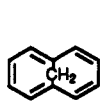
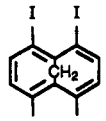
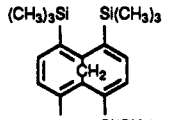
Table I. Structural Parameters

	compound		
			
	2	1a	1c
	Bond Distances (Å)		
C_1–C_2	1.403 (3)	1.380 (10)	
C_2–C_3	1.379 (4)	1.421 (10)	
C_3–C_4	1.417 (4)	1.383 (10)	1.35
C_4–C_5	1.378 (3)	1.411 (9)	1.45
C_5–C_6	1.402 (3)	1.366 (10)	1.36
C_6–C_7	1.410 (3)	1.421 (10)	1.47
C_7–C_8	1.376 (4)	1.372 (10)	1.35
C_8–C_9	1.419 (4)	1.412 (10)	1.47
C_9–C_{10}	1.373 (3)	1.366 (10)	
C_{10}–C_1	1.405 (3)	1.429 (10)	
C_1–C_{11}	1.487 (3)	1.510 (11)	
C_{11}–C_6	1.484 (3)	1.506 (11)	1.50
C_1–C_6	2.235	2.357	2.298
	Bond Angles (deg)		
C_1–C_2–C_3	122.8	122.1 (6)	119
C_2–C_3–C_4	127.3	127.1 (6)	132
C_3–C_4–C_5	126.8	128.5 (7)	
C_4–C_5–C_6	122.7	121.8 (7)	
C_5–C_6–C_7	126.2	133.0 (7)	
C_6–C_7–C_8	122.6	121.5 (6)	
C_7–C_8–C_9	127.6	130.3 (7)	
C_8–C_9–C_{10}	127.1	130.9 (7)	126
C_9–C_{10}–C_1	123.1	121.4 (7)	118
C_{10}–C_1–C_2	126.8	132.9 (7)	128
C_1–C_{11}–C_6	97.6	102.8	100

As a consequence of the above, C_1–C_{11} and C_6–C_{11} bond lengths are lengthened from 1.487 and 1.484 for **2** to 1.510 and 1.506, respectively. Surprisingly, as seen from the side view, the torsional distortion of the bicycle is minimal (all the four iodine atoms are on one side of the C=C double bond plane) compared to the effect of "*peri*" trimethylsilyl substitution[2] or the effect of *peri* bromine substitution in 1,4,5,8-tetrabromonaphthalene.[8]

Summary

The title compound could not be prepared by traditional aromatic iodination procedures. A new approach employing an intermediate mercuration step was successful, provided mercuric acetate or trifluoroacetate are employed. The organomercurial was not characterized due to intractability but subsequent conversion to the known 2,5,7,10-tetrabromo-1,6-methano[10]annulene constitutes a proof of structure.

The tetraiodo bicycle **1a** is surprisingly only slightly distorted in an unusual fashion; the transannular distance is enlarged as are the bridge bonds and the angle subtended by the bridge carbon atoms. The π-delocalization is also somewhat decreased relative to the parent bicycle.

As expected, the carbon–iodine bonds are thermally labile; heating the solid produces a small amount of unsubstituted methano[10]annulene and a black solid.[9]

Acknowledgment. F.W. and K.D.S. thank the Office of Naval Research for support and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also thank Hugh Webb for high resolution mass spectra and Ata Shirazi for high resolution NMR spectra.

Supplementary Material Available: Tables of final atomic coordinates and anisotropic temperature factors for **1a** (5 pages); observed and calculated structure factors for **1a** (9 pages). Ordering information is given on any current masthead page.

(8) Davidova, M. A.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 258.
(9) Sturm, K. D. Unpublished Results. Results of characterization of this solid will be published elsewhere.
(10) Vogel, E. In *Aromaticity*; Ollis, W. D., Eds.; The Chemical Society Special Publications: London, 1967; No. 21, p 113.

Synthesis of Furans by Ag(I)-Promoted Cyclization of Allenyl Ketones and Aldehydes

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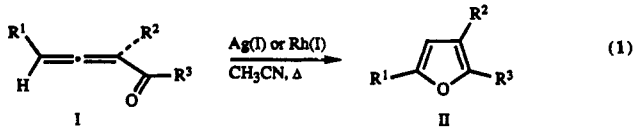
A series of conjugated allenones (**11b**, **12b**, **13c**; **18a**, **18b**; **19b**, **20b**, AB and **27d**) were prepared by [2,3] Wittig rearrangement of (propargyloxy)acetic acids or [(propargyloxy)methyl]stannanes followed by oxidation of the resultant allenylcarbinols. These allenones were readily cyclized to 2,3,5-trisubstituted furans upon treatment with $AgNO_3$–$CaCO_3$ in aqueous acetone. Under these conditions 2-(hydroxymethyl)-3,5-dialkylfurans self-condensed to give 2,2'-difurylmethanes

We recently described a new route to furans involving Ag(I)- or Rh(I)-catalyzed cyclization of allenyl ketones and aldehydes (eq 1).[1,2] The present study was undertaken to examine the applicability of that approach to furans with functionalized C2 substituents. Such systems are of interest as prototypes of intermediates for the synthesis of various natural products.[2-4]



(1)

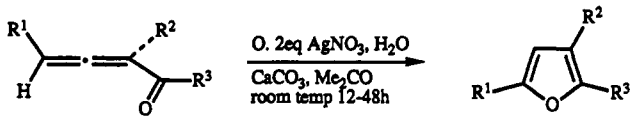
I II

R^1 = H, CH_3; R^2 = H, *n*-C_7H_{15}; R^3 = H, CH_3, $Me_2C{=}CHCH_2CH_2C(Me){=}CH$

(1) Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990**, *55*, 3450.
(2) For leading references to furan synthesis and furanoid natural products, see: Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407.
(3) Cf.: Fenical, W.; Okuda, R. K.; Bandurraga, M. M.; Clulver, P.; Jacobs, R. S. *Science* **1981**, *212*, 1512. Bandurraga, M. M.; Fenical, W.; Donovan, S. F.; Clardy, J. *J. Am. Chem. Soc.* **1982**, *104*, 6463. Wright, A. E.; Burres, N. S.; Schulte, G. K. *Tetrahedron Lett.* **1989**, *30*, 3491.
(4) Martin, S. F.; Guinn, D. E. *J. Org. Chem.* **1987**, *52*, 5588. Martin, S. F.; Zinke, P. W. *J. Am. Chem. Soc.* **1989**, *111*, 2311.

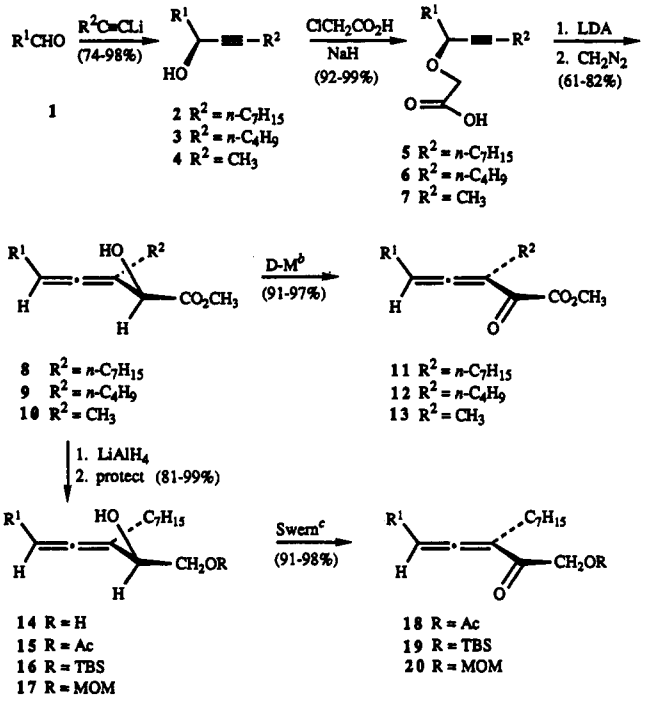
0022-3263/91/1956-0960$02.50/0

Table I. Ag(I)-Catalyzed Cyclization of Allenones to Furans



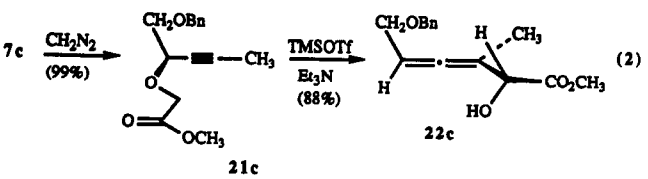
entry	allenone	R^1	R^2	R^3	furan	yield (%)
1	**11b**	CH_2	C_7H_{15}	CO_2CH_3	**28**	98
2	**12b**	CH_3	C_4H_9	CO_2CH_3	**29**	95
3	**13c**	CH_2OBn	CH_3	CO_2CH_3	**30**	91
4	**18a**	H	C_7H_{15}	CH_2OAc	**31**	88
5	**18b**	CH_3	C_7H_{15}	CH_2OAc	**32**	65
6	**19b**	CH_3	C_7H_{15}	CH_2OTBS	**33**	96
7	**20b**	CH_3	C_7H_{15}	CH_2OMOM	**34**	93
8	**26d**	$(CH_3)_2CHCH_2$	C_7H_{15}	H	**35**	95
9	**27d**	$(CH_3)_2CHCH_2$	C_7H_{15}	CH_3	**36**	99
10	**27e**	$(CH_3)_3C$	C_7H_{15}	CH_3	**37**	99

Scheme I[a]

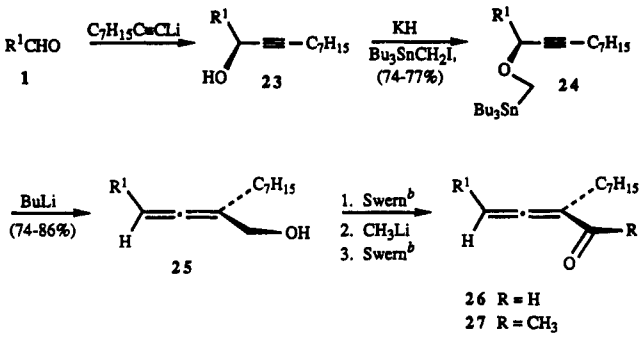


[a] **a** series, R^1 = H; **b** series, R^1 = CH_3; **c** series, R^1 = CH_2OBn. [b] Dess–Martin periodinane reagent. [c] Swern oxidation with $(COCl)_2$, Et_3N, Me_2SO.

The allenones employed in this study were prepared by [2,3] Wittig rearrangement of the propargyloxy acetic acids **5–7** followed by oxidation, as outlined in Scheme I.[5] The rearrangements afforded predominantly the diastereomeric allenyl carbinols **8–10**.[6] Owing to the base lability of the acid derivative **7c**, carbinol **10c** was obtained in poor yield.[5,6] However, an alternative method involving TMSOTf-induced rearrangement of ester **21c** afforded allenyl carbinol **22c**, epimeric with **10c**, in satisfactory yield (eq 2).[6] The allenyl alcohols were smoothly oxidized by



Scheme II[a]



[a] **d** series, R^1 = *i*-Bu; **e** series, R^1 = *t*-Bu. [b] Swern oxidation, $(COCl)_2$, Et_3N, Me_2SO.

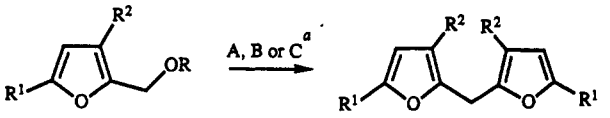
the Dess–Martin periodinane reagent[7] to the unstable α-keto esters **11–13**, which were used immediately for the furan cyclizations (Table I, entries 1–3). Other oxidizing agents proved less satisfactory. Additional allenone substrates **18–20** were prepared from hydroxy ester **8** by reduction with $LiAlH_4$ to the diol **14** and then selective acetylation or etherification of the primary alcohol followed by Swern oxidation.[8] Allenones **27d** and **27e** and the aldehyde **26d**, were prepared as outlined in Scheme II by Still [2,3] Wittig rearrangement of the stannylmethyl propargyl ethers **24** followed by oxidation.[9]

In our initial application of the allenone route to furans we employed $AgNO_3$ or $AgBF_4$ in CH_3CN at 100 °C to effect cyclization (eq 1).[1] In a related study we found that allenyl carbinols were smoothly converted to 2,5-dihydrofurans upon treatment with $AgNO_3$–$CaCO_3$ in aqueous acetone.[5] We were pleased to find that these mild conditions could also be used for the present cyclizations. Thus, treatment of the foregoing allenones with 0.2 equiv of $AgNO_3$ in aqueous acetone containing solid $CaCO_3$ yielded the furans **28–37** upon standing at room temperature for 12–48 h (Table I). Yields of all cyclizations were high except for the acetate derivative **32** (entry 5). The significance of that result will be discussed presently.

In some of our initial experiments with the α-oxygenated allenone **18b** we noted the formation of a polar byproduct. The ^1H NMR spectrum of this byproduct showed it to be a mixture of epimeric 2-hydroxy-2,5-dihydrofurans **38**. On standing overnight in the NMR sample tube ($CDCl_3$ sol-

(5) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1990**, *55*, 2995.
(6) Details will be discussed in a forthcoming paper on [2,3] Wittig rearrangements of nonracemic (propargyloxy)acetic acid derivatives. For a preliminary account, see ref 5.
(7) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4156.
(8) Mancuso, A. J.; Huang, S.-L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(9) Marshall, J. A.; Robinson, E. D.; Zapata, A. *J. Org. Chem.* **1989**, *54*, 5854.

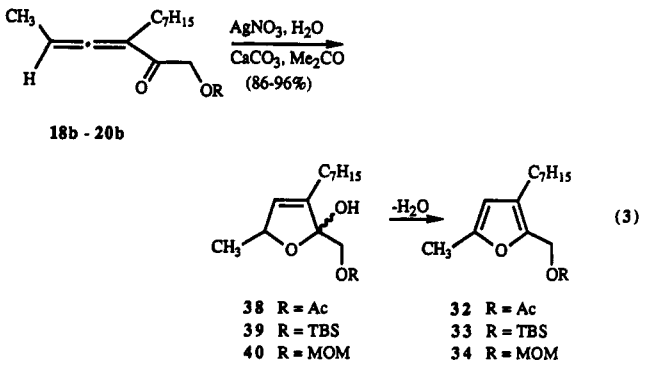
Table II. Dimerization of Furfuryl Alcohol Derivatives



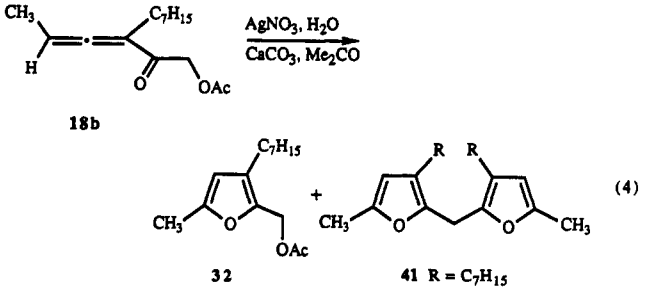
entry	R	R^2	R	furan	conditions[a]	"bisfuran"	yield (%)
1	CH_3	C_7H_{15}	Ac	32	A	41	65
2	CH_3	C_7H_{15}	H	42	A	41	70
3	CH_3	C_7H_{15}	H	42	B	41	75
4	CH_3	C_4H_9	H	43	A	48	55
5	CH_3	C_4H_9	H	43	B	48	81
6	CH_3	C_4H_9	H	43	C	48	46
7	$BnOCH_2$	CH_3	H	44	A	49	trace[b]
8	$BnOCH_2$	CH_3	H	44	B	49	40[c]
9	H	C_7H_{15}	H	45	B	–	0[d]
10	C_6H_{13}	H	H	46	B	–	0[d]
11	CH_2OH	C_7H_{15}	H	47	B	50	8[e]

[a] A = $AgNO_3$, $CaCO_3$, Me_2CO, H_2O, Δ; B = Cl_3CCO_2H, Me_2CO, H_2O, 40 °C, 1 h; C = silica gel. [b] 41% of aldehyde **51**. See eq 5. [c] 14% of aldehyde **51**. See eq 5. [d] Recovered starting material. [e] 29% of aldehyde **51** and 35% of pyranone **61**. See eq 6.

vent) or in ether solution these dihydrofurans were quantitatively converted to the furan product **32** (eq 3). Analogous behavior was noted for the TBS and MOM derivatives **19b** and **20b**.



As noted above, cyclization of the α-acetoxyallenone **18b** was significantly less efficient than that of its close analogues **19b** and **20b** (Table I, entries 5–7). This decreased efficiency could be traced to the formation of a byproduct, judged to be the bisfuranomethane **41** on the basis of ^1H NMR, ^{13}C NMR, and MS analyses (eq 4).[10]



We suspected that furan **32** was the precursor of **41** and, in fact, treatment of the former with $AgNO_3$–$CaCO_3$ in aqueous acetone confirmed this suspicion. Bisfuranomethane **41** was thereby obtained in 65–70% yield (Table II, entry 1). The conversion of furan **32** to the "dimer"

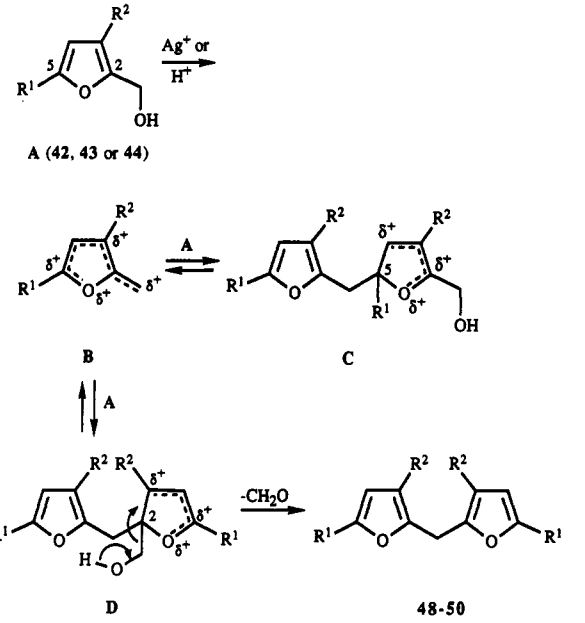


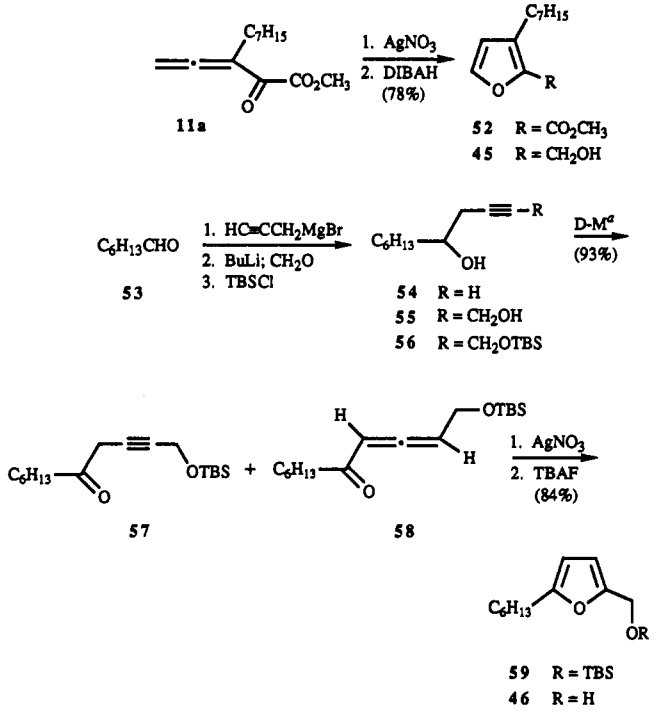
Figure 1. Pathway for dimerization of furfuryl alcohols.

bisfuranomethane **41** proceeds with loss of a CH_2OAc grouping from one of the furan moieties. Anticipating a possible mechanistic pathway for this interesting transformation, we prepared the analogous alcohols **42** and **43** by reduction of esters **28** and **29** with $LiAlH_4$. As expected, treatment of these alcohols with $AgNO_3$–$CaCO_3$ also afforded the "dimeric" products **41** and **48** (Table II, entries 2 and 4). This conversion could likewise be effected with acids such as Cl_3CCO_2H in aqueous acetone (Table II, entries 3 and 5). Presumably other mineral acids would suffice as well, but none was examined. "Dimerization" even took place upon attempted purification of alcohol **43** by chromatography on silica gel (Table II, entry 6). By deactivating the column with Et_3N we were able to prevent this undesired reaction.

A possible pathway for the formation of the bisfuran products is shown in Figure 1. Accordingly, Ag(I)- or H^+-assisted dissociation of the furfuryl alcohol A would lead to the delocalized cation B. Addition of B to the furan A at the 5- or 2-position could lead to intermediate C or D. The latter, through loss of formaldehyde, would afford the observed condensation products. Evidently this process does not take place unless the R^1 and R^2 substituents of the furan A are capable of stabilizing carbocations B and

(10) Bisfuranomethanes have previously been prepared in low yield by condensation of furans with aldehydes and ketones in the presence of Lewis acids. Ackman, R. G.; Brown, W. H.; Wright, G. F. *J. Org. Chem.* **1955**, *20*, 1147. Brown, W. H.; French, W. N. *Can. J. Chem.* **1958**, *36*, 537. Kobuke, Y.; Hanji, K.; Horiguchi, K.; Asada, M.; Nakayama, Y.; Furukawa, J. *J. Am. Chem. Soc.* **1976**, *98*, 7414.

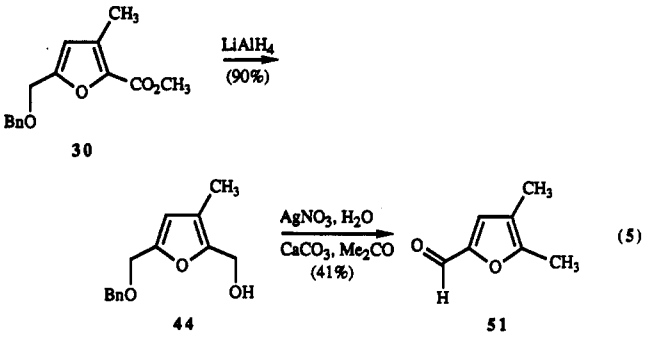
Scheme III[a]



[a] Dess–Martin periodinane reagent.

D. Thus, furans **45** (R^1 = H) and **46** (R^2 = H), prepared as shown in Scheme III, gave no bisfuranomethane products, nor were any products derived from cation C observed.

Interestingly, alcohol **44**, obtained by reduction of the [(benzyloxy)methyl]furan ester **30**, gave only a trace of bisfuranomethane **49** upon treatment with $AgNO_3$–$CaCO_3$ (Table II, entry 7). The major product in that case was aldehyde **51** (eq 5). With Cl_3CCO_2H as the catalyst, however, bisfuran **49** was the major product (Table II, entry 8).



The formation of aldehyde **51** from furan **44** (eq 5) may follow the pathway shown in Figure 2. Cation B can add to starting furan **44** to afford bisfuran **49** (Figure 1) or it can lose a proton to form the transient enol ether E whose protonolysis and debenzylation leads to the observed aldehyde **51**. Cation B could also undergo a 1,2-hydride shift followed by debenzylation and double bond isomerization in an alternative route to aldehyde **51**. Evidently the balance between isomerization and dimerization in this system is strongly influenced by reaction conditions.

As a further test of the self-condensation mechanism we prepared diol **47** and subjected it to acid treatment (eq 6). Three products were isolated from this reaction, bisfuranomethane **50** (8%), aldehyde **60** (29%), and the pyranone **61** (35%). None of the isomeric bisfuranomethanes

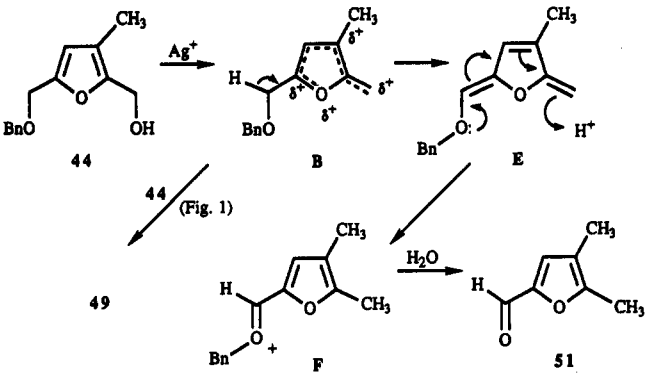
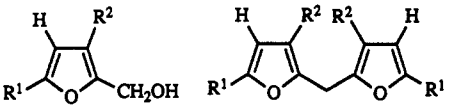


Figure 2. Pathway for pinacolic-type rearrangement of furfuryl alcohol **44**.

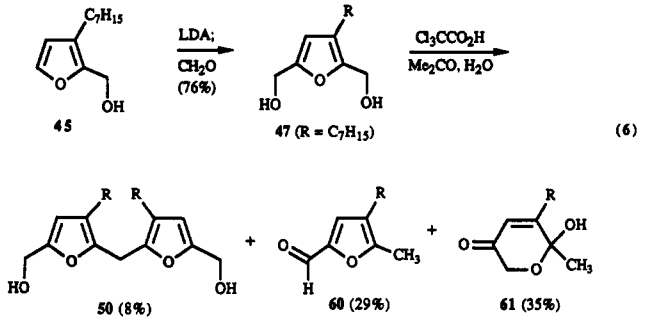
Table III. Chemical Shifts for Furan Protons



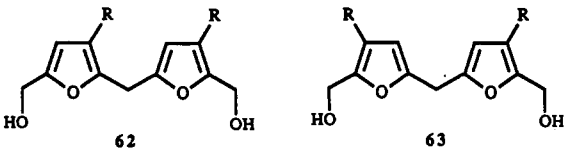
R	R^2	furan	δ	"bisfuran"	δ
CH_3	C_7H_{15}	**42**	5.82	**41**	5.75
CH_3	C_4H_9	**43**	5.82	**48**	5.75
$BnOCH_2$	CH_3	**44**	6.14	**49**	6.10
$HOCH_2$	C_7H_{15}	**47**	6.14	**50**	6.09
H	C_7H_{15}	**45**	7.30, 6.23[a]		
C_6H_{13}	H	**46**	6.16, 5.90[b]		

[a] d, J = 1.8 Hz. [b] d, J = 3.1 Hz.

62 and **63**, arising from condensation reactions involving less favored carbocations, could be detected.



The structure assignment to bisfuranomethane **50** was based on the ^1H NMR spectrum. The number of signals and their ratios required a symmetrical structure thus excluding **62**. The choice of **50** vs **63** could be made by the chemical shift of the furan proton at 6.09 ppm (vs 5.75 for bisfuranomethanes **41** and **48**) as a consequence of deshielding by the oxygen of the adjacent CH_2OH grouping (Table III).[11]



Pyranone **61** was unexpected but its formation can be readily rationalized by the sequence depicted in Figure 3.[4]

(11) Cf.: Marshall, J. A.; Grote, J.; Audia, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1186. Bhacca, N. S., Williams, D. H. *Applications of NMR Spectroscopy in Organic Chemistry*; Holden-Day Inc.: San Francisco, 1966; pp 101–102.

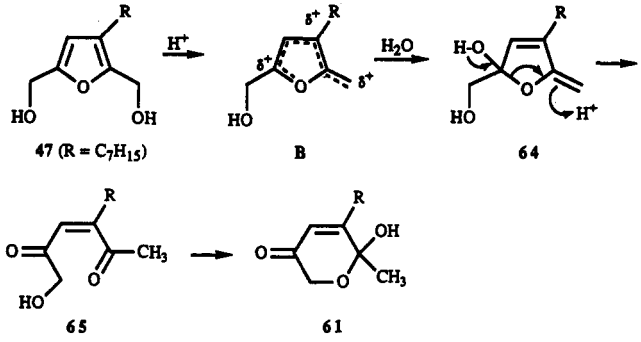


Figure 3. Pathway for conversion of diol **47** to pyranone **61**.

Although two isomeric pyranones are possible, only one was observed in keeping with the preferred formation of cation B, the precursor of all three of the observed products, **50**, **60**, and **61**.

In conclusion, we have discovered an efficient and apparently general route to furans. We have also found that 2-(hydroxymethyl)-3,5-dialkylfurans undergo cationic self-condensation leading to 2,2′-bisfuranomethanes. In view of the mild reaction conditions these methods should be well suited to the preparation of sensitive furans and bisfuranomethanes.

Experimental Section[12]

2-Decyn-1-ol (2a). To a solution of 2.00 g (16.10 mmol) of 1-nonyne in 60 mL of THF was slowly added 6.1 mL (17.71 mmol) of 2.90 M *n*-BuLi at −78 °C. The mixture was stirred for 1 h, whereupon 1.5 g (50.0 mmol) of paraformaldehyde was added. The mixture was warmed to room temperature, stirred for another 1 h, neutralized with 10% HCl, and extracted with ether. The extracts were washed with saturated aqueous $NaHCO_3$ and brine and then dried over $MgSO_4$. After removal of solvent, the residue was distilled at reduced pressure to give 2.45 g (98%) of propargylic alcohol **2a**: IR (film) 3422, 2931, 2225, 1460, 1118, 1057, 909 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.24 (dt, J = 1.7, 6.1 Hz, 2 H, CH_2OH), 2.22–2.16 (m, 2 H, propargylic CH_2), 1.51–1.26 (m, 10 H, $(CH_2)_5$), 0.87 (t, J = 6.7 Hz, 3 H, CH_2CH_3); MS m/e (%) 153 (5, M − H), 137 (61), 123 (17), 109 (43), 95 (100).

The above procedure was used to prepare the following compounds.

3-Undecyn-2-ol (2b): 92% yield; IR (film) 3357, 2929, 2248, 1455, 1155, 1076, 890 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.49 (m, 1 H, $CHOH$), 2.16 (dt, J = 1.9, 7.0 Hz, 2 H, propargylic CH_2), 1.40 (d, J = 6.5 Hz, 3 H, $CHCH_3$), 1.49–1.25 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); MS m/e (%) 167 (2, M − H), 151 (19), 109 (70), 95 (100).

3-Octyn-2-ol (3b): 74% yield; IR (film) 3363, 2930, 2859, 2247, 1457, 1156, 1078 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.51–4.47 (m, 1 H, $CHOH$), 2.18 (dt, J = 2.0 Hz, 6.9 Hz, 2 H, propargylic CH_2), 1.72 (d, J = 5.2 Hz, 1 H, OH), 1.51–1.31 (m, 4 H, CH_2CH_2), 1.41 (d, J = 6.5 Hz, 3 H, $OCHCH_3$), 0.89 (t, J = 7.2 Hz, 3 H, CH_2CH_3); MS m/e (%) 125 (3, M − H), 109 (15), 67 (100).

2-Methyl-5-tridecyn-4-ol (23d): 94% yield; IR (film) 3354, 2930, 2862, 2240, 1467, 1368, 1155, 1036 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.37 (m, 1 H, propargylic CH), 2.18 (dt, J = 2.0, 7.0 Hz, 2 H, propargylic CH_2), 1.83–1.77 (m, 1 H, $CH(CH_3)_2$), 1.64–1.26 (m, 12 H, $(CH_2)_6$), 0.92 (d, J = 6.4 Hz, 3 H, $CH(CH_3)CH_3$), 0.90 (d, J = 6.4 Hz, 3 H, $CH(CH_3)CH_3$), 0.87 (t, J = 6.9 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{26}O$ (M − H) 209.1905, found 209.1911.

2,2-Dimethyl-4-dodecyn-3-ol (23e): 87% yield; IR (film) 3424, 2930, 2859, 2225, 1463, 1363, 1040, 1004 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.99–3.95 (m, 1 H, propargylic CH), 2.19 (dt, J = 2.0, 6.9 Hz, 2 H, propargylic CH_2), 1.69 (d, J = 6.3 Hz, 1 H, OH), 1.51–1.26 (m, 10 H, $(CH_2)_5$), 0.96 (s, 9 H, $C(CH_3)_3$), 0.87 (t, J = 6.8 Hz, 3 H, CH_2CH_3); MS m/e (%) 209 (6, M^+ − H), 167 (25), 126 (30) 70 (46), 57 (100).

1-(Benzyloxy)-3-pentyn-2-ol (4c). Methylacetylene was bubbled into 20 mL of THF at −78 °C for 15 min. To the solution was added dropwise 1.0 mL (2.90 mmol) of 2.90 M *n*-BuLi at −78 °C. The mixture was stirred at −78 °C for 1 h and 410 mg (2.73 mmol) of 2-(benzyloxy)acetaldehyde in 5 mL of THF at −78 °C was added. The mixture was warmed to room temperature, stirred for 5 h, acidified with 10% HCl, and extracted with ether. The extracts were washed with saturated $NaHCO_3$ and brine and dried over $MgSO_4$. Concentration of the mixture and chromatography of the residue afforded 412 mg (79%) of alcohol **4c**: IR (film) ν 3400, 3030, 2920, 2860, 2240, 1490, 1445, 1360, 1310, 1110, 1075, 1025, 895, 740, 700 cm^{-1}; ^1H NMR (500 HMz, $CDCl_3$) δ 7.35–7.28 (m, 5 H, Ar-H), 4.61, 4.67 (AB, J = 12.0 Hz, 2 H, $PhCH_2O$), 4.53 (X of ABX, m, 1 H, $HOCH$), 3.60 (A of ABX, dd, J = 3.5, 9.8 Hz, 1 H, $BnOCH_2$), 3.50 (B of ABX, dd, J = 7.6, 9.8 Hz, 1 H, $BnOCH_2$), 2.39 (d, J = 4.4 Hz, 1 H, OH), 1.83 (d, J = 2.2 Hz, 3 H, propargylic CH_3); HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0996.

1-(Nonynyloxy)acetic Acid (5a). To a suspension of 1.37 g (57.06 mmol) of NaH in 100 mL of THF was added a solution of 2.45 g (15.88 mmol) of alcohol **2a** in 50 mL of THF at 0 °C. After 30 min, 2.25 g (23.80 mmol) of chloroacetic acid was added in several portions at 0 °C. The mixture was refluxed for 18 h, acidified with 10% HCl, and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/ether, 4:1, then ether) to yield 3.37 g (100%) of acid **5a**: IR (film) 3600–2500, 2931, 2885, 2225, 1733, 1431, 1247, 1115, 928 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.28 (t, J = 2.1 Hz, 2 H, $C{=}CCH_2O$), 4.22 (s, 2 H, OCH_2CO_2H), 2.20 (dt, J = 2.1, 4.8 Hz, 2 H, propargylic CH_2), 1.51–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.7 Hz, 3 H, CH_2CH_3); MS m/e (%) 153 (4, $M^+ - CH_2CO_2H$), 128 (100), 109 (16), 81 (40), 67 (46).

The above procedure was used to prepare the following compounds.

2-[(1-Methyl-1-nonynyl)oxy]acetic acid (5b): 92% yield; IR (film) 3600–2500, 2932, 2240, 1735, 1420, 1216, 1125, 795 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.38–4.33 (m, 1 H, $OCHCH_3$), 4.30, 4.17 (AB q, J = 16.9 Hz, 2 H, OCH_2CO_2H), 2.18 (dt, J = 1.7, 7.1 Hz, 2 H, propargylic H), 1.50–1.40 (m, 2 H, H-6), 1.45 (d, J = 6.5 Hz, 3 H, $OCHCH_3$), 1.40–1.31 (m, 8 H, $(CH_2)_4$), 0.86 (t, J = 6.6 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{22}O_3$ (M + NH_3) 244.1917, found 244.1913.

2-[(1-Methyl-1-hexynyl)oxy]acetic acid (6b): 99% yield; IR (film) 3500–2400, 2920, 2850, 2240, 1720, 1420, 1340, 1240, 1125 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.35 (m, 1 H, propargylic CH), 4.30, 4.18 (AB q, J = 16.7 Hz, OCH_2CO_2H), 2.20 (dt, J = 2.0, 6.9 Hz, 2 H, propargylic CH_2), 1.45 (d, J = 6.5 Hz, 3 H, CH_3), 1.49–1.33 (m, 4 H, CH_2CH_2), 0.89 (t, J = 7.2 Hz, 3 H, CH_2CH_3); MS m/e (%) 183 (100, M^+ − H), 153 (35).

2-[[1-[(Benzyloxy)methyl]-1-propynyl]oxy]acetic acid (7c): 99% yield; IR (film) 3600–2500, 2920, 2243, 1735, 1430 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.25 (m, 5 H, ArH), 4.65, 4.59 (AB, J = 12.1 Hz, 2 H, $PhCH_2O$), 4.33 (m, 1 H, propargylic CH), 4.33, 4.16 (AB, J = 17.2 Hz, 2 H, OCH_2CO_2H), 3.60 (m, 2 H, CH_2OBn), 1.83 (d, J = 2.2 Hz, 3 H, CH_3); MS m/e (%) 247 (2, M^+ − H), 189 (5), 160 (22), 91 (100).

Methyl 2-Hydroxy-3-heptyl-3,4-pentadienecarboxylate (8a). To a solution of 1.08 mL (7.54 mmol) of diisopropylamine in 5 mL of THF was added 2.4 mL (7.06 mmol) of 2.90 M *n*-BuLi at 0 °C. The mixture was stirred at 0 °C for 30 min and cooled to −78 °C, and 500 mg (2.36 mmol) of acid **5a** in 3 mL of THF

(12) The apparatus and methods described Levy[13] G. W. Kramer, M. M. Midland, and A. B. *Soc.* **1990**, *112*, 6679. were used to maintain an argon or nitrogen; atmosphere in the reaction flask. Anhydrous solvents were obtained by distillation from benzophenone ketyl (diethyl ether, tetrahydrofuran), P_2O_5 (dichloromethane), calcium hydride (hexamethylphosphoramide), or sodium (benzene, toluene). Proton magnetic resonance samples were prepared as dilute solutions in deuteriochloroform ($CDCl_3$). Glass capillary gas chromatography was performed on a Superox 4, 25M column. Combustion microanalyses were performed by Atlantic Laboratories, Norcross, GA. Analytical thin-layer chromatography (TLC) was used to monitor reactions. Plates precoated with E. Merck silica gel 60 F254 or 0.25 mm thickness were used. E. Merck silica gel 60 (230–400 ASTM mesh) was employed for column chromatography according to the procedure of Still, Kahn, and Mitra.[14]

(13) Brown, H. C. *Organic Syntheses via Boranes*; Wiley: New York, 1975; pp 191–202.

(14) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

was added dropwise. The reaction mixture was stirred at −78 °C for 5 h, acidified with 10% HCl, and extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was directly esterified without purification.

To a solution of the above material in 10 mL of ether was added excess diazomethane in 10 mL of ether. The reaction mixture was stirred at room temperature until the TLC showed no trace of starting material. The excess diazomethane was destroyed with acetic acid. Concentration of the mixture and chromatography of the crude product on silica gel (hexane/ether, 4:1) afforded 325 mg (61%) of allenic ester **8a**: IR (film) 3490, 2928, 2855, 1958, 1743, 1439, 1270, 1077, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.89 (m, 2 H, vinyl H), 4.58 (d, 1 H, J = 7.4 Hz, $HOCHCO_2CH_3$), 3.78 (s, 3 H, CO_2CH_3), 2.88 (d, J = 7.4 Hz, 1 H, OH), 2.04–1.93 (m, 2 H, propargylic CH_2), 1.54–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{22}O_3$ 226.1569, found 226.1565. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.88; H, 9.81.

The above procedure was used to prepare the following compounds.

Methyl 2-hydroxy-3-heptyl-3,4-hexadienecarboxylate (8b): 80% yield; a 93:7 mixture of diastereomers according to GC analysis; IR (film) 3500, 2928, 2856, 1967 1745, 1439, 1215, 1078, 1004 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.31–5.27 (m, 1 H, vinyl H), 4.53 (br s, 1 H, $HOCHCO_2Me$), 3.75 (s, 3 H, CO_2CH_3), 2.84 (br s, 1 H, OH), 2.06–1.89 (m, 2 H, vinyl CH_2), 1.65 (d, J = 7.1 Hz, 3 H, CH_3), 1.40–1.23 (m, 10 H, $(CH_2)_5$), 0.85 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{24}O_3$ 240.1725, found 244.1714. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.97; H, 10.06. Found: C, 70.02; H, 10.11.

Methyl 2-hydroxy-3-butyl-3,4-hexadienecarboxylate (9b): 82% yield; an 84:16 mixture of diastereomers according to GC analysis; IR (film) 3494, 2956, 1966, 1740, 1440, 1214, 1077 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.31 (m, 1 H, vinyl H), 4.54 (d, J = 8.0 Hz, 1 H, $OCHCO_2Me$), 3.76 (s, 3 H, CO_2CH_3), 2.81 (d, J = 8.0 Hz, 1 H, OH), 2.06–1.85 (m, 2 H, vinyl CH_2), 1.66 (d, J = 7.0 Hz, 3 H, CH_3), 1.40–1.23 (m, 4 H, CH_2CH_2), 0.88 (t, J = 7.1 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{11}H_{18}O_3$ 198.1258, found 198.1256. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.73; H, 9.16.

Methyl 2-hydroxy-3-methyl-6-(benzyloxy)-3,4-hexadienecarboxylate (10c): 20% yield; a 66.34 mixture of diastereomers according to GC analysis; IR (film) 3452, 3029, 2953, 2927, 2360, 1969, 1744, 1454, 1271, 1208, 1094, 739, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.24 (m, 5 H, ArH), 5.39 (m, 1 H, vinyl H), 4.59 (d, J = 7.1 Hz, 1 H, $HOCHCO_2Me$), 4.52 (s, 2 H, OCH_2Ar), 4.04 (d, J = 6.7 Hz, 2 H, vinyl CH_2), 3.76 (s, 3 H, CO_2CH_3), 2.95 (d, J = 7.1 Hz, 1 H, OH), 1.74 (d, J = 2.9 Hz, 3 H, vinyl CH_3); HRMS calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1218. Anal. Calcd for $C_{21}H_{30}O_4$: C, 68.69; H, 6.92. Found: C, 68.82; H, 6.85.

Methyl 2-Oxo-3-heptyl-3,4-pentadienoate (11a). To a solution of 495 mg (2.19 mmol) of allenyl alcohol **8a** in 10 mL of CH_2Cl_2 was added 976 mg (2.30 mmol) of Dess–Martin reagent in a single portion. The mixture was stirred at room temperature for 20 min and then diluted with ether. The ether layer was washed with 1 N NaOH and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/ether, 6:1) to afford 480 mg (98%) of allenyl ketone **11a**: IR (film) 2928, 2856, 1955, 1927, 1747, 1862, 1436, 1307, 1207, 1162, 1098 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.29 (t, J = 3.0 Hz, 2 H, vinyl H), 3.81 (s, 3 H, CO_2CH_3), 2.27–2.18 (m, 2 H, vinyl CH_2), 1.43–1.27 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3). This product was unstable and was best used for cyclization immediately.

The above procedure was used to prepare the following compounds.

Methyl 2-oxo-3-heptyl-3,4-hexadienoate (11b): 91% yield; IR (film) 2928, 2855, 1946, 1747, 1682, 1436, 1307, 1199, 1163, 1101 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.66 (m, 1 H, vinyl H), 3.79 (s, 3 H, CO_2CH_3), 2.20 (m, 2 H, vinyl CH_2), 1.78 (d, J = 7.4 Hz, 3 H, vinyl CH_3), 1.41–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H CH_2CH_3). This product was used for cyclization immediately.

Methyl 2-oxo-3-butyl-3,4-hexadienoate (12b): 92% yield; IR (film) 2958, 1945, 1746, 1681, 1437, 1310, 1199, 1092, 1006 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.68–5.64 (m, 1 H, vinyl H), 3.79 (s, 3 H, CO_2CH_3), 2.09 (m, 2 H, vinyl CH_2), 1.78 (d, J = 7.4 Hz, 3 H, vinyl CH_3), 1.38–1.25 (m, 4 H, $(CH_2)_2$), 0.89 (t, J = 7.3 Hz, 3 H, CH_2CH_3). This product was used for cyclization immediately.

Methyl 2-oxo-2-methyl-6-(benzyloxy)-3,4-hexadienoate (13c): 97% yield; IR (film) 3060, 2860, 1951, 1745, 1682, 1454, 1313, 1208, 1041, 740 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.28 (m, 5 H, ArH), 5.78 (m, 1 H, vinyl H), 4.53 (s, 2 H, $PhCH_2O$), 4.16 (d, J = 7.0 Hz, 2 H, CH_2OBn), 3.78 (s, 3 H, CO_2CH_3), 1.87 (d, J = 2.6 Hz, 3 H, CH_3). This product was used for cyclization immediately.

3-Heptyl-3,4-pentadiene-1,2-diol (14a). To a solution of 185 mg (0.82 mmol) of allenic alcohol **8a** in 5 mL of ether was added dropwise 1.6 mL (1.60 mmol) of 1.0 M $LiAlH_4$ at 0 °C. The mixture was stirred for an additional 1 h at 0 °C, acidified with 10% HCl, and diluted with ether. The organic layer was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/ether 1:1) to afford 131 mg (81%) of diol **14a**: IR (film) 3356, 2926, 2855, 1956, 1458, 1080, 845 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.96–4.87 (m, 2 H, 2 vinyl H), 4.07 (m, 1 H, CHOH), 3.72 (m, 1 H, CH_2OH), 3.57 (m, 1 H, CH_2OH), 2.00–1.94 (m, 2 H, vinyl CH_2), 1.43–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); MS m/e (%) 180 (15, $M^+ - H_2O$), 137 (32), 107 (34), 96 (60), 83 (100).

The above procedure was used to prepare the following compound:

3-Heptyl-3,4-hexadiene-1,2-diol (14b): 99% yield; IR (film) 3340, 2930, 2900, 2830, 1955, 1620, 1445, 1360, 1060, 865 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.33 (m, 1 H, vinyl H), 4.05 (m, 1 H, HOCH), 3.70–3.66 (m, 1 H, CH_2OH), 3.56–3.52 (m, 1 H, CH_2OH), 1.98–1.88 (m, 2 H, vinyl CH_2), 1.98–1.88 (m, 2 H, $HOCHCH_2OH$, overlap with vinyl CH_2), 1.68 (d, J = 6.9 Hz, 3 H, vinyl CH_3), 1.41–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{24}O_2$ ($M - H_2O$) 194.1671, found 194.1671.

1-Acetoxy-3-heptyl-3,4-pentadien-2-ol (15a). To a mixture of 105 mg (0.53 mmol) of diol **14a** and 0.22 mL (1.59 mmol) of Et_3N in 6 mL of CH_2Cl_2 was added dropwise 0.055 mL (0.58 mmol) of Ac_2O. The resulting mixture was stirred at room temperature overnight and then diluted with ether. The ether layer was washed with aqueous $NaHCO_3$ and brine and dried over $MgSO_4$. Concentration of the extracts and chromatography of the residue on silica gel (hexane/ether, 3:1) afforded 116 mg (91%) of allenic alcohol **15a**: IR (film) 3442, 2928, 2855, 1962, 1745, 1378, 1245, 1040 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.91 (m, 2 H, vinyl H), 4.21 (A of ABX, dd, J = 3.0, 11.9 Hz, 1 H, $AcOCH_2$), 4.21 (X of ABX, m, 1 H, CHOH), 4.08 (B of ABX, dd, J = 8.2, 11.9 Hz, 1 H, $AcOCH_2$), 2.08 (s, 3 H, CH_3CO), 2.01 (d, J = 5.7 Hz, 1 H, OH), 1.99 (m, 2 H, vinyl CH_2), 1.40–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{24}O_3$ 240.1725, found 240.1720.

The above procedure was used to prepare the following compound.

1-Acetoxy-3-heptyl-3,4-hexadien-2-ol (15b): 90% yield; IR (film) 3420, 2950, 2920, 2850, 1960, 1730, 1370, 1225, 1035 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.30 (m, 1 H, vinyl H), 5.28 (s, 1 H, OH), 4.19 (A of ABX, dd, J = 3.0, 11.9 Hz, 1 H, $AcOCH_2$), 4.16 (X of ABX, m, 1 H, HOCH), 4.05 (B of ABX, dd, J = 8.1, 11.9 Hz, 1 H, $AcOCH_2$), 2.08 (s, 3 H, CH_3CO), 1.96 (m, 2 H, vinyl CH_2), 1.67 (d, J = 7.0 Hz, 3 H, CH_3), 1.40–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{26}O_3$ ($M + NH_3$) 272.2224, found 272.2237.

1-[(*tert*-Butyldimethylsilyl)oxy]-3-heptyl-3,4-hexadien-2-ol (16b). A mixture of 141 mg (0.66 mmol) of diol **14b**, 105 mg (0.70 mmol) of TBSCl, and 90 mg (1.33 mmol) of imidazole in 5 mL of DMF was stirred at room temperature overnight and then diluted with ether. the ether layer was washed with 1% HCl and saturated $NaHCO_3$ and dried over $MgSO_4$. Concentration of the mixture and chromatography of the residue on silica gel (hexane/ether, 4:1) afforded 203 mg (94%) of allenic alcohol **16b**: IR (film) ν 3461, 2928, 2857, 1960, 1463, 1362, 1255, 1113, 1006, 838, 777, 735 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.21 (m, 1 H, vinyl H), 4.02 (X of ABX, m, 1 H, CHOH), 3.67 (A of ABX, dd, J = 3.6, 10.1 Hz, 1 H, $TBSOCH_2$), 3.51 (B of ABX, dd, J = 7.3, 10.1 Hz, 1 H, $TBSOCH_2$), 2.47 (d, J = 4.3 Hz, OH), 1.96 (m, 2 H, vinyl CH_2), 1.65 (d, J = 7.0 Hz, 3 H, vinyl CH_3), 1.40–1.26 (m, 10 H, $(CH_2)_5$), 0.88 (s, 9 H, $(CH_3)_3C$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.05 (s, 6 H, $Si(CH_3)_2$); HRMS calcd for $C_{19}H_{38}O_2Si$ 326.2634, found 326.2641.

1-(Methoxymethyl)-3-heptyl-3,4-hexadien-2-ol (17b). To a mixture of 150 mg (0.71 mmol) of diol **14b**, 0.25 mL (1.41 mmol) of diisopropylethylamine, and 9 mg (0.071 mmol) of DMAP in 10 mL of CH_2Cl_2 was added 0.06 mL of chloromethyl methyl ether. The mixture was stirred at room temperature overnight and then diluted with ether. The organic layer was washed with dilute HCl, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 3:1) to afford 98 mg (55%) of allenic alcohol **17b**: IR (film) 3420, 2920, 2850, 1960, 1450, 1430, 1205, 1135, 1105, 1030, 915 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.26 (m, 1 H, vinyl H), 4.67, 4.65 (AB, J = 6.6 Hz, 2 H, OCH_2O), 4.17 (X of ABX, m, 1 H, HOC*H*), 3.69 (A of ABX, dd, J = 3.0, 10.5 Hz, 1 H, $MOMOCH_2$), 4.48 (B of ABX, dd, J = 7.6, 10.5 Hz, 1 H, $MOMOCH_2$), 3.37 (s, 3 H, OCH_3), 2.47 (d, J = 4.7 Hz, 1 H, OH), 1.98 (m, 2 H, vinyl CH_2), 1.66 (d, J = 7.0 Hz, 3 H, vinyl CH_3), 1.41–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{27}O_3$ (M – H) 255.1956, found 255.1960.

1-Acetoxy-3-heptyl-3,4-pentadien-2-one (18a). To a solution of 0.040 mL (0.44 mmol) of oxalyl chloride in 2 mL of CH_2Cl_2 at –78 °C was added 0.060 mL (0.87 mmol) of DMSO and, after 5 min, a solution of 70 mg (0.29 mmol) of alcohol **15a** in 2 mL of CH_2Cl_2 was added. The mixture was stirred at –78 °C for another 30 min, and then 0.24 mL (1.78 mmol) of Et_3N was added. The cooling bath was removed, and the mixture was diluted with ether and washed with 10% HCl. The ether layer was dried over $MgSO_4$ and concentrated. Chromatography of the residue on silica gel (hexane/ether, 10:1) afforded 56 mg (96%) of allenic ketone **18a**: IR (film) 2960, 2928, 2856, 1934, 1755, 1699, 1417, 1376, 1218, 1077, 846 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (t, J = 3.0 Hz, 2 H, vinyl H), 4.97 (s, 2 H, $AcOCH_2$), 2.15 (s, 3 H, CH_3CO), 2.15 (m, 2 H, vinyl CH_2, overlap with AcO), 1.40–1.24 (m, 10 H, $(CH_2)_5$), 0.85 (t, J = 6.6 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1565.

The above procedure was used to prepare the following compounds.

1-Acetoxy-3-heptyl-3,4-hexadien-2-one (18b): 97% yield, IR (film) 2920, 2850, 1940, 1740, 1680, 1410, 1370, 1260, 1230, 1200, 1080 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.63–5.59 (m, 1 H, vinyl H), 4.97, 4.90 (AB q, J = 16.3 Hz, 2 H, $AcOCH_2$), 2.15 (s, 3 H, CH_3CO), 2.15 (m, 2 H, vinyl CH_2) 1.80 (d, J = 7.3 Hz, 3 H, vinyl CH_3), 1.35–1.24 (m, 10 H, $(CH_2)_5$), 0.85 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{25}O_3$ (M + H) 253.1804, found 253.1821.

1-[(*tert*-Butyldimethylsilyl)oxy]-3-heptyl-3,4-hexadien-2-one (19b): 98% yield; IR (film) 2928, 2857, 1946, 1699, 1463, 1361, 1254, 1150, 1101, 910, 839, 779, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.50 (m, 1 H, vinyl H), 4.55 (s, 2 H, OCH_2CO), 2.15 (m, 2 H, vinyl CH_2), 1.77 (d, J = 7.7 Hz, 3 H, vinyl CH_3), 1.41–1.14 (m, 10 H, $(CH_2)_5$), 0.89 (m, 9 H, $(CH_3)_3C$), 0.85 (t, J = 7.0 Hz, 3 H, CH_2CH_3), 0.075, 0.065 (ds, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{19}H_{36}O_2Si$ 309.2250, found 309.2247.

1-(Methoxymethoxy)-3-heptyl-3,4-hexadien-2-one (20b): 91% yield; IR (film) 2920, 2850, 1945, 1685, 1440, 1365, 1205, 1145, 1120, 1055, 920 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.55 (m, 1 H, vinyl H), 4.68 (s, 2 H, OCH_2O), 4.52, 4.43 (AB q, J = 16.9 Hz, 2 H, OCH_2CO), 3.37 (s, 3 H, OCH_3), 2.16 (m, 2 H, vinyl CH_2), 1.79 (d, J = 7.3 Hz, 3 H, vinyl CH_3), 1.40–1.24 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{26}O_3$ 254.1878, found 254.1882.

Methyl 2-[[1-[(Benzyloxy)methyl]-2-butynyl]oxy]acetate (21c). A solution of 248 mg (1.00 mmol) of acid **7c** in 10 mL of Et_2O was treated with excess CH_2N_2. The mixture was stirred at room temperature for several minutes, and then excess CH_2N_2 was destroyed with acetic acid. After concentration, the residue was chromatographed on silica gel (hexane/ether, 2:1) to yield 262 mg (99%) of ester **21c**: IR (film) 3030, 2920, 2862, 2243, 1756, 1497, 1210, 1129, 1028, 739, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.24 (m, 5 H, ArH), 4.64 4.59 (AB q, J = 12.2 Hz, 2 H, $PhCH_2O$), 4.47 (m, 1 H, propargylic CH), 4.33, 4.25 (AB q, J = 16.4 Hz, 2 H, OCH_2CO_2Me), 3.73 (s, 3 H, CO_2CH_3), 3.70–3.61 (m, 2 H, $BnOCH_2$), 1.83 (d, J = 2.2 Hz, 3 H, propargylic CH_3); HRMS calcd for $C_{15}H_{18}O_4$ 262.1205, found 262.1218.

Methyl 2-Hydroxy-3-methyl-6-(benzyloxy)-3,4-hexadienecarboxylate (22c). To a mixture of 200 mg (0.77 mmol) of ester **21c** and 0.13 mL (0.93 mmol) of Et_3N in 5 mL of CH_2Cl_2 was added 0.20 mL (1.00 mmol) of TMSOTf at 0 °C. After being stirred at reflux for 16 h and being cooled to room temperature, the mixture was treated with 2.0 mL (2.00 mmol) of 1 M Bu_4NF. Water was added followed, after 10 min, by ether. The ether layer was washed with water, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 1:1) to give 176 mg (88%) of allenic alcohol **10c**: IR (film) 3452, 3029, 2953, 2927, 2360, 1969, 1744, 1454, 1271, 1208, 1094, 739, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.24 (m, 5 H, ArH), 5.39 (m, 1 H, vinyl H), 4.59 (d, J = 7, 1 Hz, 1 H, $HOCHCO_2Me$), 4.52 (s, 2 H, OCH_2Ar), 4.04 (d, J = 6.7 Hz, 2 H, vinyl CH_2), 3.76 (s, 3 H, CO_2CH_3), 2.95 (d, J = 7.1 Hz, 1 H, OH), 1.74 (d, J = 2.9 Hz, 3 H, vinyl CH_3); HRMS calcd for $C_{15}H_{18}O_4$ (M + H) 263.1283, found 263.1269. Anal. Calcd for $C_{21}H_{30}O_4$: C, 68.69; H, 6.92. Found: C, 68.82; H, 6.85.

2-Methyl-4-[(tributylstannyl)methoxy]-5-tridecyne (24d). To a suspension of 750 mg (4.69 mmol) of KH (25% in oil, washed by hexane) in 5 mL of THF was added 660 mg (3.12 mmol) of alcohol **21d** in 3 mL of THF. After 15 min, 1.60 g (3.71 mmol) of ICH_2SnBu_3 was added. After being stirred at room temperature overnight, the mixture was quenched with dilute HCl and extracted with ether. The extract was washed with brine and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel (hexane/ether, 20:1) to afford 1.19 g (74%) of ether **24d**: IR (film) 2926, 2233, 1465, 1377, 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.00, 3.54 (AB q, J = 10.2 Hz, 2 H, OCH_2SnBu_3), 3.85 (m, 1 H, propargylic CH), 2.20 (dt, J = 2.0, 7.4 Hz, 2 H, propargylic CH_2), 1.78 (m, 1 H, $CH(CH_3)_2$), 1.54–0.84 (m, 42 H, $(CH_2)_5CH_3$, $(C_4H_9)_3Sn$, and $CHCH_2CH(CH_3)_2$); HRMS calcd for $C_{27}H_{54}OSn$ (M – C_4H_9) 453.2494, found 453.2488. Anal. Calcd for $C_{27}H_{54}OSn$: C, 63.17; H, 10.60. Found: C, 63.28; H, 10.57.

The above procedure was used to prepare the following compound.

2,2-Dimethyl-3-[(tributylstannyl)methoxy]-4-dodecyne (24e): 77% yield; IR (film) 2927, 2225, 1464, 1056 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.00, 3.54 (AB q, J = 10.2 Hz, 2 H, OCH_2SnBu_3), 3.85 (m, 1 H, propargylic CH), 2.20 (dt, J = 2.0, 7.4 Hz, 2 H, propargylic CH_2), 1.50–0.78 (m, 49 H, $(C_4H_9)_3Sn$, $C(CH_3)_3$, and $(CH_2)_5$); HRMS calcd for $C_{27}H_{54}OSn$ (M – C_4H_9) 453.2494, found 453.2490. Anal. Calcd for $C_{27}H_{54}OSn$: C, 63.17; H, 10.60. Found: C, 62.96; H, 10.67.

2-Heptyl-6-methyl-2,3-heptadien-1-ol (25d). To a solution of 513 mg (1.00 mmol) of propargylic ether **24d** in 10 mL of THF was added dropwise 0.38 mL (1.10 mmol) of 2.90 M *n*-BuLi at –78 °C. The mixture was stirred at –78 °C for 13 h, quenched with aqueous NH_4Cl and 10% HCl, and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/ether, 2:1) to afford 193 mg (86%) of allenic alcohol **23d**: IR (film) 3326, 2926, 2855, 1964, 1465, 1382, 1024 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.25 (m, 1 H, vinyl H), 3.96 (m, 2 H, $HOCH_2$), 1.97 (m, 2 H, vinyl CH_2), 1.90 (t, J = 7.1 Hz, 2 H, vinyl CH_2CH), 1.63 (m, 1 H, $CH(CH_3)_2$), 1.55–1.26 (m, 10 H, $(CH_2)_5$), 0.91 (d, J = 6.6 Hz, 6 H, $CH(CH_2)_3$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{28}O$ 224.2140, found 224.2139. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29, H, 12.58. Found: C, 80.31; H, 12.49.

The above procedure was used to prepare the following compound.

2-Heptyl-5,5-dimethyl-2,3-hexadien-1-ol (25e): 74% yield; IR (film 3342, 2927, 2857, 1963, 1461, 1362, 1014 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.35 (t, J = 3.1 Hz, 1 H, vinyl H), 3.98 (m, 2 H, CH_2OH), 1.95 (m, 2 H, vinyl CH_2), 1.40–1.26 (m, 10 H, $(CH_2)_5$), 1.02 (s, 9 H, $C(CH_3)_3$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{28}O$ 224.2140, found 224.2145. Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.16; H, 12.56.

2-Heptyl-6-methyl-2,3-heptadienal (26d). To a solution of 0.050 mL (0.57 mmol) of oxalyl chloride in 2 mL of CH_2Cl_2 at –78 °C was added 0.080 mL (1.13 mmol) of DMSO. After 5 min, a solution of 100 mg (0.45 mmol) of allenic alcohol **25d** in 2 mL of CH_2Cl_2 was added, followed after 30 min by 0.34 mL (2.44 mmol) of Et_3N. The cooling bath was removed, and the mixture was diluted with ether and washed with 10% HCl. The ether layer was dried over $MgSO_4$ and concentrated. Chromatography of the residue on silica gel (hexane/ether, 10:1) afforded 93 mg (94%) of allenic aldehyde **26d**: IR (film) 2927, 2855, 1944, 1687, 1465, 1368, 1199 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1 H, CHO),

5.64 (m, 1 H, vinyl H), 2.14 (m, 2 H, vinyl CH_2), 2.05 (t, J = 6.7 Hz, 2 H, CH_2CH), 1.72 (m, 1 H, $CH(CH_3)_2$), 1.40–1.25 (m, 10 H, $(CH_2)_5$), 0.95 (d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3). This aldehyde was immediately used for the cyclization.

The above procedure was used to prepare the following compound.

2-Heptyl-5,5-dimethyl-2,3-hexadienal (26e): 91% yield; IR (film) 2927, 2857, 1943, 1687, 1462, 1364, 1173 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1 H, CHO), 5.71 (m, 1 H, vinyl H), 2.16 (m, 2 H, vinyl CH_2), 1.40–1.25 (m, 10 H, $(CH_2)_5$), 1.11 (s, 9 H, $C(CH_3)_3$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3). This aldehyde was immediately used for the cyclization.

3-Heptyl-7-methyl-3,4-octadien-2-one (27d). To a solution of 70 mg (0.31 mmol) of aldehyde **26d** in 5 mL of THF was added dropwise 0.30 mL (0.41 mmol) of 1.4 M MeLi at −78 °C. After 10 min, the mixture was acidified with 10% HCl and extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 4:1) to yield 62 mg (83%) of allenic alcohol: IR (film) 3340, 2927, 1961, 1465, 1367, 1083 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.26 (m, 1 H, vinyl H), 4.15 (m, 1 H, $HOCHCH_3$), 1.96 (m, 2 H, vinyl CH_2), 1.94–1.87 (m, 2 H, CH_2CH), 1.64 (m, 1 H, $CH(CH_3)_2$), 1.44–1.25 (m, 10 H, $(CH_2)_5$), 1.27 (dd, J = 6.3 Hz, 3 H, $HOCHCH_3$), 0.91 (d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$), 0.86 (t, J = 6.7 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{16}H_{30}O$ 238.2297, found 238.2297.

To a solution of 0.02 mL (0.24 mmol) of oxalyl chloride in 2 mL of CH_2Cl_2 at −78 °C was added 0.04 mL (0.56 mmol) of DMSO and, after 5 min, a solution of 36 mg (0.15 mmol) of the above allenic alcohol in 2 mL of CH_2Cl_2 was added. After 30 min, 0.21 mL (1.50 mmol) of Et_3N was added. The cooling bath was removed, and the mixture was diluted with ether and washed with 10% HCl. The extract was dried over $MgSO_4$ and concentrated. Chromatography of the residue on silica gel (hexane/ether, 10:1) afforded 34 mg (95%) of allenic ketone **27d**: IR (film) 2926, 1944, 1681, 1466, 1356, 1236 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.50 (m, 1 H, vinyl H), 2.24 (s, 3 H, CH_3CO), 2.13 (m, 2 H, vinyl CH_2), 2.05 (t, J = 6.8 Hz, 2 H, CH_2CH), 1.74 (m, 1 H, $CH(CH_3)_2$), 1.40–1.25 (m, 10 H, $(CH_2)_5$), 0.95 (d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$), 0.85 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2140.

The above procedure was used to prepare the following compound.

3-Heptyl-6,6-dimethyl-3,4-pentadien-2-one (27e): 62% yield; IR (film) 2927, 2857, 1944, 1680, 1462, 1362, 1240 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.54 (t, J = 2.8 Hz, 1 H, vinyl H), 2.24 (s, 3 H, CH_3CO), 2.13 (m, 2 H, vinyl CH_2), 1.40–1.25 (m, 10 H, $(CH_2)_5$), 1.11 (s, 9 H, $C(CH_3)_3$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2139.

2-(Methoxycarbonyl)-3-heptyl-5-methylfuran (28). A mixture of 43 mg (0.18 mmol) of allenyl ketone **11b**, 6 mg (0.036 mmol) of $AgNO_3$, and 14 mg (0.15 mmol) of $CaCO_3$ in 1.5 mL of acetone/H_2O (3:2) was stirred at room temperature in the dark overnight. After extraction with ether the product was purified by column chromatography on silica gel (hexane/ether, 8:1) to afford 42 mg (98%) of furan **28**: IR (film) 2927, 2855, 1712, 1610, 1546, 1437, 1400, 1306, 1193, 1154, 1112, 1070, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.01 (s, 1 H, vinyl H), 3.85 (s, 3 H, CO_2CH_3), 2.72 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 2.31 (d, J = 0.8 Hz, 3 H, vinyl CH_3), 1.53–1.28 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.15678. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.69; H, 9.41.

The above procedure was used to prepare the following compounds.

2-(Methoxycarbonyl)-3-butyl-5-methylfuran (29): 95% yield; IR (film) 2956, 1712, 1610, 1547, 1437, 1400, 1314, 1162, 1109, 1056, 812 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.01 (s, 1 H, vinyl H), 3.85 (s, 3 H, CO_2CH_3), 2.73 (t, J = 7.8 Hz, 2 H, vinyl CH_2), 2.31 (d, J = 0.9 Hz, 3 H, vinyl CH_3), 1.57–1.30 (m, 4 H, $(CH_2)_2$), 0.90 (t, J = 7.3 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{11}H_{16}O_3$ 196.1099, found 196.1096. Anal. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22. Found: C, 67.40; H, 8.24.

2-(Methoxycarbonyl)-3-methyl-5-[(benzyloxy)methyl]-furan (30): 91% yield; IR (film) 3030, 2950, 2854, 1717, 1613, 1548, 1439, 1356, 1298, 1170, 1101, 740, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.24 (m, 5 H, ArH), 6.29 (s, 1 H, H-4), 4.56 (s, 2 H, $PhCH_2O$), 4.47 (s, 2 H, $BnOCH_2$), 3.87 (s, 3 H, CO_2CH_3), 2.32 (s, 3 H, CH_3); HRMS calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1044. Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.22; H, 6.20 Found: C, 69.06; H, 6.23.

2-(Acetoxymethyl)-3-heptylfuran (31): 88% yield; IR (film) 2930, 2855, 1745, 1459, 1375, 1232, 1021, 969 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 1.8 Hz, 1 H, H-5), 6.25 (d, J = 1.8 Hz, 1 H, H-4), 5.01 (s, 2 H, $AcOCH_2$), 2.41 (t, J = 7.3 Hz, 2 H, vinyl CH_2), 2.06 (s, 3 H, CH_3CO), 1.53–1.27 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1565. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.44; H, 9.28.

2-(Acetoxymethyl)-3-heptyl-5-methylfuran (32): 44% yield; IR (film) 2920, 2860, 1730, 1570, 1440, 1370, 1230, 1115, 965, 920, 790 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.84 (s, 1 H, vinyl H), 4.96 (s, 2 H, $AcOCH_2$), 2.32 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 2.24 (d, J = 0.9 Hz, 3 H, vinyl CH_3), 2.05 (s, 3 H, CH_3CO), 1.46–1.25 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{24}O_3$ 252.1725, found 252.1728. Anal. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59. Found: C, 71.52; H, 9.64.

Continued elution (hexane/ether, 2:1) afforded 6 mg (21%) of the hemiacetal intermediate (cf. **38**), which was transformed into furan **32** quantitatively upon standing in $CDCl_3$ overnight. A small amount of dimer **41** was also found in the early chromatographic fractions.

2-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-3-heptyl-5-methylfuran (33): 96% yield; IR (film) 2928, 2856, 1573, 1463, 1400, 1254, 1061, 838, 776 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.79 (s, 1 H, vinyl H), 4.52 (s, 2 H, $TBSOCH_2$), 2.31 (t, J = 7.8 Hz, 2 H, vinyl CH_2), 2.22 (d, J = 0.9 Hz, 3 H, vinyl CH_3), 1.46–1.25 (m, 10 H, $(CH_2)_5$), 0.88 (m, 9 H, $(CH_3)_3C$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.05 (s, 6 H, $(CH_3)_2Si$); MS m/e (%) 267 (86, $M^+ - C_4H_9$), 193 (100), 183 (20), 109 (57).

2-[(Methoxymethoxy)methyl]-3-heptyl-5-methylfuran (34): 93% yield; IR (film) 2929, 2856, 1573, 1466, 1397, 1149, 1099, 1039, 990, 927, 797 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.82 (s, 1 H, vinyl H), 4.64 (s, 2 H, OCH_2O), 4.43 (s, 2 H, OCH_2Ar), 3.38 (s, 3 H, OCH_3), 2.33 (t, J = 7.6 Hz, 2 H, vinyl CH_2), 2.23 (d, J = 0.9 Hz, 3 H, vinyl CH_3), 1.47–1.24 (m, 10 H, $(CH_2)_5$), 0.85 (t, J = 7.1 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{26}O_3$ 254.1882, found 254.1878. Anal. Calcd for $C_{15}H_{26}O_3$: C, 70.83; H, 10.30. Found: C, 71.12; H, 10.40.

2-Methyl-3-heptyl-5-isobutylfuran (36): 99% yield; IR (film) 2927, 2856, 1575, 1466, 1384, 1219 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (s, 1 H, H-4), 2.37 (d, J = 7.0 Hz, 2 H, $ArCH_2CH(CH_3)_2$), 2.23 (t, J = 7.5 Hz, 2 H, $ArCH_2(CH_2)_5CH_3$)), 2.14 (s, 3 H, CH_3), 1.88 (m, 1 H, $CH(CH_3)_2$), 1.45–1.26 (m, 10 H, $(CH_2)_5$), 0.90 (d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2138. Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.39; H, 11.89.

2-Methyl-3-heptyl-5-*tert*-butylfuran (37): 99% yield; IR (film) 2926, 2856, 1568, 1460, 1361, 1288, 1191, 1100 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.71 (s, 1 H, H-4), 2.22 (t, J = 7.5 Hz, 2 H, $ArCH_2$), 2.14 (s, 3 H, CH_3), 1.45–1.27 (m, 10 H, $(CH_2)_5$), 1.22 (s, 9 H, $(CH_3)_3$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{16}H_{28}O$ 236.2140, found 236.2139. Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.94. Found: C, 81.36; H, 11.89.

3-Heptyl-5-isobutylfuran (35). A mixture of 43 mg (0.19 mmol) of allenic aldehyde **26d**, 7 mg (0.04 mmol) of silver nitrate, and 15 mg (0.15 mmol) of calcium carbonate in 1.5 mL of acetone/water (3:2) was stirred at room temperature in the dark for 24 h. Ether was added, and the ether layer was washed with water and dried over $MgSO_4$. Concentration of the solution and chromatography of the residue (hexane) afforded 33 mg (77%) of furan **35**: IR (film) 2927, 2856, 1548, 1465, 1384, 1125, 938, 799 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1 H, H-2), 5.84 (s, 1 H, H-4), 2.41 (d, J = 7.0 Hz, 2 H, $ArCH_2CH(CH_3)_2$, 2.33 (t, J = 6.8 Hz, 2 H, $ArCH_2(CH_2)_5CH_3$)), 1.91 (m, 1 H, $CH(CH_3)_2$), 1.52–1.27 (m, 10 H, $(CH_2)_5$), 0.90 (d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{15}H_{26}O$ 222.1984, found 222.1975. Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.78. Found: C, 81.23; H, 11.72.

Continued elution (hexane/ether, 3:1) afforded the hemiacetal intermediate (cf. **38**), which was transformed into furan **35**

quantitatively upon standing in $CDCl_3$ overnight.

2-[(3-Heptyl-5-methyl-2-furyl)methyl]-3-heptyl-5-methylfuran (41). A. From Furfuryl Acetate 32. A mixture of 50 mg (0.20 mmol) of acetate **32** and 34 mg (0.20 mmol) of $AgNO_3$ in 2 mL of acetone/H_2O (3:2) was refluxed in the dark under N_2 for 24 h. The mixture was cooled to room temperature, diluted with water, and then extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 30:1) to give 24 mg (65%) of bisfuranomethane **41**: IR (film) 2920, 2850, 1570, 1450, 1370, 1250, 1115, 970, 790 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (s, 2 H, 2 vinyl H), 3.75 (s, 2 H, CH_2), 2.24 (t, J = 7.6 Hz, 4 H, 2 vinyl CH_2), 2.19 (s, 6 H, 2 vinyl CH_3), 1.42–1.26 (m, 20 H, 2 $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 6 H, 2 CH_2CH_3; ^{13}C NMR (500 MHz, $CDCl_3$) δ 149.9, 145.3, 121.1, 108.0, 32.3, 30.9, 29.8, 29.6, 25.1, 24.0, 23.1, 14.5, 13.9; HRMS calcd for $C_{25}H_{40}O_2$ 372.3028, found 372.3024.

B. From Furfuryl Alcohol 42. Method A. A mixture of 50 mg (0.24 mmol) of furan **42** and 40 mg (0.24 mmol) of $AgNO_3$ in 3 mL of acetone/H_2O (3:2) was refluxed in the dark under N_2 for 24 h. The mixture was cooled to room temperature, diluted with water, and extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 30:1) to give 31 mg (70%) of bisfuranomethane **41** with spectral properties identical with those in part A.

Method B. A mixture of 32 mg (0.15 mmol) of furan **42** and a catalytic amount of trichloroacetic acid in 3 mL of acetone/H_2O (3:2) was heated at 40 °C under N_2 for 1 h. The mixture was cooled to room temperature, diluted with water and then extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 30:1) to give 21 mg (75%) of bisfuranomethane **41**.

The above procedures were used to prepare the following compound:

2-[(3-Butyl-5-methyl-2-furyl)methyl]-3-butyl-5-methylfuran (48). Method A: 55% yield; IR (film) 2927, 2858, 1577, 1456, 1258, 1121, 797 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.75 (s, 2 H, 2 vinyl H), 3.75 (s, 2 H, $ArCH_2Ar$), 2.25 (t, J = 7.2 Hz, 4 H, 2 vinyl CH_2), 2.18 (s, 6 H, 2 CH_3), 1.42–1.30 (m, 8 H, 2 CH_2CH_2), 0.88 (t, J = 7.2 Hz, 6 H, 2 CH_2CH_3); HRMS calcd for $C_{19}H_{28}O_2$ 288.2089, found 288.2083.

Method B: 81% yield.

Method C. To a solution of 62 mg (0.32 mmol) of furan ester **29** in 5 mL of ether was added dropwise 0.95 mL (0.95 mmol) of 1 M DIBAH at 0 °C. After 30 min, the mixture was diluted with ether and washed with dilute HCl and saturated $NaHCO_3$. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 30:1) to give 21 mg (46%) of bisfuranomethane **48** directly.

2-(Hydroxymethyl)-3-heptyl-5-methylfuran (42). To a solution of 65 mg (0.27 mmol) of furan ester **28** in 5 mL of ether was added dropwise 0.82 mL (0.82 mmol) of a 1 M DIBAH at 0 °C. The mixture was stirred at 0 °C for 1 h, acidified with dilute HCl, and extracted with ether. The extract was washed with saturated $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was purified, by column chromatography on silica gel deactivated with Et_3N (hexane/ether, 4:1) to give 53 mg (92%) of alcohol **42**: IR (film) 3320, 2920, 2865, 1565, 1445, 1260, 1110, 985, 910, 790 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (s, 1 H, vinyl H), 4.50 (d, J = 5.7 Hz, 2 H, $HOCH_2$), 2.33 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 2.23 (d, J = 1.0 Hz, 3 H, vinyl CH_3), 1.49–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{22}O_2$ 210.1620, found 210.1629.

The above procedure was used to prepare the following compounds.

2-(Hydroxymethyl)-3-butyl-5-methylfuran (43): 95% yield; IR (film) 3354, 2929, 1574, 1456, 1270, 1119, 990 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (s, 1 H, vinyl H), 4.50 (d, J = 5.2 Hz, 2 H, $HOCH_2$), 2.34 (t, J = 7.7 Hz, 2 H, vinyl CH_2), 2.23 (d, J = 0.7 Hz, 3 H, vinyl CH_3), 1.49–1.27 (m, 2 H, $(CH_2)_2$), 0.89 (t, J = 7.2 Hz, 3 H, CH_2CH_3); MS m/e (%) 167 (55, M^+ – H), 154 (100), 137 (47), 111 (55), 97 (76).

2-(Hydroxymethoxy)-3-methyl-5-[(benzyloxy)methyl]-furan (44): 90% yield; IR (film) 3387, 3029, 2926, 1454, 1358, 1152, 1069, 1004, 738, 699 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.34–7.24 (m, 5 H, PhH), 6.14 (s, 1 H, vinyl H), 4.55 (d, J = 6.0 Hz, 2 H, $HOCH_2$), 4.54 (s, 2 H, $PhOCH_2$), 4.41 (s, 2 H, $BnOCH_2$), 2.01 (s, 3 H, CH_3), 1.59 (t, J = 6.0 Hz, 1 H, OH); HRMS calcd for $C_{14}H_{16}O_3$ 232.1099, found 232.1097. Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.30; H, 6.98.

2-(Hydroxymethyl)-3-heptylfuran (45). A mixture of 45 mg (0.20 mmol) of allenyl ketone **11a**, 7 mg (0.04 mmol) of $AgNO_3$, and 16 mg (0.16 mmol) of $CaCO_3$ in 1.5 mL of acetone/H_2O (3:2) was stirred at room temperature in the dark for 48 h. The product was extracted with ether, and the extract was washed with water, dried over $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ether, 8:1) to afford 35 mg (78%) of furan **52**: IR (film) 2928, 2855, 1716, 1596, 1490, 1439, 1409, 1298, 1196, 1120, 890, 783 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 1.7 Hz, 1 H, H-5), 6.38 (d, J = 1.7 Hz, 1 H, H-4), 3.88 (s, 3 H, CO_2CH_3), 2.77 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 1.56–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1411. Anal. Calcd for $C_{13}H_{22}O_3$: C, 69.62; H, 8.99. Found: C, 69.46; H, 8.96.

To a solution of 65 mg (0.29 mmol) of the above furan ester in 5 mL of ether was added dropwise 0.87 mL (0.87 mmol) of 1 M DIBAH at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, quenched with dilute HCl, and extracted with ether. The extract was washed with saturated $NaHCO_3$ and dried over $MgSO_4$. After concentration, the residue was chromatographed on silica gel (hexane/ether, 2:1) to yield 56 mg (99%) of furfuryl alcohol **45**: IR (film) 3343, 2927, 2855, 1465, 1150, 1004, 892, 734 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 1.8 Hz, 1 H, H-5), 6.23 (d, J = 1.8 Hz, 1 H, H-4), 4.55 (d, J = 5.8 Hz, 2 H, $HOCH_2$), 2.39 (t, J = 7.6 Hz, 3 H, vinyl CH_2), 1.54–1.27 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.1 Hz, 3 H, CH_2CH_3; HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196.1457.

2,5-Bis(hydroxymethyl)-3-heptylfuran (47). To a solution of 226 mg (1.15 mmol) of furfuryl alcohol **45** in 10 mL of THF was added dropwise 1.0 mL (2.53 mmol) of 2.44 M *n*-BuLi at –78 °C. The mixture was stirred at –78 °C for 1 h, and then 100 mg (3.33 mmol) of paraformaldehyde was added in a single portion. The mixture was allowed to warm to room temperature, stirred for 1 h, quenched with dilute HCl and extracted with ether. The extract was washed with saturated $NaHCO_3$ and dried over $MgSO_4$. Concentration of the mixture and chromatography of the residue on silica gel deactivated with Et_3N (hexane/ether, 1:2) afforded 198 mg (76%) of diol **47**: IR (film) 3358, 2926, 2855, 1461, 1016 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.14 (s, 1 H, vinyl H), 4.54 (s, 4 H, 2 $HOCH_2$), 2.36 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 1.49–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{22}O_3$ 226.1569, found 226.1568. Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.05; H, 9.83.

2-[[3-Methyl-5-(benzyloxy)-2-furyl]methyl]-3-methyl-5-(benzyloxy)furan (49). A mixture of 79 mg (0.34 mmol) of furan alcohol **44** and a catalytic amount of trichloroacetic acid in 3 mL of acetone/H_2O (3:2) was heated at 40 °C under N_2 for 1 h. The mixture was cooled to room temperature, diluted with water, and then extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 2:1) to give 14 mg (40%) of bisfuranomethane **49**: IR (film) 3067, 3029, 2923, 2862, 1573, 1451, 1406, 1231, 1072, 822, 746, 693 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.32–7.24 (m, 10 H, 2 ArH), 6.10 (s, 2 H, 2 vinyl H), 4.50 (s, 4 H, 2 $PhCH_2O$), 4.36 (s, 4 H, 2 OCH_2Ar), 3.87 (s, 2 H, CH_2), 1.91 (s, 6 H, 2 CH_3); MS m/e (%) 416 (1, M^+), 91 (100).

Continued elution afforded 3 mg (14%) of aldehyde **60** and 3 mg (16%) of benzyl alcohol.

4,5-Dimethyl-2-formylfuran (51). A mixture of 165 mg (0.71 mmol) of furan alcohol **44** and 120 mg (0.71 mmol) of $AgNO_3$ in 5 mL of acetone/H_2O (3:2) was heated at 40 °C in the dark under N_2 for 24 h. The mixture was cooled to room temperature, diluted with water, and then extracted with ether. The extracts were dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 2:1) to give 36 mg (41%) of aldehyde **51**: IR (film) 2926, 1674, 1609, 1526, 1318, 1161, 802 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1 H, CHO), 7.02 (s, 1 H, vinyl H), 2.31 (d, J = 0.6 Hz, 3 H, 4-CH_3), 2.00 (d, J = 0.5 Hz, 5-CH_3); MS m/e (%) 124 (100, M^+), 123 (76), 95 (22), 67 (60).

Continued elution afforded 42 mg (54%) of benzyl alcohol.

Acid-Catalyzed Isomerization/Dimerization of Diol 47. A mixture of 100 mg (0.44 mmol) of diol **47** and 16 mg (0.10 mmol) of trichloroacetic acid in 5 mL of acetone/H_2O (5:1) was heated at 40 °C for 6 h, quenched with water, and extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (hexane/ether, 1:1) to give 27 mg (29%) of aldehyde **60** as the first fraction: IR (film) 2928, 2856, 1681, 1525, 1466, 1316, 1143, 950, 807, 725 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 9.25 (s, 1 H, CHO), 7.05 (s, 1 H, vinyl H), 2.34 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 2.31 (s, 3 H, CH_3), 1.50–1.26 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.1 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1456.

Continued elution afforded 35 mg (35%) of pyranone **61** as the second fraction: IR (film) 3388, 2929, 2857, 1672, 1465, 1377, 1285, 1098, 930, 885 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90 (s, 1 H, vinyl H), 4.47, 4.07 (AB q, J = 16.8 Hz, 2 H, OCH_2), 2.57 (m, 1 H, OH), 2.38–2.22 (m, 2 H, vinyl CH_2), 1.61 (s, 3 H, CH_3), 1.58–1.27 (m, 10 H, $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{13}H_{22}O_3$ 226.1569, found 226.1570.

Further elution (ether) yielded 7 mg (8%) of bisfuranomethane **50** as the third fraction: IR (film) 3388, 2925, 2855, 1463, 1015, 978, 814 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.09 (s, 2 H, 2 vinyl H), 4.48 (s, 4 H, 2 $HOCH_2$), 3.47 (s, 2 H, CH_2), 2.27 (t, J = 7.8 Hz, 4 H, 2 vinyl CH_2), 1.44–1.25 (m, 20 H, 2 $(CH_2)_5$), 0.86 (t, J = 7.0 Hz, 6 H, 2 CH_2CH_3); HRMS calcd for $C_{25}H_{40}O_4$ 404.2927, found 404.2926.

1-Decyn-4-ol (54). To a mixture of 212 mg (8.76 mmol) of Mg powder and a catalytic amount of $HgCl_2$ in 10 mL of Et_2O was added dropwise 781 mg (6.57 mmol) of propargyl bromide in 5 mL of Et_2O over 20 min. Heptanal (**53**) 0.59 mL (4.38 mmol) was added dropwise. After being stirred for 10 min at room temperature, the mixture was acidified with 10% HCl and extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel to afford 562 mg (83%) of alcohol **54**: IR (film) 3350, 3313, 2931, 2858, 2120, 1467, 1378, 1125, 1050, 952, 850 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.74 (m, 1 H, $CHOH$), 2.46–2.25 (m, 2 H, propargylic CH_2), 2.04 (t, J = 2.6 Hz, 1 H, C≡CH), 1.86 (d, J = 5.0 Hz, 1 H, OH), 1.55–1.27 (m, 8 H, $(CH_2)_4$), 0.87 (t, J = 6.9 Hz, 3 H, CH_2CH_3); MS m/e (%) 153 (1, M^+ – H), 121 (3), 115 (16), 97 (49), 55 (100).

2-Undecyne-1,5-diol (55). To a stirred solution of 495 mg (3.21 mmol) of alcohol **54** in 15 mL of THF was added dropwise 2.76 mL (6.74 mmol) of 2.44 M n-BuLi in hexane at −78 °C. After 30 min, 289 mg (9.63 mmol) of paraformaldehyde was added in one portion. The mixture was allowed to warm to room temperature, stirred for 1 h, acidified with 10% HCl, and extracted with ether. The extract was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel to afford 561 mg (95%) of diol **55**: IR (film) 3357, 2929, 2858, 2225, 1459, 1137, 1015 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.25 (m, 2 H, CH_2OH), 3.73 (m, 1 H, $CHOH$), 2.50–2.29 (m, 2 H, propargylic CH_2), 1.97 (m, 1 H, OH), 1.78 (m, 1 H, OH), 1.52–1.27 (m, 8 H, $(CH_2)_4$), 0.86 (t, J = 7.0 Hz, 3 H, CH_2CH_3); HRMS calcd for $C_{11}H_{20}O_2$ 184.1463, found 184.1462.

1-[(*tert*-Butyldimethylsilyl)oxy]-2-undecyn-5-ol (56). To a mixture of 558 mg (3.02 mmol) of alcohol **55** and 412 mg (6.05 mmol) of imidazole in 10 mL of CH_2Cl_2 was added 456 mg (3.02 mmol) of TBSCl. The resulting mixture was stirred at room temperature for 3 h and then it was acidified with 10% HCl and extracted with ether. The ether layer was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel to yield 787 mg (87%) of alcohol **56**: IR (film) 3405, 2930, 2858, 2234, 1464, 1255, 1140, 1081, 838, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.30 (t, J = 2.1 Hz, 2 H, CH_2OTBS), 3.70 (m, 1 H, $CHOH$), 2.50–2.33 (m, 2 H, propargylic CH_2), 1.83 (m, 1 H, OH), 1.50–1.27 (m, 8 H, $(CH_2)_4$), 0.89 (s, 9 H, $(CH_3)_3CSi$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.09 (s, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{17}H_{34}O_2Si$ – C_4H_9 241.1624, found 241.1623.

1-[(*tert*-Butyldimethylsilyl)oxy]-2,3-undecadien-5-one (58) and 1-[(*tert*-Butyldimethylsilyl)oxy]-2-undecyn-5-one (57). A solution of 300 mg (1.01 mmol) of alcohol **56** and 450 mg (1.06 mmol) of Dess–Martin reagent[7] in 5 mL of CH_2Cl_2 was stirred at room temperature for 20 min. Ether was added, and the solution was washed with 1 N NaOH, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 8:1) to yield 272 mg (93%) of allenic ketone **58** and homopropargylic ketone **57** as a 1.2:1 mixture according to the ^1H NMR spectrum: IR (film) of mixture 2930, 2858, 1950, 1726, 1685, 1464, 1362, 1255, 1085, 838, 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) for **58** δ 5.81–5.78 (m, 1 H, vinyl H-4), 5.70 (q, J = 60 Hz, 1 H, vinyl H-2), 4.34–4.29 (m, 2 H, CH_2OTBS), 2.55 (t, J = 7.7 Hz, 2 H, CH_2CO), 1.56–1.26 (m, 8 H, $(CH_2)_4$), 0.88 (s, 9 H, $(CH_3)_3CSi$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.07 (s, 6 H, $(CH_3)_2Si$); ^1H NMR (300 MHz, $CDCl_3$) for **57** δ 4.34–4.29 (m, 2 H, CH_2OTBS), 3.25 (t, J = 2.2 Hz, 2 H, $COCH_2CC$), 2.57 (t, J = 7.7 Hz, 2 H, CH_2CO), 1.56–1.26 (m, 8 H, $(CH_2)_4$), 0.90 (s, 9 H, $(CH_3)_3CSi$), 0.86 (t, J = 6.9 Hz, 3 H, CH_2CH_3), 0.10 (s, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{17}H_{32}O_2Si$ (M – CH_3) 281.1937, found 281.1939.

1-[(*tert*-Butyldimethylsilyl)oxy]-5-hexylfuran (59). A mixture of 264 mg (0.89 mmol) of ketones **57** and **58**, 31 mg (0.18 mmol) of $AgNO_3$, and 71 mg (0.71 mmol) of $CaCO_3$ in 4 mL of acetone/water (3:2) was stirred at room temperature in the dark for 4 h. Ether was added, and the ether layer was washed with water, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane) to afforded 221 mg (84%) of furan **59**: IR (film) 2929, 2858, 1561, 1464, 1255, 1079, 1019, 838, 779 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.08 (d, J = 3.0 Hz, 1 H, vinyl H-4), 5.87 (d, J = 3.0 Hz, 1 H, vinyl H-3), 4.57 (s, 2 H, CH_2OTBS), 2.57 (t, J = 7.5 Hz, 2 H, vinyl CH_2), 1.60–1.28 (m, 8 H, $(CH_2)_4$), 0.88 (s, 9 H, $(CH_3)_3CSi$), 0.86 (t, J = 6.8 Hz, 3 H, CH_2CH_3), 0.05 (s, 6 H, $(CH_3)_2Si$); HRMS calcd for $C_{17}H_{33}O_2Si$ (M – H) 295.2093, found 295.2095. Anal. Calcd for $C_{17}H_{32}O_2Si$: C, 68.86; H, 10.88. Found: C, 68.76; H, 10.91.

1-(Hydroxymethyl)-5-hexylfuran (46). To a solution of 212 mg (0.71 mmol) of furan **59** in 5 mL of THF was added 1.4 mL (1.4 mmol) of 1 M Bu_4NF, followed by 170 mg (2.84 mmol) of acetic acid. The reaction mixture was stirred at room temperature for 1 h. Ether was added, and the ether layer was washed with water and aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel (hexane/ether, 1:1) to afford 124 mg (96%) of furan **46**: IR (film) 3355, 3106, 2929, 2860, 1560, 1465, 1378, 1182, 1013, 784 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.16 (d, J = 3.1 Hz, 1 H, vinyl H-4), 5.90 (d, J = 3.1 Hz, 1 H, vinyl H-3), 4.54 (s, 2 H, CH_2OTBS), 2.58 (t, J = 7.6 Hz, 2 H, vinyl CH_2), 2.37 (t, J = 7.6 Hz, 1 H, OH), 1.61–1.28 (m, 8 H, $(CH_2)_4$), 0.87 (t, J = 6.8 Hz, 3 H, CH_2CH_3; HRMS calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1311. Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.30; H, 10.00.

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Supplementary Material Available: ^1H NMR spectra for compounds **2a,b, 3b, 4c, 5a,b, 6b, 7c, 11a,b, 12b, 13c, 14a,b, 15a,b, 16b, 17b, 18a,b, 19b, 21c, 23d,e, 25d,e, 26b,d,e, 27d,e, 28, 33, 41–46, 48–51, 54–61** (54 pages). Ordering information is given on any current masthead page.