Room-Temperature Palladium-Catalyzed Allyl Cross-Coupling Reaction with Boronic Acids Using Phosphine-Free Hydrazone Ligands

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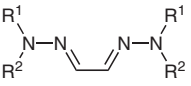
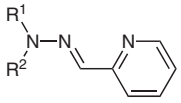
Abstract: Palladium-catalyzed allyl cross-coupling reaction of allylic acetates with a variety of boronic acids at room temperature using a catalytic amount of $Pd(OAc)_2$ with phosphine-free hydrazone as a ligand gave the allylbenzene derivatives in good yields.

Key words: palladium, catalysis, allyl cross-coupling, boronic acid, hydrazones



1a: R^1 = Ph, R^2 = Me
1b: R^1,R^2 = $(CH_2)_6$
1c: R^1,R^2 = $(CH_2)_5$
1d: R^1,R^2 = $(CH_2)_4$



2a: R^1,R^2 = $(CH_2)_6$
2b: R^1,R^2 = $(CH_2)_5$

Figure 1 Hydrazone ligands **1** and **2**

Palladium-catalyzed C–C bond formation reactions have been recognized as powerful tools in multiple organic transformations.[1] Palladium-catalyzed cross-coupling of aryl and vinyl halides with aryl- and vinylboronic acids (Suzuki–Miyaura coupling)[2] has especially gained popularity due to broad functional group tolerance, the availability of boronic acid substrates, and the lack of toxic by-products. On the other hand, a 1,3-diarylpropene framework constitutes an important structural assembly in many molecules of biological importance.[3] The palladium-catalyzed allyl cross-coupling reaction of cinnamyl acetate with arylboronic acids provides a powerful tool for the synthesis of 1,3-diarylpropenes. Previously allyl cross-coupling reactions of allylic acetates using $PdCl_2(TFP)_2$ with KF as a fluoride source,[4] resin-supported Pd-bis(PPh_3) complex[5] and $Pd_2(dba)_3{\cdot}CHCl_3$–PPh_3 under microwave irradiation conditions[6] were reported. However, phosphines in palladium complexes are often air-sensitive. Although phosphine-free palladium catalytic systems have also been reported,[7] these reactions require additional tetra-*n*-butyl ammonium salt as an activator, heating conditions, or long times to complete the reaction. We recently demonstrated air-stable phosphine-free hydrazone as an effective ligand for palladium-catalyzed C–C bond formation such as the Suzuki–Miyaura,[8] Mizoroki–Heck,[9] Sonogashira, and Hiyama cross-coupling reactions.[10] We now report the use of phosphine-free hydrazone ligands **1** and **2** (Figure 1) for a palladium-catalyzed allyl cross-coupling reaction of allylic acetates with boronic acids at room temperature.

We examined the allyl cross-coupling reaction of cinnamyl acetate and phenylboronic acid in the presence of 2 mol% of Pd catalyst for one hour under an argon atmosphere at room temperature to determine the optimum reaction conditions (Table 1).

The effect of various hydrazone ligands was investigated using $Pd(OAc)_2$ with K_2CO_3 as a base (Table 1, entries 1–5). In the presence of hydrazone **1a**, which is the effective ligand for the Suzuki–Miyaura reaction of aryl halides, 1,3-diphenylpropene (**3a**) was obtained in moderate yield (Table 1, entry 1). In this reaction, small amounts of **4**[11] and **5**[12] were also obtained as by-products. The use of hydrazone **1c** with a 6-membered ring as a ligand led to high yield (Table 1, entry 3). On the other hand, hydrazone **2a** was not effective for this reaction (Table 1, entry 5). Next, the effect of various palladium sources was investigated (Table 1, entries 3 and 6–9). $Pd(OAc)_2$ proved to be the best palladium source for this reaction. Several bases were also tested (Table 1, entries 3 and 10–13). Although the use of fluoride salts such as KF and CsF led to good yields (Table 1, entries 12 and 13), K_2CO_3 was found to be the most effective base in this reaction (entry 3). Finally the effect of various solvents was investigated (Table 1, entries 3 and 14–20). The DMF–H_2O (3:1) mixture was found to be the solvent of choice. Other solvents proved less effective in this reaction.

The effect of leaving groups of cinnamyl esters in this reaction was investigated (Table 2, entries 1–3). Using cinnamyl benzoate and pivalate instead of acetate, the yields were decreased (Table 2, entry 1 vs. entries 2 and 3). Based on these results, the allyl cross-coupling reaction of cinnamyl and allyl acetate with various boronic acids was investigated (Table 2, entries 4–14).[13]

Using *p*-tolylboronic acid led to good yields of the desired products (Table 2, entry 4). With 4-methoxyphenylboronic acid (2 equiv), the reaction gave the corresponding product with moderate yield after one hour (Table 2, entry 5). In the reaction of 4-trifluoromethylphenylboronic acid longer reaction times, such as 24 h, were necessary

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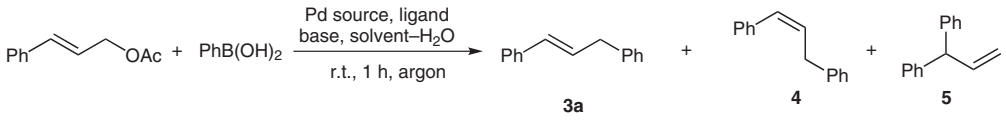
Table 1 Optimization of Reaction Conditions for Phenylation of Cinnamyl Acetate[a]

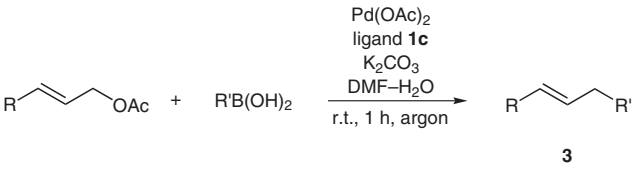


Entry	Ligand	Pd source	Base	Solvent	**3a/4/5**[b]	Yield (%)[c]
1	**1a**	$Pd(OAc)_2$	K_2CO_3	DMF	98.0/1.5/0.5	78
2	**1b**	$Pd(OAc)_2$	K_2CO_3	DMF	99.0/0.8/0.2	92
3	**1c**	**$Pd(OAc)_2$**	**K_2CO_3**	**DMF**	**99.0/0.8/0.2**	**94**
4	**1d**	$Pd(OAc)_2$	K_2CO_3	DMF	98.8/0.9/0.3	89
5	**2a**	$Pd(OAc)_2$	K_2CO_3	DMF	98.5/1.0/0.5	69
6	**1c**	$PdCl_2$	K_2CO_3	DMF	97.8/1.3/0.9	71
7	**1c**	$[PdCl(allyl)]_2$	K_2CO_3	DMF	98.9/1.0/0.1	92
8	**1c**	$PdCl_2(MeCN)_2$	K_2CO_3	DMF	98.8/1.0/0.2	88
9	**1c**	$Pd(acac)_2$	K_2CO_3	DMF	99.0/0.5/0.5	5
10	**1c**	$Pd(OAc)_2$	K_3PO_4	DMF	98.1/1.0/0.9	86
11	**1c**	$Pd(OAc)_2$	Cs_2CO_3	DMF	98.6/1.1/0.3	69
12	**1c**	$Pd(OAc)_2$	CsF	DMF	98.8/1.1/0.1	89
13	**1c**	$Pd(OAc)_2$	KF	DMF	98.8/1.1/0.1	79
14	**1c**	$Pd(OAc)_2$	K_2CO_3	NMP	98.9/0.8/0.3	92
15	**1c**	$Pd(OAc)_2$	K_2CO_3	MeOH	98.4/1.1/0.5	72
16	**1c**	$Pd(OAc)_2$	K_2CO_3	MeCN	98.8/1.1/0.1	52
17	**1c**	$Pd(OAc)_2$	K_2CO_3	DMSO	98.2/1.4/0.4	57
18	**1c**	$Pd(OAc)_2$	K_2CO_3	DMF[d]	98.8/0.9/0.3	64
19	**1c**	$Pd(OAc)_2$	K_2CO_3	DMF[e]	99.0/0.8/0.2	75
20	**1c**	$Pd(OAc)_2$	K_2CO_3	DMF[f]	97.9/1.4/0.7	52

[a] Reaction conditions: cinnamyl acetate (0.5 mmol), phenylboronic acid (0.6 mmol), base (1.0 mmol), solvent (1.5 mL), H_2O (0.5 mL), palladium source (0.01 mmol), ligand (0.01 mmol).
[b] Determined by ^1H NMR.
[c] Isolated yields.
[d] In this reaction, DMF (2 mL) was added in the absence of H_2O.
[e] In this reaction, a mixture of DMF (1.9 mL) and H_2O (0.1 mL) was added.
[f] In this reaction, a mixture of DMF (1 mL) and H_2O (1 mL) was added.

(Table 2, entry 6). The reactions of other arylboronic acids led to good yields after one hour (Table 2, entries 7–9). The reactions of cinnamyl acetate derivatives with phenylboronic acid also led to good yields after one hour (Table 2, entries 10–12). Next we investigated the reaction of allyl acetate. Using 1-naphthaleneboronic acid led to good yield of 1-allylnaphthalene (Table 2, entry 13). Moreover, we investigated the vinylation of cinnamyl acetate for the preparation of 1,4-diene. The 1,4-diene framework also constitutes an important structural assembly in many molecules of biological importance[14] in addition to its applications in organic synthesis.[15] Recently, the reaction of vinyltrifluoroborate with allyl acetate was reported.[16] In this case, 1,4-dienes were obtained using $PdCl_2(dppf)\cdot CH_2Cl_2$ under microwave irradiation at 80 °C. On the other hand, in our case, the reaction of 2-phenylvinylboronic acid with cinnamyl acetate gave a high yield of the corresponding 1,4-diene-type product **3l** after one hour at room temperature under phosphine-free conditions (Table 2, entry 14).

Table 2 Allyl Cross-Coupling Reaction of Cinnamyl Esters and Allyl Acetate with Boronic Acids[a]



Entry	R	R′	Product	Yield (%)[b]
1	Ph	Ph	**3a**	94
2	Ph[c]	Ph	**3a**	83
3	Ph[d]	Ph	**3a**	79
4	Ph	*p*-MeC_6H_4	**3b**	85
5[e]	Ph	*p*-$MeOC_6H_4$	**3c**	64
6[f]	Ph	*p*-$CF_3C_6H_4$	**3d**	71
7	Ph	3,5-$Me_2C_6H_3$	**3e**	92
8	Ph	*o*-MeC_6H_4	**3f**	92
9	Ph	1-Naph	**3g**	79
10	*p*-MeC_6H_4	Ph	**3h**	80
11	*p*-$MeOC_6H_4$	Ph	**3i**	77
12	*p*-$NO_2C_6H_4$	Ph	**3j**	86
13	H	1-Naph	**3k**	88
14	Ph	*trans*-PhCH=CH	**3l**	96[g]

[a] Reaction conditions: acetate (0.5 mmol), boronic acid (0.6 mmol), K_2CO_3 (1.0 mmol), DMF (1.5 mL), H_2O (0.5 mL), $Pd(OAc)_2$ (2 mol%), ligand **1c** (2 mol%), r.t., 1 h, under argon.
[b] Isolated yields (GC–MS purities of all products were >98%).
[c] This reaction was carried out using benzoate instead of acetate.
[d] This reaction was carried out using pivalate instead of acetate.
[e] This reaction was carried out using 4-methoxyphenylboronic acid (1.0 mmol).
[f] This reaction was carried out for 24 h.
[g] GC–MS purity of **3l** was 94.9%.

We also tried the reaction of disubstituted allylic acetates such as prenyl acetate with 1-naphthaleneboronic acid. Using similar conditions as the reaction with cinnamyl acetate (Table 3, entry 1), the corresponding product, however, was not obtained. In this case, naphthalene, which was the reduced product of 1-naphthaleneboronic acid, was obtained. Consequently, we attempted to optimize the coupling conditions of prenyl acetate with 1-naphthaleneboronic acid (Table 3). When DMF was used as a solvent in the absence of H_2O, a small amount of reaction product **3m** was obtained (Table 3, entry 2). Using 5 mol% of $Pd(OAc)_2$ and ligand **1c** for 24 hours increased the yield of **3m** to 15% (Table 3, entry 3). The allyl cross-coupling conditions were optimized using a variety of bases (K_2CO_3, CsF, Cs_2CO_3), solvents (DMF, MeCN, MeOH), and ligands (**1a**, **1c**, **2a**, **2b**[17]) (Table 3, entries 3–10). We found the following optimized conditions: 5 mol% of the $Pd(OAc)_2$/hydrazone **2a** system and 2.6 equivalents of Cs_2CO_3 as a base in MeCN at room temperature under an argon atmosphere for 24 hours (Table 3, entry 9).[18] Based on these results, the reaction of geranyl acetate, neryl acetate, and linalyl acetate with 1-naphthaleneboronic acid was investigated (Table 3, entries 11–13). Although these allylic acetates easily gave β-hydride-eliminated 1,3-diene products via π-allylpalladium intermediate using palladium catalyst such as a catalytic amount of $Pd(PPh_3)_4$,[19] an *E*/*Z* mixture of product **3n** was obtained with good yields in all cases.

In conclusion, we found that the palladium-catalyzed allyl cross-coupling reaction of allylic acetates with boronic acids at room temperature using a catalytic amount of $Pd(OAc)_2$ with phosphine-free hydrazone **1c** or **2a** as a ligand gave the allylbenzene derivatives in good yields.

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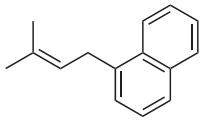
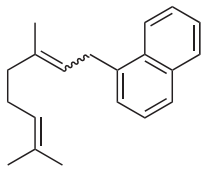
Table 3 Allyl Cross-Coupling Reaction of Disubstituted Allylic Acetates with 1-Naphthaleneboronic Acid[a]

Entry	Allylic acetate	Ligand	Base	Solvent	Product	Yield (%)[b]
1[c]	prenyl acetate	**1c**	K_2CO_3	DMF–H_2O (3:1)		0
2[c]		**1c**	K_2CO_3	DMF		3
3		**1c**	K_2CO_3	DMF		15
4		**1c**	CsF	DMF		6
5		**1c**	Cs_2CO_3	DMF		22
6		**1c**	Cs_2CO_3	MeCN	**3m**	47
7		**1c**	Cs_2CO_3	MeOH		1
8		**1a**	Cs_2CO_3	MeCN		37
9		**2a**	Cs_2CO_3	MeCN		62
10		**2b**	Cs_2CO_3	MeCN		37
11	geranyl acetate	**2a**	Cs_2CO_3	MeCN		69[d]
12	neryl acetate	**2a**	Cs_2CO_3	MeCN		68[e]
13	linalyl acetate	**2a**	Cs_2CO_3	MeCN		70[f]
					3n	

[a] Reaction conditions: acetate (0.5 mmol), 1-naphthaleneboronic acid (0.6 mmol), base (1.3 mmol), solvent (2 mL), $Pd(OAc)_2$ (5 mol%), ligand (5 mol%), r.t., 24 h, under argon.
[b] Isolated yields (GC–MS purities of all products were >98%).
[c] This reaction was carried out using $Pd(OAc)_2$ (2 mol%) and ligand **1c** with K_2CO_3 (1.0 mmol) for 1 h.
[d] *E*/*Z* mixture = 66:34.
[e] *E*/*Z* mixture = 48:52.
[f] *E*/*Z* mixture = 62:38.

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(13) **General Procedure for Allyl Cross-Coupling Reaction of Cinnamyl and Allyl Acetate with Boronic Acids (Table 2)**: To a mixture of acetate (0.5 mmol), K_2CO_3 (138.2 mg, 1.0 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), and ligand **1c** (2.22 mg, 0.01 mmol) in DMF (1.5 mL) and H_2O (0.5 mL) was added boronic acid (0.6 mmol) at r.t. under an atmosphere of argon. After 1 h, the mixture was diluted with EtOAc and H_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography. All prepared compounds **3** (except for **3e**) were known and identified by ^1H NMR, ^{13}C NMR, and MS. **Analytical Data of 3e (Table 2, entry 7)**: colorless oil. IR (neat): 1604 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.29 (s, 6 H), 3.47 (d, *J* = 6.5 Hz, 2 H), 6.33 (dt, *J* = 15.7, 6.6 Hz, 1 H), 6.45 (d, *J* = 15.9 Hz, 1 H), 6.86 (s, 3 H), 7.16–7.37 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ = 21.1, 39.2, 126.1, 126.4, 127.0, 127.8, 128.5, 129.4, 130.8, 137.5, 138.0, 140.0. MS (EI, relative intensity): *m*/*z* = 222 (86) [M^+]. HRMS (FAB–MS): *m*/*z* calcd for $C_{17}H_{18}$: 222.1409; found: 222.1408. GC–MS purity: 98.5%.

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(17) **Preparation of Hydrazone 2b**: To a solution of *N*-aminopiperidine (0.060 g, 0.60 mmol) in MeOH (2.0 mL) was added 2-pyridinecarboxaldehyde (0.054 g, 0.51 mmol) and the mixture was stirred for 24 h at r.t. The mixture was directly concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane–EtOAc, 4:1). Yield: 0.092 g, 0.49 mmol, 96%; colorless oil. IR (neat): 1572 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.51–1.59 (m, 2 H), 1.66–1.79 (m, 4 H), 3.24 (t, *J* = 5.6 Hz, 4 H), 7.08–7.12 (m, 1 H), 7.59–7.64 (m, 2 H), 7.83 (dd, *J* = 8.1, 0.8 Hz, 1 H), 8.50 (dd, *J* = 4.8, 0.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 24.4, 25.4, 52.0, 119.4, 122.3, 134.3, 136.5, 149.4, 156.3. MS (EI, relative intensity): *m*/*z* = 189 (11) [M^+]. HRMS (FAB–MS): *m*/*z* calcd for $C_{11}H_{15}N_3$: 189.1266; found: 189.1280.

(18) **General Procedure for Allyl Cross-Coupling Reaction of Disubstituted Allylic Acetates with 1-Naphthaleneboronic Acid (Table 3)**: To a mixture of acetate (0.5 mmol), Cs_2CO_3 (423.6 mg, 1.3 mmol), $Pd(OAc)_2$ (5.61 mg, 0.025

mmol), and ligand **2a** (5.08 mg, 0.025 mmol) in MeCN (2 mL) was added 1-naphthaleneboronic acid (103.2 mg, 0.6 mmol) at r.t. under an atmosphere of argon. After 24 h, the mixture was diluted with EtOAc and H_2O. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography. Compounds **3m** and **3n** were known and identified by ^1H NMR, ^{13}C NMR, and MS.

(19) Keinan, E.; Kumar, S.; Dangur, V.; Vaya, J. *J. Am. Chem. Soc.* **1994**, *116*, 11151.

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