Palladium-Catalyzed Cyclization of ω-Haloallenes. A New General Route to Common, Medium, and Large Ring Compounds via Cyclic Carbopalladation

Shengming Ma and Ei-ichi Negishi*

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Received February 9, 1995[⊗]

Abstract: A series of ω-haloallenes (**4**−**32**) as well as related ω-haloalkenes (**41**−**45**) were prepared through the application of known procedures. Their cyclization in the presence of a catalytic amount of $Cl_2Pd(PPh_3)_2$, a base, *e.g.*, K_2CO_3, and other appropriate reagents was investigated mostly under two sets of conditions (conditions I and II). The results summarized in Table 1 reveal the following: (1) The Pd-catalyzed cyclization reaction of ω-haloallenes gives the desired five- through twelve-membered and twenty-membered ring products in respectable yields. (2) The use of the dilute solution technique and *n*-Bu_4NCl is advantageous in the synthesis of eight-membered and larger rings. (3) Formation of a carbon−carbon bond uniformly takes place at the central carbon of an allene. (4) The corresponding reaction of ω-haloalkenes fails to give eight- and nine-membered rings and displays an intriguing endo−exo cyclization mode vs ring size profile. (5) The eight-membered ring products were exclusively *Z*, and the eleven-, twelve-, and twenty-membered ring products were *E*. The stereochemistry of the nine- and ten-membered rings depends on other factors as well. The putative allylpalladium intermediates can be trapped with external nucleophiles, such as malonate esters, organostannanes, phenols, and amines, to give the corresponding derivatives. The results support the oxidative addition−carbopalladation mechanism leading to the formation of allylpalladium intermediates. The results also indicate that the extents of the actual cyclization process itself may be considerably higher than indicated by the yields of the dehydropalladation products and that some undesirable side reactions, such as double bond isomerization, can be circumvented through trapping with nucleophiles.

Cyclic carbopalladation[1−11] has emerged as a potentially general and versatile method for the preparation of both simple and complex cyclic compounds. Earlier studies employed almost exclusively alkenes[1−3] as π-systems. More recently, alkynes[4,6] and conjugated dienes[7] have also been employed. In our systematic development of the cascade carbopalladation methodology,[6a−c,g−i] it became desirable to investigate cyclic carbopalladation of allenes.[12] Although intermolecular carbo-

[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1995.

(1) For reviews dealing with early works, see: (a) Heck, R. F. *Org. React.* **1982**, *27*, 345. (b) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985.

(2) For early studies on the synthesis of heterocycles, see: (a) Mori, M.; Chiba, M.; Ban, Y. *Tetrahedron Lett.* **1977**, *18*, 1073. (b) Mori, M.; Ban, Y. *Tetrahedron Lett.* **1979**, *20*, 1133; **1982**, *23*, 5315. (c) Terpko, M. O.; Heck, R. F. *J. Am. Chem. Soc.* **1979**, *101*, 5281.

(3) For early studies on the synthesis of carbocycles, see: (a) Narula, C. K.; Mak, K. T.; Heck, R. F. *J. Org. Chem.* **1983**, *48*, 2792. (b) Grigg, R.; Stevenson, P.; Worakun, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1073; *Tetrahedron* **1988**, *44*, 2033, 2049, 4967. (c) Tour, J. M.; Negishi, E. *J. Am. Chem. Soc.* **1985**, *107*, 8289. (d) Abelman, M. M.; Oh, T.; Overman, L. E. *J. Org. Chem.* **1987**, *52*, 4133. (e) Negishi, E.; Zhang, Y.; O'Connor, B. *Tetrahedron Lett.* **1988**, *29*, 2915. (f) O'Connor, B.; Zhang, Y.; Negishi, E.; Luo, F. T.; Cheng, J. W. *Tetrahedron Lett.* **1988**, *29*, 3903. (g) Zhang, Y.; O'Connor, B.; Negishi, E. *J. Org. Chem.* **1988**, *53*, 5588. (h) Larock, R. C.; Song, H.; Baker, B. E.; Gong, W. H. *Tetrahedron Lett.* **1988**, *29*, 2919.

(4) For early works on intramolecular carbopalladation of alkynes, see: (a) Burns, B.; Grigg, R.; Sridharan, V.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4325. (b) Burns, B.; Grigg, R.; Ratananukul, P.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakum, T. *Tetrahedron Lett.* **1988**, *29*, 5565. (c) Burns, B.; Grigg, R.; Sridharan, V.; Stevenson, P.; Sukirthalingam, S.; Worakun, T. *Tetrahedron Lett.* **1989**, *30*, 1135. (d) Luo, F. T.; Chou, F. L.; Wang, R. T. *J. Org. Chem.* **1990**, *55*, 4846. (e) Negishi, E.; Noda, Y.; Lamaty, F.; Vawter, E. J. *Tetrahedron Lett.* **1990**, *31*, 4393. (f) Nuss, J. M.; Levine, B. H.; Rennels, R. A.; Heravi, M. M. *Tetrahedron Lett.* **1991**, *32*, 5243. (g) Nuss, J. M.; Murphy, M. M.; Rennels, R. A.; Heravi, M. H.; Mohr, B. J. *Tetrahedron Lett.* **1993**, *34*, 3079.

(5) For cyclic cascade carbopalladation of alkenes, see: (a) Abelman, M. M.; Overman, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 2328. (b) Carpenter, N. E.; Kucera, D. J.; Overman, L. E. *J. Org. Chem.* **1989**, *54*, 5846.

(6) For cyclic cascade carbopalladation of alkynes, see: (a) (review) Negishi, E. *Pure Appl. Chem.* **1992**, *64*, 323. (b) Zhang, Y.; Negishi, E. *J. Am. Chem. Soc.* **1989**, *111*, 3454. (c) Zhang, Y.; Wu, G.; Agnel, G.; Negishi, E. *J. Am. Chem. Soc.* **1990**, *112*, 8590. (d) Grigg, R.; Dorrity, M. J.; Malone, J. F.; Sridharan, V.; Sukirthalingam, S. *Tetrahedron Lett.* **1990**, *31*, 1343. (e) Meyer, F. E.,; de Meijere, A. *Synlett* **1991**, 777. (f) Meyer, F. E.; Parsons, P. J.; de Meijere, A. *J. Org. Chem.* **1991**, *56*, 6487. (g) Negishi, E.; Harring, L. S.; Owczarczyk, Z.; Mohamud, M. M.; Ay, M. *Tetrahedron Lett.* **1992**, *33*, 3253. (h) Negishi, E.; Ay, M.; Sugihara, T. *Tetrahedron* **1993**, *49*, 5471. (i) Sugihara, T.; Copéret, C.; Owczarczyk, Z.; Harring, L. S.; Negishi, E. *J. Am. Chem. Soc.* **1994**, *116*, 7923.

(7) For cyclic carbopalladation of conjugated dienes, see: (a) Burns, B.; Grigg, R.; Ratananukul, R.; Sridharan, V.; Stevenson, P.; Worakun, T. *Tetrahedron Lett.* **1988**, *29*, 4329. (b) Grigg, R.; Sridharan, V.; Sukirthalingam, S.; Worakun, T. *Tetrahedron Lett.* **1989**, *30*, 1139.

(8) For related Pd-catalyzed cycloisomerizations of enynes and related compounds lacking carbon−halogen and related electrophilic functional groups, see: Trost, B. M. *Acc. Chem. Res.* **1990**, *23*, 34 and references therein.

(9) (a) (review) Oppolzer, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds., Pergamon Press: Oxford, 1991; Vol. 5, p 29. (b) Oppolzer, W.; Gaudin, J. M. *Helv. Chim. Acta* **1987**, *70*, 1477. (c) For a related reaction involving a different procedure, see: Negishi, E.; Iyer, S.; Rousset, C. J. *Tetrahedron Lett.* **1989**, *30*, 291.

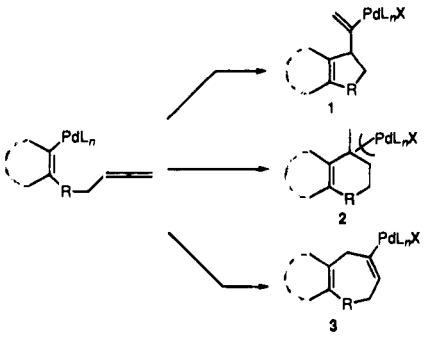
(10) For applications of cyclic carbopalladation to natural product synthesis, see: (a) Abelman, M. M.; Overman, L. E.; Tran, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 6959. (b) Crimins, D. L.; Baevsky, M. F.; Hong, H. *J. Am. Chem. Soc.* **1992**, *114*, 10971. (c) Hudlicky, T.; Olivo, H. F. *J. Am. Chem. Soc.* **1992**, *114*, 9694. (d) Hong, C. Y.; Kado, N.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 11028. (e) Rawal, V. H.; Michoud, C.; Monestel, R. F. *J. Am. Chem. Soc.* **1993**, *115*, 3030. (f) Masters, J. J.; Jung, D. K.; Bornmann, W. G.; Danishefsky, S. J. *Tetrahedron Lett.* **1993**, *34*, 7253.

(11) For asymmetric cyclic carbopalladation, see: (a) Sata, Y.; Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1989**, *54*, 4738. See also ref 56. (b) Ashimori, A.; Overman, L. E. *J. Org. Chem.* **1992**, *57*, 4571 and references therein.

(12) Ma, S.; Negishi, E. *J. Org. Chem.* **1994**, *59*, 4730.

0002-7863/95/1517-6345$09.00/0

Scheme 1



palladation of allenes[13] was well-documented, its intramolecular version did not appear to have been previously studied.

In principle, cyclic carbopalladation of allenes can give rise to three organopalladium derivatives (**1**–**3**) (Scheme 1). In view of the previously studied intermolecular carbopalladation of allenes which has been shown to give allylpalladium derivatives, preferential formation of **2** may be predicted. On the other hand, the Pd-catalyzed cyclization of aminoallenes[14] has been shown to give alkenylpalladium species. The ring size increases by one atom in going from **1** to **2** as well as from **2** to **3**. This may also play a significant role in determining the course of the reaction.

In our preliminary study[12] we found that, in accord with the results of intermolecular carbopalladation of allenes, the reaction exclusively produced allylpalladium derivatives **2** containing seven- or eight-membered rings. Since the reaction of the corresponding alkenes did not lead to the formation of eight-membered rings in detectable yield (<5%) under comparable conditions, the intramolecular carbopalladation of allenes appeared to be a considerably more favorable cyclization process than the corresponding alkene reaction. In each case, formation of a seven- or eight-membered ring exclusively occurred in competition with formation of a six- or seven-membered ring, respectively. These interesting and potentially useful features prompted us to undertake a more systematic investigation. We now report full details of such a systematic study including the results of our preliminary investigation.

Results and Discussion

A number of satisfactory methods are known for the preparation of allenes,[15] and all of the starting allenes (**4**–**32**) were prepared through the application of known procedures (Scheme 2). Thus, **4** was prepared by treating **33** with EtMgBr, while a similar S_N2' displacement reaction of **34** and **35** with propargylic bromides provided **5**–**7**. Those allenes having a longer polymethylene tether, *i.e.*, **19**, **23**, and **24**, were prepared by successive treatment of α,ω-bis(halomagnesio)alkanes with *o*-halobenzyl bromides and propargyl bromide in one pot. Those allenes that contain only one malonate unit, *i.e.*, **8**–**12**, **15**, **16**, **20**, and **21**, were prepared by a two-step alkylation of diethyl malonate with 4-bromo-1,2-butadiene (2,3-pentadienyl bromide for **10**) and an appropriate organic halide. Of those that contain two malonate units, **25**–**28** were prepared by double alkylation with α,ω-dibromoalkanes of **37** or **38** and then **36**. Similarly, base-promoted alkylation of appropriate malonates with **39**, prepared by the base-promoted reaction of **36** with **40**, provided **29**–**32**. Finally, ether-containing allenes, *i.e.*, **13**, **14**, **17**, **18**, and **22**, were prepared by the reaction of *o*-bromo- or *o*-iodobenzyl bromide with the corresponding sodium allenolates (Scheme 2). For the sake of comparison, several alkene derivatives, *i.e.*, **41**–**45**, were also prepared in manners similar to the preparation of the corresponding allenes, *i.e.*, **17**, **19**, **25**, **27**, and **28**, respectively.

For the Pd-catalyzed cyclization of ω-haloallenes we initially employed a set of conditions consisting of treatment of an ω-haloallene with 5 mol % $Cl_2Pd(PPh_3)_2$, K_2CO_3 (5 equiv), and EtOH (10 equiv) at a concentration of 0.025–0.05 M in DMF (conditions I). However, our more recent studies (*vide infra*) have indicated that, in some cases, more satisfactory results are obtained by lowering the substrate concentration to $(2-4) \times 10^{-3}$ M and using *n*-Bu_4NCl[16] (1 equiv) as an added reagent (conditions II). Under conditions I and/or II ω-haloallenes **5**–**20** and **22**–**28** all cyclized to give cyclic conjugated dienes via presumed dehydropalladation. The corresponding reaction of **4**, however, did not afford any monomeric cyclization product in detectable yield. The experimental results are summarized in Table 1.

The results summarized in Table 1 reveal the following noteworthy features.

First, the Pd-catalyzed cyclization of ω-haloallenes provides a novel and potentially general cyclization method applicable to the synthesis of common, medium, and large rings. Thus, five- through twelve-membered and twenty-membered rings have been synthesized in ≥40% yields in most cases. The formation of six-membered rings by this reaction deserves special attention. The reaction of **7** afforded α-methylnaphthalene as the only monocyclization product in 66% yield (76% by NMR). The initially formed cyclization product must have undergone double C=C bond migration. The reaction of **8** provided only a 23% yield of the desired product **47** (Chart 1). However, its dimer **48**, presumably formed via its Diels–Alder reaction, was also present to the extent of 12%. When the reaction was run at 110–120 °C for 6 h at the concentration of 0.05 M, the yields of **47** and **48** were 12% and 42%, respectively. Since **48** displays only one set of ^{13}C NMR signals, it appears to correspond to one of the four regioisomers **48a**–**d**.

Second, carbon–carbon bond formation takes place invariably at the central carbon atom of an allene in accord with the known regiochemistry of the intermolecular carbopalladation of allenes.[13] Thus, the mode of cyclization is uniformly exo with respect to the C=C bond distal to ω-halogen. In the reaction of terminal allenes, *exo*-methylene derivatives are usually obtained, unless further double bond isomerization is favored by aromatization, *e.g.*, conversion of **7** to α-methylnaphthalene, or other factors.

Third, five- through eight-membered rings can be obtained in reasonable yields in most cases under the initially adopted conditions (conditions I). As summarized in Table 2, the formation of nine-membered rings was more sluggish and prone to competing side reactions, especially dimerization and somewhat mysterious but known dehalogenation.[3d,17] These difficulties can be alleviated through the use of the dilute solution

(13) For intermolecular carbopalladation of allenes, see: (a) Shimizu, I.; Tsuji, J. *Chem. Lett.* **1984**, 233. (b) Ahmar, M.; Cazes, B.; Goré, J. *Tetrahedron Lett.* **1984**, *25*, 4505. (c) (review) Cazes, B. *Pure Appl. Chem.* **1990**, *62*, 1867. (d) Larock, R. C.; Berrios-Pena, N. G.; Fried, C. A. *J. Org. Chem.* **1991**, *56*, 2615. (e) Besson, L.; Bazin, J.; Gore, J.; Cazes, B. *Tetrahedron Lett.* **1994**, *35*, 2881. (f) Larock, R. C.; Zenner, J. M. *J. Org. Chem.* **1995**, *60*, 482.

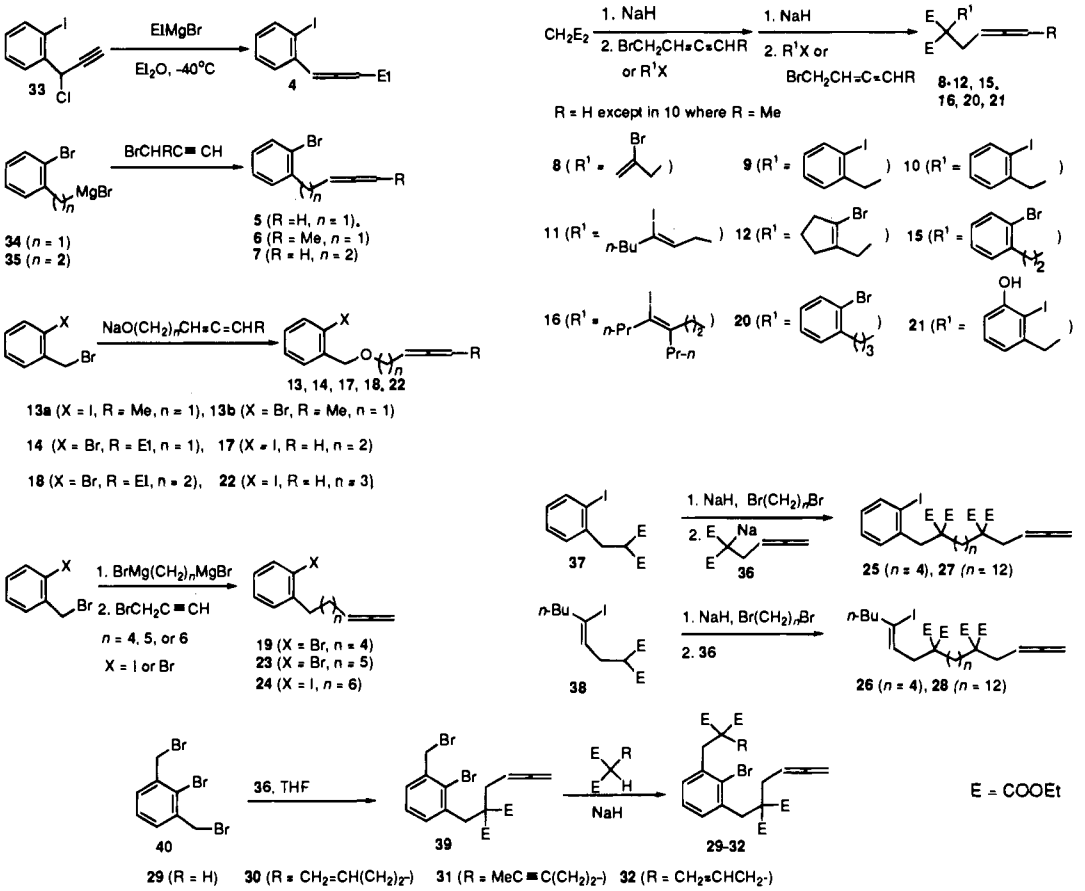
(14) (a) Fox, D. N. A.; Lathbury, D.; Mahon, M. F.; Malloy, K. C.; Gallagher, T. *J. Am. Chem. Soc.* **1991**, *113*, 2652. (b) Kimura, M.; Fugami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1992**, *57*, 6377.

(15) (a) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1988. (b) *The Chemistry of Ketenes, Allenes, and Related Compounds Part 1*; Patai, S., Ed.; John Wiley & Sons: New York, 1980; p 157.

(16) (a) Jeffery, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1287. (b) Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667. (c) Jeffery, T. *Synthesis* **1987**, 70.

(17) Zask, A.; Helquist, P. *J. Org. Chem.* **1978**, *43*, 1619.

Scheme 2



technique ($(2-4) \times 10^{-3}$ M) and *n*-Bu_4NCl[16] (conditions II). On the other hand, the use of Ag_2CO_3[3d] was not effective.

Fourth, contrast between the Pd-catalyzed cyclization of allenes and that of the corresponding alkenes is striking and intriguing. The results obtained with **17**, **19**, **25**, **27**, and **28** are compared with those obtained with **41**−**45** in Scheme 3. In sharp contrast with the facile formation of the desired eight- and nine-membered rings, *i.e.*, **57** and **60**, from **17** and **19**, respectively, the corresponding reactions of **41** and **42** under comparable reaction conditions failed to yield the desired monocyclization products to detectable extents. In these cases, dehalogenation rather than cyclic dimer formation appears to be the major side reaction. In the reaction of **43**, a monocyclization product (**74**) was produced but only in 18% yield, while **25** gave **65** in 50% yield. As might be expected, even the alkene cyclization reaction appears to be reasonably satisfactory for the synthesis of large rings. Thus, **44** was converted to **76** in 66% yield, while the corresponding reaction of **27** produced **67** in 86% yield. Interestingly, the endo-mode cyclization[18] is observed in the formation of **74**, **76**, and **78**. In the reaction of **44**, the amount of the exo-mode cyclization product **77** was <5%, if any, making this process >93% endo-selective. Since exo-mode cyclization is predominant in the formation of five- through seven-membered rings,[1-11] the observed high endo selectivity initially appeared puzzling. However, the observed endo selectivity must be a reflection of the well-known regiochemistry of intermolecular carbopalladation of monosubstituted alkenes, which reportedly places 80% of the carbon group of an organopalladium derivative at the terminal position.[19] Thus, in the absence of overriding stereoelectronic constraints, the regiochemistry of carbopalladation in the formation of large rings is expected to be the same as or similar to that of intermolecular carbopalladation.

Fifth, the stereochemistry of the allene cyclization reaction is also interesting. As might be expected from the well-known relative thermodynamic stability,[20] eight-membered rings are exclusively *Z* judging from the ^1H NMR coupling constants of 10−11 Hz for the endocyclic C=C bonds, while the twelve- and twenty-membered rings are *E* (J = 16−17 Hz). On the other hand, the *E*/*Z* ratio of the nine- and ten-membered rings is a function of other factors as well. Thus, **60** and **62** are *Z* (J = 10.5 Hz), whereas **61** is *E* (J = 16.8 Hz), although all of them are nine-membered. The ten-membered ring product **63** is a 73/27 mixture of the *E* and *Z* isomers, but **64** containing an eleven-membered ring is exclusively *E*. The alkenyl side chain in **54** and **58** is >97% *E*. On the other hand, the alkylidene side chains in **46** and **59** are 79% and 73% *E*, respectively.

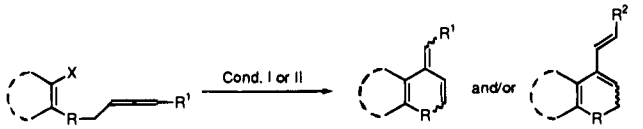
In the comparison of allenes with alkenes discussed above we mainly relied on the yields of the desired cyclization products. High product yields are a consequence of either a high rate of the desired process or low rates of any competing side reactions, provided that the product is stable under the reaction conditions. In view of higher strain energies of allenes[15b] relative to those of alkenes, a higher reactivity of allenes toward organopalladiums may be anticipated. To probe this point in a simple manner, the reaction of iodobenzene with

(18) (a) For other endo-mode cyclic carbopalladation and related reactions, see: Owczarczyk, Z.; Lamaty, F.; Vawter, E. J.; Negishi, E. *J. Am. Chem. Soc.* **1992**, *114*, 10091 and references therein. (b) For endo-mode acylpalladation, see: Negishi, E.; Tour, J. M. *Tetrahedron Lett.* **1986**, *27*, 4869.

(19) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133.

(20) (a) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York, 1990; Part A, p 161. (b) Turner, R. B.; Meader, W. R. *J. Am. Chem. Soc.* **1957**, *79*, 4133. (c) Cope, A. C.; Moore, P. T.; Moore, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1744.

Table 1. Pd-Catalyzed Cyclization of ω-Haloallenes via Cyclic Carbopalladation

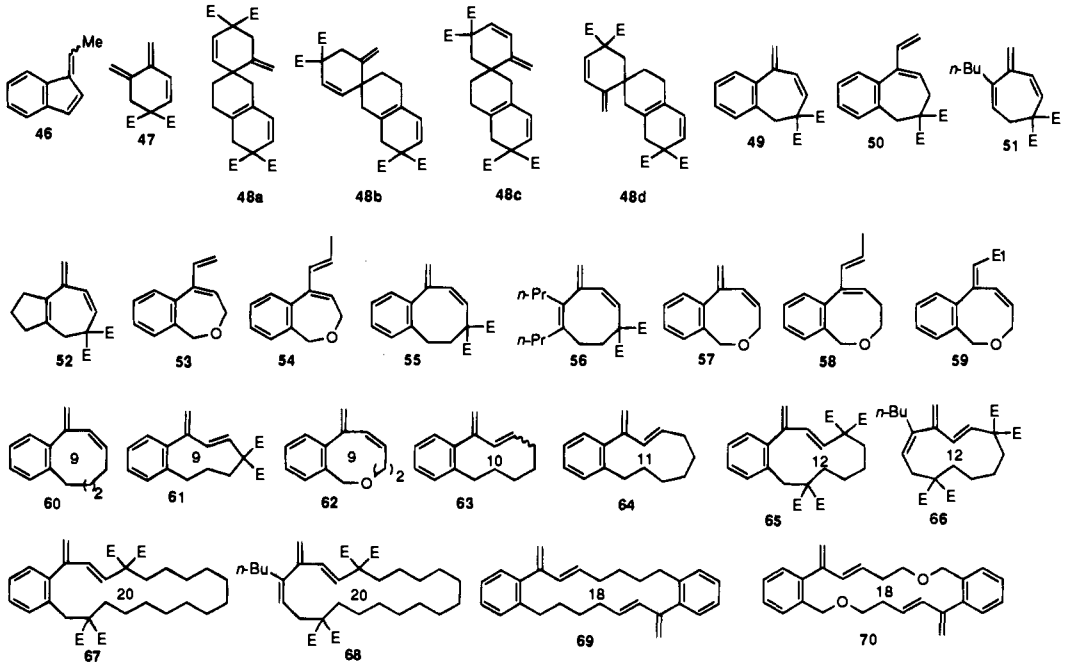


R = 0 - 15 atom tether. R^1 = H, Me, or Et. R^2 = R^1 • CH_2. X = I or Br.

ω-haloallene	cond[a]	concn, M	temp, °C	time, h	product	yield,[b] %	other notes
5	I	0.05	80	4	*c*	69	
6	I	0.025	80	3	**46**	50	*E*/*Z* = 79/21
7	I	0.025	80	2	*d*	66 (76)	
8	I	0.025	80	4	**47** and **48**	35	**47** (23%), **48** (12%)
9	I	0.05	120	4	**49**	65	
10	I	0.05	120	22	**50**	58	
11	I	0.025	120	3	**51**	66	
12	I	0.05	120	4	**52**	58	
13a	I	0.05	100	5	**53**	60 (71)	
13b	I	0.05	100	4	**53**	60	
14	I	0.05	100	4	**54**	61	
15	I	0.05	120	22	**55**	56	
16	II	0.013	80, then 120	17, then 27	**56**	23 (43)	
17	I	0.05	100	2	**57**	52 (74)	
18	I	0.05	100	3	**58** and **59**	– (76)	**58** (41% by NMR) **59** (35% by NMR)
19	II	2×10^{-3}	120	12	**60**	55	
20	II	2×10^{-3}	120	42	**61**	62	
22	II	4×10^{-3}	60	41	**62**	33	**70** (18%)
23	II	2×10^{-3}	120	16	**63**	48	*E*/*Z* = 73/27
24	II	2×10^{-3}	120	12	**64**	40 (57)	
25	II	2×10^{-3}	80	29	**65**	50	
26	II	2×10^{-3}	120	60	**66**	27	*e* (26%)
27	II	2×10^{-3}	120	5	**67**	86	
28	II	2×10^{-3}	80	37	**68**	– (47)	

[a] Conditions I: 5% $Cl_2Pd(PPh_3)_2$, K_2CO_3 (5 equiv), EtOH (10 equiv), DMF. Conditions II: 5% $Cl_2Pd(PPh_3)_2$, K_2CO_3 (5 equiv), *n*-Bu_4NCl (1 equiv), DMF. [b] Isolated yield. The numbers in parentheses are determined by NMR spectroscopy with an internal standard. [c] Benzofulvene. [d] α-Methylnaphthalene. [e] Deiodination product.

Chart 1



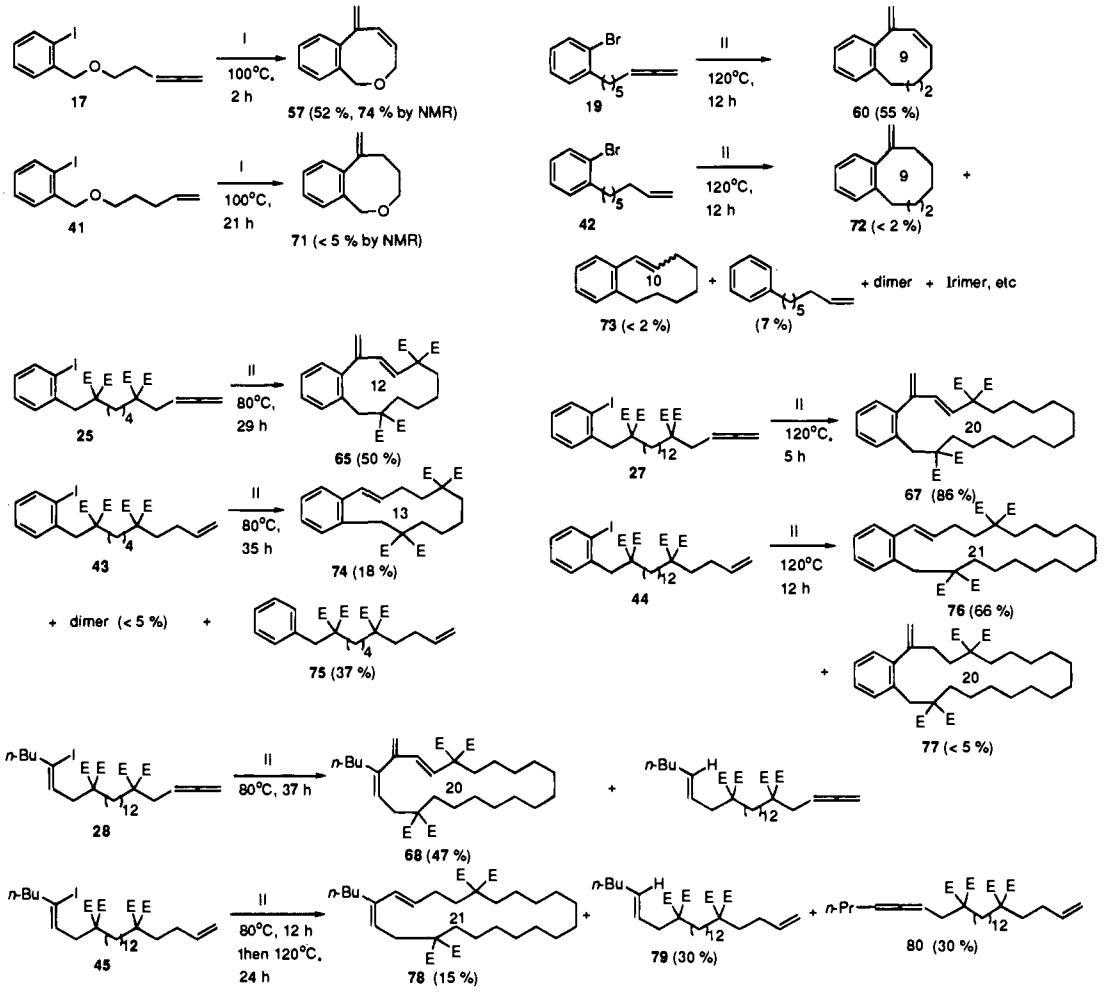
2 molar equivalents each of 1,2-octadiene and 1-octene in the presence of 5 mol % $Cl_2Pd(PPh_3)_2$ under conditions II was carried out. The reaction produced (3*E*)-2-phenyl-1,3-octadiene in 47% yield without producing (*E*)-1-phenyl-1-octene, even though the latter compound was obtained in 20% yield in the absence of 1,2-octadiene. Since the reported yields of the Heck substitution reaction between iodobenzene and 1-alkenes are typically around 40%,[19] the 20% yield observed above is low, making comparison of 1,2-octadiene with 1-octene inaccurate. Even so, the results clearly indicate that allenes react substantially faster than similarly structured alkenes. For further comparison of allenes with alkenes and alkynes, **30**–**32** were

Table 2. Effects of the Reaction Conditions on the Yields of Nine-Membered Rings Formed via Pd-Catalyzed Cyclic Carbopalladation of ω-Haloallenes

ω-Haloallene	cond	concn, M	temp, °C	time, h	product	yield,[a] %	yields, other, %
19	I	0.017	80	45	**60**	17	**69** (17), [b](13)
19	II	0.016	80	72	**60**	46	**69** (12), **19** (7)
19	II	0.016	120	3	**60**	42	**69** (22)
19	II	2×10^{-3}	120	12	**60**	55	**69** (<2−3)
20	I	0.025	120	5	**61**	30	*c* (<2), *d* (30)
20	I	0.018	80	112	**61**	55	*c* (<2), *d* (7)
20	II	2×10^{-3}	120	42	**61**	62	*c* (<2), *d* (<1)

[a] By NMR. [b] 6,7-Octadienylbenzene. [c] Dimeric products. [d] 4,4-Bis(ethoxycarbonyl)-6,7-nonadienylbenzene.

Scheme 3



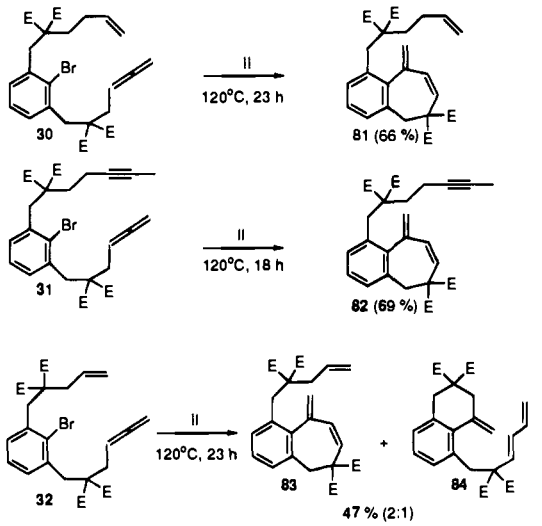
I = 5 % $Cl_2Pd(PPh_3)_2$, K_2CO_3 (5 equiv) and EtOH (10 equiv), DMF;
II = 5 % $Cl_2Pd(PPh_3)_2$, K_2CO_3 (5 equiv) and *n*-Bu_4NCl (1 equiv), DMF

subjected to conditions II at 120 °C. Both **30** and **31** were selectively and cleanly converted to **81** (66%) and **82** (69%), respectively, without an indication of competitive cyclization involving the alkene and alkyne groups (Scheme 4). In the reaction of **32**, however, the monocyclization products consisted of a 31% yield of **83** and a 16% yield of **84**, which was tentatively identified. These results indicate that the Pd-catalyzed allene cyclization reaction is substantially faster than the corresponding reaction of alkenes or possibly even alkynes and that the rate of formation of a seven-membered ring via allene cyclization is comparable or even somewhat faster than that of a six-membered ring via alkene cyclization. We attribute the favorable results reported herein mainly to the enhanced reactivity of the allenic substrates relative to that of the corresponding alkenes and alkynes rather than the lack or paucity of competitive side reactions.

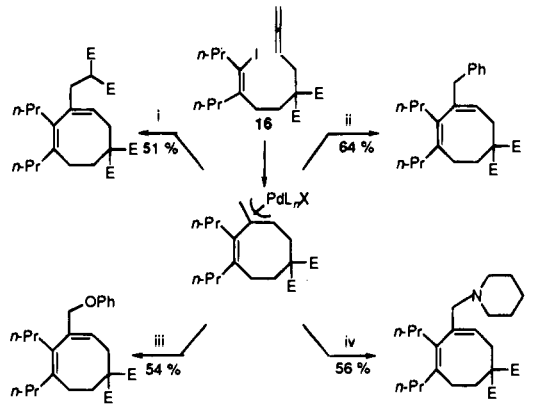
All of the allene cyclization reactions discussed herein were carried out with only a catalytic amount of $Cl_2Pd(PPh_3)_2$, and their mechanistic details were not rigorously investigated. Nonetheless, the available data clearly point to the conversion of ω-haloallenes into allylpalladium intermediates **2** via oxidative addition−cyclic carbopalladation, which must then undergo dehydropalladation to give conjugated dienes as the products. Rather than attempt to establish the intermediacy of **2** using the stoichiometric amount of a Pd−phosphine complex, we chose to trap the putative intermediates **2** by known reactions of allylpalladium species.[21] To this end, **16** was selected as a text substrate, and diethyl malonate, $PhSnBu_3$,[22] PhOH,[21] and

(21) For reviews, see: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: West Berlin, 1980.

Scheme 4



Scheme 5



i: I, CH_2E_2 (3 equiv), 0.05 M, 120°C, 23 h;
ii: II, $PhSn(n\text{-}Bu)_3$ (2.2 equiv), 0.014 M, 120°C, 11 h;
iii: II, PhOH (5 equiv), 0.013 M, 80°C, 24 h, 120°C, 7 h;
iv: II, piperidine (2 equiv), 0.014 M, 80°C, 9 h.

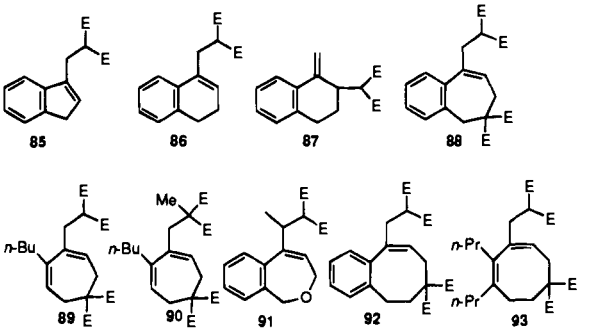
piperidine[21] were used as four representative trapping agents. As the results summarized in Scheme 5 indicate, the expected products were obtained in 51−64% yields via exclusive attack by the nucleophiles at the less-hindered *exo*-methylene carbon atom. These results not only strongly support the mechanism discussed above but also further demonstrate the synthetic utility of the cyclization methodology herein presented. It should be noted that the observed yields are considerably higher than that of the conjugated dienes **56**, *i.e.*, 23%, suggesting that the conjugated diene products, such as **56**, must be rather unstable and that the actual extent of the cyclization process itself may be considerably higher than indicated in Table 1. Further examples of trapping with diethyl malonate are summarized in Table 3. It is noteworthy that the allylpalladium intermediate derived from **7** can be trapped to give **86** and **87** before its decomposition to yield α-methylnaphthalene. Trapping of the allylpalladium intermediate derived from **11** with diethyl α-methylmalonate was sluggish under conditions I, producing the desired compound **90** only in 15% yield along with a 50% yield of **51**. Under conditions II, however, **90** was obtained in 50% yield along with only a 4% yield of **51**. Finally, the reactions of **21** and **29** to give **94** and **95**, respectively, provide examples of intramolecular trapping, and conversion of **53** into

(22) For a review see: Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

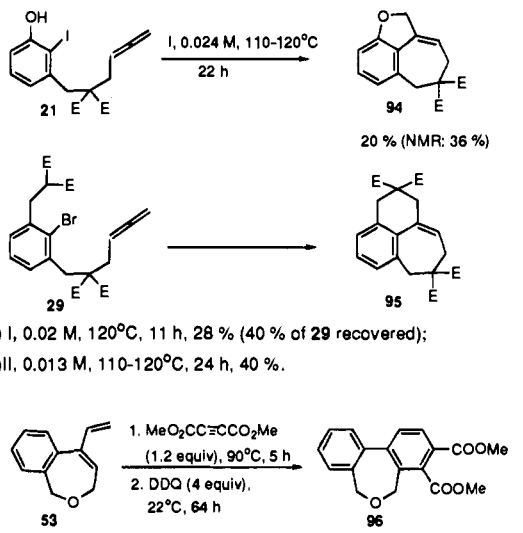
Table 3. Trapping of Allylpalladium Derivatives with Diethyl Malonate[a]

ω-haloallene	cond	concn, M	temp, °C	time, h	product	yield,[b] %
5	I	0.024	120	2	**85**	61
7	I	0.024	120	5	**86** and **87**	55[c]
9	I	0.05	120	4	**88**	87
11	I	0.024	120	3	**89**	73
11	I[d]	0.024	120	4	**90**	15[e]
11	II[d]	0.024	120	4	**90**	50[f]
13a	I	0.05	120	5	**91**	73
15	I	0.05	120	3	**92**	84
16	I	0.05	120	23	**93**	51

[a] 3 equiv used. [b] Isolated yield. [c] An 86:14 mixture of **86** and **87**. [d] Diethyl α-methylmalonate was used as a trapping agent. [e] A 50% yield of **51** was also obtained. [f] A 4% yield of **51** was produced.



96 via cyclic carbopalladation−Diels−Alder reaction−oxidation represents a novel route to fused tricyclic biaryls.



Conclusions

(1) A new and potentially general cyclization method based on catalytic intramolecular carbopalladation of ω-haloallenes has been discovered and developed. It has been applied to the synthesis of five- through twelve-membered and twenty-membered rings in respectable yields. The use of the dilute solution technique and $n\text{-}Bu_4NCl$ as a reagent is advantageous in the synthesis of eight-membered and larger rings.

(2) Comparative studies indicate that, under comparable reaction conditions, the corresponding reaction of ω-haloalkenes fails to yield eight- and nine-membered rings. Formation of large rings via cyclization of ω-haloalkenes proceeds via endo-mode cyclization. On the other hand, formation of a carbon−carbon bond at the central carbon of an allene group to give an allylpalladium derivative has been uniformly observed in the cyclization of ω-haloallenes. The favorable ring size−product

yield profile and the uniform regioselectivity make the Pd-catalyzed ω-haloallene cyclization distinct from the previously known alkene cyclization reaction and provide a highly promising synthetic method.

(3) The available comparative data suggest that the favorable results obtained with ω-haloallenes mainly stem from a high reactivity of allenes toward organopalladium species rather than the lack or paucity of competing side reactions.

(4) Trapping of the putative allylpalladium intermediates with various nucleophiles, such as malonate esters, organostannanes, phenols, and amines, provides the corresponding products in respectable yields. These results not only support the oxidative addition−carbopalladation mechanism but also extend the synthetic utility of this cyclization methodology. The results further indicate that the extents of the cyclization process itself may be considerably higher than indicated by the yields of the dehydropalladation products and that some undesirable side reactions, such as double bond isomerization, can be circumvented.

(5) Some attendant regiochemical and stereochemical details have also been investigated.

Applications of this new and potentially general cyclization method to the synthesis of natural products and other organic compounds are currently being conducted.

Experimental Section

General Procedures. All cyclization reactions were conducted under a dry Ar atmosphere. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Gemini-200 spectrometer using Me_4Si as the internal reference. NMR yields were determined by using methylene bromide as the internal reference. All commercially available reagents were used without further purification unless otherwise stated. THF was distilled from sodium benzophenone ketyl. DMF was distilled from CaH_2 and stored over molecular sieves 4A. $Cl_2Pd(PPh_3)_2$ was prepared as reported.[23]

ω-(2′-Halophenyl)-1,2-allenes. Compounds **4**−**7** were prepared by the reaction of the corresponding Grignard reagents with propargylic bromides in ether at −40 °C according to the literature method.[24]

(a) Preparation of 4-(2′-Bromophenyl)-1,2-butadiene (5). Representative Procedure. Propargyl bromide (80% in toluene, 1.11 mL, 1.19 g, 10 mmol) in ether (4 mL) was added at −40 °C to (2-bromobenzyl)magnesium bromide in ether, prepared from 2-bromobenzyl bromide (2.50 g, 10 mmol) and Mg (240 mg, 10 mmol) in ether, and the reaction mixture was stirred overnight at 23 °C. The reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel (*n*-hexane) to afford 1.11 g (53% yield) of **5**: ^1H NMR δ 3.4−3.5 (m, 2H), 4.65−4.75 (m, 2H), 5.2−5.4 (m, 1H), 7.0−7.1 (m, 1H), 7.15−7.35 (m, 2H), 7.55 (d, J = 6.8 Hz, 1H); ^{13}C NMR δ 35.38, 75.47, 88.09, 124.44, 127.43, 127.90, 130.32, 132.68, 139.54, 209.15; IR (neat) 1956 cm^{-1}; HRMS calcd for $C_{10}H_{10}Br$ (M^+ + 1) 208.9966, found 208.9965.

(b) 1-(2′-Bromophenyl)-2,3-pentadiene (6). 3-Bromo-1-butyne was used instead of propargyl bromide (35−40% yield): ^1H NMR δ 1.65 (dd, J = 3.2 and 7.4 Hz, 3H), 3.45 (dd, J = 2.7 and 6.8 Hz, 2H), 5.0−5.15 (m, 1H), 5.15−5.3 (m, 1H), 7.0−7.2 (m, 1H), 7.2−7.35 (m, 2H), 7.55 (d, J = 6.8 Hz, 1H); ^{13}C NMR δ 14.21, 36.04, 86.41, 88.21, 124.46, 127.37, 127.75, 130.30, 132.62, 139.89, 205.52; IR (neat) 1966 cm^{-1}; HRMS calcd for $C_{11}H_{12}Br$ (M^+ + 1) 223.0122, found 223.0117.

(c) 5-(2′-Bromophenyl)-1,2-pentadiene (7). [2-(2′-Bromophenyl)-ethyl]magnesium bromide was used instead of (2-bromobenzyl)-magnesium bromide (35−40% yield): ^1H NMR δ 2.2−2.4 (m, 2H), 2.75−2.9 (m, 2H), 4.65−4.75 (m, 2H), 5.05−5.25 (m, 1H), 6.95−7.1 (m, 1H), 7.15−7.3 (m, 2H), 7.55 (d, J = 7.9 Hz, 1H); ^{13}C NMR δ 28.25, 35.61, 75.29, 89.12, 124.44, 127.30, 127.61, 130.42, 132.74, 140.87, 208.53; IR (neat) 1956 cm^{-1}; MS *m/e* 223/225 (M^+ + 1).

(23) Jenkin, J. M.; Verkade, J. G. *Inorg. Synth.* **1968**, *11*, 108.

(24) Brandsma, L.; Arens, J. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 734.

(d) 1-(2′-Iodophenyl)-1,2-pentadiene (4). **4** was prepared similarly in 70% yield by the reaction of EtMgBr with 3-chloro-3-(2′-iodophenyl)-1-propyne: ^1H NMR δ 1.06 (t, J = 6.8 Hz, 3H), 2.0−2.45 (m, 2H), 5.55−5.75 (m, 1H), 6.4−6.6 (m, 1H), 6.82 (td J = 8.5 and 1.2 Hz, 1H), 7.25 (t, J = 8.5 Hz, 1H), 7.35−7.45 (m, 1H), 7.78 (d, J = 8.5 Hz, 1H); ^{13}C NMR δ 13.39, 21.79, 96.84, 98.27, 99.30, 127.51, 128.11, 137.60, 139.42, 205.87; IR (neat) 1946 cm^{-1}; HRMS calcd for $C_{11}H_{11}I$ (M^+) 269.9906, found 269.9909.

Allenes with One Malonate Unit. Compounds **8**−**12**, **15**, **16**, **20**, and **21** were prepared by two-step alkylation with the corresponding bromide or iodide and NaH in THF. 4-Bromo-1,2-butadiene was prepared from 2,3-butadienol[25] using PBr_3. 3-(2′-Bromophenyl)propyl bromide,[26] 1,4-diiodo-3-*n*-propyl-3(*Z*)-heptene,[27] and 3-iodo-2(*Z*)-heptenyl bromide[28] were prepared as reported.

(a) 7-Bromo-5,5-bis(ethoxycarbonyl)-1,2,7-octatriene (8). Representative Procedure. To a suspension of NaH (115 mg, 95%, 4.55 mmol) in THF (10 mL) was added 5,5-bis(ethoxycarbonyl)-1,2-pentadiene (640 mg, 3.01 mmol) in THF (3 mL). After 10 min at room temperature, 2,3-dibromo-1-propene (810 mg × 80% = 648 mg, 3.24 mmol) in THF (5 mL) was added at room temperature. The reaction was stirred overnight, quenched with water, extracted with ether, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) to afford **8** (60% yield): ^1H NMR δ 1.25 (t, J = 7.7 Hz, 6H), 2.75 (dt, J = 2.3 and 7.8 Hz, 2H), 3.20 (s, 2H), 4.1−4.3 (m, 4H), 4.6−4.75 (m, 2H), 4.85−5.1 (m, 1H), 5.60 (d, J = 1.2 Hz, 1H), 5.70 (d, J = 1.2 Hz, 1H); ^{13}C NMR δ 13.93, 30.77, 42.74, 57.09, 61.61, 74.85, 84.11, 122.12, 127.08, 169.91, 210.02; IR (neat) 1956, 1736, 1626 cm^{-1}; HRMS calcd for $C_{14}H_{20}BrO_4$ (M^+ + 1) 331.0545, found 331.0541.

(b) 6-(2′-Iodophenyl)-5,5-bis(ethoxycarbonyl)-1,2-hexadiene (9). 5,5-Bis(ethoxycarbonyl)-1,2-pentadiene was alkylated similarly in 91% yield with 2-iodobenzyl bromide: ^1H NMR δ 1.21 (t, J = 7.6 Hz, 6H), 2.6−2.7 (m, 2H), 3.54 (s, 2H), 4.0−4.3 (m, 4H), 4.6−4.75 (m, 2H), 5.05−5.25 (m, 1H), 6.8−6.95 (m, 1H), 7.25−7.35 (m, 2H), 7.85 (d, J = 7.7 Hz, 1H); ^{13}C NMR δ 13.89, 32.89, 42.17, 58.92, 61.44, 74.72, 85.02, 102.81, 128.03, 128.46, 130.21, 139.76, 139.84, 170.50, 209.91; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{18}H_{21}IO_4$ (M^+) 428.0485, found 428.0469.

(c) 6,6-Bis(ethoxycarbonyl)-7-(2′-iodophenyl)-2,3-heptadiene (10). 2-[2′,2′-Bis(ethoxycarbonyl)ethyl]-1-iodobenzene was alkylated similarly in 85% yield with 2,3-pentadienyl bromide: ^1H NMR δ 1.20 (t, J = 8.6 Hz, 6H), 1.6−1.7 (m, 3H), 2.6−2.7 (m, 2H), 3.52 (s, 2H), 4.16 (q, J = 8.6 Hz, 4H), 5.0−5.15 (m, 2H), 6.85−7.0 (m, 1H), 7.20−7.35 (m, 2H), 7.85 (d, J = 8.8 Hz, 1H); ^{13}C NMR δ 13.90, 14.22, 33.43, 41.96, 58.86, 61.41, 85.06, 85.75, 102.78, 127.99, 128.41, 130.33, 139.84, 139.95, 170.59, 206.53; IR (neat) 1966 cm^{-1}; HRMS calcd for $C_{19}H_{22}IO_4$ (M^+) 442.0641, found 442.0637.

(d) 5,5-Bis(ethoxycarbonyl)-8-iodo-1,2,7(*Z*)-dodecatriene (11). 5,5-Bis(ethoxycarbonyl)-1,2-pentadiene was alkylated similarly in 72% with 3-iodo-2(*Z*)-heptenyl bromide: ^1H NMR δ 0.90 (t, J = 7.3 Hz, 3H), 1.25 (t, J = 7.8 Hz, 6H), 1.2−1.4 (m, 2H), 1.4−1.6 (m, 2H), 2.46 (t, J = 7.2 Hz, 2H), 2.55−2.65 (dt, J = 1.5 and 8.0 Hz, 2H), 2.78 (d, J = 7.8 Hz, 2H), 4.20 (q, J = 7.8 Hz, 4H), 4.65−4.75 (m, 2H), 4.9−5.1 (m, 1H), 5.40 (t, J = 7.8 Hz, 1H); ^{13}C NMR δ 13.77, 14.04, 21.19, 31.33, 32.49, 39.47, 45.23, 57.16, 61.39, 74.68, 84.27, 112.94, 128.62, 170.43, 209.99; IR (neat) 1956, 1732, 1628 cm^{-1}; HRMS calcd for $C_{18}H_{28}IO_4$ 435.1032, found 435.1031.

(e) 5,5-Bis(ethoxycarbonyl)-6-(2′-bromo-1′-cyclopentenyl)-1,2-hexadiene (12). 5,5-Bis(ethoxycarbonyl)-1,2-pentadiene was alkylated similarly in 46% yield with 1-(bromomethyl)-2-bromo-1-cyclopentene: ^1H NMR δ 1.22 (t, J = 8.1 Hz, 6H), 1.75−1.95 (m, 2H), 2.1−2.25 (m, 2H), 2.55−2.65 (m, 4H), 2.88 (s, 2H), 4.05−4.25 (m, 4H), 4.55−4.65 (m, 2H), 5.0−5.2 (m, 1H); ^{13}C NMR δ 14.00, 22.03, 32.65, 33.30, 34.05, 39.83, 57.03, 61.38, 74.47, 84.75, 121.11, 135.85, 170.75,

(25) Olsson, L. I.; Claesson, A. *Acta Chem. Scand., B.* **1977**, *31*, 614.

(26) Beeby, M. H.; Mann, F. G. *J. Chem. Soc.* **1951**, 411.

(27) Negishi, E.; Holmes, S. J.; Tour, J.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336; Takahashi, T.; Kageyama, M.; Denisov, V.; Hara, R.; Negishi, E. *Tetrahedron Lett.* **1993**, *34*, 687.

(28) Corey, E. J.; Katzenellenbogen, J. A.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 4245; Corey, E. J.; Kim, C. U.; Takeda, M. *Tetrahedron Lett.* **1972**, 4339.

209.89; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{17}H_{24}BrO_4$ (M^+ + 1) 371.0858, found 371.0857.

(f) 7-(2′-Bromophenyl)-5,5−bis(ethoxycarbonyl)-1,2-heptadiene (15). 1,1-Bis(ethoxycarbonyl)-3-(2′-bromophenyl)propane was alkylated similarly in 70% yield with 4-bromo-1,2-butadiene: ^1H NMR δ 1.27 (t, J = 8.2 Hz, 6H), 2.15−2.25 (m, 2H), 2.6−2.8 (m, 4H), 4.22 (q, J = 8.2 Hz, 4H), 4.65−4.75 (m, 2H), 4.95−5.15 (m, 1H), 7.0−7.15 (m, 1H), 7.15−7.3 (m, 2H), 7.55 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 14.09, 30.88, 31.94, 42.42, 57.41, 61.31, 74.74, 84.30, 124.17, 127.55, 127.79, 130.37, 132.76, 140.67, 170.77, 209.93; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{19}H_{23}BrO_4$ (M^+) 394.0780, found 394.0776.

(g) 5,5-Bis(ethoxycarbonyl)-8-*n*-propyl-9-iodo-1,2,8(*Z*)-dodecatriene (16). 8,8-Bis(ethoxycarbonyl)-4-iodo-5-*n*-propyl-4(Z)-octene was alkylated similarly in 94% with 4-bromo-1,2-butadiene: ^1H NMR δ 0.90 (t, J = 7.0 Hz, 6H), 1.25 (t, J = 7.8 Hz, 6H), 1.3−1.65 (m, 4H), 1.9−2.25 (m, 6H), 2.45 (t, J = 7.0 Hz, 2H), 2.6−2.75 (m, 2H), 4.22 (q, J = 7.8 Hz, 4H), 4.6−4.75 (m, 2H), 4.95−5.15 (m, 1H); ^{13}C NMR δ 12.80, 13.93, 14.06, 21.90, 22.92, 29.30, 31.65, 33.44, 37.00, 42.89, 57.15, 61.22, 74.62, 84.36, 105.68, 142.64, 170.77, 209.81; IR (neat) 1956, 1732, 1628 cm^{-1}; HRMS calcd for $C_{21}H_{34}IO_4$ (M^+ + 1) 477.1502, found 477.1483.

(h) 5,5-Bis(ethoxycarbonyl)-8-(2′-bromophenyl)-1,2-octadiene (20). 5,5-Bis(ethoxycarbonyl)-1,2-pentadiene was alkylated similarly in 80% yield with 3-(2′-bromophenyl)propyl bromide at 70 °C: ^1H NMR δ 1.24 (t, J = 8.0 Hz, 6H), 1.4−1.6 (m, 2H), 1.9−2.1(m, 2H), 2.62 (dt, J = 8.4 and 1.5 Hz, 2H), 2.75 (t, J = 8.2 Hz, 2H), 4.18 (q, J = 8.0 Hz, 4H), 4.55−4.70 (m, 2H), 4.8−5.0 (m, 1H), 7.0−7.1 (m, 1H), 7.15−7.25 (m, 2H), 7.52 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 14.03, 24.23, 31.57, 31.78, 36.22, 57.49, 61.17, 74.50, 84.19, 124.32, 127.33, 127.57, 130.29, 132.72, 141.00, 170.95, 209.87; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{20}H_{25}BrO_4$ (M^+) 408.0936, found 408.0940.

(i) 1-[2′,2′-Bis(ethoxycarbonyl)-4′,5′-hexadienyl]-3-hydroxy-2-iodobenzene (21). 1-[2′,2′-Bis(ethoxycarbonyl)ethyl]-3-hydroxy-2-iodobenzene was alkylated in 55% yield similarly with 4-bromo-1,2-butadiene: ^1H NMR δ 1.22 (t, J = 7.8 Hz, 6H), 2.6−2.75 (m, 2H), 3.56 (s, 2H), 4.05−4.3 (m, 4H), 4.6−4.75 (m, 2H), 5.05−5.2 (m, 1H), 6.1−6.7 (bs, 1H), 6.75−6.9 (m, 2H), 7.10 (t, J = 8.6 Hz, 1H); ^{13}C NMR δ 13.84, 32.70, 42.49, 58.89, 61.50, 74.74, 84.89, 95.17, 113.29, 122.02, 128.97, 140.66, 155.01, 170.55, 209.84; IR (paraffin oil) 3378, 1950, 1736, 1700, 1592, 1572 cm^{-1}; HRMS calcd for $C_{18}H_{22}IO_5$ (M^+ + 1) 445.0512, found 445.0516.

ω-(2′-Halophenyl)-1,2-allenes with a Longer Polymethylene Tether. Compounds **19**, **23**, and **24** were prepared according to the following procedure.

(a) 8-(2′-Bromophenyl)-1,2-octadiene (19). Representative Procedure. To 2-bromobenzyl bromide (9.4 g, 37.6 mmol) in ether (20 mL) was added at 0 °C 1,4-bis(bromomagnesio)butane in ether (40 mL), prepared from 1-bromo-4-chlorobutane (12.8 g, 74.6 mmol) and Mg (18 g, 760 mmol) and then transferred by a syringe. After 4.5 h at 0 °C, the solution was cooled to −40 °C, and then propargyl bromide (80% in toluene) (16.8 mL, 150 mmol) was added at such a rate that the temperature was controlled around −35 to −45 °C. This mixture was stirred overnight, quenched with water, extracted with ether, dried over $MgSO_4$, and evaporated. Vacuum distillation afforded a fraction containing the expected product **19**, which was further purified by chromatography on silica gel (*n*-hexane) to afford 3.58 g (36% yield) of **19**: ^1H NMR δ 1.2−1.7 (m, 6H), 1.9−2.1 (m, 2H), 2.70 (t, J = 8.0 Hz, 2H), 4.55−4.7 (m, 2H), 5.0−5.2 (m, 1H), 6.95−7.1 (m, 1H), 7.15−7.3 (m, 2H), 7.50 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 28.14, 28.76, 28.88, 29.68, 36.13, 74.61, 89.92, 124.42, 127.27, 127.33, 130.24, 132.70, 141.95, 208.49; IR (neat) 1956 cm^{-1}; HRMS calcd for $C_{14}H_{17}Br$ (M^+) 264.0514, found 264.0506.

(b) 9-(2′-Bromophenyl)-1,2-nonadiene (23). 1,5-Dibromopentane was used instead of 1-bromo-4-chlorobutane (35% yield): ^1H NMR δ 1.25−1.5 (m, 6H), 1.5−1.7 (m, 2H), 1.9−2.1 (m, 2H), 2.70 (t, J = 8.1 Hz, 2H), 4.6−4.7 (m, 2H), 5.0−5.2 (m, 1H), 6.95−7.1 (m, 1H), 7.15−7.3 (m, 2H), 7.55 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 28.21, 28.85, 29.01, 29.13, 29.84, 36.14, 74.57, 90.01, 124.42, 127.26, 127.31, 130.24, 132.69, 142.01, 208.46; IR (neat) 1956 cm^{-1}; MS *m/e* 279/281 (M^+ + 1).

(c) 10-(2′-Iodophenyl)-1,2-decadiene (24). 1,6-Dibromohexane and 2-iodobenzyl bromide were used instead of 1-bromo-4-chlorobutane and 2-bromobenzyl bromide, respectively (6% yield): ^1H NMR δ 1.2−1.5 (m, 8H), 1.5−1.65 (m, 2H), 1.9−2.1 (m, 2H), 2.70 (t, J = 8.2 Hz, 2H), 4.6−4.7 (m, 2H), 5.0−5.2 (m, 1H), 6.80−6.95 (m, 1H), 7.15−7.3 (m, 2H), 7.82 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 28.24, 28.99, 20.08, 29.08, 29.22, 29.27, 30.22, 40.84, 74.56, 90.06, 100.06, 127.48, 128.19, 129.28, 139.39, 145.33, 208.46; IR (neat) 1956 cm^{-1}; HRMS calcd for $C_{16}H_{22}I$ (M^+ + 1) 341.0766, found 341.0749.

Allenes with Two Malonate Units. Compounds **25**−**32** were prepared by two-step alkylation of α,ω-dibromoalkane with the corresponding monosubstituted diethyl malonates in DMF or THF at room tempurature using NaH as the base. 2-Bromo-1,3-bis(bromomethyl)benzene was prepared according to the literature method.[29]

(a) 5,5,10,10-Tetrakis(ethoxycarbonyl)-11-(2′-iodophenyl)-1,2-undecadiene (25). Representative Procedure. Step 1. 2-(2′,2′-Bis-[ethoxycarbonyl)ethyl]iodobenzene (3.0 g, 8 mmol) in DMF (5 mL) was added to a suspension of NaH (95%, 300 mg, 11.9 mmol) in DMF (5 mL). After 10 min at room temperature, 1,4-dibromobutane (3.45 g, 16 mmol) was added to this mixture, and the reaction mixture was stirred overnight at room temperature, diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. The crude product was further purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 20/1) to afford 2.96 g (73% yield) of 6-(2′-iodophenyl)-5,5-bis-(ethoxycarbonyl)hexyl bromide.

Step 2. 5,5-Bis(ethoxycarbonyl)-1,2-pentadiene (244 mg, 1.15 mmol) in DMF (2.5 mL) was added to a suspension of NaH (95%, 45 mg, 1.78 mmol) in DMF (2.5 mL). After 10 min at room temperature, 6-(2′-iodophenyl)-5,5-bis(ethoxycarbonyl)hexyl bromide (710 mg, 1.20 mmol) was added to this mixture, and the reaction mixture was stirred overnight at room temperature, diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. The crude product was further purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to afford 630 mg (69% yield) of **25**: ^1H NMR δ 1.1−1.45 (m, 16H), 1.75−2.0 (m, 4H), 2.5−2.65 (m, 2H), 3.48 (s, 2H), 4.15 (q, J = 8.1 Hz, 8H), 4.6−4.7 (m, 2H), 4.8−5.0 (m, 1H), 6.8−6.95 (m, 1H), 7.1−7.3 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 13.66, 13.81, 23.80, 24.60, 31.42, 31.52, 32.47, 42.03, 57.17, 58.53, 60.82, 60.97, 74.27, 84.02, 102.44, 127.75, 128.19, 129.73, 139.57, 139.65, 170.63, 170.69, 209.60; IR (neat) 1956, 1730 cm^{-1}; HRMS calcd for $C_{29}H_{40}O_8$ (M^+ + 1) 643.1768, found 643.1743.

(b) 13-Iodo-5,5,10,10-tetrakis(ethoxycarbonyl)-1,2,12(*Z*)-heptadecatriene (26). 1,1-Bis(ethoxycarbonyl)-4-iodo-3(*Z*)-octene was used instead of 2-[2′,2′-bis(ethoxycarbonyl)ethyl]iodobenzene (71% yield): ^1H NMR δ 0.90 (t, J = 7.0 Hz, 3H), 1.15−1.35 (m, 18H), 1.35−1.55 (m, 2H), 1.8−2.0 (m, 4H), 2.45 (t, J = 6.8 Hz, 2H), 2.55−2.65 (m, 2H), 2.65−2.8 (m, 2H), 4.18 (q, J = 7.4 Hz, 8H), 4.6−4.7 (m, 2H), 4.85−5.0 (m, 1H), 5.32 (t, J = 6.9 Hz, 1H); ^{13}C NMR δ 13.72, 14.02, 21.17, 24.04, 24.34, 31.31, 31.67, 31.79, 32.36, 39.47, 45.16, 56.93, 57.46, 61.10, 61.22, 74.49, 84.24, 112.84, 128.80, 170.97, 209.87; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{29}H_{46}IO_8$ (M^+ + 1) 649.2237, found 649.2224.

(c) 5,5,18,18-Tetrakis(ethoxycarbonyl)-19-(2′-iodophenyl)-1,2-nonadecadiene (27). 1,12-Dibromododecane was used instead of 1,4-dibromobutane (52% yield): ^1H NMR δ 1.4−1.1 (m, 32H), 1.8−2.0 (m, 4H), 2.5−2.7 (m, 2H), 3.50 (s, 2H), 4.1−4.25 (m, 8H), 4.6−4.7 (m, 2H), 4.85−5.05 (m, 1H), 6.8−6.95 (m, 1H), 7.15−7.25 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 13.93, 14.09, 22.63, 23.75, 24.55, 29.30, 29.51, 29.59, 29.76, 31.57, 31.80, 31.96, 33.18, 42.36, 57.62, 58.89, 61.09, 61.23, 74.41, 84.39, 102.77, 127.99, 128.36, 130.02, 139.86, 140.13, 171.22, 171.26, 209.91; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{37}H_{56}IO_8$ (M^+ + 1) 755.3020, found 755.3037.

(d) 21-Iodo-5,5,18,18-Tetrakis(ethoxycarbonyl)-1,2,20(*Z*)-pentacosatriene (28). 1,1-Bis(ethoxycarbonyl)-4-iodo-3(*Z*)-octene and 1,-12-dibromododecane were used instead of 2-[2′,2′-bis(ethoxycarbonyl)-ethyl]iodobenzene and 1,4-dibromobutane, respectively (53% yield): ^1H NMR δ 0.90 (t, J = 6.8 Hz, 3H), 1.0−1.35 (m, 34H), 1.35−1.6 (m, 2H), 1.75−1.95 (m, 4H), 2.45 (t, J = 7.5 Hz, 2H), 2.55−2.7 (m, 2H), 2.7−2.8 (m, 2H), 4.18 (q, J = 7.7 Hz, 8H), 4.6−4.7 (m, 2H), 4.85−5.05 (m, 1H), 5.35 (t, J = 6.9 Hz, 1H); ^{13}C NMR δ 13.78, 14.07, 21.19, 23.74, 24.02, 29.29, 29.51, 29.58, 29.75, 31.33, 31.78, 31.95, 32.62, 39.47, 45.19, 57.04, 57.60, 61.08, 61.19, 74.38, 84.37, 112.69,

(29) Vogtle, F. *Chem. Ber.* **1969**, *102*, 1784.

128.99, 171.21, 209.89; IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{37}H_{62}IO_8$ ($M^+ + 1$) 761.3489, found 761.3497.

(e) 3-[2′,2′-Bis(ethoxycarbonyl)ethyl]-1-[2′,2′-bis(ethoxycarbonyl)-4′,5′-hexadienyl)-2-bromobenzene (29). In step 1, 5,5-bis(ethoxycarbonyl)-1,2-pentadiene was alkylated similarly with 2-bromo-1,3-bis(bromomethyl)benzene in THF, and the corresponding product was alkylated with diethyl malonate in THF in step 2 in 76% yield: ^1H NMR δ 1.22 (t, J = 8.2 Hz, 12H), 2.55−2.65 (m, 2H), 3.36 (d, J = 8.3 Hz, 2H), 3.58 (s, 2H), 3.84 (t, J = 8.3 Hz, 1H), 4.0−4.3 (m, 8H), 4.6−4.75 (m, 2H), 5.05−5.25 (m, 1H), 7.05−7.25 (m, 3H); ^{13}C NMR δ 13.78, 13.85, 32,44, 36.23, 37.84, 51.27, 58.66, 61.26, 61.32, 74.56, 84.85, 126.59, 128.15, 130.03, 137.08, 137.67, 168.52, 170.37, 209.80; IR (neat) 1956, 1734 cm^{-1}; HRMS calcd for $C_{26}H_{33}BrO_8$ (M^+) 552.1359, found 552.1359.

(f) 1-[2′,2′-Bis(ethoxycarbonyl)-4′,5′-hexadienyl]-3-[2′,2′-bis(ethoxycarbonyl)-5′-hexenyl]-2-bromobenzene (30). **30** was prepared according to the method described for **29** using 5,5-bis(ethoxycarbonyl)-1-pentene instead of diethyl malonate in 53% yield: ^1H NMR δ 1.15−1.3 (m, 12H), 1.85−2.0 (m, 2H), 2.0−2.15 (m, 2H), 2.55−2.65 (m, 2H), 3.06 (s, 2H), 3.08 (s, 2H), 4.05−4.3 (m, 8H), 4.6−4.7 (m, 2H), 4.95 (d, J = 8.3 Hz, 1H), 5.02 (d, J = 17.3 Hz, 1H), 5.05−5.25 (m, 1H), 5.65−5.9 (m, 1H), 7.0−7.2 (m, 3H); ^{13}C NMR δ 13.87, 28.89, 31.82, 32.36, 38.49, 38.74, 58.44, 58.75, 61.24, 61.34, 74.62, 84.99, 114.88, 126.37, 129.72, 129.81, 130.00, 137.05, 137.14, 137.47, 170.52, 171.01, 209.85; IR (neat) 1956, 1732, 1642 cm^{-1}; HRMS calcd for $C_{30}H_{40}BrO_8$ ($M^+ + 1$) 607.1907, found 607.1913.

(g) 1-[2′,2′-Bis(ethoxycarbonyl)-4′,5′-hexadienyl]-3-[2′,2′-bis(ethoxycarbonyl)-5′-heptynyl]-2-bromobenzene (31). **31** was prepared according to the method described for **29** using 6,6-bis(ethoxycarbonyl)-2-hexyne instead of diethyl malonate in 76% yield: ^1H NMR δ 1.22 (t, J = 7.4 Hz, 12H), 1.73 (s, 3H), 2.0−2.25 (m, 4H), 2.55−2.7 (m, 2H), 3.55 (s, 2H), 3.58 (s, 2H), 4.05−4.25 (m, 8H), 4.6−4.7 (m, 2H), 5.05−5.25 (m, 1H), 7.05−7.20 (m, 3H); ^{13}C NMR δ 3.32, 13.78, 14.63, 32.24, 38.38, 38.71, 58.09, 58.67, 61.25, 74.54, 75.73, 77.82, 84.92, 126.33, 129.61, 129.74, 129.98, 136.84, 137.03, 170.39, 170.54, 209.79; IR (neat) 2258, 1956, 1728 cm^{-1}; HRMS calcd for $C_{31}H_{40}BrO_8$ ($M^+ + 1$) 619.1907, found 619.1907.

(h) 1-[2′,2′-Bis(ethoxycarbonyl)-4′,5′-hexadienyl]-3-[2′,2′-bis(ethoxycarbonyl)-4′-pentenyl]-2-bromobenzene (32). **32** was prepared according to the method described for **29** using 4,4−bis(ethoxycarbonyl)-1-butene instead of diethyl malonate in 35−40% yield: ^1H NMR δ 1.2−1.3 (m, 12H), 2.5−2.7 (m, 4H), 3.56 (s, 2H), 3.58 (s, 2H), 4.0−4.25 (m, 8H), 4.6−4.75 (m, 2H), 5.0−5.2 (m, 3H), 5.7−5.95 (m, 1H), 7.0−7.2 (m, 3H); ^{13}C NMR δ 13.85, 32.34, 37.67, 38.40, 38.77, 58.62, 58.69, 61.24, 61.29, 74.60, 118.75, 126.31, 129.81, 129.86, 129.94, 132.94, 136.97, 137.11, 170.47, 170.64, 209.82; IR (neat) 1956, 1734, 1640, 1578 cm^{-1}; HRMS calcd for $C_{29}H_{37}BrO_8$ (M^+) 592.1672, found 592.1666.

Allenyl Ethers. Allenyl ethers **13a**, **13b**, **14**, **17**, **18**, and **22** were prepared according to the following procedure.

(a) 2-Iodobenzyl 4,5-Hexadienyl Ether (22). Representative Procedure. 4,5-Hexadienol[30] (270 mg, 2.76 mmol) in THF (2.5 mL) was added to a suspension of NaH in THF (2.5 mL) at room temperature. After 10 min at room temperature, 2-iodobenzyl bromide (0.94 g, 3.16 mmol) was added to the above mixture. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with water, extracted with ether, dried over $MgSO_4$, and evaporated. The crude product was further purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 100/1) to afford 612 mg (71% yield) of **22**: ^1H NMR δ 1.7−1.9 (m, 2H), 2.05−2.2 (m, 2H), 3.58 (dt, J = 7.1 and 1.3 Hz, 2H), 4.45 (s, 2H), 4.55−4.75 (m, 2H), 5.0−5.2 (m, 1H), 6.95 (t, J = 7.2 Hz, 1H), 7.2−7.55 (m, 2H), 7.80 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 24.77, 29.00, 70.03, 75.07, 76.53, 89.49, 97.68, 128.10, 128.57, 128.97, 139.01, 140.69, 208.44; IR (neat) 1956 cm^{-1}; HRMS calcd for $C_{13}H_{16}IO$ ($M^+ + 1$) 315.0246, found 315.0233.

(b) 2-Iodobenzyl 2,3-Pentadienyl Ether (13a). 2,3-Pentadienol was used instead of 4,5-hexadienol (79% yield): ^1H NMR δ 1.6−1.75 (m, 3H), 4.05−4.15 (m, 2H), 4.52 (s, 2H), 5.1−5.35 (m, 2H), 6.97 (t, J = Hz, 1H), 7.25−7.5 (m, 2H), 7.85 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 14.17, 69.07, 75.32, 86.66, 87.56, 97.74, 128.16, 128.73, 129.06, 130.09, 140.56, 206.03; IR (neat) 1966 cm^{-1}; MS 301 (M^+).

(c) 2-Bromobenzyl 2,3-Pentadienyl Ether (13b). 2-Bromobenzyl bromide and 2,3-pentadienol were used instead of 2-iodobenzyl bromide and 4,5-hexadienol, respectively (64% yield): ^1H NMR δ 1.6−1.75 (m, 3H), 4.05−4.15 (m, 2H), 4.58 (s, 2H), 5.1−5.3 (m, 2H), 7.05−7.2 (m, 1H), 7.2−7.4 (m, 1H), 7.4−7.6 (m, 2H); ^{13}C NMR δ 14.00, 69.40, 70.80, 86.40, 87.80, 122.40, 127.40, 128.60, 129.00, 132.40, 137.60, 206.00; IR (neat) 1944 cm^{-1}; HRMS calcd for $C_{12}H_{13}BrO$ (M^+) 252.0150, found 252.0147.

(d) 2-Bromobenzyl 2,3-Hexadienyl Ether (14). 2-Bromobenzyl bromide and 2,3-hexadienol were used instead of 2-iodobenzyl bromide and 4,5-hexadienol, respectively (71% yield): ^1H NMR δ 1.04 (t, J = 8.1 Hz, 3H), 1.95−2.15 (m, 2H), 4.05−4.15 (m, 2H), 4.60 (s, 2H), 5.2−5.35 (m, 2H), 7.12 (td, J = 8.2 and 1.2 Hz, 1H), 7.30 (td, J = 8.2 and 1.2 Hz, 1H), 7.50 (t, J = 8.2 Hz, 2H); ^{13}C NMR δ 13.40, 21.66, 69.27, 70.83, 88.85, 93.75, 122.61, 127.31, 128.76, 128.99, 132.41, 137.72, 204.82; IR (neat) 1964 cm^{-1}; MS *m/e* 267/269 ($M^+ + 1$).

(e) 2-Iodobenzyl 3,4-Pentadienyl Ether (17). 3,4-Pentadienol was used instead of 4,5-hexadienol (73% yield): ^1H NMR δ 2.3−2.45 (m, 2H), 4.50 (s, 2H), 4.64 (t, J = 7.8 Hz, 2H), 4.65−4.75 (m, 2H), 5.1−5.25 (m, 1H), 6.96 (t, J = 8.3 Hz, 1H), 7.34 (t, J = 8.3 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H); ^{13}C NMR δ 28.77, 70.08, 75.01, 76.36, 86.66, 97.63, 128.14, 128.58, 129.03, 139.04, 140.57, 208.88; IR (neat) 1956 cm^{-1}; HRMS calcd for $C_{12}H_{14}IO$ ($M^+ + 1$) 301.0089, found 301.0086.

(f) 2-Bromobenzyl 3,4-Heptadienyl Ether (18). 2-Bromobenzyl bromide and 3,4-heptadienol were used instead of 2-iodobenzyl bromide and 4,5-hexadienol, respectively (77% yield): ^1H NMR δ 1.00 (t, J = 7.4 Hz, 3H), 1.9−2.1 (m, 2H), 2.25−2.45 (m, 2H), 3.63 (t, J = 7.4 Hz, 2H), 4.60 (s, 2H), 5.1−5.25 (m, 2H), 7.15 (td, J = 7.9 and 1.2 Hz, 1H), 7.30 (t, J = 7.9 Hz, 1H), 7.45−7.6 (m, 2H); ^{13}C NMR δ 13.37, 21.84, 29.51, 70.43, 72.07, 88.01, 93.07, 122.51, 127.32, 128.73, 128.88, 132.39, 137.85, 204.05; IR (neat) 1964 cm^{-1}; MS *m/e* 281/283 ($M^+ + 1$).

ω-Haloalkenes. (a) 2-Iodobenzyl 4-Pentenyl Ether (41). **41** was prepared in 96% yield according to the procedure described for **17** using 4-pentenol instead of 3,4-pentadienol: ^1H NMR δ 1.65−1.85 (m, 2H), 2.1−2.25 (m, 2H), 3.56 (t, J = 7.2 Hz, 2H), 4.48 (s, 2H), 4.96 (d, J = 8.2 Hz, 1H), 5.04 (d, J = 17.2 Hz, 1H), 5.7−5.95 (m, 1H), 6.9−7.05 (m, 1H), 7.3−7.6 (m, 2H), 7.82 (d, J = 8.6 Hz, 1H); ^{13}C NMR δ 28.93, 30.36, 70.20, 76.56, 97.70, 114.78, 128.15, 128.61, 129.02, 138.22, 139.07, 140.76; HRMS calcd for $C_{12}H_{15}IO$ (M^+) 302.0168, found 302.0158.

(b) 8-(2′-Bromophenyl)-1-octene (42). **42** was prepared in 36% yield according to the procedure described for **19** using allyl bromide instead of propargyl bromide: ^1H NMR δ 1.2−1.5 (6H), 1.5−1.7 (m, 2H), 1.9−2.15 (m, 2H), 2.70 (t, J = 8.1 Hz, 2H), 4.92 (d, J = 10.0 Hz, 1H), 5.00 (d, J = 16.0 Hz, 1H), 5.65−5.95 (m, 1H), 6.9−7.1 (m, 1H), 7.1−7.25 (m, 2H), 7.50 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 28.83, 28.91, 29.19, 29.84, 33.76, 36.15, 114.19, 124.42, 127.24, 127.28, 130.21, 132.68, 139.03, 141.99; IR (neat) 1640, 1566 cm^{-1}; HRMS calcd for $C_{14}H_{19}Br$ (M^+) 266.0670, found 266.0675.

(c) 5,5,10,10-Tetrakis(ethoxycarbonyl)-11-(2′-iodophenyl)-1-undecene (43). **43** was prepared in 70% yield according to the procedure described for **25** using 5,5-bis(ethoxycarbonyl)-1-pentene instead of 5,5-bis(ethoxycarbonyl)-1,2-pentadiene: ^1H NMR δ 1.1−1.45 (m, 14H), 1.75−2.0 (m, 10H), 3.50 (s, 2H), 4.18 (q, J = 7.2 Hz, 8H), 4.95 (d, J = 8.5 Hz, 1H), 5.04 (d, J = 14.8 Hz, 1H), 5.65−5.95 (m, 1H), 6.8−6.95 (m, 1H), 7.1−7.25 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 13.93, 14.08, 24.25, 25.01, 28.35, 31.44, 32.05, 32.82, 42.43, 57.15, 58.88, 61.04, 61.30, 102.75, 114.95, 128.04, 128.46, 129.99, 137.61, 139.89, 139.96, 171.10, 171.56; IR (neat) 1730, 1642 cm^{-1}; HRMS calcd for $C_{29}H_{42}IO_8$ ($M^+ + 1$) 645.1924, found 645.1910.

(d) 5,5,18,18-Tetrakis(ethoxycarbonyl)-19-(2′-iodophenyl)-1-nonadecene (44). **44** was prepared in 35−45% yield according to the procedure described for **27** using 5,5-bis(ethoxycarbonyl)-1-pentene instead of 5,5-bis(ethoxycarbonyl)-1,2-pentadiene: ^1H NMR δ 1.1−1.35 (m, 32H), 1.8−2.0 (m, 8H), 3.48 (s, 2H), 4.1−4.25 (m, 8H), 4.96 (d, J = 8.6 Hz, 1H), 5.04 (d, J = 17.2 Hz, 1H), 5.65−5.9 (m, 1H), 6.8−6.95 (m, 1H), 7.15−7.25 (m, 2H), 7.85 (d, J = 8.0 Hz, 1H); ^{13}C NMR δ 13.81, 13.96, 23.72, 24.39, 28.23, 29.16, 29.37, 29.42, 29.57,

(30) Crabbe, P.; Fillion, H.; Andre, D.; Luche, J. *J. Chem. Soc., Chem. Commun.* **1979**, 859.

29.66, 31.28, 32.06, 33.04, 42.23, 57.07, 58.73, 60.82, 61.06, 102.64, 114.74, 127.85, 128.24, 129.90, 137.56, 139.71, 139.98, 171.07, 171.54; IR (neat) 1730, 1630 cm^{-1}; HRMS calcd for $C_{37}H_{58}IO_8$ ($M^+ + 1$) 757.3176, found 757.3192.

(e) 21-Iodo-5,5,18,18-tetrakis(ethoxycarbonyl)-1,20(*Z*)-pentacosadiene (45). **45** was prepared in 40% yield according to the procedure described for **28** using 5,5-bis(ethoxycarbonyl)-1-pentene instead of 5,5-bis(ethoxycarbonyl)-1,2-pentadiene: ^1H NMR δ 0.85−0.95 (m, 3H), 1.0−1.3 (m, 34H), 1.3−1.55 (m, 2H), 1.75−2.0 (m, 8H), 2.4−2.5 (m, 2H), 2.65−2.8 (m, 2H), 4.05−4.25 (m, 8H), 4.94 (d, J = 9.4 Hz, 1H), 5.03 (d, J = 16.5 Hz, 1H), 5.25−5.4 (m, 1H), 5.65−5.8 (m, 1H); ^{13}C NMR δ 13.67, 13.96, 21.06, 23.73, 23.89, 28.25, 29.16, 29.38, 29.45, 29.62, 29.67, 31.20, 31.30, 32.07, 32.49, 39.35, 45.07, 56.91, 57.09, 60.82, 61.05, 112.53, 114.74, 128.91, 137.56, 171.04, 171.55; IR (neat) 1732, 1642 cm^{-1}; HRMS calcd for $C_{37}H_{63}IO_8$ (M^+) 763.3646, found 763.3663.

Pd-Catalyzed Cyclization of ω-Haloallenes. (a) Cyclization of 4-(2′-bromophenyl)-1,2-butadiene (5). Representative Procedure (Conditions I). To 4-(2′-bromophenyl)-1,2-butadiene (**5**) (105 mg, 0.50 mmol), K_2CO_3 (340 mg, 2.46 mmol), and EtOH (300 μL, 5 mmol) in DMF (10 mL) was added $Cl_2Pd(PPh_3)_2$ (18 mg, 5 mol %) under argon. The reaction was complete in 4 h at 80 °C as monitored by TLC, and then the mixture was diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. Further purification by chromatography on silica gel (*n*-hexane) afforded 45 mg (69%) of 1-methylene-1*H*-indene:[31] ^1H NMR δ 5.68 (s, 1H), 6.00 (s, 1H), 6.45 (d, J = 6.3 Hz, 1H), 6.82 (d, J = 6.3 Hz, 1H), 7.0−7.3 (m, 4H); IR (neat) 1692, 1604 cm^{-1}; MS *m/e* 128 (M^+).

(b) 1-Ethylidene-1*H*-indene (46). Cyclization of **6** (52 mg, 0.233 mmol) afforded 19 mg (57%) of **46**: ^1H NMR δ 2.15 (d, J = 8.3 Hz, 3H, *E*), 2.35 (d, J = 8.3 Hz, 3H, *Z*), 6.45 (q, J = 8.3 Hz, 1H, *Z*), 6.70 (q, J = 8.3 Hz, 1H, *E*), 6.82 (d, J = 6.2 Hz, 1H), 6.90 (d, J = 6.2 Hz, 1H), 7.2−7.65 (m, 4H); IR (neat) 1650, 1604 cm^{-1}; HRMS calcd for $C_{11}H_{10}$ (M^+) 142.0783, found 142.0775.

(c) 1-Methylnaphthalene.[32] Cyclization of **7** (55 mg, 0.247 mmol) afforded 23 mg (66%) of 1-methylnaphthalene: ^1H NMR δ 2.68 (s, 3H), 7.25−7.6 (m, 4H), 7.70 (d, J = 7.6 Hz, 1H), 7.8−7.9 (m, 1H), 7.95−8.05 (m, 1H); ^{13}C NMR δ 19.37, 124.08, 125.51, 125.55, 125.68, 126.35, 126.53, 128.50, 132.58, 133.52, 134.23; IR (neat) 1598, 1510 cm^{-1}; MS *m/e* 142 (M^+).

(d) Cyclization of **8** (85 mg, 0.257 mmol) at 120 °C afforded 8 mg (12%) of 6,6-bis(ethoxycarbonyl)-3,4-dimethylenecyclohexene (**47**) and 27 mg (42%) of **48**. Data for **47**: ^1H NMR δ 1.2−1.35 (m, 6H), 2.91 (s, 1H), 4.1−4.3 (m, 4H), 4.95 (s, 1H), 5.00 (s, 1H), 5.38 (s, 2H), 6.02 (d, J = 9.7 Hz, 1H), 6.36 (d, J = 9.7 Hz, 1H). Data for **48**: ^1H NMR δ 1.2−1.3 (m, 12H), 1.55−1.7 (m, 2H), 1.95−2.3 (m, 4H), 2.68 (s, 2H), 2.88 (s, 2H), 4.1−4.3 (m, 8H), 4.77 (s, 1H), 4.95 (s, 1H), 5.70 (d, J = 9.5 Hz, 1H), 5.80 (d, J = 7.2 Hz, 1H), 5.85 (d, J = 7.2 Hz, 1H), 5.88 (d, J = 9.5 Hz, 1H); ^{13}C NMR δ 13.98, 25.03, 32.13, 34.14, 36.04, 39.82, 40.38, 54.73, 58.13, 61.50, 61.62, 61.68, 111.27, 120.10, 123.42, 124.06, 126.72, 129.46, 139.25, 146.17, 169.86, 170.52, 170.73; IR (neat) 1736, 1648, 1604 cm^{-1}; HRMS calcd for $C_{28}H_{36}O_8$ (M^+) 500.2410, found 500.2394.

(e) 6,6-Bis(ethoxycarbonyl)-3-methylene-1,2-benzo-1,4-cycloheptadiene (49). Cyclization of **9** (110 mg, 0.257 mmol) afforded 50 mg (73%) of **49**: ^1H NMR δ 1.25 (t, J = 7.0 Hz, 6H), 3.52 (s, 2H), 4.18 (q, J = 7.0 Hz, 4H), 5.43 (s, 1H), 5.53 (s, 1H), 5.80 (d, J = 11.7 Hz, 1H), 6.58 (d, J = 11.7 Hz, 1H), 7.15−7.4 (m, 4H); ^{13}C NMR δ 13.95, 38.86, 59.18, 61.73, 121.29, 126.47, 127.11, 127.72, 127.87, 130.20, 132.52, 133.65, 141.11, 145.18, 169.55; IR (neat) 1736, 1592, 1570 cm^{-1}; HRMS calcd for $C_{18}H_{20}O_4$ 300.1362, found 300.1356.

(f) 6,6-Bis(ethoxycarbonyl)-3-vinyl-1,2-benzo-1,3-cycloheptadiene (50). Cyclization of **10** (110 mg, 0.249 mmol) afforded 45 mg (58%) of **50**: ^1H NMR δ 1.26 (t, J = 6.7 Hz, 6H), 2.40 (d, J = 8.0 Hz, 2H), 3.10 (s, 2H), 4.20 (q, J = 6.7 Hz, 4H), 5.14 (d, J = 10.0 Hz, 1H), 5.22 (d, J = 17.6 Hz, 1H), 6.20 (t, J = 8.0 Hz, 1H), 6.55 (dd, J = 10.0 and 17.6 Hz, 1H), 7.2−7.5 (m, 4H); ^{13}C NMR δ 14.04, 31.00, 37.29, 61.42, 67.03, 115.46, 126.45, 127.22, 127.80, 128.51, 130.62, 132.40, 136.90, 137.53, 142.07, 171.03; IR (neat) 1716, 1600 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4$ 314.1518, found 314.1514.

(31) Bernardon, C.; Deberby, A. *J. Org. Chem.* **1982**, *47*, 463.
(32) Hollenstein, V. R.; Mooser, A. *Angew. Chem.* **1974**, *86*, 595.

(g) 6,6-Bis(ethoxycarbonyl)-2-*n*-butyl-3-methylene-1,4-cycloheptadiene (51). Cyclization of **11** (100 mg, 0.23 mmol) afforded 47 mg (66%) of **51**: ^1H NMR δ 0.88 (t, J = 7.7 Hz, 3H), 1.15−1.45 (m, 10H), 2.24 (t, J = 6.4 Hz, 2H), 2.78 (d, J = 6.2 Hz, 2H), 4.1−4.3 (m, 4H), 5.31 (s, 1H), 5.34 (s, 1H), 5.68 (t, J = 6.2 Hz, 1H), 5.82 (d, J = 12.2 Hz, 1H), 6.27 (d, J = 12.2 Hz, 1H); ^{13}C NMR δ 13.86, 14.00, 22.05, 30.62, 32.00, 36.40, 58.17, 61.63, 121.09, 122.72, 126.86, 133.23, 142.17, 143.15, 170.01; IR (neat) 1736, 1638, 1572 cm^{-1}; HRMS calcd for $C_{18}H_{26}O_4$ (M^+) 306.1831, found 306.1826.

(h) 6,6-Bis(ethoxycarbonyl)-3-methylene-1,2-cyclopent-1′-eno-1,4-cycloheptadiene (52). Cyclization of **12** (90 mg, 0.243 mmol) afforded 41 mg (66%) of **52**: ^1H NMR δ 1.25 (t, J = 7.8 Hz, 6H), 1.7−1.95 (m, 2H), 2.5−2.7 (m, 4H), 2.88 (s, 2H), 4.20 (q, J = 7.80 Hz, 4H), 5.12 (s, 2H), 5.90 (d, J = 11.6 Hz, 1H), 6.25 (d, J = 11.6 Hz, 1H); ^{13}C NMR δ 13.99, 21.64, 34.80, 35.66, 41.37, 58.38, 61.66, 119.55, 126.48, 133.18, 133.63, 138.29, 140.47, 170.08; IR (neat) 1736, 1650, 1560 cm^{-1}; HRMS calcd for $C_{17}H_{22}O_4$ 290.1518, found 290.1519.

(i) 5-Vinyl-1,3-dihydro-2-benzoxepin (53). Cyclization of **13a** (150 mg, 0.5 mmol) afforded 50 mg (58%) of **53**: ^1H NMR δ 3.90 (d, J = 6.7 Hz, 2H), 4.43 (s, 2H), 5.29 (d, J = 10.7 Hz, 1H), 5.40 (d, J = 17.5 Hz, 1H), 6.22 (t, J = 6.7 Hz, 1H), 6.62 (dd, J = 10.7 and 17.5 Hz, 1H), 7.2−7.6 (m, 4H); ^{13}C NMR δ 62.81, 68.16, 117.61, 126.68, 127.84, 128.07, 128.17, 129.57, 137.08, 137.75, 137.90, 144.36; IR (neat) 1602, 1572 cm^{-1}; HRMS calcd for $C_{12}H_{12}O$ 172.0888, found 172.0890.

(j) 5-(1′-Propenyl)-1,3-dihydro-2-benzoxepin (54). Cyclization of **14** (140 mg, 0.524 mmol) afforded 59 mg (61%) of **54:** >97% *E*; ^1H NMR δ 1.82 (dd, J = 7.5 and 1.2 Hz, 3H), 3.82 (d, J = 6.7 Hz, 2H), 4.40 (s, 2H), 5.88 (dq, J = 16.2 and 7.5 Hz, 1H), 6.10 (t, J = 6.7 Hz, 1H), 6.30 (d, J = 16.2 Hz, 1H); ^{13}C NMR δ 18.39, 62.35, 67.85, 123.97, 127.72, 127.90, 128.12, 129.50, 129.64, 131.40, 137.58, 138.83, 144.61; IR (neat) 1590, 1570 cm^{-1}; HRMS calcd for $C_{13}H_{14}O$ 186.1045, found 186.1039.

(k) 6,6-Bis(ethoxycarbonyl)-3-methylene-1,2-benzo-1,4−cyclooctadiene (55). Cyclization of **15** (195 mg, 0.494 mmol) afforded 86 mg (56%) of **55:** ^1H NMR δ 1.10 (t, J = 7.0 Hz, 6H), 2.4−2.55 (m, 2H), 2.8−2.9 (m, 2H), 3.80 (q, J = 7.0 Hz, 4H), 5.22 (bs, 1H), 5.44 (bs, 1H), 5.72 (d, J = 12.3 Hz, 1H), 6.65 (d, J = 12.3 Hz, 1H), 7.05−7.3 (m, 4H); ^{13}C NMR δ 13.65, 29.62, 35.48, 58.37, 61.57, 123.59, 124.89, 126.61, 128.13, 128.52, 129.95, 136.28, 137.27, 139.16, 146.75, 170.50; IR (neat) 1716, 1586, 1566 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4$ (M^+) 314.1518, found 314.1516.

(l) 6,6-Bis(ethoxycarbonyl)-1,2-di-*n*-propyl-3-methylene-1,4-cyclooctadiene (56). Cyclization of **16** (60 mg, 0.126 mmol) afforded 10 mg (23%, 43% by NMR) of **56:** ^1H NMR δ 0.8−1.0 (m, 6H), 1.15−1.5 (m, 10H), 1.9−2.4 (m, 8H), 4.0−4.3 (m, 4H), 5.15 (s, 1H), 5.28 (s, 1H), 5.70 (d, J = 11.7 Hz, 1H), 6.38 (d, J = 11.7 Hz, 1H); ^{13}C NMR δ 13.88, 14.57, 14.94, 21.94, 22.09, 28.49, 32.25, 34.60, 35.85, 58.57, 61.68, 120.92, 122.97, 133.19, 136.43, 137.62, 147.50, 171.31; IR (neat) 1736, 1630, 1570 cm^{-1}; HRMS calcd for $C_{21}H_{33}O_4$ ($M^+ + 1$) 349.2379, found 349.2361.

(m) 6-Methylene-1,3-dihydro-2-benzoxocin (57). Cyclization of **17** (150 mg, 0.50 mmol) afforded 45 mg (52%) of **57:** ^1H NMR δ 3.80 (d, J = 7.9 Hz, 2H), 4.70 (s, 2H), 5.22 (bs, 1H), 5.4 (bs, 1H), 5.60 (dt, J = 11.9 and 7.9 Hz, 1H), 6.74 (d, J = 11.9 Hz, 1H), 7.2−7.5 (m, 4H); ^{13}C NMR δ 57.49, 65.85, 121.58, 123.61, 128.01, 128.92, 129.18, 130.92, 132.65, 140.25, 142.02, 146.26; IR (neat) 1686, 1584, 1568 cm^{-1}; HRMS calcd for $C_{12}H_{12}O$ (M^+) 172.0888, found 172.0883.

(n) 6-(1′-Propenyl)-3,4-dihydro-1*H*-2-benzoxocin (58) and 6-Propylidene-1,3-dihydro-2-benzoxocin (59). Cyclization of **18** (140 mg, 0.50 mmol) afforded 58 mg (58%) of a mixture of **58** (41% by NMR) and **59** (35% by NMR). This mixture could be separated carefully by high-resolution preparative TLC (*n*-hexane/ethyl acetate = 40/1). Data for **58**: >97% *E*; ^1H NMR δ 1.72 (d, J = 8.0 Hz, 3H), 1.75−1.9 (m, 1H), 2.15−2.4 (m, 1H), 3.25−3.45 (m, 1H), 3.8−4.0 (m, 1H), 4.0−4.2 (m, 1H), 4.6−4.8 (m, 1H), 5.2−5.45 (m, 1H), 5.86 (t, J = 8.0 Hz, 1H), 6.30 (d, J = 16.0 Hz, 1H); ^{13}C NMR δ 18.20, 30.80, 66.60, 71.10, 127.30, 127.70, 128.00, 128.80, 129.50, 131.00, 134.20, 136.30, 137.80, 140.50; IR (neat) 1718, 1618 cm^{-1}; HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1200. Data for **59**: ^1H NMR δ 0.99 (t, J = 7.8 Hz, 3H, *E*), 1.12 (t, J = 7.8 Hz, 3H, *Z*), 1.9−2.1 (m, 2H, *E*), 2.38 (m, 2H, *Z*), 3.28 (d, J = 8.0 Hz, 2H, *Z*), 3.63 (d, J = 8.0 Hz, 2H, *E*), 4.65 (s, 2H, *E*), 4.70 (s, 2H, *Z*), 5.4−5.9 (m, 2H), 6.68 (d, J = 12.2 Hz, 1H, *E*), 6.96

(d, J = 12.2 Hz, 1H, *Z*), IR (neat) 1716, 1560, 1530 cm^{-1}; HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1204.

(**o**) **6,6-Bis(ethoxycarbonyl)-3-methylene-1,2-benzo-1,4(*E*)-cyclononadiene (61).** Cyclization of **20** (110 mg, 0.269 mmol) afforded 55 mg (containing 4,4-bis(ethoxycarbonyl)-6,7-octadienylbenzene (total 7%)) (55%) of **61**: ^1H NMR δ 1.15−1.35 (m, 6H), 2.1−3.05 (m, 6H), 4.05−4.35 (m, 4H), 5.26 (s, 1H), 5.28 (s, 1H), 5.85 (d, J = 16.8, 1H), 6.42 (d, J = 16.8 Hz, 1H), 7.05−7.35 (m, 4H); ^{13}C NMR δ 13.88, 25.60, 37.20, 41.50, 61.40, 61.60, 126.60, 128.20, 128.80, 129.30, 131.00, 132.00, 135.40, 142.00, 143.40, 148.40, 170.00, 170.60; IR (neat) 1736, 1640, 1600 cm^{-1}; HRMS calcd for $C_{20}H_{24}O_4$ (M^+) 328.1675, found 328.1675. The following data were assigned to 4,4-bis(ethoxycarbonyl)-6,7-octadienylbenzene: ^1H NMR δ 1.15−1.35 (m, 6H), 1.45−1.65 (m, 2H), 1.9−2.05 (m, 2H), 2.55−2.7 (m, 4H), 4.05−4.35 (m, 4H), 4.55−4.65 (m, 2H), 4.8−5.0 (m, 1H), 7.05−7.35 (m, 4H).

Pd-Catalyzed Cyclization of ω-Haloallenes. (a) Cyclization of 8-(2′-bromophenyl)-1,2-octadiene (19). Representative Procedure (Conditions II). To 8-(2′-bromophenyl)-1,2-octadiene (**19**) (65 mg, 0.245 mmol), K_2CO_3 (170 mg, 1.23 mmol), and *n*-Bu_4NCl (70 mg, 0.25 mmol) in DMF (120 mL) was added $Cl_2Pd(PPh_3)_2$ (10 mg, 5 mol %) under argon. Then the mixture was cooled to −78 °C, degassed by vacuum, and purged with argon several times. After that, the air was completely removed, and reaction was carried out at 120 °C for 12 h (monitored by TLC). Then the mixture was first diluted with ether (200 mL), washed with saturated aqueous solution of NaCl (3 × 30 mL) and then water (3 × 30 mL), dried over $MgSO_4$, and evaporated. The crude product was further purified by chromatography on silica gel (*n*-hexane) to afford 25 mg (55%) of 3-methylene-1,2-benzo-1,4-(*Z*)-cyclononadiene (**60**): ^1H NMR δ 1.45−1.65 (m, 2H), 1.65−1.8 (m, 2H), 1.85−2.05 (m, 2H), 2.82 (t, J = 7.7 Hz, 2H), 4.97 (d, J = 1.2 Hz, 1H), 5.29 (d, J = 1.2 Hz, 1H), 5.57 (dt, J = 11.7 and 8.1 Hz, 1H), 6.33 (d, J = 11.7 Hz, 1H), 7.0−7.3 (m, 4H); ^{13}C NMR δ 23.36, 26.01, 26.32, 31.53, 119.49, 125.81, 127.42, 129.21, 129.43, 132.21, 132.34, 141.75, 142.05, 148.49; IR (neat) 1638, 1586 cm^{-1}; HRMS calcd for $C_{14}H_{16}$ (M^+) 184.1252, found 184.1250. At a concentration of 0.016 M at 115−120 °C, cyclization of **19** (65 mg, 0.245 mmol) afforded 19 mg of **60** (42%) and 10 mg (22%) of 5,16-dimethylene-8,9,10,11,19,-20,21,22-octahydro-5*H*,16*H*-dibenzo[*a*,*j*]cyclooctadecene (**69**): ^1H NMR δ 1.05−1.3 (m, 4H), 1.4−1.6 (m, 4H), 2.0−2.15 (m, 4H), 2.67 (t, J = 6.6 Hz, 4H), 4.82 (s, 2H), 5.06 (dt, J = 16.3 and 6.5 Hz, 2H), 5.25 (s, 2H), 6.30 (d, J = 16.3 Hz, 2H), 6.95−7.35 (m, 8H); ^{13}C NMR δ 29.22, 30.54, 31.96, 33.52, 115.93, 124.86, 127.03, 128.35, 129.64, 133.30, 135.02, 139.99, 140.14, 147.53; IR (neat) 1630, 1596 cm^{-1}; HRMS calcd for $C_{28}H_{32}$ (M^+) 368.2504, found 368.2505.

(**b**) Cyclization of **20** (30 mg, 0.073 mmol) afforded 15 mg of **61** (62%) as the only product.

(**c**) **7-Methylene-3,4-dihydro-1*H*-2-benzoxonin (62).** Cyclization of **22** (75 mg, 0.239 mmol) afforded 23 mg of a mixture of **62** and **70**, which was separated by preparative TLC on silica gel (*n*-hexane/ethyl acetate = 100/1). Data for **62**: ^1H NMR δ 1.8−1.95 (m, 2H), 3.62 (t, J = 6.2 Hz, 2H), 4.75 (s, 2H), 4.97 (s, 1H), 5.32 (s, 1H), 5.65 (dt, J = 11.4 and 8.8 Hz, 1H), 6.50 (d, J = 11.4 Hz, 1H), 7.0−7.4 (m, 4H); ^{13}C NMR δ 27.51, 67.54, 73.36, 117.73, 126.88, 127.13, 128.30, 129.88, 135.52, 138.09, 142.48, 148.46; IR (neat) 1630, 1588 cm^{-1}; HRMS calcd for $C_{13}H_{14}O$ (M^+) 186.1045, found 186.1044. Data for 5,16-dimethylene-8,9,19,20-tetrahydro-5*H*,11*H*,16*H*,22*H*-dibenzo[*c*,*l*][10,21]-dioxacyclooctadecin (**70**): ^1H NMR δ 2.37 (q, J = 7.4 Hz, 4H), 3.05 (t, J = 7.4 Hz, 4H), 4.39 (s, 4H), 4.85 (d, J = 1.8 Hz, 2H), 5.00 (dt, J = 16.0 and 7.4 Hz, 2H), 5.25 (d, J = 1.8 Hz, 2H), 6.38 (d, J = 16.0 Hz, 2H), 6.95−7.05 (m, 2H), 7.15−7.35 (m, 4H), 7.45−7.55 (m, 2H); ^{13}C NMR δ 34.00, 69.64, 69.78, 117.44, 126.97, 127.57, 127.92, 129.36, 130.77, 134.59, 136.42, 139.27, 146.48; IR (neat) 1654, 1598 cm^{-1}; HRMS calcd for $C_{26}H_{29}O_2$ (M^+ + 1) 373.2168, found 373.2157.

(**d**) **3-Methylene-1,2-benzo-1,4-cyclodecadiene (63).** Cyclization of **23** (70 mg, 0.251 mmol) afforded 24 mg (48%) of **63**: ^1H NMR δ 1.2−1.9 (m, 6H), 2.1−2.25 (m, 2H), 2.5−2.7 (m, 2H), 4.80 (s, 1H, *Z*), 4.95 (s, 1H, *Z*), 5.08 (s, 1H, *E*), 5.20 (s, 1H, *E*), 5.25−5.38 (m, 1H, *Z*), 5.52 (dt, J = 7.2 and 15.8 Hz, 1H, *E*), 6.30 (d, J = 11.8 Hz, 1H, *Z*), 6.45 (d, J = 15.8, 1H, *E*), 7.05−7.35 (m, 4H); IR (neat) 1696, 1600 cm^{-1}; HRMS calcd for $C_{15}H_{19}$ (M^+) 199.1487, found 199.1481.

(**e**) **3-Methylene-1,2-benzo-1,4(*E*)-cycloundecadiene (64).** Cyclization of **24** (20 mg, 0.059 mmol) afforded 5 mg (40%) of **64**: ^1H NMR δ 1.1−1.8 (m, 8H), 2.1−2.3 (m, 2H), 2.4−2.6 (m, 2H), 4.98 (d, J = 1.7 Hz, 1H), 5.22 (d, J = 1.7 Hz, 1H), 5.23 (dt, J = 8.2 and 16.5 Hz, 1H), 6.40 (d, J = 16.5 Hz, 1H), 7.1−7.35 (m, 4H); ^{13}C NMR 21.78, 24.98, 26.78, 27.60, 28.47, 33.54, 116.31, 125.45, 127.50, 128.39, 129.61, 134.03, 134.53, 140.90, 140.98, 148.90; IR (neat) 1630, 1598 cm^{-1}; HRMS calcd for $C_{16}H_{21}$ (M^+ + 1) 213.1643, found 213.1632.

(**f**) **3-Methylene-6,6,11,11-tetrakis(ethoxycarbonyl)-1,2-benzo-1,4-(*E*)-cyclododecadiene (65).** Cyclization of **25** (85 mg, 0.132 mmol) afforded 41 mg (purity 83%;, 50%) of **65**: ^1H NMR δ 1.15−1.7 (m, 16H), 1.9−2.1 (m, 4H), 3.30 (s, 2H), 4.1−4.3 (m, 8H), 5.00 (s, 1H), 5.46 (s, 1H), 5.62 (d, J = 16.8 Hz, 1H), 6.60 (d, J = 16.8 Hz, 1H), 6.85−7.3 (m, 4H); ^{13}C NMR δ 13.95, 14.01, 23.04, 23.64, 29.36, 32.59, 34.41, 58.04, 59.69, 61.08, 61.25, 61.40, 119.33, 126.25, 127.42, 128.17, 130.16, 131.43, 134.21, 134.41, 140.91, 146.40, 171.44; IR (neat) 1732, 1630, 1596 cm^{-1}; HRMS calcd for $C_{29}H_{39}O_8$ 515.2645, found 515.2625.

(**g**) **2-*n*-Butyl-3-methylene-6,6,11,11-tetrakis(ethoxycarbonyl)-1(*Z*),4(*E*)-cyclododecadiene (66).** Cyclization of **26** (47 mg, 0.073 mmol) afforded 20 mg of a 1/1 mixture of **66** (27%) and 5,5,10,10-tetrakis(ethoxycarbonyl)-1,2,12-heptadecatriene (26%). Data for **66**: ^1H NMR δ 0.8−0.95 (m, 3H), 1.1−1.5 (m, 20H), 1.55−2.7 (m, 8H), 4.18 (q, J = 6.9 Hz, 8H), 4.82 (s, 1H), 5.00 (t, J = 7.7 Hz, 1H), 5.18 (s, 1H), 5.90 (d, J = 16.5 Hz, 1H), 6.32 (d, J = 16.5 Hz, 1H); IR (neat) 1732, 1630, 1596 cm^{-1}; HRMS calcd for $C_{29}H_{45}O_8$ (M^+ + 1) 521.3114, found 521.3105. The following data were assigned to 5,5,10,10-tetrakis(ethoxycarbonyl)-1,2,12-heptadecatriene: ^1H NMR δ 0.8−0.95 (3H), 1.1−1.5 (m, 20H), 1.55−2.7 (m, 10H), 4.1−4.3 (m, 8H), 4.6−4.7 (m, 2H), 4.75−5.15 (m, 3H); IR (neat) 1956, 1732 cm^{-1}; HRMS calcd for $C_{29}H_{47}O_8$ (M^+ + 1) 523.3271, found 523.3245.

(**h**) **3-Methylene-6,6,19,19-tetrakis(ethoxycarbonyl)-1,2-benzo-1,4-(*E*)-cycloeicosadiene (67).** Cyclization of **27** (95 mg, 0.126 mmol) afforded 68 mg (86%) of **67**: ^1H NMR δ 1.1−1.5 (m, 32H), 1.65−1.85 (m, 2H), 2.0−2.2 (m, 2H), 3.24 (s, 2H), 4.0−4.25 (m, 8H), 5.16 (d, J = 1.6 Hz, 1H), 5.42 (d, J = 1.6 Hz, 1H), 5.60 (d, J = 16.9 Hz, 1H), 6.40 (d, J = 16.9 Hz, 1H), 7.0−7.1 (m, 1H), 7.1−7.3 (m, 3H); ^{13}C NMR δ 13.91, 13.97, 22.90, 23.53, 26.31, 26.57, 27.16, 27.52, 28.00, 28.27, 28.58, 33.24, 33.72, 34.95, 59.48, 59.51, 60.83, 61.33, 120.17, 126.61, 127.23, 129.54, 130.14, 130.30, 133.26, 135.17, 139.98, 147.23, 170.37, 171.55; IR (neat) 1734, 1654, 1602 cm^{-1}; HRMS calcd for $C_{37}H_{54}O_8$ (M^+) 626.3819, found 626.3813.

(**i**) **2-*n*-Butyl-3-methylene-6,6,19,19-tetrakis(ethoxycarbonyl)-1(*Z*),4(*E*)-cycloeicosadiene (68).** Cyclization of **28** (95 mg, 0.125 mmol) afforded 43 mg of a 87/13 mixture of **68** and 5,5,18,18-tetrakis-(ethoxycarbonyl)-1,2,20-pentacosatriene. Data for **68**: ^1H NMR δ 0.8−1.0 (m, 3H), 1.0−1.7 (m, 36H), 1.7−2.85 (m, 8H), 4.1−4.3 (m, 8H), 4.83 (d, J = 1.7 Hz, 1H), 5.17 (d, J = 1.7 Hz, 1H), 5.35 (t, J = 7.4 Hz, 1H), 6.00 (d, J = 16.7 Hz, 1H), 6.12 (d, J = 16.7 Hz, 1H); IR (neat) 1734, 1596 cm^{-1}; HRMS calcd for $C_{37}H_{61}O_8$ (M^+ + 1) 633.4366, found 633.4379. The following data were assigned to 5,5,18,18-tetrakis(ethoxycarbonyl)-1,2,20-pentacosatriene: ^1H NMR δ 0.8−1.0 (m, 3H), 1.0−1.7 (m, 36H), 1.7−2.85 (m, 10H), 4.1−4.3 (m, 8H), 4.6−4.7 (m, 2H), 4.8−5.25 (m, 3H); IR (neat) 1958, 1734 cm^{-1}; HRMS calcd for $C_{37}H_{63}O_8$ (M^+ + 1) 635.4523, found 635.4510.

Pd-Catalyzed Cyclization of ω-Haloalkenes. (a) Cyclization of 41. Following the procedure described for that of **17** (conditions I), the ^1H NMR spectrum of the crude product mixture showed that the formation of **71** was less than 5%, if any.

(**b**) **Cyclization of 42.** Following the procedure described for that of **19**, **42** (65 mg, 0.244 mmol) afforded 3 mg (7%) of 8-phenyl-1-octene and 26 mg of dimer and trimer, etc. The formation of nine- or ten-membered products, i.e., **72** and **73**, is less than 2%. Data for 8-phenyl-1-octene: ^1H NMR δ 1.2−1.5 (m, 6H), 1.5−1.75 (m, 2H), 1.95−2.15 (m, 2H), 2.50 (t, J = 8.8 Hz, 2H), 4.93 (d, J = 9.0 Hz, 1H), 5.00 (d, J = 16.3 Hz, 1H), 5.7−5.95 (m, 1H), 7.05−7.35 (m, 5H); IR (neat) 1640, 1604 cm^{-1}; HRMS calcd for $C_{14}H_{20}$ (M^+) 188.1565, found 188.1565.

(**c**) **Cyclization of 43.** Following the procedure described for that of **25**, **43** (80 mg, 0.124 mmol) afforded 35 mg of a 1/2 mixture of 7,7,12,12-tetrakis(ethoxycarbonyl)-1,2-benzo-1,3(*E*)-cyclotridecadiene (**74**) (18%) and 11-phenyl-5,5,10,10-tetrakis(ethoxycarbonyl)-undecene (**75**) (37%). Data for **74**: ^1H NMR δ 1.0−2.3(m, 24H), 3.32 (s, 2H), 4.0−4.3 (m, 8H), 5.9−6.15 (m, 1H), 6.62 (d, J = 16.5 Hz, 1H), 6.85−7.4 (m, 4H); HRMS calcd for $C_{29}H_{41}O_8$ (M^+ + 1) 517.2801,

found 517.2806. The following data were assigned to **75**: ^{1}H NMR 1.0−2.3 (m, 24H), 3.20 (d, J = 1.9 Hz, 2H), 4.0−4.3 (m, 8H), 4.95 (d, J = 8.6 Hz, 1H), 5.02 (d, J = 16.7 Hz, 1H), 5.65−5.9 (m, 1H), 6.85−7.4 (m, 5H),; IR 1736, 1642, 1604 cm^{-1}; HRMS calcd for $C_{29}H_{43}O_8$ (M^+ + 1) 519.2958, found 519.2947.

(d) Cyclization of 44. Following the procedure described for that of **27**, **44** (95 mg, 0.126 mmol) afforded 52 mg (66%) of **7**,7,20,20-tetrakis(ethoxycarbonyl)-1,2-benzo-1,3(*E*)-cycloheneicosadiene (**76**): ^{1}H NMR δ 1.1−1.45 (m, 32H), 1.55−1.7(m, 2H), 1.85−2.0 (m, 2H), 2.05−2.15 (m, 4H), 3.34 (s, 2H), 4.1−4.3 (m, 8H), 5.95 (dt, J = 15.8 and 2.7 Hz, 1H), 6.70 (d, J = 15.8 Hz, 1H), 6.9−7.45 (m, 4H); ^{13}C NMR δ 19.99, 14.07, 21.90, 24.49, 26.55, 26.71, 27.47, 27.92, 28.02, 28.16, 28.95, 29.76, 30.73, 31.23, 32.25, 34.40, 57.15, 59.38, 61.06, 126.86, 126.93, 128.85, 129.81, 131.81, 133.81, 138.17, 171.59, 171.68; IR (neat) 1736, 1654, 1600 cm^{-1}; HRMS calcd for $C_{37}H_{57}O8$ (M^+ + 1) 629.4053, found 629.4028.

(e) Cyclization of 45. Following the procedure described for that of **28**, **45** (95 mg, 0.125 mmol) afforded 59 mg (66%) of a mixture of **78**−**80**. Data for **78**: ^{1}H NMR δ 0.7−0.9 (m, 3H), 0.95−2.8 (m, 48H), 4.0−4.2 (m, 8H), 5.6−5.9 (m, 2H), 6.32 (d, J = 16.2 Hz, 1H); IR (neat) 1732 cm^{-1}; HRMS calcd for $C_{37}H_{63}O_8$ (M^++1) 635.4523, found 635.4503. Data for **79:** ^{1}H NMR δ 0.7−0.9 (m, 3H), 0.95−2.8 (m, 48H), 4.0−4.2 (m, 8H), 4.95 (d, J = 8.5 Hz, 1H), 5.05 (d, J = 17.3 Hz, 1H), 5.6−5.9 (m, 3H); IR (neat) 1732 cm^{-1}; HRMS calcd for $C_{37}H_{65}O_8$ (M^+ + 1) 637.4679, found 637.4653. Data for **80**: ^{1}H NMR δ 0.7−0.9 (m, 3H), 0.95−2.8 (m, 46H), 4.0−4.2 (m, 8H), 4.95 (d, J = 8.5 Hz, 1H), 5.05 (d, J = 17.3 Hz, 1H), 5.3−5.9 (m, 3H); ^{13}C NMR δ 205.67; IR (neat) 1964, 1732 cm^{-1}.

Reaction of Iodobenzene, 1-Octene, and 1,2-Octadiene under the Catalysis of $Cl_2Pd(PPh_3)_2$ in DMF. To iodobenzene (195 mg, 0.98 mmol), 1-octene (220 mg, 1.96 mmol), 1,2-octadiene (226 mg, containing 9.6 mol % toluene, 1.88 mmol), K_2CO_3 (690 mg, 5 mmol), and n-Bu_4NCl (280 mg, 1 mmol) in DMF (5 mL) was added $Cl_2Pd(PPh_3)_2$ (35 mg, 5 mol %) under argon. The reaction was run at 80 °C for 23 h. The mixture was diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. The crude product was analyzed by ^{1}H NMR spectra. Further purification via chromatography on silica gel (n-hexane) afforded 43 mg (23%, 43% by NMR) of 2-phenyl-1,3(*E*)-octadiene: ^{1}H NMR δ 0.7−0.95 (m, 3H), 1.0−1.7 (m, 4H), 2.0−2.2 (m, 2H), 5.05 (s, 1H), 5.19 (s, 1H), 5.65 (dt, J = 15.6 and 7.0 Hz, 1H), 6.30 (d, J = 15.6 Hz, 1H), 7.1−7.5 (m, 5H); ^{13}C NMR δ 13.95, 22.29, 31.35, 32.54, 114.48, 126.35, 127.24, 128.01, 128.24, 131.27, 134.59, 140.73, 148.15; IR (neat) 1644, 1596 cm^{-1}; HRMS calcd for $C_{14}H_{18}$ (M^+) 186.1409, found 186.1403.

Reaction of Iodobenzene and 1-Octene under the Catalysis of $Cl_2Pd(PPh_3)_2$ in DMF. To iodobenzene (195 mg, 0.98 mmol), 1-octene (220 mg, 1.96 mmol), K_2CO_3 (690 mg, 5 mmol), and n-Bu_4NCl (280 mg, 1 mmol) in DMF (5 mL) was added $Cl_2Pd(PPh_3)_2$ (35 mg, 5 mol %) under argon. The reaction was run at 80 °C for 23 h. The mixture was diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. The crude product was analyzed by ^{1}H NMR spectra. Further purification via chromatography on silica gel (n-hexane) afforded 33 mg (18%, 30% by NMR) of a 86/14 mixture of 1-phenyl-1(*E*)-octene and 2-phenyl-1-octene. Data for 1-phenyl-1(*E*)-octene: ^{1}H NMR δ 0.8−0.95 (m, 3H), 1.2−1.55 (m, 8H), 2.1−2.3 (m, 2H), 6.22 (dt, J = 15.9 and 6.8 Hz, 1H), 6.40 (d, J = 15.9 Hz, 1H), 7.1−7.5 (m, 5H); ^{13}C NMR δ 14.10, 22.63, 28.91, 29.35, 31.76, 33.05, 125.87, 126.70, 128.43, 129.65, 131.23, 137.94; IR (neat) 1654, 1600 cm^{-1}; HRMS calcd for $C_{14}H_{20}$ (M^+) 188.1565, found 188.1565. The following data were assigned to 2-phenyl-1-octene: ^{1}H NMR δ 0.8−0.95 (m, 3H), 1.2−1.55 (m, 8H), 2.4−2.55 (m, 2H), 5.04 (s, 1H), 5.26 (s, 1H), 7.1−7.5 (m, 5H).

Intramolecular Comparsion of Reactivities of an Allene with an Alkene or an Alkyne. (a) Cyclization of 30. Following the procedure described for **19**, **30** (96 mg, 0.158 mmol) afforded 55 mg (66%) of 3′-[2″,2″-bis(ethoxycarbonyl)-5″-hexenyl]-3-methylene-6,6-bis(ethoxycarbonyl)-1,2-benzo-1,4-cycloheptadiene (**81**): ^{1}H NMR δ 1.05 (t, J = 6.9 Hz, 3H), 1.15−1.35 (m, 9H), 1.5−2.0 (m, 4H), 3.22 (d, J = 10.7 Hz, 1H), 3.29 (d, J = 10.7 Hz, 1H), 3.60 (d, J = 13.5 Hz, 1H), 3.90 (d, J = 13.5 Hz, 1H), 3.96 (q, J = 6.9 Hz, 2H), 4.1−4.35 (m, 6H), 4.92 (d, J = 7.7 Hz, 1H), 4.97 (d, J = 15.4 Hz, 1H), 5.22 (s, 1H), 5.60 (s, 1H), 5.6−5.75 (m, 1H), 5.76 (d, J = 11.5 Hz, 1H), 6.53 (d, J = 11.5 Hz, 1H), 6.9−7.1 (m, 3H); ^{13}C NMR δ 13.95, 14.02, 28.94, 30.89, 33.79, 38.37, 59.11, 59.31, 61.07, 61.24, 61.46, 62.04, 114.71, 121.57, 126.69, 126.85, 128.41, 128.82, 132.57, 132.72, 134.41, 137.88, 141.56, 143.11, 169.03, 170.15, 171.35, 171.50; IR (neat) 1736, 1642, 1596 cm^{-1}; HRMS calcd for $C_{30}H_{39}O_8$ (M^+ + 1) 527.2645, found 527.2645.

(b) Cyclization of 31. Following the procedure described for **19**, **31** (75 mg, 0.121 mmol) afforded 45 mg (69%) of 3′-[2″,2″-bis(ethoxycarbonyl)-5″-heptynyl]-3-methylene-6,6-bis(ethoxycarbonyl)-1,2-benzo-1,4-cycloheptadiene (**82**): ^{1}H NMR δ 1.05 (t, J = 7.5 Hz, 3H), 1.15−1.4 (m, 9H), 1.73 (s, 3H), 1.85−2.2 (m, 4H), 3.20 (d, J = 13.3 Hz, 1H), 3.28 (d, J = 13.3 Hz, 1H), 3.60 (d, J = 13.5 Hz, 1H), 3.85 (d, J = 13.7 Hz, 1H), 3.95 (q, J = 7.5 Hz, 2H), 4.05−4.35 (m, 6H), 5.20 (s, 1H), 5.60 (s, 1H), 5.77 (d, J = 11.7 Hz, 1H), 6.62 (d, J = 11.7 Hz, 1H), 6.9−7.15 (m, 3H); ^{13}C NMR δ 3.43, 13.89, 13.94, 14.56, 31.37, 33.78, 38.28, 58.80, 59.31, 61.08, 61.34, 61.42, 62.00, 75.74, 78.16, 121.31, 126.66, 126.72, 128.49, 128.99, 132.41, 134.41, 141.71, 143.19, 169.04, 170.18, 170.86, 171.10; IR (neat) 1732, 1584, 1590 cm^{-1}; HRMS calcd for $C_{31}H_{39}O_8$ (M^+ + 1) 539.2645, found 539.2629.

(c) Cyclization of 32. Following the procedure described for **19**, **32** (75 mg, 0.126 mmol) afforded 30 mg (47%) of a 2/1 mixture of 3′-[2″,2″-bis(ethoxycarbonyl)-4″-pentenyl]-3-methylene-6,6-bis(ethoxycarbonyl)-1,2-benzo-1,4-cycloheptadiene (**83**) and **84** (tentatively assigned). Data for **83**: ^{1}H NMR δ 1.0−1.4 (m, 12H), 2.15−2.6 (m, 2H), 3.1−3.35 (m, 2H), 3.62 (d, J = 14.0 Hz, 1H), 3.90 (d, J = 14.0 Hz, 1H), 3.95 (q, J = 6.4 Hz, 2H), 4.05−4.35 (m, 6H), 4.8−5.05 (m, 2H), 5.15 (s, 1H), 5.52 (s, 1H), 5.55−5.8 (m, 1H), 5.78 (d, J = 11.8 Hz, 1H), 6.54 (d, J = 11.8 Hz, 1H), 6.95−7.2 (m, 3H); IR (neat) 1734 cm^{-1}; HRMS calcd for $C_{29}H_{32}O_8$ (M^+) 512.2410, found 512.2411. The following data were assigned to **84**: ^{1}H NMR δ 1.0−1.4 (m, 12H), 2.15−2.6(m, 2H), 2.9−4.0 (m, 4H), 3.8−4.4 (m, 8H), 5.05 (s, 1H), 5.22 (s, 1H), 4.8−5.85 (m, 4H), 6.95−7.2 (m, 3H).

Pd-Catalyzed Cyclization of ω-Haloallenes in the Presence of Nucleophiles. (a) Cyclization of 9-Iodo-8-*n*-propyl-1,2,8(*Z*)-dodecatriene (16) in the Presence of Diethyl Malonate. Representative Procedure (Conditions I). To 9-iodo-8-n-propyl-1,2,8(*Z*)-dodecatriene (**16**) (120 mg, 0.252 mmol), K_2CO_3 (170 mg, 1.23 mmol), EtOH (150 μL, 2.5 mmol), and diethyl malonate (120 mg, 0.75 mmol) in DMF (5 mL) was added $Cl_2Pd(PPh_3)_2$ (10 mg, 5 mol %) under argon. The reaction was complete in 23 h at 120 °C as monitored by TLC, and then the mixture was diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. Further purification by chromatography on silica gel (n-hexane/ethyl acetate = 20/1) afforded 65 mg (51%) of 6,6-bis(ethoxycarbonyl)-3-[2′,2′-bis(ethoxycarbonyl)ethyl]-1,2-di-n-propyl-1,3-cyclooctadiene: ^{1}H NMR δ 0.8−1.0 (m, 6H), 1.1−1.6 (m, 16H), 1.8−2.1 (m, 4H), 2.15−2.45 (m, 4H), 2.55−2.9 (m, 3H), 3.27 (dd, J = 3.9 and 9.8 Hz, 1H), 4.05−4.35 (m, 8H), 5.44 (t, J = 7.8 Hz, 1H); ^{13}C NMR δ 13.90, 13.93, 14.11, 14.31, 14.40, 21.55, 21.89, 28.32, 30.23, 30.82, 31.92, 34.09, 34.40, 50.56, 53.47, 60.91, 61.25, 61.30, 61.45, 124.09, 131.65, 139.07, 141.13, 168.86, 169.31, 170.20, 173.32; IR (neat) 1732, 1640 cm^{-1}; HRMS calcd for $C_{28}H_{44}O_8$ (M^+) 508.3036, found 508.3046.

(b) Cyclization of 9-Iodo-8-*n*-propyl-1,2,8(*Z*)-dodecatriene (16) in the Presence of $PhSn(n\text{-}Bu)_3$. Representative Procedure (Conditions II). To 9-iodo-8-n-propyl-1,2,8(*Z*)-dodecatriene (**16**) (65 mg, 0.137 mmol), K_2CO_3 (85 mg, 0.62 mmol), n-Bu_4NCl (35 mg, 0.126 mmol), and $PhSn(n\text{-}Bu)_3$ (100 μL, 97%, 109 mg, 0.297 mmol) in DMF (10 mL) was added $Cl_2Pd(PPh_3)_2$ (10 mg, 5 mol %) under argon. The reaction was complete in 11 h at 120 °C as monitored by TLC, and then the mixture was diluted with ether, washed with water, dried over $MgSO_4$, and evaporated. Further purification by chromatography on silica gel (n-hexane/ethyl acetate = 20/1) afforded 37 mg (64%) of 3-benzyl-6,6-bis(ethoxycarbonyl)-1,2-di-n-propyl-1,3-cyclooctadiene: ^{1}H NMR δ 0.78 (t, J = 7.3 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H), 1.1−1.5 (m, 11H), 1.7−2.4 (m, 9H), 2.6−2.8 (m, 1H), 3.36 (s, 2H), 4.05−4.2 (m, 4H), 5.28 (dd, J_1 = 7.4 and 8.7 Hz, 1H), 7.0−7.3 (m, 5H); ^{13}C NMR δ 14.00, 14.10, 14.51, 21.50, 21.58, 28.13, 30.27, 31.00, 31.96, 33.64, 41.78, 53.81, 60.75, 61.19, 122.29, 125.75, 127.92, 129.00, 132.90, 137.16, 139.45, 144.73, 170.55, 173.48; IR (neat) 1732, 1650, 1602 cm^{-1}; HRMS $C_{27}H_{38}O_4$ (M^+) 426.2770, found 426.2779.

(c) Cyclization of 9-Iodo-8-*n*-propyl-1,2,8(*Z*)-dodecatriene (16) in the Presence of Phenol (Conditions II). Cyclization of **16** (60 mg, 0.126 mmol) in the presence of phenol (55 mg, 0.585 mmol) afforded 30 mg (54%) of 6,6-bis(ethoxycarbonyl)-1,2-di-*n*-propyl-3-phenoxymethyl-1,3-cyclooctadiene: ^{1}H NMR δ 0.8−1.0 (m, 6H), 1.1−1.50 (m, 10H), 1.75−2.45 (m, 9H), 2.65−2.85 (m, 1H), 4.05−4.25 (m, 4H), 4.45 (d, J = 11.5 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 5.68 (t, J = 7.9 Hz, 1H), 6.75−7.00 (m, 3H), 7.15−7.35 (m, 2H); ^{13}C NMR δ 14.02, 14.11, 14.20, 14.44, 21.66, 21.81, 28.16, 30.23, 31.05, 31.85, 33.93, 53.57, 60.87, 61.34, 69.73, 114.89, 120.57, 123.78, 129.24, 131.38, 138.94, 141.10, 158.64, 170.35, 173.31; IR (neat) 1734, 1600, 1595 cm^{-1}; HRMS calcd for $C_{27}H_{39}O_5$ (M^++1) 443.2798, found 443.2780.

(d) Cyclization of 9-Iodo-8-*n*-propyl-1,2,8(*Z*)-dodecatriene (16) in the Presence of Piperidine (Conditions II). Cyclization of **16** (65 mg, 0.137 mmol) in the presence of pyrrolidine (25 μL, 21 mg, 0.30 mmol) afforded 33 mg (56%) of 6,6-bis(ethoxycarbonyl)-1,2-di-*n*-propyl-3-piperidinylmethyl-1,3-cyclooctadiene: ^{1}H NMR δ 0.86 (t, J = 7.3 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H), 1.1−1.6 (m, 16H), 1.75−2.45 (m, 13H), 2.65−2.8 (m, 1H), 3.83 (d, J = 14.7 Hz, 1H), 3.00 (d, J = 14.7 Hz, 1H), 4.1−4.3 (m, 4H), 5.50 (dd, J = 7.1 and 9.3 Hz, 1H); ^{13}C NMR δ 14.05, 14.20, 14.52, 21.66, 21.71, 24.47, 26.14, 28.36, 30.33, 31.14, 32.03, 33.87, 53.60, 54.64, 60.79, 61.21, 63.30, 122.07, 133.94, 136.43, 142.67, 170.81, 173.53; IR (neat) 1732, 1650 cm^{-1}; HRMS $C_{26}H_{43}NO_4$ (M^+) 433.3192, found 433.3188.

(e) Cyclization of 5 in the Presence of Diethyl Malonate (Conditions I). **5** (50 mg, 0.239 mmol) afforded 42 mg (61%) of 3-[2′,2′-bis(ethoxycarbonyl)ethyl]-1*H*-indene (**85**): ^{1}H NMR δ 1.25 (t, J = 7.2 Hz, 6H), 3.18 (d, J = 7.6 Hz, 2H), 3.32 (d, J = 1.6 Hz, 2H), 3.81 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.2 Hz, 4H), 6.27 (t, J = 1.6 Hz, 1H), 7.15−7.5 (m, 4H); ^{13}C NMR δ 14.02, 26.81, 37.88, 50.90, 61.56, 118.78, 123.76, 124.82, 126.11, 129.40, 129.40, 140.56, 144.02, 144.08, 169.09; IR (neat) 1734, 1600 cm^{-1}; HRMS calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1374.

(f) Cyclization of 7 in the Presence of Diethyl Malonate (Conditions I). **7** (54 mg, 0.242 mmol) afforded 50 mg (55%) of a mixture of 3-[2′,2′-bis(ethoxycarbonyl)ethyl]-1,2-benzo-1,3-cyclohexadiene (**86**) and 3-methylene-4-[bis(ethoxycarbonyl)methyl]-1,2-benzo-1-cyclohexene (**87**). Data for **86**: ^{1}H NMR δ 1.25 (t, J = 7.5 Hz, 6H), 2.15−2.3 (m, 2H), 2.70 (t, J = 8.0 Hz, 2H), 3.10 (d, J = 8.1 Hz, 2H), 3.64 (t, J = 8.1 Hz, 1H), 4.18 (q, J = 7.5 Hz, 4H), 5.94 (t, J = 4.0 Hz, 1H), 7.1−7.3 (m, 4H); ^{13}C NMR δ 14.05, 22.99, 28.14, 31.74, 51.04, 61.33, 122.16, 126.46, 126.90, 127.40, 127.71, 132.68, 133.67, 136.73, 169.16; IR (neat) 1748, 1630 cm^{-1}; HRMS calcd for $C_{18}H_{22}O_4$ (M^+) 302.1518, found 302.1515. The following ^{1}H NMR data were assigned to **87**: 1.15−1.35 (m, 6H), 1.95−2.1 (m, 2H), 2.8−2.95 (m, 2H), 3.3−3.45 (m, 1H), 3.54 (d, J = 10.4 Hz, 1H), 4.05−4.3 (m, 4H), 5.08 (s, 1H), 5.45 (s, 1H), 7.1−7.55 (m, 4H).

(g) Cyclization of 9 in the Presence of Diethyl Malonate (Conditions I). **9** (95 mg, 0.222 mmol) afforded 89 mg (87%) of 6,6-bis(ethoxycarbonyl)-3-[2′,2′-bis(ethoxycarbonyl)ethyl]-1,2-benzo-1,3-cycloheptadiene (**88**): ^{1}H NMR δ 1.05−1.25 (m, 12H), 2.22 (d, J = 7.3 Hz, 2H), 2.97 (s, 2H), 3.02 (d, J = 7.8 Hz, 2H), 3.28 (t, J = 7.1 Hz, 1H), 4.2−3.95 (m, 8H), 5.96 (t, J = 7.3 Hz, 1H), 7.05−7.3 (m, 4H); ^{13}C NMR δ 13.87, 13.98, 30.70, 35.14, 37.31, 51.34, 61.29, 67.59, 125.78, 126.04, 126.92, 127.22, 130.79, 137.37, 138.58, 139.03, 168.84, 170.97; IR (neat) 1734, 1600 cm^{-1}; HRMS calcd for $C_{25}H_{32}O_8$ (M^+) 460.2097, found 460.2092.

(h) Cyclization of 11 in the Presence of Diethyl Malonate (Conditions I). **11** (100 mg, 0.23 mmol) afforded 57 mg (53%) of 6,6-bis(ethoxycarbonyl)-3-[2′,2′-bis(ethoxycarbonyl)ethyl]-2-*n*-butyl-1,3-cycloheptadiene (**89**): ^{1}H NMR δ 0.87 (t, J = 7.5 Hz, 3H), 1.35−1.4 (m, 16H), 2.05−2.2 (m, 2H), 2.32 (d, J = 5.8 Hz, 2H), 2.35 (d, J = 7.8 Hz, 2H), 2.74 (d, J = 6.2 Hz, 2H), 3.35 (t, J = 7.8 Hz, 1H), 4.1−4.3 (m, 8H), 5.98 (t, J = 6.2 Hz, 1H), 6.02 (t, J = 5.8 Hz, 1H); ^{13}C NMR δ 13.90, 13.98, 14.02, 22.49, 30.67, 31.34, 31.68, 33.28, 33.85, 51.52, 61.15, 61.41, 71.38, 126.90, 128.41, 140.13, 142.93, 168.97, 171.48; IR (neat) 1734, 1645 cm^{-1}; HRMS calcd for $C_{25}H_{38}O_8$ (M^+) 466.2567, found 466.2572.

(i) Cyclization of 11 in the Presence of Diethyl Methylmalonate (Conditions II). **11** (51 mg, 0.118 mmol) afforded 28 mg (50%) of 2-*n*-Butyl-6,6-bis(ethoxycarbonyl)-3-[2′,2′-bis(ethoxycarbonyl)propyl]-1,3-cycloheptadiene (**90**): ^{1}H NMR δ 0.87 (t, J = 6.4 Hz, 3H), 1.15−1.3 (m, 16H), 1.36 (s, 3H), 2.05−2.2 (m, 2H), 2.34 (d, J = 6.8 Hz, 4H), 2.74 (s, 2H), 4.0−4.25 (m, 8H), 5.95 (t, J = 6.8 Hz, 1H), 6.00 (t, J = 6.8 Hz, 1H); ^{13}C NMR δ 13.94, 14.04, 19.59, 22.58, 30.56, 31.31, 32.00, 34.40, 38.49, 54.16, 61.13, 71.69, 125.82, 131.65, 138.53, 144.55, 171.61, 171.99; IR (neat) 1732, 1640 cm^{-1}; HRMS calcd for $C_{26}H_{41}O_8$ (M^+ + 1) 481.2801, found 481.2777.

(j) Cyclization of 13a in the Presence of Diethyl Malonate (Conditions I). **13a** (75 mg, 0.25 mmol) afforded 61 mg (73%) of 5-[2′,2′-bis(ethoxycarbonyl)-1′-methylethyl]-1,3-dihydro-2-benzoxepin (**91**): ^{1}H NMR δ 1.14 (d, J = 7.0 Hz, 3H), 1.22 (d, J = 6.3 Hz, 3H), 1.28 (t, J = 7.0 Hz, 3H), 3.5−3.85 (m, 4H), 4.08 (q, J = 7.0 Hz, 2H), 4.15−4.3 (m, 2H), 4.30 (d, J = 10.5 Hz, 1H), 4.38 (d, J = 10.5 Hz, 1H), 6.05 (t, J = 6.7 Hz, 1H), 7.3−7.65 (m, 4H); ^{13}C NMR δ 13.93, 14.09, 18.94, 38.34, 57.26, 61.39, 61.50, 61.68, 67.72, 122.37, 126.03, 128.15, 128.44, 129.57, 137.51, 140.64, 149.63, 168.20, 168.28; IR (neat) 1732 cm^{-1}; HRMS calcd for $C_{19}H_{24}O_5$ (M^+) 332.1624, found 332.1621.

(k) Cyclization of 15 in the Presence of Diethyl Malonate (Conditions I). **15** (105 mg, 0.266 mmol) afforded 95 mg (84%) of 6,6-bis(ethoxycarbonyl)-3-[2′,2′-bis(ethoxycarbonyl)ethyl]-1,2-benzo-1,3-cyclooctadiene (**92**): ^{1}H NMR δ 1.1−1.6 (m, 13H), 1.90 (dd, J = 8.6 and 13.2 Hz, 1H), 2.6−2.85 (m, 4H), 2.95−3.1 (m, 2H), 3.25 (dd, J = 5.1 and 8.6 Hz, 1H), 4.0−4.4 (m, 8H), 5.68 (dd, J = 7.1 and 9.7 Hz, 1H), 7.15−7.3 (m, 4H); ^{13}C NMR δ 13.84, 13.90, 14.09, 29.48, 31.43, 34.96, 37.16, 50.42, 53.76, 61.04, 61.30, 61.38, 124.80, 126.03, 126.55, 127.97, 129.71, 137.10, 139.79, 142.10, 168.73, 168.85, 170.09, 172.69; IR (neat) 1734 cm^{-1}; HRMS calcd for $C_{26}H_{34}O8$ (M^+) 474.2254, found 474.2248.

(l) Cyclization of 21 under Conditions I in the Absence of Diethyl Malonate. **21** (110 mg, 0.248 mmol) afforded 16 mg (20%, 34% by NMR) of 7,7-bis(ethoxycarbonyl)-8-hydro-2*H*,6*H*-furano[*jk*]benzocycloheptene (**94**): ^{1}H NMR δ 1.12 (t, J = 7.7 Hz, 6H), 2.9−3.0 (m, 2H), 3.43 (s, 2H), 4.05−4.2 (m, 4H), 5.06 (d, J = 2.3 Hz, 1H), 5.08 (d, J = 2.3 Hz, 1H), 5.55−5.65 (m, 1H), 6.65 (d, J = 7.8 Hz, 1H), 6.72 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H); ^{13}C NMR δ 13.96, 36.00, 40.40, 54.90, 61.80, 75.00, 108.00, 112.40, 113.90, 121.80, 130.00, 135.00, 136.00, 163.90, 170.80; IR (neat) 1734, 1600 cm^{-1}; HRMS calcd for $C_{18}H_{20}O_5$ (M^+) 316.1311, found 316.1305.

(m) Cyclization of 29 under Conditions II in the Absence of Diethyl Malonate. **21** (70 mg, 0.126 mmol) afforded 25 mg (40%) of 3,9-dihydro-2,2,8,8-tetrakis(ethoxycarbonyl)-1*H*,7*H*-cyclohexa[*jk*]-benzocycloheptene (**95**): ^{1}H NMR δ 1.15−1.35 (m, 12H), 2.38 (d, J = 6.7 Hz, 2H), 3.00 (s, 2H), 3.08 (s, 2H), 3.28 (s, 2H), 4.05−4.3 (m, 8H), 5.96 (t, J = 6.7 Hz, 1H), 7.05−7.3 (m, 3H); ^{13}C NMR δ 14.06, 31.55, 34.91, 37.64, 37.92, 55.29, 61.42, 61.50, 68.19, 125.14, 126.70, 127.18, 128.93, 134.02, 135.58, 135.94, 136.15, 170.81, 171.23; IR (neat) 1734, 1600 cm^{-1}; HRMS calcd for $C_{26}H_{33}O_8$ (M^+ + 1) 473.2175, found 473.2151.

Diels−Alder Reaction of 53 with Dimethyl Acetylenedicarboxylate and Oxidation of the Diels−Alder Product. A mixture of **53** (35 mg, 0.2 mmol) and dimethyl acetylenedicarboxylate (45 μL, 52 mg, 0.366 mmol) was heated at 90 °C with stirring for 5 h. After cooling to room temperature, benzene (anhydrous, 3 mL) and DDQ (92 mg × 98% = 90 mg, 0.397 mmol) were added, and the mixture was stirred at 23 °C. After 46 h, another portion of DDQ (92 mg × 98% = 90 mg, 0.397 mmol) was added, and the reaction mixture was stirred at 23 °C for another 18 h. After evaporation, the crude product was purified by chromatography on silica gel (*n*-hexane/ethyl acetate = 10/1) to afford 37 mg (58%) of 3,4-bis(methoxycarbonyl)-5,7-dihydrodibenz[*c*,*e*]oxepin (**96**): ^{1}H NMR δ 3.95 (s, 3H), 4.05 (s, 3H), 4.32 (s, 2H), 4.40 (s, 2H), 7.40−7.60 (m, 4H), 7.67 (d, J = 7.2 Hz, 1H), 8.15 (d, J = 7.2 Hz, 1H); ^{13}C NMR 52.65, 52.98, 63.26, 67.53, 127.17, 127.70, 128.44, 129.18, 129.55, 129.84, 130.41, 132.10, 134.92, 136.18, 139.49, 146.50, 165.71, 169.00; IR (neat) 1728, 1594 cm^{-1}; HRMS calcd for $C_{18}H_{16}O_5$ 312.0998, found 312.1001.

Acknowledgment. We thank the National Institutes of Health (Grant GM 36792) and Purdue Cancer Center for support of this work and Johnson Matthey for a loan of $PdCl_2$.

JA950441W