Zeolite-Mediated Cyclization of an Epoxide-Containing Polyene[†]

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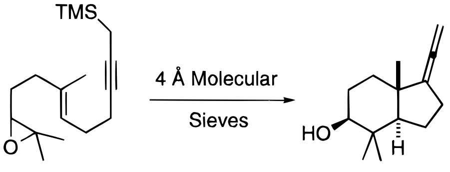
The utility of zeolites as promoters for the cyclization of an epoxide-containing polyene has been investigated. Reaction of polyene **1** with oven-dried 4 Å molecular sieves (type A zeolite) proceeds efficiently to generate bicyclic alcohol **2** in a 90% isolated yield. The reaction is sensitive to a variety of factors, including solvent type, water content, and zeolite acidity. Reactivity is apparently due to the zeolite lattice, since alumina and silica either are unreactive or generate a complex mixture of epoxide ring-opened products. Compared to the aluminum-based Lewis acid Me_2AlCl, the zeolite-promoted cyclization of **1** was a more facile reaction, providing excellent product recovery after filtration. These results indicate that zeolites represent a new class of promoters in biomimetic polyene cyclizations.

Introduction

Biomimetic polyene cyclization represents an important method for the preparation of polycycles with controlled stereochemistry. While substantial progress has been made with the introduction of acetal and allylic alcohol functionalities as initiating groups in these cyclization reactions,[1] few successful applications of the epoxide functionality, the normal initiator for many naturally-occurring cyclases, have been demonstrated.[2] Unfortunately, known methodology for the cyclization of epoxide-containing polyenes using aluminum- and titanium-based Lewis acids[3] can result in low yields and the production of both partially cyclized and rearranged byproducts. Because of the importance of epoxides in biological cyclizations[4] and their synthetic utility in generating lanostane-type A ring systems, the development of new promoters for the biomimetic cyclization of epoxide-containing polyenes continues to be an active area of research.

The utility of zeolites as selective adsorbents and as cracking catalysts in the petroleum industry has been known for many years.[5,6] However, zeolites have also been examined as catalysts for other synthetic transformations.[7] Examples of zeolite-promoted reactions include Friedel−Crafts alkylation and acylation,[8,9] aldol condensations,[10] photochemical and acid-catalyzed cyclizations,[11,12] and ring-opening reactions.[13] Modification of the zeolite either by the introduction of reactive metal centers or by reagent “doping” has expanded the range of reactions now available with this porous material.[14]

Scheme 1



1 **2**

Because of the known properties of zeolites as superacids and as cavity-selective catalysts, we became interested in determining the utility of these materials in generating polycycles by polyene cyclization methodology. Herein, we report our initial results involving the zeolite-induced bicyclization of polyene **1,** which possesses an epoxide initiator and a silicon (propargylic silane) terminator (Scheme 1). Cyclizations of this polyene using $(i\text{-PrO})TiCl_3$ and Me_2AlCl were also examined so that a comparison between traditional Lewis acid promoters and zeolite methodology could be made. Reaction of polyene **1** with oven-dried 4 Å molecular sieves in refluxing $CHCl_3$ for 40 min results in conversion of starting material to bicyclic product **2**. As described below, the reaction requires the proper balance between solvent type, water content, and zeolite acidity.

Results and Discussion

Polyene **1** was synthesized in seven steps (37% overall yield) from 3-chloropropionaldehyde diethyl acetal using the procedures developed by Johnson and co-workers for the construction of larger polyene skeletons (Scheme 2).[15] The final step of the reaction sequence, formation of the

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[†] This paper is dedicated to the memory of William S. Johnson.

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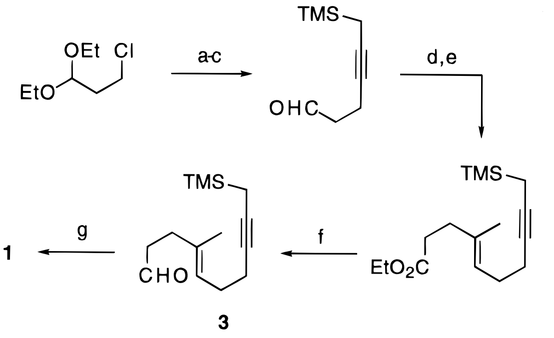
Scheme 2. Synthesis of Polyene 1[a]



[a] Conditions: (a) Li acetylide·EDA, DMSO (79%); (b) *n*-BuLi, then Me_3SiCH_2I (99%); (c) PPTS, acetone/H_2O (quantitative); (d) $CH_2{=}C(CH_3)MgBr$, THF (85%); (e) $CH_3C(OEt)_3$, propionic acid (74%); (f) DIBALH, THF, −94 °C (97%); (g) $(CH_3)_2CHSPh_2BF_4$, *t*-BuLi, THF, −78 °C (78%).

gem-dimethyl epoxide from aldehyde **3**, was troublesome due to the instability of diphenylsulfonium isopropylide. Reactions with the sulfur ylide required the rigorous exclusion of both air and moisture and, because of its thermal instability were typically conducted between −78 and −60 °C. Under these conditions, epoxide **1** was formed in 75−80% isolated yield. Diphenylsulfonium isopropylide was generated from diphenylisopropylsulfonium tetrafluoroborate, prepared by the method of Julia and co-workers, involving triflic acid-induced addition of phenyl sulfide to 2-propanol, followed by anion exchange with tetrafluoroboric acid.[16] Although the alternative condensation of phenyl sulfide with 2-iodopropane in the presence of silver tetrafluoroborate[17] provided higher reaction yields (45−55% compared to 10−25%), the resulting salt contained unidentified contaminants that led to difficulties in epoxide isolation.

To determine optimal conditions for the cyclization of polyene **1**, small-scale reactions (2−5 mg) were performed. Several potential factors responsible for zeolite reactivity were explored, and the results of these experiments are summarized below.

Solvent Effects. Results from the cyclization of **1** with 4 Å molecular sieves (type A zeolite, Na form) using several different solvents are presented in Table 1. The cyclization of polyene **1** occurred in a variety of nonpolar and halogenated solvents but was significantly inhibited when coordinating solvents were used. Although temperature had an important effect on reaction rate (toluene at rt *versus* reflux), the use of lower-boiling halogenated solvents increased both the rate and the selectivity of the reaction. Thus, cyclization of polyene **1** using toluene as solvent (at reflux) occurred within 5 h to provide **2** and a mixture of epoxide ring-opened and partially cyclized materials, while reaction of **1** in refluxing $CHCl_3$ required only 40 min for complete consumption of starting material to yield bicycle **2** as the sole reaction product. The inhibitory effects of both THF and CH_3CN suggest that these solvents compete with the reactant for coordinating sites on the zeolite,[18] thus impeding cyclization chemistry.

Water Content. A qualitative examination of differing amounts of water present within the zeolite was undertaken to determine its effect on the cyclization of epoxide-containing polyene **1**. A sample of 4 Å molecular sieves was separated into three portions and subjected to different activation methods (unactivated, dried at 110 °C overnight, and dried at 500 °C for 5 h). The results of these experiments (Table 2) indicate that small amounts of water are essential in order for efficient cyclization to proceed. In addition to slowing down the reaction rate, too much water resulted in an increase in byproduct formation. Compared to either oven-dried or untreated zeolites, those that were activated at 500 °C not only were significantly less effective promoters of the bicyclization of **1** but also yielded proportionately higher quantities of O-silylated bicycle **4** (Figure 1).

Table 1. Effect of Different Solvents on the Cyclization of Polyene 1[a]

	reaction conditions		recovered materials (%)[b]	
solvent	temp (°C)	time	bicycles **2** (**4**)	polyene **1**
toluene	25	2 days	0	92[c]
toluene	110	5 h	43 (6)	0[d]
benzene	80	5 h	65	0[e]
CH_3CN	82	4 h	6	79[f]
THF	66	4.5 h	0	100
hexane	68	4.5 h	60 (18)	0[g]
CCl_4	76	3.5 h	64 (5)	18[h]
CH_2Cl_2	40	3.5 h	100 (0)	0
$CHCl_3$[i]	61	40 min	100 (0)	0

[a] Reaction conditions: 2 mg of polyene **1** and 30 mg of oven-dried, crushed 4 Å molecular sieves in 5 mL of solvent, at reflux. [b] GC yield of isolated reaction mixture. [c] Byproduct composition: 5% **5** and 3% **6**. [d] Byproduct composition: 9% **7**, 16% **5**, 6% **6**, remainder (<4% each) unidentified. [e] Byproduct composition: 19% **6**, remainder (<5% each) unidentified. [f] Byproduct composition: 15% **5**. [g] Remaining material (<5% each) unidentified. [h] Byproduct composition: 7% **7**, 6% **5**. [i] Distilled from K_2CO_3 prior to use.

Table 2. Effect of Water Content on the Cyclization of Polyene 1[a]

	recovered materials (%)[b]			
zeolite type	bicycles **2 (4)**	ketone **5**	bicyclic ether **7**	polyene **1**
110 °C dried zeolite	70	0	0	30
unactivated zeolite	36 (10)	6	3	45
500 °C dried zeolite	23 (32)	9	4	5[c]

[a] Reaction conditions: 3.5 mg of polyene **1** and 70 mg of crushed 4 Å molecular sieves in 4 mL of $CHCl_3$ at reflux for 30 min. [b] GC yield of isolated reaction mixture. [c] Remaining material (<4% each) unidentified.

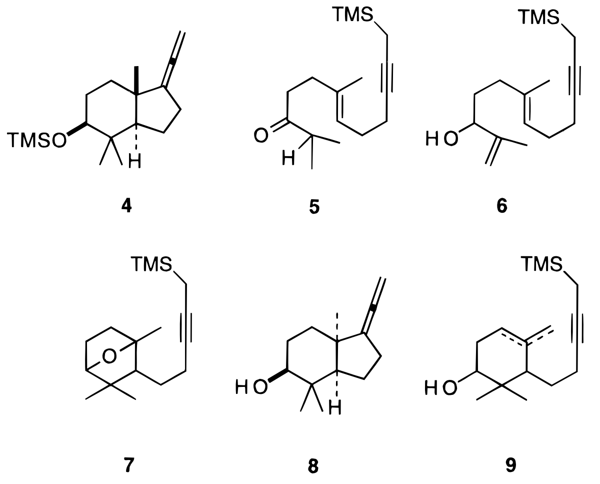


Figure 1. Byproducts identified in the reaction of **1** with 4 Å molecular sieves under nonoptimal cyclization conditions.

Zeolite Equivalents. The amount of accessible zeolite surface present was found to be related to the cyclization rate of polyene **1** (Table 3). Thus, the reaction

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Table 3. Effect of Zeolite Quantity on the Cyclization of Polyene 1[a]

zeolite equivalents (by weight)	solvent	reaction time[b]
10	toluene	8 h[c]
20	toluene	5 h
30	toluene	3.5 h
15	CHCl$_3$[d]	2.5 h
20	CHCl$_3$[d]	1.5 h
30	CHCl$_3$[d]	40 min

[a] Reaction conditions: 3 mg of polyene **1** in 4 mL of solvent at reflux. [b] Time required for complete consumption of starting material. [c] 2% starting material remaining. [d] Distilled from K$_2$CO$_3$ prior to use.

was faster when crushed *versus* pellet zeolite was used, and the rate increased with increasing zeolite content and stirring rate. These results are expected for heterogeneous reactions that require adsorption onto a solid surface. Although the reaction proceeds smoothly within 2.5 h when using 15 equiv (by weight) of crushed 4 Å molecular sieves, the reaction time can conveniently be modulated by the presence of more or less zeolite, resulting in no change in the yield of product formed.

Byproduct Characterization. The structures of the reaction byproducts were determined by combining several crude reaction mixtures from nonoptimized reactions and isolating the compounds by flash chromatography. The fractions thus obtained were then analyzed by ^{1}H NMR and cross-correlated with the corresponding GC retention times. Results indicated that the major byproducts were typically TMS ether **4**, epoxide ring-opened products **5** and **6**, and bridging bicyclic ether **7** (Figure 1). Although compounds **5** and **7**, which result from premature termination of the cyclization process, are commonly seen in the cyclization of related epoxide-containing polyenes using titanium- and aluminum-based Lewis acids,[3] alcohol **6** is not, suggesting that there are subtle differences in the acidity between zeolites and these conventional cyclization promoters. In addition, significant amounts of byproducts were formed in toluene and when improperly dried zeolites were used. Surprisingly, little if any *cis*-fused bicycle **8** and monocyclic alcohols **9** were formed under any of the zeolite-promoted reactions so far examined.

Effect of Different Catalysts and Acid Strength. The effectiveness of 4 Å molecular sieves in promoting the bicyclization of polyene **1** can be ascribed to the acidic property of zeolites. For every aluminum center that is present in an aluminosilicate zeolite, a cation (metal cation or proton) is required for charge neutralization. From both structural and theoretical studies, it is now established that zeolite activity is a result of increased acidity due to the Al−O−Si linkages.[19] Proposed catalytic mechanisms all involve the initial formation of a Lewis acid−Lewis base complex by coordination of the substrate to either a proton or a metal cation at the Al−O−Si cluster.

Experiments were performed to determine whether the observed reactivity is the result of characteristics unique to zeolites. First, to establish the prerequisite for the aluminosilicate structure, the cyclization of polyene **1** was attempted using either silica gel or neutral alumina. Second, to test the effect of zeolite acidity on cyclization efficiency, type A zeolite (Na form) was ion-exchanged with lithium, potassium, and cesium according to previously reported procedures[20] and then reacted with polyene **1**. The results from these studies are summarized in Table 4.

Table 4. Reactivity of Silica, Alumina, and Cation-Exchanged Zeolites

reaction conditions[a]		recovered material (%)[b]		
cyclization promoter	time (h)	bicycles **2 (4)**	polyene **1**	byproducts
none[c]	30		100	
SiO$_2$	1		100	
Al$_2$O$_3$	0.5		100	
LiA[d]	1	100		
NaA[d]	1	83 (2)		15[e]
KA[d]	1	39 (0)		61[f]
CsA[d]	0.5	12 (2)	71	15[g]

[a] Reaction conditions: (a) SiO$_2$ reactions, 2.5 mg of polyene **1** and 50 mg of SiO$_2$ in 4 mL of reluxing CHCl$_3$; (b) AlO$_2$ reactions, 3 mg of polyene **1** and 90 mg of AlO$_2$ in 4 mL of refluxing CHCl$_3$; (c) zeolite reactions, 3.5 mg of polyene **1** and 70 mg of cation-exchanged zeolite in 4 mL of refluxing CHCl$_3$. [b] GC yield of isolated reaction mixture. [c] Reaction performed in toluene. [d] Prepared by soaking Na-form zeolite A in 1 M solution of the appropriate chloride salt, followed by filtration, washing the solid with deionized water, and drying at 110 °C overnight. [e] The sole byproduct for this reaction was bicyclic ether **7**. [f] Byproduct composition: 24% **5**, 13% **6**, 10% **7**, remainder (<5% each) unidentified. [g] Byproduct composition: 5% **5**, 3% **6**, 2% **7**, remainder unidentified.

Reaction of polyene **1** with either silica or neutral alumina resulted in no reaction when conditions identical to the zeolite-promoted cyclization were used. However, the use of acidic alumina (data not shown) resulted in the formation of 28% bicyclic products, along with 18% byproducts (1 h reflux in toluene), suggesting that acidity may play an important role in the observed reactivity.[21] Since the relative acidity within the zeolite cavity is, in part, a function of the type of neutralizing cation, the acid strength of a particular zeolite can be modified by simple cation exchange. For zeolite type X, the relative acidity trend has been determined to be HX (proton-exchanged zeolite X) > LiX > NaX > KX > CsX.[22] Cyclization of **1** using ion-exchanged zeolite A showed a direct correlation with this acidity trend. Thus, lithium-exchanged zeolite A was the most effective promoter, while the activity of CsA was greatly diminished. For reactions involving K- and Cs-exchanged zeolite A, a much higher proportion of unwanted byproducts was formed, including a significant amount of ketone **5** (Figure 1).

To compare the efficiency of zeolite-mediated reactions with conventional biomimetic polyene cyclization promoters, reactions of **1** with (i-PrO)TiCl$_3$ and with Me$_2$AlCl were performed. Using the mixed titanium reagent, conversion of **1** into bicycle **2** proceeded smoothly,[23] while reaction of **1** with the aluminum-based Lewis acid resulted in recovery of starting material and of partially cyclized products (including compounds **7** and **9**) and ketone **5** (data not shown).[24]

Desilylation. NMR studies were performed to determine the mode of desilylation upon cyclization of polyene **1**. Reaction of epoxide **1** with 4 Å molecular sieves in

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(23) The Ti(i-OPr)Cl$_3$-promoted cyclization of **1** was performed using the procedure described in ref 3a. Reaction of **1** (9 mg, 0.03 mmol) with 10 equiv of Ti(i-OPr)Cl$_3$ in CH$_2$Cl$_2$ at −78 °C gave **2** (5 mg, 76%).

(24) The Me$_2$AlCl-promoted cyclization of **1** was performed using the procedure reported ref 3c.

$CDCl_3$, followed by NMR analysis of the filtrate, indicated a 2:1 ratio of bicycle **2** to hexamethyldisiloxane. This result, in addition to the nearly quantitative mass recovery of cyclic products, indicates that loss of the TMS group from the polyene is mediated by trace amounts of water retained in the zeolite lattice, as opposed to silylation of the zeolite surface. In situations where there is insufficient water available to mediate desilylation, the hydroxyl moiety of the bicycle participates in the termination step to provide bicycle **4**.

Conclusion

The studies described above indicate that molecular sieves hold promise as a new class of promoters in the cyclization of epoxide-containing polyenes. The zeolite-induced cyclization of epoxypolyene **1** proceeds cleanly, yielding bicycle **2** in excellent yield when halogenated solvents are used. Reactivity results from the zeolite structure and is enhanced with the use of acidic aluminosilicates. Compared to traditional Lewis acid cyclizations, the zeolite-mediated reaction is more convenient, requiring only filtration for product recovery. Work is currently under way to expand the scope of this reaction to higher-order polyene cyclizations and to larger-pore zeolites for use in stereoselective ring-forming reactions.

Experimental Section

General Methods. Unless otherwise stated, all chemicals and solvents were obtained from commercial sources and were used without further purification. Molecular sieves (4 Å, both powder and pellet forms) were purchased from Aldrich Chemical Co. THF was distilled from sodium benzophenone ketyl, $CHCl_3$ was distilled from K_2CO_3, and benzene and toluene were distilled from CaH_2. ^{1}H and ^{13}C NMR spectra were recorded on a GE QE-300 spectrometer at 300 and 75 MHz, respectively. Flash chromatography was performed using silica gel 60 (230−400 mesh, EM Science). Gas chromatography (GC) was performed on a Hewlett-Packard Model 5890 gas chromatograph equipped with a flame ionization detector, using a DB5-HT 30 m capillary column (J & W Scientific) and the following temperature gradient: 150 °C for 1 min, 10 °C/min to 325 °C for 5 min. Elemental analyses were performed by Desert Analytics Laboratory, Tucson, AZ.

Isopropyldiphenylsulfonium Tetrafluoroborate. To a solution of phenyl sulfide (10.3 g, 55 mmol) in 2-propanol (50 mL, 12 equiv) was added trifluoromethanesulfonic acid (30 mL, 6 equiv) dropwise at 0 °C. The reaction mixture was allowed to warm to rt over 0.5 h and then heated to 45 °C for 3 days. After cooling the dark brown reaction mixture, water and ether were added (50 mL each), and the resulting two layers were separated. The lower aqueous layer was extracted with ether (3 × 50 mL), and the combined organic extracts were washed (brine), dried ($MgSO_4$), and concentrated *in vacuo*. The resulting light brown oil was dissolved in ethanol (50 mL) and treated with fluoroboric acid (48% solution, 24 mL, 3.3 equiv). After the mixture was stirred for 1 h at rt, the reaction was quenched by the addition of water (20 mL) and CH_2Cl_2 (150 mL). The aqueous layer was extracted with CH_2Cl_2 (4 × 20 mL), and the combined organic layers were washed (brine), dried ($MgSO_4$), and concentrated *in vacuo* to give a light brown semisolid, which was triturated with petroleum ether (3 × 15 mL). The crude product was recrystallized from CH_3OH/ether (1:1) to provide the sulfonium salt as a fine white powder (2.2 g, 13%): mp 116.5−118.4 °C (lit.[16] mp 123 °C).

(6*E*)-2,3-Epoxy-2,6-dimethyl-12-(trimethylsilyl)-6-dodecen-10-yne (1). To a suspension of isopropyldiphenylsulfonium tetrafluoroborate (948 mg, 3 mmol) in THF (12 mL) was added dropwise at −78 °C *tert*-butyllithium (1.7 M solution in hexanes, 2.6 mmol). After the resulting yellow reaction mixture was stirred for 30−40 min, a solution of aldehyde **3**[15] (236 mg, 1 mmol) in THF (2 mL) was added. The light yellow reaction mixture was stirred between −78 and −60 °C for 1.5 h and then quenched by the addition of saturated aqueous NH_4Cl (2 mL). After warming to rt, the two layers were separated, and the aqueous layer was extracted with ether (3 × 5 mL). The combined organic layers were washed (brine), dried ($MgSO_4$), and concetrated *in vacuo* to give a light yellow oil. Flash chromatography using a hexane to 5% EtOAc/hexane gradient gave **1** as a colorless oil (206 mg, 74%): t_R = 9.40 min; IR (neat) 2952, 2917, 2217, 1652, 1248 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.22 (br s, 1 H), 2.69 (t, 1 H, J = 6 Hz), 2.15 (br m, 6 H), 1.61 (br m, 5 H), 1.39 (s, 2 H), 1.28 (s, 3 H), 1.24 (s, 3 H), 0.07 (s, 9 H); ^{13}C NMR δ 135.0, 123.9, 78.6, 76.6, 64.1, 58.2, 36.3, 28.1, 27.4, 24.8, 19.4, 18.7, 16.1, 6.9, −2.2. Anal. Calcd for $C_{17}H_{30}OSi$: C, 73.31; H, 10.86. Found: C, 73.03; H, 10.74.

Preparative-Scale Cyclization Procedure. To a suspension of oven-dried (110 °C, overnight), crushed 4 Å molecular sieves (3.3 g, 30-fold excess by weight compared to **1**) in $CHCl_3$ (100 mL) at rt was added a solution of **1** (111 mg, 0.4 mmole) in 5 mL of $CHCl_3$. The mixture was stirred under argon and heated to reflux for 2 h. The flask was then cooled to rt, the suspension was filtered through a fritted glass funnel, and the recovered zeolite was rinsed consecutively with ether and methanol (3 × 10 mL each). The combined filtrate was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography using 5% EtOAc/hexane as eluent to provide bicycles **2** and **4** (61 and 18 mg, respectively, 90% yield), along with ketone **5** (3.8 mg) and bicyclic ether **7** (5.5 mg). Bicycle **2**: t_R = 7.32 min; IR (neat) 3459, 2966, 1955, 1700, 1036, 852 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.68 (m, 2 H), 3.32 (dd, 1 H, J = 11 Hz, 5 Hz), 2.59 (m, 1 H), 2.41 (m, 1 H), 1.8−1.2 (br m, 7 H), 1.02 (s, 3 H), 0.99 (s, 3 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 200.0, 112.8, 79.8, 56.9, 44.2, 38.6, 34.8, 28.8, 28.5, 27.2, 21.1, 20.5, 15.2. Anal. Calcd for $C_{14}H_{22}O$: C, 81.49; H 10.75. Found: C, 81.20; H, 10.43.

Byproduct Characterization. Bicycle 4: t_R = 8.05 min; IR (neat) 2956, 1963, 1253, 1098, 1057, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.67 (m, 2 H), 3.27 (dd, 1 H, J = 11.1, 4.4 Hz), 2.58 (m, 1 H), 2.41 (m, 1 H), 1.78−1.22 (m, 7 H), 1.01 (s, 3 H), 0.88 (s, 3 H), 0.82 (s, 3 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 199.9, 113.1, 80.3, 56.9, 44.1, 38.9, 34.8, 29.1, 28.9, 27.2, 21.1, 20.5, 15.6, 0.4.

(6*E*)-2,6-Dimethyl-12-(trimethylsilyl)-6-dodecen-10-yn-3-one (5): t_R = 9.75 min; IR (neat) 2961, 1716, 1253, 862 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.18 (m, 1 H), 2.63 (septet, 1 H, J = 6.6 Hz), 2.54 (t, 2 H, J = 8.1 Hz), 2.23 (t, 2 H, J = 8.1 Hz), 2.15 (br s, 4 H), 1.61 (s, 3 H), 1.41 (s, 2 H), 1.08 (d, 6 H, J = 6.6 Hz), 0.08 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 214.5, 134.9, 123.6, 78.6, 77.5, 40.8, 39.0, 33.4, 28.0, 19.3, 18.2, 16.2, 6.9, −2.1.

(6*E*)-2,6-Dimethyl-12-(trimethylsilyl)-1,6-dodecandien-10-yn-3-ol (6): t_R = 10.04 min; IR (neat) 3378, 2960, 2224, 1656, 1250, 1056, 844 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.23 (br m, 1 H), 4.94 (s, 1 H), 4.84 (s, 1 H), 4.05 (dd, 1 H, J = 6.3, 6.3 Hz), 2.16 (br s, 4 H), 2.03 (m, 2 H), 1.73 (s, 2 H), 1.62 (s, 3 H), 1.57 (s, 3 H), 1.41 (s, 2 H), 0.08 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 147.5, 135.7, 123.7, 111.0, 78.6, 77.4, 75.6, 35.7, 33.1, 28.1, 19.4, 17.6, 16.1, 6.9, −2.1.

1,3,3-Trimethyl-2-[5-(trimethylsilyl)-3-pentynyl]-7-oxabicyclo[2.2.1]heptane (7): t_R = 8.94 min; IR (neat) 2963, 2132, 1247, 1006 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.72 (d, 1 H, J = 5.2 Hz), 2.24−2.05 (m, 3 H), 1.92 (m, 1 H), 1.80−1.47 (m, 5 H), 1.43 (br s, 2 H), 1.32 (s, 3 H), 1.06 (s, 3 H), 0.99 (s, 3 H), 0.09 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 86.6, 86.1, 77.8, 77.2, 54.1, 45.2, 38.9, 27.6, 26.0, 25.7, 23.4, 19.0, 18.8, 6.9, −2.1.

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