Palladium-Catalyzed 1-Methylene-2-propenylation Reactions of Aryl Bromides with 3,4-Alkadien-1-ols via Carbon–Carbon Bond Cleavage for the Synthesis of 2-Aryl-1,3-butadiene Derivatives

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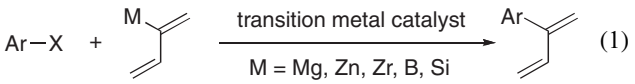
A method for the synthesis of 2-aryl-1,3-alkadienes has been developed. Treatment of aryl bromides with 3,4-alkadien-1-ols in the presence of a palladium catalyst results in 1-methylene-2-propenyl group transfer to aryl bromides. Taking advantage of palladium-mediated retro-allylation as an sp^3C–sp^3C bond cleavage reaction, one can regard 3,4-alkadien-1-ols as 1-methylene-2-propenyl metal equivalents that are easy to prepare and are not sensitive to air and moisture. In the event that the Diels–Alder dimerization of the product during the 1-methylene-2-propenylation reaction is problematic, addition of *N*-methylpyrrole to the reaction mixture can efficiently suppress the dimerization. The reactions of aryl bromides with 2-substituted 3,4-alkadien-1-ols yield the corresponding (*E*)-2-aryl-1,3-alkadienes stereoselectively.

Conjugated dienes are an important class of compounds that can undergo numerous organic transformations. Among them, 2-aryl-1,3-alkadienes are useful precursors in organic synthesis[1] as well as in polymer chemistry.[2] Development of new and convenient methods for the preparation of 2-aryl-1,3-alkadienes is thus important. Cross-coupling reactions of aryl halides with 1-methylene-2-propenylmetal reagents may provide an easy access to 2-aryl-1,3-alkadienes (eq 1).[3] However, the reactions often result in moderate yields because the products are prone to undergo polymerization or Diels–Alder dimerization during the synthesis. Moreover, the preparations of 1-methylene-2-propenylmetal reagents are not always facile and functional group compatibility is far from satisfactory.



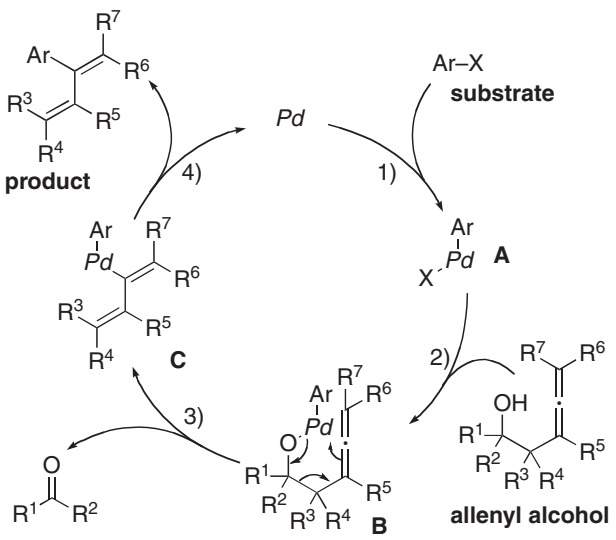
(1)

We have reported palladium-catalyzed regiospecific and stereoselective allylations of aryl halides with homoallyl alcohols via retro-allylation.[4–6] We envisioned that the allyl-transfer reaction via retro-allylation would be extended to the synthesis of 2-aryl-1,3-alkadienes as outlined in Scheme 1. After oxidative addition (Step 1), ligand exchange (Step 2) would occur to afford palladium alkoxide **B**. Carbon–carbon bond cleavage would then proceed via a six-membered cyclic transition state, providing aryl(1-methylene-2-propenyl)-palladium **C** selectively (Step 3). The subsequent reductive elimination (Step 4) would furnish 2-aryl-1,3-alkadienes. Notably, any type of allenyl alcohol is readily available in two steps from homoallyl alcohols via the corresponding dibromocyclopropyl alcohols,[7] which would allow us to prepare a wider variety of 2-aryl-1,3-alkadienes.

Similar palladium-catalyzed reactions of aryl halides with 3,4-alkadien-1-ols were reported to afford 2-aryl-1,3-alkadienes.[8] However, the scope of the reaction was narrow and particularly, the synthesis of 2-aryl-1,3-butadienes resulted in moderate yields. It was proposed that the reaction would begin with carbopalladation followed by β-carbon elimination, which is different from our working hypothesis.

Results and Discussion

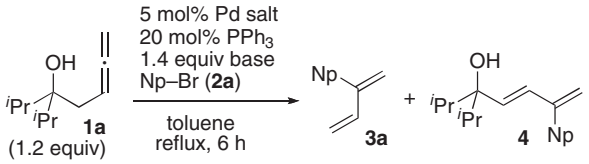
Optimization. The reaction of 1-bromonaphthalene (**2a**, Np = 1-naphthyl) with allenyl alcohol **1a** was examined as a model reaction. As the initial trial, treatment of **2a** with **1a** in the presence of cesium carbonate (obtained from Wako Pure



Scheme 1. Working hypothesis.

Published on the web March 12, 2009; doi:10.1246/bcsj.82.393

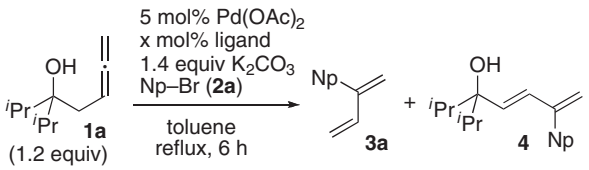
Table 1. Effect of Base and Palladium Precursor[a)]



Entry	Pd salt	Base	**3a**/%[a)]	**4**/%[a)]	**2a**/%[a)]
1	$Pd(OAc)_2$	Cs_2CO_3[b)]	54	15	8
2	$Pd(OAc)_2$	Cs_2CO_3[c)]	75	3	0
3	$Pd(OAc)_2$	K_2CO_3	75	9	9
4	$Pd(OAc)_2$	Na_2CO_3	8	15	65
5	$Pd(OAc)_2$	K_3PO_4	50	14	0
6	$PdCl_2$	K_2CO_3	46	16	33
7	$[(\pi\text{-allyl})PdCl]_2$[d)]	K_2CO_3	11	23	36
8	$Pd_2(dba)_3$[d)]	K_2CO_3	15	22	48

a) Determined by ^{1}H NMR analysis of crude products. b) From Wako Pure Chemical Co. (mean particle diameter: ca. 60 μm). c) From Chemetall (mean particle diameter: ca. 20 μm). d) 2.5 mol % of the palladium precursor was used.

Table 2. Ligand Effect



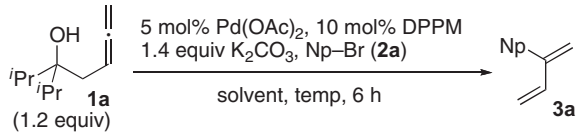
Entry	Ligand	x/mol %	**3a**/%[a)]	**4**/%[a)]	**2a**/%[a)]
1	PPh_3	20	75	9	9
2	$P(2\text{-}MeC_6H_4)_3$	20	56	10	0
3	$P(4\text{-}FC_6H_4)_3$	20	65	8	0
4	$P(2\text{-furyl})_3$	20	75	11	0
5	$P(OPh)_3$	20	32	10	0
6	$P(^cC_6H_{11})_3$	20	26	7	46
7	$P(^cC_6H_{11})_3$	10	54	12	0
8	PMe_3	20	56	0	9
9	PBu_3	20	18	0	66
10	DPPM	10	76	0	12
11	DPPM	5	54	14	0
12	DPPE	10	53	1	28
13	DPPP	10	64	11	0

a) Determined by ^{1}H NMR analysis of crude products.

Chemical Co.) in refluxing toluene for 6 h afforded 2-(1-naphthyl)-1,3-butadiene (**3a**) in 54% yield along with remaining **2a** (Table 1, Entry 1). The only detectable by-product was alcohol **4**, which carbopalladation of **2a** followed by β-hydride elimination would yield.[9] The use of finely milled cesium carbonate, which is available from Chemetall, increased the yield of **3a** to 75% (Entry 2). Potassium carbonate was as effective as the milled cesium carbonate (Entry 3). Sodium carbonate and potassium phosphate were less efficient (Entries 4 and 5). Cost-efficient potassium carbonate was chosen as the best base. Palladium acetate was far superior to other palladium salts such as palladium chloride (Entries 6–8).

The results of ligand screening are summarized in Table 2.

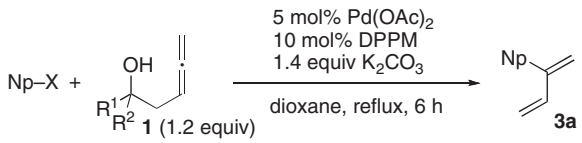
Table 3. Solvent Effect



Entry	Solvent	Temp/°C	**3a**/%[a)]	**2a**/%[a)]
1	Toluene	111 (reflux)	76	12
2	1,4-Dioxane	101 (reflux)	88 (79[b)])	0
3	Benzene	80 (reflux)	0	100
4	DMF	110	67	0
5	DMSO	110	38	0

a) Determined by ^{1}H NMR analysis of crude products. b) Isolated yield.

Table 4. Effect of Leaving Group X and Substituent R



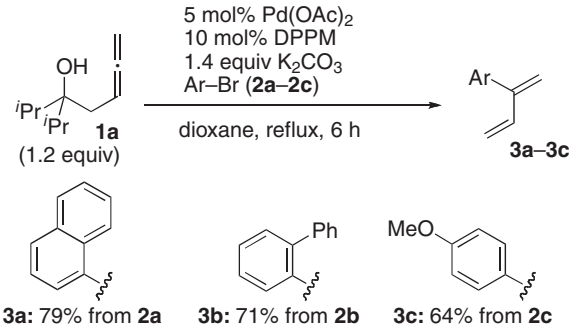
Entry	X	**1**	R^1	R^2	**3a**/%[a)]
1	Br	**1a**	^{i}Pr	^{i}Pr	88
2	OTf	**1a**	^{i}Pr	^{i}Pr	76
3	Cl	**1a**	^{i}Pr	^{i}Pr	8[b)]
4	I	**1a**	^{i}Pr	^{i}Pr	20[c)]
5	Br	**1b**	Me	Me	49[d)]
6	Br	**1c**	Ph	Ph	62
7	Br	**1d**	Ph	H	34

a) Determined by ^{1}H NMR analysis of crude products. b) 71% of 1-chloronaphthalene was recovered. c) 60% of 1-iodonaphthalene was recovered. d) 35% of 1-bromonaphthalene was recovered.

Monodentate triarylphosphine ligands, triphenyl phosphite, and tricyclohexylphosphine gave mixtures of **3a** and **4** (Entries 1–7). Although trimethylphosphine and tributylphosphine suppressed the formation of **4**, the yields of **3a** were moderate (Entries 8 and 9). Interestingly, the use of 10 mol % of bis(diphenylphosphino)methane (DPPM) proved to furnish **3a** selectively in high yield without affording **4** (Entry 10). Decreasing the amount of DPPM to 5 mol % resulted in contamination with **4** (Entry 11). The catalytic activity was diminished when 1,2-bis(diphenylphosphino)ethane (DPPE) was used (Entry 12). The use of bidentate 1,3-bis(diphenylphosphino)propane (DPPP) provided a mixture of **3a** and **4** (Entry 13). Overall, there are no clear correlations between the characters of phosphine ligands and yields and selectivities.

Among the solvents tested, 1,4-dioxane was the best (Table 3, Entry 2). Temperatures higher than 100 °C were essential for the reaction: the reaction in boiling benzene resulted in recovery of the starting materials (Entry 3). The reactions in polar solvents such as DMF and DMSO provided **3a** with unidentified by-products (Entries 4 and 5).

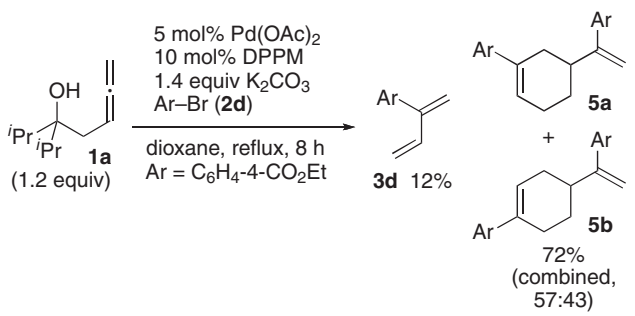
Not only 1-bromonaphthalene but also 1-naphthyl trifluoromethanesulfonate underwent the reaction as well (Table 4, Entry 2). 1-Chloronaphthalene resisted the reaction (Entry 3).



Scheme 2. Reactions of sterically demanding or electron-rich aryl bromides with **1a**.

The reaction of 1-iodonaphthalene suffered from low conversion (Entry 4). The efficiency of the reaction with **1b** was unsatisfactory (Entry 5). The smaller methyl groups would retard the carbon–carbon bond cleavage process that utilizes the release of the steric congestion around the hydroxy group. Diphenyl-substituted alcohol **1c** was the less efficient 1-methylene-2-propenyl donor than **1a** (Entry 6). The reaction of secondary alcohol **1d**[8] proceeded with low efficiency under the present reaction conditions (Entry 7). The triethylsilyl ether of **1a** failed to react under the reaction conditions.

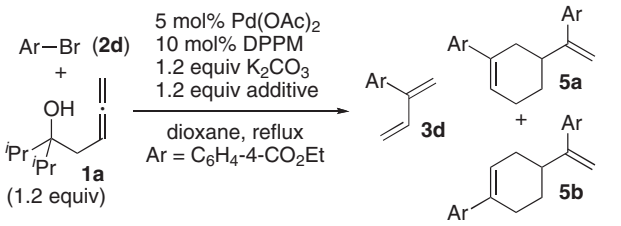
Reactions of Aryl Bromides with 1a. With the optimized conditions in hand, several aryl bromides were subjected to the reactions (Scheme 2). The reactions of **2a**, 2-bromobiphenyl (**2b**), and 4-bromoanisole (**2c**) with **1a** provided the corresponding arylated 1,3-butadienes (**3a**–**3c**) in good isolated yields. However, the reaction of ethyl 4-bromobenzoate (**2d**) provided **3d** in only 12% yield, albeit with full conversion (eq 2). In the crude reaction mixture, we detected significant amounts of **5a** and **5b** (**5a**/**5b** or **5b**/**5a** = 57:43), which resulted from the Diels–Alder dimerization of the initial product **3d**. Sterically demanding aryl group or electron-rich aryl group of **3a**–**3c** could fortunately prevent the dimerization. This transformation thus proved to lack generality.

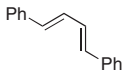


(2)

Development of Alternate Conditions to Suppress Diels–Alder Dimerization. After struggling to minimize the undesired dimerization reaction, we finally found that addition of another conjugated diene could inhibit the Diels–Alder reaction (Table 5, Entries 1 and 2). An unconjugated diene, 1,5-cyclooctadiene, was ineffective (Entry 3). Configurationally regulated 1,2,3,4-tetramethylcyclopentadiene was a potent inhibitor of the Diels–Alder reaction (Entry 4). Intriguingly, additions of 5-membered heteroaromatic compounds efficiently

Table 5. Effect of Additive in the Reaction of **2d** with **1a**



Entry	Additive	Time/h	**3d**/%[a]	**5a** + **5b**/%[a]
1		3	45	17
2		4.5	45	27
3		6	17	66
4		6.5	44	50
5		6	55	14
6[b]		6	39	0
7		9.5	71	18
8[c]		6	58	12
9		6	59	29

a) Determined by ^{1}H NMR analysis of crude products. b) 50% of **2d** was recovered. c) 25% of **2d** was recovered.

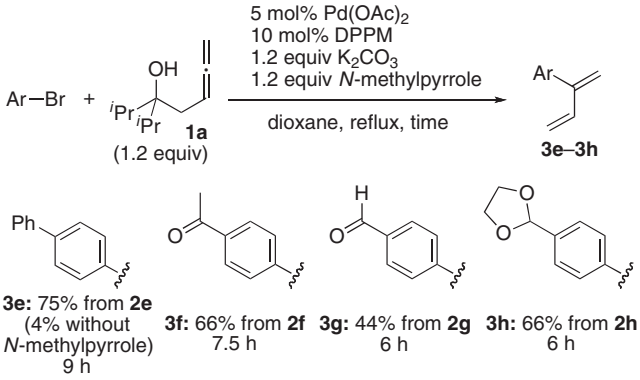
inhibited the side reaction (Entries 5–9). Among them, *N*-methylpyrrole suppressed the formation of **5** most efficiently without diminishing the conversion of **2d** (Entry 7).

Without suffering from the dimerization reaction, not only ethyl 4-bromobenzoate (**2d**) but also other aryl bromides **2e**–**2h** of some generality were converted to the corresponding arylated butadienes in good yield (Scheme 3). Although the reaction of 4-bromobenzaldehyde (**2g**) was unsatisfactory, the corresponding acetal **2h** was converted more efficiently.

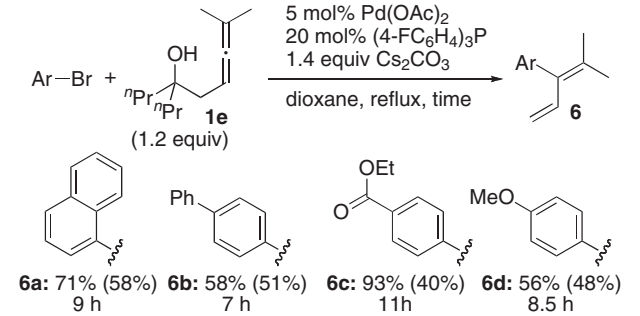
We have no exact ideas how the additives could suppress the Diels–Alder reaction. Probably, these additives would coordinate to palladium, deactivating the catalytic performance of palladium for the Diels–Alder reaction.[10]

Unfortunately, no reactions took place when heteroaromatic halides were used as substrates. The reaction of 2- or 3-bromopyridine or 2-bromothiophene with **1a** resulted in recovery of the starting materials.

Scope of Allenyl Alcohols. Allenyl alcohol **1e** was readily prepared in two steps from 2-methyl-3-butyn-2-ol via Johnson–Claisen rearrangement.[11,12] Alcohol **1e** reacted with aryl bromides without suffering from the Diels–Alder dimerization (Scheme 4). In reactions with **1e**, tri(4-fluorophenyl)phosphine was more effective than DPPM. The more basic cesium carbonate (Wako) was used instead of potassium carbonate



Scheme 3. Reactions of aryl bromides with **1a** in the presence of *N*-methylpyrrole.



[a] Yields obtained by using 10 mol% DPPM are in parentheses.

Scheme 4. Reactions with allenyl alcohol **1e**[a].

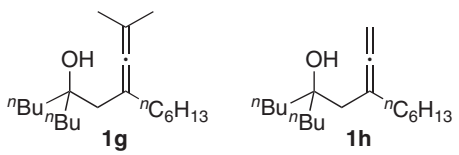
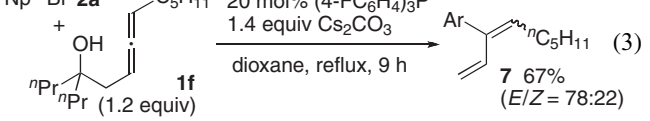


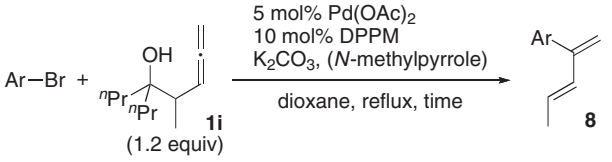
Figure 1. Allenyl alcohols that failed to yield conjugated dienes.

(Scheme 1, Step 2). Alcohol **1f**[12] having a 1,3-disubstituted allene moiety was transformed into the corresponding diene **7** with slight E stereoselectivity (eq 3). The low stereoselectivity stemmed from facile isomerization of the initially formed E isomer into the Z isomer. Because of steric reasons, no reaction took place when tetrasubstituted allene **1g** was used (Figure 1).[12] The reaction of **1h** gave a complex mixture.



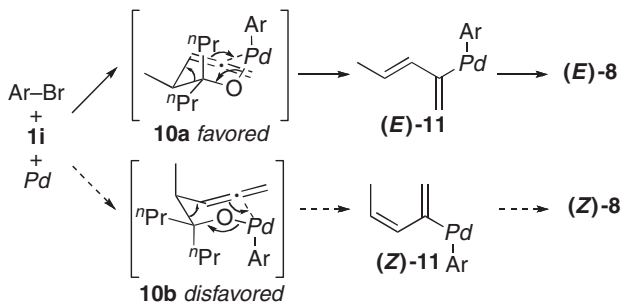
Allenyl alcohol **1i**,[12] bearing a branched methyl group at the carbon next to the hydroxylated carbon, reacted with various aryl bromides to yield (*E*)-2-aryl-1,3-pentadienes **8** stereoselectively (Table 6). No Z isomers were observed. In the event the Diels–Alder dimerization of **8** is problematic, *N*-methylpyrrole should be added to avoid the side reaction (Entries 4–8). The reactions of allenyl alcohols **1j** and **1k** also yielded the corresponding (*E*)-dienes exclusively (eq 4).[12]

Table 6. Reactions with **1i** for Stereoselective Synthesis of (*E*)-2-Aryl-1,3-pentadienes **8**

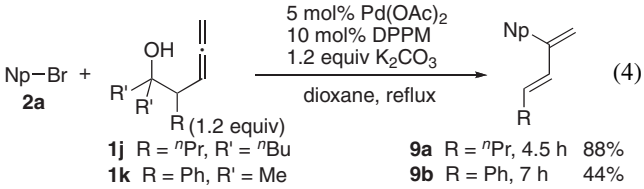


Entry	Ar–Br **2**	Conditions[a]	Time /h	**8**	Yield /%
1	Np–Br (**2a**)	A	10	**8a**	94
2	2-PhC$_6$H$_4$Br (**2b**)	A	11	**8b**	91
3	4-MeOC$_6$H$_4$Br (**2c**)	A	6	**8c**	57
4	4-EtOC(=O)C$_6$H$_4$Br (**2d**)	B	8.5	**8d**	68
5	4-PhC$_6$H$_4$Br (**2e**)	B	9	**8e**	72
6	4-AcC$_6$H$_4$Br (**2f**)	B	7.5	**8f**	50
7	4-HC(=O)C$_6$H$_4$Br (**2g**)	B	9	**8g**	41
8	4-[CH(OCH$_2$CH$_2$O)]-C$_6$H$_4$Br (**2h**)	B	10.5	**8h**	67

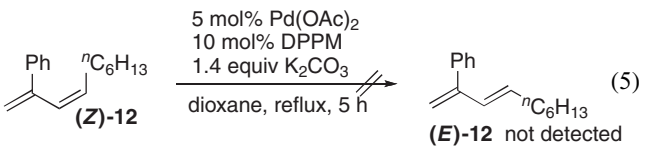
a) Conditions A: 0.17 M **2**, 1.4 equiv K_2CO_3, without *N*-methylpyrrole; Conditions B: 0.067 M **2**, 1.2 equiv K_2CO_3, 1.2 equiv *N*-methylpyrrole.



Scheme 5. Explanation of the stereoselectivity.



The stereoselective formation of the E isomers is rationalized as follows (Scheme 5). Upon the palladium-mediated retro-allylation reaction of **1i**, a chair-like transition state **10a** with the methyl group at the pseudoequatorial position would be the most favorable, compared to other possible transition states including another chair transition state **10b** having a pseudoaxial methyl group.[13] Formation of (*E*)-**11** would be thus favored. Intermediate (*E*)-**11** would undergo smooth reductive elimination to provide (*E*)-**8** exclusively. We excluded the possibility of the isomerization of (*Z*)-**8** into (*E*)-**8** in situ by a control experiment: exposure of (*Z*)-**12** to the reaction conditions gave rise to no observable isomerization (eq 5).



Conclusion

We have developed a method for the synthesis of 2-aryl-1,3-alkadienes: palladium-catalyzed 1-methylene-2-propenylation reactions of aryl bromides with 3,4-alkadien-1-ols. Palladium-mediated retro-allylation allows 3,4-alkadien-1-ols to act as 1-methylene-2-propenyl metals. The alcohols are practically inert under air and readily available. Stereoselective synthesis of (*E*)-2-aryl-1,3-pentadienes highlights the synthetic advantage of the present strategy.

Experimental

General. ^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were recorded in $CDCl_3$. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.00 ppm for ^{1}H and relative to $CDCl_3$ at 77.2 ppm for ^{13}C unless otherwise noted. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra (EI unless otherwise noted) were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene, 1,4-dioxane, and benzene were stored over slices of sodium. DMF and DMSO were distilled from calcium hydride prior to use. Cesium carbonate (standard particle size), potassium carbonate, sodium carbonate, and potassium phosphate were purchased from Wako Pure Chemical Co. Finely milled cesium carbonate was obtained from Chemetall and was stored and handled under inert atmosphere. DPPM and tri(4-fluorophenyl)phosphine were purchased from Wako Pure Chemical and Aldrich, respectively. Palladium acetate and *N*-methylpyrrole were obtained from TCI. All reactions were carried out under argon atmosphere. Allenyl alcohols **1** were synthesized as described in the following.

Typical Procedure for the Preparation of Allenyl Alcohols 1a–1d, 1i, and 1k. Synthesis of **1a** is representative. Allylmagnesium chloride was prepared from magnesium (0.875 g, 36.0 mmol) and allyl chloride (2.44 mL, 30.0 mmol) in THF (27 mL) under argon at 0 °C. The Grignard reagent obtained was placed in a 100-mL reaction flask under argon. A solution of 2,4-dimethyl-3-pentanone (3.54 mL, 25 mmol) in THF (25 mL) was added dropwise to the Grignard reagent at 0 °C. The resulting mixture was stirred for 1 h at room temperature. The reaction was quenched with 1 M hydrochloric acid (30 mL). Extractive workup followed by silica gel column purification (hexane/ethyl acetate = 10:1) afforded 2-methyl-3-methylethyl-5-hexen-3-ol (3.75 g, 24.0 mmol, 96%) as a colorless oil.

Tetrabutylammonium bromide (0.774 g, 2.4 mmol) was placed in a 100-mL reaction flask equipped with a Dimroth condenser under argon. Potassium hydroxide (50 wt % aqueous solution, 24.0 mL, 0.34 mol) and bromoform (10.5 mL, 0.12 mol) were added at 0 °C. After the mixture was stirred for 10 min, 2-methyl-3-methylethyl-5-hexen-3-ol (3.75 g, 24.0 mmol) in dichloromethane (24 mL) was added. The resulting mixture was stirred at reflux for 12 h. The mixture was cooled to room temperature. After water (25 mL) was added, the mixture was filtered through a pad of Celite. The product was extracted with ethyl acetate (30 mL × 3), and the combined organic phase was dried over anhydrous sodium sulfate. After evaporation, chromatographic purification on silica gel (hexane/ethyl acetate = 10:1) provided 3-(2,2-dibromocyclopropyl)methyl-2,4-dimethylpentan-3-ol (5.83 g, 17.8 mmol, 74%) as a pale brown oil.

Magnesium (1.30 g, 53.4 mmol) was placed in a 100-mL reaction flask. Bromoethane (3.32 mL, 44.5 mmol) in THF (41.0 mL) was added dropwise at room temperature under argon. Ethylmagnesium bromide thus obtained was transferred to a 300-mL reaction flask. A solution of 3-(2,2-dibromocyclopropyl)-methyl-2,4-dimethylpentan-3-ol (5.83 g, 17.8 mmol) in THF (36.0 mL) was added dropwise at 0 °C. After the addition was completed, the mixture was stirred for 2 h at ambient temperature. After a saturated ammonium chloride solution (20 mL) was added, the product was extracted with ethyl acetate. Concentration followed by purification on silica gel (hexane/ethyl acetate = 10:1) yielded 2-methyl-3-methylethyl-5,6-heptadien-3-ol (**1a**, 2.43 g, 14.4 mmol, 81%) as a colorless oil.

Typical Procedure for the Preparation of Allenyl Alcohols 1e–1h and 1j. Synthesis of **1e** is representative. A 100-mL reaction flask, equipped with a Dean–Stark trap was charged with argon. To this flask, 2-methyl-3-butyn-2-ol (2.91 mL, 30.0 mmol), triethyl orthoacetate (32.8 mL, 180 mmol), and propionic acid (0.34 mL, 4.5 mmol) were sequentially added dropwise. The resulting mixture was heated at reflux (bath temp. 150 °C) for 10 h. After being cooled to ambient temperature, the mixture was diluted with ether (30 mL). The organic phase was washed with 1 M sulfuric acid (180 mL × 2), a saturated sodium hydrogencarbonate solution (100 mL), and brine (50 mL). The residue was purified on silica gel (hexane/ethyl acetate = 20:1) to give ethyl 5-methyl-3,4-hexadienoate (2.28 g, 14.8 mmol, 49%) as a yellow oil.

A 100-mL reaction flask was charged with propylmagnesium bromide prepared from magnesium (0.95 g, 39 mmol) and 1-bromopropane (2.96 mL, 32.6 mmol) in THF (30 mL). Ethyl 5-methyl-3,4-hexadienoate (2.28 g, 14.8 mmol) in THF (30 mL) was added dropwise to the mixture at 0 °C. The resulting mixture was stirred for 5.5 h at room temperature. The reaction was quenched with a saturated ammonium chloride solution (10 mL). Extractive workup and silica gel column purification (hexane/ethyl acetate = 20:1) yielded 8-methyl-4-propyl-6,7-nonadien-4-ol (2.27 g, 11.5 mmol, 78%) as a pale yellow oil.

Typical Procedure for the Palladium-Catalyzed Reactions of Aryl Bromides 2 with Allenyl Alcohols 1 in the Absence of *N*-Methylpyrrole. The reaction of 1-bromonaphthalene (**2a**) with **1a** (Table 3, Entry 2) is representative. Potassium carbonate (80 mg, 0.58 mmol) was placed in a 30-mL reaction flask equipped with a Dimroth condenser. The base was dried in vacuo with a hair dryer for 2 min. Under an atmosphere of argon, palladium acetate (4.5 mg, 0.020 mmol) and DPPM (15.4 mg, 0.040 mmol) were added to the flask. Dioxane (2.4 mL), alkadienol **1a** (80.8 mg, 0.48 mmol), and 1-bromonaphthalene (**2a**, 93.2 mg, 0.40 mmol) were sequentially added. The whole mixture was heated at reflux for 6 h. After the mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with hexane (20 mL × 3). The combined organic layer was dried over anhydrous sodium sulfate and was concentrated under reduced pressure. Chromatographic purification (hexane/ethyl acetate = 80:1) yield-

ed 1-(1-methylene-2-propenyl)naphthalene (**3a**, 57 mg, 0.32 mmol, 79%).

Typical Procedure for the Palladium-Catalyzed Reactions in the Presence of *N*-Methylpyrrole. The reaction of 4-bromobiphenyl (**2e**) with **1a** (Scheme 3) is representative. Potassium carbonate (66 mg, 0.48 mmol) was placed in a 30-mL reaction flask and was dried in vacuo. Palladium acetate (4.5 mg, 0.020 mmol) and DPPM (15.4 mg, 0.040 mmol) were then added under argon. Dioxane (4 mL), alkadienol **1a** (80.8 mg, 0.48 mmol), 4-bromobiphenyl (**2e**, 93.2 mg, 0.40 mmol), and *N*-methylpyrrole (0.043 mL, 0.48 mmol) were sequentially added. The whole mixture was heated at reflux for 9 h. After the mixture was cooled to room temperature, water (20 mL) was added. The product was extracted with hexane (20 mL × 3). The combined organic layer was dried and concentrated. The residual oil was purified on silica gel with hexane as an eluent to afford 1-(1-methylene-2-propenyl)-4-phenylbenzene (**3e**, 61.9 mg, 0.30 mmol, 75%). As an exception, the reaction of **2h** with **1a** was performed in 2.4 mL of dioxane (Scheme 3).

Characterization Data. Spectral data for **1b**,[14] **1c**,[15] **1d**,[8] **3a**,[8] **3c**,[8] and **6a**[16] are found in the literature.

2-Methyl-3-methylethyl-5,6-heptadien-3-ol (1a): Oil. IR (neat): 3490, 2965, 2880, 1956, 1471, 1386, 977, 948, 842 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.93–0.99 (m, 12H), 1.23 (s, 1H), 1.95 (sep, $J = 7.0$ Hz, 2H), 2.26 (dd, $J = 8.5$, 3.0 Hz, 2H), 4.66 (dd, $J = 6.5$, 3.0 Hz, 2H), 5.08–5.15 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 17.52, 17.76, 33.29, 34.23, 74.26, 86.40, 209.93; HRMS Found: m/z 168.1514. Calcd for $C_{11}H_{20}O$: 168.1514.

8-Methyl-4-propyl-6,7-nonadien-4-ol (1e): Oil. IR (neat): 3389, 2958, 2873, 1969, 1454, 1233, 1134, 1021, 862, 822 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91 (t, $J = 7.5$ Hz, 6H), 1.28–1.37 (m, 4H), 1.41–1.46 (m, 4H), 1.42 (s, 1H), 1.68 (d, $J = 3.0$ Hz, 6H), 2.09 (d, $J = 8.0$ Hz, 2H), 4.92 (tsep, $J = 8.0$, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.94, 17.00, 20.79, 39.64, 41.59, 74.58, 83.94, 94.56, 203.90; Found: C, 79.65; H, 12.47%. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32%.

4-Propyl-6,7-tridecadien-4-ol (1f): Oil. IR (neat): 3390, 2958, 2932, 2873, 1962, 1458, 1378, 1132, 977, 874 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.89 (t, $J = 7.0$ Hz, 3H), 0.92 (t, $J = 7.0$ Hz, 6H), 1.27–1.36 (m, 8H), 1.38–1.47 (m, 6H), 1.40 (s, 1H), 1.95–2.01 (m, 2H), 2.11–2.15 (m, 2H), 5.02–5.11 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.31, 14.92 (2 peaks merge), 16.98, 17.03, 22.72, 29.09, 29.16, 31.56, 39.65, 41.52, 41.68, 74.60, 85.94, 90.62, 205.82; Found: C, 80.34; H, 12.89%. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68%.

5-Butyl-7-(2-methyl-1-propenylidene)tridecan-5-ol (1g): Oil. IR (neat): 3446, 2931, 2360, 1456, 1379, 1135, 1059 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86–0.93 (m, 9H), 1.22–1.33 (m, 14H), 1.33–1.40 (m, 2H), 1.43–1.51 (m, 4H), 1.57 (s, 1H), 1.68 (s, 6H), 1.92 (t, $J = 7.0$ Hz, 2H), 2.05 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 14.33 (2 peaks merge), 14.36, 21.03 (2 peaks merge), 22.92, 23.64 (2 peaks merge), 26.22 (2 peaks merge), 27.85, 29.11, 32.07, 35.20, 38.91 (2 peaks merge), 42.29, 74.86, 96.25, 98.34, 199.60; Found: C, 81.48; H, 13.17%. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07%.

5-Butyl-7-vinylidenetridecan-5-ol (1h): Oil. IR (neat): 3447, 2859, 1954, 1456, 1379, 841 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.86–0.93 (m, 9H), 1.22–1.35 (m, 14H), 1.38–1.45 (m, 2H), 1.46–1.51 (m, 4H), 1.76 (s, 1H), 1.98 (tt, $J = 7.5$, 3.5 Hz, 2H), 2.11 (t, $J = 2.5$ Hz, 2H), 4.70 (tt, $J = 3.5$, 2.5 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 14.33 (2 peaks merge), 22.86, 23.52, 26.14, 27.81, 29.17, 31.95, 34.20, 39.03, 42.07, 75.47, 75.86, 99.88, 207.29; HRMS Found: m/z 280.2765. Calcd for $C_{19}H_{36}O$: 280.2766.

5-Methyl-4-propyl-6,7-octadien-4-ol (1i): Oil. IR (neat): 3475, 2959, 2874, 1956, 1458, 1379, 1126, 961, 840 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.91–0.94 (m, 6H), 1.02 (d, $J = 7.0$ Hz, 3H), 1.25 (s, 1H), 1.27–1.51 (m, 8H), 2.31–2.38 (m, 1H), 4.70 (dt, $J = 6.5$, 2.5 Hz, 2H), 5.18 (dt, $J = 8.5$, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.59, 14.98, 15.01, 16.74, 16.79, 38.62, 39.53, 40.74, 75.23, 76.12, 92.04, 208.77; HRMS Found: m/z 182.1668. Calcd for $C_{12}H_{22}O$: 182.1671.

5-Butyl-4-propyl-1,2-nonadien-5-ol (1j): Oil. IR (neat): 3446, 2936, 1956, 1456, 1379, 997, 837 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.87–0.95 (m, 9H), 1.20–1.36 (m, 10H), 1.41–1.52 (m, 6H), 1.47 (s, 1H), 2.17 (t, $J = 10.0$ Hz, 1H), 4.67 (dd, $J = 6.5$, 1.5 Hz, 2H), 4.96 (dt, $J = 10.0$, 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 14.30, 14.37 (2 peaks merge), 21.56, 23.63, 23.66, 25.62 (2 peaks merge), 31.17, 36.56, 36.85, 47.63, 74.32, 76.27, 90.29, 209.52; HRMS Found: m/z 237.2218. Calcd for $C_{16}H_{30}O$ [$M^+ - H$]: 237.2214.

2-Methyl-3-phenyl-4,5-hexadien-2-ol (1k): Oil. IR (neat): 3447, 2973, 2933, 1956, 1452, 1373, 1198, 1150, 874, 844, 742, 702 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.18 (s, 3H), 1.25 (s, 3H), 1.56 (s, 1H), 3.35 (dt, $J = 9.5$, 1.5 Hz, 1H), 4.69 (ddd, $J = 11.0$, 6.5, 1.5 Hz, 1H), 4.74 (ddd, $J = 11.0$, 6.5, 1.5 Hz, 1H), 5.59 (dt, $J = 9.5$, 6.5 Hz, 1H), 7.25–7.30 (m, 3H), 7.30–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 27.92, 27.95, 57.25, 73.13, 75.36, 90.27, 127.09, 128.42, 129.38, 140.95, 209.29; Found: C, 82.94; H, 8.85%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

1-(1-Methylene-2-propenyl)-2-phenylbenzene (3b): Oil. IR (neat): 3086, 3058, 3022, 1588, 1479, 1448, 1435, 1009, 989, 905, 745, 699 cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.81 (d, $J = 17.5$ Hz, 1H), 5.01–5.05 (m, 1H), 5.02 (d, $J = 10.5$ Hz, 1H), 5.26–5.29 (m, 1H), 6.41 (dd, $J = 17.5$, 10.5 Hz, 1H), 7.24–7.41 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 117.31, 120.11, 126.85, 127.10, 127.77, 127.94, 129.14, 130.28, 130.68, 138.34, 139.00, 141.24, 142.04, 148.31; Found: C, 93.20; H, 7.00%. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84%.

Ethyl 4-(1-Methylene-2-propenyl)benzoate (3d): Oil. IR (neat): 2981, 1719, 1609, 1367, 1275, 1178, 1103, 1020, 907, 863, 781, 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.40 (t, $J = 7.0$ Hz, 3H), 4.39 (q, $J = 7.0$ Hz, 2H), 5.15 (d, $J = 17.5$ Hz, 1H), 5.23 (d, $J = 10.0$ Hz, 1H), 5.24–5.27 (m, 1H), 5.35–5.38 (m, 1H), 6.62 (dd, $J = 17.5$, 10.0 Hz, 1H), 7.37–7.40 (m, 2H), 8.01–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.58, 61.16, 117.76, 118.05, 128.47, 129.66, 129.80, 137.82, 144.57, 147.71, 166.71; Found: C, 77.01; H, 6.80%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

1-(1-Methylene-2-propenyl)-4-phenylbenzene (3e): Solid. IR (nujol): 2924, 2855, 1577, 1485, 1448, 996, 928, 906, 842, 773, 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.25 (d, $J = 10.5$ Hz, 1H), 5.26–5.28 (m, 1H), 5.27 (d, $J = 17.5$ Hz, 1H), 5.32–5.35 (m, 1H), 6.65 (dd, $J = 17.5$, 10.5 Hz, 1H), 7.33–7.38 (m, 1H), 7.39–7.48 (m, 4H), 7.57–7.64 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 117.06, 117.47, 127.08, 127.27, 127.51, 128.86, 128.99, 138.26, 138.90, 140.57, 141.04, 147.99; HRMS Found: m/z 206.1093. Calcd for $C_{16}H_{14}$: 206.1096. mp: 48.2–49.1 °C.

1-[4-(1-Methylene-2-propenyl)phenyl]ethanone (3f): Oil. IR (neat): 3090, 1684, 1605, 1401, 1358, 1267, 1016, 992, 957, 907, 848 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.62 (s, 3H), 5.16 (d, $J = 17.0$ Hz, 1H), 5.25 (d, $J = 11.0$ Hz, 1H), 5.26 (s, 1H), 5.38 (s, 1H), 6.62 (dd, $J = 17.0$, 11.0 Hz, 1H), 7.40–7.44 (m, 2H), 7.93–7.97 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 26.87, 117.82, 118.18, 128.50, 128.70, 136.44, 137.73, 144.88, 147.57, 198.01; Found: C, 83.47; H, 6.94%. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02%.

4-(1-Methylene-2-propenyl)benzaldehyde (3g): Oil. IR (neat): 2833, 1699, 1606, 1589, 1565, 1387, 1305, 1210, 1170, 992, 909, 838 cm^{-1}; ^1H NMR ($CDCl_3$): δ 5.16 (d, $J = 17.5$ Hz, 1H), 5.26 (d, $J = 10.5$ Hz, 1H), 5.27–5.30 (m, 1H), 5.39–5.42 (m,

1H), 6.63 (dd, $J = 17.5$, 10.5 Hz, 1H), 7.48–7.51 (m, 2H), 7.86–7.90 (m, 2H), 10.03 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 117.97, 118.53, 129.15, 129.89, 135.76, 137.61, 146.33, 147.48, 192.17; HRMS Found: m/z 158.0729. Calcd for $C_{11}H_{10}O$: 158.0732.

2-[4-(1-Methylene-2-propenyl)phenyl]-1,3-dioxolane (3h): Oil. IR (neat): 3089, 2954, 2885, 1588, 1417, 1385, 1222, 1082, 1019, 943, 906, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.02–4.09 (m, 2H), 4.12–4.19 (m, 2H), 5.17 (d, $J = 16.0$ Hz, 1H), 5.18–5.22 (m, 1H), 5.21 (d, $J = 11.0$ Hz, 1H), 5.29–5.32 (m, 1H), 5.83 (s, 1H), 6.61 (dd, $J = 16.0$, 11.0 Hz, 1H), 7.32–7.36 (m, 2H), 7.45–7.49 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 65.58, 103.84, 117.45, 117.52, 126.48, 128.59, 137.22, 138.20, 140.93, 148.11; Found: C, 77.10; H, 7.06%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

1-(2-Methyl-1-vinyl-1-propenyl)-4-phenylbenzene (6b): Oil. IR (neat): 3027, 2910, 1601, 1486, 1448, 1009, 986, 903, 837, 769, 738, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.63 (s, 3H), 1.99 (s, 3H), 4.60 (d, $J = 17.0$ Hz, 1H), 5.02 (d, $J = 11.0$ Hz, 1H), 7.01 (dd, $J = 17.0$, 11.0 Hz, 1H), 7.12–7.16 (m, 2H), 7.32–7.37 (m, 1H), 7.42–7.48 (m, 2H), 7.57–7.61 (m, 2H), 7.62–7.66 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 20.15, 23.39, 115.18, 126.92, 127.21, 127.29, 128.94, 130.70, 133.35, 135.39, 135.85, 139.18, 139.73, 141.27; Found: C, 92.07; H, 7.96%. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74%.

Ethyl 4-(2-Methyl-1-vinyl-1-propenyl)benzoate (6c): Oil. IR (neat): 2983, 2909, 1718, 1608, 1367, 1272, 1176, 1098, 1022, 777, 719 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.40 (t, $J = 7.0$ Hz, 3H), 1.55 (s, 3H), 1.97 (s, 3H), 4.39 (q, $J = 7.0$ Hz, 2H), 4.45 (d, $J = 17.0$ Hz, 1H), 5.00 (d, $J = 7.0$ Hz, 1H), 6.96 (dd, $J = 17.0$, 10.5 Hz, 1H), 7.13–7.15 (m, 2H), 8.01–8.05 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.59, 20.12, 23.23, 61.07, 115.36, 128.81, 129.60, 130.38, 133.65, 135.11, 135.42, 145.90, 166.95; Found: C, 78.29; H, 7.96%. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88%.

1-Methoxy-4-(2-methyl-1-vinyl-1-propenyl)benzene (6d): Oil. IR (neat): 2909, 2834, 1609, 1511, 1285, 1243, 1174, 1104, 1038, 903, 830 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.58 (s, 3H), 1.95 (s, 3H), 3.83 (s, 3H), 4.54 (dd, $J = 17.0$, 1.5 Hz, 1H), 4.99 (dd, $J = 10.5$, 1.5 Hz, 1H), 6.87–6.91 (m, 2H), 6.96–6.99 (m, 2H), 6.98 (dd, $J = 17.0$, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 20.10, 23.31, 55.39, 113.60, 114.92, 131.26, 132.88, 133.27, 135.26, 136.15, 158.18; Found: C, 82.69; H, 8.64%. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57%.

1-(1-Vinyl-1-heptenyl)naphthalene (E:Z = 78:22 Mixture) (7): Oil. IR (neat): 3044, 2956, 2926, 2856, 1593, 1507, 987, 906, 800, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.78 (t, $J = 7.0$ Hz, 0.78 × 3H), 0.93 (t, $J = 7.0$ Hz, 0.22 × 3H), 1.08–1.18 (m, 0.78 × 4H), 1.26–1.34 (m, 0.78 × 2H), 1.35–1.44 (m, 0.22 × 4H), 1.49–1.57 (m, 0.22 × 2H), 1.76 (q, $J = 7.5$ Hz, 0.78 × 2H), 2.44 (q, $J = 7.5$ Hz, 0.22 × 2H), 4.41 (d, $J = 7.5$ Hz, 0.78 × 1H), 4.61 (d, $J = 17.5$ Hz, 0.22 × 1H), 4.92 (d, $J = 11.0$ Hz, 0.78 × 1H), 5.08–5.13 (m, 0.22 × 1H), 5.61 (t, $J = 7.5$ Hz, 0.22 × 1H), 6.00 (t, $J = 7.5$ Hz, 0.78 × 1H), 6.70 (dd, $J = 17.5$, 11.0 Hz, 0.78 × 1H), 7.06 (dd, $J = 17.5$, 10.5 Hz, 0.22 × 1H), 7.20–7.24 (m, 0.78 × 1H), 7.27–7.30 (m, 0.22 × 1H), 7.39–7.52 (m, 3H), 7.76–7.88 (m, 3H); ^{13}C NMR ($CDCl_3$): δ 14.14, 14.33, 22.62, 22.80, 28.02, 29.22, 29.43, 29.62, 31.56, 31.79, 114.62, 117.38, 125.61, 125.63, 125.69, 125.72, 125.85, 125.93, 126.25, 126.71, 127.24, 127.26, 127.41, 127.43, 128.26, 128.33, 132.11, 132.56, 133.70, 133.71, 133.78, 135.15, 136.05, 136.15, 138.46, 139.85, 139.89, 140.80; Found: C, 91.35; H, 9.02%. Calcd for $C_{19}H_{22}$: C, 91.14; H, 8.86%.

(*E*)-1-(1-Methylene-2-butenyl)naphthalene (8a): Oil. IR (neat): 3016, 2911, 2851, 1591, 1504, 1448, 1436, 1255, 964, 894, 802, 778 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.68 (dd, $J = 6.5$, 1.0 Hz, 3H), 5.08 (d, $J = 1.5$ Hz, 1H), 5.17 (dq, $J = 15.5$, 6.5 Hz, 1H), 5.45 (dd, $J = 1.5$, 1.0 Hz, 1H), 6.47 (dd, $J = 15.5$, 1.0 Hz, 1H), 7.29–7.32 (m, 1H), 7.40–7.48 (m, 3H), 7.78–7.82 (m, 1H), 7.83–7.86 (m, 1H), 7.89–7.93 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 18.34, 116.89, 125.52, 125.81, 125.86, 126.64, 126.66, 127.61, 128.24, 130.08, 132.08, 133.66, 134.19, 139.06, 147.39; Found: C, 92.61; H, 7.39%. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26%.

(*E*)-1-(Methylene-2-butenyl)-2-phenylbenzene (8b): Oil. IR (neat): 3059, 3021, 1599, 1478, 1448, 1435, 1009, 965, 890, 769, 745, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.61 (dd, $J = 6.5$, 1.5 Hz, 3H), 4.85 (d, $J = 1.5$ Hz, 1H), 5.11 (dd, $J = 1.5$, 1.5 Hz, 1H), 5.28 (dq, $J = 15.5$, 6.5 Hz, 1H), 6.09 (dd, $J = 15.5$, 1.5 Hz, 1H), 7.23–7.38 (m, 9H); ^{13}C NMR ($CDCl_3$): δ 18.21, 117.15, 126.81, 127.03, 127.57, 127.87, 129.06, 129.54, 130.19, 130.60, 133.65, 139.45, 141.17, 142.18, 148.11; Found: C, 92.46; H, 7.46%. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32%.

(*E*)-1-Methoxy-4-(1-methylene-2-butenyl)benzene (8c): Oil. IR (neat): 2934, 2912, 2835, 1609, 1511, 1442, 1286, 1246, 1178, 1036, 969, 886, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.78 (dd, $J = 6.5$, 1.5 Hz, 3H), 3.82 (s, 3H), 5.01 (d, $J = 1.5$ Hz, 1H), 5.11 (d, $J = 1.5$ Hz, 1H), 5.68 (dq, $J = 15.5$, 6.5 Hz, 1H), 6.30 (d, $J = 15.5$ Hz, 1H), 6.86–6.89 (m, 2H), 7.23–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 18.47, 55.48, 113.63, 113.74, 129.12, 129.50, 133.10, 133.35, 147.73, 159.16; Found: C, 82.62; H, 8.24%. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%.

Ethyl (*E*)-4-(1-Methylene-2-butenyl)benzoate (8d): Oil. IR (neat): 2981, 1718, 1610, 1404, 1367, 1273, 1176, 1128, 1103, 1020, 967, 863, 781, 717 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.40 (t, $J = 7.0$ Hz, 3H), 1.79 (dd, $J = 6.5$, 1.5 Hz, 3H), 4.38 (q, $J = 7.0$ Hz, 2H), 5.08 (m, 1H), 5.22 (m, 1H), 5.63 (dq, $J = 16.0$, 6.5 Hz, 1H), 6.31 (dd, $J = 16.0$, 1.0 Hz, 1H), 7.35–7.39 (m, 2H), 8.00–8.03 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 14.58, 18.52, 61.13, 115.47, 128.44, 129.57, 129.60, 129.80, 132.39, 145.60, 147.59, 166.74; HRMS Found: m/z 216.1150. Calcd for $C_{14}H_{16}O_2$: 216.1150.

(*E*)-1-(1-Methylene-2-butenyl)-4-phenylbenzene (8e): Oil. IR (neat): 2924, 2853, 1486, 1443, 1007, 978, 890, 851, 772, 741, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.81 (dd, $J = 7.0$, 2.0 Hz, 3H), 5.11 (m, 1H), 5.19–5.22 (m, 1H), 5.74 (dq, $J = 15.5$, 7.0 Hz, 1H), 6.35 (dd, $J = 15.5$, 2.0 Hz, 1H), 7.33–7.37 (m, 1H), 7.38–7.42 (m, 2H), 7.42–7.47 (m, 2H), 7.56–7.59 (m, 2H), 7.60–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 18.52, 114.55, 127.00, 127.27, 127.46, 128.86, 128.99, 129.42, 132.81, 139.92, 140.41, 141.11, 147.90; HRMS Found: m/z 220.1252. Calcd for $C_{17}H_{16}$: 220.1252.

(*E*)-1-[4-(1-Methylene-2-butenyl)phenyl]ethanone (8f): Oil. IR (neat): 2931, 2855, 1683, 1602, 1407, 1358, 1269, 1015, 958, 827 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.79 (dd, $J = 7.0$, 2.0 Hz, 3H), 2.61 (s, 3H), 5.09 (m, 1H), 5.23 (m, 1H), 5.62 (dq, $J = 15.5$, 7.0 Hz, 1H), 6.32 (dd, $J = 15.5$, 2.0 Hz, 1H), 7.38–7.42 (m, 2H), 7.92–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 18.53, 26.86, 115.61, 128.42, 128.68, 129.87, 132.31, 136.28, 145.93, 147.46, 198.02; HRMS Found: m/z 186.1044. Calcd for $C_{13}H_{14}O$: 186.1045.

(*E*)-4-(1-Methylene-2-butenyl)benzaldehyde (8g): Oil. IR (neat): 2914, 1699, 1606, 1564, 1386, 1304, 1210, 1169, 968, 896, 840, 757, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.79 (dd, $J = 7.0$, 2.0 Hz, 3H), 5.11 (m, 1H), 5.26 (m, 1H), 5.62 (dq, $J = 15.5$, 7.0 Hz, 1H), 6.32 (dd, $J = 15.5$, 2.0 Hz, 1H), 7.46–7.49 (m, 2H), 7.84–7.87 (m, 2H), 10.0 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 18.55, 115.94, 129.12, 129.82, 130.02, 132.18, 135.62, 147.35, 147.39, 192.19; HRMS Found: m/z 172.0888. Calcd for $C_{12}H_{12}O$: 172.0888.

(*E*)-2-[4-(1-Methylene-2-butenyl)phenyl]-1,3-dioxolane (8h): Oil. IR (neat): 2882, 1597, 1421, 1387, 1304, 1221, 1080, 1019, 968, 890, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 1.77 (dd, $J = 7.0$, 2.0 Hz,

3H), 4.03–4.09 (m, 2H), 4.12–4.18 (m, 2H), 5.03 (m, 1H), 5.15–5.18 (m, 1H), 5.63 (dq, $J = 15.5$, 7.0 Hz, 1H), 5.83 (s, 1H), 6.31 (dd, $J = 15.5$, 2.0 Hz, 1H), 7.31–7.34 (m, 2H), 7.44–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 18.48, 65.57, 103.87, 114.84, 126.37, 128.57, 129.57, 132.78, 137.01, 141.95, 148.01; Found: C, 77.46; H, 7.54%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

(*E*)-1-(1-Methylene-2-hexenyl)naphthalene (9a): Oil. IR (neat): 3044, 2958, 2928, 2871, 967, 893, 802, 779 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 0.81 (t, $J = 7.5$ Hz, 3H), 1.29 (tq, $J = 7.5$, 7.5 Hz, 2H), 2.00 (dt, $J = 7.5$, 7.5 Hz, 2H), 5.10 (d, $J = 2.5$ Hz, 1H), 5.16 (dt, $J = 15.5$, 7.5 Hz, 1H), 5.46 (d, $J = 2.5$ Hz, 1H), 6.45 (d, $J = 15.5$ Hz, 1H), 7.30–7.33 (m, 1H), 7.40–7.49 (m, 3H), 7.79–7.82 (m, 1H), 7.83–7.87 (m, 1H), 7.90–7.94 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 13.87, 22.36, 34.93, 117.11, 125.54, 125.78, 125.80, 126.65, 126.74, 127.60, 128.21, 132.09, 132.95, 133.66, 135.36, 139.11, 147.51; Found: C, 91.94; H, 8.35%. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16%.

(*E*)-1-[1-Methylene-3-phenyl-2-propenyl]naphthalene (9b): Solid. IR (nujol): 2923, 2854, 1591, 1578, 1505, 1493, 1454, 1377, 962, 800, 777, 754, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.30 (d, $J = 2.0$ Hz, 1H), 5.71 (d, $J = 2.0$ Hz, 1H), 6.02 (d, $J = 16.5$ Hz, 1H), 7.16–7.21 (m, 1H), 7.22–7.31 (m, 5H), 7.37–7.45 (m, 2H), 7.45–7.54 (m, 2H), 7.85–7.91 (m, 2H), 7.92–7.96 (m, 1H); ^{13}C NMR ($CDCl_3$): δ 120.18, 125.60, 125.96, 126.11, 126.54, 126.74, 126.90, 127.81, 127.94, 128.30, 128.71, 131.60, 132.09, 132.60, 133.72, 137.23, 138.30, 147.32; HRMS Found: m/z 256.1250. Calcd for $C_{20}H_{16}$: 256.1252. mp: 75.5–76.3 °C.

This work was supported by Grants-in-Aid for Scientific Research and GCOE Research from MEXT and JSPS. S.H. and K.H. thank JSPS for financial support. H.Y. acknowledges financial support through the Eisai Award of Synthetic Organic Chemistry, Japan, and from Kyoto University. Finely milled cesium carbonate was a gift from Chemetall GmbH.

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