A Method for the Stereoselective Construction of 4-Alkoxy-5-alkylidenecyclopentenones by the Tandem Ring Expansion–Functionalization of 1-Alkynylcyclobutenols Using a Palladium–Mercury Cocatalytic System

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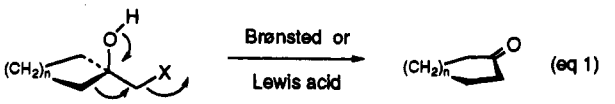
1-(1-Alkynyl)-4-methoxy-4-methyl-2-cyclobutenols, prepared by nucleophilic functionalization of cyclobutenediones, were transformed with high stereoselectivity into 4-methoxy-4-methyl-5-alkylidenecyclopentenones. The action of stoichiometric $Hg(OCOCF_3)_2$ and then metathesis with NaCl produced 5-(1-(chloromercurio)alkylidene)-4-methoxy-4-methyl-2-cyclopentenones which were stereospecifically functionalized by palladium-mediated allylation and hydroxybutenylation. Treatment with Br_2/DMSO led to stereospecific bromodemercuration. The 1-(1-alkynyl)-4-methoxy-4-methyl-2-cyclobutenols underwent efficient and very stereoselective tandem ring expansion–functionalizations in the presence of three different allylic chlorides and a catalyst system composed of 10% $Hg(OCOCF_3)_2$ and 10% $PdCl_2$. All products can be obtained with a stereoselectivity greater than 99:1 at the exocyclic alkene.

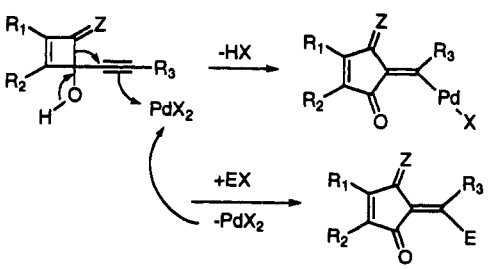
Introduction

Electrophile-induced ring expansion protocols provide the synthetic organic chemist with useful methods for the construction of larger rings from smaller ones.[1-21] Typically, these procedures are initiated by the action of a Brønsted or Lewis acid on a small-ring cycloalkanol bearing a suitable ionizable heteroatom substituent on an atom adjacent to the ring (eq 1). The Lewis acidity of various



(eq 1)

higher oxidation state transition-metal species implies that they should be competent reagents for electrophilically induced ring expansions. Two synthetically useful opportunities accrue from the use of Lewis acidic transition-metal reagents to induce a ring expansion. First, the tendency of transition-metal species to bind to unsaturated polarizable moieties such as alkenes or alkynes presents a broadened opportunity for ring expansions by using carbon–carbon unsaturation attached to the ring rather than adjacent heteroatom substituents. Second, the carbon–transition-metal bond that results from the ring expansion step should be amenable to further carbon–carbon bond-forming procedures using well-established procedures such as Heck-like reactions or cross-couplings. On the basis of these ideas, it was previously demonstrated that 4-alkynyl-4-hydroxy-2-cyclobutenones and 4-alkynyl-4-hydroxy-2-cyclobutenone acetals (and the corresponding benzo analogues) would participate in efficient and highly stereoselective tandem ring expansion–functionalization sequences in the presence of a palladium(II) catalyst and a suitable electrophile (H^+, NBS, allyl bromide) (eq 2).[12,14,15,22] In order to extend this process to the direct



(eq 2)

Z = O, OCH_2CH_2O

construction of 4-alkoxy-5-alkylidenecyclopentenones 1, a substructure present in a number of naturally occurring molecules with established cytotoxic activity, the palla-

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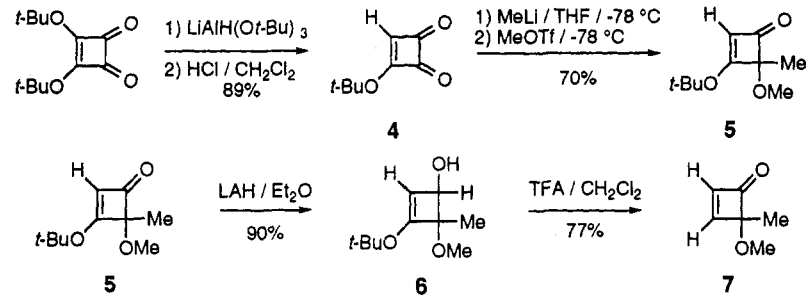
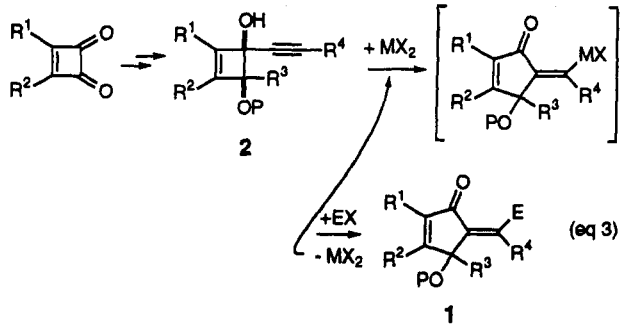
Scheme 1

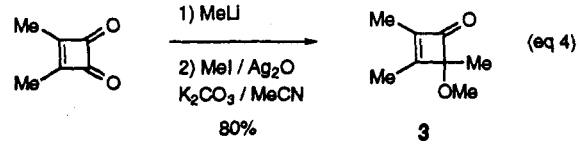


dium(II)-catalyzed ring expansion–functionalization of 4-alkoxy-4-subtituted-1-(1-alkynyl)-2-cyclobutenols **2** was studied (eq 3). The results of that investigation including the discovery of an effective palladium–mercury-cocatalyzed ring expansion–functionalization are described herein. Related metal-mediated ring expansion processes have been documented recently.[3,5,7,23]



Results and Discussion

The projected ring expansion–functionalization study depicted in eq 3 required a general method for construction of 4-alkoxy-4-substituted-1-(1-alkynyl)-2-cyclobutenols **2**. Synthetic approaches were developed to two representative 4-methoxy-4-methyl-2-cyclobutenones, **3** and **7**. The synthesis of 2,3-dimethyl-4-methoxy-4-methyl-2-cyclobutenone (**3**) from dimethylcyclobutenedione was straightforward (eq 4). On a small scale, 1,2-addition of



methyllithium followed by direct alkoxide quench with $CH_3OSO_2CF_3$ gave **3** in good yield. However, on larger scale, better reproducibility was achieved by prior isolation of the 4-hydroxy-4-methyl-2-cyclobutenone followed by O-methylation with $MeI/Ag_2O/K_2CO_3$ in CH_3CN.[24] Using the latter conditions, cyclobutenone **3** was readily prepared in 80% yield. The "parent" cyclobutenone system **7**, prepared by the sequence of reactions shown in Scheme 1, required an alternate synthetic entry because of the instability of the parent 3-cyclobutene-1,2-dione.[25–28] Following established protocol,[29] 3,4-di-*tert*-butoxy-3-cyclobutene-1,2-dione[30] was treated with $LiAlH(O\text{-}t\text{-}Bu)_3$ and the 1,2-adduct rearranged with acid to give 3-*tert*-butoxy-3-cyclobutene-1,2-dione (**4**) in excellent yield. Addition of MeLi to the more reactive carbonyl group and methylation of the alkoxide produced 3-*tert*-butoxy-4-methoxy-4-methyl-2-cyclobutenone (**5**). Lithium aluminum hydride reduction of **5** followed by quenching with NH_4Cl led to 3-*tert*-butoxy-4-methoxy-4-methyl-2-cyclobutenol (**6**) in excellent yield. This material when dissolved in CH_2Cl_2 and treated with trifluoroacetic acid (0.9 equiv) cleanly lost the elements of *tert*-butyl alcohol and produced the desired 4-methoxy-4-methyl-2-cyclobutenone (**7**) in 77% yield. The process was less efficient using catalytic trifluoroacetic acid, and a biphasic acid treatment (aqueous HCl/CH_2Cl_2) led to the formation of ring-opened products. The logical alternative of directly quenching the LAH reaction with trifluoroacetic acid (or trifluoroacetic anhydride) was rendered unsatisfactory by the presence of aluminum salts. Of some interest, the chemistry depicted in Scheme 1 could be carried out up to the formation of the analog of **6** by beginning with diisopropoxysquarate. However, attempted formation of **7** by elimination of 2-propanol with trifluoroacetic acid did not proceed cleanly. 4-Methoxy-4-methyl-2-cyclobutenone (**7**) is a colorless oil that can be stored at −4 °C for a few days under an inert atmosphere. Its reactivity parallels that of other 2,3-unsubstituted cyclobutenones,[31,32] and it is a potent lachrymator, necessitating proper care when being handled.

From ketones **3** and **7** a variety of 1-(1-alkynyl)-4-methoxy-4-methyl-2-cyclobutenols (**8**) were prepared in very good to excellent yields by addition of lithium acetylides (Table 1). The relative stereochemistry of the substituents of **8** bear comment. In all cases studied, only one diastereomer was formed. Though not rigorously confirmed, spectroscopic studies on **8d** and **8h** suggest assignment as the *cis* diastereomer. Infrared spectra in CCl_4 showed hydrogen-bound OH stretching frequencies (**8d** at 3543 cm^{-1} and **8h** at 3612 and 3510 cm^{-1}) that were unchanged on dilution, indicative of intramolecular H-bonding. Similarly, OH resonances appeared at 2.95 (**8d**) and 3.34 (**8h**) ppm in the ^1H NMR spectra and were not significantly affected by changes in concentration.

With a variety of 1-alkynyl-4-methoxy-4-methyl-2-cyclobutenols in hand, an investigation of the palladium-

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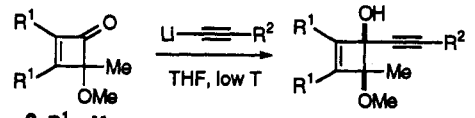
Table 1. Preparation of 1-Alkynyl-4-methoxy-4-methyl-2-cyclobutenols

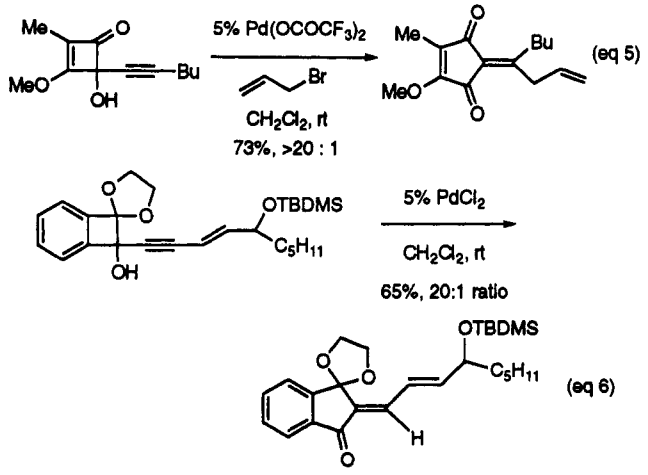


3, R^1 = Me
7, R^1 = H
8

entry	R^1	R^2	compd	yield, %
1	Me	$SiMe_3$	**8a**	72
2	Me	H	**8b**	80[a]
3	Me	*n*-Pr	**8c**	96
4	Me	*n*-Bu	**8d**	91
5	Me	$(CH_2)_4OSi$-*t*-$BuMe_2$	**8e**	92
6	Me	$(CH_2)_4OH$	**8f**	80[b]
7	Me	$(CH_2)_7CH_3$	**8g**	97
8	H	*n*-Bu	**8h**	87
9	H	H	**8i**	70[c]

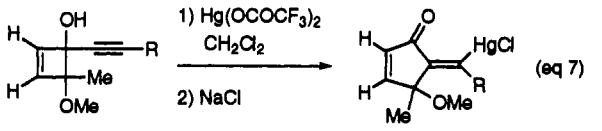
[a] Prepared from **8a** by treatment with $KF{\cdot}2H_2O$/MeOH. [b] Prepared from **8e** by treatment with Bu_4NF in THF. [c] Prepared by addition of $LiC{\equiv}CSiMe_3$ to **7** followed by desilylation with $KF{\cdot}2H_2O$/MeOH.

catalyzed ring expansion–functionalization was begun. In earlier studies of the palladium(II)-catalyzed ring expansion–functionalization of alkynylcyclobutenol derivatives, it was noted that the efficiency of the reaction varied with the substituents attached to the migrating carbon (4-carbon) of the cyclobutenol ring. In consonance with the ability of the migrating group to support positive charge, palladium-catalyzed ring expansion–functionalization occurred efficiently with a migrating carbonyl carbon (eq 5)[15] or ketal carbon (eq 6),[14] but not with a simple methylene group.[8]



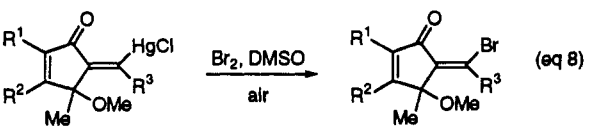
Given the diminished migratory aptitude of the CH_2 group, it was not surprising that treatment of the 4-methoxy-4-methylalkynylcyclobutenol **8d** and allyl bromide with catalytic or stoichiometric Pd(II) sources {$Pd(OCOCF_3)_2$, $PdCl_2$, $Pd(OCOCH_3)_2$} under a variety of conditions (room temperature to reflux in various solvents up to 5-day reaction times) led at best to only traces of the anticipated ring expansion–allylation product **9** (Scheme 2). On the presumption that a stronger Lewis acid was required to induce the desired ring expansion process, alkynylcyclobutenol **8d** was exposed to stoichiometric $Hg(OCOCF_3)_2$,[3] a Lewis acid more electrophilic than the PdX_2 sources used above. Gratifyingly, after ligand exchange with chloride, the 4-methoxy-5-alkylidenecyclopentenone mercurial **10a** was obtained in 78% yield. One predominant stereoisomer was seen by ^1H NMR (>15:1 ratio), and consistent with previously documented palladium-catalyzed ring expansions of alkynylcyclobutenols,[12,15] it was assigned the *Z*-configuration. The methylene group of $C{=}C(HgCl)CH_2C_3H_7$, which in the major isomer is *anti* to the ketone, appears upfield of that in the minor isomer. The initial difficulty in generating the ring expanded and functionalized product **9** by Pd(II) catalysis alone was circumvented by treatment of the isolated vinylmercurial **10a** with catalytic Li_2PdCl_4 and allyl bromide.[33] The two-step protocol of stoichiometric Hg(II)-induced ring expansion and Pd(II)-catalyzed functionalization provided the alkylidenecyclopentenone **9** in 69% isolated yield over two steps in high diastereoselectivity (Scheme 2).

The successful $Hg(OCOCF_3)_2$-induced ring expansion of **8d** depicted in Scheme 2 prompted a brief exploration of the same process using two substrates not bearing cyclobutene double-bond substituents (Table 1, **8h** and **8i**). In contrast to the facile room-temperature formation of **10a** shown in Scheme 2, the more sensitive substrates **8h** and **8i** required lower temperature reaction (−23 °C) with $Hg(OCOCF_3)_2$ in order to produce good yields of ring-expanded vinylmercurials (eq 7). Each formed with very high stereoselectivity (99:1) and was assigned the *Z*-configuration shown. Treatment of the alkynylcyclobutenols **8h** and **8i** with $Hg(OCOCF_3)_2$ at room temperature produced ring-opened materials.



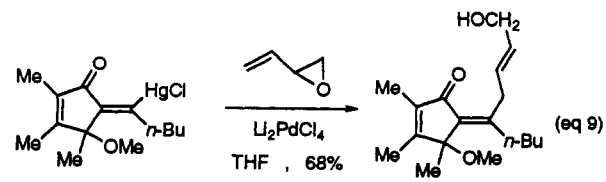
8h, R = *n*-Bu
8i, R = H
10b, R = *n*-Bu, 59%
10c, R = H, 61%

The three vinylmercurials, **10a–c**, were efficiently functionalized in different ways. Stereospecific brominolysis was achieved using Br_2 in DMSO[34,35] at room temperature open to the air and produced the synthetically useful vinyl bromides **11a–c** in excellent yields (eq 8). In addition to the already described efficient palladium-catalyzed allylation of vinylmercurial **10a**, a related stoichiometric palladium-mediated hydroxybutenylation with butadiene monoepoxide[36] was easily accomplished and gave stereospecifically the alkylidenecyclopentenone **12** in 68% yield (eq 9).



10a-c **11a-c**

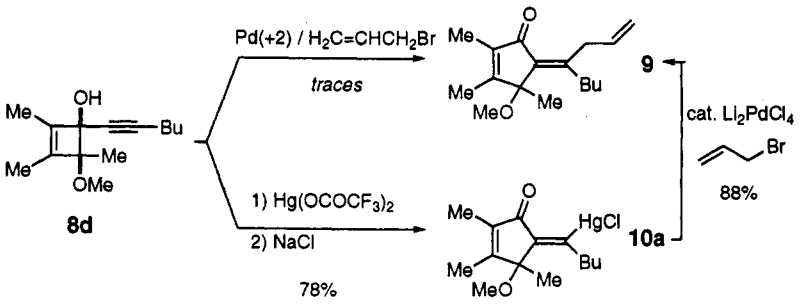
$R^1 = R^2 = Me$, $R^3 = n$-Bu: yield 90%
$R^1 = R^2 = H$, $R^3 = n$-Bu: yield 89%
$R^1 = R^2 = H$, $R^3 = H$: yield 89%



10a **12**

On consideration of the overall process of stoichiometric Hg(II)-induced ring expansion and palladium-catalyzed

Scheme 2



Scheme 3

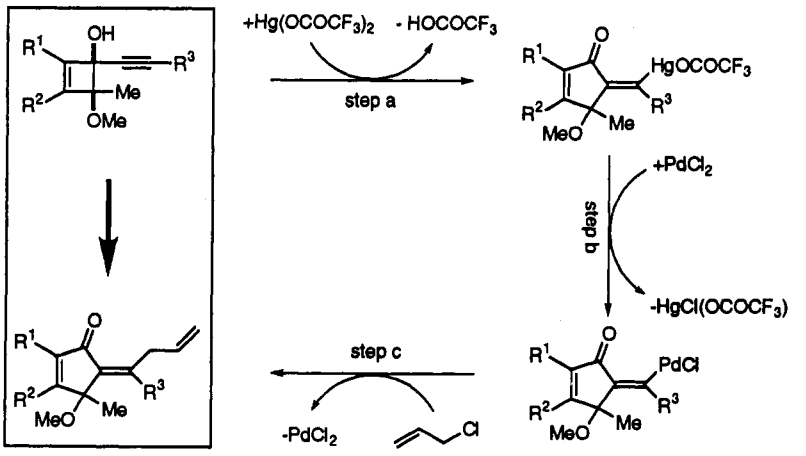
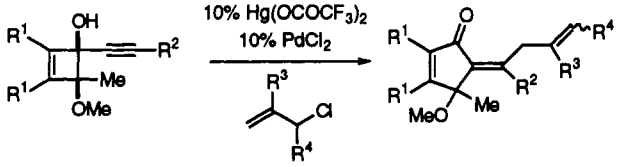


Table 2. Mercury/Palladium Cocatalyzed Ring Expansion–Functionalization



entry	R^1	R^2	R^3	R^4	solvent	product	yield, %
1	Me	*n*-Bu	H	H	THF	**9a**	81
2	Me	*n*-Pr	H	H	THF	**9b**	70
3	Me	H	H	H	THF, propylene oxide	**9c**	81
4	Me	$(CH_2)_3CH_2OH$	H	H	*N*-methylpyrrolidone	**9d**	77
5	Me	$(CH_2)_7CH_3$	H	H	THF, propylene oxide	**9e**	76
6	H	*n*-Bu	H	H	*N*-methylpyrrolidone, degassed	**9f**	77
7	Me	*n*-Pr	H	Me	THF, propylene oxide	**9g**	89
8	Me	*n*-Bu	H	Me	THF, propylene oxide	**9h**	92
9	H	*n*-Bu	Me	H	*N*-methylpyrrolidone	**9i**	70

vinylmercurial functionalization, it is apparent that both *palladium and mercury* can function in substoichiometric roles (Scheme 3). Ring expansion induced by a mercury(II) salt produces a vinylmercurial (Scheme 3, step a) that undergoes transmetalation with a palladium(II) salt, producing a vinylpalladium intermediate and *regenerating a mercury(II) species that could remain a competent ring expansion reagent* (Scheme 3, step b). Reaction of the alkenylpalladium intermediate with an allylic halide produces the observed product alkylidenecyclopentenone and *regenerates a palladium(II) salt, thus rendering the process catalytic in palladium* (Scheme 3, step c).

In agreement with the arguments put forth, alkynylcyclobutenols **8b–d,f–h** underwent efficient and highly stereoselective tandem ring expansion–functionalizations in the presence of three different allylic chlorides and a catalyst system composed of 10% $Hg(OCOCF_3)_2$ and 10% $PdCl_2$ (Table 2). All products were obtained with a stereoselectivity greater than 99:1 at the exocyclic alkene. A number of observations are of interest. Allylic chlorides, not bromides, were required for facile catalysis, apparent to secure the *in situ* formation of the effective electrophile $HgCl_2$. The alkynylcyclobutenol **8e** bearing an O-silylated hydroxybutane side chain did not participate in efficient Hg/Pd-cocatalyzed ring expansion–functionalization. In contrast, and for reasons that are not understood, the analogous free alcohol **8f** efficiently gave the alkylidenecyclopentenone **9d**. In four cases (Table 2, entries 3, 5, 7, and 8), geometric isomerization of the exocyclic double bond of the alkylidenecyclopentene was problematic, but could be overcome. For example, ^1H NMR monitoring of the reaction of **8b** with allyl chloride in the

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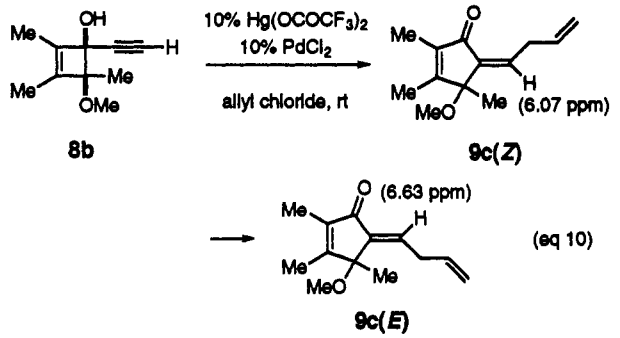
presence of 10% $Hg(OCOCF_3)_2$ and 10% $PdCl_2$ in THF at room temperature demonstrated the initial formation of the *Z*-alkylidene isomer (eq 10, =CH—R at 6.07 ppm). This quickly isomerized to the more stable *E*-alkylidene isomer (=CH—R at 6.63 ppm). On the presumption that alkylidene isomerization is facilitated by the trifluoroacetic acid generated in the first step of the catalytic cycle (Scheme 3, step a), propylene oxide was added as an acid scavenger. This tactic effectively prevented scrambling of the double-bond stereochemistry and led to the isolated yields of the (*Z*)-alkylidenecyclopentenones depicted in Table 2. Finally, the sequential ring expansion–functionalization protocol was successfully extended to two additional allylic halides. 3-Chloro-1-butene proved a facile coupling partner, producing alkylidenecyclopentenones **9g** and **9h** as mixtures of stereoisomers at the trisubstituted double bond. 2-Methyl-3-chloro-1-propene also participated in the tandem ring expansion–functionalization process, although at a slower rate than 3-chloro-1-propene or 3-chloro-1-butene. In this case THF and CH_2Cl_2 were ineffective as solvents, and a solvent change to *N*-methylpyrrolidone was required to support effective catalysis.



(eq 10)

Conclusions

The action of a Lewis acidic metal efficiently transforms 1-alkynyl-4-methoxy-4-methyl-2-cyclobutenols into 4-methoxy-2-methyl-5-alkylidene-2-cyclopentenones with high stereoselectivity at the exocyclic double bond. The use of stoichiometric $Hg(OCOCF_3)_2$ followed by NaCl metathesis produces 5(*E*)-(1-(chloromercurio)alkylidene)-4-methoxy-4-methyl-2-cyclopentenones in high yield. The mercury was efficiently replaced by bromine with retention of stereochemistry or with allylic and hydroxybutenyl groups through palladium-mediated processes. An effective and highly stereoselective synthesis of functionalized 4-methoxy-4-methyl-5-alkylidene-2-cyclopentenones was developed through the action of cocatalytic $PdCl_2$ and $Hg(OCOCF_3)_2$ on 1-alkynyl-4-methoxy-4-methyl-2-cyclobutenols in the presence of various allylic halides.

Experimental Section

Materials and Methods. All solvents were dried before use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium and benzophenone. Acetonitrile, dichloromethane, and trimethylsilyl chloride were distilled from calcium hydride. Anhydrous *N*-methylpyrrolidone was purchased from Aldrich in Sure/Seal botles. The purification of other solvents and reagents is noted in the individual experimental procedures. All infrared spectra were obtained using a dilute solution of the sample in dry CH_2Cl_2 or CCl_4 in KCl cells unless otherwise noted. All ^1H NMR spectra were obtained at 300 MHz on a General Electric QE-300 spectrometer or at 360 MHz on a Nicolet NMR-360. In addition, all ^{13}C NMR spectra were obtained at 75.5 MHz on a General Electric QE-300 spectrometer. All ^1H NMR absorptions are expressed in parts per million (δ) relative to tetramethylsilane (TMS) or chloroform (7.26 ppm) as internal standards; all ^{13}C NMR absorptions are relative to $CDCl_3$ (77.0) as the internal standard unless stated otherwise. Routine column chromatography was performed with flash grade silica gel 60 (EM Science) with compressed air or dry nitrogen as the source of positive pressure. Analytical thin layer chromatography was performed on precoated silica gel plates (60 F_{254}) obtained from EM Reagents. Compounds were visualized by the use of UV light (254 nm) and/or a variety of stains: vanillin (5% w/v vanillin in 5% v/v sulfuric acid in 50% aqueous ethanol), phosphomolybdic acid (10% w/v in ethanol), anisaldehyde (5% w/v *p*-anisaldehyde in 5% v/v of sulfuric acid in 50% ethanol), and halo stain (0.5 g of $ZnCl_2$, 0.5 g of diphenylamine in 100 mL of acetone).

Starting Materials. 3,4-Dimethyl-3-cyclobutene-1,2-dione[29] and 3,4-di-*tert*-butoxy-3-cyclobutene-1,2-dione[30] were prepared according to literature procedures.

Synthesis of 4-Methoxy-4-methyl-2-cyclobutenones. 4-Methoxy-2,3,4-trimethyl-2-cyclobutenone (3). On a small scale, 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one was prepared as follows: A solution of 3,4-dimethyl-3-cyclobutene-1,2-dione (0.20 g, 1.82 mmol) in 10 mL of THF under an argon atmosphere was cooled to −78 °C and MeLi (1.4 M in Et_2O, 1.30 mL, 1 equiv) was added dropwise. The reaction was kept at −78 °C and monitored by TLC (SiO_2, 2:1 hexanes:EtOAc) for the disappearance of the starting material. After 30 min, the reaction was quenched at −78 °C with methyl trifluoromethanesulfonate (0.20 mL, 1 equiv). After 15 min of stirring, 5 mL of water was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was extracted with Et_2O and the combined organic layers were dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude residue consisting of a mixture of a major product (UV, R_f = 0.44) and a byproduct (UV, R_f = 0.5) was purified via flash chromatography (30 g of SiO_2, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2). Removal of solvent provided 0.22 g (1.54 mmol, 85%) of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one as a yellow oil: IR (CH_2Cl_2) 3060, 2935, 2833, 1760, 1640, 1441, 1382, 1310, 1187, 1144, 1065, 969 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.07 (s, 3 H), 1.97 (s, 3 H), 1.57 (s, 3 H), 1.22 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 196.3, 179.6, 147.3, 95.6, 52.0, 17.4, 10.3, 6.6; MS (HR EI) *m/e* (relative intensity) 140 (M^+, 9), 126 (34), 125 (100), 111 (19), 99 (10), 97 (13), 95 (13), 91 (19), 83 (17), 81 (25), 79 (15), 77 (17), 73 (15), 71 (21), 70 (17), 69 (35), 67 (20), 60 (24), 57 (43); calcd for $C_8H_{12}O_2$ 140.0837234, found 140.0837298 (error (4.6 × 10^{-6})%). Anal. Calcd for $C_8H_{12}O_2$: C, 68.55; H, 8.63. Found: C, 68.26; H, 8.54.

When the former procedure was repeated on a larger scale, the percentage of the byproduct (R_f = 0.5 in 2:1 hexanes:EtOAc) increased. To circumvent this drawback, isolation of 4-hydroxy-2,3,4-trimethyl-2-cyclobuten-1-one followed by methylation to 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one was found to be more convenient. The 4-hydroxy-2,3,4-trimethyl-2-cyclobuten-1-one was prepared as follows: A solution of 3,4-dimethyl-3-cyclobutene-1,2-dione (2.81 g, 0.025 mol) in 40 mL of THF under an argon atmosphere was cooled to −78 °C and MeLi (1.4 M in Et_2O, 18.3 mL, 1 equiv) was added dropwise. The reaction mixture was kept at −78 °C and monitored by TLC for disappearance of starting material (SiO_2, 2:1 hexanes:EtOAc). After 30 min, the reaction was quenched at −78 °C with 20 mL of a 19% aqueous solution of HCl. The mixture was diluted with 40 mL of Et_2O and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 15 mL) and the combined organic layers were dried over Na_2SO_4 and filtered. The solvents were removed and the residue was passed through a small plug of SiO_2 with CH_2Cl_2. The solvent was evaporated to give 2.46 g (0.019 mol, 78%) of 4-hydroxy-2,3,4-trimethyl-2-cyclobuten-1-one as a yellow oil: ^1H NMR ($CDCl_3$, 300 MHz) δ 3.96 (br s, 1 H), 2.04 (s, 3 H), 1.58 (s, 3 H), 1.33 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 197.7, 180.9, 146.1, 90.2, 18.5, 9.8, 7.0. The compound can be stored in the refrigerator under nitrogen only for a short period of time. The transformation into the 4-methoxy derivative can be achieved in a quantitative yield either by reaction of 4-hydroxy-2,3,4-trimethyl-2-cyclobuten-1-one with a mixture of 5 equiv of K_2CO_3, 2 equiv of Ag_2O, and 4 equiv of CH_3I in acetonitrile at

room temperature for 30 h[24] or by reaction of 4-hydroxy-2,3,4-trimethyl-2-cyclobuten-1-one with a mixture of 1.3 equiv of Ag_2O and 5 equiv of $CaSO_4$ in excess of CH_3I for 3 days at room temperature.[37]

4-Methoxy-4-methyl-2-cyclobutenone (7). 2,3-Di-*tert*-butoxy-4-hydroxy-2-cyclobuten-1-one. A solution of 3,4-di-*tert*-butoxy-3-cyclobutene-1,2-dione (8.0 g, 35.3 mmol) in 300 mL of THF under an argon atmosphere was cooled to −23 °C, and lithium tri-*tert*-butoxyaluminum hydride (1.0 M in THF, 42 mL, 1.2 equiv) was added dropwise. The reaction was kept at −23 °C for 30 min and stirring was maintained for 12 h at room temperature. TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed formation of a new compound (UV, R_f = 0.28). The reaction mixture was quenched with 40 mL of a 20% aqueous solution of potassium sodium tartrate. The aqueous layer was extracted with Et_2O (three 100-mL portions) and the combined organic layers were dried over $MgSO_4$ and filtered. Concentration of the organic layers, filtration through a short silca gel plug, and recrystallization from Et_2O/hexanes left 7.89 g (34.6 mmol, 98%) of 2,3-di-*tert*-butoxy-4-hydroxy-2-cyclobuten-1-one as a white solid that can be stored under argon: mp 102 °C; IR (CCl_4) 3355, 2983, 2936, 1760, 1679, 1602, 1476, 1397, 1154 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.79 (d, J = 4.8 Hz, 1 H), 4.43 (s, 1 H), 1.49 (s, 9 H), 1.39 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 185.3, 166.6, 130.8, 84.2, 80.2, 77.0, 28.7 (3 C), 28.5 (3 C). Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.04; H, 8.82.

3-*tert*-Butoxy-3-cyclobutene-1,2-dione (4). 2,3-Di-*tert*-butoxy-4-hydroxy-2-cyclobuten-1-one (7.89 g, 34.6 mmol) was dissolved in 280 mL of CH_2Cl_2 under an argon atmosphere at room temperature and 25 drops of concentrated HCl were added. After 12 h of stirring at room temperature, the reaction mixture was quenched with 150 mL of a saturated aqueous solution of sodium bicarbonate. TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed the presence of a single compound having the same R_f as the starting material. After separation of the layers, the organic layer was washed with brine, dried over $MgSO_4$, and filtered. After evaporation of the solvent, flash chromatography of the crude residue (SiO_2, 2:1 hexanes:EtOAc) and recrystallization from Et_2O/hexanes gave 4.85 g (31.5 mmol, 91%) of 3-*tert*-butoxy-3-cyclobutene-1,2-dione as a crystalline white solid which can be stored under argon: mp 55 °C; IR (CCl_4) 2983, 2933, 1791, 1774, 1707, 1665, 1561, 1396, 1375, 1289 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.49 (s, 1 H), 1.56 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 199.3, 196.0, 193.8, 164.9, 88.7, 27.8 (3 C); MS (high resolution EI) m/e (relative intensity) 154 (M^+, 1), 125 (3), 112 (6), 71 (31), 57 (100), 56 (20), 53 (20); calcd for $C_8H_{10}O_3$ 154.0629883, found 154.0629943 (error (3.89 × 10^{-6})%). Anal. Calcd for $C_8H_{10}O_3$: C, 62.33; H, 6.54. Found: C, 62.40; H, 6.52.

3-*tert*-Butoxy-4-methoxy-4-methyl-2-cyclobuten-1-one (5). A solution of 3-*tert*-butoxy-3-cyclobutene-1,2-dione (2.0 g, 12.99 mmol) in 50 mL of THF under an argon atmosphere was cooled to −78 °C and MeLi (1.4 M in Et_2O, 10.20 mL, 1.1 equiv) was added dropwise. The reaction was kept at −78 °C and monitored by TLC (SiO_2, 2:1 hexanes:EtOAc) for the disappearance of starting material. After 20 min the reaction mixture was quenched at −78 °C with methyl trifluoromethanesulfonate (1.62 mL, 1.1 equiv). Stirring was maintained for 30 min at −78 °C; then at −23 °C 10 mL of water was added and the reaction mixture was allowed to warm to room temperature. It was extracted with three 17-mL portions of Et_2O and the combined organic layers were dried over Na_2SO_4 and filtered. After evaporation of the solvent, the crude residue consisting of a major product (UV, R_f = 0.36) and a byproduct (UV, R_f = 0.76) was flash chromatographed (SiO_2, 2:1 hexanes:EtOAc). Removal of the solvent and recrystallization from Et_2O/hexanes gave 1.69 g (9.09 mmol, 70%) of 3-*tert*-butoxy-4-methoxy-4-methyl-2-cyclobuten-1-one as white flakes which can be stored under argon: mp 104 °C; IR (CCl_4) 2989, 2931, 2831, 1766, 1679, 1573, 1459, 1397, 1374, 1328 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.15 (s, 1 H), 3.31 (s, OMe, 3 H), 1.52 (s, 9 H), 1.41 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 192.9, 185.5, 111.7, 94.9, 85.5, 52.5, 27.3 (3 C), 17.4. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.05; H, 8.73.

3-*tert*-Butoxy-3-methoxy-4-methyl-2-cyclobuten-1-ol (6). A solution of 3-*tert*-butoxy-4-methoxy-4-methyl-2-cyclobuten-1-one (1.0 g, 5.38 mmol) in 30 mL of Et_2O under an argon atmosphere was treated with lithium aluminum hydride (1.0 M in Et_2O, 2.0 mL, 1.5 equiv). TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed the formation of a new compound (R_f = 0.38, phosphomolybdic acid stain). After 30 min the reaction mixture was quenched with 7 mL of a 10% aqueous solution of ammonium chloride. After separation of the layers, the aqueous layer was extracted with two 10-mL portions of Et_2O. The combined organic layers were washed with 20 mL of brine, dried over Na_2SO_4, and filtered. After evaporation of the solvent, the yellow residue was purified by flash chromatography (SiO_2, 2:1 hexanes:EtOAc). Evaporation of the solvent and recrystallization from Et_2O/hexanes at low temperature gave 0.90 g (4.84 mmol, 90%) of 3-*tert*-butoxy-4-methoxy-4-methyl-2-cyclobuten-1-ol as a white solid which can be stored under argon: mp 35–6 °C; IR (CCl_4) 3444, 2985, 1773, 1679, 1432, 1372, 1208, 1136 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.76 (s, 1 H), 4.12 (d, J = 9.2 Hz, 1 H), 3.40 (s, 3 H), 2.33 (d, J = 9.2 Hz, 1 H), 1.35 (s, 9 H), 1.34 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 157.1, 105.1, 84.3, 79.4, 73.2, 53.1, 27.5 (3 C), 16.9; MS (high resolution EI) m/e (relative intensity) 130 (M^+ − C_4H_8, 100), 116 (76), 97 (84), 71 (15), 69 (15), 59 (19), 58 (65). Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.21; H, 9.71.

4-Methoxy-4-methyl-2-cyclobutenone (7). 3-*tert*-Butoxy-4-methoxy-4-methyl-2-cyclobuten-1-ol (0.62 g, 3.32 mmol) was dissolved in 20 mL of methylene chloride under an argon atmosphere and trifluoroacetic acid (0.18 mL, 0.9 equiv) was added dropwise. The reaction mixture turned orange. TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed the formation of a new compound (UV, R_f = 0.50). The reaction mixture was passed through a plug of anhydrous sodium carbonate. Evaporation of the solvent left an orange residue that was purified by flash chromatography (SiO_2, 40:60 hexanes:Et_2O) to give 0.28 g (2.55 mmol, 77%) of 4-methoxy-4-methyl-2-cyclobutenone as a colorless oil. 4-Methoxy-4-methyl-2-cyclobutenone is a potent lacrymator. It can be stored under a dry argon atmosphere at −4 °C for a few days: IR (CCl_4) 2985, 2933, 2833, 1777, 1297, 1158, 1069 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.55 (d, J = 2.9 Hz, 1 H), 6.45 (d, J = 2.9 Hz, 1 H), 3.27 (s, 3 H), 1.47 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 196.6, 174.2, 143.3, 98.8, 53.2, 19.6; MS (high resolution EI) m/e (relative intensity) 112 (M^+, 77), 97 (M^+ − CH_3, 100), 83 (39), 69 (34), 61 (50); calcd for $C_6H_8O_2$ 112.052425, found 112.0524296 (error (4.10 × 10^{-6})%).

Synthesis of 4-Methoxy-4-methyl-1-alkynyl-2-cyclobutenols. 4-Methoxy-2,3,4-trimethyl-1-((trimethylsilyl)ethynyl)-2-cyclobuten-1-ol (8a). A solution of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one (0.80 g, 5.71 mmol) in 4 mL of THF under an argon atmosphere was cooled to −23 °C and added via cannula to approximately 2.0 equiv of lithium (trimethylsilyl)-acetylide, formed by treating (trimethylsilyl)acetylene (1.60 mL) in 7 mL of THF at −23 °C with *n*-butyllithium (2.5 M in hexanes, 4.6 mL) and stirring for 30 min at −23 °C. After 60 min, analysis by TLC showed consumption of starting material and the formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.63, UV). The reaction mixture was quenched at −23 °C with 20 mL of saturated aqueous NaCl and after 10 min allowed to warm to room temperature. The mixture was extracted with Et_2O (4 × 15 mL), dried over Na_2SO_4, filtered, concentrated, and chromatographed (50 g of flash silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column). Removal of solvent at reduced pressure gave 0.98 g (4.11 mmol, 72%) of 4-methoxy-2,3,4-trimethyl-1-((trimethylsilyl)ethynyl)-2-cyclobuten-1-ol that was recrystallized from Et_2O to give a white solid: mp 84 °C; IR (CCl_4, c = 0.14 M) 3579, 2966, 2916, 2833, 2165, 1441, 1376, 1250, 1200, 1144, 1094, 1075, 1050, 1027, 1005 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.32 (s, 3 H), 2.96 (s, 1 H), 1.59 (s, 3 H), 1.56 (s, 3 H), 1.37 (s, 3 H), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 145.1, 144.6, 103.0, 91.7, 84.3, 76.4, 52.8, 15.8, 9.5, 8.1, −0.5 (3 carbons); MS (HR EI) m/e (relative intensity) 238 (M^+, 1), 206 (25), 192 (77), 191 (82), 177 (50), 149 (22), 113 (47), 108 (39), 107 (19), 105 (14), 97 (26), 91 (19), 89 (14), 83 (17), 81 (20), 79 (12), 75 (41), 73 (100), 59 (17), 55 (12); calcd for $C_{13}H_{22}O_2Si$ 238.1388984, found 238.1388245 (error (3.10 × 10^{-5})%). Anal. Calcd for $C_{13}H_{22}O_2Si$: C, 65.50; H, 9.30. Found: C, 65.43; H, 9.27.

1-Ethynyl-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (8b). In a 50-mL round-bottomed flask, 1-((trimethylsilyl)-

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ethynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (0.13 g, 0.54 mmol) was dissolved in 7 mL of MeOH at room temperature under an argon atmosphere. Potassium fluoride dihydrate (0.06 g, 1.2 equiv) was added and the reaction mixture turned orange. After 24 h of stirring analysis by TLC (SiO_2, 2:1 hexanes:EtOAc) showed consumption of the starting material and formation of a new compound (R_f = 0.47, UV). The reaction mixture was diluted with water (20 mL) and extracted with three 15-mL portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified via flash chromatography (20 g of silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column) and recrystallized from Et_2O to give 0.08 g (0.50 mmol, 93%) of 1-ethynyl-4-methoxy-2,3,4-trimethyl-2-cyclobutenol as a off-white solid: mp 89.5 °C; IR (CCl_4, c = 0.11 mol/L) 3541, 3313, 2968, 2916, 2833, 2118, 1443, 1376, 1347, 1308, 1258, 1200, 1142, 1092, 1071, 999 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.36 (s, 3 H), 2.95 (s, 1 H), 2.55 (s, 1 H), 1.63 (s, 3 H), 1.60 (s, 3 H), 1.43 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 145.4, 144.1, 84.1, 81.4, 75.9, 74.9, 52.7, 15.8, 9.3, 7.9. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.37; H, 8.53.

4-Methoxy-1-(1-pentynyl)-2,3,4-trimethyl-2-cyclobuten-1-ol (8c). Following the protocol for **8a**, a solution of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one (0.50 g, 3.57 mmol) in 4 mL of THF was treated with approximately 2.0 equiv of 1-pentynyllithium, formed by treating 1-pentyne (0.70 mL) in 5 mL of THF at −4 °C with *n*-butyllithium (2.8 mL, 2.5 M in hexanes). TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed formation of a new compound (UV, R_f = 0.41). Flash chromatography (40 g of silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column) and removal of the solvent at reduced pressure gave 0.71 g (3.41 mmol, 96%) of 4-methoxy-1-(1-pentyny)-2,3,4-trimethyl-2-cyclobutenol as a yellow oil: IR (CCl_4) 3539, 2968, 2939, 2875, 2833, 2240, 1443, 1376, 1308, 1277, 1258, 1200, 1177, 1148, 1121, 1052, 1009, 947, 909 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.35 (s, 3 H), 2.87 (s, 1 H), 2.20 (t, J = 7.0 Hz, 2 H), 1.62 (s, 3 H), 1.58 (s, 3 H), 1.51 (app hext, J = 7.2 Hz, 2 H), 1.40 (s, 3 H), 0.95 (t, J = 7.4 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.7, 144.2, 87.4, 84.5, 77.5, 76.2, 52.5, 22.0, 20.7, 15.8, 13.2, 9.1, 7.8. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.70; H, 9.56.

1-(1-Hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (8d). A solution of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one (0.79 g, 5.70 mmol) in 4 mL of THF under an argon atmosphere was cooled to −4 °C and added via cannula to approximately 2.0 equiv of 1-hexynyllithium, formed by treating 1-hexyne (1.31 mL) in 10 mL of THF at −4 °C with *n*-butyllithium (4.6 mL, 2.5 M in hexanes) and stirring 30 min at −4 °C. After 30 min, TLC monitoring indicated consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.47, UV). The reaction mixture was quenched at −4 °C with 10 mL of a 10% aqueous solution of NH_4Cl, allowed to warm to room temperature, extracted with Et_2O (3 × 10 mL), dried over Na_2SO_4, and filtered. The crude product was purified by flash chromatography (40 g of silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column) to give 1.15 g (5.18 mmol, 91%) of 1-(1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol as a yellow oil: IR (neat) 3425, 2962, 2937, 2875, 2236, 1764, 1698, 1638, 1443, 1376, 1202, 1181, 1121, 1084, 1050 cm^{-1}; IR (CH_2Cl_2, c = 0.3 mol/L) 3531, 2964, 2875, 2834, 2254, 1769, 1443, 1378, 1308, 1270, 1262, 1146, 1119, 1038, 911 cm^{-1}; IR (CCl_4, c = 0.05 mol/L) 3543, 2962, 2939, 2875, 2832, 2238, 1771, 1443, 1376, 1200, 1148, 1121, 1084, 1050 cm^{-1}; IR (CCl_4, c = 0.01 mol/L) 3540, 2961, 2937, 2862, 2357, 1766, 1439 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.26 (s, 3 H), 2.95 (s, 1 H), 2.14 (t, J = 6.8 Hz, 2 H), 1.52 (s, 3 H), 1.49 (s, 3 H), 1.41–1.25 (m, 4 H), 1.31 (s, 3 H), 0.79 (t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.6, 144.1, 87.4, 84.5, 77.3, 76.2, 52.4, 30.6, 21.6, 18.3, 15.8, 13.3, 9.1, 7.7. Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.74; H, 9.92.

1-(6-(*tert*-Butyldimethylsiloxy)-1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (8e). Following the protocol for **8a**, a solution of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one (0.37 g, 2.60 mmol) in 2 mL of THF was treated at −78 °C with approximately 1.5 equiv of (6-(*tert*-butyldimethylsiloxy)-1-hexynyl)lithium, formed by treating 6-(*tert*-butyldimethylsiloxy)-1-hexyne (0.84 g) in 5 mL of THF at −4 °C with *n*-butyllithium (2.5 M in hexanes, 1.56 mL). TLC monitoring indicated consumption of starting material and formation of a new compound (SiO_2, 2.1 hexanes:EtOAc, R_f = 0.61, UV). The reaction mixture was quenched with 10 mL of a saturated aqueous solution of NaCl. Workup and then flash chromatography (40 g of silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column) gave 0.85 g (2.40 mmol, 92%) of 1-(6-*tert*-butyldimethylsiloxy)-1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol as a white semisolid: IR (CCl_4) 3538, 3424, 2931, 2860, 2833, 2740, 2242, 1764, 1632, 1472, 1463, 1443, 1387, 1376, 1362, 1291, 1256, 1200, 1148, 1106, 1050, 1007, 909 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.58 (app t, J = 5.7 Hz, 2 H), 3.34 (s, 3 H), 2.87 (s, 1 H), 2.24 (app t, J = 6.4 Hz, 2 H), 1.61 (s, 3 H), 1.58 (s, 3 H), 1.58–1.52 (m, 4 H), 1.39 (s, 3 H), 0.85 (s, 9 H), 0.01 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.9, 144.4, 87.6, 84.6, 77.6, 76.3, 62.6, 52.7, 31.9, 25.9 (3 C), 25.2, 18.7, 18.3, 15.9, 9.4, 8.0, −5.4 (2 C); MS (high resolution EI) m/e (relative intensity) 352 (M^+, 1), 263 (30), 189 (42), 188 (14), 173 (14), 171 (20), 149 (23), 148 (11), 147 (12), 145 (17), 123 (17), 119 (11), 113 (54), 105 (13), 91 (16), 89 (22), 81 (17), 79 (13), 77 (11), 75 (100), 73 (68), 67 (10), 59 (16), 55 (12); calcd for $C_{20}H_{36}O_3Si$ 352.2433569, found 352.2431793 (error (5.04 × 10^{-5})%). Anal. Calcd for $C_{20}H_{36}O_3Si$: C, 68.13; H, 10.29. Found: C, 68.33 H, 10.23.

1-(6-Hydroxy-1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (8f). In a 50-mL round-bottomed flask, 1-(6-(*tert*-butyldimethylsiloxy)-1-hexynyl)-4-methoxy-1,2,3-trimethyl-2-cyclobutenol (0.36 g, 1.0 mmol) was dissolved in 15 mL of THF under an argon atmosphere. The solution was cooled to 0 °C and 1.5 mL (1.5 equiv) of a solution of tetra-*n*-butylammonium fluoride (approximately 1.0 M in THF) was added. The reaction mixture was allowed to warm to room temperature and stirred for 25 min. TLC monitoring indicated consumption of starting material and formation of a new compound (SiO_2, 1:1 hexanes:EtOAc, R_f = 0.11, phosphomolybdic acid). At room temperature 10 mL of water was added and the crude product was extracted with two 12-mL portions of Et_2O. The combined organic layers were dried over $MgSO_4$ and filtered, and the crude product was purified via flash chromatography (SiO_2, 1:1 hexanes:EtOAc, 15 × 3 cm^2 column) and then recrystallized from hexanes to give 0.19 g (0.79 mmol, 80%) of 1-(6-hydroxy-1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobutenol as a white solid: mp 61–2 °C; IR (CH_2Cl_2) 3618, 3508, 3053, 2944, 2236, 1443, 1119, 1044 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.64 (app t, J = 6.0 Hz, 2 H), 3.36 (s, 3 H), 2.90 (s, 1 H), 2.40 (s, 1 H), 2.28 (app t, J = 6.6 and 6.2 Hz, 2 H), 1.62 (s, 3 H), 1.59 (s, 3 H), 1.50–1.70 (m, 4 H), 1.40 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.7, 144.4, 87.3, 84.6, 77.7, 76.2, 62.0, 52.6, 31.7, 24.9, 18.6, 15.9, 9.3, 7.9. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.42; H, 9.27.

1-(1-Decynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (8g). Following the protocol for **8a**, a solution of 4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-one (0.20 g, 1.43 mmol) in 4 mL of THF was treated with approximately 2.0 equiv of 1-decynyllithium, formed by treating 1-decyne (0.52 mL) in 20 mL of THF at −4 °C with *n*-butyllithium (2.5 M in hexanes, 1.15 mL). Monitoring by TLC showed the disappearance of starting material and the formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.63, UV). Workup and flash chromatography (40 g of silica gel, 230–400 mesh, 2:1 hexanes:EtOAc, 15 × 3 cm^2 column) gave 0.39 g (1.38 mmol, 97%) of 1-(1-decynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol as a yellow oil: IR (CH_2Cl_2) 3529, 3305, 2933, 2858, 2236, 1443, 1374, 1121, 1042 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.34 (s, 3 H), 2.88 (s, 1 H), 2.20 (t, J = 6.9 Hz, 2 H), 1.60 (s, 3 H), 1.57 (s, 3 H), 1.28–1.50 (m, 2 H), 1.38 (s, 3 H), 1.22 (br s, 10 H), 0.84 (app t, J = 6.0, 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.5, 144.3, 87.8, 84.6, 77.4, 76.3, 52.7, 31.7, 29.1, 29.0, 28.7, 28.7, 22.6, 18.8, 15.8, 14.0, 9.3, 7.9. Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: C, 77.53; H, 10.81.

1-(1-Hexynyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol (8h). A solution of 4-methoxy-4-methyl-2-cyclobutenone (0.10 g, 0.89 mmol) in 4 mL of THF under an argon atmosphere was cooled to −4 °C and added via cannula to approximately 2.0 equiv of 1-hexynyllithium, formed by treating 1-hexyne (0.21 mL) in 8 mL of THF at −4 °C with *n*-butyllithium (2.5 M in hexanes, 0.71 mL) and stirring for 30 min at −4 °C. After 30 min, analysis by TLC indicated consumption of starting material and formation

of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.51, phosphomolybdic acid). The reaction was quenched at −4 °C with 10 mL of a 10% aqueous solution of NH_4Cl. After 15 min the reaction mixture was allowed to warm to room temperature and was extracted with two 10-mL portions of Et_2O. The combined organic layers were dried over $MgSO_4$ and filtered, and the crude orange residue was flash chromatographed (SiO_2, 2:1 hexanes:EtOAc) to give 0.15 g (0.77 mmol, 87%) of 1-(1-hexynyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol as a yellow oil: IR (neat) 3431 (ν_{OH}), 2960, 2935, 2875, 2833, 2238, 1785, 1715, 1461, 1368, 1300, 1223, 1198, 1140, 1127, 1102, 1059 cm^{-1}; IR (CCl_4, c = 0.1 mol/L) 3612 (weak ν_{OH}) and 3510 (ν_{OH}), 2962, 2937, 2875, 2833, 2240, 1786, 1715, 1625, 1196, 1140, 1127, 1100, 1063 cm^{-1}; IR (CCl_4, c = 0.01 mol/L) 3610 (weak ν_{OH}) and 3513 (ν_{OH}), 2962, 2937, 2875, 2833, 2240, 1786, 1665, 1626, 1368, 1196, 1140, 1100, 1063 cm^{-1}; IR (CCl_4, c = 0.001 mol/L) 3610 (weak ν_{OH}) and 3510 (ν_{OH}), 2962, 2937, 2877, 2833, 2236, 1786, 1665, 1549, 1368, 1250, 1196, 1138, 1100, 1065, 1003 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.39 (s, 2 H), 3.37 (s, 3 H), 3.34 (s, 1 H), 2.25 (app t, J = 6.9 Hz, 2 H), 1.35–1.51 (m, 4 H), 1.47 (s, 3 H), 0.88 (app t, J = 7.1 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 144.3, 142.6, 88.6, 86.1, 77.6, 76.0, 52.3, 30.7, 21.9, 18.6, 18.0, 13.6; MS (high resolution EI) m/e (relative intensity) 194 (M^+, 18), 179 (14), 151 (13), 109 (13), 97 (13), 91 (19), 85 (100), 79 (15), 77 (13), 55 (47); calcd for $C_{12}H_{18}O_2$ 194.130671, found 194.1306800 (error (4.64 × 10^{-6})%).

1-Ethynyl-4-methoxy-4-methyl-2-cyclobuten-1-ol (8i). Following the protocol for **8a**, a solution of 4-methoxy-4-methyl-2-cyclobutenone (0.15 g, 1.34 mmol) in 3 mL of THF under an argon atmosphere was cooled to −23 °C and added via cannula to approximately 2.0 equiv of lithium (trimethylsilyl)acetylide, formed by treating (trimethylsilyl)acetylene (0.38 mL) in 7 mL of THF at −23 °C with n-butyllithium (2.5 M in hexanes, 1.1 mL) and stirring for 30 min at −23 °C. After 30 min TLC analysis indicated consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.67, phosphomolybdic acid). The reaction mixture was quenched at −23 °C with 3 mL of brine and then allowed to warm to room temperature and extracted with two 10-mL portions of Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated, the crude orange residue was dissolved in 7 mL of methanol under an argon atmosphere, and potassium fluoride dihydrate (0.13 g, 1.34 mmol) was added at room temperature. Analysis by TLC indicated formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.53, phosphomolybdic acid). The reaction mixture was quenched with 10 mL of water and extracted with three 12-mL portions of Et_2O, and the combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude residue was flash chromatographed (SiO_2, 2:1 hexanes:EtOAc) and then recrystallized from Et_2O/hexanes to give 0.13 g (0.93 mmol, 70%) of 1-ethynyl-4-methoxy-4-methyl-2-cyclobuten-1-ol as a white solid: mp 76 °C; IR (CCl_4) 3504, 3313, 2981, 2937, 2833, 2104, 1451, 1374, 1198, 1098 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.45 (d, J = 2.9 Hz, 1 H), 6.41 (d, J = 2.9 Hz, 1 H), 3.39 (s, overlapping O*Me* and O*H*, 4 H), 2.64 (s, 1 H), 1.51 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 143.6, 143.6, 85.6, 81.4, 77.2, 75.6, 52.4, 18.0; MS (high resolution EI) m/e (relative intensity) 138 (M^+, 39), 123 ($M^+ - CH_3$, 45), 112 (23), 107 (11), 99 (14), 95 (52), 85 (100), 77 (62), 75 (17), 67 (21), 57 (73), 55 (58), 53 (47); calcd for $C_8H_{10}O_2$ 138.0680742, found 138.0680797 (error (3.9 × 10^{-6})%).

Stoichiometric Hg(OCOCF$_3$)$_2$-Induced Ring Expansions. 5(*Z*)-(1-(Chloromercurio)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (10a). A solution of 1-(1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (0.1 g, 0.45 mmol) in 10 mL of CH_2Cl_2 under an argon atmosphere was treated at room temperature with $Hg(OCOCF_3)_2$ (0.19 g, 1 equiv). The yellow solution turned orange, green, and finally black. After 30 min of stirring at room temperature, TLC monitoring (SiO_2, CH_2Cl_2) indicated the disappearance of starting material and 20 mL of an aqueous saturated solution of NaCl was added causing a color change to brown. After 1 h of stirring at room temperature, the layers were separated and the aqueous layer was extracted with two 10-mL portions of Et_2O. The combined organic layers were dried over Na_2SO_4, filtered, and evaporated and the crude residue was purified by flash chromatography (SiO_2, 2:1 hexanes:EtOAc). Removal of the solvent and recrystallization from CH_2Cl_2 provided 0.16 g (0.35 mmol, 78%) of 5(*Z*)-(1-(chloromercurio)-pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (R_f = 0.6, UV) as a crystalline yellow solid deduced to be the *Z*-isomer (>15:1, *Z*:*E*) from the chemical shift of the minor isomer resonances (see discussion in the text): mp 88 °C; IR (CH_2Cl_2) 3051, 2962, 2935, 2875, 2829, 1673 (major), 1656 (minor), 1606, 1563, 1439, 1389, 1372, 1329, 1264, 1221, 1183, 1115, 1055, 1005 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.83 (s, 3 H), 2.65 (app t, J = 7.6 Hz, 2 H), 1.96 (s, 3 H), 1.79 (s, 3 H), 1.61–1.50 (m, 2 H), 1.43 (s, 3 H), 1.44–1.34 (m, 2 H), 0.91 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 193.6, 168.7, 163.8, 140.9, 139.0, 83.7, 51.3, 35.0, 34.2, 24.0, 22.7, 14.0, 10.8, 8.5; MS (HR EI) m/e (relative intensity) 458 (M^+, 0.5), 221 (48), 190 (22), 189 (18), 188 (13), 135 (26), 119 (16), 105 (15), 95 (10), 91 (24), 83 (10), 81 (17), 79 (12), 77 (15), 71 (14), 69 (28), 67 (12), 65 (10), 57 (22), 55 (29), 53 (12); calcd for $C_{14}H_{21}O_2HgCl$ 458.0936229, found 458.0936398 (error (3.7 × 10^{-6})%).

5(*Z*)-(1-(Chloromercurio)pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (10b). A solution of 1-(1-hexynyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol (0.3 g, 1.58 mmol) in 12 mL of degassed CH_2Cl_2 under an argon atmosphere was cooled to −23 °C and treated with $Hg(OCOCF_3)_2$ (0.67 g, 1 equiv). The yellow solution turned orange and then pink. Stirring was maintained for 2 h at −23 °C; then the reaction mixture was quenched with 4 mL of degassed brine. After warming to room temperature, the reaction mixture was extracted with six 8-mL portions of CH_2Cl_2, and the combined organic layers were dried over $MgSO_4$ and filtered through a short plug of Celite. After evaporation of the solvent, the yellow crude product was purified by flash chromatography (SiO_2, CH_2Cl_2) to give a byproduct (UV, R_f = 0.58) and 0.39 g (0.93 mmol, 59%) of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (UV, R_f = 0.52) that was recrystallized from Et_2O/hexanes. The off-white solid could be stored under an inert atmosphere at low temperature (−4 °C): mp 89–90 °C; IR (CH_2Cl_2) 3064, 2964, 2877, 1686, 1611, 1335, 1216, 1115 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38 (d, J = 6.0 Hz, 1 H), 6.46 (d, J = 6.0 Hz, 1 H), 3.02 (s, 3 H), 2.73–2.67 (m, 2 H), 1.60 (m, 2 H), 1.56 (s, 3 H), 1.40 (m, 2 H), 0.95 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 194.4, 166.1, 164.6, 141.0, 134.7, 83.6, 52.1, 34.5, 34.9, 25.3, 22.7, 14.0; MS (low resolution EI) m/e (relative intensity) 430 (M^+, 56), 431 ($(M + H)^+$, 100); MS (high resolution EI) m/e (relative intensity) 398 ($(M - CH_4O)^+$, 10), 193 (63), 162 (30), 161 (22), 160 (14), 119 (15), 112 (100), 105 (19), 91 (45), 80 (18), 77 (27), 65 (23).

5(*Z*)-(1-(Chloromercurio)methylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (10c). A solution of 1-ethynyl-4-methoxy-4-methyl-2-cyclobuten-1-ol (0.12 g, 0.89 mmol) in 5 mL of degassed CH_2Cl_2 under an argon atmosphere was cooled to −23 °C and treated with $Hg(OCOCF_3)_2$ (0.38 g, 1 equiv). The yellow solution turned orange and then brown. Stirring was maintained for 1 h at −23 °C; then the reaction mixture was quenched with 3 mL of degassed brine at 0 °C. After warming to room temperature, the reaction mixture was extracted with three 8-mL portions of CH_2Cl_2 and the combined organic layers were dried with $MgSO_4$ and filtered through a short plug of Celite. After evaporation of the solvent, the crude yellow product was purified by flash chromatography (SiO_2, 2:1 hexanes:EtOAc), giving 0.20 g (0.54 mmol, 61%) of 5(*Z*)-(1-(chloromercurio)methylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (UV, R_f = 0.34). The white solid could be stored under an inert atmosphere at low temperature (at −4 °C): mp 151–152 °C (Et_2O); IR (CH_2Cl_2) 3056, 2985, 2937, 2831, 1696, 1657, 1638, 1626, 1455, 1335, 1218, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.50 (d, J = 6.2 Hz, 1 H), 6.78 (t, $J(^1H–C–^{199}Hg)$ = 127.5 Hz, 1 H), 6.56 (d, J = 6.2 Hz, 1 H), 3.03 (s, 3 H), 1.53 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 193.5, 164.1, 151.9, 139.5, 135.4, 82.1, 52.1, 25.9; MS (high resolution EI) m/e (relative intensity) 374 (M^+, 6), 361 (25), 359 (57), 358 (30), 357 (41), 356 (26), 341 (10), 313 (9), 237 (12), 137 (31); calcd for $C_8H_9O_2HgCl$ 373.9997277, found 373.9997394 (error (3.13 × 10^{-6})%).

Functionalization of Vinylmercurials. Synthesis of 5(*Z*)-(1-bromopentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (11a) by bromination of 5(*Z*)-(1-(chloromercurio)-pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopentenone (**10a**). In a 25-mL round-bottomed flask opened to air a solution of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (35 mg, 0.077 mmol) in 4 mL of dry DMSO

was treated with bromine (48 μL, 1.2 equiv). After 5 min of stirring at room temperature, TLC analysis showed consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.7, UV). Hexanes (10 mL) and then water (5 mL) were added to the reaction mixture. After extraction with Et_2O, the combined organic layers were dried over Na_2SO_4, filtered, and evaporated, and the crude product was purified by preparative thin layer chromatography (silica gel 60 F_{254} precoated plate, 20 × 20 cm², pretreated with a mixture of 10% of NEt_3 and 90% of the following mixture of solvents, 2:1 hexanes:EtOAc). After evaporation of the solvent, 21 mg (0.07 mmol, 90%) of 5(*Z*)-(1-bromopentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one was isolated as a yellow oil: IR (CCl_4) 2962, 2935, 2875, 2827, 1700, 1671, 1617, 1256, 1210, 1113, 1053 cm⁻¹; ¹H NMR ($CDCl_3$, 300 MHz) δ 3.07–2.97 (m, 1 H), 2.90 (s, 3 H), 2.59–2.69 (m, 1 H), 1.90 (s, 3 H), 1.79 (s, 3 H), 1.76–1.69 (m, 1 H), 1.65–1.56 (m, 1 H), 1.35–1.45 (m, 2 H), 1.44 (s, 3 H), 0.95 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR ($CDCl_3$, 75.5 MHz) δ 191.4, 162.5, 140.8, 135.3, 132.5, 84.6, 51.2, 38.2, 30.6, 24.4, 22.5, 13.9,, 10.1, 8.5; MS (HR EI) *m/e* (relative intensity) 300 (M^+, 4), 222 (15), 221 (100), 189 (26), 135 (23), 119 (15), 105 (12), 91 (16), 77 (12); calcd for $C_{14}H_{21}O_2Br$ 300.0725348, found 300.0724912 (error (1.45 × 10^{-5})%).

Synthesis of **5(*Z*)-(1-bromopentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (11b)** by bromination of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-4-methyl-2-cyclopentenone (**10b**). In a 50-mL round-bottomed flask opened to air a solution of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (0.1 g, 0.23 mmol) in 4 mL of dry DMSO was treated with 12 μL (1 equiv) of bromine. After 8 min of stirring at room temperature, TLC analysis showed consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.73, UV). Et_2O (10 mL) and then water (4 mL) were added to the reaction mixture. After extraction with Et_2O, the combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude mixture was purified by flash chromatography (SiO_2 pretreatment with a 2:1 mixture of hexanes:EtOAc containing 10% Et_3N). After evaporation of the solvent, 0.056 g (0.205 mmol, 89%) of 5(*Z*)-(1-bromopentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one was isolated as a yellow oil: IR (CCl_4) 2964, 2935, 2877, 2829, 1711, 1623, 1598, 1241, 1200, 1117, 1063 cm⁻¹; ¹H NMR ($CDCl_3$, 300 MHz) δ 7.05 (d, *J* = 6.0 Hz, 1 H), 6.40 (d, *J* = 6.0 Hz, 1 H), 3.07 (s, 3 H), 2.96–3.04 (ddd, *J* = 5.1, 10.5 and 15.5 Hz, 1 H), 2.62–2.72 (ddd, *J* = 5.1, 10.5 and 15.5 Hz, 1 H), 1.78–1.70 (m, 1 H), 1.64–1.56 (m, 1 H), 1.54 (s, 3 H), 1.36–1.48 (m, 2 H), 0.95 (t, *J* = 7.3 Hz, 3 H); ¹³C NMR ($CDCl_3$, 75.5 MHz) δ 191.9, 159.4, 137.3, 136.5, 132.7, 84.5, 52.1, 38.6, 30.5, 25.8, 22.5, 13.9; MS (high resolution EI) *m/e* (relative intensity) 272 (M^+, 8), 259 (14), 257 (14), 242 (14), 240 (14), 193 (100), 177 (20), 161 (19), 151 (22), 107 (16), 105 (23), 91 (57), 85 (15), 79 (22), 77 (35), 69 (21), 65 (32), 63 (16), 55 (15), 53 (16), 51 (24); calcd for $C_{12}H_{17}O_2Br$ 272.0412364, found 272.0411911 (error (1.66 × 10^{-5})%).

Synthesis of **5(*Z*)-(1-bromopentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (11c)** by bromination of 5(*Z*)-(1-(chloromercurio)methylidene)-4-methoxy-4-methyl-2-cyclopentenone (**10c**). In a 50-mL round-bottomed flask opened to the air, a solution of 5(*Z*)-(1-(chloromercurio)methylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (0.1 g, 0.28 mmol) in 4 mL of dry DMSO was treated with bromine (14 μL, 1 equiv). After 8 min of stirring at room temperature, TLC analysis showed consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.34, UV). Et_2O (10 mL) and then water (4 mL) were added to the reaction mixture. After extraction with Et_2O, the combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by flash chromatography (SiO_2 pretreated with a 2:1 mixture of hexanes:EtOAc containing 10% Et_3N). After evaporation of the solvent and recrystallization from Et_2O, 0.056 g (0.25 mmol, 89%) of 5(*Z*)-(1-bromomethylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one was isolated as a white solid: mp 70 °C; IR (CCl_4) 2989, 2829, 2337, 1715, 1621, 1374, 1329, 1285, 1133, 1119, 1065 cm⁻¹; ¹H NMR ($CDCl_3$, 300 MHz) δ 7.17 (d, *J* = 6.0 Hz, 1 H), 6.89 (s, 1 H), 6.46 (d, *J* = 6.0 Hz, 1 H), 3.08 (s, 3 H), 1.51 (s, 3 H); ¹³C NMR ($CDCl_3$, 75.5 MHz) δ 192.1, 159.5, 139.8, 137.4, 113.4, 83.5, 52.0, 26.6; MS (high resolution EI) *m/e* (relative intensity) 216 (M^+, 19), 203 (97), 201 (M^+ – 15, 100), 187 (39), 185 (40), 159 (22), 157 (23), 137 (77), 122 (31), 109 (28), 105 (20), 83 (18), 78 (57), 77 (57), 63 (19), 53 (26), 52 (26); calcd for $C_8H_9O_2Br$ 215.9786396, found 215.9785907 (error (2.26 × 10^{-5})%).

Synthesis of **5(*Z*)-(1-allylpentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopentenone (9a)** by palladium-catalyzed allylation of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopentenone (**10a**). A solution of **10a** (38 mg, 0.084 mmol) in THF (4 mL) under a dry argon atmosphere was cooled to –78 °C and LiCl (2 mg, 60 mol %), $PdCl_2$ (4 mg, 30 mol %), and allyl bromide (0.07 mL, 0.84 mmol, 10 equiv) were added. After 30 min at –78 °C, the red solution was allowed to warm to room temperature and stirred overnight. TLC monitoring (SiO_2, 2:1 hexanes:EtOAc) showed the disappearance of the starting material (R_f = 0.6) and the formation of a new spot (R_f = 0.7) which was UV active and stained with phosphomolybdic acid. The mixture was quenched with NH_4Cl (satd aqueous solution, 10 mL) and extracted with Et_2O (2 × 7 mL), and the combined organic layers were washed with saturated aqueous NaCl (2 × 10 mL) and dried (Na_2SO_4). After filtration and evaporation the residue was purified by preparative-layer chromatography (SiO_2, CH_2Cl_2) to provide 18 mg (88%) of a yellow oil that analyzed as 5(*Z*)-(1-allylpentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one: IR (CH_2Cl_2) 1679, 1638, 1625 cm⁻¹; ¹H NMR ($CDCl_3$, 300 MHz) δ 5.85–5.71 (m, 1 H), 5.08 (dd, *J* = 17.2 and 1.4 Hz, 1 H), 4.98 (dd, *J* = 9.9 and 1.4 Hz, 1 H), 3.90 (dd, *J* = 13.3 and 6.3 Hz, 1 H), 3.39 (dd, *J* = 13.3 and 7.2 Hz, 1 H), 2.84 (s, 3 H), 2.64–2.54 (m, 1 H), 2.31–2.21 (m, 1 H), 1.87 (s, 3 H), 1.74 (s, 3 H), 1.50–1.36 (m, 4 H), 1.43 (s, 3 H), 0.93 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR ($CDCl_3$, 75.5 MHz) δ 195.0, 163.0, 153.0, 140.4, 136.2, 130.4, 115.7, 82.7, 50.8, 34.9, 31.7, 29.4, 24.5, 23.3, 14.0, 10.2, 8.2; MS (LREI) *m/e* (relative intensity) 262 (M^+, 74), 247 (57), 231 (100), 230 (26), 215 (43), 201 (31), 188 (32), 187 (41), 175 (20), 174 (21), 173 (69), 159 (20), 158 (29), 145 (35), 131 (23), 125 (20), 105 (20), 91 (35), 55 (20); MS (HREI) calcd for $C_{17}H_{26}O_2$ 262.19327, found 262.19328 (error (4.77 × 10^{-6})%).

Synthesis of **5(*Z*)-[1-(4-hydroxy-2(*E*)-butenyl)pentylidene]-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (12)** by palladium-mediated hydroxybutenylation of **10a**. A solution of 5(*Z*)-(1-(chloromercurio)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (48 mg, 0.10 mmol) in 5 mL of THF and 0.25 mL of water under an argon atmosphere was treated with LiCl (9 mg, 2 equiv), butadiene monoepoxide (17 μL, 2 equiv), and $PdCl_2$ (19 mg, 1 equiv). After 1 day of stirring at room temperature, TLC monitoring showed consumption of starting material and formation of a new compound (SiO_2, 2:1 hexanes:EtOAc, R_f = 0.2, UV). The reaction mixture was quenched with 4 mL of a 5% aqueous solution of NH_4Cl and extracted with Et_2O. After purification by flash chromatography (silica gel, 2:1 hexanes:EtOAc), 20 mg (0.068 mmol, 68%) of 5(*Z*)-[1-(4-hydroxy-2(*E*)-butenyl)pentylidene]-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one was isolated as an orange oil: IR (CH_2Cl_2) 3068, 3056, 2962, 2935, 2875, 1679, 1627, 1438, 1383, 1324, 1109, 1058, 974 cm⁻¹; ¹H NMR ($CDCl_3$, 300 MHz) δ 5.65–5.71 (m, 2 H), 4.05–4.06 (d, *J* = 4.3 Hz, 2 H), 3.78–3.84 (m, 1 H), 3.38–3.45 (m, 1 H), 2.82 (s, 3 H), 2.51–2.61 (m, 1 H), 2.21–2.31 (m, 1 H), 1.87 (s, 3 H), 1.73 (s, 3 H), 1.57–1.27 (m, 5 H), 1.41 (s, 3 H), 0.92–0.85 (m, 3 H); ¹³C NMR ($CDCl_3$, 75.5 MHz) δ 195.0, 163.2, 152.9, 140.5, 130.5 (2 C), 130.4, 82.7, 63.7, 50.9, 33.3, 31.8, 29.4, 24.5, 23.3, 14.0, 10.2, 8.2; MS (HR EI) *m/e* (relative intensity) 292 (M^+, 9), 275 (20), 274 (M^+ – 18, 100), 247 (84), 243 (27), 242 (36), 232 (39), 227 (30), 217 (33), 215 (35), 213 (32), 201 (20), 199 (26), 187 (35), 185 (43), 173 (40), 171 (27), 159 (24), 157 (41), 145 (20), 129 (45), 128 (22), 117 (21), 113 (24), 105 (27), 97 (33), 95 (25), 91 (58), 85 (30), 83 (34), 81 (35), 79 (29), 77 (35), 71 (46), 69 (53), 67 (29), 65 (20), 58 (85), 53 (26); calcd for $C_{18}H_{28}O_3$ 292.2038311, found 292.2038450 (error (4.75 × 10^{-6})%).

$Hg(OCOCF_3)_2$/$PdCl_2$-Cocatalyzed Ring Expansion–Functionalizations. 5(*Z*)-(1-Allylpentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9a). Following the same protocol as described below for **9c**, 5(*Z*)-(1-allylpentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (0.110 g, 0.42 mmol, 81%) was prepared in THF from 1-(1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobutenol (0.116 mg, 0.52 mmol). 5(*Z*)-(1-Allylpentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV,

R_f = 0.44, with CH_2Cl_2 as eluant) is an orange oil showing the same spectroscopic data as listed earlier.

5(Z)-(1-Allylbutylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9b). Following the protocol for **9c**, 5(Z)-(1-allylbutylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (0.083 g, 0.33 mmol, 70%) was prepared in THF from 4-(1-pentynyl)-4-methoxy-1,2,3-trimethyl-2-cyclobutenol (0.1 g, 0.48 mmol). 5(Z)-(1-Allylbutylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV, R_f = 0.55, with CH_2Cl_2 as eluant) is an orange oil showing the following: IR (CCl_4) 3080, 2964, 2935, 2875, 2825, 1684, 1627, 1436, 1383, 1370, 1322, 1248, 1208, 1111, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.84–5.71 (m, 1 H), 5.07 (dd, J = 17.0, 1.1 Hz, 1 H), 4.97 (d, J = 9.8 Hz, 1 H), 3.90 (dd, J = 13.3, 6.5 Hz, 1 H), 3.38 (dd, J = 13.3, 6.9 Hz, 1 H), 2.84 (s, 3 H), 2.62–2.52 (m, 1 H), 2.29–2.19 (m, 1 H), 1.87 (s, 3 H), 1.74 (s, 3 H), 1.66–1.53 (m, 2 H), 1.42 (s, 3 H), 0.97 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 195.0, 163.0, 152.9, 140.5, 136.2, 130.5, 115.7, 82.7, 50.8, 34.8, 34.0, 24.5, 20.6, 14.7, 10.2, 8.2; MS (HR EI) m/e (relative intensity) 248 (M^+, 10), 247 (21), 246 (19), 234 (17), 233 (100), 217 (13), 216 (13), 207 (30), 202 (13), 201 (38), 187 (17), 175 (16), 173 (26), 159 (14), 145 (14), 135 (14), 119 (13), 105 (18), 91 (28), 79 (13), 77 (19), 69 (13), 55 (22); calcd for $C_{16}H_{24}O_2$ 248.1776186, found 248.1776302 (error (4.67 × 10^{-6})%).

5(Z)-(1-Allylmethylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9c(Z)). In a 25-mL round-bottomed flask under an argon atmosphere, 1-ethynyl-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (0.1 g, 0.60 mmol) was dissolved in a mixture of 5 mL of dry THF and 1.0 mL (25 equiv) of propylene oxide. $Hg(OCOCF_3)_2$ (0.025 g, 10 mol %), $PdCl_2$ (0.01 g, 10 mol %), and allyl chloride (0.5 mL, 10 equiv) were added at 0 °C. Once the reagents had all dissolved, the ice bath was removed and the reaction mixture was allowed to warm to room temperature and stirred at room temperature for 18 h. TLC monitoring (SiO_2, CH_2Cl_2) showed consumption of starting material and formation of a new compound (R_f = 0.49, UV). The reaction mixture was quenched with 7 mL of a 5% aqueous solution of NH_4Cl then extracted with two 12-mL portions of Et_2O. The combined organic layers were dried over $MgSO_4$ and filtered. After evaporation of solvent, the residue was purified by flash chromatography (20 g of silica gel, 230–400 mesh, methylene chloride as eluant, 15 × 3 cm^2 column), yielding 100 mg (0.48 mmol, 81%) of 5(Z)-(1-allylmethylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one as an orange oil: IR (CCl_4) 3083, 2983, 2933, 2825, 1696, 1669, 1646, 1438, 1385, 1370, 1354, 1316, 1242, 1212, 1115, 1063, 1023 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.08 (t, J = 7.6 Hz, 1 H), 5.09 (m, 1 H), 5.03 (d, J = 17.3 Hz, 1 H), 5.03 (d, J = 10.0 Hz, 1 H), 3.73–3.63 (m, 1 H), 3.58–3.48 (m, 1 H), 2.87 (s, 3 H), 1.90 (s, 3 H), 1.77 (s, 3 H), 1.37 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 195.11, 163.33, 141.36, 136.15, 135.59, 135.54, 115.89, 81.27, 50.70, 31.16, 24.99, 10.69, 7.99; MS (HR EI) m/e (relative intensity) 206 (M^+, 43), 205 (28), 192 (14), 191 (100), 174 (55), 173 (39), 163 (14), 161 (18), 160 (25), 159 (90), 157 (20), 146 (21), 145 (14), 142 (18), 131 (64), 129 (18), 119 (13), 117 (18), 115 (18), 105 (21), 105 (13), 91 (34), 79 (12), 77 (22), 65 (15); calcd for $C_{13}H_{18}O_2$ 206.130671, found 206.130680 (error (4.37 × 10^{-6})%).

In the absence of propylene oxide, the minor isomer **9c(E)**, 5(E)-(1-allylmethylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one, can be isolated as an orange oil by chromatography as described above: IR (CCl_4) 2931, 2860, 1704, 1673, 1644, 1588, 1457, 1383, 1324, 1250, 1206, 1117, 1063 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.64 (t, J = 7.9 Hz, 1 H), 5.93–5.80 (m, 1 H), 5.14–5.05 (m, 2 H), 3.17–3.13 (m, 2 H), 2.87 (s, 3 H), 1.93 (s, 3 H), 1.80 (s, 3 H), 1.45 (s, 3 H).

5(Z)-(1-Allyl-4-hydroxypentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9d). Following the protocol for **9c**, 5(Z)-(1-allyl-4-hydroxypentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (0.197 g, 0.62 mmol) was prepared in NMP in 77% yield from 1-(6-hydroxy-1-hexynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (0.227 g, 0.81 mmol). 5(Z)-(1-Allyl-4-hydroxypentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV, R_f = 0.52, with 2:1 hexanes:EtOAc as eluant) is an orange oil showing the following: IR (CH_2Cl_2) 3618, 2987, 2939, 1679, 1625, 1436, 1385, 1324, 1109, 1057 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.80 (m, 1 H), 5.07 (dd, J = 17.4, 1.3 Hz, 1 H), 5.02 (dd, J = 10.2, 0.9 Hz, 1 H), 3.85 (dd, J = 13.4, 6.4 Hz, 1 H), 3.67 (t, J = 5.7 Hz, 2 H), 3.45 (dd, J = 13.4, 6.8 Hz, 1 H), 2.86 (s, 3 H), 2.60 (m, 1 H), 2.33 (m, 1 H), 1.88 (s, 3 H), 1.75 (s, 3 H), 1.50–1.70 (m, 5 H), 1.44 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 194.9, 163.0, 152.3, 140.6, 136.1, 130.7, 115.9, 82.7, 62.5, 50.9, 34.8, 33.0, 31.5, 24.5, 23.4, 10.2, 8.2; MS (HR EI) m/e (relative intensity) 278 (M^+, 18), 263 (65), 247 (53), 246 (100), 231 (26), 213 (29), 205 (33), 201 (37), 188 (32), 187 (86), 175 (47), 174 (33), 173 (74), 159 (34), 145 (44), 131 (26), 105 (34), 91 (54), 77 (32); calcd for $C_{17}H_{26}O_3$ 278.1881819, found 278.1881950 (error (4.71 × 10^{-6})%).

5(Z)-(1-Allylnonylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9e). Following the protocol for **9c**, 5(Z)-(1-allylnonylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (0.063 g, 0.23 mmol) was prepared in THF containing 20 equiv of propylene oxide in 76% yield from 1-(1-decynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobuten-1-ol (0.074 g, 0.30 mmol). 5(Z)-(1-Allylnonylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV, R_f = 0.80, with 2:1 hexanes:EtOAc as eluant) is a orange oil showing the following: IR (CH_2Cl_2) 2931, 2858, 1679, 1625, 1437, 1109, 911 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.70 (m, 1 H), 5.03 (dd, J = 17.0, 1.1 Hz, 1 H), 4.94 (d, J = 9.8 Hz, 1 H), 3.86 (dd, J = 13.3, 6.2 Hz, 1 H), 3.35 (dd, J = 13.3, 6.9 Hz, 1 H), 2.82 (s, 3 H), 2.55 (m, 1 H), 2.23 (m, 1 H), 1.85 (s, 3 H), 1.72 (s, 3 H), 1.23–1.59 (br m, 12 H), 1.40 (s, 3 H), 0.83 (dd, J = 5.2, 6.9 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 194.8, 162.9, 153.0, 140.4, 136.1, 130.3, 115.7, 82.6, 50.7, 34.8, 31.9, 31.8, 30.2, 29.3, 29.2, 27.2, 24.4, 22.6, 14.0, 10.1, 8.1; MS (HR EI) m/e (relative intensity) 318 (M^+, 52), 303 (59), 288 (22), 287 (100), 286 (21), 271 (29), 220 (21), 201 (42), 189 (21), 188 (45), 187 (43), 175 (29), 174 (28), 173 (70), 159 (28), 145 (36), 131 (23), 105 (24), 91 (36), 55 (31); calcd for $C_{21}H_{34}O_2$ 318.2558646, found 318.2558806 (error (5.03 × 10^{-6})%).

5(Z)-(1-Allylpentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (9f). In a 25-mL round-bottomed flask under an argon atmosphere, 1-(1-hexenyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol (64 mg, 0.33 mmol) was dissolved in 6 mL of degassed NMP. At −14 °C were added $Hg(OCOCF_3)_2$ (14 mg, 10 mol %), $PdCl_2$ (6 mg, 10 mol %), and allyl chloride (66 μL, 2 equiv). Once the reagents had all dissolved, the cold bath was removed and the reaction mixture was allowed to stir at room temperature for 48 h. TLC monitoring (SiO_2, CH_2Cl_2) showed consumption of starting material and the formation of a new compound (UV, R_f = 0.31) and a byproduct (UV, R_f = 0.51). The reaction mixture was quenched with 10 mL of water and the crude product was extracted with four 10-mL portions of Et_2O. The combined organic layers were dried over Na_2SO_4 and filtered. After evaporation of the solvent, the residue was purified by preparative thin layer chromatography (silica gel 60 F_{254} precoated plate, 20 × 20 cm^2, CH_2Cl_2 as eluant), giving 59 mg (0.25 mmol, 77%) of 5(Z)-(1-allylpentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one as a yellow oil: IR (CCl_4) 2961, 2933, 1679, 1631, 1432, 1206, 1136 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.06 (d, J = 6.1 Hz, 1 H), 6.28 (d, J = 6.1 Hz, 1 H), 5.75 (m, 1 H), 5.08 (dd, J = 1.6, 17.1 Hz, 1 H), 4.99 (dd, J = 1.5, 10.0 Hz, 1 H), 3.85 (dd, J = 6.4, 13.3 Hz, 1 H), 3.35 (dd, J = 7.1, 13.3 Hz, 1 H), 3.00 (s, 3 H), 2.56 (m, 1 H), 2.26 (m, 1 H), 1.52 (s, 3 H), 1.36–1.53 (m, 4 H), 0.92 (app t, J = 6.8 and 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 195.7, 160.4, 155.4, 136.6, 135.7, 130.4, 116.1, 82.9, 51.6, 35.0, 32.1, 29.3, 25.9, 23.3, 14.0; MS (high resolution EI) m/e (relative intensity) 234 (M^+, 57), 219 (M^+ − 15, 100), 205 (38), 177 (80), 160 (32), 159 (56), 146 (50), 145 (54), 131 (48), 117 (50), 112 (86), 105 (31), 97 (42), 91 (78), 79 (33), 77 (42), 69 (31); calcd for $C_{15}H_{22}O_2$ 234.1619694, found 234.1619803 (error (4.61 × 10^{-6})%).

5(Z)-(1-(2-Butenyl)butylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9g). Following the protocol for **9c**, 1-(1-pentynyl)-4-methoxy-2,3,4-trimethyl-2-cyclobutenol (0.100 g, 0.48 mmol) with 3-chlorobut-1-ene (0.5 mL, 4.8 mmol) in 10 mL of THF containing 25 equiv of propylene oxide (0.67 mL) gave 89% of 5(Z)-(1-(2-butenyl)butylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (0.115 g, 0.43 mmol) as a mixture of *cis* and *trans* butenyl isomers. 5(Z)-(1-(2-Butenyl)butylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV, R_f = 0.57 with CH_2Cl_2 as eluant) is a yellow oil showing the following: IR (CCl_4) 2966, 2937, 2875, 2825, 1685, 1629, 1436, 1383, 1320, 1243, 1111, 1059 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.52–5.26 (m, 2 H), 3.94 (dd, J = 13.7, 6.4 Hz, 0.60 H), 3.80 (dd, J = 13.2, 5.8 Hz, 0.40 H),

3.40 (dd, J = 13.7, 7.6 Hz, 0.60 H), 3.29 (dd, J = 13.2, 6.4 Hz, 0.40 H), 2.83 (s, 1.2 H), 2.82 (s, 1.8 H), 2.62–2.49 (m, 1 H), 2.27–2.15 (m, 1 H), 1.86 (s, 3 H), 1.73 (s, 3 H), 1.66 (d, J = 6.6 Hz, 0.60 × 3 H), 1.59 (dd, J = 5.9, 1.1 Hz, 0.40 × 3 H), 1.6–1.5 (m, 2 H), 1.40 (s, 3 H), 0.90 (t, J = 7.3 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, as a mixture of the isomers of the butenyl chain) δ 195.1, 195.0, 162.8 (2 C), 154.4, 154.0, 140.4 (2 C), 130.0, 129.9, 128.5, 128.0, 126.4, 125.0, 82.6 (2 C), 50.7, 50.7, 33.8, 33.8, 33.4, 28.0, 24.5 (2 C), 20.7, 20.6, 17.9, 14.7, 14.6, 13.0, 10.1 (2 C), 8.1 (2 C); MS (high resolution EI) m/e (relative intensity) 262 (M^+, 65), 247 (34), 234 (17), 233 (100), 232 (15), 231 (75), 230 (15), 216 (16), 215 (88), 203 (18), 201 (54), 202 (18), 188 (14), 187 (58), 173 (16), 173 (22), 163 (66), 159 (20), 149 (18), 145 (16), 95 (13), 91 (32), 79 (16), 77 (24); calcd for $C_{17}H_{26}O_2$ 262.1932678, found 262.1932803 (error (4.77 × 10^{-6})%).

5(*Z*)-(1-(2-Butenyl)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (9h). Following the protocol for **9c**, 1-(1-hexynyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol (0.03 g, 0.13 mmol) and 3-chlorobut-1-ene (0.13 mL, 1.3 mmol) in 5 mL of THF containing 25 equiv of propylene oxide (0.23 mL) gave 0.032 g (92%) of 5(*Z*)-(1-(2-butenyl)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one as a 37:63 mixture of the butenyl group stereoisomers. 5(*E*)-(1-(2-Butenyl)pentylidene)-4-methoxy-2,3,4-trimethyl-2-cyclopenten-1-one (UV, R_f = 0.42, with CH_2Cl_2 as eluant) is a yellow oil showing the following: IR (CCl_4) 2962, 2935, 2863, 2825, 1685, 1629, 1438, 1381, 1370, 1320, 1241, 1200, 1111, 1075, 1059, 969 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.53–5.26 (m, 2 H), 3.94 (dd, J = 13.7, 6.5 Hz, 0.63 H), 3.80 (dd, J = 13.3, 6.2 Hz, 0.37 H), 3.41 (dd, J = 13.7, 7.5 Hz, 0.63 H), 3.30 (dd, J = 13.3, 6.75 Hz, 0.37 H), 2.83 (s, 3 H), 2.62–2.51 (m, 1 H), 2.29–2.18 (m, 1 H), 1.86 (s, 3 H), 1.74 (s, 3 H), 1.67 (d, J = 6.6 Hz, 0.63 × 3 H), 1.61 (d, J = 6.0 Hz, 0.37 × 3 H), 1.36–1.53 (m, 4 H), 1.41 (s, 3 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, as a mixture of the isomers of the butenyl chain) δ 195.1 (2 C), 162.8 (2 C), 154.6, 154.2, 140.4 (2 C), 129.9, 129.8, 128.5, 128.0, 126.4, 125.0, 82.7 (2 C), 50.8, 50.7, 33.5, 31.6, 31.4, 29.4, 29.4, 28.1, 24.5 (2 C), 23.4, 23.3, 17.9, 13.9 (2 C), 13.1, 10.1 (2 C), 8.1 (2 C); MS (high resolution EI) m/e (relative intensity) 276 (M^+, 77), 261 (24), 247 (51), 245 (76), 229 (78), 217 (18), 215 (29), 201 (38), 192 (19), 191 (46), 188 (21), 187 (100), 173 (32), 159 (33), 149 (17), 145 (24), 135 (16), 131 (20), 129 (16), 125 (22), 119 (22), 117 (18), 115 (18), 105 (34), 97 (22), 93 (21), 91 (55), 90 (33), 79 (44), 65 (23), 55 (45), 53 (28); calcd for $C_{18}H_{28}O_2$ 276.208917, found 276.2089304 (error (4.85 × 10^{-6})%).

5(*Z*)-(1-(2-Methylallyl)pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (9i). Following the protocol for **9c**, 1-(1-hexynyl)-4-methoxy-4-methyl-2-cyclobuten-1-ol (0.030 g, 0.13 mmol) and methallyl chloride (0.13 mL, 1.3 mmol) in 5 mL of NMP for 30 h gave 0.025 g (70%) of 5(*Z*)-(1-(2-methylallyl)-pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one (UV, R_f = 0.39, with CH_2Cl_2 as eluant). 5(*Z*)-(1-(2-Methylallyl)pentylidene)-4-methoxy-4-methyl-2-cyclopenten-1-one is a yellow oil showing the following: IR (CCl_4) 2962, 2933, 2862, 2825, 1684, 1671, 1627, 1439, 1382, 1320, 1111 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.75 (s, 1 H), 4.66 (s, 1 H), 3.95 (d, J = 14.0 Hz, 1H), 3.45 (d, J = 14.0 Hz, 1 H), 2.89 (s, 3 H), 2.60–2.51 (m, 1 H), 2.24–2.34 (m, 1 H), 1.89 (s, 3 H), 1.75 (s, 3 H), 1.70 (s, 3 H), 1.49–1.36 (m, 4 H), 1.45 (s, 3 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 195.0, 162.9, 153.0, 144.0, 140.6, 131.6, 111.1, 82.9, 51.0, 37.3, 31.2, 29.7, 24.6, 23.4, 22.6, 14.0, 10.2, 8.2; MS (high resolution EI) m/e (relative intensity) 276 (M^+, 11), 261 (100), 245 (24), 229 (34), 201 (21), 187 (34), 125 (21); calcd for $C_{18}H_{28}O_2$ 276.208917, found 276.2089304 (error (4.85 × 10^{-6})%).

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra for compounds **7**, **8h,i**, **9a,b**, **9c(*Z*)**, **9c(*E*)**, **9d,e**, **9g–i**, **10a–c**, **11a–c**, and **12** and ^{1}H NMR spectra for compounds **9c(*E*)** and **9f** (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.