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An efficient Pd(II)-(2-aminonicotinaldehyde) complex as complementary catalyst for the Suzuki-Miyaura coupling in water

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ABSTRACT

An efficient new Pd(II)-(2-aminonicotinaldehyde)-catalyzed Suzuki-Miyaura coupling of the aryl halides (Br, Cl and I) and organoboronic acids at moderate temperature in water is described. Low catalyst loading, easy accessibility, being an air-stable catalyst, functional group compatibility, and water as the reaction medium are some of the key features of this synthetic method. This protocol is also applicable for gram scale.

The direct carbon–carbon bond formation reactions are the most important synthetic tools for organic chemists [1] as they play vital role in the synthesis of building blocks for various biologically active products, material sciences, supramolecular chemistry and catalysis [2]. The transition-metal catalysts are ubiquitous in the carbon–carbon bond formations namely, Suzuki [3], Heck [4], Sonogashira [5], Stille [6], Hiyama [7], Negishi [8], Kumada [9], and Murahashi [10] reactions. Among these, palladium-catalyzed cross-couplings, reactions of arylboronic acid with aryl halide, known as the Suzuki-Miyaura reaction, which is the leading methodologies for the construction of C—C bond in the synthesis of biaryls become popular because of its wide applications in various fields (Fig. 1) [11]. In this decade, the Suzuki cross-coupling of organoboronic acid, organoborane [12], organoboronate esters [13], KF_4-borates[14] and arylhalides has been massively employed to unsymmetrical biaryls *via* sp^2-sp^2 linkage since its initial reporting by Akira Suzuki [3]. There has been a deep-rooted interest in the exploration of palladium complexes due to their wide use as homogeneous and heterogeneous catalyst for carbon–carbon bond formation reactions in high turnover numbers (TON) [15]. Later, a number of modifications have been appeared in palladium complexity to increase the efficacy of the catalyst including activity, stability, and functional group compatibility [16]. The ligands which are used in most of the catalysts are phosphenes [17], *N*-Heterocyclic carbenes (NHCs) [18] and bidentate P,N ligands [19]. Recent past has witnesed a tremendous increment in ways to develop and design novel phosphorus free palladium catalysts for robust, active, higher turnover number and functional group tolerance at low costs [20]. In literature we found that only few pyridine based bidentate ligands for palladium catalyzed cross coupling reactions [21].

In continuation of our effort towards the sustainable chemistry employing metal catalysis under green reaction conditions [22], we searched for a robust, inexpensive and biologically relevant monodentate pyridine based-Pd(II)-catalysts for Suzuki-Miyaura coupling reaction [23]. Water is ubiquitous in nature and a desirable medium for chemical reactions which falls in line with the principles of green chemistry [24].

Herewith, we report an efficient, less expensive, easily accessible, air-stable Pd(II)-(2-aminonicotinaldehyde) (Pd(II)-ANA, **C4**) complex as a complementary catalyst for the Suzuki-Miyaura reaction with low catalyst loading in water (Figure 2). The use of most abundant water as a reaction medium makes protocol convenient, environmentally benign and safe to handle.

In our initial screening experiments, the reaction between phenylboronic acid **1a** and 4-bromoanisole **2e** with catalysts **C1-C4** (Figure 3) was investigated to optimize the reaction conditions, and only the key facts are reported in Table 1.

Firstly, we have initiated the optimization of the reaction conditions using phenylboronic acid **1a** and 4-bromoanisole **2e** and we are delighted to observe that the formation of corresponding cross-coupled product **3f** was in 78% along with the self coupled product of

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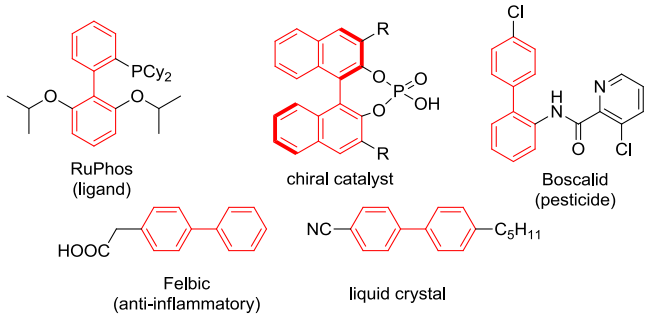


Figure 1. Some examples of functional biaryls.

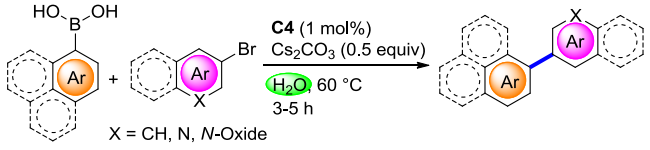


Figure 2. Pd(II)ANA-Catalyzed Suzuki-Miyaura coupling to access biaryl derivatives.

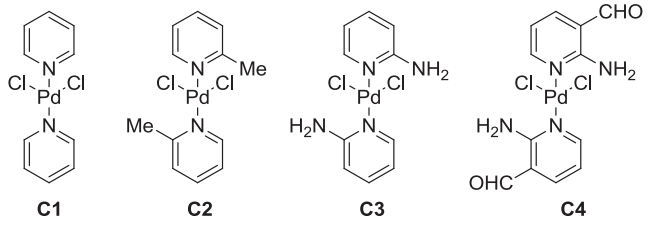
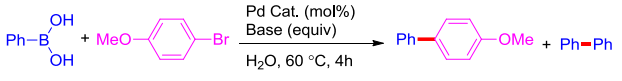


Figure 3. Pyridine-based monodentate Pd(II) complexes.

Table 1
Optimization of the Reaction Conditions.[a]



Entry	Catalyst (mol%)	Base (equiv)	Yield[b]	
			3f	**3a**
1	C1	Cs_2CO_3	78	20
2	C2	Cs_2CO_3	83	16
3	C3	Cs_2CO_3	80	18
4	**C4**	**Cs_2CO_3**	**96**	**n.d**
5	C4	K_2CO_3	90	n.d
6	C4	Na_2CO_3	88	10
7	C4	KO^{t}Bu	95	n.d
8	C4	$NaHCO_3$	86	Trace
9	C4	NaOH	22	n.d
10	C4	Cs_2CO_3	52[c]	n.d
11	C4	Cs_2CO_3	80[d]	n.d
12	C4	Cs_2CO_3	78[e]	n.d

[a] Reaction Conditions: Phenylboronic acid **1a** (0.5 mmol), 4-bromoanisole **2e** (0.5 mmol), catalyst (1.0 mol%), base (0.5 equiv), water (1.0 mL) at 60 °C.
[b] Yields are of isolated pure products.
[c] Room temperature, [d]40 °C, [e]Base 0.3 equiv., n.d = Not detected.

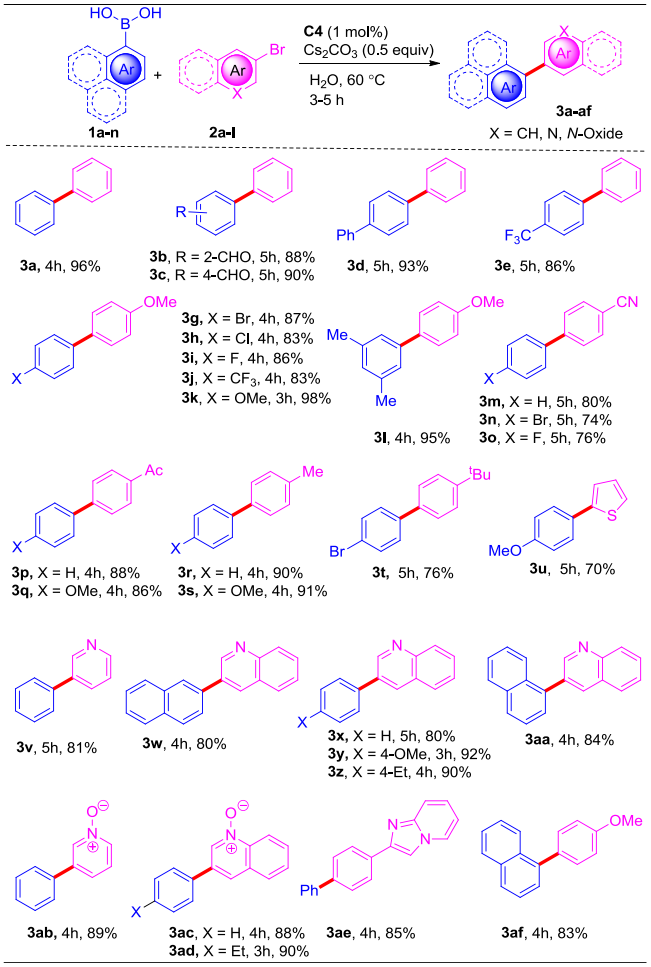
boronic acid **3a** (20%) employing 1.0 mol% of Pd(II) complex of pyridine **C1** and 0.5 equivalents of Cs_2CO_3 in water (Table 1, entry 1). These results prompted us to optimize the reaction conditions to improve the product yield by changing the different pyridine based ligands on palladium metal and reaction conditions. The Pd(II) complexes of 2-methylpyridine **C2**, 2-aminopyridine **C3** were successful to yield the cross-coupled product **3f** in 80–83% along with the self-coupled product **3a** in 16–18% (Table 1, entry 2–3).

Inspiringly, we found that the yield was improved to 96% by use of Pd(II) complex of 2-aminonicotinaldehyde **C4**, this catalyst was found to be highly active and gave unsymmetrical biphenyl **3f** as a solo product. (Table 1, entry 4).

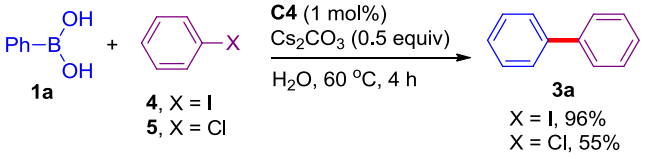
The effect of various bases on the model reaction were also screened (Table 1, entries 5–8). Notably, K_2CO_3, Na_2CO_3, KO^{t}Bu and $NaHCO_3$ gave the desired product **3f** in 86–95% respectively, whereas NaOH gave cross-coupled product in low yield (Table 1, entry 9). Lowering the reaction temperature or the amount of the base showed the inferior results (Table 1, entries 10–12).

With the preferred conditions for the Suzuki reaction in hand, we next examined the scope of the substrates and synthesised a library of compounds listed in Table 2. Initiated with a substituted arylboronic acids **1a-n** and bromobenzene **2a-l** as substrates. The phenylboronic acid **1a** readily reacted with bromobenzene **2a** to deliver biphenyl **3a** in 96% yield**.** Notably**,** electron withdrawing groups on boronic acid (**1b** and **1c**) did not hamper the reaction

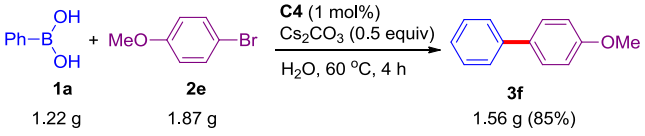
Table 2
Reaction of Diverse Arylboronic Acids **1** and Arylbromides **2**.[a,b]



[a] Reaction Condition: Arylboronic acid **1** (0.5 mmol), arylbromide **2** (0.5 mmol), catalyst **C4** (1 mol%), Cs_2CO_3 (0.5 equiv), H_2O (1.0 mL) at 60 °C.
[b] Yields are of isolated pure products.



Scheme 1. Suzuki-Miyaura Reaction of Chloro- and Iodobenzene.



Scheme 2. Gram-Scale Reaction.

yields (**3b-c**). The 4-biphenylboronic acid **1d** was similarly reacted and turned-out as *para*-terphenyl **3d** in 93%. It was observed that the halogen substituted arylboronic acids were also reacted smoothly to give the corresponding cross-coupled products **3g-j**, **3n-o** in good yields (83–87%). Whereas, electron-rich arylboronic acids gave marginally high yields with various bromobenzenes (**3k-m**, **3p-s**). We also found that 4-bromo phenylboronic acid **1g** reacted with 4-*tert*-butyl bomobenzene **2f** to furnish the desired substituted biphenyl **3t** in 76% of yield.

Further, the protocol was extended to explore the substrate scope of heteroaryl bromides. The 2-bromothiophene readily reacted with 4-bromoanisole **2b** and yielded desired product **3u** in 70%. Likewise, 3-bromopyridine and 3-bromoquinoline **2h-i** cross-coupled with various arylboronic acids to deliver desired products **3v-3aa** in good yields (80–90%). Pyridine *N*-oxide and quinoline *N*-oxide also smoothly coupled with arylboronic acid under the optimized conditions (**3ab-ad**) without deoxygenation of *N*-oxide. It is worth noting that the pyridine *N*-oxides gave better yields than its counter pyridine derivatives. We also found that 4-imidazopyridine bromobenzene **2l** and 1-naphthaleneboronic acid **2n** delivered cross-coupled biphenyls **3ae-af** in 83–85%.

Furthermore, we extended the optimized protocol to investigate the reactivity of other halobenzenes and found that the iodobenzene **4** was comparable to the bromobenzene (Scheme 1). Whereas, chlorobenzene **5** gave less yield compare to bromo and iodo benzenes**.**

Finally, we investigated the efficiency of this protocol for gram scale reaction using phenylboronic acid **1a** and 4-bomoanisole **2b** under the standard condition, gave **3f** in 85% of yield (Scheme 2).

In conclusion, an efficient, easily accessible, air-stable Pd(II)ANA-catalyzed Suzuki-Miyaura coupling reaction is achieved in water at moderate temperature to produce unsymmetrical biaryls with functional group diversities. The protocol is simple and efficient at low catalyst loading. The protocol demonstrated at gram scale preparation of biphenyl derivatives for commercial applications.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.06.051.

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