30.3, 24.1; exact mass calcd for $C_8H_{15}NO_3$ ($M^{\bullet+}$ + H^+) 174.1131, found 174.1130.

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Supplementary Material Available: ^1H and ^{13}C NMR for all compounds (51 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfiche version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Radical Cyclization of (Bromomethyl)dimethylsilyl Propargyl Ethers. Regio-, Chemo-, and Stereoselectivity

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Radical cyclization of (bromomethyl)dimethylsilyl propargyl ether derivatives 1 is a powerful reaction with a high degree of regio-, chemo-, and stereoselectivity. Trisubstituted olefins 3, cyclopentene derivatives 5, and diquinane system 7j are obtained in good yields by a judicious choice of unsaturated substituents. Triquinane frameworks could be obtained stereoselectively from a suitable acyclic substrate of type 1 in a one-pot reaction. First attempts have not yet allowed us to aim at this goal due to interesting (1,5) hydrogen transfers. Moreover, we have intercepted, for the first time, the α-cyclopropyl radical which is involved in the Stork–Beckwith mechanism of the 5-versus 6-membered ring formation in the vinyl radical cyclization.

Introduction

Over the last ten years, tin hydride based methods have greatly expanded the repertoire of bond-forming reactions at the disposal of the synthetic organic chemist.[1] Recently, radical cyclizations of (bromomethyl)dimethylsilyl allyl ethers have been used[2] to provide 1,3-diols after a Tamao oxidation.[3] We subsequently applied this reaction to propargyl ethers 1, which leads to a new type of heterocycle easily converted regio- and stereoselectivity into di- and trisubstituted functionalized double bonds of type 3.[4] The intermediate exocyclic vinyl radical 2 involved in this reaction can be trapped intramolecularly to afford regioselectively functionalized unsaturated five-membered carbocycles 5 in high yields.[5] Moreover, a remarkable 3,5-cis stereoselectivity is observed.[6] Very recently, a new strategy for [3 + 2] annulation involving a homoallyl radical and an electron-deficient alkene receptor has been developed.[7] Therefore, 4 appears to be a convenient intermediate in such a process and, indeed, radical cyclization of 4-[(bromomethyl)dimethylsiloxy]-2-methyl-1-undecen-5-yne (1j) in the presence of acrylonitrile leads stereoselectively via a sequence of intra-, intra-, inter-, and intramolecular processes to diquinane system 7j (Scheme I). This one-pot reaction allows the consecutive formation of four carbon–carbon bonds with two contiguous quaternary centers and controls the stereoselective construction of four stereogenic centers.[6] Work in our laboratory is aimed at developing a one-pot stereoselective synthesis of angular and linear triquinane frameworks from acyclic substrates (Scheme II). We have examined the behavior of β-silyl radical intermediate 6, which could be trapped by unsaturation present either on substituent R^3 to give an angular triquinane or on substituent R^1 to give a linear triquinane. Radical cyclizations have been used successfully in syntheses of triquinanes from cyclic substrates,[8] but stereoselectivity was not observed with acyclic ones.[9]

Table I. Stereoselective H-Abstraction of Trisubstituted Vinyl Radicals 2

entry	R^1	R^2	R^3	X	olefin[a] *E*-3:*Z*-3	yield (%)
1a	CH_3	CH_3	$CH_2CH{=}CH_2$	OH	70:30	67
1b	CH_3	CH_3	$(CH_2)_2CH{=}CH_2$	OH	75:25	75
1b	CH_3	CH_3	$(CH_2)_4CH{=}CH_2$	OH	95:5[b]	70
1d	CH_3	CH_3	$(CH_2)_3OTHP$	$SiMe_3$	0:100	60
1e	H	n-C_4H_9	n-C_4H_9	OH	100:0[b]	65
1f	CH_3	CH_3	C_6H_5	OH	25:75[c]	84
1g	CH_3	CH_3	$SiMe_3$	OH	35:65	85

[a] The stereoselectivity of olefins 3 was assigned by γ-gauche effects in the ^{13}C-NMR spectra and confirmed by ^1H-NMR NOE measurements. The chemical shift of CH_2OH is 58 ppm for the *E* olefin versus 68 ppm for the *Z* olefin. [b] Radical-induced intramolecular (1,5) hydrogen atom transfers are well known. The inter- vs intramolecular mode for hydrogen abstraction of the very reactive vinyl radicals 2c and 2e have not yet been established. However, a (1,5) hydrogen shift can be ruled out because the resulting 5-hexenyl radical should give a 5-*exo-trig* cyclization.[12] Studies using Bu_3SnD are in progress in our laboratory in order to confirm that the tin hydride is the hydrogen donor. [c] The formation of a 25:75 ratio of *E*:*Z* olefins 3 is kinetically controlled. The thermodynamic ratio of 99:1 for *Z*:*E* heterocycles 2′ was obtained by AM1 calculations.

Stereoselective Hydrogen Abstraction by Trisubstituted Vinyl Radicals. Stereoselectivity in free-radical

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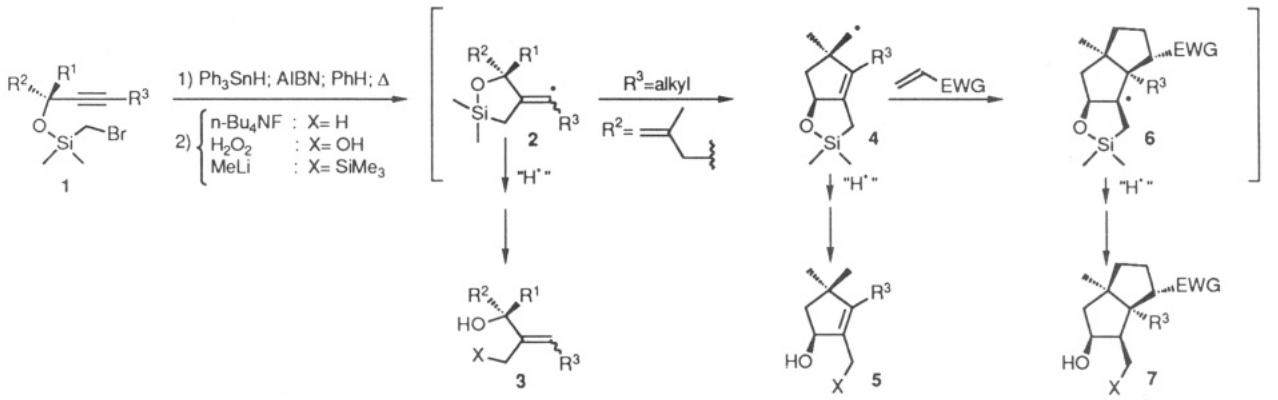
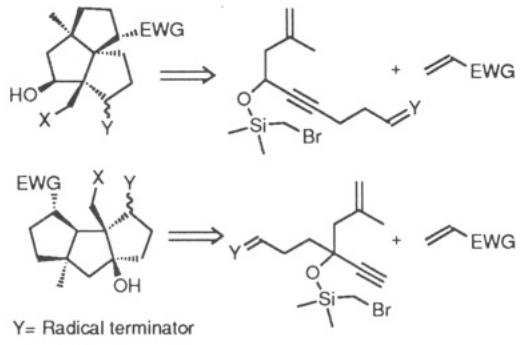
0022-3263/92/1957-3085$03.00/0

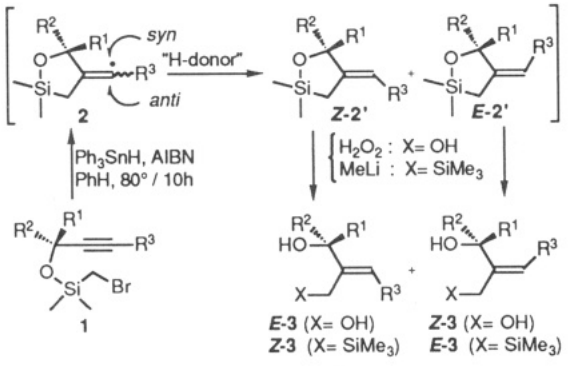
Scheme I



Scheme II



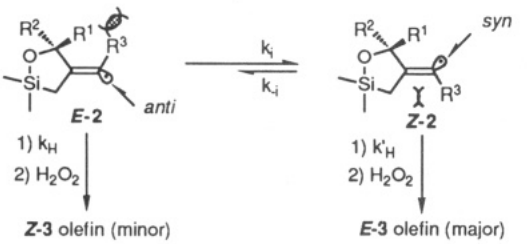
Scheme III. Stereoselective H-Abstraction of Trisubstituted Vinyl Radicals



chemistry is of great importance[10] and previous studies[11] have demonstated that a complete spectrum of configurational stability exists for vicinally disubstituted vinyl radicals. Radical cyclization of (bromomethyl)dimethylsilyl propargyl ethers gave an unexpectedly high degree of stereoselectivity during hydrogen abstraction by trisubstituted vinyl radicals **2** (Scheme III and Table I). Propargyl ethers **1** are obtained quantitatively by silylation of propargyl alcohols with commercial (bromomethyl)chlorodimethylsilane in the presence of a catalytic amount of 4-(dimethylamino)pyridine (DMAP) at room temperature.[2b] The radical cyclization of **1** is carried out in refluxing benzene (0.025 M) with AIBN (0.1 equiv) by slow addition of Ph_3SnH[13] (2×10^{-4} mol/h, 1.1 equiv) with a syringe pump to avoid reduction of the stabilized α-silyl radical[14] initially generated. After completion of the reaction, the crude product was subjected to oxidation (30% H_2O_2, $KHCO_3$, THF/MeOH (1/1), Δ 3–5 h) to give 1,3-diols in good yields. The sensitive heterocycle **2′** can be converted to allylsilanes by treatment with methyllithium at −30 °C in ether.

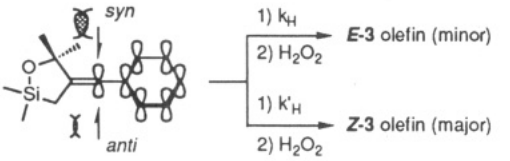
When R^3 is an alkyl chain, 100% stereoselectivity can be reached with the syn approach[15] of the hydrogen donor which occurs in either an inter- or eventually intramolecular fashion[12] (Scheme III and entries **1c–1e** of Table I). This remarkable stereoselectivity can be explained by bent vinyl radical **2** in which inversion of the sp^2 carbon is fast relative to H-abstraction.[11] Owing to this angular attack, the steric hindrance of the H-donor is not expected to have an important effect on the stereoselectivity observed. Furthermore, 1,3-allylic interactions between R^3 and R^1 or R^2 substituents, by far the more important factor, easily explain the stereochemistry of H-abstraction. These interactions are expected to be more severe in cyclic systems due to an annelated ring effect[16] (Scheme IV).

Scheme IV. Angular Attack on the sp^2-Hybridized Vinyl Radical by an H-Donor[a]



[a] $k_H < k_i, k_{-i}$, where k_i and k_{-i} are rates of isomerization; k_H and k'_H are rates of H-abstraction.

Scheme V. Perpendicular Attack of the sp-Hybridized Vinyl Radical by an H-Donor



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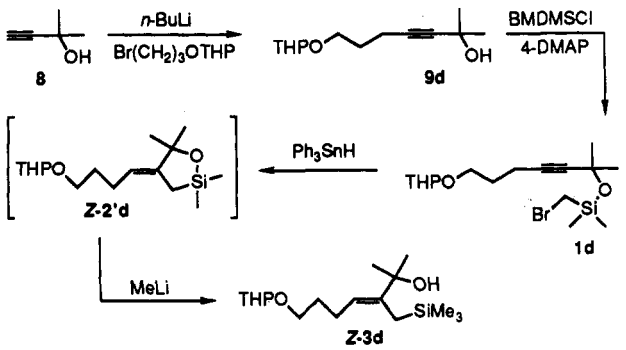
(15) Syn and anti refer to the direction of H-abstraction relative to the more bulky substituent.

Scheme VI



Very recently, the stereochemistry of intermolecular iodine-atom transfer to trisubstituted vinyl radicals has been studied in which a ring effect is also present.[10d] They found a reversed stereoselectivity for iodine capture.[17]

When R^3 is a phenyl or TMS group, the stereoselectivity is reversed and kinetically-controlled. Intermolecular hydrogen abstraction occurs via an anti approach[15] of the hydrogen donor leading to the less stable *Z*-**3** olefin (see footnote *c* and entries **1f** and **1g** of Table I). This stereocontrol, already observed in the case of a disubstituted α-phenyl radical,[10c] is in good agreement with a linear vinyl radical structure in which the steric hindrance of the incoming Ph_3SnH with methyl substituents becomes the predominant factor. Supported by CNDO calculations,[11a] this linear structure is consistent with the radical-stabilizing effect of the phenyl group.[11c,18] Again, the five-membered heterocycle increases the difference in steric hindrance between the syn and anti perpendicular attack of H-donor (Scheme V). As part of our ongoing program aimed at illustrating the synthetic importance of this approach, we accomplished a short, efficient, stereoselective synthesis of the terpenoid building block (*Z*)-2-methyl-7-(2-tetrahydropyranyloxy)-3-(trimethylsilylmethyl)-3-hepten-2-ol[19] (*Z*-**3d**) by the radical cyclization of **1d** (Scheme VI).

Propargyl ether **1d** is readily obtained in two steps: (i) condensation of the lithium derivative **8** with 1-bromo-3-(2-tetrahydropyranyloxy)propane in THF gives **9d** in 70% yield; (ii) quantitative silylation leads to **1d**. Radical cyclization of **1d** followed by treatment with methyllithium affords the pure *Z* stereoisomer of **3d** in 60% yield.

Regioselective Intramolecular Cyclization of Vinyl Radicals 2. *External* and *internal* vinyl radical cyclizations have been extensively studied,[20,21] and a 5-*exo* cyclization was found to be largely favored over a 6-*endo* ring-closure. However, this preference may be inverted sterically[20c] or by inducing reversibility.[20-23] Thus high dilution[20b,21] and germanium hydride[22] or tetramethyltetrahydrofuran[23] as solvent were found to increase the 6-*endo* product due to rearrangement of the kinetically generated homoallyl radical. The exocyclic vinyl radical **2** can be trapped intramolecularly by a double bond connected to C-3 (internal vinyl radical) or to C-1 (external vinyl radical) to give products which could be used as an access to functionalized carbocycles. We first studied the radical cyclizations of variously substituted derivatives of propargyl ethers **1** with an alkenyl chain connected to C-3.

Homoallyl propargyl alcohols **9** were synthesized in excellent yields by a 2,3-Wittig reaction[24] of allyl propargyl ethers **11** (Scheme VII and Table II). Propargyl ethers **1** were then obtained quantitatively by silylation.

(Bromomethyl)dimethylsilyl propargyl ethers were submitted to the radical cyclization under the same conditions as described above (Scheme VIII and Table III). Importantly, when R^1 and R^3 are H or alkyl, the 5-*exo* ring closure leading to **5** is 90 to 100% regioselective (entries **1h** to **1o**). The steric hindrance of methyl substitution (entries **1h**, **1j**, **1o**) at the site of attack can thus be completely surmounted. The five-membered transition state with a short carbon–carbon double bond is by far the most favored. Due to a shorter C–O versus C–C bond, a similar regiocontrol has also been reported involving radical cyclization leading to oxygenated ring products.[27] Moreover, our cyclization is highly diastereoselective, as shown in the next part of this article. In contrast, when R^3 is a phenyl group (entry **1p**), the reaction led a to a 42:58 mixture of **5p** and **13p** (arising from α-cyclopropyl radical (**I**)). Faster addition of the mediator, more concentrated solutions, or the use of germanium hydride were without effect on the regioselectivity. The regioisomer **13p** was isolated as a single stereoisomer whose stereochemistry was established by X-ray crystallography. The diastereoselectivity may be due to a 1,3-diaxial interaction between the C–O bond and the incoming Ph_3SnH which favors the syn stereoisomer for compound **13p** (Scheme IX).

Table II

entry	R^1	R^3	R	reaction time	yield (%)
9h	H	H	Me	no reaction[a]	
9i	H	$SiMe_3$	Me	immediate	100
9j	H	n-C_5H_{11}	Me	1 h	90
9k	n-C_5H_{11}	$SiMe_3$	Me	immediate	100
9l	H	H	H	no reaction[a]	
9m	H	$SiMe_3$	H	immediate	100
9n	H	n-C_5H_{11}	H	immediate	100

[a] Compounds **9h** and **9l** were obtained by desilylation (KF in DMSO)[26] of **9i** and **9m**.

Table III. Regioselectivity of the Cyclization of the *Internal* Vinyl Radical 2

entry	R^1	R^3	R	ratio 5/13 (%)	yield (%)
1h	H	H	Me	100/0	65
1j	H	n-C_5H_{11}	Me	90/10	79
1l	H	H	H	100/0[c]	60
1n	H	C_5H_{11}	H	100/0[c]	67
1o[a]	n-C_5H_{11}	H	Me	100/0	75
1p[b]	H	C_6H_5	Me	42/58	80

[a] Alcohol **9o** was obtained by desilylation (KF in DMSO) of **9k**. [b] Alcohol **9p** was obtained by the reaction of methallylmagnesium chloride with 3-phenyl-2-propynal in 94% isolated yield. [c] The cyclopentene derivative is obtained as a single stereoisomer whose stereochemistry has not yet been confirmed (3,5-cis stereoselectivity).

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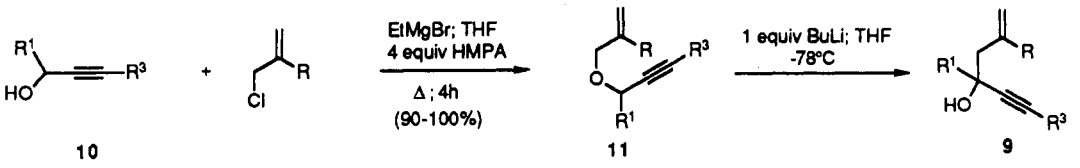
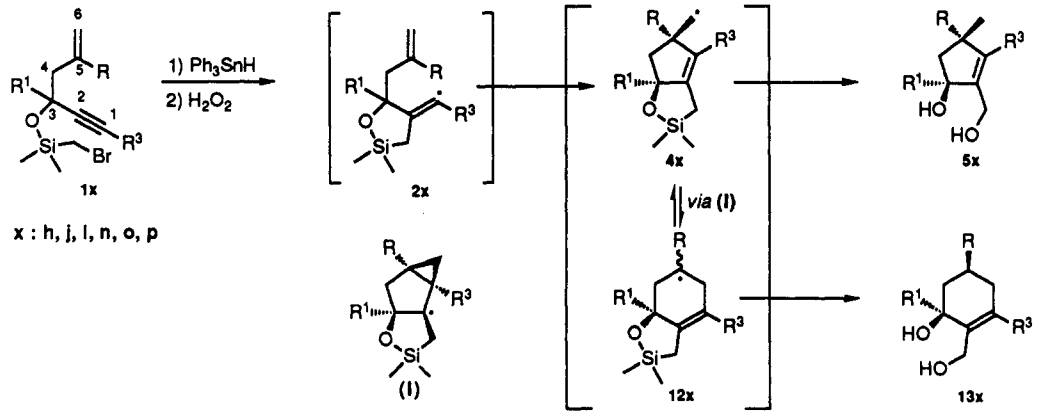
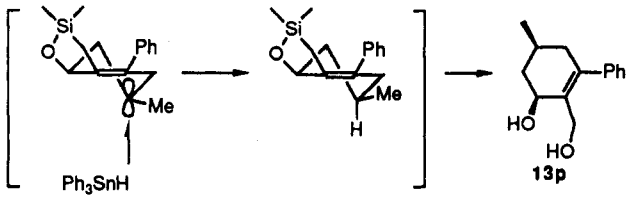
Scheme VII



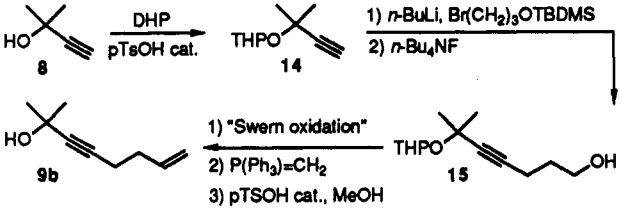
Scheme VIII. Regioselectivity of the *Internal* Vinyl Radical



Scheme IX



Scheme X



We pursued the study of the regioselectivity of the radical cyclization of propargyl ethers bearing an alkenyl chain connected to C-1. Substrates with an olefinic side chain of various lengths (n = 1–4) linked to C-1 were easily synthesized. For n = 1, we allylated 3-methyl-1-propyne-3-ol (8) using allyl bromide.[28] For n = 3 and 4, the lithium derivative of 8 was condensed with the corresponding bromides. This route was unsuccessful with 4-bromo-1-butene (n = 2); the synthesis of alcohol **9b** (48% overall yield from 8) is outlined in the Scheme X. Results of the radical cyclizations are illustrated in the Scheme XI.

Cyclic products were obtained only from substrate **1q** where n = 3. Diols **18** and **19** in a 5:95 ratio were isolated in 89% overall yield after Tamao oxidation. The selective formation of the rearranged endo compound, via the α-cyclopropyl radical (**II**), may be explained by three $A^{1,3}$ interactions present in intermediate **16** against only one 1,3-allylic interaction in radical **17**. This is, in our opinion, the first example in which the nearly exclusive formation of six-membered ring product is completely due to steric hindrance in the transition state. When n = 1, 2, and 4, the corresponding propargyl ethers gave trisubstituted olefins **3a–c** (entries **1a**, **1b**, **1c** of Table I and Scheme III). These results are in agreement with the known behavior of α-cyclopropyl and α-cyclobutyl radicals[31] and also with the unfavorable 6-*exo-trig* cyclization process.[32]

Stereoselective Synthesis of a Functionalized Diquinane Framework. When an allyl chain is connected to C-3, two consecutive regioselective cyclizations allow the formation of homoallyl radical intermediate **4** (Scheme VIII) which is a convenient substrate for a [3 + 2] annulation.[8] Another five-membered carbocycle was created by this strategy as illustrated by the following example. 4-[(Bromomethyl)dimethylsiloxy]-2-methyl-1-undecen-5-yne (**1j**) was refluxed in benzene (0.01 M) in the presence of 10 equiv of acrylonitrile and a benzene solution of Ph_3SnH (0.05 M, 1.1 equiv) containing 0.1 equiv of AIBN was slowly added (2×10^{-4} mol/h) by a syringe pump. The mixture was allowed to reflux for 5 additional hours. The volatile material was removed and the crude mixture subjected to Tamao oxidation to give **7j** in 51% yield. When only 3 equiv of acrylonitrile were used, a mixture of **7j** and **5j** (monocyclic product) in a 70:30 ratio was isolated in the same overall yield. Moreover, the diastereoselectivity observed in the formation of **7j** was impressive; within the detection limits of high-field ^{1}H- and ^{13}C-NMR analysis, the product was a single stereoisomer. Its structure and stereochemistry were established by 2D NMR and ^{1}H-NMR NOE measurements (Scheme XII).

This remarkable 3,5-cis stereoselectivity is consistent with the reaction of vinyl radical **2j**[20] through the more reactive **2j lk**[33] versus conformation **2j ul** (Scheme XIII). This 1,3-asymmetric induction due to steric[34,35] (chairlike

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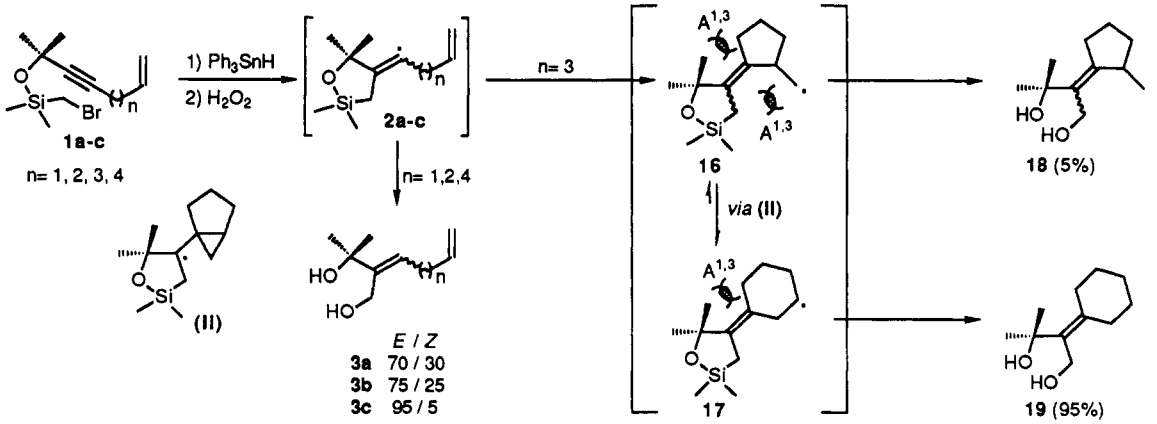
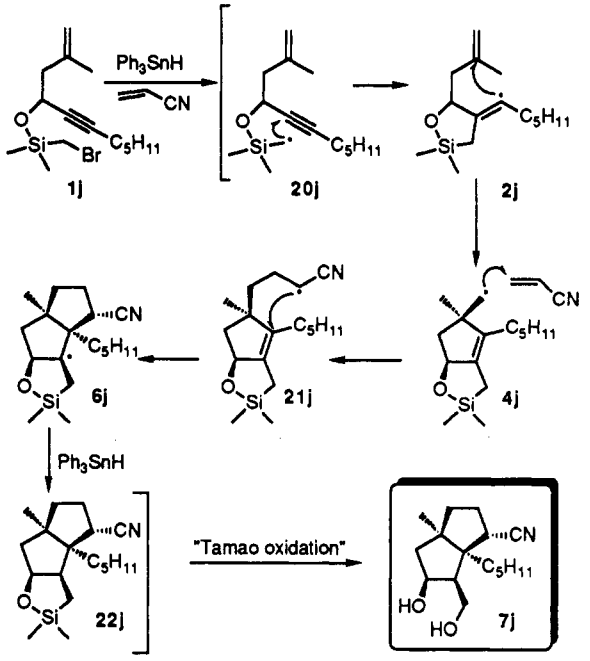
(35) Rajan, Babu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759.

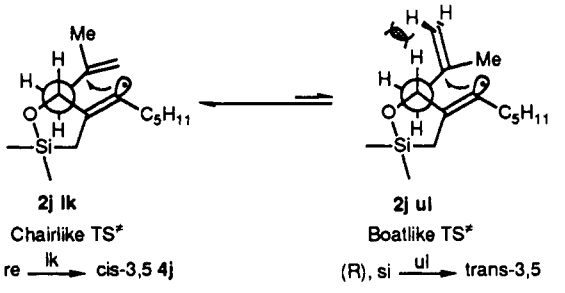
Scheme XI



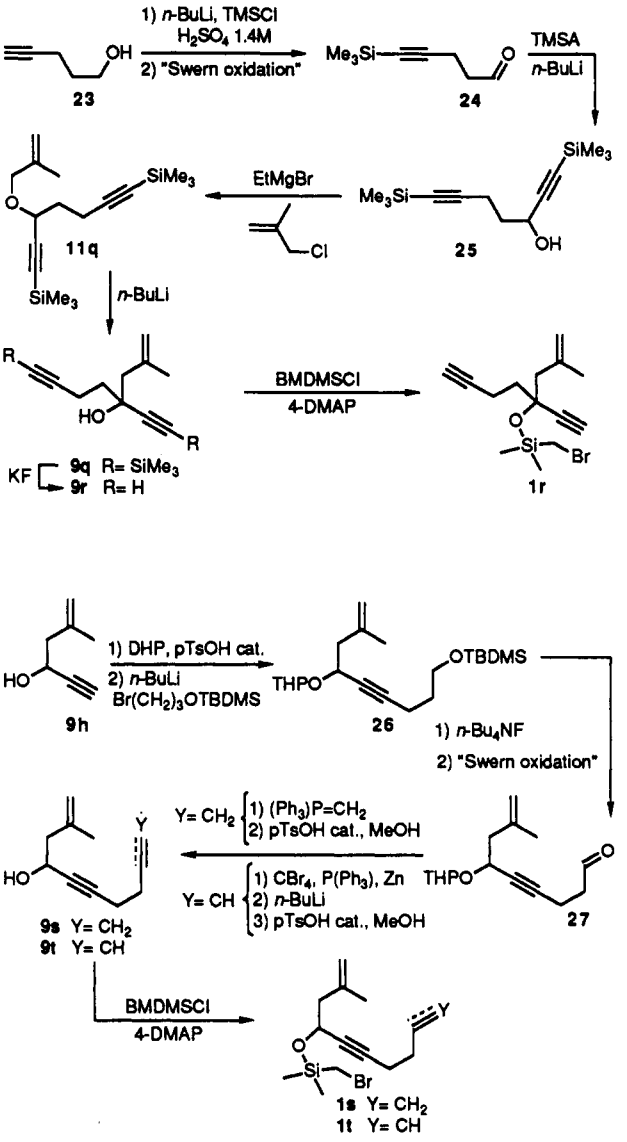
Scheme XII



Scheme XIII



Scheme XIV

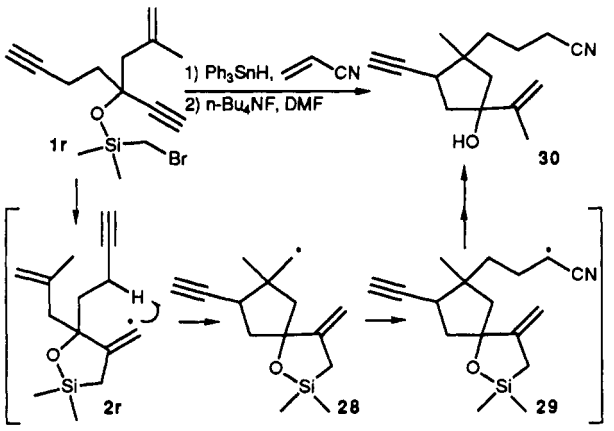


transition state) and perhaps electronic effects[36] directed the creation of all additional stereocenters since intermediate **22j** must have a cis–syn–cis configuration and therefore **21j** will cyclize with the cyano group on the convex face of the incipient tricyclic skeleton. Finally, a noteworthy feature of this sequence is the reduction of radical **6j** instead of its further trapping by acrylonitrile which is probably due to steric hindrance. This one-pot reaction allows the stereoselective formation of diquinane framework **7j** with the consecutive formation of four carbon–carbon bonds with two contiguous quaternary centers and the stereoselective formation of four stereogenic centers. Our next challenge is to apply this strategy to build, in one-pot, the angular and linear triquinane frameworks from acyclic substrate **1**, when substituents on C-1 and C-3 respectively will be suitable radical terminators (Scheme II).

First Attempts at Stereoselective Synthesis of Triquinane Frameworks. We began with the syntheses of the acyclic substrates, which were achieved in only a few

(36) Zahouilly, M.; Smadja, W.; Journet, M.; Malacria, M. *Tetrahedron Lett.* **1991**, *32*, 3683.

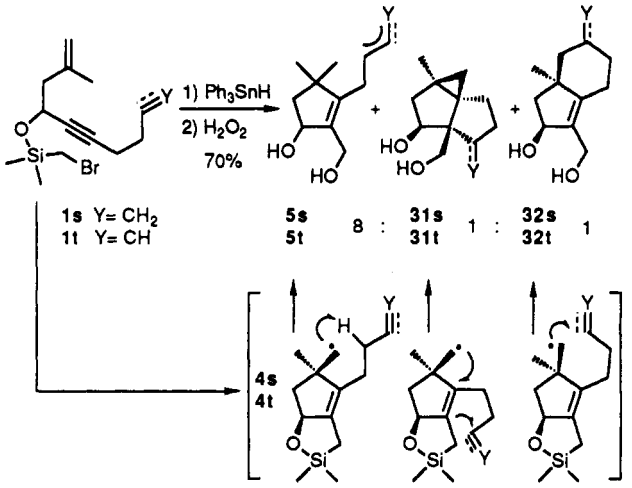
Scheme XV



steps in very good yields (Scheme XIV). Alcohol **23** was silylated on the terminal alkyne function and then oxidized[29] to aldehyde **24** in 93% yield. The lithium derivative of (trimethylsilyl)acetylene was condensed with **24** in THF at −78 °C to afford alcohol **25** (99% yield), which was etherified with β-methallyl chloride (91%) by methodology described by Marshall.[25] Allyl propargyl ether **11q** was subjected to a 2,3-Wittig reaction and the acetylenic functions were desilylated with 5 equiv of KF in DMSO at room temperature[26] to give **9r** in 85% yield. Finally, **9r** was silylated in 99% yield to furnish (bromomethyl)-dimethylsilyl propargyl ether **1r**. This potential precursor of the linear triquinane framework was thus prepared in 70% overall yield. Synthesis of the other type of acyclic substrate (angular triquinane) was conducted as follows: propargyl alcohol **9h** (see footnote *a* of Table II) was treated with 3 equiv of 3,4-dihydropyran in CH_2Cl_2 at room temperature with a catalytic amount of *p*-TsOH to give the tetrahydropyranyl ether in 99% yield as a 1:1 mixture of diastereoisomers. Its lithium derivative was added to 1-bromo-3-(*tert*-butyldimethylsiloxy)propane in THF to provide **26** in 75% yield. Silyl ether **26** was quantitatively desilylated with *n*-Bu_4NF in THF, and the corresponding alcohol was subjected to a Swern oxidation (94%). One-carbon homologation of aldehyde **27** was next accomplished in two different ways: (i) alcohol **9s** was obtained by a Wittig methylenation[30] (77%) followed by the quantitative deprotection of the tetrahydropyranyl ether with a catalytic amount of *p*-TsOH in MeOH at room temperature; (ii) alcohol **9t** was obtained by a Corey–Fuchs reaction[37] (78%) followed by deprotection. Finally, silylation of **9s** and **9t** provided **1s** and **1t** in 53% overall yield from alcohol **9h**. We subjected propargyl ether **1r** to the conditions of radical cyclization in the presence of 10 equiv of acrylonitrile followed by a Tamao oxidation. Unfortunately, this led to a complex mixture of products probably due to the instability of the diol. So, we repeated the cyclization of **1r** and treated the crude mixture with 5 equiv of *n*-Bu_4NF in DMF at 70 °C.[38] Under these conditions, compound **30** was isolated as a mixture of stereoisomers in 50% yield (Scheme XV).

This result can be explained by the preference of vinyl radical **2r** to undergo a (1,5) hydrogen shift involving the activated propargyl hydrogen rather than a 5-*exo-trig* cyclization. The propargylic radical intermediate thus produced can cyclize via a 5-*exo-trig* cyclization to give radical intermediate **28**, which is then trapped by acrylonitrile. Finally, **29** is reduced by the stannane and converted in situ to compound **30** by the fluoride anion. A quaternary

Scheme XVI



center at the propargyl position may be necessary if this (1,5) hydrogen transfer is to be avoided. We next applied our approach to angular triquinanes, starting in a similar way from **1s** and **1t**. Unfortunately, **1t** provided **5t** in 20% yield accompanied by many other unidentified products. **1s** gave a complex mixture. To understand this problem, the cyclization of **1s** and **1t** was performed in the absence of acrylonitrile in order to verify the compatibility of the unsaturated chain connected to C-1. The results of this radical cyclization are depicted in the Scheme XVI.

Once again, the limiting factor of this approach is a (1,5) hydrogen shift because compound **5s** results from a migration of the terminal double bond. This hydrogen transfer is the major process (56%) occuring but two others are also observed. First of all, intermediates **4s** and **4t** undergo a 3-*exo-trig* cyclization and the resulting β-silyl radical is trapped by the unsaturation to furnish cyclopropanes **31s** and **31t** as single stereoisomers in 7% yield. This is the first example which proves the mechanism proposed by Stork[20b] and Beckwith[21] for the formation of the rearranged 6-*endo* products via an α-cyclopropyl radical. Finally, the formation of **32s** and **32t** results from 6-*exo* cyclization of the homoallyl radical **4** on the radical terminator Y. Compound **32t** is isolated in 7% yield as a single stereoisomer and **32s** is a 1:1 mixture of diastereoisomers (7%) due to lack of control of the stereoselectivity during the creation of the last stereogenic center. As in the case of the linear triquinane approach, a quaternary center at the propargyl or allyl position seems to be necessary to avoid hydrogen transfer.

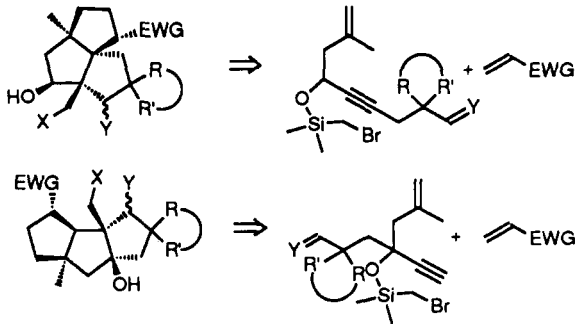
Conclusions

The radical cyclization of (bromomethyl)dimethylsilyl propargyl ethers is a powerful reaction with a very effective control of regio-, chemo-, and stereoselectivity. Diallyl 1,3-diols, not easily accessible by other ways,[39] are synthesized in very high yields. By judicious choice of substituents on the (bromomethyl)dimethylsilyl propargyl ether derivatives, we can obtain regio- and stereoselectively trisubstituted double bonds, five-membered unsaturated carbocycles, or the diquinane system. Moreover, we have intercepted, for the first time, the α-cyclopropyl radical which is involved in the Stork-Beckwith mechanism of the 5- versus 6-membered ring formation in the vinyl radical cyclization.

Unfortunately, we have not yet succeeded in the stereoselective synthesis of angular and linear triquinane

(37) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.
(38) Stork, G.; Mah, R. *Tetrahedron Lett.* **1989**, *30*, 3609.
(39) Crozet, M. P.; Archaimbault, G.; Vanelle, P.; Nougier, R. *Tetrahedron Lett.* **1985**, *26*, 5133.

Scheme XVII[a]



[a] Y = radical terminator.

frameworks from acyclic substrates. This could be achieved if (1,5) hydrogen shift can be avoided by including a quaternary center in the right position (Scheme XVII). Work aimed toward this goal is currently in progress in our laboratory.

Experimental Section

Synthesis of Allyl Propargyl Ethers. General Procedure. To a stirred, cooled (0 °C) solution of propargyl alcohol **10** (10 mmol) and 5 mg of 1,10-phenanthroline in HMPA (7.0 mL, 40 mmol) and THF (50 mL) was added dropwise EtMgBr (2.0 M in THF, 5.0 mL, 10 mmol). Allyl halide (β-methallyl chloride or allyl bromide, 15 mmol) was added and the reaction mixture was heated to reflux. After 4 h, the organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum and the residue purified by flash chromatography with a mixture of petroleum ether and ether (95:5) as eluent to yield **11** (90–100%) as a colorless liquid.

3-(2-Methyl-2-propenoxy)-1-propyne (11h): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.80 (1 H, br s), 4.74 (1 H, br s), 3.93 (2 H, d, J = 2.3 Hz), 3.78 (2 H, s), 2.30 (1 H, J = 2.3 Hz), 1.56 (3 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.2, 113.0, 79.7, 74.2, 73.5, 56.8, 19.4; IR (neat) 3300, 3080, 2110, 1650, 900 cm^{-1}; bp 43–45 °C at ~15 Torr.

3-(2-Methyl-2-propenoxy)-1-(trimethylsilyl)-1-propyne (11i): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.93 (1 H, br s), 4.86 (1 H, br s), 4.05 (2 H, s), 3.91 (2 H, s), 1.69 (3 H, s), 0.12 (9 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.4, 113.1, 101.6, 91.1, 73.5, 57.7, 19.5, –0.2; IR (neat) 3080, 2180, 1660, 900 cm^{-1}. Anal. Calcd for $C_{10}H_{18}OSi$: C, 65.87; H, 99.5. Found: C, 65.65; H, 10.04.

1-(2-Methyl-2-propenoxy)-2-octyne (11j): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.96–4.89 (2 H, m), 4.09 (2 H, t, J = 2.0 Hz), 3.93 (2 H, s), 2.19 (2 H, tt, J = 6.9, 2.0 Hz), 1.72 (3 H, s), 1.53–1.24 (6 H, m), 0.88 (3 H, t, J = 6.9 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.7, 112.6, 86.9, 75.9, 73.3, 57.5, 31.0, 28.3, 22.1, 19.5, 18.7, 13.9; IR (neat) 3080, 2220, 1660, 900 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.90; H, 11.11.

3-(2-Methyl-2-propenoxy)-1-(trimethylsilyl)-1-octyne (11k): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.97 (1 H, br s), 4.88 (1 H, br s), 3.99 (2 H, AB, J = 21.5 Hz), 3.97 (1 H, t, J = 6.5 Hz), 1.73 (3 H, s), 1.61–1.15 (8 H, m), 0.87 (3 H, t, J = 6.7 Hz), 0.16 (9 H, s); IR (neat) 3080, 2170, 1660, 900 cm^{-1}.

3-(2-Propenoxy)-1-(trimethylsilyl)-1-propyne (11m): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.95–5.75 (1 H, m), 5.28–5.12 (2 H, m), 4.08 (2 H, s), 4.00 (2 H, d, J = 5.6 Hz), 0.13 (9 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 134.0, 117.7, 101.4, 91.2, 70.5, 57.8, –0.2; IR (neat) 3080, 2170, 1650, 995, 920 cm^{-1}.

1-(2-Propenoxy)-2-octyne (11n): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.99–5.80 (1 H, m), 5.40–5.16 (2 H, m), 4.11 (2 H, t, J = 2.0 Hz), 4.03 (2 H, d, J = 5.8 Hz), 2.19 (2 H, tt, J = 6.0, 2.0 Hz), 1.53–1.23 (6 H, m), 0.88 (3 H, t, J = 6.8 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 134.3, 117.5, 93.4, 82.3, 70.4, 57.7, 31.0, 28.3, 22.2, 18.5, 13.9; IR (neat) 3080, 2220, 1650, 990 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.40; H, 10.92.

3-(2-Methyl-2-propenoxy)-1,7-bis(trimethylsilyl)-1,6-heptadiyne (11q): ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.96 (1 H, br s), 4.88 (1 H, br s), 4.15 (1 H, t, J = 6.5 Hz), 3.99 (2 H, AB, J = 19.6 Hz), 2.38 (2 H, td, J = 7.5, 3.8 Hz), 1.90 (2 H, qd, J = 6.7, 1.9 Hz), 1.73 (3 H, br s), 0.15 (9 H, s), 0.12 (9 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.8, 112.8, 106.2, 104.1, 90.6, 84.9, 72.6, 67.2, 34.6, 19.6, 15.9, 0.1; IR (neat) 3075, 2170, 1650, 1250, 1070, 900 cm^{-1}.

Synthesis of Homoallyl Propargyl Alcohols via a 2,3-Wittig Reaction. General Procedure. To a stirred solution of **11** (10 mmol) in THF (50 mL) was added n-butyllithium (1.6 M in hexanes, 6.25 mL, 10 mmol) at –78 °C under nitrogen. The reaction mixture was then washed with brine and dried over Na_2SO_4. After removing the solvent under vacuum, the residue was purified by flash column chromatography with a mixture of petroleum ether and ether (1:1) as eluent to yield **9** (90–100%) as a colorless liquid.

5-Methyl-1-(trimethylsilyl)-5-hexen-1-yn-3-ol (9i): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.91–4.88 (1 H, m), 4.84–4.83 (1 H, m), 4.47 (1 H, t, J = 6.6 Hz), 2.43 (2 H, d, J = 6.6 Hz), 1.78 (3 H, s), 0.15 (9 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.0, 114.2, 106.5, 89.5, 60.9, 46.1, 22.6, –0.2; IR (neat) 3350, 3080, 2180, 1650, 890 cm^{-1}.

2-Methyl-1-undecen-5-yn-4-ol (9j): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.88–4.80 (2 H, m), 4.45 (1 H, tt, J = 6.7, 2.0 Hz), 2.38 (2 H, d, J = 6.7 Hz), 2.16 (2 H, td, J = 7.0, 2.0 Hz), 1.76 (3 H, s), 1.52–1.22 (6 H, m), 0.87 (3 H, t, J = 7.1 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.3, 114.0, 85.6, 80.8, 60.6, 48.5, 31.0, 28.3, 22.6, 22.2, 18.6, 13.9; IR (neat) 3350, 3080, 2230, 1650, 900 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.70; H, 11.28.

1-Undecen-5-yn-4-ol (9n): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.94–5.73 (1 H, m), 5.16–5.07 (2 H, m), 4.35 (1 H, tt, J = 6.9, 2.0 Hz), 2.42 (2 H, t, J = 7.0 Hz), 2.18 (2 H, td, J = 6.9, 2.0 Hz), 1.48–1.16 (6 H, m), 0.88 (3 H, t, J = 6.8 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 133.5, 118.3, 85.8, 80.7, 61.8, 42.5, 31.0, 28.3, 22.1, 18.6, 13.9; IR (neat) 3350, 3080, 2220, 1640, 990 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.36; H, 11.00.

3-(2-Methyl-2-propenyl)-1,7-bis(trimethylsilyl)-1,6-heptadiyn-3-ol (9q): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.97 (1 H, br s), 4.83 (1 H, br s), 2.52 (1 H, t, J = 8.2 Hz), 2.48 (1 H, t, J = 7.0 Hz), 2.37 (2 H, AB, J = 12.9 Hz), 1.91 (3 H, s), 1.86 (2 H, t, J = 7.7 Hz), 0.133 (9 H, s), 0.130 (9 H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.3, 115.9, 107.4, 107.1, 89.7, 84.8, 69.0, 50.0, 40.7, 24.3, 15.3, 0.0, –0.3; IR (neat) 3520, 3450, 3080, 2170, 1650, 1250, 1080, 900 cm^{-1}.

Desilylation of Acetylenic Functions. General Procedure. To a stirred solution of **9i** (1.82 g, 10 mmol) in DMSO (50 mL) was added KF (1.45 g, 25 mmol). After 1 h at room temperature, the reaction mixture was extracted with ether, washed with brine, dried over Na_2SO_4, and concentrated under vacuum. The product was flash chromatographed with a mixture of petroleum ether and ether (1:1) as eluent to afford **9h** (1.1 g, 100%): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.87 (1 H, br s), 4.82 (1 H, br s), 4.47 (1 H, td, J = 6.8, 2.0 Hz), 2.44 (1 H, d, J = 2.0 Hz), 2.42 (2 H, d, J = 6.8 Hz), 1.76 (3 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 140.8, 114.2, 84.6, 72.9, 60.3, 45.9, 22.5; IR (neat) 3350, 3300, 3080, 2120, 1650, 900 cm^{-1}.

5-Hexen-1-yn-3-ol (9l): 100%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.93–5.72 (1 H, m), 5.18–5.08 (1 H, m), 4.35 (1 H, td, J = 6.3, 2.1 Hz), 2.43 (1 H, d, J = 2.1 Hz), 2.42 (2 H, t, J = 6.8 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 132.7, 118.8, 84.2, 73.1, 61.2, 41.7; IR (neat) 3350, 3300, 3080, 2120, 1650, 995 cm^{-1}.

5-Methyl-3-pentyl-5-hexen-1-yn-3-ol (9o): 100%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.97 (1 H, br s), 4.84 (1 H, br s), 2.43 (1 H, s), 2.38 (2 H, AB, J = 11.5 Hz), 1.92 (3 H, s), 1.69–1.50 (4 H, m), 1.33–1.28 (4 H, m), 0.88 (3 H, t, J = 6.5 Hz); IR (neat) 3450, 3300, 3080, 2100, 1640, 890 cm^{-1}.

3-(2-Methyl-2-propenyl)-1,6-heptadiyn-3-ol (9r): 100%; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.99–4.95 (1 H, m), 4.84–4.83 (1 H, m), 2.49 (1 H, td, J = 8.0, 2.8 Hz), 2.48 (1 H, s), 2.44 (1 H, td, J = 8.0, 2.8 Hz), 2.39 (1 H, s), 2.37 (1 H, s), 1.95 (1 H, t, J = 2.8 Hz), 1.90 (3 H, s), 1.89 (1 H, t, J = 6.5 Hz), 1.88 (1 H, t, J = 6.5 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.1, 116.1, 85.7, 84.1, 73.5, 68.7, 68.6, 49.9, 40.7, 24.3, 13.8; IR (neat) 3520, 3450, 3300, 3080, 2120, 1640, 900 cm^{-1}.

Synthesis of (Bromomethyl)dimethylsilyl Propargyl Ethers. General Procedure. To a solution of propargyl alcohol **9** (10 mmol) and 4-DMAP (122 mg, 1 mmol) in CH_2Cl_2 (50 mL) were added triethylamine (1.4 mL, 11 mmol) and (bromomethyl)chlorodimethylsilane (1.35 mL, 10 mmol) at 0 °C under nitrogen. The mixture was stirred for 15 min at room temperature. The organic phase was washed with brine and then dried over

Na_2SO_4. After evaporation of the solvent, the residue was chromatographed with a mixture of petroleum ether and ether (95:5) as eluent to yield 1 (95 to 100%) as a clear oil.

6-[(Bromomethyl)dimethylsiloxy]-6-methyl-1-hepten-4-yne (1a): ^{1}H-NMR (80 MHz, $CDCl_3$) δ 6.11–5.57 (1 H, m), 5.38–5.06 (2 H, m), 2.61 (2 H, s), 2.49–2.34 (2 H, m), 1.51 (6 H, s), 0.35 (6 H, s); IR (neat) 3080, 1640, 1250, 1150, 910 cm^{-1}. Anal. Calcd for $C_{11}H_{19}OSiBr$: C, 48.00; H, 6.96. Found: C, 47.85; H, 6.94.

7-[(Bromomethyl)dimethylsiloxy]-7-methyl-1-octen-5-yne (1b): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.89–5.75 (1 H, m), 5.10–4.99 (2 H, m), 2.57 (2 H, s), 2.26 (4 H, s), 1.44 (6 H, s), 0.31 (6 H, s); IR (neat) 3080, 1640, 1250, 1150, 910 cm^{-1}.

9-[(Bromomethyl)dimethylsiloxy]-9-methyl-1-decen-7-yne (1c): ^{1}H-NMR (80 MHz, $CDCl_3$) δ 6.08–5.58 (1 H, m), 5.15–4.88 (2 H, m), 2.59 (2 H, s), 2.30–1.97 (4 H, m), 1.67–1.42 (4 H, m), 1.47 (6 H, s), 0.34 (6 H, s); IR (neat) 3080, 2240, 1250, 1150, 840 cm^{-1}. Anal. Calcd for $C_{14}H_{25}OSiBr$: C, 52.99; H, 7.94. Found: C, 52.83; H, 7.98.

2-[(Bromomethyl)dimethylsiloxy]-2-methyl-7-(2-tetrahydropyranyloxy)-3-heptyne (1d): ^{1}H-NMR (80 MHz, $CDCl_3$) δ 4.45 (1 H, br s), 3.95–2.81 (4 H, m), 2.47 (2 H, s), 2.42–2.11 (8 H, m), 1.46 (6 H, s), 0.32 (6 H, s); IR (neat) 2240, 1250, 840 cm^{-1}. Anal. Calcd for $C_{16}H_{29}O_3SiBr$: C, 50.92; H, 7.74. Found: C, 50.78; H, 7.75.

7-[(Bromomethyl)dimethylsiloxy]-5-undecyne (1e): ^{1}H-NMR (80 MHz, $CDCl_3$) δ 4.27–4.19 (1 H, m), 2.49 (2 H, s), 2.16–2.09 (2 H, m), 1.65–1.02 (10 H, m), 0.87 (3 H, t, J = 7.1 Hz), 0.27 (6 H, s); IR (neat) 2230, 1250, 1150 cm^{-1}; bp 98–100 °C at 1 Torr. Anal. Calcd for $C_{14}H_{27}OSiBr$: C, 52.65; H, 8.52. Found: C, 52.61; H, 8.54.

3-[(Bromomethyl)dimethylsiloxy]-3-methyl-1-phenyl-1-butyne (1f): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.44–7.37 (2 H, m), 7.35–7.30 (3 H, m), 2.64 (2 H, s), 1.59 (6 H, s), 0.39 (6 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 131.4, 128.4, 122.7, 93.9, 83.6, 67.5, 33.0, 17.6, –1.1; IR (neat) 3080, 3060, 2230, 1600, 1250, 1150 cm^{-1}.

3-[(Bromomethyl)dimethylsiloxy]-3-methyl-1-(trimethylsilyl)-1-butyne (1g): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 2.59 (2 H, s), 1.45 (6 H, s), 0.33 (6 H, s), 0.16 (9 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 110.6, 87.9, 67.2, 32.9, 17.5, –0.2, –1.1; IR (neat) 2150, 1250, 1150 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-1-hexen-5-yne (1h): ^{1}H-NMR (80 MHz, $CDCl_3$) δ 4.80–4.76 (2 H, m), 4.50 (1 H, td, J = 6.5, 2.0 Hz), 2.49 (2 H, s), 2.40 (1 H, d, J = 2.0 Hz), 2.35 (2 H, d, J = 6.5 Hz), 1.71 (3 H, s), 0.27 (6 H, s); IR (neat) 3300, 3080, 2120, 1650, 1260, 1080, 900 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-1-undecen-5-yne (1j): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.82–4.80 (1 H, m), 4.76–4.75 (1 H, m), 4.51 (1 H, tt, J = 6.9, 2.0 Hz), 2.54 (2 H, AB), 2.35 (2 H, ABX), 2.17 (2 H, td, J = 6.9, 2.0 Hz), 1.74 (3 H, s), 1.51–1.24 (6 H, m), 0.88 (3 H, t, J = 6.9 Hz), 0.30 (6 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.3, 113.3, 85.9, 80.9, 62.7, 47.0, 31.0, 28.8, 22.9, 22.2, 18.6, 16.4, 13.9, –2.7; IR (neat) 3080, 2240, 1650, 1260, 1080, 900 cm^{-1}; MS (m/z) 317, 315, 277, 275, 153, 151, 125, 123, 75, 41, 29.

4-[(Bromomethyl)dimethylsiloxy]-1-hexen-5-yne (1l): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.89–5.72 (1 H, m), 5.17–5.08 (2 H, m), 4.43 (1 H, td, J = 6.5, 2.1 Hz), 2.53 (2 H, AB), 2.45 (1 H, d, J = 2.1 Hz), 2.43 (2 H, ABX), 0.31 (6 H, 3); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 133.2, 118.2, 84.3, 73.4, 62.8, 42.7, 16.1, –2.6; IR (neat) 3300, 3080, 2120, 1650, 1080, 990, 920 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-1-undecen-5-yne (1n): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.89–5.72 (1 H, m), 5.14–5.04 (2 H, m), 4.41 (1 H, tt, J = 6.4, 1.9 Hz), 2.53 (2 H, AB), 2.39 (2 H, ABX), 2.17 (2 H, td, J = 6.9, 1.9 Hz), 1.52–1.25 (6 H, m), 0.88 (3 H, t, J = 7.0 Hz), 0.30 (6H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 133.9, 117.5, 86.1, 63.3, 43.3, 31.0, 28.2, 22.1, 18.6, 13.9, –2.6; IR (neat) 3080, 2220, 1640, 1250, 1080, 990 cm^{-1}. Anal. Calcd for $C_{14}H_{25}OSiBr$: C, 52.99; H, 7.94. Found: C, 52.74; H, 8.02.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-4-pentyl-1-hexen-5-yne (1o): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.89–4.87 (2 H, m), 2.58 (2 H, s), 2.53 (1 H, s), 2.38 (2 H, s), 1.83 (3 H, s), 1.66–1.55 (2 H, m), 1.51–1.26 (6 H, m), 0.88 (3 H, t, J = 6.5 Hz), 0.33 (6 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 141.2, 115.4, 87.2, 74.4, 72.6, 50.4, 42.6, 31.9, 24.4, 24.0, 22.6, 17.5, 14.0, –1.1; IR (neat) 3300, 3080, 2100, 1640, 1250, 1070, 890 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-6-phenyl-1-hexen-5-yne (1p): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.44–7.29 (5 H, m), 4.89–4.86 (2 H, m), 4.78 (1 H, t, J = 7.0 Hz), 2.53 (2 H, s), 2.43 (2 H, d, J = 7.0 Hz), 1.75 (3 H, br s), 0.30 (6 H, s); IR (neat) 3080, 2250, 1650, 1260, 1085, 900 cm^{-1}. Anal. Calcd for $C_{16}H_{21}OSiBr$: C, 56.97; H, 6.27. Found: C, 56.89; H, 6.25.

4-[(Bromomethyl)dimethylsiloxy]-4-ethynyl-2-methyl-1-octen-7-yne (1r): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.91–4.89 (1 H, m), 4.79–4.78 (1 H, m), 2.58 (1 H, s), 2.57 (2 H, s), 2.41 (2 H, s), 2.37 (2 H, td, J = 8.2, 2.7 Hz), 1.93 (1 H, t, J = 2.7 Hz), 1.89 (2 H, t, J = 8.2 Hz), 0.34 (3 H, s), 0.33 (3 H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.6, 116.1, 85.8, 84.1, 75.3, 71.6, 68.2, 50.6, 41.1, 24.3, 17.2, 13.9, –1.1; IR (neat) 3300, 3080, 2110, 1640, 1250, 1085, 895 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-1,9-decadien-5-yne (1s): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.89–5.76 (1 H, m), 5.09–4.99 (2 H, m), 4.81–4.76 (2 H, m), 4.51 (1 H, br t, J = 6.7 Hz), 2.53 (2 H, AB), 2.34 (2 H, ABX), 2.25 (4 H, br s), 1.74 (3 H, s), 0.29 (6 H, s); IR (neat) 3080, 2225, 1640, 1250, 1070, 910, 890 cm^{-1}.

4-[(Bromomethyl)dimethylsiloxy]-2-methyl-1-decene-5,9-diyne (1t): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.82–4.81 (1 H, m), 4.77–4.76 (1 H, m), 4.52 (1 H, tt, J = 6.7, 2.7 Hz), 2.55 (2 H, AB), 2.44–2.30 (6 H, m), 2.00 (1 H, t, J = 2.5 Hz), 1.74 (3 H, s), 0.30 (3 H, s), 0.29 (3 H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.3, 113.5, 83.6, 82.6, 82.1, 69.4, 62.5, 46.8, 23.0, 18.8, 18.6, 16.5, –2.5, –2.7; IR (neat) 3300, 3080, 2225, 2120, 1250, 1080, 890 cm^{-1}.

Radical Cyclization of (Bromomethyl)dimethylsilyl Propargyl Ethers 1. General Procedure. A benzene solution (10 mL) of Ph_3SnH (580 mg, 1.65 mmol) containing AIBN (21 mg, 0.15 mmol) was added by a syringe pump over 8 h to a solution of (bromomethyl)dimethylsilyl propargyl ether 1 (1.5 mmol) in refluxing benzene (60 mL) under argon. After completion of the addition, the mixture was allowed to reflux for 5 additional hours. The solvent was then removed under reduced pressure and the heterocyclic intermediate was transformed in situ in 3 different ways.

Method A. Treatment with H_2O_2. The residue was placed in a 1:1 mixture of MeOH/THF (30 mL) with $KHCO_3$ (750 mg, 7.5 mmol) and then refluxed. H_2O_2 (30%, 5.0 mL, 43 mmol) was added and the solution was stirred for 3 h. The reaction mixture was filtered through Celite and extracted with ether. After being washed with aqueous 10% $NaHSO_3$ and with brine, the organic layer was dried over Na_2SO_4 and evaporated. The product was purified by flash column chromatography with ether as eluent.

Method B. Treatment with MeLi. After being dissolved in pentane (5 mL), the stannane residue precipitated and was eliminated by filtration under argon. After evaporation under vacuum, the pentane was replaced by ether (30 mL) and methyllithium (1.6 M in ether, 940 μL, 1.5 mmol) was added at –30 °C. The mixture was stirred for 1 h under argon. The organic phase was washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed with a mixture of petroleum ether and ether (1:1) as eluent.

Method C. Treatment with n-Bu_4NF. The residue was placed in DMF (40 mL) with n-Bu_4NF (1.0 M in THF, 7.5 mL, 7.5 mmol) under argon. The solution was stirred at 70 °C for 8 h. The reaction mixture was extracted with ether, washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The product was flash chromatographed with a mixture of petroleum ether and ether (1:1) as eluent.

(*E*)- and (*Z*)-2-(3-Butenylidene)-3-methyl-1,3-butanediol (3a). ***E*-3a**: oil (47%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.85–5.66 (2 H, m), 5.07–4.93 (2 H, m), 4.29 (2 H, s), 2.31–2.06 (2 H, m), 1.41 (6 H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.2, 136.1, 128.9, 114.2, 74.1, 58.6, 39.7, 30.1; IR (neat) 3350, 3080, 1640, 1000, 915 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.06; H, 10.35. ***Z*-3a**: oil (21%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.86–5.65 (2 H, m), 5.05–4.90 (2 H, m), 4.17 (2 H, s), 2.30–2.05 (2 H, m), 1.41 (6 H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 144.4, 136.0, 114.4, 73.5, 68.5, 39.9, 31.1; IR (neat) 3350, 3080, 1640, 1000, 920 cm^{-1}. Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.11; H, 10.37.

(*E*)- and (*Z*)-3-Methyl-2-(3-pentenylidene)-1,3-butanediol (3b). ***E*-3b**: oil (56%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.83–5.66 (1 H, m), 5.51 (1 H, t, J = 6.8 Hz), 5.02–4.92 (2 H, m), 4.26 (2 H,

s), 2.24–2.08 (4 H, m), 1.35 (6 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 143.9, 137.9, 126.7, 115.1, 74.1, 58.2, 33.7, 29.9, 27.0; IR (neat) 3350, 3080, 1640, 980, 910 cm^{-1}. ***Z*-3b**: oil (19%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 5.89–5.69 (1 H, m), 5.33 (1 H, t, J = 6.9 Hz), 5.06–4.95 (2 H, m), 4.15 (2 H, s), 2.23 (2 H, t, J = 6.6 Hz), 2.13 (2 H, t, J = 6.6 Hz), 1.44 (6 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 145.5, 138.1, 128.9, 115.4, 73.9, 69.0, 34.2, 31.1, 28.7; IR (neat) 3350, 3080, 1640, 980, 910 cm^{-1}.

(*E*)-3-Methyl-2-(3-octenylidene)-1,3-butanediol (*E*-3c): oil (66.5%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.79–5.64 (1 H, m), 5.51–5.29 (2 H, m), 4.98–4.85 (1 H, m), 4.23 (2 H, s), 2.10–1.87 (4 H, m), 1.59–1.53 (4 H, m), 1.32 (6 H, s); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 143.5, 138.9, 127.5, 114.5, 74.2, 58.2, 33.6, 32.0, 29.6, 29.2, 26.5; IR (neat) 3350, 3080, 1660, 1640, 1000 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.75; H, 11.14.

(*E*)- and (*Z*)-3-Methyl-2-[(trimethylsilyl)methylidene]-1,3-butanediol (3g). *E*-3g: oil (30%); ^{1}H-NMR (200 MHz, C_6D_6) δ 5.65 (1 H, s), 4.39 (2 H, s), 1.35 (6 H, s), 0.18 (9 H, s); ^{13}C-NMR (50 MHz, C_6D_6) δ 162.5, 125.1, 75.3, 63.2, 30.5, 0.6; IR (neat) 3350, 1610, 1250, 1150, 1010 cm^{-1}. ***Z*-3g**: mp 75–76 °C (55%); ^{1}H-NMR (200 MHz, C_6D_6) δ 5.68 (1 H, t, J = 1.4 Hz), 3.85 (2 H, d, J = 1.4 Hz), 1.11 (6 H, s), 0.31 (9 H, s); ^{13}C-NMR (50 MHz, C_6D_6) δ 163.4, 122.7, 73.8, 65.3, 30.0, 2.4; IR ($CHCl_3$) 3400, 1610, 1250, 1150, 1010 cm^{-1}; MS (m/z) 173, 155, 137, 131, 109, 97, 75, 59, 43. Anal. Calcd for $C_9H_{20}O_2Si$: C, 57.39; H, 10.70. Found: C, 57.56; H, 10.69.

2-(Hydroxymethyl)-4-methyl-2-cyclopentenol (5l): oil (60%); ^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.65 (1 H, s), 4.81–4.79 (1 H, m), 4.27 (2 H, s), 2.61–2.53 (3 H, m), 1.08 (3 H, d, J = 6.7 Hz); ^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.7, 135.7, 78.0, 10.5, 43.0, 37.4, 21.6.

2-(Hydroxymethyl)-4-methyl-3-pentyl-2-cyclopentenol (5n): oil (67%); ^{1}H-NMR (200 MHz, C_6D_6) δ 5.93–4.89 (1 H, m), 4.39 (2 H, AB, J = 19.5 Hz), 2.48–2.39 (2 H, m), 2.25–1.92 (3 H, m), 1.49–1.15 (6 H, m), 1.10 (3 H, d, J = 6.5 Hz), 0.91 (3 H, t, J = 6.7 Hz); ^{13}C-NMR (50 MHz, C_6D_6) δ 146.7, 136.8, 78.4, 58.4, 41.8, 39.5, 32.1, 28.2, 26.3, 22.8, 20.2, 14.1; IR (neat) 3350, 1050, 1010 cm^{-1}.

2-(Hydroxymethyl)-4,4-dimethyl-3-phenyl-2-cyclopentenol (5p): mp 135–136 °C (33.5%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 7.27–7.22 (3 H, m), 7.06–7.02 (2 H, m), 4.97 (1 H, dd, J = 7.3, 5.0 Hz), 3.99 (2 H, AB, J = 10.9 Hz), 2.19 (1 H, dd, J = 13.1, 7.3 Hz), 1.71 (1 H, dd, J = 13.1, 5.0 Hz), 1.07 (3 H, s), 1.01 (3 H, s); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 151.4, 137.5, 135.9, 128.9, 127.9, 127.1, 76.1, 58.4, 49.6, 46.5, 28.7, 28.0; IR (neat) 3400, 3080, 1600, 1050, 1000 cm^{-1}; MS (m/z) 200, 169, 155, 141, 128, 105, 91, 77, 51, 41. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.10; H, 8.35.

***cis*-2-(Hydroxymethyl)-5-methyl-3-phenyl-2-cyclohexenol (13p)**: mp 64–66 °C (46.5%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33–7.12 (5 H, m), 4.61–4.57 (1 H, m), 4.12 (2 H, AB, J = 16.6 Hz), 2.34 (1 H, dd, J = 13.5, 3.5 Hz), 2.09 (1 H, dd, J = 13.5, 3.5 Hz), 2.01–1.82 (2 H, m), 1.37 (1 H, AB, J = 11.3 Hz), 1.00 (3 H, d, J = 6.5 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 141.6, 139.2, 133.8, 128.2, 128.1, 127.1, 70.6, 61.7, 41.3, 41.1, 28.0, 21.8; IR (neat) 3350, 3050, 1650, 1600, 1060 cm^{-1}; MS (m/e) 200, 187, 115, 91, 77, 43. Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.06; H, 8.27.

3-(3-Butynyl)-2-(hydroxymethyl)-4,4-dimethyl-2-cyclopentenol (5t): oil (56%); ^{1}H-NMR (200 MHz, C_6D_6) δ 5.01 (1 H, dd, J = 7.1, 4.5 Hz), 4.43 (2 H, AB, J = 18.0 Hz), 2.35–2.29 (4 H, m), 2.15 (1 H, dd, J = 13.1, 7.1 Hz), 2.04 (1 H, t, J = 2.3 Hz), 1.83 (1 H, dd, J = 13.1, 4.5, Hz), 1.22 (3 H, s), 1.03 (3 H, s); ^{13}C-NMR (100 MHz, C_6D_6) δ 147.8, 137.9, 84.4, 77.1, 69.8, 58.9, 49.8, 46.2, 28.9, 24.6, 20.0; IR (neat) 3350, 3300, 2110 cm^{-1}.

3-Methyl-2-(2-methylcyclopentylidene)-1,3-butanediol (18): oil (4.5%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.30 (2 H, AB, J = 10.1 Hz), 2.91–2.86 (1 H, m), 2.46–2.29 (2 H, m), 1.79–1.27 (4 H, m), 1.46 (3 H, s), 1.45 (3 H, s), 1.01 (3 H, d, J = 7.0 Hz); IR (neat) 3400, 1380, 1120 cm^{-1}; MS (m/z) 166, 148, 133, 120, 105, 93, 91, 79, 59, 43, 41, 31.

4-[2-Ethynyl-4-hydroxy-1-methyl-4-(1-methylethenyl)-cyclopentyl]butanenitrile (30): oil (50%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.99 (1 H, br s), 4.83–4.81 (1 H, m), 2.98–2.79 (1 H, m), 2.49–1.08 (10 H, m), 2.03 (1 H, d, J = 2.3 Hz), 1.77 (3 H, s), 0.90 (3 H, s); IR (neat) 3450, 3300, 2240, 2110, 1100, 910 cm^{-1}.

2-Hydroxy-1-(hydroxymethyl)-4,9-dimethyltricyclo-[4.3.0.0^{4,8}]nonane (31s): oil (7%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.24 (1 H, t, J = 7.9 Hz), 3.62 (2 H, AB, J = 28.7 Hz), 2.14–1.96 (2 H, m), 1.85–1.76 (1 H, m), 1.67–1.47 (2 H, m), 1.33–1.24 (2 H, m), 1.05 (3 H, d, J = 7.1 Hz), 0.89 (1 H, d, J = 5.0 Hz), 0.35 (1 H, d, J = 5.0 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 65.4, 57.2, 45.1, 41.3, 39.7, 33.7, 26.7, 24.1, 22.8, 21.9, 18.5, 15.7; IR (neat) 3350, 3040, 1380, 1020 cm^{-1}.

3-Hydroxy-2-(hydroxymethyl)-5,7-dimethylbicyclo-[4.3.0]non-1-ene (32s): oil as a mixture of 1:1 diastereoisomers (7%); ^{1}H-NMR (200 MHz, $CDCl_3$) δ 4.97–4.94 (1 H, m), 4.26 (2 H, AB, J = 15.3 Hz), 2.47–1.12 (9 H, m), 1.04 and 1.01 (3 H, s), 0.95 and 0.85 (3 H, d, J = 6.5 Hz); ^{13}C-NMR (50 MHz, $CDCl_3$) δ 149.0, 148.5, 132.5, 131.6, 78.3, 78.1, 58.1, 52.1, 50.8, 50.5, 48.3, 47.2, 45.8, 45.1, 40.8, 35.7, 31.8, 31.6, 28.4, 28.0, 24.8, 23.1, 20.9, 19.1; IR (neat) 3350, 1100, 1050 cm^{-1}.

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Supplementary Material Available: ^{1}H NMR spectra for **11k, 9, 9o, 1b, 1s, 18, 30,** and **32s** and ^{1}H and ^{13}C NMR spectra for **11h, 11m, 11q, 9q, 9h, 9l, 9r, 1f, 1g, 1j, 1l, 1o, 1r, 1t, *E*-3b, *Z*-3b, *E*-3g, 5l, 5n, 5t,** and **31s** (50 pages). Ordering information is given on any current masthead page.