Cross-Coupling of Aryl Halides and Allyl Acetates with Arylboron Reagents in Water Using an Amphiphilic Resin-Supported Palladium Catalyst

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Owing to increasing environmental concerns about harmful and resource-consuming solvent waste,[1] the chemistry of organic transformations in water is presently undergoing very rapid growth.[2] In addition, the development of immobilized reagents has been attracting significant interest for their practical advantages.[3] There is good reason to believe that immobilized catalysts exhibiting high catalytic activity in aqueous media offer a viable clean alternative to more traditional methods of accomplishing many organic reactions. We have recently reported the design and preparation of amphiphilic resin-supported triarylphosphine−palladium complexes bound to a poly(ethylene glycol)−polystyrene graft copolymer (PEG−PS resin) which exhibit high catalytic activity in allylic substitution reactions of allyl acetates with various nucleophiles in aqueous media under mild reaction conditions.[7] As a part of our efforts to develop the wide utility of these catalysts, we examined the palladium−catalyzed cross-coupling reaction in water. We describe herein the arylation of aryl halides and allyl acetates with arylboron reagents in aqueous media which is catalyzed by the amphiphilic PEG−PS resin-supported triarylphosphine−palladium complexes.

Table 1. Cross-Coupling of Aryl Halides with Arylboron Reagents in Water Catalyzed by Palladium−Phosphine Complexes

entry	aryl halide	arylboron	catalyst	product	yield %
1	C_6H_5I (**4a**)	**5**	Pd−PEP (**2**)	**8a**	88
2		**5**	Pd−$(PEP)_2$ (**3**)	**8a**	80
3		**5**	Pd/TPPTS[a]	**8a**	59
4		**5**	$Pd(PPh_3)_4$	**8a**	0
5		**6**	**2**	**9a**	91
6		**7**	**2**	**10a**	72
7[b]		$NaBPh_4$	**2**	**8a**	84
8	C_6H_5Br (**4a′**)	**5**	**2**	**8a**	77
9		**6**	**2**	**9a**	82
10		**7**	**2**	**10a**	70
11[b]		$NaBPh_4$	**2**	**8a**	67
12[c]	2-$CH_3C_6H_4I$ (**4b**)	**5**	**2**	**8b**	66
13		**6**	**2**	**9b**	80
14		**7**	**2**	**10b**	72
15[b]		$NaBPh_4$	**2**	**9a**	67
16	4-$CH_3C_6H_4I$ (**4c**)	**5**	**2**	**9a**	85
17		**6**	**2**	**9c**	79
18		**7**	**2**	**10c**	67
19[b]		$NaBPh_4$	**2**	**9a**	70

[a] A catalyst generated in situ by mixing $[PdCl(\pi-C_3H_5)]_2$ and TPPTS (2 mol % Pd, Pd/P = 1/1) was used. [b] Without KOH. [c] Three mol % Pd of **2** was used.

The transition-metal-catalyzed cross-coupling of aryl and alkenyl halides with various organometal reagents is a useful means of carbon−carbon bond formation. The palladium−catalyzed cross-coupling using organoboron reagents, so-called Suzuki−Miyaura coupling, is one of the representatives.[8] Several palladium−phosphine complexes were examined for the coupling reaction of iodobenzene with phenylboronic acid in water, the Suzuki−Miyaura coupling having been well-documented to take place in aqueous organic media.[8] It was found that resin-supported palladium−phosphine complexes catalyze the coupling reaction to give biphenyl in high yield. The PEG−PS resin-supported palladium−monophosphine complex Pd−PEP[9] (**2**) was readily prepared by treatment of resin-supported phosphine **1**[7a] with an excess amount of di(μ-chloro)bis(η^3-allyl)dipalladium(II) ($[PdCl(\eta^3-C_3H_5)]_2$) (Pd/P > 1/1) followed by removal of unimmobilized $[PdCl(\eta^3-C_3H_5)]_2$ by washing three times with chloroform (Scheme 1). The gel-phase $^{13}C\{^1H\}$ NMR of **2** exhibited a singlet signal at 61.4 ppm and two doublet signals at 80.0 ppm ($^2J_{C-P}$ = 31 Hz) and 118.3 ppm ($^2J_{C-P}$ = 5 Hz), demonstrating that its structure is PdCl(η^3-allyl)(phosphine).[10] A mixture of iodobenzene (**4a**) and phenylboronic acid (**5**) was agitated in water with shaking on a wrist-action shaker in the presence of 4.5 equiv of potassium hydroxide and 2 mol % palladium of Pd−PEP complex **2** at 25 °C for 24 h to give biphenyl **8a** in 88% yield (Table 1, entry 1, and Scheme 2). The coupling with

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(1) For example, see: Anastas, P. T., Williamson, T. C., Eds.; *Green Chemistry*; ACS Symposium Series 626; American Chemical Society: Washington: DC, 1996, and references therein.

(2) For recent reviews, see: (a) Li, C.-J.; Chan, T.-H. *Organic Reactions in Aqueous Media*; Wiley: New York, 1997. (b) Grieco, P. A., Ed.; *Organic Synthesis in Water*; Kluwer Academic Publishers: Dordrecht, 1997.

(3) For recent reviews, see: (a) Bunin, B. A. *Combinatorial Index*; Academic Press: London, 1998; p 262. (b) Obrecht, D.; Villalgordo, J. M. *Solid-Supported Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries;* Tetrahedron Organic Chemistry Series Vol. 17, Elsevier: Oxford, 1998; p 44.

(4) For a review, see: Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1524−1544.

(5) For recent examples of reactions catalyzed by palladium−phosphine complexes performed in aqueous media, see: (a) Genêt, J. P.; Blart, E.; Savignac, M. *Synlett* **1992**, 715. (b) Genêt, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Paris, J.-M. *Tetrahedron Lett.* **1993**, *34*, 4189. (c) Lemaire-Audoire, S.; Savignac, M.; Blart, E.; Pourcelot, G.; Genêt, J. P. *Tetrahedron Lett.* **1994**, *35*, 8783. (d) Genêt, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Lemaire-Audoire, S.; Paris, J.-M.; Bernard, J.-M. *Tetrahedron* **1994**, *50*, 497. (e) Blart, E.; Genêt, J. P.; Safi, M.; Savignac, M.; Sinou, D. *Tetrahedron* **1994**, *50*, 505. (f) Amatore, C.; Blart, E.; Genêt, J. P.; Jutand, A.; Lemaire-Audoire, S.; Savignac, M. *J. Org. Chem.* **1995**, *60*, 6829. (g) Lemaire-Audoire, S.; Savignac, M.; Dupuis, C.; Genêt, J. P. *Tetrahedron Lett.* **1996**, *37*, 2003. (h) Bumagin, N. A.; Bykov, V. V.; Sukhomlinova, L. I.; Tolstaya, T. P.; Beletskaya, I. P. *J. Organomet. Chem.* **1995**, *486*, 259.

(6) Very recently, Bergbreiter and Liu have reported water-soluble polymer-bound, recoverable palladium(0)−phosphine catalysts; see: Bergbreiter, D. E.; Liu, Y.-S. *Tetarhedron Lett.* **1997**, *38*, 7843.

(7) (a) Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett.* **1997**, *38*, 3557. (b) Uozumi, Y.; Danjo, H.; Hayashi, T. *Tetrahedron Lett.* **1998**, *39*, 8303.

(8) For a review, see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457.

(9) The abbreviation PEP comes from PEG−PS resin (PE)-supported phosphine (P).

(10) The values of the coupling constants are in the typical range for PdCl(η^3-allyl)(phosphine) complexes. For recent relevant papers on NMR studies of π-allylpalladium complexes, see: (a) Hayashi, T.; Kawatsura, M.; Uozumi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 1681. (b) Pregosin, P. S.; Salzman, R.; Togni, A. *Organometallics* **1995**, *14*, 842.

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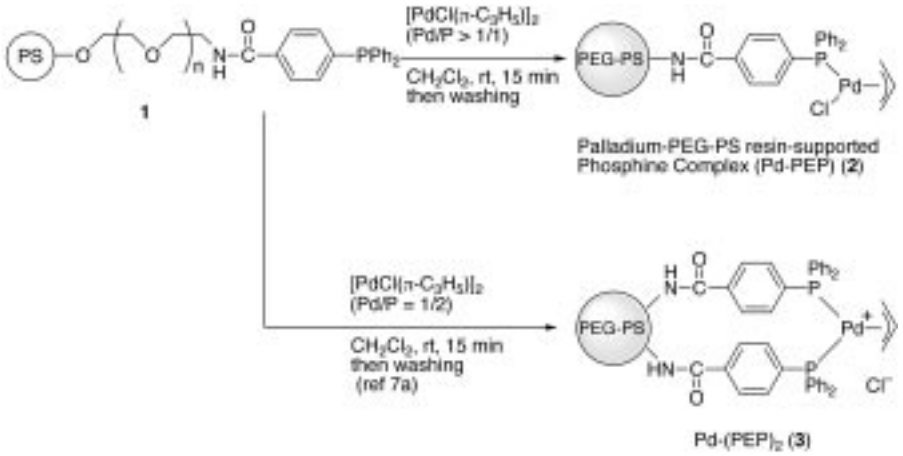
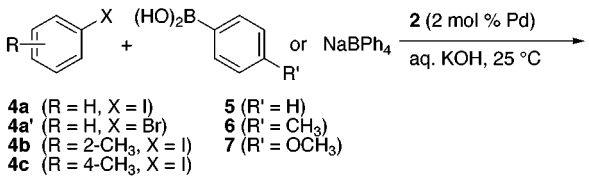
Scheme 1

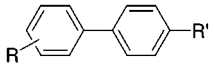


Scheme 2



4a (R = H, X = I)
4a' (R = H, X = Br)
4b (R = 2-CH_3, X = I)
4c (R = 4-CH_3, X = I)

5 (R' = H)
6 (R' = CH_3)
7 (R' = OCH_3)



8a-b (R' = H)
9a-c (R' = CH_3)
10a-c (R' = OCH_3)

(**a**: R = H, **b**: R = 2-CH_3, **c**: R = 4-CH_3)

resin-supported palladium−bis(triarylphosphine) complex **3** (Pd−$(PEP)_2$)[7a] gave 80% yield of **8a** (entry 2). The cross-coupling using water-soluble phosphine ligand TPPTS[11,12] showed lower catalytic activity under the reaction conditions giving 59% yield of **8a** (entry 3). Palladium−triphenylphosphine complex did not catalyze the reaction in water owing to its insolubility (entry 4). The arylation with 4-methylphenylboronic acid (**6**) and 4-methoxyphenylboronic acid (**7**) gave biaryls **9a** and **10a** in 91% and 72% yields, respectively, under the same reaction conditions (entries 5 and 6). The coupling reaction of **4a** with sodium tetraphenylborate took place without base to give 84% of **8a**. Bromobenzene (**4a′**) also underwent the cross-coupling with arylboron reagents at 25 °C by use of Pd−PEP catalyst in water. The reaction of **4a′** with **5**, **6**, and **7** gave biaryls **8a**, **9a**, and **10a** in 77%, 82%, and 70% yield, respectively (entries 8−10). It has been well-documented that Suzuki−Miyaura coupling of aryl halides with arylboronic acids catalyzed by palladium−phosphine complexes requires a reaction temperature around 80 °C even for aryl iodides.[8] This immobilized Pd−PEP (**2**) shows catalytic activity in water higher than that of other homogeneous palladium−phosphine complexes so far reported for the present transformation,[8,13] while immobilization of catalysts often causes decrease of catalytic activity in general. The reaction of *o*- and *p*-iodotoluene (**4b** and **4c**) with **5**−**7** gave the corresponding biaryls under the same reaction conditions in 66−85% yield (entries 12−19).

Encouraged by the results obtained in the Suzuki−Miyaura coupling, we examined the application of Pd−PEP (**2**) to the allylic arylation using arylboron reagents. Compared to the significant development of the Suzuki−Miyaura coupling, rather surprisingly only scattered attention has been paid to the use of arylboron reagents for the arylation of allyl alcohol derivatives.[14] In particular, only a few works on the catalytic allylic arylation of 1,3-disubstituted secondary allyl esters have been reported so far.[15] Recently, Kobayashi et al. have developed nickel-catalyzed arylation of allylic carbonates with lithium organoborates.[16] It was found that Pd−PEP complex **2** catalyzes allylic arylation of secondary and primary allyl acetates with arylboronic acid and sodium tetraphenylborate at 25 °C in water (Scheme 3). The results obtained are summarized in Table 2, which also includes those obtained with triphenylphosphine and TPPTS[11] for comparison. A mixture of cinnamyl acetate **11a**, phenylboronic acid (1.5 equiv), and potassium carbonate (4.5 equiv) in water was shaken in the presence of 2 mol % palladium of Pd−PEP **2** at 25 °C for 24 h to give 99% yield of 1,3-diphenylpropene (**12a**) (Table 2, entry 1). The resin-supported catalyst was readily recovered by simple filtration and could be taken on to the next series of the reaction. Thus, after completion of the reaction, the resin-supported catalyst was washed twice with THF and water under nitrogen atmosphere in the Merrifield vessel. To the reaction vessel were charged aqueous potassium carbonate, allyl acetate **11a**, and phenylboronic acid (**5**), and the entire mixture was agitated under the same reaction conditions to give 80% yield of **12a**. The allylic arylation with sodium tetraphenylborate took place to give 99% yield of **12a** (entry 3). The Pd−PEP showed much lower catalytic activity in

(11) TPPTS = triphenylphosphinetrisulfonate sodium salt. Sinou, D. *Bull. Soc. Chim. Fr.* **1987**, *3*, 480.

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(15) Palladium-catalyzed arylation of 1,3-diphenyl-2-propenyl acetate and 2-cyclohexenyl acetate with sodium tetraphenylborate has been reported; see: Legros, J.-Y.; Fiaud, J.-C. *Tetrahedron Lett.* **1990**, *31*, 7453.

(16) (a) Kobayashi, Y.; Mizojiri, R.; Ikeda, E. *J. Org. Chem.* **1996**, *61*, 5391. (b) Kobayashi, Y.; Takahisa, E.; Usmani, S. B. *Tetrahedron Lett.* **1998**, *39*, 597. (c) Usmani, S. B.; Takahisa, E.; Kobayashi, Y. *Tetrahedron Lett.* **1998**, *39*, 601.

Scheme 3

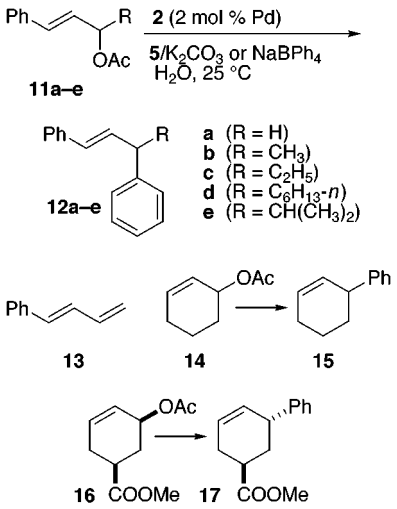


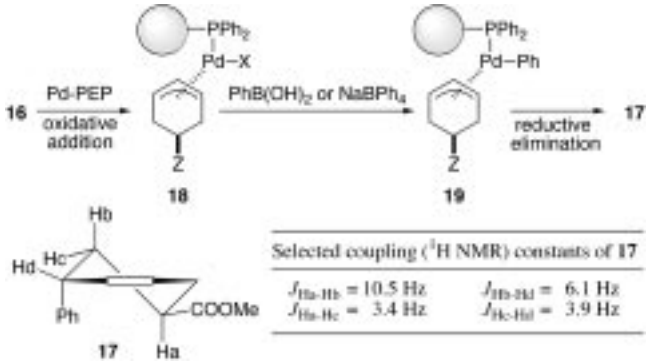
Table 2. Arylation of Allylic Acetates in Water Catalyzed by Pd−PEP (2)[a]

entry	allyl acetate	reagent	catalyst	product	yield (%)
1	**11a**	**5**	Pd(PEP) (**2**)	**12a**	99
2	**11a**	**5**	$Pd(PEP)_2$ (**3**)	**12a**	80
3[b]	**11a**	$NaBPh_4$	**2**	**12a**	99
4[c]	**11a**	**5**	**2**	**12a**	29
5	**11b**	**5**	**2**	**12b**	99
6	**11b**	**5**	Pd/TPPTS[d]	**12b**	15
7[e]	**11b**	**5**	$Pd(PPh_3)_4$	**12b**	no reaction
8[f]	**11b**	**5**	$Pd(PPh_3)_4$	**12b**	14[g]
9[b]	**11b**	$NaBPh_4$	**2**	**12b**	99
10	**11c**	**5**	**2**	**12c**	90
11[b]	**11c**	$NaBPh_4$	**2**	**12c**	94
12	**11d**	**5**	**2**	**12d**	85
13[b]	**11e**	$NaBPh_4$	**2**	**12e**	81[h]
14	**14**	**5**	**2**	**15**	90
15	**16**	**5**	**2**	**17**	45
16[b]	**16**	$NaBPh_4$	**2**	**17**	96

[a] All reactions were carried out in the presence of 2 mol % Pd of catalyst at 25 °C for 24 h, unless otherwise noted. [b] Without K_2CO_3. [c] Carried out in aqueous benzene solvent (H_2O/benzene = 1.0/5.0). [d] A catalyst generated in situ by mixing $[PdCl(\pi-C_3H_5)]_2$ and TPPTS (2 mol % Pd, Pd/P = 1/1) was used. [e] At 25 °C in aq. Na_2CO_3/benzene (1/5). [f] Reflux in aqueous Na_2CO_3/benzene (1/5). [g] 38% yield of 1-phenylbutadiene (**13**) was obtained. [h] 10% yield of regioisomeric product, 1,1-diphenyl-4-methylpent-2-ene, was obtained.

organic reaction media. The allylic arylation of **11a** with **5** in aqueous benzene (H_2O/benzene = 1/5) gave 29% yield of **12a** under otherwise the same reaction conditions (entry 4). This allylic arylation system using Pd−PEP catalyst, arylboron reagents, and genuine aqueous reaction media was also successfully applied to other substrates which have substituents on their C1 and C3 positions. Thus, reaction of 1-phenyl-3-acetoxybutene (**11b**) with phenylboronic acid was catalyzed by 2 mol % palladium of Pd−PEP in aqueous potassium carbonate to give 99% yield of 1,3-diphenylbutene (**12b**) as a single regioisomer (entry 5). Palladium−TPPTS complex generated in situ exhibited much lower catalytic activity under the present conditions to give 15% yield of **12b** (entry 6). Tetrakis(triphenylphosphine)palladium did not catalyze the present reaction at 25 °C in aqueous benzene solvent, and the reaction at higher temperature resulted in the formation of conjugated 1,3-diene **13** as a major product (entries 7 and 8). Secondary allylic acetates, 3-acetoxy-1-phenylpentene (**11c**), 3-acetoxy-1-phenylnonene (**11d**),

Scheme 4



and 3-acetoxy-4-methyl-1-phenylpentene (**11e**) also underwent the alkylation to give **12c**, **12d**, and **12e** in 94%, 85%, and 81% yield, respectively (entries 10−13). The Pd−PEP catalyst is also effective for the arylation of 2-cyclohexenyl acetate (**14**) in aqueous potassium carbonate to give 3-phenylcyclohexene (**15**) in 90% yield (entry 14).

The Pd−PEP catalyzed arylation was found to proceed with inversion of configuration with respect to the stereogenic carbon center where the arylation took place. Thus, the reaction of *cis*-3-acetoxy-5-carbomethoxy-1-cyclohexene (**16**) with phenylboronic acid in the presence of Pd−PEP (2 mol % of Pd) and potassium carbonate in water at 25 °C gave 3-phenyl-5-carbomethoxy-1-cyclohexene (**17**) in 45% yield as a single diastereoisomer (Table 2, entry 15). The chemical yield of arylation was improved by use of sodium tetraphenylborate to 96% without loss of stereoselectivity (entry 16). The stereochemistry of **17** was assigned to be trans by comparison of the ^1H NMR spectrum with reported data (Scheme 4).[17] This catalytic arylation must proceed via the π-allylpalladium intermediate **18**, which is formed by the oxidative addition of allylic acetates to a palladium(0) species. The stereochemistry upon oxidative addition to palladium(0) complexes coordinated with phosphine ligands has been reported to be inversion with allylic acetates.[18] It is deduced from the overall inversion of configuration observed here in the catalytic arylation that the stereochemistry upon arylation of π-allylpalladium is retention, indicating that the aryl group attacks the palladium atom of the π-allylpalladium intermediate to form the π-allyl(aryl)palladium intermediate **19** and reductive elimination gives the allylarene **17**. The inversion of configuration at catalytic allylic arylation has been also observed in the nickel-catalyzed arylation of allylic carbonates with lithium arylborate.[16a]

Experimental Section

General. The amphiphilic resin-supported triarylphosphine **1** was prepared on commercially available polystyrene−polyethylene graft copolymer beads, TentaGel S-NH_2 (Rapp Polymere, Germany) or ArgoGel NH_2 (Argonaut Technologies, CA), according to the reported procedure.[7a] Compounds **5**−**7**, and **11a** were purchased from Aldrich Chemical Co. Inc., and **4a**, **4a′**, **4b**, and **4c** were purchased from Wako Chemical Co. Inc. The agitation of the reaction mixture was performed on a wrist-action shaker (Burrel Scientific, Inc.). Acetates **14** and **16** were

(17) Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833. Also see ref 16a.
(18) Hayashi, T.; Hagihara, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* **1983**, *105*, 7767.

prepared according to the reported procedure.[19] Compounds **8a**,**b**, **9a**−**c**, **10a**−**c**, **11a**−**c**, **11e**, **12a**−**d**, and **13**−**17** are known compounds.[20] Authentic samples of **8a**,**b**, **9a**,**b**, and **10a** are commercially available.

Preparation of Palladium−PEP Complex 2. A Merrifield vessel was charged with 1.04 g of resin-supported phosphine **1**[7a] (loading value, 0.123 mmol/g) and 20 mL of dichloromethane. To the suspension was added 22.5 mg of di(μ-chloro)bis(η^3-allyl)-dipalladium(II) (0.062 mmol) at room temperature, and the mixture was shaken on a wrist-action shaker at room temperature for 15 min. After filtration, the resin beads were washed three times with dichloromethane (20 mL × 3) and dried under reduced pressure to give 1.06 g of **2**: ^{13}C NMR (gel-phase) δ 39.9, 61.4, 69.7, 70.6, 80.0 (d, $^2J_{C-P}$ = 31 Hz), 118.3 (d, $^2j_{C-P}$ = 5 Hz), 127.2, 127.7, 128.8, 130.8, 131.6, 132.0, 134.0, 136.5, 166.7; ^{31}P NMR (gel-phase) δ 23.2 (s).

General Procedure for the Cross-Coupling. Method A: Reaction of Aryl Halides with Arylboronic Acids. A Merrifield vessel was charged with aryl halide (0.5 mmol), arylboronic acid (0.75 mmol), 1.5 M KOH aqueous solution (1.5 mL), and Pd−PEP **2** (0.01 mmol Pd), and the mixture was shaken on a wrist-action shaker at 25 °C for 24 h under nitrogen. The reaction mixture was filtered, and the resin was extracted four times with chloroform (6 mL × 4). The combined extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (eluent, pentane) to give the coupling product.

Method B: Reaction of Aryl Halides with Sodium Tetraphenylborate. A Merrifield vessel was charged with aryl halide (0.5 mmol), sodium tetraphenylborate (0.75 mmol), 1.5 mL of water, and Pd−PEP **2** (0.01 mmol Pd), and the mixture was shaken on a wrist-action shaker at 25 °C for 24 h under nitrogen. The reaction mixture was filtered, and the resin was extracted four times with chloroform (6 mL × 4). The combined extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (eluent, pentane) to give coupling product.

All products in Table 1 were characterized by comparison of their mass spectra and/or ^{1}H NMR spectra with those of authentic samples or reported data.[20]

Preparation of Allyl Acetates (11b−e). A typical procedure is given for the preparation of **3-Acetoxy-1-phenylbutene (11b)**.[20,21] To a solution of cinnamaldehyde (2.64 g, 20 mmol) in 30 mL of THF was added a 0.87 M solution (THF) of MeMgBr (34 mL, 30 mmol) at 0 °C, and the entire mixture was stirred for 2 h. The reaction mixture was diluted with 30 mL of ether and quenched with a small amount of saturated NH_4Cl. The resulting suspension was filtered through Celite, and the filter cake was rinsed three times with ether. The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (hexane/EtOAc = 3/1) to give 1-phenyl-1-buten-3-ol. To a solution of 1-phenyl-1-buten-3-ol in 20 mL of dichloromethane was added pyridine (5 mL) and acetic anhydride (5 mL) at 0 °C, and the mixture was stirred at ambient temperature for 2 h. The reaction mixture was concentrated under reduced pressure, and the residue was diluted with ether. The mixture was washed with water and saturated $CuSO_4$ and dried over Na_2SO_4. After removal of the solvent, chromatography on silica gel (hexane/EtOAc = 10/1) followed by Kugelrohr distillation (pot temperature 135 °C/4 mmHg) gave 2.96 g (78% for two steps) of 3-acetoxy-1-phenylbutene (**11b**) as a colorless oil: ^{1}H NMR δ 1.25 (d, J = 6.6 Hz, 3H), 2.07 (s, 3H), 5.53 (quint, J = 6.6 Hz, 1H), 6.18 (dd, J = 6.6, 16.1 Hz, 1H), 6.60 (d, J = 16.1 Hz, 1H), 7.23−7.39 (m, 5H). **3-Acetoxy-1-phenyl-1-pentene (11c):**[20] ^{1}H NMR δ 0.94 (t, J = 7.6 Hz, 3H), 1.73 (dq, J = 6.9, 7.6 Hz, 2H), 2.08 (s, 3H), 5.34 (dt, J = 6.9, 7.3 Hz, 1H), 6.12 (dd, J = 7.3, 16.2 Hz, 1H), 6.60 (d, J = 16.2 Hz, 1H), 7.24−7.40 (m, 5H). **3-Acetoxy-1-phenyl-1-nonene (11d):** ^{1}H NMR δ 0.88 (t, J = 6.8 Hz, 3H), 1.25−1.33 (m, 8H), 1.61−1.76 (m, 2H), 2.07 (s, 3H), 5.39 (dt, J = 6.6, 7.3 Hz, 1H), 6.12 (dd, J = 7.3, 16.1 Hz, 1H), 6.60 (d, J = 16.1 Hz, 1H), 7.22−7.39 (m, 5H); ^{13}C{^{1}H} NMR δ 14.1, 21.3, 22.6, 25.2, 29.1, 31.7, 34.6, 74.8, 126.6, 127.8, 127.9, 128.6, 132.4, 136.5, 170.3. Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.14; H, 9.09. **3-Acetoxy-4-methyl-1-phenyl-1-pentene (11e):**[20] ^{1}H NMR δ 0.95 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.96 (octet, J = 6.6 Hz, 1H), 2.09 (s, 3H), 5.21 (dd, J = 6.6, 7.6 Hz, 1H), 6.12 (dd, J = 7.6, 15.8 Hz, 1H), 6.60 (d, J = 15.8 Hz, 1H), 7.24−7.41 (m, 5H).

General Procedure for the Allylic Arylation. Method A: Reaction of Allyl Acetates with Arylboronic Acids. A Merrifield vessel was charged with arylboronic acid (0.75 mmol), potassium carbonate (2.3 mmol), Pd−PEP **2** (0.01 mmol Pd), and 1.5 mL of water. To the mixture was added allyl acetate (0.5 mmol) at ambient temperature, and the reaction mixture was shaken on a wrist-action shaker at 25 °C for 24 h under nitrogen. The reaction mixture was filtered, and the resin was extracted four times with chloroform (6 mL × 4). The combined extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (eluent, pentane) to give the arylation product.

Method B: Reaction of Aryl Halides with Sodium Tetraphenylborate. A Merrifield vessel was charged with sodium tetraphenylborate (0.75 mmol), Pd−PEP **2** (0.01 mmol Pd), and 1.5 mL of water. To the mixture was added allyl acetate (0.5 mmol) at ambient temperature, and the reaction mixture was shaken on a wrist-action shaker at 25 °C for 24 h under nitrogen. The reaction mixture was filtered, and the resin was extracted four times with chloroform (6 mL × 4). The combined extract was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was chromatographed on silica gel (eluent, pentane) to give the arylation product.

Products **12a**,[14a] **12b**,[21] **12c**,[22] **12d**,[23] **13**,[24] **15**,[25] and **17**[16a] were characterized by comparison of their mass spectra and/or ^{1}H NMR spectra with those of authentic samples and/or reported data.[20] **1,3-Diphenyl-1-pentene (12c):** ^{1}H NMR δ 0.91 (t, J = 7.3 Hz, 3H), 1.78−1.89 (m, 2H), 3.31 (quint, J = 7.3 Hz, 1H), 6.33 (dd, J = 7.3, 15.8 Hz, 1H), 6.40 (d, J = 15.8 Hz, 1H), 7.16−7.35 (m, 10H); ^{13}C{^{1}H} NMR δ 12.3, 28.8, 51.0, 126.1, 126.2, 127.0, 127.7, 128.5, 129.5, 134.2, 137.6, 144.5. Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.54, H, 8.46. **1,3-Diphenyl-1-nonene (12d):**[22] ^{1}H NMR δ 0.86 (t, J = 7.1 Hz, 3H), 1.24−1.37 (m, 8H), 1.79 (dt, J = 6.8, 7.3 Hz, 2H), 3.40 (dt, J = 7.3, 7.3 Hz, 1H), 6.32 (dd, J = 7.3, 15.8 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 7.16−7.35 (m, 10H); ^{13}C{^{1}H} NMR δ 14.1, 22.7, 27.6, 29.3, 31.8, 35.9, 49.2, 126.1, 126.2, 127.0, 127.6, 128.4, 128.5, 129.3, 134.5, 137.7, 144.8. Anal. Calcd for $C_{21}H_{26}$: C, 90.59; H, 9.41. Found: C, 90.57; H, 9.36. **1,3-Diphenyl-4-methyl-1-pentene (12e):** ^{1}H NMR δ 0.71 (d, J = 6.6 Hz, 3H), 1.00 (d, J = 6.6 Hz, 3H), 2.00−2.09 (m, 1H), 3.02−3.07 (m, 1H), 6.38−6.39 (m, 2H), 7.17−7.35 (m, 10H); ^{13}C{^{1}H} NMR δ 20.9, 21.2, 33.2, 57.6, 126.0, 126.1, 127.0, 128.0, 128.4, 128.6, 130.3, 133.2, 137.7, 144.3. Anal. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.23; H, 8.61. **5-Methoxycarbonyl-3-phenyl-1-cyclohexene (17):**[16a] ^{1}H NMR δ 1.97 (ddd, J = 3.4, 3.9, 13.2 Hz, 1H), 2.16 (ddd, J = 6.1, 10.5, 13.2 Hz, 1H), 2.33−2.37 (m, 2H), 2.58−2.65 (m, 1H), 3.54−3.60 (m, 1H), 5.76−5.80 (m, 1H), 5.93−5.98 (m, 1H), 7.20−7.33 (m, 5H).

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(19) CAS numbers for these compounds are supplied as follows: **8a** [92-52-4]; **8b** [643-58-3]; **9a** [644-08-6]; **9b** [611-61-0]; **9c** [613-33-2]; **10a** [613-37-6]; **10b** [92495-54-0]; **10c** [53040-92-9]; **11a** [103-54-8]; **11b** [74457-38-8]; **11c** [113334-98-8]; **11e** [108814-27-3]; **12a** [3412-44-0]; **12b** [7302-01-4]; **12c** [189322-54-1], [189322-53-0]; **12d** [203316-75-0]; **13** [16939-57-4]; **14** [76704-31-9]; **15** [15232-96-9]; **16** [11518-98-1], [60729-55-7]; **17** [82342-65-2].

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Supporting Information Available: $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ gel-phase NMR spectra of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Additions and Corrections

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Page 9156. The structures should be numbered as follows: In eq 2, compounds **12** and **13** should be read as compounds **5** and **6**, respectively. In eq 3, compounds **14** and **15** should be read as compounds **7** and **8**, respectively. In eq 4, compounds **16** and **17** should be read as compounds **9** and **10**, respectively. In eq 5, compounds **18** and **19** should be read as compounds **11** and **12**, respectively.

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