



Generally applicable and efficient oxidative Heck reaction of arylboronic acids with olefins catalyzed by cyclopalladated ferrocenylimine under base- and ligand-free conditions

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ABSTRACT

A mild and efficient method for oxidative Heck-type reaction of arylboronic acids with olefins catalyzed by cyclopalladated ferrocenylimine was developed. The results represent the first examples involving the palladacycle as the catalyst for such couplings. Moreover, the catalytic system could tolerate various functional groups, such as F, Cl, Br, NO₂ and CH₃O, and the substrates could be extended to a wide range of olefins from acrylic esters, α,β -unsaturated ketones to alkenes. Furthermore, the olefination could proceed well under base- and ligand-free conditions and employ oxygen as the environmentally benign oxidant.

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1. Introduction

The palladium-catalyzed carbon–carbon bond forming reactions have become one of the most important and reliable tools in a great number of synthesis during the last ten years.¹ After being firstly discovered by Heck, oxidative Heck reaction has attracted considerable attention and various systems under palladium catalysis have been developed.^{2–4} Notably, Larhed and co-workers firstly reported a Pd(II)/dmphen catalytic version for the olefination of organoboronic acids with olefins using O₂ as the oxidant.^{3g} Subsequently, Jung and co-workers developed the first base-free oxidative Heck reaction.^{4d} Very recently, Jiao and co-workers demonstrated a palladium-catalyzed ligand-free protocol for highly selective control of β -H elimination in the oxidative Heck-type reactions of allyl esters with AgOAc/CuF₂ and KHF₂ as the oxidants and additive, respectively.⁵ However, the reported methods mostly required a high catalyst loading, higher temperature and relatively longer reaction time as well as the participation of bases, ligands and metal salts additives. Therefore, the more mild, convenient and efficient catalytic system should still be developed.

Palladacycles have emerged as a new family of palladium catalysts in carbon–carbon and carbon–heteroatom bonds forming

reactions since more than ten years ago.⁶ We found a novel kind of palladacyclic catalysts: cyclopalladated ferrocenylimines are often stable and convenient to be prepared and easy to handle and can be used as important alternatives to simple palladium species.⁷ We have investigated their applications in catalytic reactions, such as Heck reaction,^{8,9} Suzuki reaction,¹⁰ Sonogashira reaction and cross-coupling of arylboronic acids/esters with terminal alkynes.¹¹ To the best of our knowledge, there were no examples of palladacycles as catalysts for oxidative Heck reaction. Herein we would like to report a palladacycle-catalyzed general and mild efficient system for oxidative Heck reaction of arylboronic acids with various olefins using O₂ as the oxidant under the base- and ligand-free conditions (Fig. 1).

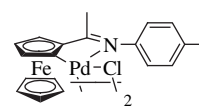


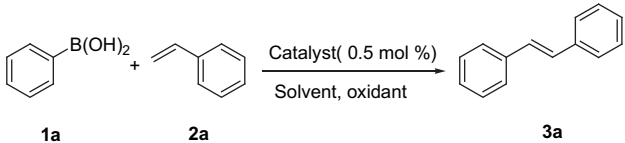
Figure 1. Palladacycle.

2. Results and discussion

We initially screened the reaction conditions using phenylboronic acid and styrene as starting substrates. The results for the oxidative Heck reaction were summarized in Table 1. After various solvents were examined, the polar solvent DMF indeed gave the

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Table 1
Effect of the solvents and oxidants on the oxidative Heck reaction of phenylboronic acid with styrene^a



Entry	Solvent	Temp (°C)	Time (h)	Oxidant	Yield ^b (%)
1	DCE	50	12	air	trace
2	CH ₃ NO ₂	50	12	air	5
3	DMA	50	12	air	23
4	THF	50	12	air	7
5	Toluene	50	12	air	trace
6	DMF	50	12	air	60
7	DMF	50	12	air	43 ^c
8	DMF	50	6	CuCl ₂	trace
9	DMF	50	6	Cu(OAc) ₂	trace
10	DMF	50	6	Cu(OTf) ₂	33
11	DMF	50	6	K ₂ S ₂ O ₈	trace
12	DMF	50	6	Ag ₂ O	trace
13	DMF	50	6	BQ	44
14	DMF	50	6	oxone	trace
15	DMF	50	3	O ₂	91
16	DMF	50	3	O ₂	40 ^d
17	DMF	23	3	O ₂	38
18	DMF	50	6	N ₂	trace

^a Reaction conditions: styrene 0.25 mmol, phenylboronic acid 0.5 mmol, oxidants 0.25 mmol (entries 8–14) and 0.5 mol % of catalyst in 1.5 mL solvent.

^b Yields are given for isolated products.

^c With the addition of Na₂CO₃ (1 mmol).

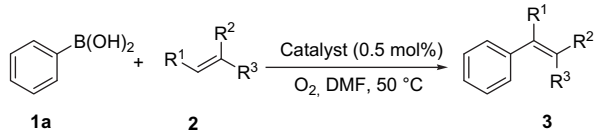
^d 0.25 mol % of the catalyst.

best value for the reaction (entries 1–6, Table 1). However, the addition of base would lead to a lower yield of the desired product and homo-coupling of phenylboronic acid (entry 7, Table 1). Among the oxidants screened, O₂ was the best choice and the desired product was obtained with a yield of 91%, while the other oxidants were relatively ineffective for this reaction (entries 8–15, Table 1). Under a lower loading of the catalyst and temperature, the yields dropped sharply (entries 16–17, Table 1). When the reaction was performed under oxidant-free conditions, only trace amount of the product was obtained (entries 18, Table 1).

With the optimized conditions in hand, the reactions of phenylboronic acid with various olefins were investigated (Table 2). Generally, the reaction proceeded well to afford the desired products in high yields. Either electronic effect or steric effect has no significant influence on the reactions. For the aryl olefins bearing electron-donating groups, desired products were also isolated in moderate to excellent yields (entries 1–4, Table 2). For the olefins containing electron-withdrawing groups, the reactions proceeded smoothly generating the products in high yields (entries 5–9, Table 2). On the other hand, the olefin with a sterically hindered group (**2b**) also underwent the olefination and led to a moderate yield of 76% (entry 1, Table 2). Moreover, for other kinds of electron-poor olefins, the similar yields were also obtained with those of the olefins containing electron-withdrawing groups and (*E*)/(*Z*) stereoselectivity would be higher than 99:1. For example, the reaction of acrylonitrile afforded exclusively the (*E*) coupling product in good isolated yield (entry 14, Table 2); the reaction of ethyl vinyl ketone provided desired products in moderate yield (entry 15, Table 2), and trace amount of byproduct of homo-coupling of phenylboronic acid was observed (entries 10–16, Table 2). However, only low yields were isolated for the reaction of allyl acetate (**2r**) and allyl alcohol (**2s**) (entries 17–18, Table 2), and reaction did not occur for vinylcyclohexane and vinylcyclopentane (entries 19–20, Table 2).

Subsequently, we explored the scope and the utility of this method for the olefination of various arylboronic acids with styrene

Table 2
Oxidative Heck reaction of phenylboronic acid with the olefins^a



Entry	Olefin	Product	Yield ^b (%)
1	2b	3b	76
2	2c	3c	99
3	2d	3d	87
4	2e	3e	73
5	2f	3f	99
6	2g	3g	91
7	2h	3h	99
8	2i	3i	99
9	2j	3j	99
10	2k	3k	82
11	2l	3l	83

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