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Palladium-catalyzed decarboxylative coupling of benzoic acid derivatives using hydrazone ligands

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ABSTRACT

Palladium-catalyzed decarboxylative coupling of benzoic acid derivatives with arylboroxins gave biaryls using a catalytic amount of $Pd(TFA)_2$–hydrazone **1d** system with Ag_2CO_3 at 80 °C in good yields. We also found that decarboxylative coupling with aryl(trialkoxy)silanes gave biaryls using a $Pd(TFA)_2$–hydrazone **1g** system with AgF in good yields.

Palladium-catalyzed coupling reactions of aryl halides with aryl organometallics, such as the Suzuki–Miyaura coupling and Hiyama coupling, have become common and convenient synthetic methods in organic chemistry for biaryl compounds.[1] On the other hand, the Myers group reported a palladium-catalyzed decarboxylative Heck reaction of benzoic acid derivatives, instead of aryl halides, with olefins in 2002.[2] After the Gooßen group[3] and the Forgione group[4] independently reported the palladium-catalyzed decarboxylative coupling of benzoic acid derivatives, instead of arylboronic acids, with aryl bromides in 2006, the Becht group[5] and the Liu group[6] also reported the palladium-catalyzed decarboxylative coupling with aryl halides. More recently, the Liu group[7] and the Tan group[8] reported the palladium-catalyzed decarboxylative coupling of benzoic acid derivatives with arylboronic acids or six-membered boronic acid esters under high reaction temperature (120–130 °C). However, palladium-catalyzed decarboxylative coupling of benzoic acids with other arylboronic acid derivatives, such as arylboroxins, and aryl(trialkoxy)silanes has not been reported. We recently demonstrated air-stable hydrazone as an effective ligand in such palladium-catalyzed C—C bond formations as the Suzuki–Miyaura coupling[9] the Mizoroki–Heck type reaction,[10] the Sonogashira coupling,[11] the Hiyama coupling,[11a] and the allyl cross-coupling reactions.[12] We now report the use of hydrazone ligands **1**–**3** (Fig. 1) for a palladium-catalyzed decarboxylative coupling of benzoic acids with arylboroxins and aryl(trialkoxy)silanes.

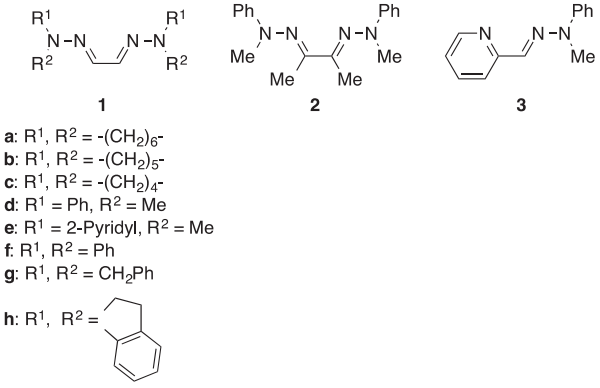

Figure 1. Hydrazone ligands.

Initially, we sought the optimal reaction conditions for a palladium-catalyzed decarboxylative coupling of the benzoic acid derivative with arylboroxin using the hydrazone ligand. 2,4,6-Trimethoxybenzoic acid and tri-*p*-tolylboroxin (**3a**) were chosen as model substrates with 7.5 mol % of Pd catalyst for 2 h under an air atmosphere at 80 °C (Table 1). Using 7.5 mol % of hydrazone **1a** as a ligand, we observed that the decarboxylative coupling in the presence of $Pd(TFA)_2$ with Ag_2CO_3 in DMSO as a solvent proceeded to give the corresponding product **4a** in 38% yield (Table 1, entry 1). We tested other hydrazones **1b**–**e**, **1h**, **2**, and **3** and found that hydrazone **1d** was an effective ligand for this reaction (entry 4). Without ligand, the reaction gave low yields of the desired

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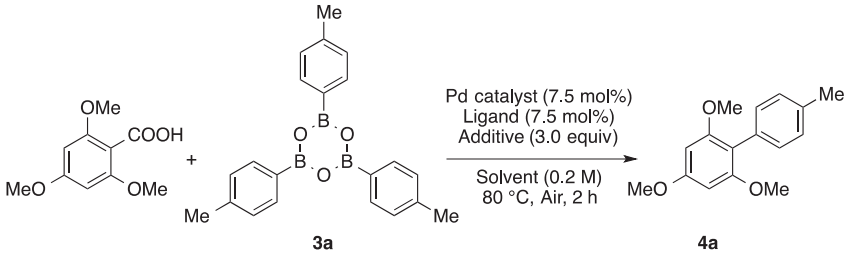
Table 1
Optimization of reaction conditions for the palladium-catalyzed decarboxylative coupling of 2,4,6-trimethoxybenzoic acid with tri-*p*-tolylboroxin[a]



3a **4a**

Entry	Ligand	Pd catalyst	Additive	Solvent	Yield[b] (%)
1	**1a**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	38
2	**1b**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	24
3	**1c**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	44
4	**1d**	**$Pd(TFA)_2$**	**Ag_2CO_3**	**DMSO**	**71**
5	**1e**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	10
6	**1h**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	52
7	**2**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	58
8	**3**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	Trace
9	—	$Pd(TFA)_2$	Ag_2CO_3	DMSO	36
10	PPh_3 (15 mol %)	$Pd(TFA)_2$	Ag_2CO_3	DMSO	43
11[c]	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	63
12[d]	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	29
13[e]	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	6
14[f]	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMSO	23
15	**1d**	$Pd(OAc)_2$	Ag_2CO_3	DMSO	27
16	**1d**	$Pd(acac)_2$	Ag_2CO_3	DMSO	22
17	**1d**	$PdCl_2$	Ag_2CO_3	DMSO	37
18	**1d**	$PdCl_2(MeCN)_2$	Ag_2CO_3	DMSO	31
19	**1d**	$Pd_2(dba)_3{\cdot}CHCl_3$	Ag_2CO_3	DMSO	44
20	**1d**	$Pd(TFA)_2$	Ag_2O	DMSO	30
21	**1d**	$Pd(TFA)_2$	AgOAc (6.0 equiv)	DMSO	30
22	**1d**	$Pd(TFA)_2$	AgF (6.0 equiv)	DMSO	28
23	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMSO/H_2O (3:1)	45
24	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMAc	10
25	**1d**	$Pd(TFA)_2$	Ag_2CO_3	DMF	7
26	**1d**	$Pd(TFA)_2$	Ag_2CO_3	NMP	Trace
27	**1d**	$Pd(TFA)_2$	Ag_2CO_3	PhMe	0

[a] Reaction conditions: 2,4,6-trimethoxybenzoic acid, tri-*p*-tolylboroxin (0.67 equiv), ligand (7.5 mol %), Pd source (Pd = 7.5 mol %), additive (3.0 equiv), solvent (0.2 M) at 80 °C for 2 h under air.
[b] Isolated yields.
[c] 0.40 mmol of *p*-tolylboronic acid was used instead of tri-*p*-tolylboroxin.
[d] 0.40 mmol of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)toluene was used instead of tri-*p*-tolylboroxin.
[e] 0.40 mmol of *p*-tolylboronic acid MIDA ester was used instead of tri-*p*-tolylboroxin.
[f] 0.40 mmol of potassium *p*-tolyltrifluoroborate was used instead of tri-*p*-tolylboroxin.

product (entry 9). Using PPh_3 as the ligand, the reaction also gave low yields of the desired product (entry 10). When we used other organoboron compounds including *p*-tolylboronic acid, the yields decreased (entries 11–14). We also investigated the effect of various palladium sources (entry 4 vs entries 15–19), additives (entry 4 vs entries 20–22), and solvents (entry 4 vs entries 23–27). Using $Pd(TFA)_2$ with Ag_2CO_3 in DMSO led to good yields for this reaction (entry 4).

Under optimized reaction conditions, the effect of various arylboroxins in the decarboxylative coupling was investigated using 2,4,6-trimethoxybenzoic acid (Table 2).[13] Using tri-*p*-tolylboroxin (**3a**), tri-*m*-tolylboroxin (**3b**) and triphenylboroxin (**3d**) led to good yields of the corresponding products (entries 1, 2 and 4). *Para*- and *meta*-substituted arylboroxins also gave products with moderate to good yields (entries 5–8). Unfortunately, the reaction with tri-*o*-tolylboroxin (**3c**) and tri-1-naphthylboroxin (**3i**) did not give the corresponding products **4c** and **4i** (entries 3 and 9). Tri-2-naphthylboroxin (**3j**) and tri-3,4-dichlorophenylboroxin (**3k**) led to good yields of the corresponding products (entries 10 and 11). The reaction of 2,4,6-triethoxybenzoic acid with tri-*p*-anisylboroxin (**3h**) gave the corresponding product **4l** in 15% yield (entry 12). We also tested the reaction of 2,3,4,6-tetramethoxybenzoic acid and 2,6-dimethoxybenzoic acid. The reaction with tri-3,4-dichlorophenylboroxin (**3k**) gave the corresponding products **4m** and **4n** in low yields (entries 13 and 14).

We next tried the use of the hydrazone ligand for a palladium-catalyzed decarboxylative coupling with aryl(trialkoxy)silanes instead of arylboroxins. We sought the optimal reaction conditions for decarboxylative coupling of 2,4,6-trimethoxybenzoic acid with *p*-tolyl(triethoxy)silane (**5a**) as model substrates with 7.5 mol % of Pd catalyst for 2 h under an air atmosphere at 100 °C (Table 3). Using 7.5 mol % of hydrazone **1d** as a ligand, we observed that the decarboxylative coupling in the presence of $Pd(TFA)_2$ with AgF in DMAc as a solvent proceeded to give the corresponding product **4a** in 53% yield (Table 3, entry 1). We tested other hydrazones **1e**–**h**, **2**, and **3** and found that hydrazone **1g** was an effective ligand for this reaction (entry 4). Without ligand, the reaction gave low yields of the desired product (entry 8). Using PPh_3 as a ligand, the reaction also gave low yields of the desired product (entry 9). We investigated the effect of various palladium sources and additives (entries 10–15). Using $Pd(TFA)_2$ with AgF led to good yields for this reaction (entry 4). Several solvents were also tested