for $C_{18}H_{24}O_2$ 272.17763, found 272.17749.

2-(3-Hydroxy-3-methylhepta-1,6-dien-1-ylidene)cyclohexanol (**2g**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (7%). Further elution with 25:75 EtOAc/hexanes afforded the diastereomeric mixture of **2g** as an oil: ^{1}H NMR δ 1.2-1.4 (m, 6H), 1.5-1.8 (m, 4H), 2.0-2.1 (m, 4H), 2.3 (br d, J = 13.9 Hz, 1H, H-3), 3.1 (br s, $W_{1/2}$ = 23.8 Hz, 2H, O*H*), 4.0 (m, 1H, H-1), 4.9-5.0 (m, 2H, H-7'), 5.3-5.4 (m, 1H, *H*-C=C=), 5.7-5.9 (m, 1H, H-6'); ^{13}C NMR δ 23.4 , 23.6, 23.9, 26.5, 26.7, 26.8, 27.1, 27.2, 28.2, 28.6, 29.8, 30.1, 30.2, 30.4, 35.7, 35.8, 35.9, 41.0, 41.2, 41.7, 69.1, 69.1, 69.2, 71.6, 71.6, 71.8, 71.9, 102.8, 103.2, 103.2, 110.9, 111.2, 111.7, 114.2, 138.7, 138.9, 192.8, 193.2; IR (neat) ν 3500-3200, 1970 cm^{-1}; HRMS calcd for $C_{14}H_{22}O_2$ 222.16198, found 222.16173.

5-Hydroxy-7-(2-hydroxycyclohexylidene)-5-methylhept-6-enenitrile (**2h**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (7%). Further elution with 50:50 EtOAc/hexanes afforded the diastereomeric mixture of **2h** as a colorless oil: ^{1}H NMR δ 1.2-1.5 (m, 6H), 1.5-1.8 (m, 6H), 1.9-2.1 (m, 2H), 2.3-2.7 (m, 5H), 4.1 (m, 1H, C*H*-OH), 5.4 (m, 1H, *H*-C=C=); ^{13}C NMR δ 17.5, 20.5, 22.6, 23.5, 23.6, 23.8 , 23.8, 26.6, 26.8, 28.1, 28.8, 30.0, 30.2, 30.4, 31.9, 36.0, 36.3, 40.8, 41.3, 69.2, 69.3, 71.4, 71.5, 103.0, 103.2, 103.3, 112.5, 119.8, 192.6, 192.8; IR (neat) ν 3600-3100, 2240, 1970, 1640 cm^{-1}; HRMS calcd for $C_{14}H_{19}NO$ (M-H_2O) 217.14666, found 217.14645.

Methyl 12-hexyl-12-hydroxy-14-(2-hydroxycyclohexylidene)tetradec-13-enoate (**2i**). Elution with 10:90 EtOAc/hexanes provided iodide **3a** (5%). Further elution with 25:75 EtOAc/hexanes afforded the diastereomeric mixture of **2i** as a colorless oil. The diastereomers were separated by HPLC (Column 1, 10 mL/min, 25:75 EtOAc/hexanes). **(1*S**,1'*R**)-Isomer (*syn*-2i)**: t_R = 27 min; colorless oil; ^{1}H NMR δ 0.8-0.9 (m, 3H, C*H*$_3$), 1.3-2.1 (m, 37H), 2.2-2.3 (m, 2H), 2.4 (br d, J = 13.0 Hz, 1H), 3.66 (s, 3H, CO_2-C*H*$_3$), 3.8-4.0 (m,

1H, C*H*-OH), 5.37 (t, *J* = 3.3 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 14.1, 22.6, 23.7, 24.9, 26.8, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7, 30.0, 30.1, 31.8, 34.1, 36.3, 40.9, 51.4, 69.0, 73.6, 103.6, 112.5, 174.3, 192.3; HRMS calcd for $C_{27}H_{48}O_4$ 436.35526, found 436.35592. **(1*S**,1'*S**)-Isomer (*anti*-2i)**: t_R = 31 min; colorless oil; ^{1}H NMR δ 0.86 (t, *J* = 5.95 Hz, 3H, C*H*$_3$), 1.3-2.0 (m, 37H), 2.3 (m, 2H), 2.4 (br d, *J* = 12.5 Hz, 1H), 3.65 (s, 3H, CO_2-C*H*$_3$), 4.0-4.1 (m, 1H, C*H*-OH), 5.36 (t, *J* = 2.7 Hz, 1H, *H*-C=C=); ^{13}C NMR δ 14.1, 22.6, 23.6, 23.7, 23.8, 24.9, 26.7, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7, 30.0, 30.1, 31.8, 34.1, 35.9, 41.0, 51.4, 69.0, 73.9, 103.3, 112.2, 174.3, 192.4; IR (neat, mixture of isomers) ν 3600-3150, 1970, 1740 cm^{-1}. Anal. Calcd for $C_{27}H_{48}O_4$: C, 74.26; H, 11.08. Found: C, 74.40; H, 11.16.

(1S,1'S*)-2-[2-(1-Hydroxycyclohexyl)prop-1-en-1-ylidene]cyclohexanol* (***anti*-2j**). Eluent: 40:60 EtOAc/hexanes. Colorless solid: mp 97-99°C; ^{1}H NMR δ 1.2-1.7 (m, 15H), 1.76 (s, 3H, C*H*$_3$), 1.7-1.8 (m, 1H), 1.9-2.1 (m, 2H), 2.3-2.4 (m, 2H), 3.90 (dd, *J* = 8.8, 4.6 Hz, 1H, H-1); ^{13}C NMR δ 15.1, 22.4, 22.5, 23.8, 25.7, 26.9, 30.2, 36.1, 36.3, 36.9, 69.3, 72.4, 109.1, 110.8, 191.7; IR (KBr) ν 3300, 1960, 950 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_2$: C, 76.21; H, 10.24. Found: C, 76.32; H, 10.31.

2-[2-(1-Hydroxycyclohexy)-2-phenylethenylidene)]cyclohexanol (**2k**). Eluent: 30:70 EtOAc/hexanes. The isomers were separated by HPLC (Column 2, 6 mL/min, 35:65 EtOAc/hexanes). Data for the less polar isomer (68% of mixture): ^{1}H NMR δ 1.2-1.8 (m, 15H), 2.0-2.2 (m, 4H), 2.49 (br d, *J* = 12.6 Hz, 1H), 4.11 (br s, $W_{1/2}$ = 7.0 Hz, 1H, O*H*), 7.2-7.3 (m, 3H), 7.51 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR δ 22.5, 22.7, 23.5, 25.6, 26.6, 29.8, 36.0, 37.0, 38.0, 69.5, 73.4, 109.9, 116.5, 126.8, 127.9, 129.2, 136.8, 195.4; IR ($CHCl_3$) ν 3540, 3340, 1960 cm^{-1}; HRMS calcd for $C_{20}H_{26}O_2$ 298.19328, found 298.19392. Data for the more polar isomer (32% of mixture): ^{1}H NMR δ 1.3-2.1 (m, 15H), 2.5 (d, *J* = 11.6 Hz, 1H), 4.0 (m, 1H, C*H*-OH), 7.2-7.3 (m, 3H), 7.4-7.5 (m, 2H); ^{13}C NMR δ 22.5, 22.8, 24.0, 25.7, 26.8, 30.3, 36.1, 36.9, 38.1, 69.4, 73.2, 110.3, 117.0, 126.9, 128.0, 129.3, 136.7, 194.7; IR ($CHCl_3$) ν 3600, 3400, 1960 cm^{-1}; HRMS calcd for $C_{20}H_{26}O_2$ 298.19328, found 298.19392.

6-(tert-Butyldiphenylsilyloxy)-4-(1-hydroxycyclohexyl)-2-hexylhexa-2,3-dien-1-ol (**2l**). First eluted with 5:95 EtOAc/hexanes were enyne **4d** and recovered **1d** (5%). Further elution with 10:90 EtOAc/hexanes afforded iodide **3d**. Finally, diol **2l** was eluted with 20:80 EtOAc/hexanes as an oil: ^{1}H NMR δ 0.87 (t, *J* = 6.8 Hz, 3H, C*H*$_3$), 1.05 (s, 9H, (C*H*$_3$)$_3$-C), 1.1-1.7 (m, 19H), 1.9-2.0 (m, 2H), 2.2-2.4 (m, 3H), 3.73 (t, *J* = 6.3 Hz, 2H, H-6), 3.96 (s, 2H, H-1), 7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 14.1, 19.0, 22.2, 22.3, 22.6, 25.6, 26.8, 27.9, 29.2, 29.5, 30.4, 31.6, 36.9, 37.3, 62.8, 64.3, 72.0, 109.7, 114.2, 127.7, 129.7, 133.3, 135.5, 194.9; IR (neat) ν 3360, 1900, 1110 cm^{-1}; HRMS calcd for $C_{34}H_{50}O_3Si$ 534.352924, found 534.353584. Data for **6-(tert-butyldiphenylsilyloxy)-2-hexyl-1-iodohex-3-yne-2-ol (3d)**: unstable oil; ^{1}H NMR δ 0.87 (distorted t, 3H, C*H*$_3$), 1.06 (s, 9H, (C*H*$_3$)$_3$-C), 1.3 (m, 6H), 1.4-1.5 (m, 2H), 1.7-1.8 (m, 2H), 2.21 (s, 1H, O*H*), 2.49 (t, *J* = 6.8 Hz, 2H, H-5), 3.37 (d, *J* = 10.1 Hz, 1H, H-1), 3.46 (d, *J* = 10.0 Hz, 1H, H-1), 3.77 (t, *J* = 6.8 Hz, 2H, H-6), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 14.0, 19.1, 20.8, 22.5, 22.8, 24.8, 26.8, 29.2, 31.6, 40.6, 62.2, 69.3, 81.2, 83.1, 127.6, 129.7, 133.5, 135.5; IR (neat) ν 3450, 2240, 1110 cm^{-1}.

3-Ethyltrideca-4,5-dien-3,7-diol (**2m**). Elution with 5:95 EtOAc/hexanes led to enynes **4f** (73:27*E*/*Z*:) and recovered **1f** (21%). Further elution with 10:90 EtOAc/hexanes afforded ketone **5**[28] followed by diols **2m** as an oil: ^{1}H NMR δ 0.8-0.9 (m, 9H, C*H*$_3$), 1.2-1.4 (m, 8H), 1.4-1.6 (m, 6H), 2.10 (br s, $W_{1/2}$ = 18.2 Hz, O*H*), 2.31 and 2.38 (br s, $W_{1/2}$ = 44.7 Hz, O*H*), 2.90 (br s, $W_{1/2}$ = 21.4 Hz, O*H*), 4.1 (m, 1H, H-7), 5.24 (dd, *J* = 6.2, 2.1 Hz, H-4), 5.30 (dd, *J* = 6.3, 2.3 Hz, H-4), 5.37 (t, *J* = 6.4 Hz, H-6), 5.44 (t, *J* = 6.1 Hz, H-6); ^{13}C NMR δ 8.0, 8.0, 14.0, 22.6, 25.4, 25.5, 29.1, 31.8, 32.8, 32.9, 37.4, 69.8, 70.3, 74.2, 74.3, 99.5, 100.7, 101.4, 200.0, 200.2; IR (neat) ν 3300, 1960 cm^{-1}; HRMS calcd for $C_{15}H_{26}O$ (M-H_2O) 223.206162, found

223.206291.

5-(1-Hydroxycyclohexyl)-3-methylpenta-3,4-diene-1,2-diol (**2n**). Eluent: EtOAc. First eluted was diol **6** followed by the solid triol **2n** that was further purified by HPLC (Column 2, 6 mL/min, EtOAc): mp 74-76°C; ^{1}H NMR δ 1.4-1.6 (m, 8H), 1.70 (d, *J* = 2.8 Hz, 3H, C*H*$_3$), 1.72 (d, *J* = 2.9 Hz, 3H, C*H*$_3$), 3.5-3.7 (m, 2H, H-1), 4.02 (br s, 4H, H-2, O*H*), 5.3 and 5.4 (t, *J* = 2.5 Hz, 1H, H-5); ^{13}C NMR δ 15.7, 16.0, 22.3, 22.4, 22.5, 22.6, 25.4, 37.9, 37.9, 38.6, 38.7, 64.4, 64.5, 71.1, 72.6, 72.7, 101.7, 102.8, 103.1, 103.7, 198.3, 198.6; IR ($CHCl_3$) ν 3400, 1965 cm^{-1}; HRMS calcd for $C_{12}H_{19}O_3$ (M-1) 211.13342, found 211.13273. Data for **3-methylpenta-3,4-dien-1,2-diol (6)**: ^{1}H NMR δ 1.74 (t, *J* = 3.2 Hz, 3H), 1.9-2.0 (br s, 2H, O*H*), 3.59 (dd, *J* = 11.3, 6.7 Hz, 1H, H-1), 3.73 (dd, *J* = 11.3, 3.5 Hz, 1H, H-1), 4.05 (m, 1H, H-2), 4.85 (m, 2H, H-5); ^{13}C NMR δ 15.2, 65.0, 72.2, 77.8, 99.3, 204.8; IR ($CHCl_3$) ν 3300, 1960 cm^{-1}; HRMS calcd for $C_6H_{10}O_2$ 114.06808, found 114.06728.

1-Benzyloxy-5-(1-hydroxycyclohexyl)-3-methylpenta-3,4-dien-2-ol (**2o**). Eluent: 35:65 EtOAc/hexanes. Oil: ^{1}H NMR δ 1.2-1.6 (m, 10H), 1.73 (t, *J* = 2.9 Hz, 3H, C*H*$_3$), 2.94 (br s, 1H, O*H*), 3.32 (br s, 1H, O*H*), 3.4-3.6 (m, 2H), 4.18 (br s, $W_{1/2}$ = 19.0 Hz, 1H), 4.54 (s, 2H, O-C*H*$_2$-Ph), 5.3 and 5.4 (m, 1H, *H*-C=C=C), 7.2-7.3 (m, 5H); ^{13}C NMR δ 15.6, 22.3, 22.4, 25.4, 37.9, 38.5, 38.6, 70.6, 71.0, 71.2, 72.3, 72.6, 73.3, 102.3, 102.7, 103.2, 103.5, 127.6, 127.7, 128.3, 137.6, 137.7, 198.2, 198.4; IR (neat) ν 3380, 1970 cm^{-1}. Anal. calcd for $C_{19}H_{26}O_3$: C, 74.45; H, 8.67; found: C, 74.38; H, 8.54.

1-(tert-Butyldiphenylsilyloxy)-5-(1-hydroxycyclohexyl)-3-methylpenta-3,4-dien-2-ol (**2p**). Eluent: 25:75 EtOAc/hexanes. Oil: ^{1}H NMR δ 1.08 (s, 9H, (C*H*$_3$)$_3$-C), 1.2-1.6 (m, 10H), 1.67 (d, *J* = 2.9 Hz, 3H, C$_3$-C*H*$_3$, *syn*-isomer), 1.71 (d, *J* = 2.9 Hz, 3H, C$_3$-C*H*$_3$, *anti*-isomer), 2.50 (d, *J* = 4.1 Hz, 1H, O*H*), 2.70 (d, *J* = 5.2 Hz, 1H, O*H*), 3.64 (dd, *J* = 10.3, 7.2 Hz, 1H, H-1), 3.75 (dd, *J* = 10.3, 4.1 Hz, 1H, H-1), 4.1 (m, 1H, H-2), 5.3 (m, 1H, H-5), 7.3-7.5 (m, 6H), 7.7-7.8 (m, 4H); ^{13}C NMR δ 15.4, 15.7, 19.2, 22.4, 25.4, 26.8, 38.1, 38.4, 66.4, 66.7, 70.1, 72.5, 102.2, 102.8, 103.2, 127.7, 129.8, 133.0, 133.5, 198.4; IR ($CHCl_3$) ν 3380, 1930, 1430, 1115 cm^{-1}; HRMS calcd for $C_{28}H_{36}O_2Si$ (M-H_2O) 432.248373, found 432.248459.

(2R,4S*)-[1-(tert-Butyldiphenylsilyloxy)-5-(1-hydroxycyclohexyl)-3-methylhexa-3,4-dien-2-ol* (**2q**). Elution with 5:95 EtOAc/hexanes afforded enyne **4j** and allene **9**. Further elution with 20:80 EtOAc/hexanes afforded dimer **7** followed by the mixture of diols **2q** and **8**, that were separated by HPLC (Column 1, 12 mL/min, 25:75 EtOAc/hexanes). **(2*R**,4*S**)-Isomer (*anti*-2q)**: t_R = 22 min; oil; ^{1}H NMR δ 1.07 (s, 9H, (C*H*$_3$)$_3$-C), 1.1-1.2 (m, 1H), 1.4-1.6 (m, 10H), 1.66 (s, 3H), 1.67 (s, 3H), 2.60 (d, *J* = 4.1 Hz, 1H, O*H*), 3.60 (dd, *J* = 10.3, 7.0 Hz, 1H, H-1), 3.71 (dd, *J* = 10.3, 3.6 Hz, 1H, H-1), 4.1 (m, 1H, H-2), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 14.2, 15.8, 19.2, 22.2, 22.3, 25.6, 26.8, 36.2, 36.6, 66.8, 72.1, 72.9, 101.1, 109.5, 127.7, 129.8, 133.1, 135.6, 197.2; IR ($CHCl_3$) ν 3400, 1970, 1120 cm^{-1}. Anal. calcd for $C_{29}H_{40}O_3Si$: C, 74.96; H, 8.68. Found: C, 74.62; H, 8.56. **(2*R**,4*R**)-Isomer (*syn*-2q)**: t_R = 27 min; oil; mp 75-77°C; ^{1}H NMR δ 1.07 (s, 9H, (C*H*$_3$)$_3$-C), 1.2-1.7 (m, 11H), 1.66 (s, 3H), 1.68 (s, 3H), 2.48 (br s, $W_{1/2}$=10.9 Hz, 1H, O*H*), 3.60 (dd, *J* = 10.3, 7.4 Hz, 1H, H-1), 3.71 (dd, *J* = 10.3, 3.9 Hz, 1H, H-1), 4.1 (m, 1H, H-2), 7.3-7.5 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 14.3, 15.7, 19.2, 22.2, 25.6, 26.8, 36.3, 36.6, 67.1, 72.1, 72.9, 101.1, 109.2, 127.7, 129.8, 133.1, 135.6, 196.9; IR ($CHCl_3$) ν 3300, 1970, 1110 cm^{-1}. Anal. calcd for $C_{29}H_{40}O_3Si$: C, 74.96; H, 8.68. Found: C, 74.73 ; H, 8.73. Data for **1-(tert-Butyldiphenylsilyloxy)-3-methylhexa-3,4-dien-2-ol (9)**: Oil; ^{1}H NMR δ 1.07 (s, 9H, (C*H*$_3$)$_3$-C), 1.6-1.7 (m, 6H, H-6 and C$_3$-C*H*$_3$), 3.64 (dd, *J* = 10.2, 6.5 Hz, 1H, H-1), 3.73 (dd, *J* = 10.2, 3.8 Hz, 1H, H-1), 4.1 (m, 1H, H-2), 5.1-5.2 (m, 1H, H-5), 7.3-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 14.5, 15.5, 15.7, 19.3, 26.8, 66.5, 72.6, 87.9, 99.1, 127.7, 129.6, 129.8, 133.2, 134.8, 135.6, 201.4; IR (neat) ν 3400,

1975, 1115 cm^{-1}; HRMS calcd for $C_{23}H_{30}O_2Si$ 366.201509, found 366.201777. Data for **1,10-Di(tert-butyldiphenylsilyloxy)-3,5,6,8-tetramethyldeca-3,4,6,7-tetraene-2,9-diol (7)**: Oil; ^1H NMR δ 1.06 (s, 9H, $(CH_3)_3$-C), 1.6 (m, 3H, CH_3), 1.7 (m, 3H, CH_3), 2.4 (m, 1H, O*H*), 3.62 (dd, J = 10.1, 7.1 Hz, 1H), 3.72 (dd, J = 10.1, 3.9 Hz, 1H), 4.1-4.2 (m, 1H), 7.3-7.4 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 15.5, 15.7, 17.8, 19.2, 26.8, 66.8, 67.2, 73.0, 101.8, 102.3, 127.7, 129.8, 133.2, 135.6, 200.7, 200.8; IR ($CHCl_3$) ν 3550, 3450, 1600, 1110 cm^{-1}; HRMS calcd for $C_{46}H_{58}O_4Si_2$ 730.38737, found 730.38742. Data for **(2R*,4S*)-2-(tert-Butyldiphenylsilyloxy)-5-(1-hydroxycyclohexyl)-3-methylhexa-3,4-dien-1-ol (8)**: t_R = 19 min; oil; ^1H NMR δ 1.08 (s, 9H, $(CH_3)_3$-C), 1.2-1.6 (m, 14H), 1.56 (s overlapped with m at 1.2-1.6, CH_3), 1.72 (s, 3H, CH_3), 3.50 (apparent d, 2H, H-1), 4.27 (apparent t, 1H, H-2), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 13.4, 14.3, 19.4, 21.9, 22.0, 25.4, 27.0, 35.3, 36.3, 64.5, 72.0, 75.3, 100.6, 107.5, 127.5, 127.7, 129.7, 129.8, 133.5, 133.9, 135.7, 135.8, 197.5; IR ($CHCl_3$) ν 3300, 1970, 1110 cm^{-1}; HRMS calcd for $C_{29}H_{40}O_3Si$ (M-H_2O) 446.26411, found 446.26282.

4-(1,2-Epoxycyclohexyl)-2-methylbut-3-yn-2-ol (**13**). n-BuLi (1.42 M, 2 mL, 2.85 mmol) was added dropwise to a solution of 1-ethynylcyclohexene (0.300 g, 2.83 mmol) in THF (3.3 mL) at -78°C and the resulting solution stirred at this temperature for 15 min, allowed to warm to room temperature over 1 h and recooled to -78°C. A solution of acetone (0.164 g, 2.83 mmol) in THF (1.5 mL) was slowly added, the reaction mixture allowed to reach 25°C and kept at this temperature for 3 h. Brine (5 mL) was added and the aqueous layer was extracted with diethyl ether (3 x 15 mL). The residue after evaporation was purified by flash chromatography (12:88 EtOAc/hexanes) to afford **4-(1-cyclohexenyl)-2-methylbut-3-yn-2-ol** (0.350 g, 76%): ^1H NMR δ 1.48 (s, 6H, CH_3), 1.5-1.6 (m, 4H), 2.0-2.1 (m, 4H), 2.5 (br s, 1H, O*H*), 6.0 (m, 1H, *H*-C=C); ^{13}C NMR δ 21.3, 22.1, 25.4, 29.0, 31.1, 31.4, 65.3, 83.6, 91.1, 120.0, 134.6. This material 0.260 g (1.83 mmol) was treated with MCPBA according to the General Epoxidation Procedure. The title epoxide **13** was obtained after purification by flash chromatography (10:90 EtOAc/hexanes): ^1H NMR δ 1.1-1.4 (m, 4H), 1.45 (s, 6H), 1.8-2.0 (m, 1H), 2.0-2.1 (m), 2.61 (br s, O*H*), 3.27 (t, J = 2.2 Hz, 1H); ^{13}C NMR δ 18.7, 19.2, 23.9, 29.6, 31.2, 50.1, 59.9, 64.8, 82.1, 86.7; IR (neat) ν 3400, 1170 cm^{-1}.

*Preparation of **anti-2d** from 13*. LAH (0.088 g, 2.33 mmol) was added to alcohol **13** (0.070 g, 0.388 mmol) in THF (18 mL) and the mixture was refluxed for 6 h. Water (5 mL) was added and the whole extracted with EtOAc (5 x 15 mL). The residue after evaporation was purified by flash chromatography (30:70 EtOAc/hexanes) to yield allene ***anti*-2d** (0.050 g) contaminated with an unknown impurity. Further purification under the same conditions yielded a pure sample of ***anti*-2d**.

1-[(1,2-Epoxycyclohexyl)ethynyl]cyclohexanol (**14**). The procedure previously described for **13** was applied to cyclohexanone to afford, after flash chromatography (10:90 EtOAc/hexanes), the epoxide **14** (64% over two steps) as a yellowish oil: ^1H NMR δ 1.1-1.6 (m, 12H), 1.7-2.2 (m, 6H), 2.30 (br s, $W_{1/2}$ = 50.0 Hz, 1H, O*H*), 3.28 (s, 1H, C*H*-O); ^{13}C NMR δ 18.8, 19.3, 23.1, 24.0, 25.0, 29.8, 39.7, 50.2, 60.0, 68.4, 84.5, 85.7; IR ($CHCl_3$) ν 3400, 1070 cm^{-1}; HRMS calcd for $C_{14}H_{20}O_2$ 220.14633, found 220.14607.

*Preparation of **syn-2j** from 14*. MeLi (1.6 M, 4.3 mL, 6.8 mmol) was added dropwise to a suspension of CuI (0.65 g, 3.4 mmol) in THF (35 mL) at -25°C. After stirring at that temperature for 45 min a solution of **14** in THF (1 mL) was added, the mixture was stirred at -25°C further 30 min and allowed to reach room temperature overnight. A 1:1 mixture of sat NH_4Cl and 3% NH_4OH (10 mL) was added and the mixture was stirred 1 h. The aqueous layer was extracted with diethyl ether (3 x 15 mL) and the combined organic layers were washed with water (2 x 10 mL). Flash chromatography (35:65 EtOAc/hexanes) of the residue after evaporation afforded a 7:5:1 mixture of alkyne **15**, ***syn*-2j** and diol **2a** (0.160 g, 100%) that were separated by HPLC (Column 1, 12 mL/min, 70:30 EtOAc/hexanes). Data for **2-(1-Hydroxycyclohexyl)ethynyl-2-**

methylcyclohexanol (15): t_R = 27 min; mp 104°C; ^{1}H NMR δ 1.2-1.3 (m, 6H), 1.29 (s, overlapped with m at 1.2-1.3, C*H*$_3$), 1.4-1.6 (m, 9H), 1.6-1.9 (m, 8H), 3.13 (dd, *J* = 10.8, 3.9 Hz, 1H, H-1); ^{13}C NMR δ 22.7, 23.7, 23.7, 24.9, 25.2, 26.9, 32.6, 38.5, 40.0, 40.3, 40.4, 68.8, 76.5, 86.8, 88.5; IR ($CHCl_3$) ν 3340 cm^{-1}; HRMS calcd for $C_{15}H_{24}O_2$: 236.177630, found 236.177115. Anal. calcd for $C_{15}H_{24}O_2$: C, 76.27; H, 10.17. Found: C, 75.85; H, 10.33. Data for **(1*S**,1'*R**)-2-[2-(1-hydroxycyclohexyl)prop-1-en-1-ylidene]cyclohexanol (*syn*-2j)**: t_R = 34 min; mp 110-111°C; ^{1}H NMR δ 1.3-1.8 (m, 18H), 1.77 (s, overlapped with m at 1.3-1.8, C*H*$_3$), 1.9-2.1 (m, 2H), 2.34 (apparent d, *J* = 14.2 Hz, 1H), 3.9 (m, 1H, H-1); ^{13}C NMR δ 14.7, 22.4, 22.6, 24.0, 25.7, 26.9, 30.5, 36.2, 36.3, 37.0, 69.2, 72.2, 109.5, 111.6, 191.0; HRMS calcd for $C_{15}H_{24}O_2$ 236.177630, found 236.178569.

(3'S,4'S*)-1-[5-(tert-Butyldiphenylsilyloxy)-3,4-epoxy-3-methylpent-1-ynyl]cyclohexanol* **(16)**. The procedure used in the preparation of epoxide **13** was followed from (*E*)-5-(*tert*-butyldiphenylsilyloxy)-3-methylpent-3-en-1-yne and cyclohexanone to yield, after flash chromatography (15:85 EtOAc/hexanes), the epoxide **16** (26 %, two steps) as as oil: ^{1}H NMR δ 1.07 (s, 9H, (C*H*$_3$)$_3$-C), 1.34 (s, 3H, C*H*$_3$), 1.5-1.7 (m, 8H), 1.9 (m, 2H), 1.98 (s, 1H, O*H*), 3.37 (t, *J* = 5.2 Hz, 1H, C*H*-O), 3.76 (d, *J* = 5.2 Hz, 2H, C*H*$_2$-O), 7.4-7.5 (m, 6H), 7.7 (m, 4H); ^{13}C NMR δ 18.6, 19.2, 23.2, 25.1, 26.7, 39.7, 50.7, 62.0, 64.2, 68.5, 84.3, 85.6, 127.7, 129.8, 132.9, 133.2, 135.5; IR (neat) ν 3400, 2240, 1110 cm^{-1}. Anal. calcd for $C_{28}H_{38}O_3Si$: C, 74.96; H, 8.09. Found: C, 75.25; H, 8.16.

Preparation of syn-2q from 16. The reaction of alcohol **16** with Gilman's cuprate under conditions similar to those described above for alcohol **14** afforded, after flash chromatography (12:88 EtOAc/hexanes) and HPLC (Column 1, 10 mL/min, 25:75 EtOAc/hexanes), in order of elution, the alkyne **17** (33%), ***syn*-2q** (27%) and **2p** (14%, mixture of diastereomers). Data for **1-(tert-butyldiphenylsilyloxy)-5-(1-hydroxycyclohexyl)-3,3-dimethylpent-4-yn-2-ol (17)**: t_R = 17 min; ^{1}H NMR δ 1.06 (s, 9H, (C*H*$_3$)$_3$-C), 1.17 (s, 3H, C*H*$_3$), 1.18 (s, 3H, C*H*$_3$), 1.3-1.8 (m, 11H), 2.75 (br s, 1H, O*H*), 3.54 (dd, *J* = 8.3, 3.1 Hz, 1H, H-1), 3.72 (apparent t, 1H, H-1), 3.91 (dd, *J* = 10.0, 3.2 Hz, 1H, H-2), 7.4 (m, 6H), 7.6-7.7 (m, 4H); ^{13}C NMR δ 19.2, 23.4, 24.4, 25.1, 26.7, 26.8, 34.1, 40.1, 40.1, 65.3, 65.8, 68.5, 77.2, 85.4, 89.0, 127.8, 129.8, 133.0, 135.5; IR ($CHCl_3$) ν 3400, 1110 cm^{-1}. Anal. calcd for $C_{29}H_{40}O_3Si$: C, 74.95; H, 8.68. Found: C, 74.71; H, 8.56.

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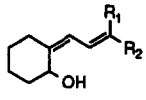

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