(br s, 1 H), 1.92 (d, J = 8.6 Hz, 1 H), 1.89 (t, J = 4.6 Hz, 1 H), 1.72 (br s, 1 H), 1.64 (d, J = 8.6 Hz, 1 H), 1.62 (dd, J = 12.4, 2.7 Hz, 1 H), 1.18 (dd, J = 12.4, 2.7 Hz, 1 H).

Mosher Ester Analysis of 23. This analysis was performed using diol **23** prepared by the $LiAlH_4$ reductions of purified cycloadducts **15** (racemic and optically active) and (−)-**18**, as well as the crude, unseparated mixtures of cycloadducts obtained from the Diels–Alder reactions of (*R*)-**1** and (*R*)-**2**. Thus, to a solution of **23** in anhydrous CH_2Cl_2 (0.1 M) were added (*R*)-(+)-MTPA-Cl (1.2 equiv), Et_3N (1.1 equiv), and catalytic DMAP. This mixture was stirred for 12 h at 23 °C under N_2. The Mosher ester derivatives were purified by preparative TLC [R_f 0.55 (2:1 ether–hexane); the diastereomeric MTPA derivatives do not separate], and the purified esters (>95% yield) were examined by high field ^1H NMR analysis. The 500-MHz ^1H NMR spectrum of Mosher ester derivative prepared from racemic **23** displays an AB pattern for the CH_2OMTPA resonance of one diastereomer (δ 4.57 and 4.46, J_{AB} = 11.3 Hz) whereas the CH_2OMTPA resonance for the second diastereomer appears as an apparent singlet at δ 4.52. The MTPA derivative of **23** prepared from purified cycloadduct (−)-**15**, however, showed essentially only the resonances at δ 4.57 and 4.46, indicating the enantiomeric purity of **15**, and hence dienophile (*R*)-**1**, to be ≥99% ee. The Mosher ester analysis of **23** prepared from the unseparated mixture of Diels–Alder adducts prepared with (*R*)-**1** had an enantiomeric purity of 96% ee, indicating that up to 2% of exo cycloadduct **17** was also produced in the Diels–Alder reaction. Parallel analyses performed with **23** deriving from purified (−)-**18** (a 98:2 mixture of **18** and **20**) as well as from the unseparated mixture of cycloadducts obtained from the Diels–Alder reaction with (*R*)-**2** indicated enantiomeric purities of 96% and 90% ee, respectively.

Acknowledgment. This research was supported by a grant from the National Institute of General Medical Sciences (GM 26782).

Registry No. **1**, 130930-48-2; **2**, 140850-05-1; **7**, 134267-57-5; **8**, 82044-23-3; **9**, 118623-64-6; **10**, 83023-80-7; **11**, 140850-04-0; **12**, 140850-78-8; **13**, 140663-04-3; **14**, 140663-05-4; **15**, 140850-06-2; **16**, 140850-09-5; **17**, 140850-10-8; **18**, 140850-07-3; **19**, 140850-08-4; **20**, 140850-79-9; **21**, 140850-11-9; **22**, 140850-12-0; **23**, 82729-80-4; **24**, 140850-13-1; **25**, 16346-63-7; PhSH, 108-98-5; PhSMgBr, 59384-25-7; L-serine, 56-45-1; pivalaldehyde, 630-19-3; cyclohexanecarboxaldehyde, 2043-61-0; cyclopentadiene, 542-92-7.

Supplementary Material Available: ^1H NMR spectra of **2**, **13**, the trans diastereomer of **13**, **21**, and **22** and procedures for the synthesis of **21** and **22** (6 pages). This material is contained in many 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.

Synthesis of 2,5-Furanocycles through Intraannular Cyclization of Macrocyclic Allenones

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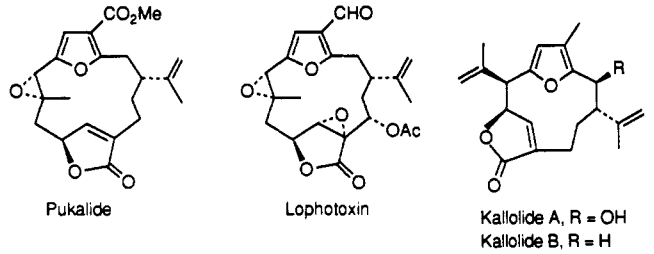
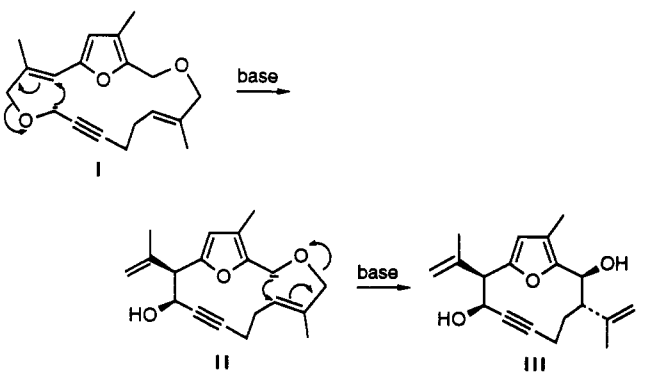
A new approach to 2,5-bridged furanocyclic compounds was demonstrated for rings of 12–14 members. Accordingly, allenylstannyl aldehydes **1.16**, **2.11**, **3.12a**, **3.12b**, **4.12**, **5.15**, and **6.12**, upon treatment with $BF_3{\cdot}OEt_2$ at −78 °C, smoothly cyclized to the homopropargylic alcohols **1.17**, **2.12**, **3.13a**, **3.13b**, **4.13**, **5.16**, and **6.13** in 87–94% yield. Oxidation and basic isomerization afforded the allenones **1.19**, **2.14**, **3.15a**, **3.15b**, **4.14**, **5.18**, and **6.15** in high yield. Intraannular cyclization to the furanocycles **1.21**, **2.15**, **3.16a**, **3.16b**, **4.16**, **5.19**, and **6.16** was effected with catalytic $AgNO_3$ and $CaCO_3$ in aqueous acetone. Furanocycles **1.21**, **2.15**, **3.16a**, and **3.16b**, with an appropriately disposed transannular (*Z*)-double bond, underwent facile intramolecular Diels–Alder cyclization in over 90% yield. The 12-membered furanocycles **4.16** and **5.19** with a transannular (*E*) double bond did not cyclize but instead were oxidized by the $AgNO_3$ catalyst to macrocyclic enediones **4.17** and **5.20**. These unusual furan reactions are presumably facilitated by ring strain (furan bending) in accord with molecular mechanics calculations.

Pukalide,[1] lophotoxin,[2] and the kallolides[3] are representative examples of marine natural products possessing a 12- or 14-membered 2,5-furanocyclic structure.[4] In connection with a program on the synthesis of biologically active cembranoid natural products we became interested in developing routes to such 2,5-furanocycles. In our initial approach we prepared the macrocyclic diether **I** hoping to effect sequential [2,3] Wittig ring contractions via **II** to the carbocyclic intermediate **III**, or a stereoisomer thereof.[5a] The conversion of **III** to kallolide A finds



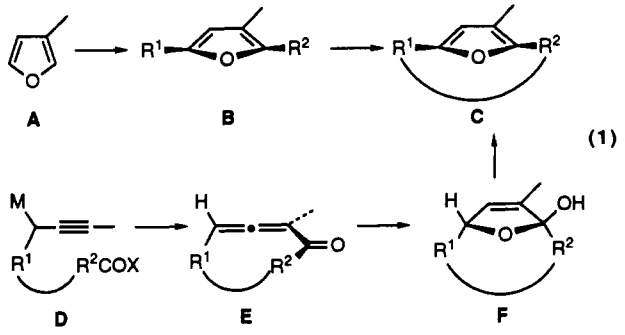


(1) Missakian, M. G.; Burneson, B. J.; Scheuer, P. J. *Tetrahedron* **1975**, *31*, 2513.
(2) Fenical, W.; Okeeda, R. K.; Bandurraga, M. M.; Culver, P.; Jacobs, R. S. *Science* **1981**, *212*, 1512.
(3) Look, S. A.; Burch, M. T.; Fenical, W.; Qui-tai, Z.; Clardy, J. *J. Org. Chem.* **1985**, *50*, 5741.
(4) For additional examples, see: Williams, D.; Andersen, R. J.; Van Duyne, C. D.; Clardy, J. *J. Org. Chem.* **1987**, *52*, 332. D'Ambroseo, M.; Fabbri, D.; Guerriero, A.; Pietra, F. *Helv. Chim. Acta.* **1987**, *70*, 63. Wright, A. E.; Bunes, N. S.; Schulte, G. K. *Tetrahedron Lett.* **1989**, *30*, 3491. Bandunaga, M. M.; Fenical, W.; Donovan, S. F.; Clardy, J. *J. Am. Chem. Soc.* **1982**, *104*, 6463. Tinto, W. F.; John, L.; Lough, A. J.; Reynolds, W. F.; McLean, S. *Tetrahedron Lett.* **1991**, *32*, 4661.
(5) (a) Marshall, J. A.; Nelson, D. J. *Tetrahedron Lett.* **1988**, *29*, 741. (b) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3451.

0022-3263/92/1957-3387$03.00/0

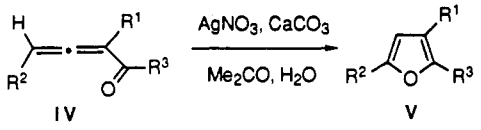
precedent in our aristolactone synthesis.[6] Unfortunately, we were unable to effect the second ring contraction. Furthermore, treatment of diether **I** with various bases afforded the rearranged product **II** in only 12% yield. Additional base treatment led to no identifiable product. Presumably, the planar arrangement of the furan ring and the linear acetylene cause structures such as **II**, and more so **III**, to be appreciably strained. This strain is felt in the transition state of the [2,3] rearrangement with a resulting decrease in efficiency. The [2,3] Wittig ring contraction of a 17-membered 2,5-furanocyclic ether also failed to afford a 14-membered analogue of pukalide.[5b]

In considering alternative approaches to kallolide A and other 2,5-furanocycles we note that in a sequence such as **A** → **B** → **C**, starting from an intact furan system, the driving force of the cyclization **B** → **C**, or in the case of **I** → **II** → **III** the ring contraction, must overcome the strain energy present in the final product as reflected in the transition state of that reaction.[7] On the other hand, if macrocyclization could be effected prior to furan introduction, then ultimate conversion to the furanocycle might be assisted by the gain in resonance energy accompanying formation of the planar furan moiety. Such an approach is illustrated in **E** → **F** → **C** (eq 1).



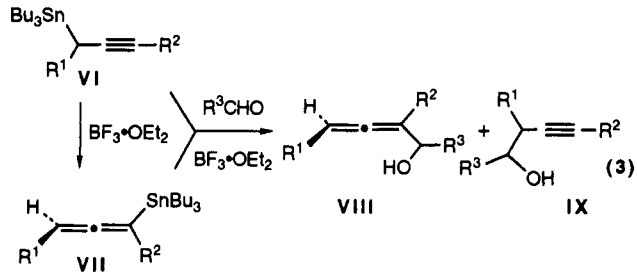
(1)

This plan was particularly attractive in light of our findings that acyclic allenones are readily converted to furans upon treatment with $AgNO_3$–$CaCO_3$ in aqueous acetone (eq 2).[8,9] We were also able to synthesize a 2,5-furano cembrane system by this methodology.[5b]



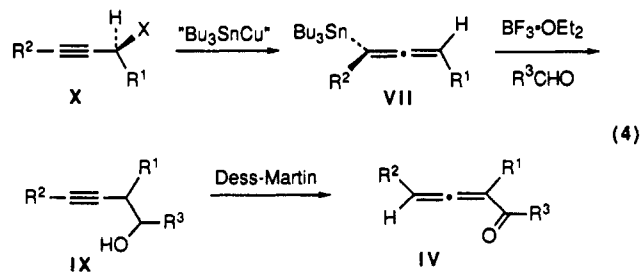
(2)

The purpose of the present study was to develop a more efficient route to macrocyclic allenones such as **E** and extend our furan methodology to prototypes of kallolide A and B. We have previously shown that allylstannanes undergo efficient intramolecular additions to aldehydes to afford 12–14-membered homoallylic alcohols.[10] Accordingly, an extension to propargylstannanes such as **D** (M = Bu_3Sn) leading to allenones **E** seemed attractive. However, we found that propargylic stannanes undergo competitive 1,3-isomerization upon treatment with BF_3·OEt_2 in the presence of aldehydes leading to a mixture of allenic and propargylic alcohols **VIII** and **IX**, favoring the latter (eq 3).[11] We also found that allenylstannanes such



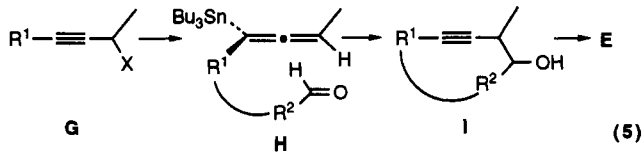
(3)

as **VII** could be efficiently prepared through S_N2' displacement of propargylic sulfonates with stannylcuprates (eq 4).[12] Furthermore, these stannanes readily add to



(4)

aldehydes affording homopropargylic alcohols **IX** as exclusive products. Oxidation of the alcohols by the Dess–Martin procedure[13] leads directly to allenic ketones **IV** as a consequence of the basic workup conditions. This sequence offers an alternative approach to macrocyclic allenones such as **E** (eq 5). We expected the cyclization step



(5)

H → **I** to be especially facile owing to the favorable anti arrangement of the Bu_3Sn and aldehyde side chain enforced by the unique allene geometry.[14]

We began our investigations with propargylic mesylate **1.13** prepared in 12 routine steps from alcohol **1.1**.[15] Addition of the Bu_3Sn cuprate, derived from Bu_3SnLi and $CuBr·SMe_2$, proceeded smoothly to afford allenylstannane **1.14** as a 1:1 mixture of diastereoisomers in 88% yield. The derived aldehyde **1.16** cyclized upon treatment with BF_3·OEt_2 in CH_2Cl_2 at −78 °C for 30 min affording ho-

(6) Marshall, J. A.; Lebreton, J. *J. Am. Chem. Soc.* **1988**, *110*, 2925.

(7) Paquette has successfully employed the Cr(II)-mediated cyclization of an allylic bromo aldehyde (Heathcock–Hiyama reaction) to produce a 12-membered 2,5-furanocyclic pseudopterolide intermediate in 20–25% yield. Paquette, L. A.; Rayner, C. M.; Doherty, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4078.

(8) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 960.

(9) In connection with their studies on [4*n*] annulenes, Sondheimer and co-workers prepared an 11-membered 2,5-furanocycle with an allenic moiety in the bridging chain through acid-catalyzed intraannular cyclization of a (presumed) 1,4-diketone. Garrath, P. J.; Nicolaou, K. C.; Sondheimer, F. *J. Org. Chem.* **1973**, *38*, 864.

(10) Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1989**, *30*, 309. Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1988**, *29*, 3899. Marshall, J. A.; Gung, W. Y. *Tetrahedron Lett.* **1988**, *29*, 1657. Marshall, J. A.; Crooks, S. L.; DeHoff, B. S. *J. Org. Chem.* **1988**, *53*, 1616. Marshall, J. A.; DeHoff, B. S.; Crooks, S. L. *Tetrahedron Lett.* **1987**, *28*, 527.

(11) Cf. Le Quan, M.; Cadiot, P. *Bull Soc. Chim. Fr.* **1965**, *45*. Le Quan, M.; Guillerm, C. *J. Organomet. Chem.* **1973**, *54*, 153. Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworths: London, 1987; pp 230–231. For a general survey of propargyl–allenyl organometallics, see: Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B., Ed. in Chief, Heathcock, C. H., Ed.; Pergamon Press: New York, 1991; Vol. 2, pp 81–98.

(12) Cf. (a) Ruitenberg, K.; Westmyze, H.; Meyer, J.; Elsevier, C. J.; Vermeer, P. *J. Organomet. Chem.* **1983**, *243*, 417. (b) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1990**, *55*, 6246.

(13) Dess, P. M.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156.

(14) For examples of allenic stereocontrol in Diels–Alder additions see: Gibs, R. A.; Okamura, W. H. *J. Am. Chem. Soc.* **1988**, *110*, 4062. Okamura, W. H.; Curtin, M. L. *Synlett.* **1990**, 1. Reich, H. J., Eisenhart, E. K.; Whipple, W. T.; Kelly, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 6432 and references cited therein.

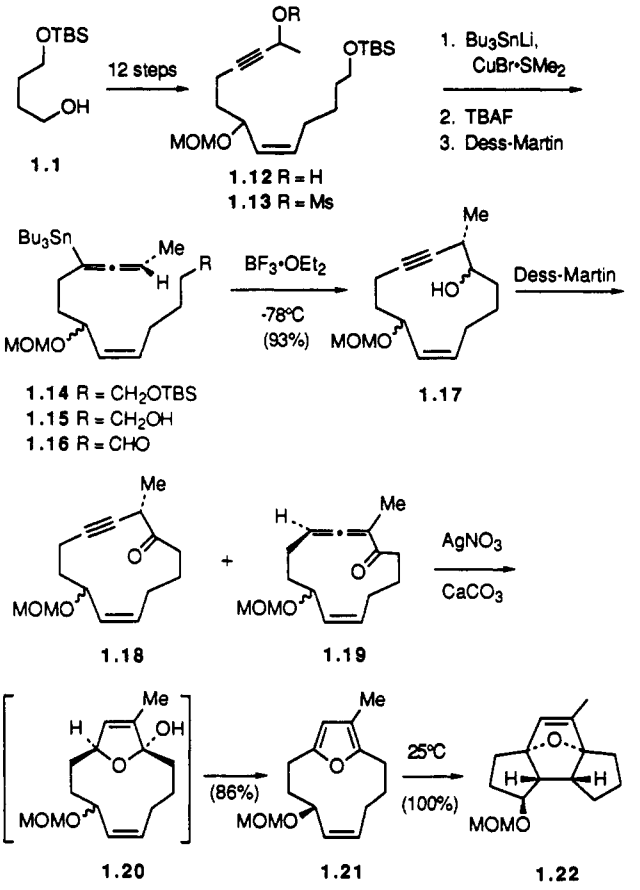
(15) An outline of the sequence and experimental procedures is available in the supplementary material.

mopropargylic alcohol **1.17** as a separable mixture of diastereomers in 93% yield. Oxidation of the mixture with the Dess–Martin periodinane reagent[13] gave the propargylic and allenic ketones **1.18** and **1.19** as a 1:3 mixture. This mixture was stirred with a catalytic amount of $AgNO_3$ and $CaCO_3$ in aqueous acetone. After several hours at room temperature, analysis by TLC showed the presence of a more polar and a less polar spot, presumed to be the dihydrofuran **1.20** and furan **1.21**. As the reaction proceeded, the polar spot gave way to two less polar spots and eventually only one of the two remained. This product, isolated in 86% yield, was not the expected furan **1.21**, but rather the derived intramolecular Diels–Alder adduct **1.22**![16]

Subsequent molecular mechanics calculations showed that the 2 and 5 positions of the furan ring are perfectly aligned with the C=C at a distance of only 3.0 Å.[17,18] Evidently, the strain energy present in **1.21** is sufficient to facilitate cycloaddition between the furan ring and the isolated double bond, two normally unreactive Diels–Alder partners.[19] More importantly, despite the apparent strain, furan **1.21** is readily formed from allenone **1.19**. Thus, as postulated, the driving force of furan aromatization can be used to offset relatively serious ring strain.

Although it is of no consequence to the immediate goals of this study we were interested in examining the intrinsic diastereoselectivity of the cyclization leading to **1.17**. We were able to separate three diastereomers of **1.17**, but stereochemistry could not be assigned. The formation of three rather than four isomers is suggestive of matched/mismatched pairing of allene and allylic OMOM chirality in the cyclization precursor **1.16**. Intermolecular additions of allenylstannanes to unbranched aliphatic aldehydes proceed with poor syn/anti selectivity.[12b] However, in the present case conformational constraints imposed by the connecting tether could lead to a preference for one diastereomer.

In order to examine this possibility we prepared the allenyl aldehyde **2.11** starting from alkyne **2.1** following a route analogous to that employed for **1.16**.[15] Cyclization was complete within 35 min affording homopropargylic alcohol **2.12** in 94% yield as a 1:1 mixture of inseparable diastereoisomers. Thus, the connecting tether per se does not engender the S_E' addition with conformationally induced diastereoselectivity, at least in the case of **2.11**.



Upon oxidation with the Dess–Martin reagent[13] alcohol **2.12** was converted to a mixture of propargylic and allenic ketones **2.13** and **2.14**. Complete isomerization to the latter was readily effected through brief treatment of the crude product mixture with Et_3N. Cyclization of allenone **2.14** to furan **2.15** was complete within 3 h at room temperature. Although furan **2.15** was the only observed product, it was obtained in low yield because of mechanical losses (volatility) during solvent removal. In view of the poor diastereoselectivity of the cyclization we did not attempt to optimize this yield. On standing at room temperature in $CHCl_3$ for 52 h furan **2.15** quantitatively cyclized to the Diels–Alder product **2.16**.

The apparent rate difference in the formation of bridged furans **1.21** and **2.15** (12 h vs 3 h) can be attributed to the presence of appreciable propargylic ketone isomer **1.18** in the starting materials for the former cyclization. When a mixture of **2.13** and **2.14** was employed, complete conversion to furan **2.15** required overnight stirring with $AgNO_3$–$CaCO_3$. Thus, isomerization of propargyl to allenyl ketone must be slow relative to furan formation under these conditions. For acyclic or larger ring cyclic systems this rate difference has no unfavorable consequence. However, for **1.21** and **2.15** the facile transannular Diels–Alder cyclization occurs at a rate comparable to isomerization thus diminishing the isolable yield of furan product. Fortunately, the isomerization can be readily effected with Et_3N prior to the furan forming step.

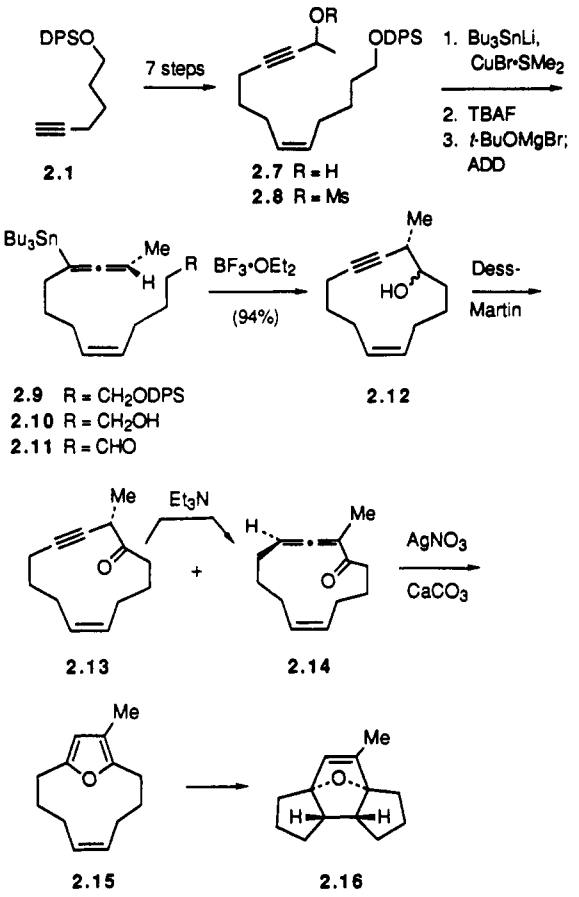
With the aim of extending the allenylstannane cyclization to larger rings and exploring the novel transannular Diels–Alder reaction on homologous 2,5-furanocycles, we synthesized the aldehydes **3.12a** and **b** starting from the DPS ether of 5-hexyn-1-ol (**2.1**) and 6-heptyn-1-ol by a sequence similar to that employed for **2.11**.[15] Upon treatment with BF_3·OEt_2 at −78 °C each aldehyde cyclized in over 90% yield to afford the 13 and 14-membered ho-

(16) For additional examples of intraannular Diels–Alder cycloadditions of macrocyclic trienes leading to tricyclic olefins see: Bérubé, G.; Deslongchamps, P. *Tetrahedron Lett.* **1987**, *28*, 5255. Deslongchamps, P. *Aldrichimica Acta* **1991**, *24*, 43. An enedione analogue of **2.15**, prepared through photooxygenation of [2.2]furanocyclophane, undergoes facile [4 + 2] cycloaddition to the 1,4-diketone derivative of **2.16**. Wasserman, H. H.; Doumaux, A. R., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 4611. The present example is remarkable in view of the poor dienophilic reactivity of isolated double bonds and the poor dienic character of furans.

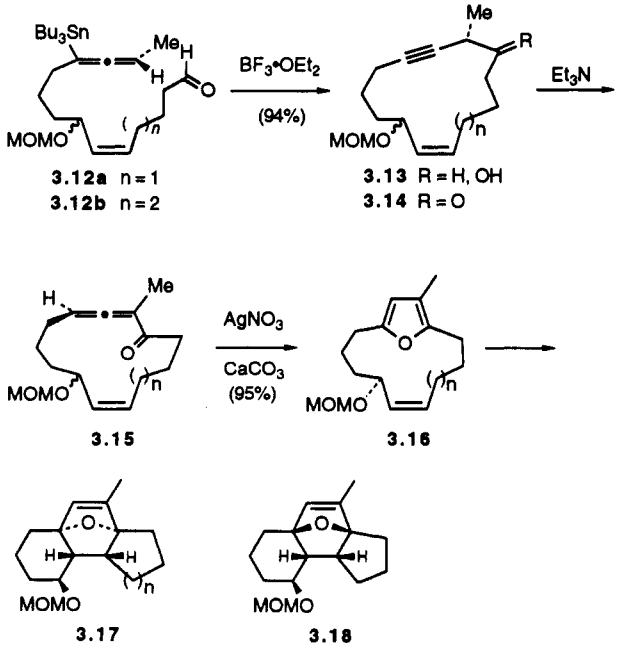
(17) The program MACROMODEL V3.1X was employed for these calculations. Conformational searching through the Monte Carlo subroutine was used to find the global minimum structure. After 200 steps, conformation 1 (lowest energy, 99.36 kJ) was found nine times and conformation 2 (next lowest energy, 107.0 kJ) was found six times. Conformation 2 has an exo arrangement of the vinylic Hs. The furan/C=C distances in this conformer are ~3.6 Å. For a description of the MACROMODEL program, see: Mohamidi, F.; Richard, N.; Guida, W.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. *J. Comput. Chem.* **1990**, *11*, 440. For a discussion of global minimum searching methods, see: Saunders, M.; Houk, K. N.; Wu, Y.-D.; Still, W. C.; Lipton, M.; Chang, G.; Guida, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 1419.

(18) For recent theoretical calculations on transition state parameters in Diels–Alder additions see: Houk, K. N.; Loncharich, R. J.; Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 9172. A distance of 2.21 Å is calculated for the forming C–C bonds in the TS for the addition of ethylene to 1,3-butadiene.

(19) Cf. Sternbach, D. D.; Rossana, D. M. *Tetrahedron Lett.* **1985**, *26*, 591.

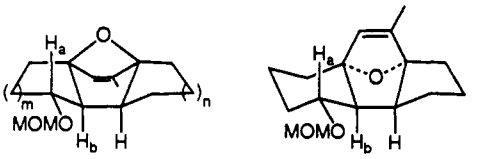


mopropargylic alcohols **3.13a** and **3.13b**, respectively, as inseparable mixtures of diastereomers. Oxidation followed by brief treatment with Et_3N led to the allenones **3.15a** and **b**. Subsequent treatment with $AgNO_3$ and $CaCO_3$ in aqueous acetone for 3 h at room temperature gave the respective furanocycles **3.16a** and **b** in 95% yield. Upon heating in toluene at 80 °C for 3 h the former cyclized to a 95:5 mixture of diastereomeric tetracyclic ethers **3.17a** and **3.18** in 98% yield. Under these conditions **3.16b** was converted to **3.17b** in 96% yield.



Assignment of stereochemistry to the transannular Diels–Alder adducts **1.22**, **3.17a/b**, and **3.18** is based upon

Table I. ^{1}H NMR Data for Transannular Diels–Alder Adducts



1.22 m = n = 1
3.17a m = 2, n = 1
3.17b m = n = 2

3.18

entry	adduct	δ Ha (ppm)	Ha/O[a] (Å)	J_{ab} (Hz)
1	**1.22**	4.1	2.93	6.7
2	**3.17a**	3.6	3.21	10.0
3	**3.18**	3.0		11.2
4	**3.17b**	3.5	3.47	11.2

[a] Calculated distance.

^{1}H NMR chemical shifts and coupling constants as summarized in Table I. Of particular significance is the distinctive chemical shift difference in the carbinyl proton (Ha) for the diastereomers **3.17a** and **3.18** (entries 2 and 3). In adduct **3.18** this proton is significantly shielded by the bridging double bond. On the other hand, the close proximity (calculated)[17] of the carbinyl proton (Ha) of **1.22** and the bridging oxygen causes appreciable deshielding. In the cyclohexyl systems **3.17a**, **3.18**, and **3.17b** the OMOM grouping assumes an equatorial orientation as indicated by the magnitude of J_{ab}.

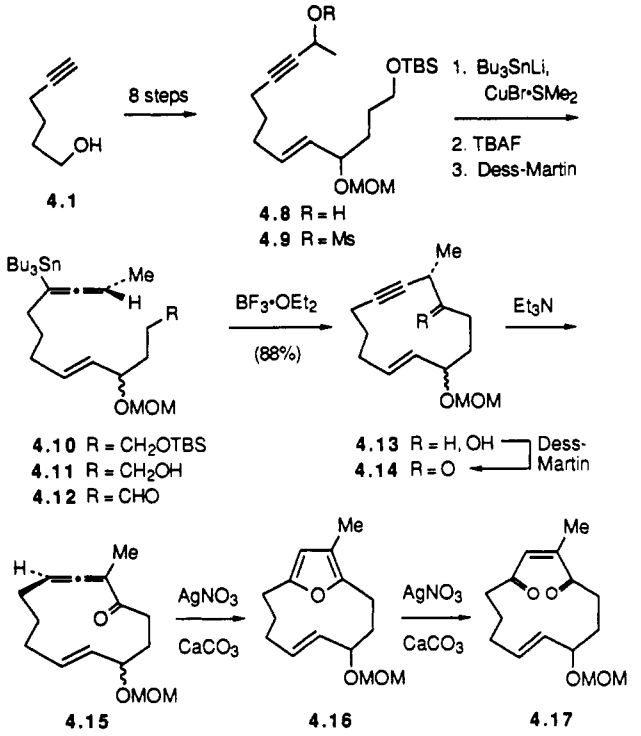
The stereoselectivity of the Diels–Alder reaction is noteworthy. Adducts **1.22**, **3.17a**, and **3.17b** arise through sterically favored transition states in which the OMOM substituent maintains an equatorial-like orientation and the double bond aligns parallel to the furan ring with the two vinylic H's directed under the ring.[20] Support for this arrangement in the ground state is found in the ^{1}H NMR spectra of the furanocycles **1.21** and **2.15**. The vinylic protons of these compounds are seen at 4.88 and 4.57 ppm, respectively, indicative of strong π shielding by the furan ring. In the homologous furanocycles these protons are relatively unshielded (5.62, 5.10 ppm for **3.16a** and 5.56, 5.23 ppm for **3.16b**).

Turning once again to the synthesis of prototypes for the kallolides, we prepared the allenyl aldehyde **4.12** in which the connecting tether incorporates an (*E*) double bond.[15] Cyclization, as before, proceeded in excellent yield to afford the homopropargylic alcohol **4.13** as an *apparent* 1:1 mixture of diastereoisomers. Oxidation with the Dess–Martin reagent yielded the propargylic ketone **4.14**, a 2:1 mixture of stereoisomers. Upon brief treatment with Et_3N ketone **4.14** isomerized to allenone **4.15** quantitatively. Cyclization to furan **4.16** proceeded in 91% yield following exposure to $AgNO_3$–$CaCO_3$ in aqueous acetone at room temperature for 4 h.

Interestingly, when propargylic ketone **4.14** was similarly treated a polar product, dione **4.17**, was slowly formed over a period of several days. In this case an excess of $AgNO_3$ was required to effect complete conversion. As expected, dione **4.17** could also be prepared through treatment of furan **4.16** with $AgNO_3$.[21] Although we did not force the issue, furan **4.16** showed no tendency to undergo trans-

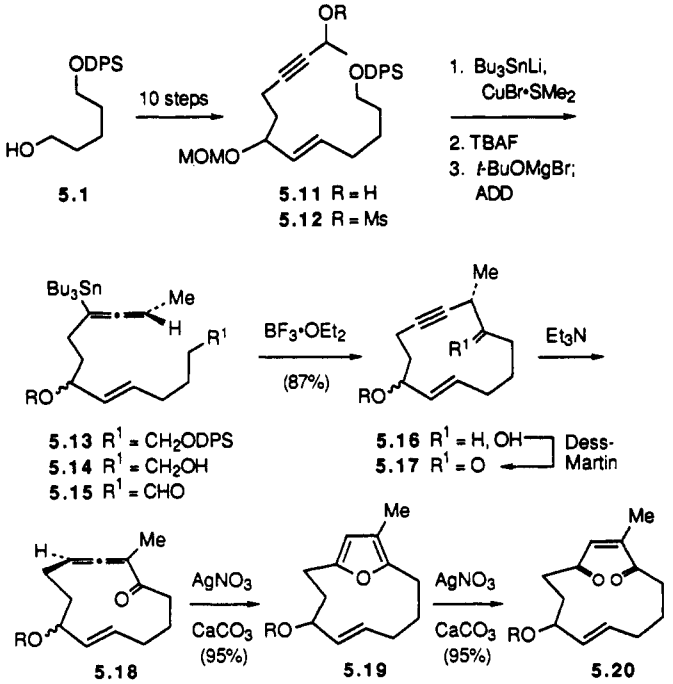
(20) This conformer was favored by ca. 7 kJ over the corresponding exo arrangement according to molecular mechanics calculations on **1.21** (OMe instead of OMOM) and **2.15**. See ref 17 for a description of the calculation protocol.

(21) A recent report describes an analogous conversion of a strained bridged furan to an ene dione upon exposure to air. Eberbach, W.; Laber, N. *Tetrahedron Lett.* **1992**, *33*, 57.

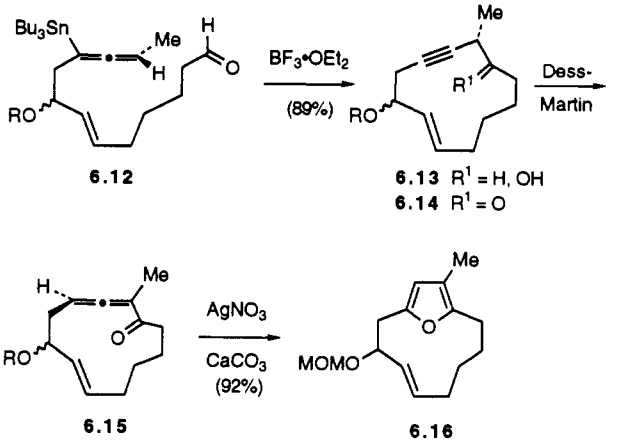


annular Diels–Alder cyclization on prolonged storage. This is to be expected as the double bond in **4.16** is not favorably arranged for cycloaddition to the furan ring. Furthermore, the product of such an addition would contain a strained trans-fused bicyclo [3.3.0] subunit. The apparent strain in the furan ring of **4.16** is evidenced by its oxidation to dione **4.17** at room temperature by the mild oxidant $AgNO_3$.

The allenyl aldehyde **5.15**, an allylic isomer of **4.12**, was subjected to a parallel sequence of reactions affording bridged furan **5.19** in high overall yield.[15] Like **4.16**, furan **5.19** was converted to dione **5.20** upon treatment with $AgNO_3$–$CaCO_3$.



The final system examined, allenyl aldehyde **6.12**, was prepared from the mono DPS ether of 1,6-hexanediol by a route analogous to that employed for **5.15**. Cyclization led to the bridged furan **6.16**, a skeletal analogue of kallolides **A** and **B**. We did not examine the possible oxidation of furan **6.16** with excess $AgNO_3$ to an ene dione analogue of kallolide C.



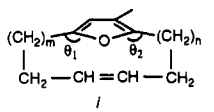
It can thus be seen that intraannular cyclization represents a viable new route to 2,5-bridged furanocycles. It is noteworthy that even the highly strained pseudopterane skeleton can be efficiently accessed through this methodology.[22] It is also clear that the intramolecular S_E' addition of allenylstannanes represents an important new method for macrocyclization.[23] While the present applications show relative modest stereoselectivity our experience with analogous intermolecular additions suggests that chirality matching could be employed in these and more complex examples.[12b] If so, the methodology could be applied to other types of macrocyclic systems with multiple stereo centers. Future studies will address this and related issues.[24]

Experimental Section[25]

(*Z*)-4-(Tributylstannyl)-7-(methoxymethoxy)-13-[(*tert*-butyldimethylsilyl)oxy]-2,3,8-tridecatriene (1.14). To a mixture of 250 mg (0.65 mmol) of alcohol **1.12** and 0.18 mL (1.30 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added 0.08 mL (0.97 mmol) of methanesulfonyl chloride at −78 °C. The resulting mixture was stirred at −78 °C for 1 h then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure yielded the crude mesylate **1.13**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.20 mL (1.37 mmol) of diisopropylamine in 6 mL of THF was added 0.81 mL (1.30 mmol) of 1.6 M *n*-BuLi in hexane at 0 °C. After 30 min, 0.33 mL (1.24 mmol) of Bu_3SnH was added. After being stirred for 20 min, the mixture was cooled to −50 °C and 255 mg (1.24 mmol) of CuBr·SMe_2 was added in

(22) A significant portion of the total strain energy of these furanocycles results from bending of the furan ring as shown by the following calculations (MACROMODEL):[17]



m	*n*	stereochem	θ_1, deg	θ_2, deg	*E*, kJ (tot energy)	bnd, kJ (bending energy)
2	2	*Z*	168.8	168.7	79.9	50.0
2	2	*E*	168.6	164.0	67.5	41.2
1	3	*E*	164.1	166.7	83.2	40.2

(23) Tius has shown that acetylide anions undergo intramolecular addition to aldehydes to afford 14-membered cembranoid propargylic alcohols. Tius, M.; Culligham, J. M. *Tetrahedron Lett.* **1989**, *30*, 3749.

(24) For a preliminary account of this work see: Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 6264.

(25) For a description of experimental protocols, see: Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 4913.

one portion. The above mesylate in 5 mL of THF was added 30 min later. The resulting mixture was stirred for 30 min with warming from −50 °C to −20 °C and allowed to stand at −20 °C for 3 h, and then it was poured into 10% ammonium hydroxide and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane–ether (30:1)) to yield 376 mg (88%) of allenylstannane **1.14**: IR (film) ν 1933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.57 (m, 1 H, vinyl H), 5.18 (t, J = 9.2 Hz, 1 H, vinyl H), 4.64, 4.47 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, vinyl H-2), 4.35 (m, 1 H, MOMOCH), 3.56 (t, J = 6.2 Hz, 2 H, $TBSOCH_2$), 3.34 (s, 3 H, CH_3O), 2.10 (m, 4 H, 2 allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 33 H, Bu_3Sn and $(CH_2)_3$), 0.87 (s, 9 H, t-Bu), 0.02 (s, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{29}H_{57}O_3Sn$ (M − Bu) 601.3099, found 601.3096. Anal. Calcd for $C_{33}H_{66}O_3SiSn$: C, 60.27; H, 10.11. Found: C, 60.34; H, 10.14.

(*Z*)-7-(Methoxymethoxy)-10-(tributylstannyl)-5,10,11-tridecatrien-1-ol (1.15). To a solution of 273 mg (0.41 mmol) of TBS ether **1.14** in 4 mL of aqueous THF was added 1.23 mL (1.23 mmol) of 1.0 M Bu_4NF in THF. The resulting mixture was stirred at room temperature for 4 h, and then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 203 mg (91%) of alcohol **1.15**: IR (film) ν 3425, 1933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.58 (m, 1 H, vinyl H), 5.18 (t, J = 9.2 Hz, 1 H, vinyl H), 4.69, 4.47 (ABq, J = 6.9 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, vinyl H-2), 4.40 (m, 1 H, MOMOCH), 3.59 (m, 2 H, $HOCH_2$), 3.35 (s, 3 H, CH_3O), 2.20–1.90 (m, 4 H, 2 allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 33 H, Bu_3Sn and $(CH_2)_3$). Anal. Calcd for $C_{27}H_{52}O_3Sn$: C, 59.68; H, 9.64. Found: C, 59.59; H, 9.65.

(*Z*)-7-(Methoxymethoxy)-10-(tributylstannyl)-5,10,11-tridecatrienal (1.16). To a solution of 170 mg (0.31 mmol) of alcohol **1.15** and 0.16 mL (0.93 mmol) of $(i\text{-}Pr)_2NEt$ in 4 mL of CH_2Cl_2 was added 199 mg (0.47 mmol) of Dess–Martin reagent in one portion. The reaction mixture was stirred at room temperature for 40 min, and then it was diluted with ether and washed with dilute NaOH. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (5:1)) to yield 109 mg (65%) of aldehyde **1.16** and 34 mg (20%) of recovered starting material: IR (film) ν 2720, 1933, 1729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.6 Hz, 1 H, CHO), 5.55 (m, 1 H, vinyl H), 5.25 (t, J = 9.2 Hz, 1 H, vinyl H), 4.64, 4.47 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.58 (m, 1 H, vinyl H-2), 4.46 (m, 1 H, MOMOCH), 3.33 (s, 3 H, CH_3O), 2.44 (dt, J = 1.6, 7.2 Hz, 2 H, CH_2CHO), 2.20–2.00 (m, 4 H, 2 allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 31 H, Bu_3Sn and $(CH_2)_2$); HRMS calcd for $C_{23}H_{41}O_3Sn$ 481.2073, found 481.2070.

(*Z*)-2-Methyl-7-(methoxymethoxy)-8-cyclododecen-3-yn-1-ol (1.17). To a solution of 0.03 mL (0.33 mmol) of $BF_3{\cdot}Et_2O$ in 15 mL of CH_2Cl_2 was added dropwise a solution of 60 mg (0.11 mmol) of allenylstannane aldehyde **1.16** in 5 mL of CH_2Cl_2 at −78 °C over 10 min. The mixture was stirred at −78 °C for 30 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 26 mg (93%) of alcohol **1.17** as a 1:1:1 separable mixture of three diastereomers: IR (film) ν for mixture 3448, 2239, 1643 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ for first fraction 5.68 (dt, J = 5.7, 10.5 Hz, 1 H, vinyl H), 5.29 (t, J = 10.5, 1 H, vinyl H), 4.79 (m, 1 H, MOMOCH), 4.65, 4.45 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.66 (m, 1 H, HOC*H*), 3.38 (s, 3 H, CH_3O), 2.80–2.20 (m, 4 H, allylic CH_2 and propargylic CH_2), 2.07–1.20 (m, 9 H, 2 $(CH_2)_2$ and CH_3CH), 1.19 (d, J = 7.1 Hz, 3 H, CH_3CH); for second fraction 5.68 (m, 1 H, vinyl H), 5.27 (t, J = 10.5 Hz, 1 H, vinyl H), 4.78 (m, 1 H, MOMOCH), 4.65, 4.46 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.44 (m, 1 H, HOC*H*), 3.37 (s, 3 H, CH_3O), 2.68–2.50 (m, 2 H, allylic CH_2), 2.30–2.18 (m, 3 H, propargylic CH_2 and CH_3CH), 2.03–1.20 (m, 8 H, 2 $(CH_2)_2$), 1.15 (d, J = 6.9 Hz, 3 H, CH_3CH); for third fraction 5.62 (dt, J = 4.4, 10.5 Hz, 1 H, vinyl H), 5.27 (t, J = 10.5 Hz, 1 H, vinyl H), 4.72–4.69 (m, 1 H, MOMOCH), 4.65, 4.46 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 3.92 (m, 1 H, HOC*H*), 3.36 (s, 3 H, CH_3O), 2.67–2.55 (m, 2 H, allylic CH_2), 2.28–2.20 (m, 3 H, propargylic CH_2 and CH_3CH), 2.03–1.20 (m, 8 H, 2 $(CH_2)_2$), 1.07 (d, J = 7.1 Hz, 3 H, CH_3CH); HRMS calcd for $C_{15}H_{24}O_3$ 252.1725, found 252.1724. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.46; H, 9.62.

(*Z*)-2-Methyl-7-(methoxymethoxy)-2,3,8-cyclododecatrienone (1.19) and (*Z*)-2-Methyl-7-(methoxymethoxy)-8-cyclododecen-3-ynone (1.18). A solution of 26 mg (0.10 mmol) of alcohol **1.17** in 1 mL of CH_2Cl_2 was treated with 66 mg (0.15 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 24 mg (92%) of a 3:1 mixture of allenyl ketone **1.18** and propargylic ketone **1.19**: IR (film) ν for mixture 1946, 1725, 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ for allenyl ketone 5.69 (m, 1 H, vinyl H), 5.56 (m, 1 H, vinyl H-2), 5.30 (t, J = 10.5 Hz, 1 H, vinyl H), 4.58 (m, 1 H, MOMCH), 4.55, 4.40 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 3.29 (s, 3 H, CH_3O), 2.35–1.40 (m, 10 H, $(CH_2)_5$), 1.80 (d, J = 2.9 Hz, 3 H, vinyl CH_3). The peaks of propargylic ketone could be seen at: δ 3.32 and 3.31 (s, 3 H, CH_3O), 3.30–3.15 (m, 1 H, CH_3CH), 1.27 and 1.20 (d, J = 6.9 Hz, 3 H, CH_3CH); HRMS calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1569.

Cyclization of Ketone 1.19 with $AgNO_3$. Furanocycle 1.21 and Tetracycle 1.22. A mixture of 23 mg (0.092 mmol) of the 3:1 mixture of **1.19** and **1.18**, 3 mg (0.018 mmol) of $AgNO_3$, and 7 mg (0.070 mmol) of $CaCO_3$ in 2 mL of aqueous acetone was stirred at room temperature in the dark for 12 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 3.5 mg (15%) of furanocycle **1.21**: IR (film) ν 1571 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.66 (s, 1 H, Ar-H), 4.88 (dt, J = 2.7, 11.1 Hz, 1 H, vinyl H), 4.61 (dt, J = 2.7, 9.4 Hz, 1 H, MOMOCH), 4.61, 4.41 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 4.57 (d, J = 11.1 Hz, 1 H, vinyl H), 3.35 (s, 3 H, CH_3O), 2.69–2.58 (m, 2 H), 2.41–2.26 (m, 2 H), 2.14–2.10 (m, 1 H), 2.04–2.00 (m, 2 H), 1.93–1.86 (m, 1 H), 1.82 (s, 3 H, vinyl CH_3), 1.55–1.40 (m, 2 H). Continued elution afforded 16.5 mg (71%) of tetracycle **1.22**: ^1H NMR (500 MHz, $CDCl_3$) δ 5.90 (d, J = 1.8 Hz, 1 H, vinyl H), 4.63, 4.60 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.08 (q, J = 6.8 Hz, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.33–2.26 (m, 1 H), 2.19–2.13 (m, 1 H), 2.01–1.95 (m, 2 H), 1.93–1.73 (m, 6 H), 1.78 (d, J = 1.8 Hz, 3 H, vinyl CH_3), 1.55–1.45 (m, 2 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 147.9, 131.1, 101.2, 97.5, 95.5, 77.9, 56.1, 55.3, 47.5, 33.5, 27.6, 26.7, 26.4, 26.0, 12.6; HRMS calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1569. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.89; H, 8.87. The furanocycle **1.21** in $CDCl_3$ was completely transformed into tricycle **1.22** upon standing at room temperature overnight.

(*Z*)-10-(Tributylstannyl)-5,10,11-tridecatrien-1-ol (2.10). To a mixture of 730 mg (1.63 mmol) of alcohol **2.7** and 0.45 mL (3.26 mmol) of Et_3N in 10 mL of CH_2Cl_2 was added 0.21 mL (2.44 mmol) of methanesulfonyl chloride at −78 °C. The resulting mixture was stirred at −78 °C for 1 h and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure yielded the crude mesylate **2.8**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.50 mL (3.42 mmol) of diisopropylamine in 10 mL of THF was added 1.25 mL (3.26 mmol) of 2.6 M n-BuLi in hexane at 0 °C. After 30 min, 0.83 mL (3.10 mmol) of Bu_3SnH was added. After being stirred for 20 min, the mixture was cooled to −50 °C and 638 mg (3.10 mmol) of $CuBr{\cdot}SMe_2$ was added in one portion. The above mesylate in 5 mL of THF was added 30 min later. The resulting mixture was stirred for 30 min with warming from −50 °C to −20 °C and allowed to stand at −20 °C for 1 h, and then it was poured into 10% ammonium hydroxide and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was directly used for the deprotecting step without purification.

To a solution of the above crude TBS–ether **2.9** in 10 mL of aqueous THF was added 3.45 mL (3.45 mmol) of 1.0 M Bu_4NF in THF. The resulting mixture was stirred at room temperature for 2 h, and then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$,

and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 606 mg (77%) of alcohol **2.10**: IR (film) ν 3333, 1933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.35 (m, 2 H, 2 vinyl H), 4.54 (m, 1 H, vinyl H-2), 3.63 (q, J = 5.5 Hz, 2 H, $HOCH_2$), 2.03 (m, 6 H, 3 vinyl CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.53–0.85 (m, 33 H, Bu_3Sn and $(CH_2)_3$); HRMS calcd for $C_{21}H_{39}OSn$ (M – Bu) 423.2018, found 423.2004. Anal. Calcd for $C_{25}H_{48}OSn$: C, 62.13; H, 10.01. Found: C, 62.22; H, 10.03.

(*Z*)-10-(Tributylstannyl)-5,10,11-tridecatrienal (2.11). To a solution of 0.06 mL (0.66 mmol) of *t*-BuOH in 3 mL of THF was added 0.31 mL (0.62 mmol) of 2.0 M EtMgBr in hexane at 0 °C, and then 200 mg (0.41 mmol) of alcohol **2.10** in 2 mL of THF was added. After 5 min, 124 mg (0.49 mmol) of ADD was added in one portion. The resulting mixture was stirred at 0 °C for 30 min, and then it was quenched with brine and extracted with ether. The extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 178 mg (89%) of aldehyde **2.11**: IR (film) ν 1930, 1715 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.6 Hz, 1 H, CHO), 5.40–5.27 (m, 2 H, 2 vinyl H), 4.56 (m, 1 H, vinyl H-2), 2.40 (dt, J = 1.6, 7.4 Hz, 2 H, CH_2CHO), 2.08–2.01 (m, 6 H, 3 vinyl CH_2), 1.58 (d, J = 6.8 Hz, 3 H, vinyl CH_3), 1.70–0.86 (m, 31 H, Bu_3Sn and $(CH_2)_2$); HRMS calcd for $C_{21}H_{37}OSn$ (M – Bu) 421.1862, found 421.1849.

(*Z*)-2-Methyl-8-cyclododecen-3-yn-1-ol (2.12). To a solution of 0.09 mL (0.92 mmol) of $BF_3{\cdot}Et_2O$ in 50 mL of CH_2Cl_2 was added dropwise a solution of 147 mg (0.31 mmol) of allenylstannane aldehyde **2.11** in 15 mL of CH_2Cl_2 at −78 °C over 30 min. The mixture was stirred at −78 °C for 5 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (2:1)) to yield 55 mg (94%) of alcohol **2.12** as a 1:1 inseparable mixture of diastereomers according to GC analysis: IR (film) ν for mixture 3440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.28 (m, 2 H, 2 vinyl H), 3.84 (m, 1 H, HOC*H*), 3.45 (m, 1 H, CH_3CH), 2.66–1.90 (m, 6 H, 2 vinyl CH_2 and propargylic CH_2), 1.67–1.15 (m, 6 H, 3 CH_2), 1.20 (d, J = 6.8 Hz, 3 H, CH_3CH). The peak of the diastereomer could be seen at: δ 1.08 (d, J = 7.1 Hz, 3 H, CH_3CH); HRMS calcd for $C_{13}H_{20}O$ 192.1514, found 192.1507. Anal. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 79.58; H, 10.23.

(*Z*)-2-Methyl-2,3,8-cyclododecatrienone (2.14). A solution of 50 mg (0.26 mmol) of alcohol **2.12** in 3 mL of CH_2Cl_2 was treated with 165 mg (0.39 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was dissolved in 2 mL of CH_2Cl_2 and treated with 0.2 mL of Et_3N. After being stirred at room temperature for 1 h, the mixture was concentrated and the residue was chromatographed on silica gel (hexane–ether (3:1)) to afford 45 mg (90%) of allenone **2.14**: IR (film) ν 1945, 1675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.43 (m, 1 H, vinyl H), 5.34 (m, 2 H, 2 vinyl H), 3.24 (m, 1 H, 1 $COCH_2$), 2.35–1.95 (m, 7 H, 3 vinyl CH_2 and 1 $COCH_2$), 1.80–1.54 (m, 4 H, 2 CH_2), 1.75 (d, J = 2.8 Hz, 3 H, vinyl CH_3); HRMS calcd for $C_{13}H_{18}O$ 190.1358; found 190.1363. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.02; H, 9.49.

Cyclization of Allenone 2.14 with $AgNO_3$. Furanocycle 2.15 and Tetracycle 2.16. A mixture of 40 mg (0.21 mmol) of allenone **2.14**, 7 mg (0.042 mmol) of $AgNO_3$, and 17 mg (0.17 mmol) of $CaCO_3$ in 2 mL of aqueous acetone was stirred at room temperature in the dark for 3 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 15 mg (38%) of furanocycle **2.15**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.63 (s, 1 H, ArH), 4.60–4.54 (m, 2 H, 2 vinyl H), 2.47 (m, 4 H, 2 allylic CH_2), 2.08 (m, 4 H, 2 $ArCH_2$), 1.83 (s, 3 H, $ArCH_3$), 1.78 (m, 4 H, $(CH_2)_2$). Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.98; H, 9.52.

The furanocycle **2.15** was quantitatively converted to Diels–Alder adduct **2.16** on standing for 52 h in $CHCl_3$ at room temperature: ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (q, J = 1.7 Hz, 1 H, ArH), 1.78 (d, J = 1.7 Hz, 3 H, $ArCH_3$), 1.93–1.50 (m, 14 H, $(CH_2)_6$) and 2 CH); HRMS calcd for $C_{13}H_{18}O$ 190.1358, found 190.1357. Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.15; H, 9.54.

(*Z*)-7-(Methoxymethoxy)-11-(tributylstannyl)-5,11,12-tetradecatrienal (3.12a). To a solution of 0.13 mL (1.32 mmol) of *t*-BuOH in 7 mL of THF was added 0.63 mL (1.24 mmol) of 2.0 M EtMgBr in hexane at 0 °C. Then 460 mg (0.82 mmol) of alcohol **3.11a** in 3 mL of THF was added. After 5 min, 251 mg (1.00 mmol) of ADD was added in one portion. The resulting mixture was stirred at 0 °C for 30 min, and then it was quenched with brine and extracted with ether. The extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 417 mg (91%) of aldehyde **3.12a**: IR (film) ν 1931, 1729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.6 Hz, 1 H, CHO), 5.51 (m, 1 H, vinyl H-5), 5.25 (t, J = 9.4 Hz, 1 H, vinyl H-6), 4.68, 4.45 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.55 (m, 1 H, vinyl H-13), 4.33 (m, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.43 (dt, J = 1.6, 8.9 Hz, 2 H, CH_2CHO), 2.12–2.05 (m, 4 H, 2 vinyl CH_2), 1.56 (d, J = 6.8 Hz, 3 H, $CHCH_3$), 1.72–0.85 (m, 33 H, Bu_3Sn and $(CH_2)_3$); HRMS calcd for $C_{24}H_{43}O_3Sn$ (M – Bu) 495.2230, found 495.2239.

(*Z*)-2-Methyl-9-cyclotridecen-3-yn-1-ol (3.13a). To a solution of 0.19 mL (1.92 mmol) of $BF_3{\cdot}Et_2O$ in 80 mL of CH_2Cl_2 was added dropwise a solution of 355 mg (0.64 mmol) of allenylstannane aldehyde **3.12a** in 30 mL of CH_2Cl_2 at −78 °C over 50 min. The mixture was stirred at −78 °C for 5 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (2:1)) to yield 160 mg (94%) of alcohol **3.13a** as an inseparable mixture of diastereomers: IR (film) ν for mixture 3450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.52–5.31 (m, 2 H, 2 vinyl H), 4.65, 4.40 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.65 (m, 1 H, MOMOCH), 3.71 (m, 1 H, HOC*H*), 3.36 (s, 3 H, CH_3O), 2.66 (m, 1 H, CH_3CH), 2.35–1.00 (m, 4 H, vinyl CH_2 and propargylic CH_2), 1.80–1.23 (m, 8 H, $(CH_2)_4$), 1.10 (d, J = 7.1 Hz, 3 H, CH_3CH). Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.14; H, 9.84. Found: C, 72.13; H, 9.78.

(*Z*)-2-Methyl-2,3,9-cyclotridecatrienone (3.15a). A solution of 145 mg (0.54 mmol) of alcohol **3.13a** in 5 mL of CH_2Cl_2 was treated with 462 mg (1.09 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was dissolved in 5 mL of CH_2Cl_2 and treated with 1.0 mL of Et_3N. After being stirred at room temperature for 24 h, the mixture was concentrated and the residue was chromatographed on silica gel (hexane–ether (3:1)) to afford 139 mg (92%) of allenone **3.15a** as a 4:1 mixture of diastereomers according to ^1HNMR analysis: IR (film) ν 1944, 1674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.53–5.20 (m, 3 H, 3 vinyl H), 4.65, 4.46 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.34 (m, 1 H, MOMOCH), 3.33 (s, 3 H, CH_3O), 3.03 (m, 1 H, 1 $COCH_2$), 2.35–1.60 (m, 11 H, 2 vinyl CH_2, 1 $COCH_2$ and 3 CH_2), 1.83 (d, J = 2.8 Hz, 3 H, vinyl CH_3). The peaks of the diastereomer could be seen at: δ 4.68, 4.46 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.46 (m, 1 H, MOMOCH), 3.38 (s, 3 H, CH_3O), 2.82 (m, 1 H, 1 $COCH_2$) and 1.78 (d, J = 2.8 Hz, 3 H, vinyl CH_3). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.78; H, 9.16.

Cyclization of Allenone 3.15a by $AgNO_3$. Furanocycle 3.16a. A mixture of 110 mg (0.42 mmol) of allenone **3.15a**, 21 mg (0.12 mmol) of $AgNO_3$, and 33 mg (0.33 mmol) of $CaCO_3$ in 5 mL of aqueous acetone was stirred at room temperature in the dark for 3 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 104 mg (95%) of furanocycle **3.16a**: IR (film) ν 2927, 1446, 1148, 1044 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (s, 1 H, ArH), 5.62 (dt, J = 4.9, 10.0 Hz, 1 H, vinyl H), 5.10 (t, J = 10.0 Hz, 1 H, vinyl H), 4.50, 4.34 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.66 (m, 1 H, MOMOCH), 3.27 (s, 3 H, CH_3O), 2.60–2.50 (m, 4 H, 2 $ArCH_2$), 2.19–1.53 (m, 8 H, $(CH_2)_4$), 1.89 (s, 3 H, $ArCH_3$). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.59; H, 9.16.

Diels–Alder Cyclization of Furanocycle 3.16a. Tetracycles 3.17a and 3.18. A solution of 30 mg (0.11 mmoL) of furanocycle **3.16a** in 1 mL of toluene was heated at 80 °C for 4 h, and then it was directly subjected to chromatography on silica gel (hexane–ether (4:1)) to afford 28 mg (93%) of tetracyclic ether **3.17a**: IR (film) ν 2927, 1446, 1148, 1044 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.56 (q, J = 1.7 Hz, 1 H, vinyl H), 4.72, 4.67 (ABq, J

= 6.8 Hz, 2 H, CH_3OCH_2O), 3.52 (dt, J = 4.0, 11.2 Hz, 1 H, MOMOCH), 3.36 (s, 3 H, CH_3O), 2.25–1.23 (m, 14 H, $(CH_2)_6$ and 2 CH), 1.77 (d, J = 1.7 Hz, vinyl CH_3). Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.75; H, 9.10. Continued elution yielded 1.5 mg (5%) of diastereomer **3.18**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (q, J = 1.7 Hz, 1 H, vinyl H), 4.64, 4.57 (ABq, J = 6.9 Hz, 2 H, CH_3OCH_2O), 3.31 (s, 3 H, CH_3O), 2.97 (dt, J = 4.0, 11.2 Hz, 1 H, MOMOCH), 2.15–1.23 (m, 14 H, $(CH_2)_6$ and 2 CH), 1.81 (d, J = 1.7 Hz, vinyl CH_3).

(*Z*)-8-(Methoxymethoxy)-12-(tributylstannyl)-6,12,13-pentadecatrienal (3.12b). To a solution of 0.06 mL (0.66 mmol) of *t*-BuOH in 4 mL of THF was added 0.31 mL (0.62 mmol) of 2.0 M EtMgBr in hexane at 0 °C, and then 200 mg (0.36 mmol) of alcohol **3.11b** in 3 mL of THF was added. After 5 min, 109 mg (0.43 mmol) of ADD was added in one portion. The resulting mixture was stirred at 0 °C for 30 min, and then it was quenched with brine and extracted with ether. The extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 181 mg (91%) of aldehyde **3.12b**: IR (film) ν 2714, 1931, 1729 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, J = 1.6 Hz, 1 H, CHO), 5.53 (m, 1 H, vinyl H-6), 5.21 (t, J = 9.4 Hz, 1 H, vinyl H-7), 4.64, 4.46 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.54 (m, 1 H, vinyl H-14), 4.35 (m, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.42 (dt, J = 1.6, 7.6 Hz, 2 H, CH_2CHO), 2.12–2.05 (m, 4 H, 2 vinyl CH_2), 1.56 (d, J = 6.8 Hz, 3 H, $CHCH_3$), 1.72–0.85 (m, 35 H, Bu_3Sn and $(CH_2)_4$); HRMS calcd for $C_{25}H_{45}O_3Sn$ (M – Bu) 509.2386, found 509.2379.

(*Z*)-8-(Methoxymethoxy)-2-methyl-9-cyclotetradecen-3-yn-1-ol (3.13b). To a solution of 0.08 mL (0.84 mmol) of $BF_3{\cdot}Et_2O$ in 40 mL of CH_2Cl_2 was added dropwise a solution of 160 mg (0.28 mmol) of allenylstannane aldehyde **3.12b** in 15 mL of CH_2Cl_2 at –78 °C over 20 min. The mixture was stirred at –78 °C for 5 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (2:1)) to yield 74 mg (94%) of alcohol **3.13b** as an inseparable mixture of diastereomers: IR (film) ν for mixture 3443 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.53–5.31 (m, 2 H, 2 vinyl H), 4.66, 4.45 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.46 (m, 1 H, MOMOCH), 3.58 (m, 1 H, HOC*H*), 3.35 (s, 3 H, CH_3O), 2.66 (m, 1 H, CH_3CH), 2.40–1.20 (m, 14 H, $(CH_2)_7$), 1.14 (d, J = 7.1 Hz, 3 H, CH_3CH); HRMS calcd for $C_{15}H_{23}O_2$ (M – MOM) 235.1698, found 235.1691. Anal. Calcd for $C_{17}H_{27}O_3$: C, 72.82; H, 10.06. Found: C, 72.95; H, 10.05.

(*Z*)-2-Methyl-2,3,9-cyclotetradecadienone (3.15b). A solution of 70 mg (0.25 mmol) of alcohol **3.13b** in 5 mL of CH_2Cl_2 was treated with 159 mg (0.37 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was dissolved in 5 mL of CH_2Cl_2 and treated with 1.0 mL of Et_3N. After being stirred at room temperature for 24 h, the mixture was concentrated and the residue was chromatographed on silica gel (hexane–ether (3:1)) to afford 68 mg (97%) of allenone **3.15b** as a 1:1 mixture of diastereomers according to ^{1}NMR analysis: IR (film) ν 1946, 1679 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58–5.27 (m, 3 H, 3 vinyl H), 4.67, 4.43 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.42 (m, 1 H, MOMOCH), 3.38 (s, 3 H, CH_3O), 3.25 (m, 1 H, 1 $COCH_2$), 2.35–1.40 (m, 13 H, 2 vinyl CH_2, 1 $COCH_2$ and 4 CH_2), 1.76 (d, J = 2.6 Hz, 3 H, vinyl CH_3). The peaks of the diastereomer could be seen at: δ 4.64, 4.47 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 3.36 (s, 3 H, CH_3O), 3.03 (m, 1 H, 1 $COCH_2$) and 1.76 (d, J = 2.8 Hz, 3 H, vinyl CH_3); HRMS calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1882.

Cyclization of Allenone 3.15b with $AgNO_3$. Furanocycle 3.16b. A mixture of 60 mg (0.22 mmol) of allenone **3.15b**, 11 mg (0.065 mmol) of $AgNO_3$, and 20 mg (0.20 mmol) of $CaCO_3$ in 3 mL of aqueous acetone was stirred at room temperature in the dark for 3 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 57 mg (95%) of furanocycle **3.16b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80 (s, 1 H, ArH), 5.56 (dt, J = 5.4, 10.9 Hz, 1 H, vinyl H), 5.23 (t, J = 10.9 Hz, 1 H, vinyl H), 4.70 (m, 1 H, MOMOCH), 4.68, 4.50 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 3.39 (s, 3 H, CH_3O), 2.71–2.57 (m, 5 H, 2 $ArCH_2$ and allylic H), 1.89–1.00 (m, 9 H, $(CH_2)_4$ and allylic H), 1.89 (s, 3 H, $ArCH_3$); HRMS calcd for $C_{17}H_{26}O_3$ 278.1882, found 278.1888. Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 72.71; H, 9.27.

Diels–Alder Cyclization of Furanocycle 3.16b. Tetracycle 3.17b. A solution of 50 mg (0.18 mmoL) of furanocycle **3.16b** in 1 mL of toluene was heated at 80 °C for 4 h, and then it was directly subjected to chromatography on silica gel (hexane–ether (4:1)) to afford 48 mg (96%) of tetracyclic ether **3.17b** as the sole product: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (q, J = 1.7 Hz, 1 H, vinyl H), 4.69 (s, 2 H, CH_3OCH_2O), 3.60 (dt, J = 4.0, 11.2 Hz, 1 H, MOMOCH), 3.35 (s, 3 H, CH_3O), 2.25–1.15 (m, 16 H, $(CH_2)_7$ and 2 CH), 1.66 (d, J = 1.7 Hz, vinyl CH_3). Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.18; H, 9.40.

(*E*)-4-(Tributylstannyl)-9-(methoxymethoxy)-13-[(*tert*-butyldimethylsilyl)oxy]-2,3,8-tridecatriene (4.10). To a mixture of 700 mg (1.82 mmol) of alcohol **4.8** and 0.51 mL (3.64 mmol) of Et_3N in 10 mL of CH_2Cl_2 was added 0.23 mL (2.73 mmol) of methanesulfonyl chloride at –78 °C. The resulting mixture was stirred at –78 °C for 1 h and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure yielded the crude mesylate **4.9**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.55 mL (3.82 mmol) of diisopropylamine in 10 mL of THF was added 1.30 mL (3.82 mmol) of 2.8 M *n*-BuLi in hexane at 0 °C. After 30 min, 0.93 mL (3.46 mmol) of Bu_3SnH was added. After being stirred for 20 min, the mixture was cooled to –50 °C and 711 mg (3.46 mmol) of $CuBr{\cdot}SMe_2$ was added in one portion. The above mesylate in 5 mL of THF was added 30 min later. The resulting mixture was stirred for 30 min with warming from –50 °C to –20 °C and allowed to stand at –20 °C for 3 h, and then it was poured into 10% ammonium hydroxide and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane–ether (30:1)) to yield 1.05 g (88%) of allenylstannane **4.10**: IR (film) ν 1933 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98 (dt, J = 7.0, 15.5 Hz, 1 H, vinyl H), 5.23 (dd, J = 8.0, 15.5 Hz, vinyl H), 4.70, 4.46 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, vinyl H-2), 3.94 (m, 1 H, MOMOCH), 3.60 (t, J = 6.6 Hz, 2 H, $TBSOCH_2$), 3.34 (s, 3 H, CH_3O), 2.10–2.00 (m, 4 H, Bu_3SnCCH_2 and allylic CH_2), 1.57 (d, J = 6.8 Hz, 3 H, vinyl CH_3), 1.54–0.88 (m, 33 H, Bu_3Sn and $(CH_2)_3$), 0.87 (s, 9 H, *t*-Bu), 0.03 (s, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{29}H_{57}O_3SiSn$ (M – Bu) 597.3094, found 597.3111.

(*E*)-4-(Methoxymethoxy)-10-(tributylstannyl)-5,10,11-tridecatrien-1-ol (4.11). To a solution of 925 mg (1.41 mmol) of TBS ether **4.10** in 15 mL of aqueous THF was added 4.23 mL (4.23 mmol) of 1.0 M Bu_4NF in THF. The resulting mixture was stirred at room temperature for 2 h, and then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 740 mg (96%) of alcohol **4.11**: IR (film) ν 3424, 1933 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (dt, J = 7.0, 15.5 Hz, 1 H, vinyl H), 5.27 (dd, J = 8.0, 15.5 Hz, vinyl H), 4.71, 4.48 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, allenyl H), 3.95 (m, 1 H, MOMOCH), 3.64 (q, J = 5.6 Hz, 2 H, $HOCH_2$), 3.35 (s, 3 H, CH_3O), 2.09–2.00 (m, 4 H, Bu_3SnCCH_2 and allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.71–0.85 (m, 33 H, Bu_3Sn and $(CH_2)_3$); HRMS calcd for $C_{27}H_{52}O_3Sn$ 540.2934, found 540.2934.

(*E*)-2-Methyl-9-(methoxymethoxy)-8-cyclododecen-3-yn-1-ol (4.13). To a solution of 200 mg (0.37 mmol) of alcohol **4.11** and 0.19 mL (1.11 mmol) of $(i\text{-}Pr)_2NEt$ in 4 mL of CH_2Cl_2 was added 187 mg (0.44 mmol) of Dess–Martin reagent in one portion. The reaction mixture was stirred at room temperature for 40 min, and then it was diluted with ether and washed with dilute NaOH. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (5:1)) to yield 53 mg (51%) of aldehyde **4.12** and 93 mg of recovered starting material: IR (film) ν 2718, 1933, 1728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, J = 1.6 Hz, 1 H, CHO), 5.59 (dt, J = 7.0, 15.6 Hz, 1 H, vinyl H), 5.28 (dd, J = 6.8, 15.6 Hz, vinyl H), 4.67, 4.51 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, allenyl H), 4.04 (m, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.41 (dt, J = 1.6, 8.9 Hz, 2 H, CH_2CHO), 2.41–2.12 (m, 2 H, Bu_3SnCCH_2),

2.04 (m, 2 H, allylic CH_2), 1.55 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 31 H, Bu_3Sn and $(CH_2)_2$); HRMS calcd for $C_{27}H_{50}O_3Sn$ 538.2777, found 538.2765.

To a solution of 0.03 mL (0.28 mmol) of $BF_3{\cdot}Et_2O$ in 15 mL of CH_2Cl_2 was added dropwise a solution of 51 mg (0.094 mmol) of allenylstannane aldehyde **4.12** in 5 mL of CH_2Cl_2 at −78 °C over 20 min. The mixture was stirred at −78 °C for 30 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (3:1)) to yield 21 mg (88%) of alcohol **4.13** as a 1:1 mixture of two diastereomers: IR (film) 3454 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.85–5.69 (m, 1 H, vinyl H), 5.32 (dd, J = 7.8, 15.5 Hz, 1 H, vinyl H), 4.68, 4.51 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.19 (m, 1 H, MOMOCH), 3.55 (m, 1 H, HOC*H*), 3.34 (s, 3 H, CH_3O), 2.72–1.40 (m, 11 H, allylic CH_2, propargylic CH_2, $(CH_2)_3$ and CH_3CH), 1.13 (d, J = 7.1 Hz, 3 H, CH_3CH). The peaks of the isomer could be seen at: δ 5.15 (dd, J = 9.0, 16.4 Hz, 1 H, vinyl H), 4.69, 4.49 (ABq, J = 6.8 Hz, 2 H, CH_3OCH_2O), 4.06 (m, 1 H, MOMOCH), 3.78 (m, 1 H, HOC*H*), 3.33 (s, 3 H, CH_3O) and 1.02 (d, J = 7.1 Hz, 3 H, CH_3CH). Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.35; H, 9.55.

(*E*)-2-Methyl-9-(methoxymethoxy)-8-cyclododecen-3-ynone (4.14). A solution of 19 mg (0.075 mmol) of alcohol **4.13** in 1 mL of CH_2Cl_2 was treated with 51 mg (0.12 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 18 mg (94%) of propargylic ketone **4.14** as a 2:1 mixture of diastereomers admixed with a trace amount of allenyl ketone **4.15**: IR (film) ν for mixture 1945, 1725, 1672 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ for propargylic ketone 5.78–5.68 (m, 1 H, vinyl H), 5.19 (dd, J = 9.3, 15.4 Hz, 1 H, vinyl H), 4.67, 4.49 (ABq, J = 6.4 Hz, 2 H, CH_3OCH_2O), 4.03 (m, 1 H, MOMOCH), 3.35 (s, 3 H, CH_3O), 3.26–2.90 (m, 1 H, propargylic CH), 2.40–2.18 (m, 6 H, $(CH_2)_3$), 1.75–1.60 (m, 4 H, $(CH_2)_2$), 1.16 (d, J = 6.9 Hz, 3 H, $CHCH_3$). The peaks of the diastereomer could be seen at: δ 4.66, 4.49 (ABq, J = 6.4 Hz, 2 H, CH_3OCH_2O), 3.34 (s, 3 H, CH_3O) and 1.26 (d, J = 7.2 Hz, 3 H, $CHCH_3$). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.88; H, 8.87.

(*E*)-2-Methyl-9-(methoxymethoxy)-2,3,8-cyclododecatrienone (4.15). A solution of 11 mg (0.044 mmol) of propargylic ketone **4.14** in 1 mL of CH_2Cl_2 was treated with 0.2 mL of Et_3N. After being stirred at room temperature for 4 h, the mixture was concentrated to give allenyl ketone **4.15** quantitatively: IR (film) ν 1946, 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.57–5.47 (m, 2 H, 2 vinyl H), 5.23 (dd, J = 8.3, 15.5 Hz, 1 H, vinyl H), 4.64, 4.48 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.93–3.87 (m, 1 H, MOMOCH), 3.32 (s, 3 H, CH_3O), 3.30–3.20 (m, 1 H, 1 $COCH_2$), 2.33–1.60 (m, 9 H, $(CH_2)_5$), 1.75 (d, J = 2.8 Hz, 3 H, vinyl CH_3).

Cyclization of Propargylic Ketone 4.14 with $AgNO_3$. Dione 4.17. A mixture of 17 mg (0.068 mmol) of ketone **4.14**, 30 mg (0.18 mmol) of $AgNO_3$, and 5 mg (0.05 mmol) of $CaCO_3$ in 1 mL of aqueous acetone was stirred at room temperature in the dark for 3 days, and then it was diluted with ether and washed with water. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (1:2)) to afford 6 mg (33%) of dione **4.17**: IR (film) ν 1694, 1615 cm^{-1}; ^1H NMR (500 MHz, CD_2Cl_2) δ 6.19 (q, J = 1.6 Hz, 1 H, vinyl H), 5.52–5.46 (m, 1 H, vinyl H), 5.20 (dd, J = 7.3, 15.9 Hz, 1 H, vinyl H), 4.60, 4.48 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.86 (m, 1 H, MOMOCH), 3.29 (s, 3 H, CH_3O), 2.53–2.40 (m, 4 H, 2 CH_2CO), 2.28–1.63 (m, 6 H, $(CH_2)_3$), 1.93 (d, J = 1.6 Hz, 3 H, vinyl CH_3); ^{13}C NMR (500 MHz, CD_2Cl_2) δ 208.4, 201.4, 150.7, 134.3, 131.5, 128.7, 94.2, 76.5, 55.4, 42.1, 36.3, 33.8, 28.9, 21.9, 20.3; MS m/e 266 (65, M^+), 238 (73), 221 (60), 205 (85), 192 (60), 123 (100).

Cyclization of Allenyl Ketone 4.15 with $AgNO_3$. Furanocycle 4.16. A mixture of 11 mg (0.044 mmol) of ketone **4.15**, 3 mg (0.018 mmol) of $AgNC_3$, and 7 mg (0.070 mmol) of $CaCO_3$ in 2 mL of aqueous acetone was stirred at room temperature in the dark for 4 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 10 mg (91%) of furanocycle **4.16**: IR (film) ν 1573 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.73 (s, 1 H, Ar-H), 5.03 (m, 1 H, vinyl H), 4.50 (dt, J = 8.6, 15.6 Hz, 1 H, vinyl H), 4.64, 4.43 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.78 (m, 1 H, MOMOCH), 3.32 (s, 3 H, CH_3O), 2.71 (m, 2 H, $ArCH_2$), 2.45 (m, 2 H, $ArCH_2$), 2.15–1.60 (m, 6 H, $(CH_2)_3$), 1.89 (s, 3 H, vinyl CH_3); ^{13}C NMR (500 MHz, $CDCl_3$) δ 152.6, 148.9, 134.6, 128.0, 116.8, 111.5, 93.2, 78.0, 55.6, 36.3, 30.4, 30.1, 29.0, 26.8, 10.2; HRMS calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1568. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.05; H, 8.86.

(*E*)-4-(Tributylstannyl)-7-(methoxymethoxy)-2,3,8-tridecatrien-13-ol (5.14). To a mixture of 150 mg (0.30 mmol) of alcohol **5.11** and 0.08 mL (0.60 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added 0.04 mL (0.45 mmol) of methanesulfonyl chloride at −78 °C. The resulting mixture was stirred at −78 °C for 1 h and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was washed with brine and dried over $MgSO_4$. Concentration under reduced pressure yielded the crude mesylate **5.12**, which was dried in vacuo and directly used for the next reaction without further purification.

To a solution of 0.09 mL (0.63 mmol) of diisopropylamine in 5 mL of THF was added 0.38 mL (0.60 mmol) of 1.6 M *n*-BuLi in hexane at 0 °C. After 30 min, 0.15 mL (0.57 mmol) of Bu_3SnH was added. After being stirred for 20 min, the mixture was cooled to −50 °C, and 117 mg (0.57 mmol) of $CuBr{\cdot}SMe_2$ was added in one portion. The above mesylate in 5 mL of THF was added 30 min later. The resulting mixture was stirred for 30 min with warming from −50 °C to −20 °C and allowed to stand at −20 °C for 3 h, and then it was poured into 10% ammonium hydroxide and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane–ether (30:1)) to yield 180 mg (76%) of allenylstannane **5.13**: IR (film) ν 1933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.66–7.35 (m, 5 H, ArH), 5.95 (dt, J = 7.0, 15.6 Hz, 1 H, vinyl H), 5.20 (dd, J = 6.8, 15.6 Hz, vinyl H), 4.69, 4.47 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.55 (m, 1 H, vinyl H-2), 3.97 (m, 1 H, MOMOCH), 3.63 (t, J = 6.3 Hz, 2 H, $DPSOCH_2$), 3.34 (s, 3 H, CH_3O), 2.10–1.97 (m, 4 H, 2 allylic CH_2), 1.57 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 33 H, Bu_3Sn and $(CH_2)_3$), 1.02 (s, 9 H, *t*-Bu).

To a solution of 180 mg (0.23 mmol) of TBS ether **5.13** in 4 mL of aqueous THF was added 0.70 mL (0.70 mmol) of Bu_4NF in THF. The resulting mixture was stirred at room temperature for 4 h, and then it was quenched with water and extracted with ether. The extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 110 mg (88%) of alcohol **5.14**: IR (film) ν 3414, 1933 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.59 (dt, J = 7.0, 15.6 Hz, 1 H, vinyl H), 5.27 (dd, J = 6.8, 15.6 Hz, vinyl H), 4.69, 4.48 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.55 (m, 1 H, vinyl H-2), 3.97 (m, 1 H, MOMOCH), 3.62 (m, 2 H, $HOCH_2$), 3.34 (s, 3 H, CH_3O), 2.15–2.20 (m, 4 H, 2 allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 33 H, Bu_3Sn and $(CH_2)_3$); HRMS calcd for $C_{27}H_{50}O_3Sn$ 538.2777, found 538.2751.

(*E*)-2-Methyl-7-(methoxymethoxy)-8-cyclododecen-3-yn-1-ol (5.16). To a solution of 0.03 mL (0.32 mmol) of *t*-BuOH in 3 mL of THF was added 0.15 mL (0.30 mmol) of 2.0 M EtMgBr in hexane at 0 °C, and then 110 mg (0.20 mmol) of alcohol **5.14** in 2 mL of THF was added. After 5 min, 339 mg (1.34 mmol) of ADD was added in one portion. The resulting mixture was stirred at 0 °C for 30 min, and then it was quenched with brine and extracted with ether. The extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 102 mg (93%) of aldehyde **5.15**: IR (film) ν 2720, 1933, 1729 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.75 (t, J = 1.6 Hz, 1 H, CHO), 5.56 (dt, J = 7.0, 15.6 Hz, 1 H, vinyl H), 5.28 (dd, J = 6.8, 15.6 Hz, vinyl H), 4.68, 4.49 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.58 (m, 1 H, vinyl H-2), 3.98 (m, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.43 (dt, J = 1.6, 8.9 Hz, 2 H, CH_2CHO), 2.07 (m, 4 H, 2 allylic CH_2), 1.58 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 31 H, Bu_3Sn and $(CH_2)_2$).

To a solution of 0.03 mL (0.33 mmol) of $BF_3{\cdot}Et_2O$ in 15 mL of CH_2Cl_2 was added dropwise a solution of 42 mg (0.077 mmol) of allenylstannane aldehyde **5.15** in 5 mL of CH_2Cl_2 at −78 °C over 10 min. The mixture was stirred at −78 °C for 30 min and

then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 17 mg (87%) of alcohol **5.16** as a 2:1 mixture of three diastereomers: IR (film) 3430, 1665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.53–5.47 (m, 1 H, 2 vinyl H), 4.70, 4.46 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.06 (m, 1 H, MOMOCH), 3.87 (m, 1 H, HOC*H*), 3.32 (s, 3 H, CH_3O), 2.65–1.23 (m, 11 H, allylic CH_2, propargylic CH_2, $(CH_2)_3$ and CH_3CH), 1.04 (d, J = 7.1 Hz, 3 H, CH_3CH). Minor peaks could be seen at: δ 4.68, 4.53 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 3.66 (m, 1 H, HOC*H*), 3.34 (s, 3 H, CH_3O) and 1.09 (d, J = 7.1 Hz, 3 H, CH_3CH); HRMS calcd for $C_{13}H_{19}O_2$ (M – MOM) 207.1385, found 207.1377. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.29; H, 9.57.

(*E*)-2-Methyl-7-(methoxymethoxy)-8-cyclododecen-3-ynone (5.17). A solution of 16 mg (0.63 mmol) of alcohol **5.16** in 1 mL of CH_2Cl_2 was treated with 40 mg (0.095 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 15 mg (95%) of propargylic ketone **5.17** as a 1:1 mixture of diastereomers admixed with a trace amount of allenyl ketone **5.18**: IR (film) ν for mixture 1945, 1725, 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ for homopropargylic ketone 5.53–5.45 (m, 2 H, vinyl H), 4.67, 4.49 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.08 (m, 1 H, MOMOCH), 3.32 (s, 3 H, CH_3O), 3.19–3.11 (m, 1 H, propargylic CH), 2.80–1.40 (m, 10 H, $(CH_2)_5$), 1.23 (d, J = 6.9 Hz, 3 H, $CHCH_3$). The peaks of diastereomer could be seen at: δ 4.67, 4.45 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 3.32 (s, 3 H, CH_3O), 1.18 (d, J = 6.9 Hz, 3 H, $CHCH_3$). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.87; H, 8.87.

(*E*)-2-Methyl-7-(methoxymethoxy)-2,3,8-cyclododecatrien-1-one (5.18). A solution of 20 mg (0.080 mmol) of propargylic ketone **5.17** in 1 mL of CH_2Cl_2 was treated with 0.2 mL of Et_3N. After being stirred at room temperature for 4 h, the mixture was concentrated to give allenyl ketone **5.18** quantitatively: IR (film) ν 1945, 1674 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.61–5.20 (m, 3 H, 3 vinyl H), 4.67, 4.50 and 4.65, 4.46 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.09–4.04 (m, 1 H, MOMOCH), 3.34 and 3.33 (s, 3 H, CH_3O), 2.53–1.55 (m, 10 H, $(CH_2)_5$), 1.76 and 1.72 (d, J = 2.8 Hz, 3 H, vinyl CH_3).

Cyclization of Allenyl Ketone 5.18 with $AgNO_3$. Furanocycle 5.19. A mixture of 20 mg (0.080 mmol) of allenone **5.18**, 4 mg (0.023 mmol) of $AgNO_3$, and 7 mg (0.07 mmol) of $CaCO_3$ in 2 mL of aqueous acetone was stirred at room temperature in the dark for 5 h, and then it was concentrated and directly subjected to chromatography on silica gel (hexane–ether (10:1)) to afford 19 mg (95%) of furanocycle **5.19**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.77 (s, 1 H, ArH), 4.86 (m, 1 H, vinyl H), 4.69 (m, 1 H, vinyl H), 4.63, 4.42 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 3.78 (m, 1 H, MOMOCH), 3.31 (s, 3 H, CH_3O), 2.73–2.41 (m, 4 H, 2 $ArCH_2$), 2.06–1.75 (m, 6 H, $(CH_2)_3$), 1.87 (s, 3 H, $ArCH_3$); ^{13}C NMR (300 MHz, $CDCl_3$) δ 152.5, 148.3, 133.2, 128.5, 116.6, 110.7, 92.8, 77.5, 55.2, 36.9, 30.4, 28.6, 24.4, 24.1, 9.9; HRMS calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1568. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 72.02; H, 8.86.

(*E*)-2-Methyl-6-(methoxymethoxy)-7-cyclododecen-3-yn-1-ol (6.13). To a solution of 0.16 mL (1.68 mmol) of *t*-BuOH in 5 mL of THF was added 0.79 mL (1.57 mmol) of 2.0 M EtMgBr in hexane at 0 °C, and then 610 mg (1.12 mmol) of alcohol **6.11** in 2 mL of THF was added. After 5 min, 339 mg (1.34 mmol) of ADD was added in one portion. The resulting mixture was stirred at 0 °C for 30 min, and then it was quenched with brine and extracted with ether. The extracts were washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 516 mg (85%) of aldehyde **6.12**: IR (film) ν 2926, 2718, 1935, 1730, 1463, 1377, 1150, 1095, 1035, 971, 919 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.74 (t, J = 1.6 Hz, 1 H, CHO), 5.59 (dt, J = 7.0, 15.6 Hz, 1 H, vinyl H), 5.28 (dd, J = 6.8, 15.6 Hz, vinyl H), 4.67, 4.51 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.53 (m, 1 H, vinyl H-2), 4.04 (m, 1 H, MOMOCH), 3.34 (s, 3 H, CH_3O), 2.41 (dt, J = 1.6, 8.9 Hz, 2 H, CH_2CHO), 2.41–2.12 (m, 2 H, Bu_3SnCCH_2), 2.04 (m, 2 H, allylic CH_2), 1.55 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.80–0.80 (m, 31 H, Bu_3Sn and $(CH_2)_2$).

To a solution of 0.05 mL (0.51 mmol) of BF_3·Et_2O in 25 mL of CH_2Cl_2 was added dropwise a solution of 92 mg (0.17 mmol) of allenylstannane aldehyde **6.12** in 10 mL of CH_2Cl_2 at –78 °C over 20 min. The mixture was stirred at –78 °C for 30 min and then quenched with saturated $NaHCO_3$ and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (3:1)) to yield 38 mg (89%) of alcohol **6.13** as a 1.8:1.6:1.2:1 mixture of four diastereomers: IR (film) 3424, 1668 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.69–5.52 (m, 1 H, vinyl H), 5.32–5.21 (m, 1 H, vinyl H), 4.72–4.47 (m, 2 H, CH_3OCH_2O), 4.18–4.08 (m, 1 H, MOMOCH), 3.45 (m, 1 H, HOC*H*), 3.33 (s, 3 H, CH_3O), 2.65–1.23 (m, 11 H, allylic CH_2, propargylic CH_2, $(CH_2)_3$ and CH_3CH), 1.04 (d, J = 7.1 Hz, 3 H, CH_3CH); HRMS calcd for $C_{15}H_{23}O_3$ (M – H) 251.1647, found 251.1644.

(*E*)-2-Methyl-6-(methoxymethoxy)-7-cyclododecen-3-ynone (6.14) and (*E*)-2-Methyl-6-(methoxymethoxy)-2,3,7-cyclododecatrienone (6.15). A solution of 35 mg (0.14 mmol) of alcohol **6.13** in 3 mL of CH_2Cl_2 was treated with 76 mg (0.095 mmol) of Dess–Martin reagent. After 10 min, the mixture was diluted with ether and washed with dilute NaOH. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 33 mg (94%) of a 3:1 mixture of allenyl ketone **6.15** and propargylic ketone **6.14**: IR (film) ν for mixture 1948, 1716, 1673 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.56–5.26 (m, 2 H, vinyl H), 4.74, 4.54 (ABq, J = 6.7 Hz, 2 H, CH_3OCH_2O), 4.10 (m, 1 H, MOMOCH), 3.37 (s, 3 H, CH_3O), 3.19–3.11 (m, 1 H, propargylic CH), 2.61–1.40 (m, 10 H, $(CH_2)_5$), 1.72 (d, J = 2.8 Hz, 3 H, vinyl CH_3). The peaks of the propargylic ketone could be seen at: δ 3.35 and 3.34 (s, 3 H, CH_3O), 3.16 (m, 1 H, CH_3CH), 1.22 and 1.21 (d, J = 7.1 Hz, 3 H, $CHCH_3$); HRMS calcd for $C_{15}H_{22}O_3$ 250.1567, found 250.1567.

Cyclization of Allenyl Ketone 6.15 with $AgNO_3$. Furanocycle 6.16. A mixture of 28 mg (0.11 mmol) of the above 3:1 mixture, 3 mg (0.018 mmol) of $AgNO_3$, and 9 mg (0.090 mmol) of $CaCO_3$ in 2 mL of aqueous acetone was stirred at room temperature in the dark for 12 h, and then it was diluted with ether and washed with water. The organic layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane–ether (4:1)) to yield 25 mg (92%) of furanocycle **6.16**: IR (film) ν 1570 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.84 (s, 1 H, Ar-H), 5.29 (dd, J = 8.1, 15.6 Hz, 1 H, vinyl H), 4.69, 4.55 (ABq, J = 6.6 Hz, 2 H, CH_3OCH_2O), 4.68 (m, 1 H, vinyl H), 3.92 (m, 1 H, MOMOCH), 3.36 (s, 3 H, CH_3O), 3.00 (dd, J = 5.2, 13.4 Hz, 1 H, $ArCH_2CHOMOM$), 2.68 (dd, J = 9.9, 13.4 Hz, 1 H, $ArCH_2CHOMOM$), 2.43 (m, 1 H, $ArCH_2CH_2$), 2.27 (m, 1 H, $ArCH_2CH_2$), 2.07–1.60 (m, 6 H, allylic CH_2 and $(CH_2)_2$), 1.87 (s, 3 H, vinyl CH_3); ^{13}C NMR (300 MHz, $CDCl_3$) δ 149.2, 148.4, 133.0, 130.2, 116.5, 110.2, 94.1, 76.6, 55.4, 34.7, 34.2, 26.1, 25.9, 24.9, 9.7; MS m/e 250 (55, M^+), 218 (27), 205 (95), 177 (45), 135 (64), 109 (100). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.84; H, 8.82.

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Supplementary Material Available: ^1H NMR spectra and experimental procedures for **1.3, 1.5, 1.6, 1.8, 1.9, 1.10, 1.11, 1.12, 2.3, 2.4, 2.6, 2.7, 3.2a, 3.5a, 3.7a, 3.8a, 3.2b, 3.5b, 3.7b, 3.8b, 3.10a, 3.10b, 3.11a, 3.11b, 4.7, 4.8, 5.6, 5.7, 5.8, 5.10, 5.11, 6.6, 6.7, 6.8, 6.9, 6.10, 6.11** and ^1H NMR spectra of **1.16, 1.18/1.19, 1.21, 2.11, 3.12a, 3.17a, 3.18, 3.12b, 4.10–4.12, 4.15, 4.17, 5.13–5.15, 5.18, 6.12, 6.13, 6.14/6.15** (73 pages). This material is contained in many 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.