JOC Article

Efficient Synthesis of 4-(2′-Alkenyl)-2,5-dihydrofurans and 5,6-Dihydro-2*H*-pyrans via the Pd-Catalyzed Cyclizative Coupling Reaction of 2,3- or 3,4-Allenols with Allylic Halides

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In the absence of a base, palladium(II) catalysts, such as $PdCl_2$, $PdCl_2(CH_3CN)_2$, $Pd(OAc)_2$, and $[(\pi\text{-}C_3H_5)PdCl]_2$, can catalyze the cyclizative coupling reaction of 2,3- or 3,4-allenols with allylic halides in DMA at room temperature to provide 2,5-dihydrofurans and 5,6-dihydro-2*H*-pyrans, respectively, in moderate to good yields. Under similar reaction conditions, nonsubstituted 2,3-allenol **1s** affords bimolecular cyclizative coupling product **5s** as the major product. The scope of the reaction and its mechanism have been studied briefly. On the basis of the experimental results, the transformation was believed to proceed via a divalent palladium-catalyzed pathway.

Introduction

2,5-Dihydrofurans and 5,6-dihydro-2*H*-pyrans, important classes of heterocyclic compounds, are useful intermediates for organic synthesis[1] and common structural units in many natural products.[2] These compounds are usually prepared via a RCM reaction,[3] Ag(I)-catalyzed rearrangement−cyclization of 4-hydroxypropargyl esters,[4] dehydration of *cis*-2-alkene-1,4-diols,[5] palladium-catalyzed reaction of cyclic alkynyl carbonates with electron-deficient alkenes,[6] Prins reaction of terminal alkene and formaldehyde,[7] reaction of oxazirconacyclopentenes with propynoates,[8] cyclization of allenols upon the addition of electrophiles,[9] and Ag(I)- or Hg(II)-catalyzed cyclization reaction of allenols.[10]

Transition metal-catalyzed cyclization of functionalized allenes bearing a nucleophilic center has attracted much attention in recent years.[11] Particularly, cyclization reaction of allenols catalyzed by Ag(I),[10] Hg(II)[10] Pd(0),[12] Ru(III),[13] or Au(III)[14] has become quite useful methodologies for the synthesis of three-, five-, or six-membered oxygen-containing heterocycles. However, Pd-catalyzed coupling−cyclization reaction of allenols with allylic halides is still unknown.

During the course of our study on the chemistry of functionalized allenes,[15−17] we have studied the Pd(0)-catalyzed coupling−cyclization reaction of 2,3-allenols

(1) (a) Marshall, J. A.; Pinney, K. G. *J. Org. Chem.* **1993**, *58*, 7180. (b) Marshall, J. A.; Yu, B. *J. Org. Chem.* **1994**, *59*, 324. (c) Yamada, O.; Ogasawara, K. *Synlett* **1995**, 427. (d) Kim, S.; Kim, K. H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1095. (e) Paolucci, C.; Musiani, L.; Venturelli, F.; Fava, A. *Synthesis* **1997**, 1415. (f) Shieh, S. J.; Fan, J. S.; Chandrasekharam, M.; Liao, F. L.; Wang, S. L.; Liu, R. S. *Organometallics* **1997**, *16*, 3987. (g) Doyle, M. P.; Forbes, D. C.; Protopopova, M. N.; Stanley, S. A.; Vasbinder, M. M.; Xavier, K. R. *J. Org. Chem.* **1997**, *62*, 7210. (h) Crotti, P.; Bussolo, L. D.; Favero, L.; Pineschi, M. *Tetrahedron* **1997**, *53*, 1417. (i) Bauer, T. *Tetrahedron* **1997**, *53*, 4763.

(2) (a) Kupchan, S. M.; Davies, V. H.; Fujita, T.; Cox, M. R.; Restivo, R. J.; Bryan, R. F. *J. Org. Chem.* **1973**, *38*, 1853. (b) Semple, J. E.; Wang, P. C.; Lysenko, Z.; Joullie, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7505.

(3) Carda, M.; Castillo, E.; Rodriguez, S.; Uriel, S.; Marco, J. A. *Synlett* **1999**, 1639.

(4) (a) Shigemasa, Y.; Yasui, M.; Ohrai, S.; Sasaki, M.; Sashiwa, H.; Saimoto, H. *J. Org. Chem.* **1991**, *56*, 910. (b) Saimoto, H.; Yasui, M.; Ohrai, S.; Oikawa, H.; Yokoyama, K.; Shigemasa, Y. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 279.

(5) Sato, F.; Kanbara, H.; Tanaka, Y. *Tetrahedron Lett.* **1984**, *25*, 5063.

(6) Darcel, C.; Bruneau, C.; Albert, M.; Dixneuf, P. H. *Chem. Commun.* **1996**, 919.

(7) Talipov, R. F.; Starikov, A. S.; Gorina, I. A.; Akmanova, N. A.; Safarov, M. G. *Zh. Org. Khim.* **1993**, *29*, 1024.

(8) Xi, C.; Kotora, M.; Takahashi, T. *Tetrahedron Lett.* **1999**, *40*, 2375.

(9) (a) Beaulieu, P. L.; Morisset, V. M.; Garratt, D. G. *Tetrahedron Lett.* **1980**, *21*, 129. (b) Smadja, W. *Chem. Rev.* **1983**, *83*, 263. (c) Bridges, A. J.; Thomas, R. D. *J. Chem. Soc. Chem. Commun.* **1984**, 694. (d) Whitby, R.; Kocienski, P. *Tetrahedron Lett.* **1987**, *28*, 3619. (e) Marshall, J. A.; Wang, X. *J. Org. Chem.* **1990**, *55*, 2995. (f) Marshall, J. A.; Wang, X. *J. Org. Chem.* **1991**, *56*, 4913.

(10) (a) Olsson, L. I.; Claesson, A. *Synthesis* **1979**, 743. (b) Nikam, S. S.; Chu, K. H.; Wang, K. K. *J. Org. Chem.* **1986**, *51*, 745. (c) Gelin, R.; Gelin, S.; Albrand, M. *Bull. Soc. Chim. Fr.* **1972**, 1946. (d) Chilot, J.-J.; Doutheau, A.; Gore, J. *Tetrahedron Lett.* **1982**, *23*, 4693. (e) Chilot, J.-J.; Doutheau, A.; Gore, J. *Bull. Soc. Chim. Fr.* **1984**, II-307. (f) Marshall, J. A.; Sehon, C. A. *J. Org. Chem.* **1995**, *60*, 5966. (g) Marshall, J. A.; Yu, R. H.; Perkins, J. F. *J. Org. Chem.* **1995**, *60*, 5550.

(11) For a review on the palladium-catalyzed chemistry of allene, see: Zimmer, R.; Dinesh, C. U.; Nadanan, E.; Hhan, F. A. *Chem. Rev.* **2000**, *100*, 3067.

(12) For the Pd(0)-catalyzed coupling−cyclization reaction of allenols with aryl or vinyl halides, see: (a) Uemura, K.; Shiraishi, D.; Noziri, M.; Inoue, Y. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1063. (b) Kang, S.-K.; Baik, T.-G.; Kulak, A. N. *Synlett* **1999**, 324. (c) Kang, S.-K.; Yamaguchi, T.; Pyun, S.-J.; Lee, Y.-T.; Baik, T.-G. *Tetrahedron Lett.* **1998**, *39*, 2127. (d) Walkup, R. D.; Guan, L.; Kim, Y. S.; Kim, S. W. *Tetrahedron Lett.* **1995**, *36*, 3805. (e) Walkup, R. D.; Guan, L.; Mosher, M. D.; Kim, Y. S.; Kim, S. W. *Synlett* **1993**, 88.

(13) For the Ru-catalyzed reaction, see: (a) Yoneda, E.; Kaneko, T.; Zhang, S.-W.; Onitsuka, K.; Takahashi, S. *Org. Lett.* **2000**, *2*, 441. (b) Trost, B. M.; Pinkerton, A. B. *J. Am. Chem. Soc.* **1999**, *121*, 10842.

(14) For the Au-catalyzed reaction, see: Hoffmann-Roder, A.; Krause, N. *Org. Lett.* **2001**, *3*, 2537.

(15) For the corresponding reaction of 1,2-allenyl ketones with organic halides to afford furans, see: (a) Ma, S.; Zhang, J. *Chem. Commun.* **2000**, 117. (b) Ma, S.; Li, L. *Org. Lett.* **2000**, *2*, 941.

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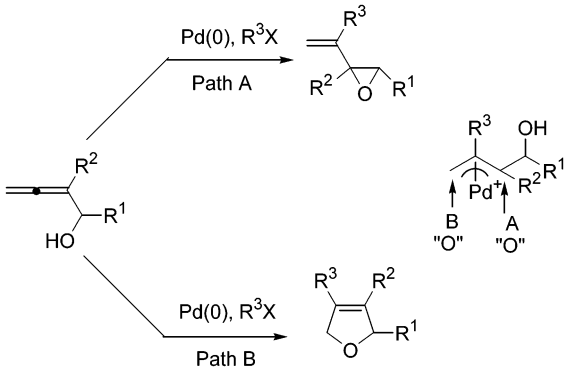
SCHEME 1

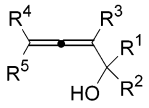


with aryl or vinyl halides.[18] In the absence of an amine,[18a] three-membered vinylic oxiranes were formed (Path A, Scheme 1) while the formation of the corresponding five-membered 2,5-dihydrofurans (Path B, Scheme 1) was not observed. Even when R^2 was introduced to increase the steric hindrance at the 2-position of 2,3-allenols, the formation of five-membered 2,5-dihydrofurans were still not observed. Due to the substituent-loading capability (up to 3) of 2,3-allenols, we are interested in the chemistry of polysubstituted 2,5-dihydrofuran-formation reaction from 2,3-allenols and organic halides. In a preliminary communication,[19] we described an efficient synthesis of 2,5-dihydrofuran via the Pd(II)-catalyzed cyclizative coupling reaction of 2,3-allenols with allylic halides. In this paper, we wish to present a full account of our observation of the reaction—the scope as well as the mechanism.

Results and Discussions

Synthesis of Starting Materials. A number of methods have been reported for the synthesis of allenols,[20] and all the requisite 2,3-allenols studied in this paper were prepared through the application of known or slightly modified procedure (Scheme 2). 2,3-Allenols **1a**−**c** were synthesized via the reduction of allenic ketones with $LiAlH_4$.[21] Allenols **1d**−**k** were prepared via the Sn(II)- or Cr(II)-mediated coupling reaction of propargylic bromides with aldehydes and ketones.[22] Primary alcohols **1l**−**n** were prepared from the DIBAL-H reduction of the corresponding allenoates.[23] 4-Substituted allenols **1o** and **1p** were obtained by the ready reductive elimination of the tetrahydropyranyloxy group from the mono-*O*-tetrahydropyran-2-yl derivatives of butyne-1,4-diols with $LiAlH_4$.[24] 2,3-Allenol **1q** was prepared via the reaction of 1,2-allenyllithium with pentanal.[25] Allenols with no-substituent on the allene moiety **1r** and **1s** were synthesized via the Cu(I)-mediated homologation of terminal propargylic alcohols.[26]

SCHEME 2



1a-s

1a $R^1 = CH_3$, $R^2 = R^4 = R^5 = H$, $R^3 = C_4H_9$-*n*
1b $R^1 = CH_3$, $R^2 = R^4 = R^5 = H$, $R^3 = CH_3$
1c $R^1 = CH_3$, $R^2 = R^4 = R^5 = H$, $R^3 = CH_2Ph$
1d $R^1 = C_4H_9$-*n*, $R^2 = R^4 = R^5 = H$, $R^3 = C_4H_9$-*n*
1e $R^1 = Ph$, $R^2 = R^4 = R^5 = H$, $R^3 = C_4H_9$-*n*
1f $R^1 = C_4H_9$-*n*, $R^2 = R^4 = R^5 = H$, $R^3 = C_3H_5$
1g $R^1 = C_4H_9$-*n*, $R^2 = R^4 = R^5 = H$, $R^3 = CO_2CH_3$
1h $R^1 = C_4H_9$-*n*, $R^2 = R^4 = R^5 = H$, $R^3 = Ph$
1i $R^1 = Ph$, $R^2 = R^4 = R^5 = H$, $R^3 = Ph$
1j $R^1 = R^2 = CH_3$, $R^3 = Ph$, $R^4 = R^5 = H$
1k $R^1 = R^2 = CH_3$, $R^3 = C_4H_9$-*n*, $R^4 = R^5 = H$
1l $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = CH_2Ph$
1m $R^1 = R^2 = R^5 = H$, $R^3 = CH_3$, $R^4 = C_6H_{13}$-*n*
1n $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = C_6H_{13}$-*n*
1o $R^1 = R^2 = CH_3$, $R^3 = R^5 = H$, $R^4 = C_4H_9$-*n*
1p R^1, $R^2 = (CH_2)_5$, $R^3 = R^5 = H$, $R^4 = C_4H_9$-*n*
1q $R^1 = C_4H_9$-*n*, $R^2 = R^3 = H$, R^4, $R^5 = (CH_2)_5$
1r $R^1 = C_4H_9$-*n*, $R^2 = R^3 = R^4 = R^5 = H$
1s R^1, $R^2 = (CH_2)_5$, $R^3 = R^4 = R^5 = H$

The synthesis of 3,4-allenols **2** is outlined in Scheme 3. The synthesis started with an ortho-Claisen rearrangement by heating the corresponding propargylic alcohols with an excess amount of triethyl orthoacetate or orthopropionate in the presence of a catalytic amount of propionic acid. The resulting 3,4-allenoates were then reduced with $LiAlH_4$ to afford 3,4-allenols **2a**−**h** in moderate to good yields.[27]

The Cyclizative Coupling Reaction of 2,3-Allenols with Allylic Halides. With different allenols in hand, the stage was set to study the Pd-catalyzed cyclizative coupling reaction. Our initial work began with the reaction of 2,3-allenol **1a** with allyl bromide **3a** in CH_3CN at room temperature using 5 mol % Pd(II) and 5 mol % Ag_2CO_3 as the cocatalyst and K_2CO_3 (1.2 equiv) as a base (entries 1−3, Table 1).[15b] To our disappointment, no cyclic product was formed. Surprisingly, the expected five-membered product, 2-methyl-3-butyl-4-allyl-2,5-dihydrofuran (**4a**), was afforded in 16% yield together with

(16) For the corresponding Pd(0)-catalyzed coupling−cyclization of 1,2-allenyl carboxylic acids with organic halides to afford *β*-substituted butenolides, see: (a) Ma, S.; Shi, Z. *J. Org. Chem.* **1998**, *63*, 6387. (b) Ma, S.; Duan, D.; Shi, Z. *Org. Lett.* **2000**, *2*, 1491.

(17) For the hydrohalogenation reaction of electron-deficient allenes, see: a) Ma, S.; Shi, Z.; Li, L. *J. Org. Chem.* **1998**, *63*, 4522. (b) Ma, S.; Li, L.; Xie, H. *J. Org. Chem.* **1999**, *64*, 5325. (c) Ma, S.; Wang, G. *Chin. J. Chem.* **1999**, *17*, 545. (d) Ma, S.; Wei, Q. *J. Org. Chem.* **1999**, *64*, 1026. (e) Ma, S.; Wei, Q. *Eur. J. Org. Chem.* **2000**, 1939.

(18) (a) Ma, S.; Zhao, S. *J. Am. Chem. Soc.* **1999**, *121*, 7943. (b) Ma, S.; Zhao, S. *J. Am. Chem. Soc.* **2001**, *123*, 5578.

(19) Ma, S.; Gao, W. *Tetrahedron Lett.* **2000**, *41*, 8933.

(20) Schuster, H. F.; Coppla, G. M. *Allenes in Organic Synthesis*; Wiley: New York, 1984.

(21) Buono, G. *Synthesis* **1981**, 872.

(22) (a) Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981**, 621. (b) Place, P.; Verniere, C.; Gore, J. *Tetrahedron* **1981**, *37*, 1359.

(23) (a) Marshall, J. A.; Woif, M. A.; Wallace, E. M. *J. Org. Chem.* **1997**, *62*, 367. (b) Ma, S.; Jiao, N.; Zhao, S.; Hou, H. *J. Org. Chem.* **2002**, *67*, 2837.

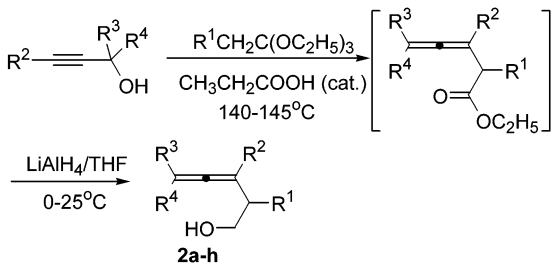
(24) Cowie, J. S.; Landor, P. D.; Landor, S. R. *J. Chem. Soc., Perkin Trans 1* **1973**, 720.

(25) (a) Clinet, J.-C.; Linstrumelle, G. *Synthesis* **1981**, 875. (b) Brandsma, L.; Verkuijsse, H. D. *Synthesis of Acetylenes, Allenes and Cumulenes*; Amsterdam, Elsevier: 1981.

(26) Crabbe, P.; Nassim, B.; Robert-Lopes, M. *Org. Synth.* **1985**, *63*, 203.

(27) (a) Lai, G.; Anderson, W. K. *Synth. Commun.* **1995**, 4087. (b) Kimura, M.; Tanaka, S.; Tamaru, Y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1689.

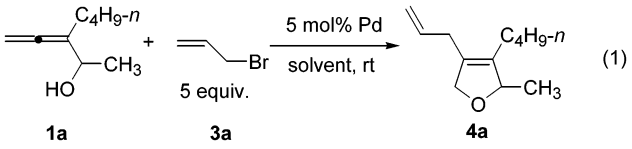
SCHEME 3[a]



2a $R^1 = CH_3$, $R^2 = C_4H_9$-*n*, $R^3 = R^4 = H$ (92%)
2b $R^1 = R^3 = R^4 = H$, $R^2 = C_4H_9$-*n* (75%)
2c[a] $R^1 = CH_3$, $R^2 = Ph$, $R^3 = R^4 = H$ (78%)
2d $R^1 = CH_3$, $R^2 = C_4H_9$-*t*, $R^3 = R^4 = H$ (70%)
2e $R^1 = C_3H_7$-*i*, $R^2 = C_4H_9$-*n*, $R^3 = R^4 = H$ (34%)
2f $R^1 = R^3 = R^4 = CH_3$, $R^2 = H$ (53%)
2g $R^1 = R^2 = R^4 = H$, $R^3 = C_4H_9$-*n* (74%)
2h $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$ (54%)

[a] DIBAL-H was used instead of $LiAlH_4$.

TABLE 1. Pd-Catalyzed Cyclizative Coupling Reaction of 3-(*n*-Butyl)-3,4-pentadien-2-ol (1a) with Allyl Bromide[a]

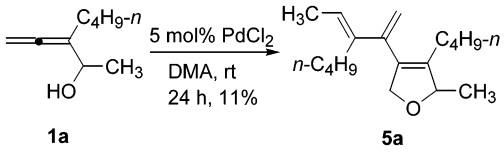


(1)

entry	catalyst	solvent	time (h)	yield **4a** (%)[i]
1	$Pd(OAc)_2$[b,c,d]	MeCN	25	NR
2	$PdCl_2$[b,d]	MeCN	46	NR
3	$PdCl_2(PhCN)_2$[b,d]	MeCN	46	NR
4	$PdCl_2(MeCN)_2$	THF	1	16
5	$PdCl_2(MeCN)_2$	DMF	25	69
6	$Pd(OAc)_2$	DMF	17	67
7	$[(\pi\text{-}C_3H_5)PdCl]_2$	DMF	49.5	48
8	$PdCl_2$	DMF	14	63
9	$PdCl_2$[e]	DMF	12	51
10	$PdCl_2$	CH_3COOH	11.5	19
11	$PdCl_2$	DMSO	12	trace
12	$PdCl_2$	PhMe	13	27
13	$PdCl_2$	DMA	12	74
14	$PdCl_2$[f]	DMA	35	65
15	$PdCl_2$[g]	DMA	5	60
16	$Pd_2(dba)_3{\cdot}CHCl_3$	DMA	46	67
17	$Pd(PPh_3)_4$	DMA	17	NR
18	$Pd(PPh_3)_4$[h]	DMA	72	72

[a] The reaction was carried out at room temperature using **1a** (1 mmol), allylic halide **3** (5 mmol), and Pd (0.05 mmol, 5 mol %) in a solvent (6 mL). [b] K_2CO_3 (120 mol %) and Ag_2CO_3 (5 mol %) were added. [c] The reaction was carriedout at room temperature for 25 h and then at 50−60 °C for 24 h. [d] 2.5 equiv of **3a** were used. [e] Allyl chloride was used instead of allyl bromide. [f] 1 mol % $PdCl_2$ was used. [g] 120 mol % K_2CO_3 was added. [h] The reaction system was exposed to air after 17 h in a N_2 atmosphere. [i] Isolated yield based on allenol **1a**.

some side products when the reaction was carried in THF using 5 mol % $PdCl_2(CH_3CN)_2$ as the catalyst *in the absence of a base* (entry 4, Table 1). The yield of **4a** was improved to 69% when DMF was applied as the solvent (entry 5, Table 1). Several other palladium catalysts including $PdCl_2$, $Pd(OAc)_2$, and $[(\pi\text{-}C_3H_5)PdCl]_2$ were tested and all proved to be effective for this transformation (entries 6−8, Table 1). Due to its ready availability, we chose $PdCl_2$ as the catalyst. Formation of a lower yield of **4a** was observed when allyl chloride was used instead of allyl bromide (compare entry 8 and entry 9, Table 1). Further study indicated the effect of solvent on the formation of 2,5-dihydrofuran **4a** was obvious and DMA was found to provide the product in the highest yield (entries 10−13, Table 1). When the reaction was carried out in the absence of allylic halides, the bimolecular cyclizative coupling product **5a** was isolated in 11% yield (eq 2).[28] The structure of **5a** was confirmed by $^1H-^1H$ NOESY spectra. The reaction in DMA with less than 5 equiv of allyl bromide afforded lower yields of **4a** which was contaminated with a significant amount of **5a** (1 equiv: 36% (**4a**), 2 equiv: 54% (**4a**)).



(2)

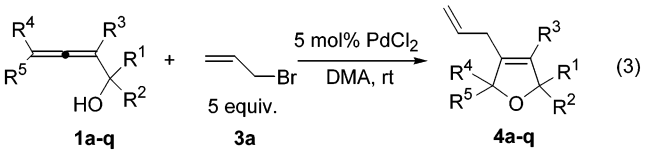
$PdCl_2$ was found to be effective even at the catalyst loading as low as 1 mol % and the corresponding reaction of **1a** with 5 equiv of allyl bromide afforded **4a** in 65% yield when the reaction time was prolonged to 35 h (entry 14, Table 1). It was interesting to note that the reaction proceeded smoothly without a base although one equiv of hydrogen halide was formed during the reaction. The addition of K_2CO_3 (1.2 equiv) did not improve the yield of the reaction (entry 15, Table 1).

The current transformation could also be catalyzed by $Pd_2(dba)_3{\cdot}CHCl_3$ (2.5 mol %) albeit slowly (entry 16, Table 1). However, it turned out that $Pd(PPh_3)_4$, one of the most commonly used Pd(0) catalysts, could not promote this reaction when the reaction was carried out in an inert atmosphere (entry 17, Table 1). After this $Pd(PPh_3)_4$ (5 mol %)-catalyzed system was exposed to air, the reaction of 2,3-allenol **1a** with allyl bromide afforded **4a** in 72% yield within 72 h (entry 18, Table 1).

To investigate the scope of the reaction, the Pd-catalyzed cyclizative coupling reaction of allyl bromide **3a** with a series of 2,3-allenols **1** was carried out under the standard conditions (eq 3). The results were summarized in Table 2. Primary, secondary, and tertiary alcohols all afforded the coupling products in good yields. The cyclizative coupling reaction of 2-substituted 2,3-allenols **1a**−**m** proceeded smoothly to afford the corresponding 4-(2′-propenyl)-2,5-dihydrofurans **4a**−**m** in moderate to good yields with the 2-position substituent R^3 being alkyl, benzyl, 2′-propenyl, methoxy carbonyl, or phenyl (entries 1−13, Table 2). When we turned to 2-nonsubstituted-4-monosubstituted 2,3-allenols **1n**−**p** ($R^3 = H$, $R^4 = n\text{-}C_6H_{13}$ or $n\text{-}C_4H_9$, entries 14−16, Table 2), the yields of the reaction depended on the substituent at the 1-position of allenols: the more substituted at 1-position, the higher yield of corresponding **4**. 4,4-Disubstituted 2,3-allenol **1q** also provided the desired product **4q** in a good yield (entry 17, Table 2).

(28) For the palladium-catalyzed dimerization reaction of 1,2-allenyl ketones, see: (a) Hashmi, A. S. K.; Choi, J.-H.; Bats, J. W. *J. Prakt. Chem.* **1999**, *341*, 342. (b) Hashmi, A. S. K.; Rupert, T. L.; Knofel, T.; Bats, J. W. *J. Org. Chem.* **1997**, *62*, 7295.

TABLE 2. $PdCl_2$-Catalyzed Cyclizative Coupling Reaction of 2,3-Allenols with Allylic Bromide[a]

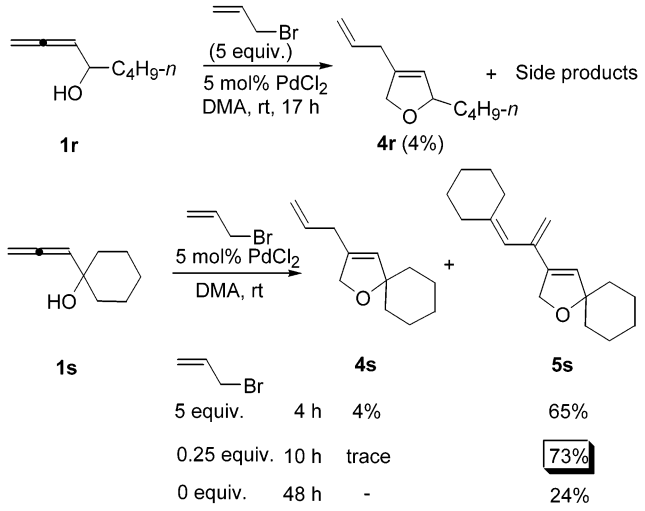


(3)

entry	2,3-allenol **1** R^1	R^2	R^3	R^4	R^5		time (h)	yield (%)[b]
1	CH_3	H	C_4H_9-*n*	H	H	(**1a**)	18.5	76 (**4a**)
2	CH_3	H	CH_3	H	H	(**1b**)	3.5	71 (**4b**)
3	CH_3	H	CH_2Ph	H	H	(**1c**)	18.5	61 (**4c**)
4	C_4H_9-*n*	H	C_4H_9-*n*	H	H	(**1d**)	10.5	81 (**4d**)
5	Ph	H	C_4H_9-*n*	H	H	(**1e**)	21	81 (**4e**)
6	C_4H_9-*n*	H	C_3H_5	H	H	(**1f**)	2	64 (**4f**)
7	C_4H_9-*n*	H	CO_2CH_3	H	H	(**1g**)	7.5	55 (**4g**)
8	C_4H_9-*n*	H	Ph	H	H	(**1h**)	14.5	68 (**4h**)
9	Ph	H	Ph	H	H	(**1i**)	14.5	60 (**4i**)
10	CH_3	CH_3	Ph	H	H	(**1j**)	9	86 (**4j**)
11	CH_3	CH_3	C_4H_9-*n*	H	H	(**1k**)	23	57 (**4k**)
12	H	H	CH_2Ph	H	H	(**1l**)	10	63 (**4l**)
13	H	H	CH_3	C_6H_{13}-*n*	H	(**1m**)	5	72 (**4m**)
14	H	H	H	C_6H_{13}-*n*	H	(**1n**)	38	32 (**4n**)
15	CH_3	CH_3	H	C_4H_9-*n*	H	(**1o**)	12	57 (**4o**)
16	$(CH_2)_5$		H	C_4H_9-*n*	H	(**1p**)	7	69 (**4p**)
17	C_4H_9-*n*	H	H	$(CH_2)_5$		(**1q**)	14	69 (**4q**)

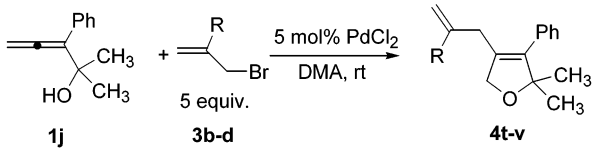
[a] The reaction was carried out at room temperature using **1** (1 mmol), allyl bromide **3a** (5 mmol), and $PdCl_2$ (0.05 mmol, 5 mol %) in DMA (6 mL). [b] Isolated yield based on **1**.

SCHEME 4



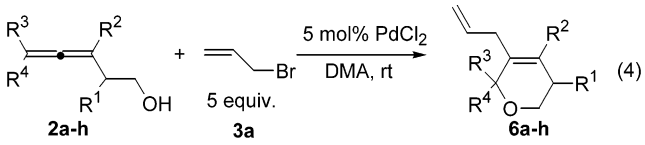
To our surprise, the reaction of nonsubstituted 2,3-allenols **1r** and **1s** with allyl bromide did not provide **4r** and **4s** as the major product (Scheme 4). Under the standard conditions, the reaction of **1r** afforded the expected product **4r** in unacceptedly low yield (4%) together with side products. We failed to determine the structure of the side products due to its high instability. The reaction of 2,3-allenol **1s** provided bimolecular cyclizative coupling product **5s** (65%) as the major product which was contaminated by 4% of **4s**. The yield of **5s** was improved to 73% when 0.25 equiv of allyl bromide was used. It should be noted that the yield of **5s** dropped to 24% and much longer reaction time was required to accomplish this transformation when the reaction was carried out in the absence of allyl bromide. The reaction mechanism is more complicated than it first appears, and the role of allyl bromide is not clear.

SCHEME 5



3b R = Ph 22.5 h **4t** (74%)
3c R = Br 19 h **4u** (71%)
3d R = C_4H_9-*n* 12.5 h **4v** (73%)

TABLE 3. $PdCl_2$-Catalyzed Cyclizative Coupling Reaction of 3,4-Allenols with Allyl Bromide[a]



(4)

entry	3,4-allenol **2** R^1	R^2	R^3	R^4		time (h)	yield (%)[b]
1	CH_3	C_4H_9-*n*	H	H	(**2a**)	48	63 (**6a**)
2	H	C_4H_9-*n*	H	H	(**2b**)	24	61 (**6b**)
3	CH_3	Ph	H	H	(**2c**)	34	78 (**6c**)
4	CH_3	C_4H_9-*t*	H	H	(**2d**)	22	48 (**6d**)
5	H	C_4H_9-*n*	C_3H_7-*i*	H	(**2e**)	20	87 (**6e**)
6	CH_3	H	CH_3	CH_3	(**2f**)	12	64 (**6f**)
7	H	H	C_4H_9-*n*	H	(**2g**)	96	34 (**6g**)[c]
8	CH_3	H	H	H	(**2h**)	24	0 (**6h**)[d]

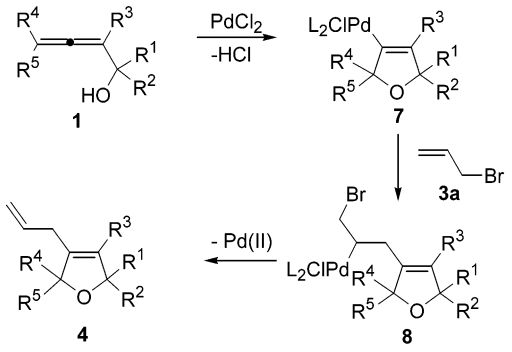
[a] The reaction was carried out at room temperature using **2** (1 mmol), allyl bromide **3a** (5 mmol), and $PdCl_2$ (0.05 mmol, 5 mol %) in DMA (6 mL). [b] Isolated yield based on **2**. [c] 33% **2g** was recovered. [d] 35% **2h** was recovered.

The scope of allylic bromides was also screened. We found that under the standard reaction conditions, the reaction of 2,3-allenol **1j** with 2-substituted allylic bromides **3b**−**d** underwent smoothly to provide the corresponding products **4t**−**v** in good yields (Scheme 5). However, when 3-phenyl-2-propenyl bromide was used, the reaction was complicated and no desired cyclic product was isolated.

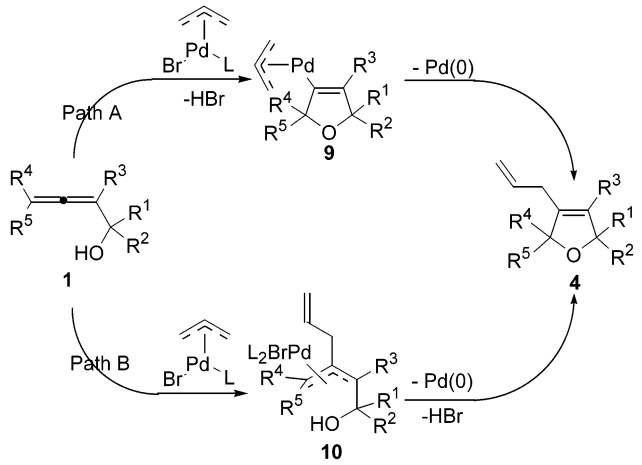
The Cyclizative Coupling Reaction of 3,4-Allenols with Allyl Bromide. Subsequently, we wish to expand the current reaction from 2,3-allenols to 3,4-allenols. Thus, under the standard conditions successfully applied for the 2,3-allenols, the reaction of 3,4-allenols **2a**−**h** with allyl bromide was studied (eq 4, Table 3), and the results were summarized in Table 3. Being similar to the results of 2,3-allenols, 3-substituted 3,4-allenols **2a**−**e** underwent cyclizative coupling reaction smoothly to afford 5,6-dihydro-2*H*-pyrans **6a**−**e** in moderate to good yields (entries 1−5, Table 3). The reaction of 5,5-disubstituted 3,4-allenol **2f** provided the desired product **6f** in 64% yield (entry 6, Table 3), while the reaction of 5-monosubstituted 3,4-allenol **2g** afforded **6g** in only 34% yield together with 33% of starting material **2g** being recovered even when the reaction time was prolonged to 96 h (entry 7, Table 3). Nonsubstituted 3,4-allenol **2h** failed to undergo the cyclizative coupling reaction (entry 8, Table 3).

Mechanistic Considerations. Two different mechanisms involving Pd(II) and Pd(0) species were proposed for the cyclizative coupling reaction of 2,3-allenols with allylic halides using 2,3-allenol **1** and allyl bromide **3a**

SCHEME 6. Pd(II)-Catalyzed Pathway



SCHEME 7. Pd(0)-Catalyzed Pathway



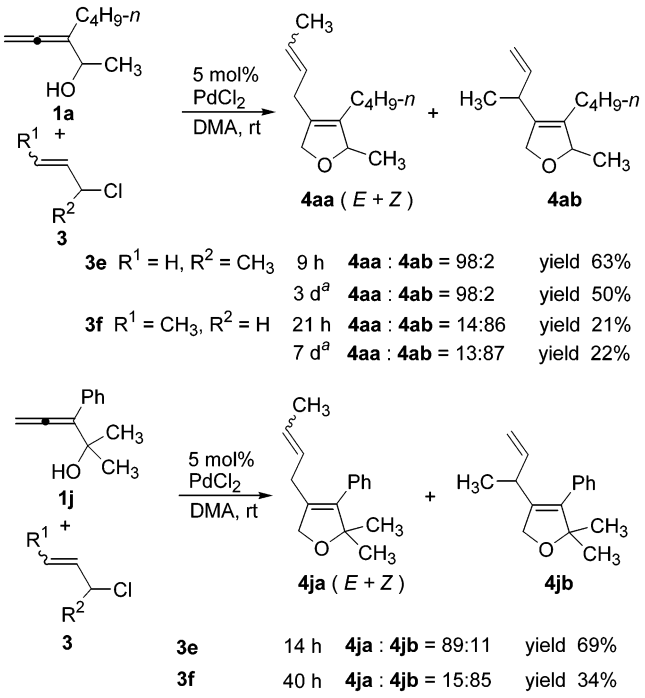
as the representative reactants as illustrated in Schemes 6 and 7, respectively.[29]

In the Pd(II)-catalyzed mechanism (Scheme 6), $PdCl_2$ coordinates with the double bond remote from the hydroxyl group in 2,3-allenol **1**. Subsequent cyclic oxypalladation affords 2,5-dihydrofuranyl palladium intermediate **7**, which reacts with allyl bromide **3a** to give *β*-bromo-*β*′-(2,5-dihydrofuranyl)palladium(II) chloride intermediate **8**, followed by dehalopalladation to provide the final product **4** and regenerate the Pd(II) species.

On the other hand, in the Pd(0)-catalyzed mechanism (Scheme 7), the oxidative addition reaction of allyl bromide **3a** with Pd(0) forms a *π*-allyl palladium(II) intermediate: in Path A, this palladium(II) intermediate interacts with the double bond remote from the hydroxyl group in 2,3-allenol **1** and subsequent cyclic oxypalladation affords intermediate **9**, which forms product **4** and regenerates the Pd(0) species via a reductive elimination reaction; in Path B, the carbopalladation of the *π*-allyl palladium(II) species with the allene moiety generates a new *π*-allyl palladium(II) intermediate **10**, and intramolecular nucleophilic substitution with the hydroxyl group furnishs **4** and the Pd(0) species.

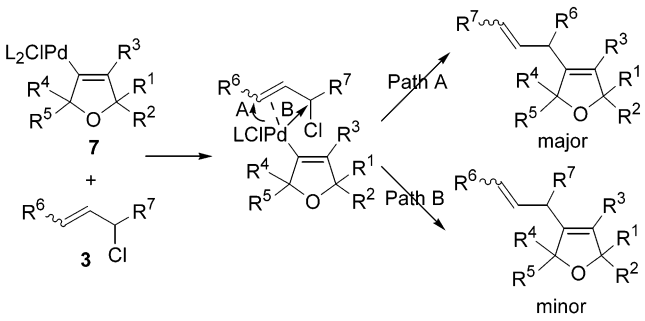
Both the Pd(II)- and Pd(0)-catalyzed mechanisms seemed possible and could account for the experimental

SCHEME 8[a]



[a] 2.5 mol% $Pd_2(dba)_3$ $CHCl_3$ was used instead of $PdCl_2$.

SCHEME 9



Path A: insertion/β-Cl elimination
Path B: coordination-directed direct replacement

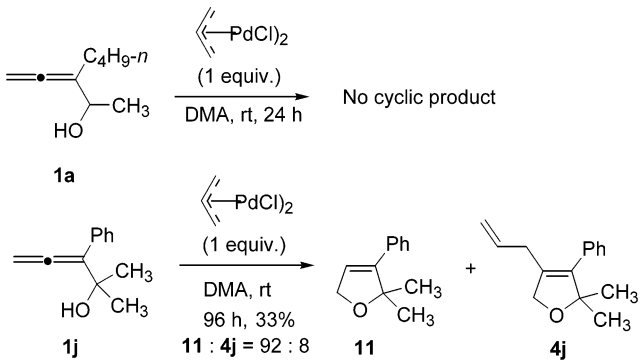
results summarized in Table 2 and Table 3. To investigate the mechanism of the current transformation, the following experiments were conducted (Scheme 8).

Based on the experimental facts outlined in Scheme 8, Pd(0)-catalyzed mechanism may be safely excluded because it predicts wrong regiochemistry in the product **4**, while the Pd(II)-catalyzed mechanism may be accepted. Moreover, it was in accordance with the fact that Pd-$(PPh_3)_4$ could not promote the reaction in an inert atmosphere (entry 17, Table 1). When the reaction system was exposed to air, $Pd(PPh_3)_4$ was readily oxidized into Pd(II), which initiated the cyclizative coupling reaction (entry 18, Table 1). Due to the increase of steric hindrance of the C═C bond in **3f**, the corresponding reaction with **3f** afforded the product **4** in relatively lower yields. The minor regioisomers in each reaction may be formed via a coordination-directed direct replacement of the chlorine atom by the corresponding palladium species **7** (Scheme 9).

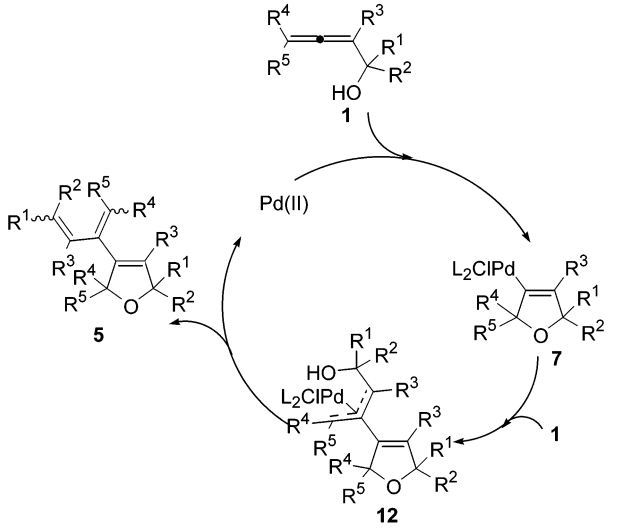
The Pd(II)-catalyzed pathway seemed to be further supported by the experimental facts that the reactions

(29) For the mechanism of Pd-catalyzed coupling−cyclization reaction of allenic amides with allylic halides, see (a) Karstens, W. F. J.; Klomp, D.; Rutjes, F. P. J. T.; Hiemstra, H. *Tetrahedron* **2001**, *57*, 5123. (b) Kimura, M.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1995**, *60*, 3764. (c) Kimura, M.; Fukami, K.; Tanaka, S.; Tamaru, Y. *J. Org. Chem.* **1992**, *57*, 6377. (d) Prasad, J. S.; Liebeskind, L. S. *Tetrahedron Lett.* **1988**, *29*, 4257.

SCHEME 10



SCHEME 11

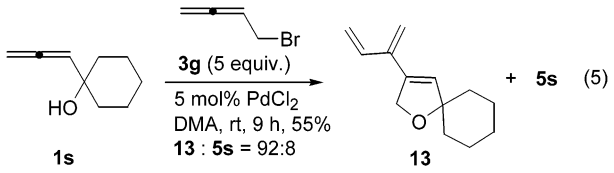


of a stoichimetric amount of (π-allyl) palladium chloride dimer with **1a** and **1j** were reluctant to undergo the transformation to provide the expected products (Scheme 10).

As enclosed from Tables 2 and 3, the substituent of allenols played a crucial role on the outcome of the reaction. For example, the reaction of 2-substituted 2,3-allenol **1a** provided desired 2,5-dihydrofuran **4a** in 76% yield (entry 1, Table 2) while nonsubstituted 2,3-allenol **1s** afforded bimolecular cyclizative coupling product **5s** as the major product in 65% yield even in the presence of 5 equiv of allyl bromide (Scheme 4). How did the great difference occur? We proposed that the bimolecular cyclizative coupling product **5** was formed via a Pd(II)-catalyzed mechanism as outlined in Scheme 11.

The transformation starts with a cyclic oxypalladation of allenol **1** to generate the 4-(2,5-dihydrofuranyl) palladium intermediate **7**, which reacts with the C_2-C_3 double bond of another molecular allenol **1**, subsequent β-hydroxyl elimination[30] provides the bimolecular cyclizative coupling product **5** and regenerates the Pd(II) species. When allyl bromide is involved, the reaction becomes more complicated. There exist at least two possible pathways for this reaction: the reaction of 4-(2,5-dihydrofuranyl) palladium intermediate **7** with another molecular allenol **1** provides the bimolecular cyclizative coupling product **5** or the reaction with allyl bromide affords cyclizative coupling product **4**. The key point here is that the reactivity of the allene moiety is high due to the absence of any substituent. The effect of the substituent of allenols was to prevent the palladium(II) intermediate **7** from interacting with another molecule of allenol to afford bimolecular cyclizative coupling product.

Palladium(II) intermediate is apt to react with the double bond of allene prior to a normal carbon−carbon double bond.[31] In fact, when 4-bromo-1,2-butadiene **3g** was used instead of allyl bromide, as expected, the reaction of 2,3-allenols **1s** provided the cyclizative coupling product **13** as major product together with bimolecular cyclizative coupling product **5s** as the minor product (eq 5).



Conclusion

In summary, we have developed a novel Pd(II)-catalyzed cyclizative coupling reaction of 2,3- or 3,4-allenols with allylic halides, which provides an efficient route to polysubstituted 2,5-dihydrofurans or 5,6-dihydro-2*H*-pyrans. The reaction conditions are mild (room temperature), the catalyst ($PdCl_2$) is readily available and air stable, the starting materials can be easily prepared, and the yields are from moderate to good. Further investigation on the chemistry of allenols is being intensively carried out in our laboratory.

Experimental Section

The Cyclizative Coupling Reaction of Allenols with Allylic Halides: General Procedure. A mixture of allenol **1** or **2** (1 mmol), allylic halide **3** (5 mmol), and $PdCl_2$ (5 mol %) was stirred in DMA (6 mL) at room temperature. When the reaction was complete as monitored by TLC, ether was added. The reaction mixture was washed with brine (three times) and dried over anhydrous sodium sulfate. The product was purified by column chromatography on silica gel (petroleum ether/ether).

(1) 3-Butyl-2-methyl-4-(2′-propenyl)-2,5-dihydrofuran (4a). The reaction of **1a** (0.105 g, 0.75 mmol) and **3a** (0.460 g, 3.80 mmol) afforded 0.102 g (76%) of **4a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.60 (m, 1 H), 5.00−4.95 (m, 2 H), 4.88−4.80 (m, 1 H), 4.60−4.42 (m, 2 H), 2.80 (d, J = 6.6 Hz, 2 H), 2.25−2.12 (m, 1 H), 2.00−1.85 (m, 1 H), 1.50−1.20 (m, 4 H), 1.23 (d, J = 6.0 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.53, 135.14, 128.97, 115.67, 83.87, 76.13, 30.17, 29.72, 24.51, 22.71, 20.59, 13.85; MS (*m*/*z*) 180 (M^+, 3.00), 43 (100); IR (neat) 1635, 1250, 1075 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ 180.1514. Found 180.1485.

(2) 2,3-Dimethyl-4-(2′-propenyl)-2,5-dihydrofuran (4b). The reaction of **1b** (0.098 g, 1.00 mmol) and **3a** (0.627 g, 5.18 mmol) afforded 0.098 g (71%) of **4b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83−5.60 (m, 1 H), 5.11−4.93 (m, 2 H), 4.81−4.67 (m, 1 H), 4.60−4.41 (m, 2 H), 2.82 (d, J = 6.4 Hz, 2 H), 1.59 (s, 3 H), 1.23 (d, J = 6.3 Hz, 3 H); MS (*m*/*z*) 138 (M^+, 10.72), 43

(30) Ma, S.; Lu, X. *J. Organomet. Chem.* **1993**, *447*, 305.

(31) Ma, S.; Negishi, E. *J. Am. Chem. Soc.* **1995**, *117*, 6345.

(100); IR (neat) 1629, 1051 cm^{-1}; HRMS calcd for $C_9H_{14}O$ 138.1045. Found 138.1020.

(3) 3-Benzyl-2-methyl-4-(2′-propenyl)-2,5-dihydrofuran (4c). The reaction of **1c** (0.143 g, 0.82 mmol) and **3a** (0.482 g, 3.98 mmol) afforded 0.107 g (61%) of **4c**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35−7.00 (m, 5 H), 5.86−5.70 (m, 1 H), 5.16−4.96 (m, 2 H), 4.78−4.45 (m, 3 H), 3.60 (d, J = 15.4 Hz, 1 H), 3.28 (d, J = 15.4 Hz, 1 H), 2.93 (d, J = 6.2 Hz, 2 H), 1.18 (d, J = 6.2 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.81, 135.10, 135.05, 131.09, 128.73, 128.71, 126.52, 116.45, 84.00, 76.43, 31.21, 30.13, 20.77; MS (m/z) 214 (M^+, 19.84), 213 (100); IR (neat) 1635, 1259, 1075 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 214.1358. Found 214.1375.

(4) 2,3-Dibutyl-4-(2′-propenyl)-2,5-dihydrofuran (4d). The reaction of **1d** (0.145 g, 0.80 mmol) and **3a** (0.647 g, 5.35 mmol) afforded 0.144 g (81%) of **4d**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.77−5.55 (m, 1 H), 5.06−4.84 (m, 2 H), 4.77−4.62 (m, 1 H), 4.52−4.30 (m, 2 H), 2.73 (d, J = 6.0 Hz, 2 H), 2.20−1.98 (m, 1 H), 1.89−1.70 (m, 1 H), 1.67−1.46 (m, 1 H), 1.42−1.10 (m, 9 H), 0.96−0.66 (m, 6 H); MS (m/z) 222 (M^+, 1.74), 165 (100); IR (neat) 1635, 1261, 1058 cm^{-1}; HRMS calcd for $C_{15}H_{25}O$ ($M^+ - 1$) 221.1905. Found 221.1926.

(5) 3-Butyl-2-phenyl-4-(2′-propenyl)-2,5-dihydrofuran (4e). The reaction of **1e** (0.173 g, 0.86 mmol) and **3a** (0.528 g, 4.36 mmol) afforded 0.168 g (81%) of **4e**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45−7.10 (m, 5 H), 5.88−5.68 (m, 1 H), 5.63 (brs, 1 H), 5.20−4.95 (m, 2 H), 4.78 (dd, J = 11.6 and 3.5 Hz, 1 H), 4.65 (d, J = 11.6 Hz, 1 H), 2.90 (d, J = 6.2 Hz, 2 H), 2.16−1.97 (m, 1 H), 1.75−1.51 (m, 1 H), 1.38−1.05 (m, 4 H), 0.81 (t, J = 6.6 Hz, 3 H); MS (m/z) 242 (M^+, 2.76), 105 (100); IR (neat) 1634, 1256, 1055 cm^{-1}; HRMS calcd for $C_{17}H_{22}O$ 242.1671. Found 242.1718.

(6) 2-Butyl-3,4-bis(2′-propenyl)-2,5-dihydrofuran (4f). The reaction of **1f** (0.111 g, 0.67 mmol) and **3a** (0.410 g, 3.39 mmol) afforded 0.088 g (64%) of **4f**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82−5.64 (m, 2 H), 5.12−4.95 (m, 4 H), 4.75 (brs, 1 H), 4.60−4.45 (m, 2 H), 2.93 (dd, J = 15.5 and 5.9 Hz, 1 H), 2.84 (d, J = 6.6 Hz, 2 H), 2.65 (dd, J = 15.5 and 5.9 Hz, 1 H), 1.72−1.55 (m, 1 H), 1.48−1.20 (m, 5 H), 0.88 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 134.80, 134.74, 132.39, 130.69, 115.81, 115.73, 87.70, 76.48, 33.80, 29.52, 29.33, 26.86, 22.73, 14.00; MS (m/z) 205 ($M^+ - 1$, 13.44), 149 (100); IR (neat) 1635, 1037 cm^{-1}; HRMS calcd for $C_{14}H_{22}O$ 206.1671. Found 206.1718.

(7) 2-Butyl-3-(methoxycarbonyl)-4-(2′-propenyl)-2,5-dihydrofuran (4g). The reaction of **1g** (0.104 g, 0.56 mmol) and **3a** (0.361 g, 2.98 mmol) afforded 0.069 g (54%) of **4g**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.90−5.69 (m, 1 H), 5.18−4.98 (m, 3 H), 4.75−4.54 (m, 2 H), 3.75 (s, 3 H), 3.33 (d, J = 5.9 Hz, 2 H), 1.90−1.75 (m, 1 H), 1.72−1.50 (m, 1 H), 1.46−1.22 (m, 4 H), 0.97−0.75 (m, 3 H); MS (m/z) 225 (M^++1, 13.05), 167 (100); IR (neat) 1662, 1634, 1259, 1039 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.27; H, 8.92.

(8) 2-Butyl-3-phenyl-4-(2′-propenyl)-2,5-dihydrofuran (4h). The reaction of **1h** (0.126 g, 0.62 mmol) and **3a** (0.400 g, 3.30 mmol) afforded 0.102 g (68%) of **4h**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.46−7.08 (m, 5 H), 5.95−5.74 (m, 1 H), 5.38−5.21 (m, 1 H), 5.20−4.97 (m, 2 H), 4.82 (dd, J = 12.4 and 5.5 Hz, 1 H), 4.68 (dd, J = 12.4 and 3.1 Hz, 1 H), 3.04 (dd, J = 15.6 and 5.8 Hz, 1 H), 2.90 (dd, J = 15.6 and 5.9 Hz, 1 H), 1.78−1.12 (m, 6 H), 0.82 (t, J = 6.6 Hz, 3 H); MS (m/z) 242 (M^+, 2.02), 185 (100); IR (neat) 1635, 1255, 1062 cm^{-1}; HRMS calcd for $C_{17}H_{22}O$ 242.1671. Found 242.1703.

(9) 2,3-Diphenyl-4-(2′-propenyl)-2,5-dihydrofuran (4i). The reaction of **1i** (0.145 g, 0.65 mmol) and **3a** (0.450 g, 3.72 mmol) afforded 0.103 g (60%) of **4i**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.30−7.16 (m, 8 H), 7.10−7.02 (m, 2 H), 6.12−6.07 (m, 1 H), 5.98−5.80 (m, 1 H), 5.25−5.12 (m, 2 H), 5.01 (dd, J = 12.8 and 5.4 Hz, 1 H), 4.82 (dd, J = 12.8 and 3.5 Hz, 1 H), 3.13 (dd, J = 15.6 and 5.9 Hz, 1 H), 3.02 (dd, J = 15.6 and 5.8 Hz, 1 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.77, 136.23, 135.03, 133.93, 133.87, 128.67, 128.54, 128.46, 128.21, 127.60, 127.57, 116.80, 91.49, 78.45, 30.73; MS (m/z) 262 (M^+, 14.84) 105 (100); IR (neat) 1634, 1253, 1066 cm^{-1}; HRMS calcd for $C_{19}H_{18}O$ 262.1358. Found 262.1345.

(10) 2,2-Dimethyl-3-phenyl-4-(2′-propenyl)-2,5-dihydrofuran (4j). The reaction of **1j** (0.070 g, 0.40 mmol) and **3a** (0.262 g, 2.16 mmol) afforded 0.074 g (86%) of **4j**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44−7.25 (m, 3 H), 7.21−7.10 (m, 2 H), 5.84−5.64 (m, 1 H), 5.11−4.92 (m, 2 H), 4.63 (s, 2 H), 2.72 (d, J = 6.0 Hz, 2 H), 1.32 (s, 6 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.97, 135.35, 135.25, 132.43, 129.28, 128.42, 127.51, 116.23, 90.35, 74.46, 30.67, 27.34; MS (m/z) 214 (M^+, 12.67), 43 (100); IR (neat) 1635, 1241, 1058 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 214.1358. Found 214.1308.

(11) 3-Butyl-2,2-dimethyl-4-(2′-propenyl)-2,5-dihydrofuran (4k). The reaction of **1k** (0.077 g, 0.50 mmol) and **3a** (0.302 g, 2.50 mmol) afforded 0.055 g (57%) of **4k**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82−5.66 (m, 1 H), 5.10−4.95 (m, 2 H), 4.43 (s, 2 H), 2.80 (d, J = 6.3 Hz, 2 H), 1.99 (t, J = 7.3 Hz, 2 H), 1.45−1.28 (m, 4 H), 1.26 (s, 6 H), 0.91 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.50, 135.12, 128.67, 115.63, 89.81, 73.94, 31.99, 29.99, 26.99, 24.74, 23.14, 13.88; MS (m/z) 193 ($M^+ - 1$, 1.54), 179 (100); IR (neat) 1634, 1253, 1056 cm^{-1}; HRMS calcd for $C_{12}H_{19}O$ ($M^+ - CH_3$) 179.1436. Found 179.1421.

(12) 3-Benzyl-4-(2′-propenyl)-2,5-dihydrofuran (4l). The reaction of **1l** (0.098 g, 0.61 mmol) and **3a** (0.354 g, 2.92 mmol) afforded 0.077 g (63%) of **4l**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40−7.05 (m, 5 H), 5.89−5.69 (m, 1 H), 5.20−5.02 (m, 2 H), 4.63 (s, 2 H), 4.52 (d, J = 4.0 Hz, 2 H), 3.45 (s, 2 H), 2.97 (d, J = 6.0 Hz, 2 H); MS (m/z) 200 (M^+, 3.04), 91 (100); IR (neat) 1636, 1266, 1061 cm^{-1}; HRMS calcd for $C_{14}H_{16}O$ 200.1201. Found 200.1154.

(13) 2-Hexyl-4-methyl-3-(2′-propenyl)-2,5-dihydrofuran (4m). The reaction of **1m** (0.170 g, 1.01 mmol) and **3a** (0.597 g, 4.93 mmol) afforded 0.152 g (72%) of **4m**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.80−5.63 (m, 1 H), 5.08−4.95 (m, 2 H), 4.75−4.65 (m, 1 H), 4.56−4.40 (m, 2 H), 2.90 (dd, J = 15.5 and 5.6 Hz, 1 H), 2.64 (dd, J = 15.5 and 6.0 Hz, 1 H), 1.72−1.54 (m, 1 H), 1.62 (s, 3 H), 1.45−1.15 (m, 9 H), 0.86 (t, J = 6.7 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 135.19, 131.41, 129.05, 115.89, 88.04, 78.42, 34.48, 32.13, 29.70, 29.60, 25.05, 22.87, 14.33, 10.07; MS (m/z) 208 (M^+, 1.23), 123 (100); IR (neat) 1638, 1045 cm^{-1}; HRMS calcd for $C_{14}H_{24}O$ 208.1827. Found 208.1820.

(14) 2-Hexyl-3-(2′-propenyl)-2,5-dihydrofuran (4n). The reaction of **1n** (0.148 g, 0.96 mmol) and **3a** (0.595 g, 4.92 mmol) afforded 0.060 g (32%) of **4n**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.92−5.76 (m, 1 H), 5.52−5.48 (m, 1 H), 5.15−5.06 (m, 2 H), 4.69 (brs, 1 H), 4.65−4.52 (m, 2 H), 2.81 (dd, J = 16.5 and 6.6 Hz, 1 H), 2.68 (dd, J = 16.5 and 6.6 Hz, 1 H), 1.70−1.55 (m, 2 H), 1.50−1.20 (m, 8 H), 0.87 (t, J = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.25, 134.97, 120.65, 116.80, 86.88, 74.77, 34.27, 32.10, 31.87, 29.68, 24.86, 22.86, 14.32; MS (m/z) 194 (M^+, 8.25), 109 (100); IR (neat) 1639, 1051 cm^{-1}; HRMS calcd for $C_{13}H_{22}O$ 194.1671. Found 194.1660.

(15) 5-Butyl-2,2-dimethyl-4-(2′-propenyl)-2,5-dihydrofuran (4o). The reaction of **1o** (0.104 g, 0.68 mmol) and **3a** (0.403 g, 3.33 mmol) afforded 0.075 g (57%) of **4o**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.84−5.68 (m, 1 H), 5.30 (d, J = 1.6 Hz, 1 H), 5.08−4.96 (m, 2 H), 4.68−4.60 (m, 1 H), 2.69 (dd, J = 16.6 and 6.5 Hz, 1 H), 2.58 (dd, J = 16.6 and 7.0 Hz, 1 H), 1.68−1.48 (m, 1 H), 1.40−1.15 (m, 5 H), 1.22 (s, 3H), 1.19 (s, 3 H), 0.87 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.38, 134.87, 129.70, 116.31, 86.00, 85.52, 34.25, 31.44, 29.07, 28.22, 26.96, 22.83, 14.01; MS (m/z) 179 ($M^+ - CH_3$, 17.12), 84 (100); IR (neat) 1639, 1245, 1081 cm^{-1}; HRMS calcd for $C_{12}H_{19}O$ ($M^+ - CH_3$) 179.1436. Found 179.1410.

(16) 2-Butyl-3-(2′-propenyl)-1-oxaspiro[4.5]dec-3-ene (4p). The reaction of **1p** (0.096 g, 0.50 mmol) and **3a** (0.313 g, 2.59 mmol) afforded 0.080 g (69%) of **4p**: liquid; ^1H NMR (300 MHz, $CDCl_3$) δ 5.95−5.74 (m, 1 H), 5.55 (s, 1 H), 5.17−5.00 (m, 2 H), 4.70−4.64 (m, 1 H), 2.77 (dd, J = 16.6 and 6.7 Hz, 1

H), 2.66 (dd, J = 16.6 and 7.0 Hz, 1 H), 1.80−1.20 (m, 16 H), 0.89 (t, J = 6.7 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 140.10, 135.03, 127.83, 116.31, 88.12, 85.00, 38.86, 37.96, 34.43, 31.70, 26.98, 25.56, 23.70, 23.62, 22.88, 14.08; MS (*m*/*z*) 234 (M^+, 12.45), 191 (100); IR (neat) 1639, 1286, 1060 cm^{-1}; HRMS calcd for $C_{16}H_{26}O$ 234.1984. Found 234.1992.

(17) 2-Butyl-4-(2′-propenyl)-1-oxaspiro[4.5]dec-3-ene (4q). The reaction of **1q** (0.065 g, 0.34 mmol) and **3a** (0.226 g, 1.87 mmol) afforded 0.054 g (69%) of **4q**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86−5.72 (m, 1 H), 5.27 (d, J = 1.5 Hz, 1 H), 5.08−4.96 (m, 2 H), 4.64−4.56 (m, 1 H), 2.62 (d, J = 6.8 Hz, 2 H), 1.76−1.16 (m, 15 H), 1.12−0.96 (m, 1 H), 0.92−0.78 (m, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.97, 135.86, 123.32, 116.47, 88.80, 83.23, 37.42, 36.69, 34.87, 31.33, 27.83, 25.63, 23.11, 22.63, 22.35, 14.36; MS (*m*/*z*) 234 (M^+, 2.90), 177 (100); IR (neat) 1639, 1144, 1082 cm^{-1}; HRMS calcd for $C_{16}H_{26}O$ 234.1984. Found 234.1973.

(18) 2-Butyl-4-(2′-propenyl)-2,5-dihydrofuran (4r). The reaction of **1r** (0.087 g, 0.69 mmol) and **3a** (0.433 g, 3.58 mmol) afforded only 5 mg (4%) of **4r**: liquid; Available data: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96−5.75 (m, 1 H), 5.44 (d, J = 1.5 Hz, 1 H), 5.16−5.00 (m, 2 H), 4.88−4.76 (m, 1 H), 4.60−4.44 (m, 2 H), 2.82 (d, J = 6.7 Hz, 2 H), 1.64−1.20 (m, 6 H), 0.90 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.59, 134.64, 123.81, 116.38, 86.67, 76.30, 35.95, 31.60, 27.37, 22.73, 13.99; MS (*m*/*z*) 166 (M^+, 0.24), 121 (100); IR (neat) 1641, 1054 cm^{-1}.

(19) The reaction of **1s** (0.133 g, 0.96 mmol) and **3a** (0.595 g, 4.92 mmol) afforded 0.007 g (4%) of **4s** and 0.081 g (65%) of **5s.**

3-(2′-Propenyl)-1-oxaspiro[4.5]dec-3-ene (4s): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88−5.75 (m, 1 H), 5.53 (s, 1 H), 5.15−5.00 (m, 2 H), 4.50 (t, J = 1.0 Hz, 2 H), 2.80 (d, J = 6.1 Hz, 2 H), 1.70−1.30 (m, 10 H); MS (*m*/*z*) 178 (M^+, 11.64), 135 (100); IR (neat) 1639, 1050 cm^{-1}; HRMS calcd for $C_{12}H_{18}O$ 178.1358. Found 178.1359.

3-(1-Cyclohexylidenemethylvinyl)-1-oxaspiro[4.5]dec-3-ene (5s): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (t, J = 1.9 Hz, 1 H), 5.69 (s, 1 H), 4.85 (s, 1 H), 4.82 (s, 1 H), 4.69 (d, J = 1.9 Hz, 2 H), 2.20−2.06 (m, 4 H), 1.68−1.25 (m, 16 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 144.34, 138.91, 137.99, 130.84, 120.11, 114.57, 90.61, 73.22, 37.46, 37.22, 30.20, 28.94, 28.33, 26.92, 25.65, 23.66; MS (*m*/*z*) 258 (M^+, 51.93), 215 (100); IR (neat) 1657, 1162, 1035 cm^{-1}; HRMS calcd for $C_{18}H_{26}O$ 258.1984. Found 258.1945.

(20) 2,2-Dimethyl-3-phenyl-4-(2′-phenyl-2′-propenyl)-2,5-dihydrofuran (4t). The reaction of **1j** (0.069 g, 0.40 mmol) and **3b** (0.385 g, 1.95 mmol) afforded 0.086 g (74%) of **4t**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−6.90 (m, 10 H), 5.33 (s, 1 H), 5.09 (s, 1 H), 4.55 (s, 2 H), 3.16 (s, 2 H), 1.27 (s, 6 H); MS (*m*/*z*) 290 (M^+, 42.71), 275 (100); IR (neat) 1624, 1248, 1058 cm^{-1}; HRMS calcd for $C_{21}H_{22}O$ 290.1671. Found 290.1680.

(21) 4-(2′-Bromo-2′-propenyl)-2,2-dimethyl-3-phenyl-2,5-dihydrofuran (4u). The reaction of **1j** (0.070 g, 0.40 mmol) and **3c** (0.412 g, 2.06 mmol) afforded 0.084 g (71%) of **4u**: solid, mp 58−58.5 °C (*n*-Hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45−7.28 (m, 3 H), 7.25−7.10 (m, 2 H), 5.60 (s, 1 H), 5.44 (s, 1 H), 4.66 (s, 2 H), 3.12 (s, 2 H), 1.34 (s, 6 H); MS (*m*/*z*) 293 ($M^+ - 1(^{81}Br)$, 6.77), 291 ($M^+ - 1(^{79}Br)$, 5.32), 279 ($M^+ - CH_3(^{81}Br)$, 99.19), 277 ($M^+ - CH_3(^{79}Br)$, 100); IR (KBr) 1623, 1240, 1057 cm^{-1}. Anal. Calcd for $C_{15}H_{17}BrO$: C, 61.45; H, 5.84. Found: C, 61.67; H, 5.89.

(22) 2,2-Dimethyl-4-(2′-butyl-2′-propenyl)-3-phenyl-2,5-dihydrofuran (4v). The reaction of **1j** (0.060 g, 0.34 mmol) and **3d** (0.345 g, 1.95 mmol) afforded 0.068 g (73%) of **4v**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42−7.26 (m, 3 H), 7.15 (d, J = 7.8 Hz, 2 H), 4.74 (s, 2 H), 4.53 (s, 2 H), 2.66 (s, 2 H), 1.91 (t, J = 6.7 Hz, 2 H), 1.35 (s, 6 H), 1.30−1.15 (m, 4 H), 0.84 (t, J = 6.9 Hz, 3 H); MS (*m*/*z*) 270 (M^+, 12.79), 255 (100); IR (neat) 1640, 1245, 1060 cm^{-1}; HRMS calcd for $C_{19}H_{26}O$ 270.1944. Found 270.1944.

(23) 4-Butyl-5-methyl-3-propenyl-5,6-dihydro-*2H*-pyran (6a). The reaction of **2a** (0.155 g, 1.01 mmol) and **3a** (0.621 g, 5.13 mmol) afforded 0.122 g (63%) of **6a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76−5.62 (m, 1 H), 5.05−4.92 (m, 2 H), 3.94 (s, 2 H), 3.67 (dd, J = 10.8 and 3.9 Hz, 1 H), 3.50 (dd, J = 10.8 and 3.7 Hz, 1 H), 2.70 (dd, J = 15.6 and 6.3 Hz, 1 H), 2.60 (dd, J = 15.6 and 6.3 Hz, 1 H), 2.25−2.05 (m, 2 H), 1.95−1.80 (m, 1 H), 1.45−1.20 (m, 4 H), 1.04 (d, J = 6.9 Hz, 3 H), 0.89 (t, J = 6.8 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 135.83, 134.86, 126.38, 115.06, 71.10, 68.14, 33.05, 31.44, 30.77, 29.27, 22.88, 16.85, 13.95; MS (*m*/*z*) 194 (M^+, 8.04), 153 (100); IR (neat) 1633, 1234, 1143 cm^{-1}; HRMS calcd for $C_{13}H_{22}O$ 194.1671. Found 194.1669.

(24) 4-Butyl-3-propenyl-5,6-dihydro-*2H*-pyran (6b). The reaction of **2b** (0.077 g, 0.55 mmol) and **3a** (0.336 g, 2.78 mmol) afforded 0.060 g (61%) of **6b**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.64 (m, 1 H), 5.10−4.96 (m, 2 H), 3.97 (s, 2 H), 3.76 (t, J = 6.5 Hz, 2 H), 2.70 (d, J = 6.1 Hz, 2 H), 2.15−1.96 (m, 4 H), 1.42−1.24 (m, 4 H), 0.91 (t, J = 7.0 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 136.04, 130.01, 126.71, 115.43, 67.96, 65.04, 33.37, 32.25, 30.40, 28.73, 22.96, 14.27; MS (*m*/*z*) 180 (M^+, 4.27), 139 (100); IR (neat) 1633, 1261, 1066 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ 180.1514. Found 180.1486.

(25) 5-Methyl-4-phenyl-3-propenyl-5,6-dihydro-*2H*-pyran (6c). The reaction of **2c** (0.180 g, 1.03 mmol) and **3a** (0.622 g, 5.14 mmol) afforded 0.172 g (78%) of **6c**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39−7.20 (m, 3 H), 7.16−7.04 (m, 2 H), 5.77−5.52 (m, 1 H), 5.06−4.91 (m, 2 H), 4.19 (d, J = 15.9 Hz, 1 H), 4.05 (dd, J = 15.9 and 1.9 Hz, 1 H), 3.90 (dd, J = 11.0 and 4.1 Hz, 1 H), 3.65 (dd, J = 11.0 and 4.0 Hz, 1 H), 2.68−2.39 (m, 3 H), 0.91 (d, J = 6.9 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 140.73, 137.39, 136.42, 129.77, 128.75, 128.33, 126.90, 116.00, 71.43, 68.23, 34.75, 34.51, 17.32; MS (*m*/*z*) 214 (M^+, 1.71), 173 (100); IR (neat) 1632, 1440, 1130 cm^{-1}; HRMS calcd for $C_{15}H_{18}O$ 214.1358. Found 214.1357.

(26) 4-*tert*-Butyl-5-methyl-3-propenyl-5,6-dihydro-*2H*-pyran (6d). The reaction of **2d** (0.151 g, 0.98 mmol) and **3a** (0.594 g, 4.91 mmol) afforded 0.092 g (48%) of **6d**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.64 (m, 1 H), 5.04−4.92 (m, 2 H), 3.91 (s, 2 H), 3.56 (dd, J = 10.3 and 1.6 Hz, 1 H), 3.45 (dd, J = 10.3 and 2.4 Hz, 1 H), 2.89−2.74 (m, 2 H), 2.15 (q, J = 6.5 Hz, 1 H), 1.13 (s, 9H), 1.11 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 142.489, 136.712, 126.570, 116.096, 71.306, 68.864, 35.575, 35.326, 31.337, 31.299, 20.187; MS (*m*/*z*) 194 (M^+, 0.54), 153 (100); IR (neat) 1635, 1133 cm^{-1}; HRMS calcd for $C_{13}H_{22}O$ 194.1671. Found 194.1624.

(27) 4-Butyl-3-propenyl-2-isopropyl-5,6-dihydro-*2H*-pyran (6e). The reaction of **2e** (0.181 g, 0.99 mmol) and **3a** (0.605 g, 5.00 mmol) afforded 0.192 g (87%) of **6e**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.64 (m, 1 H), 5.08−4.92 (m, 2 H), 3.96−3.88 (m, 2 H), 3.47 (dt, J = 10.9 and 3.0 Hz, 1 H), 2.91 (dd, J = 15.5 and 5.7 Hz, 1 H), 2.64 (dd, J = 15.5 and 7.1 Hz, 1 H), 2.36−2.08 (m, 2 H), 2.05−1.95 (m, 2 H), 1.74 (d, J = 16.2 Hz, 1 H), 1.44−1.20 (m, 4 H), 1.03 (d, J = 6.9 Hz, 3 H), 0.91 (t, J = 7.0 Hz, 3 H), 0.74 (d, J = 6.9 Hz, 3 H); MS (*m*/*z*) 222 (M^+, 0.11), 179 (100); IR (neat) 1632, 1127, 1097 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.94; H, 11.67.

(28) 3-Propenyl-2,2,5-trimethyl-5,6-dihydro-*2H*-pyran (6f). The reaction of **2f** (0.125 g, 0.99 mmol) and **3a** (0.603 g, 4.98 mmol) afforded 0.106 g (64%) of **6f**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.62 (m, 1 H), 5.26 (d, J = 1.4 Hz, 1 H), 5.04−4.92 (m, 2 H), 3.70 (dd, J = 11.2 and 5.1 Hz, 1 H), 3.24 (dd, J = 11.2 and 7.5 Hz, 1 H), 2.68−2.52 (m, 2 H), 2.28−2.16 (m, 1 H), 1.21 (s, 6 H), 0.86 (d, J = 7.4 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 141.58, 136.87, 126.25, 116.42, 74.61, 65.78, 36.40, 30.15, 26.90, 25.77, 17.64; MS (*m*/*z*) 167 (M^++1, 1.99), 151 (100); IR (neat) 1638, 1164, 1094 cm^{-1}; HRMS calcd for $C_{11}H_{18}O$ 166.1358. Found 166.1382.

(29) 2-Butyl-3-propenyl-5,6-dihydro-*2H*-pyran (6g). The reaction of **2g** (0.082 g, 0.59 mmol) and **3a** (0.386 g, 3.19 mmol) afforded 0.036 g (34%) of **6g** (33% of **2g** was recovered): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82−5.66 (m, 1 H), 5.58−5.52 (m, 1 H), 5.08−4.98 (m, 2 H), 4.05−3.94 (m, 1 H), 3.90−3.80

(m, 1 H), 3.58−3.50 (m, 1 H), 2.64 (d, J = 6.6 Hz, 2 H), 2.23−2.08 (m, 1 H), 2.02−1.90 (m, 1 H), 1.66−1.20 (m, 6 H), 0.88 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 138.37, 135.91, 120.50, 116.26, 75.45, 61.91, 37.67, 31.83, 27.13, 25.60, 22.71, 14.03; MS (m/z) 180 (M^+, 1.78), 123 (100); IR (neat) 1637, 1266, 1041 cm^{-1}; HRMS calcd for $C_{12}H_{20}O$ 180.1514. Found 180.1465.

(30) (*E* and *Z*)-4-(2′-Butenyl)-3-butyl-2-methyl-2,5-dihydrofuran (4aa). The reaction of **1a** (0.096 g, 0.69 mmol) and **3e** (0.317 g, 3.50 mmol) afforded 0.084 g (63%) of **4aa** (*E*/*Z* = 1) and **4ab (**98:2**)** as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.50−5.20 (m, 2 H), 4.82−4.65 (m, 1 H), 4.50−4.32 (m, 2 H), [2.76 (d, J = 7.3 Hz), 2.67 (d, J = 6.2 Hz), 2 H], 2.16−2.01 (m, 1 H), 1.94−1.76 (m, 1 H), 1.63−1.50 (m, 3 H), 1.40−1.08 (m, 7 H), 0.93−0.75 (m, 3 H); MS (m/z) 193 ($M^+ - 1$, 56.40), 55 (100); IR (neat) 1075 cm^{-1}; HRMS calcd for $C_{12}H_{19}O$ ($M^+ - CH_3$) 179.1436. Found 179.1481. The following data are discernible for the other stereoisomer, i.e., 3-butyl-2-methyl-4-(1′-methyl-2′-propenyl)-2,5-dihydrofuran (**4ab**): 5.83−5.61 (m, 1 H), 5.01−4.87 (m, 2 H), 3.26−3.14 (m, 1 H).

(31) 3-Butyl-2-methyl-4-(1′-methyl-2′-propenyl)-2,5-dihydrofuran (4ab). The reaction of **1a** (0.219 g, 1.56 mmol) and **3f** (0.693 g, 7.65 mmol) afforded 0.060 g (21%) of **4aa** and **4ab (**14:86**)** as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80−5.65 (m, 1 H), 5.00−4.88 (m, 2 H), 4.82−4.72 (m, 1 H), 4.56−4.36 (m, 2 H), 3.24−3.14 (m, 1 H), 2.18−2.04 (m, 1 H), 1.96−1.82 (m, 1 H), 1.40−1.12 (m, 7 H), 1.05 (dd, J = 7.1 and 0.7 Hz, 3 H), 0.95−0.75 (m, 3 H); MS (m/z) 194 (M^+, 9.12), 55 (100); IR (neat) 1078, 1020 cm^{-1}. The following data are discernible for the other stereoisomer, i.e., (*E* and *Z*)-4-(2′-butenyl)-3-butyl-2-methyl-2,5-dihydrofuran (**4aa**): 5.50−5.20 (m, 2 H), [2.76 (d, J = 7.3 Hz), 2.68 (d, J = 6.1 Hz), 2 H].

(32) (*E* and *Z*)-4-(2′-Butenyl)-2,2-Dimethyl-3-phenyl-2,5-dihydrofuran (4ja). The reaction of **1j** (0.070 g, 0.40 mmol) and **3e** (0.184 g, 2.03 mmol) afforded 0.063 g (69%) of **4ja** and **4jb (**89:11**)** as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.24 (m, 3 H), 7.20−7.08 (m, 2 H), 5.54−5.24 (m, 2 H), 4.63 (t, J = 1.2 Hz, 2 H), [2.74 (dd, J = 7.3 and 0.6 Hz), 2.66 (d, J = 6.2 Hz), 2 H], [1.64 (dt, J = 4.8 and 1.3 Hz), 1.51 (dt, J = 6.7 and 0.8 Hz), 3 H], 1.36−1.24 (m, 6 H); MS (m/z) 228 (M^+, 0.44), 213 (100); IR (neat) 1598, 1490, 1181, 1060 cm^{-1}; HRMS calcd for $C_{16}H_{20}O$ 228.1514. Found 228.1469. The following data are discernible for the other stereoisomer, i.e., 2,2-dimethyl-4-(1′-methyl-2′-propenyl)-3-phenyl-2,5-dihydrofuran (**4jb**): 5.84−5.73 (m, 1 H), 5.01−4.94 (m, 2 H), 3.06−2.97 (m, 1 H).

(33) 2,2-Dimethyl-4-(1′-methyl-2′-propenyl)-3-phenyl-2,5-dihydrofuran (4jb). The reaction of **1j** (0.131 g, 0.75 mmol) and **3f** (0.345 g, 3.81 mmol) afforded 0.055 g (34%) of **4ja** and **4jb (**15:85**)** as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.28 (m, 3 H), 7.16−7.11 (m, 2 H), 5.84−5.72 (m, 1 H), 5.02−4.94 (m, 2 H), 4.73−4.63 (m, 2 H), 3.05−2.96 (m, 1 H), 1.33 (s, 3 H), 1.30 (s, 3 H), 1.08 (d, J = 7.1 Hz, 3 H); MS (m/z) 228 (M^+, 21.57), 227 (100); IR (neat) 1249, 1147, 1057 cm^{-1}. The following data are discernible for the other stereoisomer, i.e., (*E* and *Z*)-4-(2′-butenyl)-2,2-Dimethyl-3-phenyl-2,5-dihydrofuran (**4ja**): 5.53−5.28 (m, 2 H), [2.74 (d, J = 7.4 Hz), 2.66 (d, J = 6.2 Hz), 2 H].

The Bimolecular Cyclizative Coupling Reaction of 2,3-Allenol 1a. 3-Butyl-4-(2′-ethylidene-1′-methylenehexyl)-2-methyl-2,5-dihydrofuran (5a). A mixture of allenol **1a** (0.069 g, 0.49 mmol) and $PdCl_2$ (0.005 g, 5 mol %) was stirred in DMA (3 mL) at room temperature for 24 h. Then ether was added. The reaction mixture was washed with brine (three times) and dried over anhydrous sodium sulfate. The product was purified by column chromatography on silica gel (petroleum ether/ether = 40:1) to afford 0.007 g (11%) of **5a**: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (q, J = 6.8 Hz, 1 H), 5.15 (d, J = 1.8 Hz, 1 H), 4.99−4.88 (m, 1 H), 4.84 (d, J = 1.8 Hz, 1 H), 4.65−4.50 (m, 2 H), 2.30−2.17 (m, 3 H), 1.94−1.82 (m, 1 H), 1.68 (d, J = 6.8 Hz, 3 H), 1.44−1.20 (m, 11 H), 0.95−0.83 (m, 6 H); MS (m/z) 262 (M^+, 11.43), 219 (100); IR (neat) 1456, 1060, 1018 cm^{-1}; HRMS calcd for $C_{18}H_{30}O$ 262.2297. Found 262.2303. The stereochemistry of **5a** was confirmed by the ^{1}H−^{1}H NOESY spectra.

The Coupling Reaction of 2,3-Allenol 1j with a Stoichimetric Amount of (π-Allyl) Palladium Chloride Dimer. 2,2-Dimethyl-3-phenyl-2,5-dihydrofuran (11). A mixture of allenol **1j** (0.030 g, 0.17 mmol) and (π-allyl) palladium chloride dimer (0.063 g, 0.17 mmol) was stirred in DMA (1.2 mL) at room temperature for 96 h. Then ether was added. The reaction mixture was washed with brine (three times) and dried over anhydrous sodium sulfate. The product was purified by column chromatography on silica gel (petroleum ether/ether = 40:1) to afford 0.010 g (33%) of **11** and **4j** (**11**:**4j** = 92:8) as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44−7.28 (m, 5 H), 5.98 (s, 1 H), 4.69 (d, J = 1.8 Hz, 2 H), 1.49 (s, 6 H); MS (m/z) 174 (M^+, 21.46), 159 (100); IR (neat) 1599, 1494, 1069 cm^{-1}; HRMS calcd for $C_{12}H_{14}O$ 174.1045. Found 174.1069. The following data are discernible for 2,2-dimethyl-3-phenyl-4-(2′-propenyl)-2,5-dihydrofuran (**4j**): 5.85−5.65 (m 1 H), 5.10−4.90 (m, 2 H), 2.76−2.70 (m, 2 H).

The Cyclizative Coupling Reaction of 2,3-Allenols 1s with 4-Bromo-1,2-butadiene 3g. 3-(1′-Methylenepropenyl)-1-oxaspiro[4.5]dec-3-ene (13). A mixture of allenol **1s** (0.042 g, 0.30 mmol), 4-bromo-1,2-butadiene **3g** (0.206 g, 1.55 mmol), and $PdCl_2$ (0.003 g, 5 mol %) was stirred in DMA (2 mL) at room temperature for 9 h. Then ether was added. The reaction mixture was washed with brine (three times) and dried over anhydrous sodium sulfate. The product was purified by column chromatography on silica gel (petroleum ether/ether = 40:1) to afford 0.032 g (55%) of **13** and **5s** (**13**:**5s** = 92:8) as a mixture: liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.39 (dd, J = 17.3 and 10.8 Hz, 1 H), 5.88 (s, 1 H), 5.44 (dd, J = 17.3 and 1.4 Hz, 1 H), 5.20 (s, 1 H), 5.11 (dd, J = 10.8 and 1.4 Hz, 1 H), 4.76 (s, 1 H), 4.70 (d, J = 2.0 Hz, 2 H), 1.70−1.25 (m, 10 H); MS (m/z) 190 (M^+, 9.42), 147 (100); IR (neat) 1637, 1447, 1062 cm^{-1}; HRMS calcd for $C_{13}H_{18}O$ 190.1358. Found 190.1327. The following data are discernible for 3-(1-cyclohexylidenemethylvinyl)-1-oxaspiro[4.5]dec-3-ene (**5s**): 2.20−2.05 (m, 4 H).

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Supporting Information Available: ^{1}H NMR spectra and some of the representative ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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