Stereoselective Hydrogenolysis of 1,1-Dibromo-1-alkenes and Stereospecific Synthesis of Conjugated (*Z*)-Alkenyl Compounds

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The Pd-catalyzed hydrogenolysis of 1,1-dibromoalkenes with Bu_3SnH occurs at room temperature stereoselectively to give (*Z*)-1-bromo-1-alkenes. We sought to determine the optimal reaction conditions and illustrate the scope of this method with 32 dibromoalkenes including alkenyl- and alkynyl-conjugated 1,1-dibromo-1-alkenes **7a**−**h** and 2,2-disubstituted 1,1-dibromo-1-alkenes **9a**−**f**. Triphenylphosphine was the best ligand for the Pd-catalyzed hydrogenolysis. A wide range of solvents can be used for this reaction excluding EtOH, AcOH, and $CHCl_3$. However, the reaction proceeds even in these solvents with the addition of a cosolvent or radical scavenger. The reaction of 1,1-diiodo-1-alkene (**3**) gave a mixture of (*Z*)-1-iodo-1-alkene (**4**), (*Z*)-1-tributylstannyl-1-alkene (**5**), and a terminal alkene **6**, while that of 1,1-dichloroalkene did not occur. This selectivity can be explained by the stereoselective insertion of Pd(0) to a *trans* bromine−alkenyl carbon bond, successive transmetalation with Bu_3SnH, and reductive elimination. The Suzuki and Sonogashira couplings of the resulting (*Z*)-1-bromo-1-alkenes with alkenyl(dialkoxy)borane and terminal alkyne occurred to give conjugated polyenes and enynes stereospecifically. The Pd-catalyzed hydrogenolysis of 1,1-dibromo-1-alkene and successive cross-coupling can be carried out either in a stepwise manner or in one-pot under the same Pd catalysis. These two processes should be useful for the synthesis of geometrically pure polyene and enyne with a *Z*-alkenyl unit.

Dienes and polyenes have been the subject of great interest due to their important roles in biologically active compounds. Considerable progress has recently been made in the regio- and stereocontrol of their synthesis.[1] A *Z*-alkenyl unit conjugated with an alkene or alkyne is often seen in structures of natural products, such as arachidonic acids,[2] retinoids,[3] antibiotics,[4] and marine natural products.[5] To prepare this conjugated *Z*-double bonds, several synthetic methods including the Wittig and related reactions,[6] semihydrogenation of alkyne,[7] and metal-catalyzed cross-coupling reactions[8] have been reported. To prepare geometrically pure polyenes and enynes bearing a conjugated *Z*-alkenyl group, metal-catalyzed, particularly Pd-catalyzed, cross-coupling reactions have been proven to be reliable,[9] since such reactions occur with high stereospecificity and give the resulting alkenes with retention of the configuration of the starting alkenyl halides or alkenylmetals. In such cases, geometrically pure (*Z*)-alkenyl halides or (*Z*)-alkenylmetals are required. Several methods for synthesizing (*Z*)-1-haloalkenes have been reported, e.g., Wittig-type condensations,[10] *cis* hydrogenations of 1-haloalkynes with diimine,[11] and hydrometalation of alkynes followed by replacement of the metal with halide.[12] Since these methods sometimes give unsatisfactory results, a more efficient and reliable method for the synthesis of (*Z*)-1-halo-1-alkenes is desirable, particularly in the case of conjugated 1-halodienes, such as (1*Z*,3*E*)-1-halo-1,3-dienes. In a preliminary paper, we reported a new method for synthesizing (*Z*)-1-bromo-1-alkenes and con-

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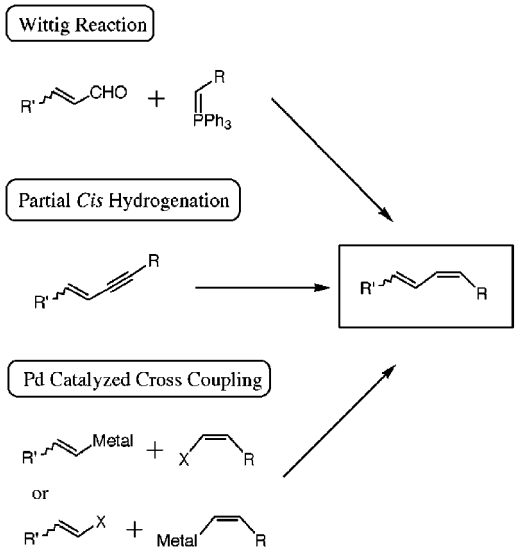
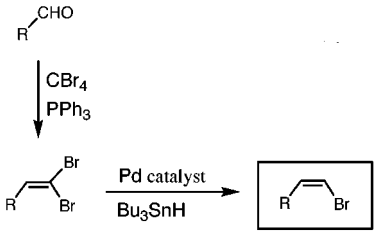
Scheme 1



Scheme 2

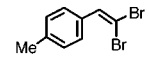
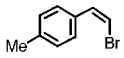
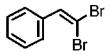
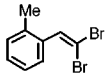
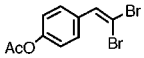
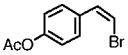
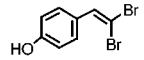
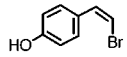
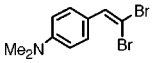
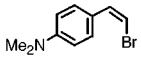
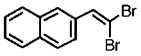
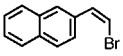
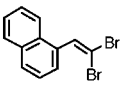
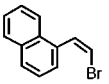
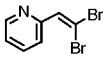
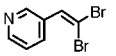
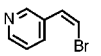
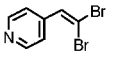
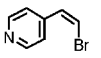
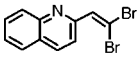
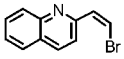
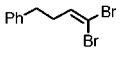
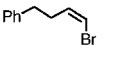
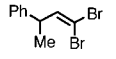
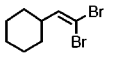
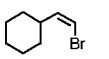
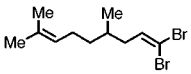
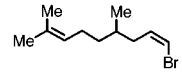
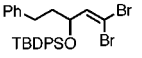
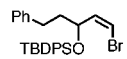
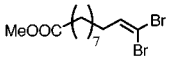
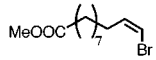


jugated polyenes and enediynes with the *Z*-alkenyl unit,[13] in which the Pd-catalyzed hydrogenolysis of 1,1-dibromo-1-alkene with Bu_3SnH gave (*Z*)-1-bromo-1-alkene stereoselectively, which coupled with alkenylboronic acid or alkyne under Pd-catalyzed conditions. In this paper, we describe the details of the hydrogenolysis of 1,1-dibromo-1-alkenes, including its mechanism, scope, and limitations and also its usefulness for the preparation of conjugated polyenes and enediynes by the Pd-catalyzed cross-coupling (Scheme 1).

Results and Discussion

Stereoselective Hydrogenolysis. Two examples of the hydrogenolysis of 1,1-dibromo-1-alkene have been reported in the literature.[14] The reaction of dibromoalkene with diethyl phosphite in the presence of triethylamine gave a mixture of *E*- and *Z*-isomers,[14a] and the radical reaction with Bu_3SnH initiated by a catalytic amount of triethylborane also gave a mixture.[14b] However, in the preliminary paper, we have revealed the stereoselective hydrogenolysis of 1,1-dibromo-1-alkene with Bu_3SnH catalyzed by $Pd(PPh_3)_4$ to give (*Z*)-1-bromoalkene exclusively.[13] For example, *β*,*β*-dibromo-4-methylstyrene (**1a**, Scheme 2, R = *p*-tolyl, and entry 1 in Table 1) was selectively reduced with 1.2 equiv of Bu_3SnH in the presence of 4 mol % of $Pd(PPh_3)_4$ in benzene

Table 1. Stereoselective Hydrogenolysis of 1,1-Dibromo-1-alkenes 1a−r

entry	dibromoalkene		time (h)	(*Z*)-bromoalkene		yield[a] (%)
1		**1a**	0.4[b]		**2a**	79
2		**1b**	0.3[b]		**2b**	76
3		**1c**	0.3[b]		**2c**	79
4		**1d**	0.3[b]		**2d**	83
5		**1e**	1.0[b]		**2e**	82
6		**1f**	0.5[b]		**2f**	90
7		**1g**	0.4[c]		**2g**	86
8		**1h**	0.1[c]		**2h**	87
9		**1i**	0.3[c]		**2i**	64
10		**1j**	0.1[c]		**2j**	62
11		**1k**	0.1[c]		**2k**	43
12		**1l**	0.3[c]		**2l**	65
13		**1m**	1.0[b]		**2m**	79
14		**1n**	0.2[b]		**2n**	84
15		**1o**	1.0[b]		**2o**	77
16		**1p**	3.5[b]		**2p**	70
17		**1q**	0.3[b]		**2q**	56
18		**1r**	1.0[b]		**2r**	80

[a] Isolated yield. [b] $Pd(PPh_3)_4$ was used as a catalyst. [c] Pd(0) catalyst was generated in situ from $Pd(OAc)_2$ and PPh_3.

at room temperature to give (*Z*)-*β*-bromo-4-methylstyrene (**2a**)[15] in 79% yield. The proton NMR spectrum indicated a coupling constant of 8.1 Hz due to the *cis* olefin of the styryl protons, and none of the corresponding *E*-isomer was detected in a NMR spectrum of the crude reaction mixtures. Aliphatic dibromoalkene, e.g., 1,1-dibromo-4-phenylbutene (**1m**) (Scheme 2, R = phenethyl, and entry 13 in Table 1), was also hydrogenolyzed under the same conditions to provide (*Z*)-1-bromo-4-phenyl-1-butene (**2m**)[16]

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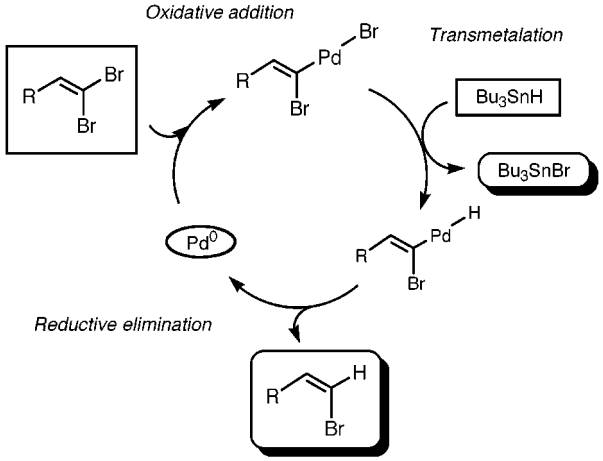
Scheme 3



in 79% yield. These results indicated that this reaction can be used for the synthesis of both aromatic and aliphatic (*Z*)-1-bromo-1-alkenes. The results for 18 dibromoalkenes are shown in Table 1. The starting dibromoalkenes were easily prepared from the corresponding aldehydes with carbon tetrabromide and triphenylphosphine by the standard procedure.[17]

β,*β*-Dibromostyrenes including naphthyl derivatives **1a**−**h** were converted to the corresponding (*Z*)-*β*-bromostyrenes **2a**−**h** in excellent yields with exclusive stereoselectivity (entries 1−8). Even in the presence of acetoxy, hydroxyl, and dimethylamino groups in the molecules, the reaction proceeded quite well (entries 4, 5, and 6). Although pyridyl-substituted dibromo- and bromoethylenes were rather unstable, hydrogenolysis of (dibromovinyl)pyridines gave the corresponding (*Z*)-bromovinylpyridines in 43−64% yields (entries 9, 10, and 11). In contrast, (*Z*)-(bromovinyl)quinoline **2l** was much more stable than pyridyl derivatives and obtained in 65% yield. The reaction of 2-alkyl-, branched alkyl-, and silyloxyalkyl-substituted 1,1-dibromoethylenes, **1m**, **1n**, **1o**, **1p**, **1q**, and **1r**, gave the corresponding (*Z*)-1-bromo-1-alkenes in good yields. The reactions of dibromoalkenes **1q** and **1r**, which have silyl ether and ester moieties, occurred to give **2q** and **2r** in 56 and 80% yields, respectively (entries 17 and 18). All of these results indicate that this hydrogenolysis takes place in a general and stereoselective manner to give *Z*-bromoalkenes.

Reaction Mechanisms. When Bu_3SnD was used as a deuterium source instead of Bu_3SnH for the reactions of **1a** and **1m**, deuterium was introduced at the *trans* position of the product. Since stereoselective hydrogenolysis did not proceed in the absence of Pd catalyst, palladium is essential for stereocontrol. On the other hand, under radical conditions initiated with Et_3B, a 1:1 mixture of *E*- and *Z*-isomers was obtained from **1a** and **1m**, respectively.

The reaction and its selectivity can be explained in terms of the typical mechanism of Pd-catalyzed reactions,[18] as shown in Scheme 3; thus, (i) highly stereoselective oxidative addition of the carbon−bromine bond located at the *trans* position of 1,1-dibromo-1-alkene to Pd(0) forming alkenylpalladium bromide, (ii) transmetalation of this *σ*-palladium complex with Bu_3SnH to generate alkenylpalladium hydride, and (iii) reductive elimination to give (*Z*)-1-bromo-1-alkene and regeneration of Pd(0) species. Eventually, this catalytic process afforded the desired (*Z*)-1-bromo-1-alkene and consumed Bu_3SnH. The high selectivity of the hydrogenolysis may be due to the oxidative addition as a key step, where Pd(0) is inserted into the sterically less hindered carbon−bromine bond. When an excess of Bu_3SnH was used, over-hydrogenolysis occurred to give a terminal alkene. The rate of the oxidative addition of 1,1-dibromo-1-alkenes to Pd(0) was estimated to be 5−20 times faster than that of (*Z*)-1-bromo-1-alkenes. Usually, 1.1−1.2 equiv of Bu_3SnH is required for the reaction, since a slight excess of Bu_3SnH is consumed in the formation of $(Bu_3Sn)_2$ as discussed later.

Table 2. Pd Catalysts for the Hydrogenolysis of 1a

entry	palladium catalysts [a]	time (min)	yield (%) **2a** [b]	yield (%) recovery of **1a** [b]
1	$Pd(PPh_3)_4$	5	87	0
2	$PdCl_2(PPh_3)_2$	60	34	50
3	$PdCl_2(CH_3CN)_2$	30	0	96
4	$Pd_2(dba)_3{\cdot}CHCl_3$	30	0	87
5	$PdCl_2$(dppf)	30	0	93
6	$PdCl_2(PPh_3)_2$+2PPh_3	30	89	0
7	$PdCl_2(CH_3CN)_2$+2PPh_3	30	84	10
8	$Pd_2(dba)_3{\cdot}CHCl_3$+2PPh_3	30	88	0
9	$PdCl_2$	30	0	87
10	$Pd(OAc)_2$	30	18	71
11	$PdCl_2$+4PPh_3 [c]	15	89	0
12	$Pd(OAc)_2$+4PPh_3 [d]	5	91	0

[a] Pd catalyst (4 mol %) was used in toluene. [b] Isolated yields. [c] Stirred for 15 min before use. [d] Stirred for 2 h before use.

Pd Catalyst and Ligand. Initially, we used Pd-$(PPh_3)_4$ as the catalyst, and it was a proper choice for this reaction. Table 2 lists several Pd catalysts and the results of the respective reactions. The reaction of **1a** with $PdCl_2(PPh_3)_2$ gave **2a** in 34% yield along with 50% recovery of **1a**. Surprisingly no hydrogenolysis of **1a** took place in the presence of $PdCl_2(CH_3CN)_2$, $PdCl_2(dba)_3{\cdot}CHCl_3$, or bidentate catalysts $PdCl_2$(dppf), even when an excess of Bu_3SnH was added. In these reactions, $(Bu_3Sn)_2$ was formed. Pd(0) has been reported to catalyze the dimerization of Bu_3SnH to generate hydrogen and $(Bu_3Sn)_2$.[19] Thus, in these particular cases, Pd catalyzed the dimerization of Bu_3SnH, which competed with the oxidative addition of alkenyl bromide to Pd(0), although the dimerization proceeded much slower with Ph_3P ligand. Interestingly, both of these pathways depend on the nature of the Pd catalyst. However, when Ph_3P was added to the reaction mixture using the above catalysts, $PdCl_2(PPh_3)_2$, $PdCl_2(CH_3CN)_2$, or $PdCl_2(dba)_3{\cdot}CHCl_3$, hydrogenolysis proceeded to give **2a** in good yields with excellent selectivity (entries 6, 7, and 8). With the addition of Ph_3P, Pd(0) may have characteristics similar to those of $Pd(PPh_3)_4$. Due to their poor solubility in

(17) Ramirez, F.; Desai, N. B.; McKelvie, N. *J. Am. Chem. Soc.* **1962**, *84*, 1745.

(18) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons Ltd.: Chichester, 1995.

(19) Four, P.; Guibe, F. *J. Org. Chem.* **1981**, *46*, 4439.

Table 3. Ligands for Pd Catalysts and the Hydrogenolysis of 1a

entry	phosphine ligand[a]	2a time (min)	2a yield[b] (%)	2a ratio[c] (Z : E)	recovery[b] of **1a** (%)
1	PPh_3	5	91	100 : 0	0
2	$(p\text{-MePh})_3P$	60	89	100 : 0	0
3	$(p\text{-MePh})PPh_2$	35	86	100 : 0	0
4	$(o\text{-MePh})_3P$	30	0	- : -	86
5	$(C_6F_5)PPh_2$	20	23	100 : 0	74
6	$(C_6F_5)_3P$	20	0	- : -	85
7	Pr^iPPh_2	5	79	85 : 15	10
8	$PrPPh_2$	10	41	87 : 13	40
9	$(Hex^c)_2PPh$	10	41	75 : 25	55
10	$(Hex^c)_3P$	20	32	60 : 40	65
11	Et_3P	5	29	88 : 12	66
12	Bu_3P	15	69	81 : 19	26
13	$(PhCH_2)_3P$	20	0	- : -	83
14	Ph_3As	20	0	- : -	88

[a] Catalysts were generated for 4 mol % of $Pd(OAc)_2$ and 16 mol % of PPh_3 by stirring in toluene for 15 min at room temperature. [b] Isolated yields. [c] Determined by ^1H NMR.

toluene, the reaction with $PdCl_2$ and $Pd(OAc)_2$ gave disappointing results (entries 9 and 10), which were also improved dramatically by the addition of Ph_3P (entries 11 and 12). When $Pd(OAc)_2$ and $PdCl_2$ were premixed with 4 equiv of Ph_3P at room temperature in benzene for 15 and 120 min, respectively, the hydrogenolysis occurred quite smoothly and stereoselectively. This *in situ* preparation of the active Pd catalyst is convenient, practical, and less expensive than the use of $Pd(PPh_3)_4$. In particular, $Pd(OAc)_2$ gave better results than $PdCl_2$ due to its better solubility and to the shorter time needed to generate the active catalyst.

Next, we examined 14 phosphine and arsine ligands. The results are summarized in Table 3. The Pd catalysts were generated by stirring $Pd(OAc)_2$ (4 mol %) and the phosphines (16 mol %) in benzene for 15 min at room temperature. The hydrogenolysis of **1a** with arylphosphines except *o*-tolylphosphine (entry 4) gave **2a** in very good yields with excellent selectivity (entries 1, 2, and 3). When an electron-withdrawing group was introduced to phosphines, e.g., as shown in entry 5, the reaction of diphenyl(pentafluorophenyl)phosphine gave **2a** in 23% yield and 74% recovery of **1a**. The use of tri(pentafluorophenyl)phosphine gave no desired product (entry 6). In these cases, Bu_3SnH was consumed to give $(Bu_3Sn)_2$ instead of **2a** (Scheme 4). The above results show that sterically hindered or electron-deficient arylphosphines are not appropriate for the hydrogenolysis catalyst. An electron-donating phosphine may appear to be preferable. However, when diphenyl(isopropyl or propyl)phosphines, in which one of the phenyl groups of triphenylphosphine was replaced with an isopropyl or propyl group, were used, the yields and selectivities declined along with the recovery of **1a** (entries 7 and 8). Importantly, the formation of *E*-isomers were observed considerably with the use of these alkyl(aryl)phosphines. Other arylalkylphosphines and trialkylphosphines gave similar results (entries 9, 10, 11, and 12). Alkylphosphine may be a good ligand for the formation of $(Bu_3Sn)_2$ and radical hydrogenolysis with Bu_3SnH. In fact, when some BHT (butylated hydroxytoluene; 2,6-di-*tert*-butyl-*p*-cresol) was added in these reactions, the formation of *E*-isomer was completely inhibited, but nevertheless the yield did not improve much. Tribenzylphoshine and triphenylarsine were totally ineffective as ligands for hydrogenolysis (entries 13 and 14).

Scheme 4

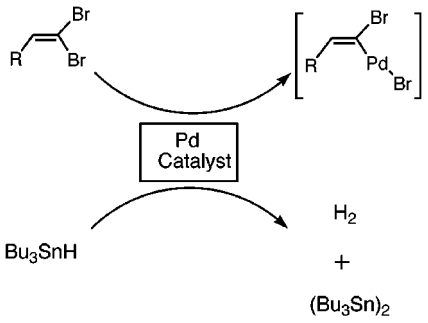


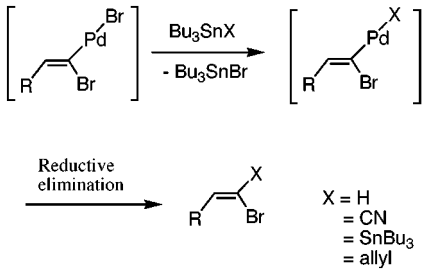
Table 4. Solvent Effect for the Hydrogenolysis of 1a

entry	solvent	reaction time (min)	yield[a] (%)	ratio (Z : E)[b]
1	Benzene	15	79	100 : 0
2	Toluene	5	87	100 : 0
3	Et_2O	15	86	100 : 0
4	DME	15	88	100 : 0
5	THF	15	78	100 : 0
6	Dioxane	10	74	100 : 0
7	EtOAc	35	88	100 : 0
8	$CHCl_3$	120	0	- : -
9	CH_2Cl_2	10	74	100 : 0
10	CH_2Cl_2 (wet)	10	71	100 : 0
11	AcOH	30	27 (69)[c]	70 : 30
12	EtOH	120	79	67 : 33
13	50% AcOH/Toluene	15	80 (14)[c]	100 : 0
14	50% EtOH/Toluene	15	87	100 : 0
15	EtOH (+ BHT)	120	78 (17)[c]	100 : 0

[a] Isolated yields. [b] Determined by ^1H NMR. [c] Recovery of the starting material.

Solvents. We examined several common solvents in this reaction. The results are listed in Table 4. A wide range of solvents are available for the hydrogenolysis. Benzene, toluene, ether, DME, THF, dioxane, and ethyl acetate could be used and gave *Z*-alkene exclusively (entries 1−7). Halogen-containing solvents generally cannot be used for the reaction of Bu_3SnH. In fact, the reaction in $CHCl_3$ did not give any **2a**, because Bu_3SnH reacted with $CHCl_3$ and was consumed very quickly (entry 8). However, the radical reaction with CH_2Cl_2 was slower than that with $CHCl_3$ and gave the desired hydrogenolysis (entry 9). The hydrogenolysis also occurred under wet conditions. Since wet solvents, e.g., wet CH_2Cl_2 (entry 10), gave yields similar to those under anhydrous conditions, the presence of a small amount of water did not influence the hydrogenolysis. The reaction of **1a** in ethanol and acetic acid took longer and gave **2a** in poor yields with unsatisfactory selectivities (entries 11 and 12). In these reactions, radical hydrogenolysis might compete with Pd-catalyzed hydrogenolysis due to the poor solubility of $Pd(PPh_3)_4$ in these solvents. This

Scheme 5

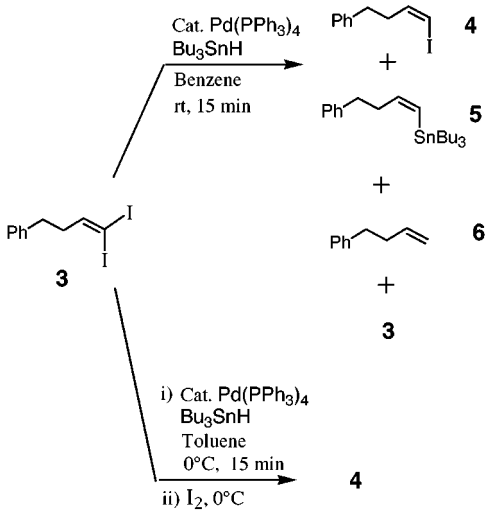


problem was nicely solved by the addition of toluene to the reaction mixture as a cosolvent (entries 13 and 14). Furthermore, this radical hydrogenolysis was also completely inhibited by the addition of BHT. This radical scavenger is effective when radical hydrogenolysis occurs. Under these conditions, even $CHCl_3$ can be used as a solvent.

Hydride Sources. Since Bu_3SnH is toxic, it is desirable to find other hydride sources. Despite our efforts to examine other reducing reagents, such as a combination of HCOOH and triethylamine, silyl hydrides including Et_3SiH and $(Me_3Si)_3SiH$, and boranes including catecholborane, 9-BBN, and BH_3 complexes, they were totally inactive for this hydrogenolysis. Only some metal borohydrides gave the desired (*Z*)-1-bromo-1-alkene. $LiBEt_3H$ was the best among them and gave (*Z*)-1-bromo-1-alkenes in yields of 50−65%, but was less satisfactory than Bu_3SnH. $NaBH_4$, $Na(CN)BH_3$, and other sodium alkoxyborohydrides were less reactive than Superhydride. Although less-toxic Ph_3SnH also gave the desired *Z*-bromoalkene exclusively, the reaction rate was slower than that with Bu_3SnH. At this stage, Bu_3SnH was found to be the best hydride reagent and delivered its hydrogen on Sn to Pd very smoothly. If this transmetalation works for other Sn−X bonds to a Pd center and the subsequent reductive elimination goes well, a new X group would be introduced to an sp^2 alkenyl carbon center steroselectively instead of *trans* bromide, as shown in Scheme 5. Although Bu_3SnCN, $(Bu_3Sn)_2$, and Bu_3Sn(allyl) were tested as other Bu_3Sn−X species, substitution did not take place.

Reactivity and Selectivity. The Pd-catalyzed transformation of alkenyl halides to alkene has been reported by Oshima et al.,[20] in which hydrogenolysis proceeded in the presence of Bu_3SnH. Alkenyl iodide was suitable as the substrate, while alkenyl bromide was not. No reaction occurred with alkenyl chloride. The hydrogenolysis of alkenyl bromide required slow addition of Bu_3SnH at a higher temperature and resulted in a poor yield. The hydrogenolysis of 1,1-dibromoalkenes took place much more mildly at room temperature, as we have described above. The reaction of 1,1-dichloro-3-phenyl-1-butene did not occur under the same reaction conditions, even in refluxing benzene using the slow addition of Bu_3SnH. On the other hand, 1,1-diiodo-3-phenyl-1-butene (**3**) reacted with Bu_3SnH (1.2 equiv) in the presence of Pd catalyst at room temperature. However, this reaction gave a mixture of (*Z*)-1-iodo-1-butene (**4**) in 27% yield, (*Z*)-1-tributylstannyl-1-butene (**5**)[16] in 11% yield, 4-phenyl-1-butene (**6**) in 3% yield, and 27% recovery of **3** (Scheme 6). The total yields improved slightly when

Scheme 6



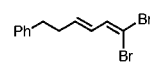
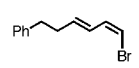
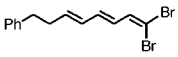
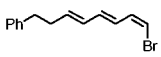
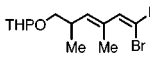
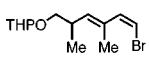
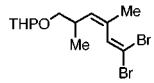
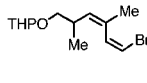
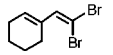
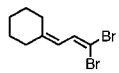
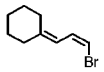
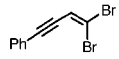
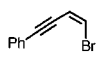
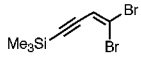
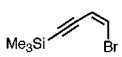
the reaction was carried out at 0 °C in toluene. The formation of **5** was unexpected. This formation was considered to be due to the reaction of **4** with $(Bu_3Sn)_2$ or Bu_3SnI, but the yield of **5** did not increase when they were added to the reaction mixtures. The iodoalkene **4** was obtained in 62% yield when the crude reaction extract was treated with iodine in $CHCl_3$ solution. Nonetheless, the hydrogenolysis of 1,1-diiodo-1-alkene was disappointing, and the mechanism of the formation of (*Z*)-1-tributylstannyl-1-butene was not clear.

Hydrogenolysis of Conjugated 1,1-Dibromoalkenes and 2,2-Disubstituted 1,1-Dibromoalkenes. Although (*Z*)-1-bromo-1-alkenes are certainly useful for *E,Z*-diene synthesis as a geometrically pure building block, 2-alkenyl- or 2-alkynyl-substituted (*Z*)-1-bromo-1-alkenes would be much more valuable for the synthesis of conjugated polyenes or enynes. The results of hydrogenolysis of 1,1-dibromopolyenes and 1,1-dibromoenynes are listed in Table 5. The reaction of (*E*)-1,1-dibromo-6-phenyl-1,3-hexadiene (**7a**) gave (1*Z*,3*E*)-1-bromo-6-phenyl-1,3-hexadine (**8a**) in an 82% yield (entry 1). (3*E*,5*E*)-1,1-Dibromo-1,3,5-triene **7b** gave (1*Z*,3*E*,5*E*)-1-bromo-1,3,5-triene **8b** in 74% yield (entry 2). No other stereoisomers were formed in these reactions. The reactivity of conjugated dibromoalkenes seemed to be greater than that of simple 1,1-dibromo-1-alkenes. Therefore, to suppress over-hydrogenolysis, a slight excess of Bu_3SnH (1.02−1.05 equiv) should be used relative to the substrates. Four additional dienes in entries 3−6, including geometrical isomers, gave the corresponding 1-bromo-1,3-dienes stereoselectively. Enynes **8g** and **8h** were obtained in 63 and 69% yields from dibromoenynes **7g** and **7h**, respectively.

Next, we were interested in the hydrogenolysis of 2,2-disubstituted 1,1-dibromoalkenes, which would give trisubstituted bromoolefines. The results for six dibromoalkenes are shown in Table 6. Due to steric hindrance of the vicinal carbon−carbon bonds, the fully substituted 1,1-dibromoolefin was anticipated to show poor reactivity. In fact, the yields of these reactions were unsatisfactory except for that with **9a**, from which **10a** was obtained in 82% yield (entry 1). In this case, the carbon−bromine bond was located *gauche* between the axial and equatorial carbon−hydrogen bonds. However, in other cases, the reactions were influenced by large steric effect of the substituent. The reaction of dialkyl-substituted com-

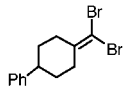
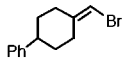
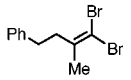
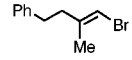
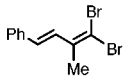
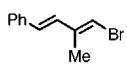
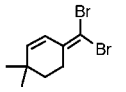
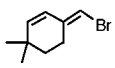
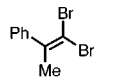
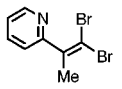
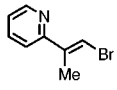
(20) Taniguchi, M.; Takeyama, Y.; Fugami, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2593.

Table 5. Stereoselective Hydrogenolysis of Conjugated 1,1-Dibromo-1-alkenes 7a−h

entry	dibromoalkene		time (h)	(*Z*)-bromoalkene		yield[a] (%)
1		**7a**	1.0[b]		**8a**	82
2		**7b**	0.3[b]		**8b**	74
3		**7c**	0.7[b]		**8c**	82
4		**7d**	0.5[b]		**8d**	88
5		**7e**	0.5[b]		**8e**	66
6		**7f**	0.8[b]		**8f**	90
7		**7g**	0.3[b]		**8g**	63
8		**7h**	1.0[b]		**8h**	69

[a] Isolated yield. [b] $Pb(PPh_3)_4$ (4 mol %) was used as catalyst.

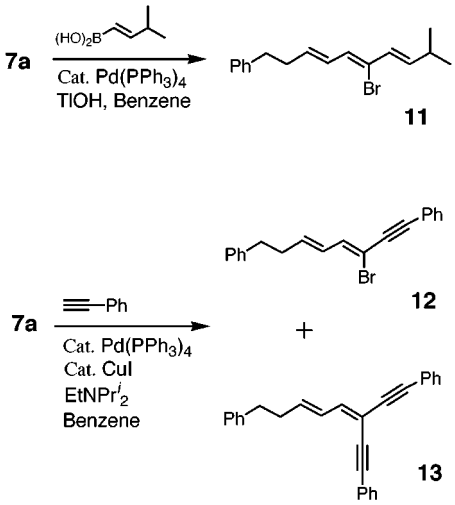
Table 6. Hydrogenolysis of Fully Substituted 1,1-Dibromo-1-alkenes 9a−f

entry	dibromoalkene	time (h)	(*Z*)-bromoalkene	yield[a] (%)	ratio[b]
1	 **9a**	2[c]	 **10a**	82	—
2	 **9b**	12[c]	 **10b**	trace	—
3	 **9c**	12[c]	 [d] **10c**	40	3 : 1
4	 **9d**	9[c]	 [d] **10d**	58	2 : 1
5	 **9e**	12[c]	 [d] **10e**	31	30 : 1
6	 **9f**	7[c]	 [d] **10f**	10	2 : 1

[a] Isolated yield. [b] Determined by ^1H NMR. [c] $Pd(PPh_3)_4$ (4 mol %) was used as catalyst. [d] The structure of the predominant isomer was indicated.

pound **9b** did not occur (entry 2). Dibromodienes **9c** and **9d** gave bromodienes **10c** and **10d** in 40 and 58% yields respectively, in which a carbon−bromine bond beside an sp^2 carbon of a cyclohexene ring is more favorably hydrogenated than that beside an sp^3 carbon (entries 3 and 4). In the case of **9e**, the *Z*-isomer of **10e** was predominantly formed in 31% yield. The stereochemical assignments of these alkenes were performed by careful NOE studies by NMR. The bulkiness of the phenyl group might affect the reaction to give a selective ratio of 30:1 (*Z*:*E*). On the other hand, the coordinating effect of the pyridine nitrogen atom contributed to the insertion of Pd, resulting in the preferred formation of the *E*-isomer of **10f** in a 2:1 ratio.

Scheme 7



Pd-Catalyzed Cross-Coupling Reaction. Although substitution of the Pd-bromine bond by Bu_3SnCN or Bu_3Sn(allyl) failed for 1,1-dibromo-1-alkene, that of alkenylboronic acid has been reported by Roush et al.[21] This Suzuki reaction[9b] of 1,1-dibromo-1,3-diene also occurred well under the TlOH-mediated conditions.[22] Thus, a mixture of **7a** with (*E*)-isopentenylboronic acid (1.2 equiv) in the presence of a catalytic amount of $Pd(PPh_3)_4$ and aqueous TlOH gave bromotriene **11** in 74% yield as a single stereoisomer (Scheme 7). On the other hand, reaction of **7a** with phenylacetylene (1.2 equiv) under Sonogashira conditions[23] gave a mixture of monoalkynyl- and dialkynyldienes **12** and **13** in 36 and 33% yields, along with 17% recovery of **7a**. These results indicate that the chemo- and stereoselectivites of 1,1-dibromo-1,3-dienes are high in Suzuki coupling, but rather low in Sonogashira coupling.

Although the Suzuki reaction of **7a** proceeded at room temperature, the reaction of **8a** with the same boronic acid did not occur under the same conditions. On the other hand, when the reaction was conducted in refluxing benzene in the presence of sodium ethoxide under typical Suzuki conditions,[24] (*E*,*Z*,*E*)-triene **14** was formed exclusively in 85% yield. If the bromotriene **11** can be debrominated with Bu_3SnH stereospecifically, (*E*,*E*,*E*)-triene, which is an isomer of **14**, would be produced. Unfortunately, the hydrogenolysis of **11** was unsuccessful due to the poor reactivity of the sterically hindered carbon−bromine bond. Sonogashira coupling of **8a** with trimethylsilylacetylene took place very nicely to give alkynyl *E*,*Z*-diene **15** in 93% yield stereospecifically. However the Heck reaction of **8a** with methyl acrylate

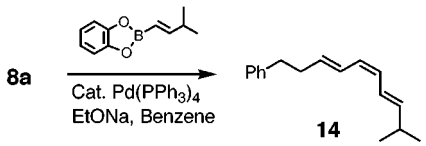
(21) (a) Roush, W. R.; Brown, B. B.; Drozda, S. E. *Tetrahedron Lett.* **1988**, *29*, 3541. (b) Roush, W. R.; Moriarty, K. J.; Brown, B. B. *Tetrahedron Lett.* **1990**, *31*, 6509.

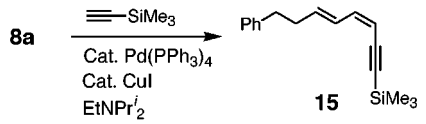
(22) Uenishi, J.; Beau, J.-M.; Armstrong, R. W.; Kishi, Y. *J. Am. Chem. Soc.* **1987**, *109*, 4756.

(23) Sonogashira, K.; Tohda, Y. Hagihara,. N. *Tetrahedron Lett.* **1975**, 4467.

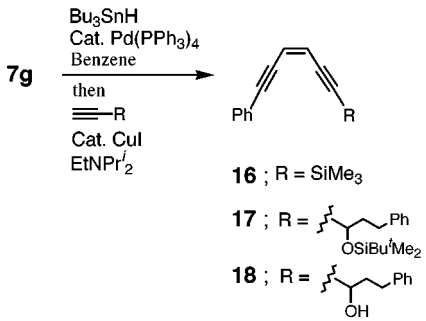
(24) The typical Suzuki conditions: *Organic Syntheses*; Wiley: New York, 1993; Collect. Vol. 8, 532.

Scheme 8





Scheme 9



exclusively gave *all-E*-trienecarboxylic acid ester, where the product might isomerize after the coupling.[25]

The hydrogenolysis, Suzuki, and Sonogashira cross-coupling reactions proceeded under Pd catalysts with a retention of configuration. If Pd(0) species are still alive in the final stage of the hydrogenolysis, and its single byproduct Bu_3SnBr does not disturb the successive cross-coupling, one-pot reaction may be possible. If these processes work well, polyenes and enynes could be obtained directly from 1,1-dibromo-1-alkenes without the isolation of unstable bromopolyenes or bromoenynes. Therefore, a one-pot reaction would be quite beneficial. As soon as the hydrogenolysis of **7a** was completed, the reaction mixture was subjected to a one-pot Suzuki reaction. The triene **14** was obtained in 54% stereoselectively. In the same manner, the one-pot Sonogashira reaction of **7a** *via* **8a** gave dienyne **15** in 61% yield (Scheme 8).

The success of the one-pot Sonogashira coupling from dibromoenyne allows the facile preparation of (*Z*)-3-hexene-1,5-diynes from (*Z*)-1,1-dibromo-1-hexen-3-yne with a Pd catalyst. Thus, after the hydrogenolysis of **7g**, product **8g** was coupled with trimethylsilylacetylene to give enediyne **16** in 70% yield. Coupling reactions with silyloxyalkyl- and hydroxyalkyl-substituted alkynes gave enediynes **17** and **18** in 64 and 54% yields, respectively (Scheme 9).

In conclusion, we have reported a mild and highly stereoselective hydrogenolysis of 1,1-dibromo-1-alkenes. This reaction is potentially useful for the general preparation of (*Z*)-1-bromo-1-alkenes. Since (*Z*)-1-bromo-1-alkenes including conjugated alkenes were obtained in geometrically pure form, they could be used as a good building block for *Z*-alkene synthesis. Pd-catalyzed cross-coupling reactions of the (*Z*)-1-bromo-1-alkenes provided polyenes or enynes bearing a *Z*-alkenyl unit in good to excellent yields stereospecifically. Several conjugated polyenes containing a *Z*-alkenyl unit have been found in natural products. Since they are mostly unstable, mild and stereospecific conditions are essential for their synthesis. With regard to the current method, we have already demonstrated the potency of the combination of selective hydrogenolysis and a mild Pd-catalyzed coupling reaction for the synthesis of unstable polyene natural products, e.g., (11*Z*)-retinal[26] and (2*Z*,4*E*,6*E*)-dehydrodendrolasin.[27]

(25) The chemical yield was less than 20% under Jeffery's improved conditions. See: Jeffery, T. *Tetrahedron Lett.* **1985**, *26*, 2667.

Experimental Section

General Procedures. All air- or moisture-sensitive reactions were carried out in flame-dried glassware under Ar atmosphere. Solvents were distilled freshly over sodium/benzophenone ketyl for THF, ether, and benzene, over P_2O_5 for CH_2Cl_2 and $CHCl_3$, over CaH_2 for hexane, toluene, DME, dioxane, and EtOH under a nitrogen atmosphere. Thin-layer chromatography (TLC) was performed with Merck $60F_{254}$ precoated silica gel plates. Column chromatography was carried out using Wako neutral alumina (200 mesh) and Merck silica gel 60 (70−230 mesh). Ph_3P was added to the NMR samples for stabilization of unstable 1-bromo-1-alkenes.

Typical Procedure of Hydrogenolysis. (i) $Pd(PPh_3)_4$-Catalyzed Reaction. To a stirred solution of dibromoalkene (1 mmol) in dry benzene or toluene (10 mL) were added $Pd(PPh_3)_4$ (4 mol %) and Bu_3SnH (1.0−1.2 mmol) successively, and the mixture was stirred at room temperature for the time indicated in the tables. After the reaction was completed, it was diluted with hexane (30−50 mL) and washed with water and brine. The hexane extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by column chromatography. If it was not specified, the column chromatography was performed with alumina using hexane as an eluent.

(ii) *In Situ* Generation of Pd(0) Species by a Combination of $Pd(OAc)_2$ and Ph_3P. An anhydrous toluene (8 mL) was added to a mixture of PPh_3 (0.16 mmol) and $Pd(OAc)_2$ (0.04 mmol) at room temperature under an Ar atmosphere, and the mixture was stirred for 15 min to generate a light yellow solution. Dibromoalkene (1 mmol) in toluene (2 mL) and Bu_3SnH (1.0−1.2 mmol) were added to the mixture. The reaction was continued for the time indicated in the tables, and the workup and purification were performed by the same procedure as described in the use of $Pd(PPh_3)_4$ catalyst.

(*Z*)-β-Bromo-4-methylstyrene (2a):[15] colorless syrup; R_f = 0.55 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (3H, s), 6.36 (1H, d, *J* = 8.1 Hz), 7.02 (1H, d, *J* = 8.1 Hz), 7.17 (2H, d, *J* = 8.1 Hz), 7.58 (2H, d, *J* = 8.1 Hz).

(*Z*)-β-Bromostyrene (2b):[28] colorless oil; R_f = 0.55 (hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 6.43 (1H, d, *J* = 8.1 Hz), 7.07 (1H, d, *J* = 8.1 Hz), 7.30−7.40 (3H, m), 7.66−7.69 (2H, m).

(*Z*)-β-Bromo-2-methylstyrene (2c):[29] colorless oil; R_f = 0.47 (hexane); ^1H NMR (300 MHz, $CDCl_3$) 2.28 (3H, s), 6.53 (1H, d, *J* = 7.8 Hz), 7.15 (1H, d, *J* = 7.8 Hz), 7.18−7.26 (3H, m), 7.56 (1H, m).

(*Z*)-4-Acetoxy-β-bromostyrene (2d): purified by silica gel column chromatography eluted with 10% EtOAc in hexane; colorless crystals; mp 46−47 °C (hexane); R_f = 0.53 (20% EtOAc in hexane); ^1H NMR (300 MHz, $CDCl_3$) δ 2.32 (3H, s), 6.44 (1H, d, *J* = 8.1 Hz), 7.05 (1H, d, *J* = 8.1 Hz), 7.10 (2H, dt, *J* = 8.7, 2.0 Hz), 7.72 (2H, dt, *J* = 8.7, 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 106.5, 121.4, 130.1, 131.4, 132.5, 150.3, 169.3; MS (EI) *m/z* (rel intensity) 242, 240 (M^+, 15, 15), 200 (base), 198 (99), 119 (9), 78 (71). Anal. Calcd for $C_{10}H_9O_2Br$: C, 49.82; H, 3.76. Found: C, 49.86; H, 3.56.

(26) Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Wada, A.; Ito, M. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 320.

(27) Uenishi, J.; Kawahama, R.; Tanio, A.; Wakabayashi, S.; Yonemitsu, O *Tetrahedron* **1997**, *53*, 2439.

(28) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424.

(29) Galamb, V.; Alper, H. *Tetrahedron Lett.* **1983**, *24*, 2965.

(*Z*)-β-Bromo-4-hydroxystyrene (2e): purified by silica gel column chromatography eluted with 10% EtOAc in hexane; colorless crystals; mp 71−72 °C (hexane); R_f = 0.42 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.01 (1H, s), 6.31 (1H, d, J = 8.1 Hz), 6.84 (2H, dm, J = 8.7 Hz), 6.99 (1H, d, J = 8.1 Hz), 7.63 (2H, dm, J = 8.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 103.7, 114.8, 127.3, 130.4, 131.3, 155.5; MS (EI) *m*/*z* (rel intensity) 200, 198 (M^+, 92, 88), 76 (base). Anal. Calcd for C_8H_7OBr: C, 48.27; H, 3.54. Found: C, 48.37; H, 3.36.

(*Z*)-β-Bromo-4-(*N*,*N*-dimethylamino)styrene (2f):[30] eluted with 5% EtOAc in hexane on alumina; pale yellow crystals; mp 49−50 °C (hexane); R_f = 0.36 (10% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.98 (6H, s), 6.16 (1H, d, J = 8.0 Hz), 6.70 (2H, d, J = 9.1 Hz), 6.93 (1H, d, J = 8.0 Hz), 7.65 (2H, d, J = 9.1 Hz).

(*Z*)-2-(β-Bromovinyl)naphthalene (2g): eluted with 5% EtOAc in hexane on alumina; Colorless crystals; mp 77−78 °C (MeOH); R_f = 0.36 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (1H, d, J = 8.1 Hz), 7.24 (1H, d, J = 8.1 Hz), 7.46−7.54 (2H, m), 7.80−7.90 (4H, m), 8.17 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 106.7, 126.3, 126.4, 126.5, 127.6, 127.7, 128.3, 128.6, 132.4, 133.0, 133.1, 136.9; MS (EI) *m*/*z* (rel intensity) 234, 232 (M^+, 93, 94), 153 (81), 152 (base). Anal. Calcd for $C_{12}H_9Br$: C, 61.83; H, 3.89. Found: C, 61.74; H, 3.78.

(*Z*)-1-(β-Bromovinyl)naphthalene (2h):[31] eluted with 2.5% EtOAc in hexane on alumina; colorless oil; R_f = 0.42 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.75 (1H, d, J = 8.0 Hz), 7.48−7.58 (3H, m), 7.60 (1H, d, J = 8.0 Hz), 7.71 (1H, dt, J = 7.2, 1.1 Hz), 7.83−7.94 (3H, m).

(*Z*)-2-(β-Bromovinyl)pyridine (2i):[32] purified by silica gel column chromatography eluted with 30% EtOAc in hexane; light brown oil; R_f = 0.25 (20% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.67 (1H, d, J = 8.5 Hz), 7.23 (1H, ddd, J = 7.8, 4.8, 1.1 Hz), 7.26 (1H, d, J = 8.5 Hz), 7.73 (1H, td, J = 7.8, 1.8 Hz), 8.04 (1H, dt, J = 7.8, 1.1 Hz), 8.64 (1H, dt, J = 4.8, 1.2 Hz).

(*Z*)-3-(β-Bromovinyl)pyridine (2j):[32] purified by silica gel column chromatography eluted with 20% EtOAc in hexane; colorless oil; R_f = 0.28 (30% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (1H, d, J = 8.2 Hz), 7.06 (1H, d, J = 8.2 Hz), 7.31 (1H, dd, J = 8.0, 4.8 Hz), 8.14 (1H, dt, J = 8.0, 1.8 Hz), 8.54 (1H, dd, J = 4.8, 1.5 Hz), 8.76 (1H, d, J = 2.0 Hz).

(*Z*)-4-(β-Bromovinyl)pyridine (2k):[32] purified by silica gel column chromatography eluted with 40% EtOAc in hexane; colorless oil; R_f = 0.32 (40% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.68 (1H, d, J = 8.3 Hz), 7.05 (1H, d, J = 8.3 Hz), 7.56 (2H, dd, J = 4.5, 1.7 Hz), 8.64 (2H, dd, J = 4.5, 1.7 Hz).

(*Z*)-2-(β-Bromovinyl)quinoline (2l): purified by silica gel column chromatography eluted with 10% EtOAc in hexane; yellow oil; R_f = 0.36 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (1H, d, J = 8.4 Hz), 7.46 (1H, d, J = 8.4 Hz), 7.55 (1H, td, J = 8.0, 0.9 Hz), 7.71 (1H, td, J = 8.0, 1.4 Hz), 8.01 (1H, dd, J = 8.0, 0.7 Hz), 8.08 (1H, d, J = 8.0 Hz), 8.12 (1H, d, J = 8.6 Hz), 8.19 (1H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.4, 121.3, 126.9, 127.3, 127.5, 129.3, 129.8, 133.8, 135.9, 148.0, 154.3; MS (EI) *m*/*z* (rel intensity) 235, 233 (M^+, 20, 20), 154 (base), 128 (39); HRMS calcd for $C_{11}H_8NBr$ M^+ 232.9840, 234.9819, found *m*/*z* 232.9821, 234.9789.

(*Z*)-1-Bromo-4-phenyl-1-butene (2m):[16] colorless oil; R_f = 0.45 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.52 (2H, td, J = 7.3, 6.9 Hz), 2.72 (2H, t, J = 7.3 Hz), 6.11 (1H, q, J = 6.9 Hz), 6.17 (1H, dt, J = 6.9, 1.1 Hz), 7.17−7.32 (5H, m).

(*Z*)-1-Bromo-3-phenyl-1-butene (2n):[33] colorless oil; R_f = 0.48 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (3H, d, J = 7.3 Hz), 4.02 (1H, qd, J = 7.3, 7.0 Hz), 6.19 (1H, q, J = 7.0 Hz), 6.22 (1H, d, J = 7.0 Hz), 7.19−7.33 (5H, m).

(*Z*)-1-Bromo-3-cyclohexylethylene (2o):[28] colorless oil; R_f = 0.80 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05−1.40 (5H, m), 1.60−1.78 (5H, m), 2.50 (1H, m), 5.92 (1H, dd, J = 8.7, 7.0 Hz), 6.04 (1H, d, J = 7.0 Hz).

(*Z*)-1-Bromo-4,8-dimethyl-1,7-nonadiene (2p):[31] colorless oil; R_f = 0.85 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91 (3H, d, J = 6.7 Hz), 1.13−1.41 (2H, m), 1.61 (3H, s), 1.55−1.65 (1H, m), 1.68 (3H, s), 1.92−2.25 (4H, m), 5.09 (1H, tm, J = 7.1 Hz), 6.09 (1H, q, J = 7.0 Hz), 6.19 (1H, dt, J = 7.0, 1.5 Hz).

(*Z*)-1-Bromo-3-(*tert*-butyldiphenylsilyl)oxy-5-phenyl-1-pentene (2q): eluted with 5% EtOAc in hexane on alumina; colorless oil; R_f = 0.41 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (9H, s), 1.74−1.94 (2H, m), 2.54−2.65 (2H, m), 4.70 (1H, qd, J = 7.3, 1.1 Hz), 6.01 (1H, dd, J = 7.3, 1.1 Hz), 6.20 (1H, t, J = 7.3 Hz), 7.05−7.09 (2H, m), 7.14 (1H, m), 7.19−7.24 (2H, m), 7.31−7.44 (6H, m), 7.62−7.70 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 27.0, 30.9, 38.9, 71.6, 106.8, 125.7, 127.5, 127.6, 128.3, 128.3, 129.6, 129.6, 133.9, 135.8, 135.9, 137.7, 137.7, 142.1; MS (EI) *m*/*z* (rel intensity) 423, 421 (M^+ − 57, 48, 45), 341 (25), 263 (18), 261 (16), 199 (base); HRMS calcd for $C_{23}H_{22}OSiBr$ $M^+ - C_4H_9$ 423.0603, 421.0623, found *m*/*z* 423.0588, 421.0641.

Methyl (*Z*)-11-bromo-10-undecenoate (2r):[34] eluted with 5% EtOAc in hexane on alumina; colorless oil; R_f = 0.43 (10% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26−1.41 (10H, m), 1.58−1.64 (2H, m), 2.14−2.22 (2H, m), 2.30 (2H, t, J = 7.6 Hz), 3.66 (3H, s), 6.07 (1H, q, J = 6.6 Hz), 6.13 (1H, d, J = 6.6 Hz).

(1*Z*,3*E*)-1-Bromo-6-phenyl-1,3-hexadiene (8a): colorless oil; R_f = 0.34 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (2H, td, J = 7.6, 6.9 Hz), 2.75 (2H, t, J = 7.6 Hz), 5.96 (1H, dt, J = 15.2, 6.9 Hz), 6.05 (1H, d, J = 7.1 Hz), 6.42 (1H, ddd, J = 15.2, 10.1, 1.1 Hz), 6.58 (1H, dd, J = 10.1, 7.1 Hz), 7.15−7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.7, 35.3, 106.0, 126.0, 126.5, 128.4, 128.4, 132.6, 138.3, 141.5; MS (EI) *m*/*z* (rel intensity) 238, 236 (M^+, 27, 23), 157 (42), 147 (2), 145 (2), 91 (base); HRMS calcd for $C_{12}H_{13}Br$ M^+ 238.0180, 236.0201, found *m*/*z* 238.0188, 236.0185.

(1*Z*,3*E*,5*E*)-1-Bromo-8-phenyl-1,3,5-octatriene (8b): yellow oil; R_f = 0.33 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (2H, td, J = 7.4, 7.0 Hz), 2.72 (2H, t, J = 7.4 Hz), 5.86 (1H, dt, J = 15.0, 7.0 Hz), 6.11 (1H, d, J = 7.1 Hz), 6.18 (1H, ddt, J = 15.0, 9.9, 1.5 Hz), 6.36 (1H, dd, J = 15.0, 9.2 Hz), 6.43 (1H, dd, J = 15.0, 9.2 Hz), 6.62 (1H, dd, J = 9.9, 7.1 Hz), 7.16−7.35 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.7, 35.4, 107.4, 125.9, 126.2, 128.3, 128.4, 130.7, 132.6, 136.5, 136.7, 141.5; MS (EI) *m*/*z* (rel intensity) 264, 262 (M^+, 96, 97), 183 (46), 173 (74), 171 (77), 156 (41), 91 (base); HRMS calcd for $C_{14}H_{15}Br$ M^+ 264.0337, 262.0357, found *m*/*z* 264.0320, 262.0347.

(1*Z*,3*E*)-1-Bromo-3,5-dimethyl-6-(2-tetrahydropyranyl)oxy-1,3-hexadiene (8c): eluted with 2.5% EtOAc in hexane on alumina; colorless oil; R_f = 0.25 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (3/2H, d, J = 7.0 Hz) and 1.04 (3/2H, d, J = 6.6 Hz), 1.46−1.88 (6H, m), 1.98 (3/2H, d, J = 1.5 Hz) and 1.99 (3/2H, d, J = 1.5 Hz), 2.80 (1H, m), 3.26 (1H, m), 3.50 (1H, m), 3.60 (1H, m), 3.86 (1H, m), 4.60 (1H, m), 5.51 (1/2H, d, J = 9.2 Hz) and 5.53 (1/2H, d, J = 8.8 Hz), 6.01 (1/2H, d, J = 8.1 Hz) and 6.02 (1/2H, d, J = 8.1 Hz), 6.53 (1/2H, d, J = 8.1 Hz) and 6.54 (1/2H, d, J = 8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 17.2 and 17.3, 19.4, 25.5, 30.6 and 30.6, 33.1 and 33.2, 62.1, 71.7 and 71.9, 98.7 and 98.8, 102.6 and 102.7, 131.6 and 131.7, 136.2, 137.9 and 138.1; MS (EI) *m*/*z* (rel intensity) 290, 288 (M^+, 2, 2), 209 (2), 167 (8), 148 (9), 146 (9), 101 (20), 85 (base); HRMS calcd for $C_{13}H_{21}O_2Br$ M^+ 290.0705, 288.0725, found *m*/*z* 290.0683, 288.0702.

(1*Z*,3*Z*)-1-Bromo-3,5-dimethyl-6-(2-tetrahydropyranyl)oxy-1,3-hexadiene (8d): eluted with 5% EtOAc in hexane on alumina; colorless oil; R_f = 0.30 (7.5% EtOAc in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (3/2H, d, J = 6.7 Hz) and 1.01 (3/2H, d, J = 6.6 Hz), 1.46−1.86 (6H, m), 1.96 (3H, s),

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2.65 (1H, m), 3.23 (1H, m), 3.48 (1H, m), 3.55 (1H, m), 3.84 (1H, m), 4.56 (1/2H, d, J = 3.7 Hz) and 4.57 (1/2H, d, J = 2.9 Hz), 5.25 (1H, m), 6.20 (1H, d, J = 7.7 Hz), 6.81 (1H, d, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.4 and 17.5, 19.4 and 19.4, 22.4, 25.5, 30.6 and 30.6, 33.8 and 33.9, 62.0 and 62.1, 71.7 and 71.9, 98.5 and 98.7, 106.8 and 106.8, 131.1 and 131.2, 132.4, 134.4 and 134.6; MS (EI) m/z (rel intensity) 290, 288 (M^+, 3, 3), 209 (4), 189 (3), 187 (3), 85 (base); HRMS calcd for $C_{13}H_{21}O_2Br$ M^+ 290.0705, 288.0725, found m/z 290.0724, 288.0735.

(*Z*)-1-[2-(1-Bromovinyl)]cyclohexene (8e): colorless oil; R_f = 0.80 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53−1.70 (4H, m), 2.05−2.15 (2H, m), 2.40−2.47 (2H, m), 5.97 (1H, d, J = 8.4 Hz), 6.00 (1H, br s), 6.49 (1H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 22.5, 25.8, 28.0, 101.4, 132.4, 134.1, 135.0; MS (EI) m/z (rel intensity) 188, 186 (M^+, 23, 23), 107 (90), 79 (base); HRMS calcd for $C_8H_{11}Br$ M^+ 188.0024, 186.0044, found m/z 187.9998, 186.0040.

(*Z*)-1-Bromo-4-cyclohexylidene-1,3-butadiene (8f): colorless oil; R_f = 0.65 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52−1.70 (6H, m), 2.17−2.24 (2H, m), 2.24−2.32 (2H, m), 6.06 (1H, d, J = 7.1 Hz), 6.10 (1H, dd, J = 10.6, 1.5 Hz), 6.86 (1H, dd, J = 10.6, 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 27.7, 28.4, 30.1, 37.5, 106.3, 117.7, 128.0, 148.7; MS (EI) m/z (rel intensity) 202, 200 (M^+, 13, 13), 181 (40), 169 (45), 151 (10), 131 (44), 121 (35), 119 (46), 69 (base); HRMS calcd for C_9H_{13}-Br M^+ 202.0180, 200.0201, found m/z 202.0198, 200.0213.

(*Z*)-1-Bromo-4-phenyl-1-buten-3-yne (8g): colorless oil; R_f = 0.34 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.53 (1H, d, J = 7.6 Hz), 6.65 (1H, d, J = 7.6 Hz), 7.32−7.38 (3H, m), 7.48−7.54 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.2, 97.1, 115.7, 117.8, 122.7, 128.4, 128.8, 131.7; MS (EI) m/z (rel intensity) 208, 206 (M^+, 60, 62), 127 (76), 101 (5), 78 (base); HRMS calcd for $C_{10}H_7Br$ M^+ 207.9711, 205.9731, found m/z 207.9736, 205.9745.

(*Z*)-1-Bromo-4-trimethylsilyl-1-buten-3-yne (8h): colorless oil; R_f = 0.46 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.23 (9H, s), 6.32 (1H, d, J = 7.7 Hz), 6.60 (1H, d, J = 7.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.3, 99.9, 103.5, 115.7, 118.8; MS (EI) m/z (rel intensity) 204, 202 (M^+, 4, 4), 122 (1), 107 (13), 69 (base); HRMS calcd for $C_7H_{11}BrSi$ M^+ 203.9793, 201.9813, found m/z 203.9799, 201.9821.

1-(Bromomethylidene)-4-phenylcyclohexane (10a): colorless crystals; mp 27−28 °C; R_f = 0.45 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45−1.60 (2H, m), 1.90−2.06 (3H, m), 2.21 (1H, m), 2.50 (1H, dm, J = 13.7 Hz), 2.70 (1H, tt, J = 12.2, 3.2 Hz), 3.03 (1H, dm, J = 13.7 Hz), 5.93 (1H, t, J = 1.8 Hz), 7.16−7.33 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.9, 33.8, 35.0, 35.2, 44.1, 98.3, 126.2, 126.8, 128.4, 143.8, 146.1; MS (EI) m/z (rel intensity) 252, 250 (M^+, 19, 19), 171 (36), 91 (base). Anal. Calcd for $C_{13}H_{15}Br$: C, 62.17; H, 6.02. Found: C, 62.34; H, 6.16.

(1*E*,3*E*)- and (1*Z*,3*E*)-1-Bromo-2-methyl-4-phenyl-1,3-butadiene (10c): *E*- and *Z*-isomers were separated by HPLC (silica gel, hexane). **1*E*,3*E*-isomer:** colorless oil; R_f = 0.51 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (3H, d, J = 0.7 Hz), 6.34 (1H, s), 6.56 (1H, d, J = 16.0 Hz), 6.71 (1H, d, J = 16.0 Hz), 7.16−7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 110.0, 126.5, 127.7, 128.7, 128.9, 129.0, 137.0, 139.8; MS (FAB) m/z 225, 223 (MH^+); HRMS calcd for $C_{11}H_{12}Br$ MH^+ 225.0102, 223.0122, found m/z 225.0111, 223.0107. **1*Z*,3*E*-isomer**: colorless oil; R_f = 0.51 (hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, d, J = 1.5 Hz), 6.16 (1H, s), 6.74 (1H, d, J = 16.2 Hz), 7.26−7.40 (4H, m), 7.49−7.54 (2H, m);^{13}C NMR (75 MHz, $CDCl_3$) δ 19.5, 105.9, 126.2, 126.9, 128.1, 128.7, 132.1, 136.7, 136.9; MS (EI) m/z (rel intensity) 224, 222 (M^+, 74, 76), 144 (24), 143 (base), 142 (58), 141 (50), 128 (99); HRMS calcd for $C_{11}H_{11}Br$ M^+ 224.0024, 222.0044, found m/z 223.9986, 222.0007.

1-(Bromomethylidene)-4,4-dimethyl-2-cyclohexene(10d): an inseparable mixture with **9d**, *E*- and *Z*-isomers of **10d**; colorless oil; R_f = 0.77 (hexane); ^{1}H and ^{13}C NMR were assigned from a mixture of the spectra. ***E*-Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (6H, s), 1.54 (2H, t, J = 6.5 Hz), 2.44 (2H, t, J = 6.5 Hz), 5.58 (1H, d, J = 9.8 Hz), 5.92 (1H, d, J = 9.8 Hz), 6.05 (1H, t, J = 1.5 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 28.5, 32.3, 35.7, 104.2, 124.6, 128.4, 140.4. ***Z*-Isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (6H, s), 1.52 (2H, t, J = 6.5 Hz), 2.36 (2H, td, J = 6.5, 1.5 Hz), 5.77 (1H, dd, J = 10.0, 1.7 Hz), 5.86 (1H, m), 6.35 (1H, dd, J = 10.0, 0.9 Hz);^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 28.7, 32.6, 36.6, 100.4, 122.1, 137.8, 144.0.

(*Z*)-β-Bromo-α-methylstyrene (10e).[35] **Major *Z*-isomer:** colorless oil; R_f = 0.57 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (3H, d, J = 1.4 Hz), 6.23 (1H, d, J = 1.4 Hz), 7.18−7.40 (5H, m).

(*E*)- and (*Z*)-1-Bromo-2-(2-pyridyl)-propene (10f): eluted with 10% EtOAc in hexane on alumina. ***E*-Isomer:** colorless oil; R_f = 0.42 (15% EtOAc in hexane);^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, d, J = 1.1 Hz), 7.15 (1H, d, J = 1.4 Hz), 7.19 (1H, ddd, J = 7.8, 5.0, 0.9 Hz), 7.37 (1H, dt, J = 7.8, 0.8 Hz), 7.66 (1H, td, J = 7.8, 1.9 Hz), 8.57 (1H, dt, J = 5.0, 0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 110.8, 120.0, 122.4, 136.6, 140.3, 149.2, 157.1; MS (FAB) m/z 200, 198 (MH^+); HRMS calcd for C_8H_9NBr MH^+ 199.9898, 197.9918, found m/z 199.9910, 197.9947. ***Z*-isomer:** colorless oil; R_f = 0.32 (15% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (3H, d, J = 1.5 Hz), 6.38 (1H, q, J = 1.5 Hz), 7.22 (1H, ddd, J = 7.7, 4.7, 1.0 Hz), 7.54 (1H, dt, J = 7.7, 0.9 Hz), 7.70 (1H, td, J = 7.7, 1.7 Hz), 8.65 (1H, dt, J = 4.7, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.4, 102.9, 122.5, 123.8, 135.9, 141.2, 149.4, 157.8; MS (FAB) m/z 200, 198 (MH^+); HRMS calcd for C_8H_9NBr MH^+ 199.9898, 197.9918, found m/z 199.9925, 197.9915.

1,1-Diiodo-4-phenyl-1-butene (3). Finely grounded carbon tetraiodide (3.87 g, 7.44 mmol) was dissolved in CH_2Cl_2 (120 mL), to which was added PPh_3 (3.9 g, 14.9 mmol) at 0 °C all at once, and the mixture was stirred for 15 min at the same temperature. Then hydrocinnamaldehyde (0.5 g, 3.72 mmol) was added. The mixture was stirred for 10 min at 0 °C and for an additional 15 min at room temperature. The reaction was diluted with hexane (100 mL) and directly purified on silica gel column chromatography. Elution with hexane gave **3** (1.0 g) in 70% yield: colorless oil; R_f = 0.52 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21−2.28 (2H, m), 2.73 (2H, t, J = 7.6 Hz), 6.98 (1H, t, J = 7.0 Hz), 7.16−7.33 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 33.4, 41.2, 126.2, 128.4, 128.5, 140.4, 151.9; MS (EI) m/z (rel intensity) 384 (M^+, 7), 257 (35), 130 (19), 91 (base); HRMS calcd for $C_{10}H_{10}I_2$ M^+ 383.8873, found m/z 383.8864.

Hydrogenolysis of 3. The hydrogenolysis of 1,1-diiodo-4-phenyl-1-butene **3** (100 mg, 0.26 mmol) was performed by the same procedure as described for 1,1-dibromo-1-alkenes. Purification was made by alumina column chromatography eluted with hexane. The first elution gave (*Z*)-4-phenyl-1-(tributylstannyl)butene (**5**)[16] (12 mg) in 11% yield, the second elution with the same eluent gave (*Z*)-4-phenyl-1-iodobutene (**4**) (18 mg) in 27% yield, and the third elution gave the recovery of starting material in 27% yield. Phenyl-1-butene (**6**)[35] was identified from the proton NMR spectrum of the crude mixture, but present in less than 5%. **(*Z*)-4-phenyl-1-(tributylstannyl)butene (5):**[16] colorless oil; R_f = 0.71 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80−0.90 (15H, m), 1.25−1.34 (6H, m), 1.40−1.50 (6H, m), 2.30−2.36 (2H, m), 2.68 (2H, t, J = 7.6 Hz), 5.84 (1H, dt, J = 12.3, 1.2 Hz), 6.55 (1H, dt, J = 12.3, 7.0 Hz), 7.15−7.30 (5H, m). **(*Z*)-4-Phenyl-1-iodobutene (4):** colorless oil; R_f = 0.55 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44−2.50 (2H, m), 2.74 (2H, t, J = 7.4 Hz), 6.21 (1H, m), 6.23 (1H, d, J = 7.4 Hz), 7.16−7.33 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.0, 36.3, 83.1, 126.0, 128.4, 128.4, 140.2, 141.0; MS (EI) m/z (rel intensity) 258 (M^+, 6), 257 (40), 131 (18), 130 (23), 91 (base); HRMS calcd for $C_{10}H_{11}I$ M^+ 257.9906, found m/z 257.9874.

Suzuki Coupling of 7a with Alkenylboronic Acid. To a degassed solution of **7a** (26 mg, 0.082 mmol), (*E*)-1-(3-methyl-1-butenyl)boronic acid (11 mg, 0.1 mmol), and $Pd(PPh_3)_4$ (9.5 mg, 8.2 μmol) in anhydrous THF (0.6 mL) was added TlOH

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(0.44 mL, 10% solution in water) at room temperature. The mixture was stirred for 1 h, diluted with hexane (30 mL), and washed with water and brine. The extract was dried over $MgSO_4$, and the solvent was removed. The residual oil was purified by column chromatography on silica gel eluted with hexane to give **11** (18.6 mg) in 74% yield: colorless oil; R_f = 0.47 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (6H, d, J = 7.0 Hz), 2.40−2.53 (3H, m), 2.75 (2H, t, J = 7.3 Hz), 5.93 (1H, dt, J = 15.0, 7.0 Hz), 6.02 (1H, d, J = 15.0 Hz), 6.10 (1H, dd, J = 15.0, 6.6 Hz), 6.37 (1H, d, J = 10.3 Hz), 6.54 (1H, ddt, J = 15.0, 10.3, 1.5 Hz), 7.17−7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 31.0, 34.9, 35.5, 121.0, 123.4, 125.9, 126.8, 128.4, 128.9, 129.9, 137.5, 141.5, 142.8; MS (EI) m/z (rel intensity) 306, 304 (M^+, 62, 61), 215 (81), 213 (82), 187 (8), 185 (9), 173 (20), 171 (19), 91 (base); HRMS calcd for $C_{17}H_{21}Br$ M^+ 306.0806, 304.0827, found m/z 306.0815, 304.0801.

Sonogashira Coupling of 7a with Phenylacetylene. To a mixture of **7a** (77 mg, 0.24 mmol), phenylacetylene (30 mg, 0.29 mmol), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol), and CuI (4.6 mg, 0.024 mmol) in anhydrous degassed benzene (2 mL) was added diisopropylamine (68 μL, 0.48 mmol). After the reaction was stirred for 1 h at room temperature, the mixture was diluted with benzene (20 mL) and water (5 mL). The benzene layer was washed with water and brine, dried over $MgSO_4$, and evaporated. The crude oil was purified by column chromatography on silica gel. Elution with hexane gave the recovery of **7a** (13 mg) in 17% yield, elution with 4% benzene in hexane gave **12** (29 mg) in 36% yield, and elution of 10% benzene in hexane gave **13** (28 mg) in 33% yield. **(3*Z*,5*E*)-3-Bromo-1,8-diphenyl-3,5-octadien-1-yne (12):** unstable light yellow oil; R_f = 0.29 (hexane);^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46−2.54 (2H, m), 2.77 (2H, t, J = 8.0 Hz), 6.08 (1H, dtd, J = 15.4, 7.0, 0.7 Hz), 6.45 (1H, ddt, J = 15.4, 10.3, 1.5 Hz), 6.79 (1H, d, J = 10.3 Hz), 7.17−7.47 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.0, 35.2, 88.7, 91.7, 99.7, 122.1, 126.0, 128.4, 128.4, 128.4, 128.8, 131.6, 131.6, 137.0, 140.3, 141.2; MS (EI) m/z (rel intensity) 338, 336 (M^+, 24, 26), 257 (19), 247 (25), 245 (25), 229 (11), 165 (base); HRMS calcd for $C_{20}H_{17}Br$ M^+ 338.0493, 336.0514, found m/z 338.0500, 336.0494. **(5*E*)-1,8-Diphenyl-3-[2-(1-phenylethynyl)]-3,5-octadien-1-yne (13):** unstable yellow oil; R_f = 0.11 (hexane);^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52−2.59 (2H, m), 2.79 (2H, t, J = 7.3 Hz), 6.07 (1H, dt, J = 14.7, 7.3 Hz), 6.75 (1H, ddt, J = 14.7, 11.4, 1.5 Hz), 6.83 (1H, d, J = 11.4 Hz), 7.17−7.55 (15H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.0, 35.3, 85.2, 88.4, 89.0, 94.1, 102.9, 122.9, 123.0, 126.0, 128.3, 128.3, 128.3, 128.4, 128.5, 128.6, 131.6, 131.6, 131.6, 139.9, 141.3, 144.6; MS (EI) m/z (rel intensity) 358 (M^+, 49), 281 (15), 265 (base); HRMS calcd for $C_{28}H_{22}$ M^+ 358.1722, found m/z 358.1725.

Synthesis of (3*E*,5*Z*,7*E*)-2-Methyl-10-phenyl-3,5,7-decatriene (14). To a solution of **8a** (50 mg, 0.21 mmol) and (*E*)-2-(3-methyl-1-butenyl)-1,3,2-benzodioxaborole (59 mg, 0.32 mmol) in anhydrous benzene (1 mL) were added $Pd(PPh_3)_4$ (10 mg, 8.4 μmol) and sodium ethoxide (2.0 M in ethanol, 0.21 mL, 0.42 mmol). The mixture was degassed quickly by bubbling with Ar and then heated for 10 min at 90 °C (bath temperature). After cooling, the mixture was diluted with hexane (30 mL), washed with water and brine, and dried over $MgSO_4$. The solvent was removed, and the residual oil was purified by column chromatography on silica gel eluted with hexane to give **14** (41 mg) in 85% yield: colorless oil; R_f = 0.34 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (6H, d, J = 6.8 Hz), 2.38 (1H, dqd, J = 6.9, 6.8, 0.9 Hz), 2.45 (2H, td, J = 7.3, 7.0 Hz), 2.73 (2H, t, J = 7.3 Hz), 5.67 (1H, dd, J = 15.1, 6.9 Hz), 5.73 (1H, dt, J = 15.1, 7.0 Hz), 5.82−5.89 (2H, m), 6.42 (1H, ddd, J = 15.1, 8.8, 1.5 Hz), 6.53 (1H, ddd, J = 15.1, 8.8, 1.5 Hz), 7.16−7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 31.4, 34.8, 35.9, 122.7, 125.8, 126.3, 127.5, 128.3, 128.3, 128.4, 134.1, 141.8, 142.7; MS (EI) m/z (rel intensity) 226 (M^+, base), 135 (99), 107 (55), 105 (17); HRMS calcd for $C_{17}H_{22}$ M^+ 226.1722, found m/z 226.1730. **One-Pot Procedure of 14 from 7a.** Hydrogenolysis of **7a** (100 mg, 0.42 mmol) was carried out under the same conditions as described for the general procedure. After the reaction was complete, (*E*)-2-(3-methyl-1-butenyl)-1,3,2-benzodioxaborole (120 mg, 0.64 mmol)-in anhydrous benzene (2 mL) and sodium ethoxide (2.0 M in ethanol, 0.64 mL, 1.28 mmol) were added and heated for 30 min at 90 °C (bath temperature). The same workup and purification described in the above experiment except column chromatography using alumina gave 52% yield of **14** and (*E*)-6-phenyl-1,3-hexadiene in 41% yield.

Synthesis of (3*Z*,5*E*)-8-Phenyl-1-trimethylsilyl-3,5-octadien-1-yne (15). To a stirred degassed solution of **8a** (100 mg, 0.42 mmol) in anhydrous benzene (2 mL) were added trimethylsilylacetylene (92 μL, 0.64 mmol), diisopropylamine (118 μL, 0.84 mmol), cuprous iodide (8 mg, 0.042 mmol), and $Pd(PPh_3)_4$ (19.4 mg, 0.017 mmol) successively to the reaction mixture. The reaction mixture was stirred at room temperature for 1 h and then diluted with hexane and washed with water and brine. The organic layer was dried over $MgSO_4$, and the solvent was evaporated. The residual oil was purified by column chromatography on silica gel eluted with hexane to give enyne **15** (100 mg) in 93% yield: colorless oil; R_f = 0.19 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (9H, s), 2.50 (2H, td, J = 7.3, 7.0 Hz), 2.76 (2H, t, J = 7.3 Hz), 5.36 (1H, d, J = 11.0 Hz), 5.94 (1H, dt, J = 15.4, 7.0 Hz), 6.37 (1H, t, J = 11.0 Hz), 6.63 (1H, ddd, J = 15.4, 11.0, 1.1 Hz), 7.16−7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.0, 34.6, 35.3, 100.4, 102.3, 107.2, 125.9, 128.2, 128.4, 128.4, 133.4, 138.1, 141.3; MS (EI) m/z (rel intensity) 254 (M^+, base), 239 (46), 181 (19), 180 (47), 163 (49), 150 (48), 135 (77); HRMS calcd for $C_{17}H_{22}Si$ M^+ 254.1490, found m/z 254.1515. **One-Pot Procedure of 15 from 7a.** Hydrogenolysis of **7a** was carried out under the same conditions as described for the general procedure. After the hydrogenolysis was complete, alkyne (1.5 equiv), diisopropylamine (6 equiv), and cuprous iodide (0.3 equiv) were added successively to the reaction mixture. The reaction was completed in 1 h. Workup of the reaction and purification described in the above experiment except column chromatography with alumina gave 61% yield of **15**.

Synthesis of Enediynes, 16, 17, and 18: General One-Pot Procedure from 1,1-Dibromo-4-phenyl-1-buten-3-yne. After the hydrogenolysis was complete, alkyne (1.5 equiv), diisopropylamine (6 equiv), and cuprous iodide (0.3 equiv) were added successively to the reaction mixture. The reaction was monitored by TLC. It was complete in 10 min with trimethylsilylacetylene, 15 min with 3-(*tert*-butyldimethylsilyl)oxy-5-phenyl-1-pentyne, and 3-hydroxy-5-phenyl-1-pentyne. The mixture was diluted with hexane (ether for the case of **18**), washed with water and brine, and dried over $MgSO_4$. The solvent was evaporated, and the residual oil was purified by alumina column chromatography.

(*Z*)-6-Phenyl-1-trimethylsilyl-3-hexen-1,5-diyne (16):[37] eluted with hexane in chromatographic purification; yield 70%; colorless oil; R_f = 0.20 (hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (9H, s), 5.90 (1H, d, J = 11.0 Hz), 6.08 (1H, d, J = 11.0 Hz), 7.32−7.36 (3H, m), 7.46−7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ −0.1, 87.1, 97.6, 102.2, 103.3, 119.3, 120.7, 123.0, 128.3, 128.6, 131.8; MS (EI) m/z (rel intensity) 224 (M^+, 98), 209 (base), 194 (36), 170 (25), 165 (60); HRMS calcd for $C_{15}H_{16}Si$ M^+ 224.1021, found m/z 224.1031.

(*Z*)-7-(*tert*-Butyldimethylsilyl)oxy-1,9-diphenyl-3-nonene-1,5-diyne (17): eluted with 2.5% EtOAc in hexane in chromatographic purification; yield 64%; colorless oil; R_f = 0.20 (2.5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (3H, s), 0.14 (3H, s), 0.90 (9H, s), 2.03−2.11 (2H, m), 2.83 (2H, tm, J = 8.4 Hz), 4.60 (1H, td, J = 6.2, 1.8 Hz), 5.90 (1H, dd, J = 11.0, 1.8 Hz), 6.03 (1H, d, J = 11.0 Hz), 7.14−7.32 (8H, m), 7.41−7.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ −5.0, −4.4, 18.2, 25.8, 31.4, 40.3, 62.9, 82.0, 86.9, 96.8, 98.9, 119.0, 119.5, 123.0, 125.8, 128.2, 128.3, 128.4, 128.5, 131.7, 141.6; MS (EI) m/z (rel intensity) 400 (M^+, 3), 343 (18), 269 (base), 209 (55); HRMS calcd for $C_{27}H_{32}OSi$ M^+ 400.2222, found m/z 400.2242.

(*Z*)-1,9-Diphenyl-7-hydroxy-3-nonen-1,5-diyne (18): eluted with 10% EtOAc in hexane in chromatographic purification; yield 54%; colorless oil; R_f = 0.25 (15% EtOAc in hexane); ^{1}H

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NMR (400 MHz, $CDCl_3$) δ 1.95 (1H, d, J = 5.1 Hz), 2.06−2.15 (2H, m), 2.86 (2H, t, J = 7.7 Hz), 4.60 (1H, dm, J = 5.1 Hz), 5.91 (1H, dd, J = 11.0, 1.8 Hz), 6.08 (1H, d, J = 11.0 Hz), 7.14−7.33 (8H, m), 7.42−7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.4, 39.2, 62.4, 82.9, 86.8, 97.3, 97.9, 118.7, 120.2, 122.8, 126.0, 128.4, 128.4, 128.5, 128.7, 131.7, 141.0; MS (EI) *m*/*z* (rel intensity) 286 (M^+, 5), 268 (base), 267 (82), 253 (23), 252 (18); HRMS calcd for $C_{21}H_{18}O$ M^+ 286.1358, found *m*/*z* 286.1346.

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Supporting Information Available: ^{13}C NMR spectra for 29 new compounds, general experimental procedures for 1,1-dibromo-1-alkenes from aldehydes, and physical and spectroscopic data for the 31 new and known compounds (41 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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