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Free-Amine Directed Arylation of Biaryl-2-amines with Aryl Iodides by Palladium Catalysis

Zunjun Liang,[†] Ruokun Feng,[†] Hong Yin,[†] and Yuhong Zhang*[,†,‡]

ZJU-NHU United R&D Center, Department of Chemistry, Zhejiang University, Hangzhou 310027, China, and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

yhzhang@zju.edu.cn

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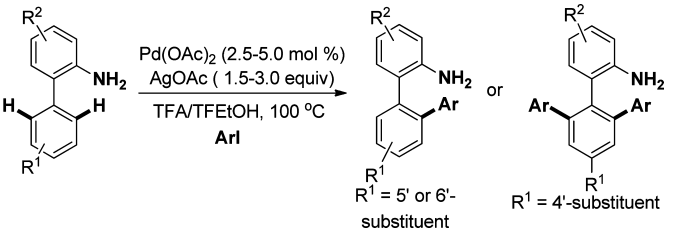
ABSTRACT



A new palladium-catalyzed free-amine directed arylation of C(sp^2)–H bonds in the presence of AgOAc and TFA is described. Biaryl-2-amines react with various aryl iodides to give the corresponding mono- or diarylated products with exclusive regioselectivity.

The biaryl linkage is an important structural motif that is prevalent in natural products, pharmaceutically active reagents, and conjugated materials.[1] Transition-metal-catalyzed direct C–H arylation reactions of arenes are increasingly viable alternatives to traditional cross-coupling reactions, which provide powerful and straightforward tools for the preparation of aryl–aryl scaffolds. For example, significant progress has been achieved in the development of a C(sp^2)–H activation reaction by palladium, ruthenium, and rhodium catalysis.[2] Among these transformations, chelation assisted C–H arylation reactions are particularly attractive due to their excellent regioselectivity and reactivity. A variety of nitrogen-containing directing groups (DGs), such as amides,[3] imines,[4] oximes,[5] and *N*-heterocycles,[6] have been shown to be efficient in these reactions. In view of the general applicability and atom economy of the directing

[†] Zhejiang University.
[‡] Lanzhou University.

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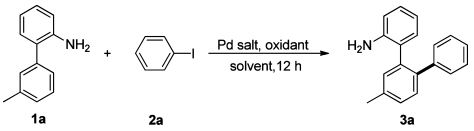
groups, expanding the scope to include simple and commonly encountered DGs is highly desirable. The amine group is one of the most prevalent nitrogen-containing groups, which has a long history of acting as a chelation group in cyclometalation reactions.[7] However, there are few reports of transition-metal-catalyzed C−H bond functionalization reactions by the use of amines as DGs,[8] especially in the case of using free amines in the direct C−H bond functionalization.[9] In 2006, Daugulis and co-workers disclosed that unsubstituted benzylamines and *N*-methylbenzylamine can be *ortho*-arylated under palladium catalysis at 130 °C.[10] In 2011, Gaunt and co-workers developed a Pd(II)-catalyzed C(sp^2)−H arylation of *β*-arylethylamines directed by *N*-aryl substituted amine.[11] Very recently, You and our group reported that *N,N*-dimethylaminomethyl could be used successfully as the directing group for Pd-catalyzed C(sp^2)−H arylation.[12]

Our ongoing research program on free-amine directed C−H activation prompted us to explore the arylation of biaryl-2-amines.[13] Herein, we report a $Pd(OAc)_2$-catalyzed C(sp^2)−H arylation of arenes with aryl iodides directed by a free-amine group in the presence of trifluoroacetic acid.

We chose 3′-methylbiphenyl-2-amine **1a** and iodobenzene **2a** as the model substrates at 100 °C for 12 h to study the arylation reaction. Initially, we used the same reaction conditions that we have reported for the alkenylation of biaryl-2-amine: 2.5 mol % $Pd(OAc)_2$ and 1.5 equiv of AgOAc in the presence of acetic acid (HOAc) (Table 1, entry 1). However, the desired C−C cross-coupling product was not detected. To our delight, such a transformation was highly promoted when trifluoroacetic acid (TFA) was utilized in place of HOAc to give the C(sp^2)−H arylation product in 86% yield (Table 1, entry 2). It should be noted that neither the Buchwald−Hartwig *N*-arylation product nor amide from TFA and amine **1a** were detected by GC-MS analysis, showing the excellent chemoselectivity for C(sp^2)−H arylation.[14] Palladium catalysts such as $PdCl_2$, $Pd(CH_3CN)_2Cl_2$, $Pd(PPh_3)_2Cl_2$, $Pd(OTFA)_2$, $Pd(PPh_3)_4$, and $Pd(dba)_2$ were also screened, and the

Table 1. Screening of the Reaction Conditions[a]



entry	catalyst	additive	acid	yield (%)[b]
1	$Pd(OAc)_2$	AgOAc	HOAc	0
2	$Pd(OAc)_2$	AgOAc	TFA	86
3	$PdCl_2$	AgOAc	TFA	75
4	$Pd(CH_3CN)_2Cl_2$	AgOAc	TFA	72
5	$Pd(PPh_3)_2Cl_2$	AgOAc	TFA	76
6	$Pd(OTFA)_2$	AgOAc	TFA	78
7	$Pd(PPh_3)_4$	AgOAc	TFA	82
8	$Pd(dba)_2$	AgOAc	TFA	77
9	$Pd(OAc)_2$	AgOAc	TFA	80[c]
10	$Pd(OAc)_2$	AgOTFA	TFA	82
11	$Pd(OAc)_2$	Ag_2O	TFA	51
12	$Pd(OAc)_2$	Ag_2CO_3	TFA	40
13	$Pd(OAc)_2$	$Cu(OAc)_2$	TFA	0
14	–	AgOAc	TFA	0
15	$Pd(OAc)_2$	–	TFA	tr[d]
16	$Pd(OAc)_2$	–	TFA	tr[e]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3.0 mmol), Pd catalyst (0.0125 mmol, 2.5 mol %), additives (0.75 mmol, 1.5 equiv), acid (1 mL), TFEtOH (1 mL), 10 min at room temperature (rt), then heated at 100 °C with stirring for 12 h. [b] Isolated yields based on biphenylamine **1a**. [c] $Pd(OAc)_2$ (1 mol %). [d] Under a O_2 atmosphere. [e] Under a N_2 atmosphere.

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results indicated that $Pd(OAc)_2$ was the best catalyst (Table 1, entries 3−8). The reaction still show high efficiency when the loading of $Pd(OAc)_2$ was decreased to 1 mol % (Table 1, entry 9). Among the additives tested, the best result was obtained by the use of AgOAc. Other silver salts, such as AgOTFA, Ag_2O, and Ag_2CO_3, were found to be inferior for this transformation (Table 1, entries 10−12). $Cu(OAc)_2$ was completely inactive (Table 1, entry 13). No product was detected without a catalyst (Table 1, entries 14). We performed the experiments in the absence of AgOAc under an oxygen or a nitrogen atmosphere. Both of the reactions gave trace amounts of the products (Table 1, entries 15 and 16), implicating that dioxygen plays little role in the transformation. Further investigation of the reaction temperature led us to establish the optimized reaction conditions as follows: 2.5 mol % of $Pd(OAc)_2$, 1.5 equiv of AgOAc, TFA (1 mL), TFEtOH (1 mL) as solvent at 100 °C for 12 h.

The scope and generality of this direct arylation reaction under the optimized conditions were investigated as shown in Figure 1. The reaction displayed good functional group tolerance toward diverse aryl iodides. Aryliodides with both electron-withdrawing and -donating groups presented excellent compatibility with the reaction conditions. In most cases, electron-deficient aryl iodides afforded the arylation products in slightly higher yields (**3d**, **3e**, **3f**, **3g**, and **3i**) than electron-rich aryl iodides (**3a**, **3b**, and **3c**). Due to the poor solubility, 1-iodo-4-(trifluoromethyl)benzene gave the arylation product in relatively lower yield (**3h**). Notably, the tolerance for bromide on the aromatic ring (**3f**) in this arylation offers an opportunity for subsequent cross-coupling, facilitating the synthesis of complex biaryl molecules. The steric hindrance played a key role in the reaction. *Meta*-substituted aryliodides generated the corresponding products in lower yields (**3j**, **3k**, and **3l**). However, an attempt to employ *ortho*-substituted aryliodide failed to afford the products.

A wide range of biphenylamine substrates were found to be compatible with this protocol (Figure 1). Both electron-rich and -poor biphenylamines participated smoothly in this transformation to afford the corresponding products in good yields (**3m**−**3s**). A variety of useful functional groups were tolerated, including methoxy (**3m**), hydroxyl (**3n**), fluoride (**3o** and **3s**), chloride (**3p**), and methyl (**3q** and **3r**). The arylation reaction was compatible with 2-(naphthalen-2-yl)aniline to give the desired product in 81% yield (**3t**). It is noteworthy that the reaction could be scaled up to 10 mmol and the arylated product **3a** can be obtained in 78% isolated yield.

When we extend the substrate scope to unsubstituted or 4′-substituted biphenylamine, a mixture of mono- and diarylated products were obtained. After intensive investigation of the reaction conditions, we obtained the optimal reaction conditions for clean diarylated products: 5 mol % $Pd(OAc)_2$, 3 equiv of AgOAc, and 10 equiv of aryl iodides. We explored the generality of the diarylation reaction, and the results were summarized in Figure 2. It is similar to the monoarylation transformation; aryl iodides with electron-donating groups (**4a**−**4c**) gave relatively

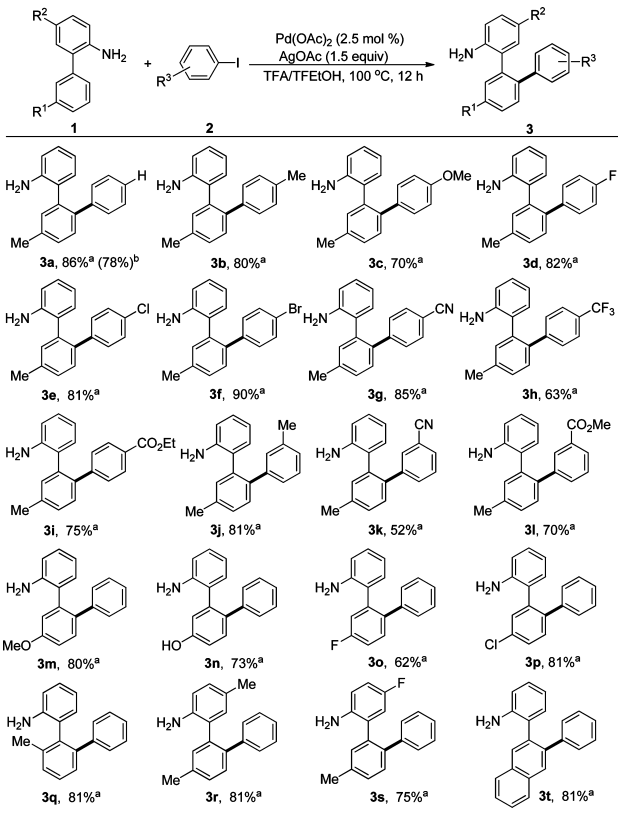


Figure 1. Monoarylation of biphenylamine. Reaction conditions: (a) biphenylamine **1** (0.5 mmol), aryl iodide **2** (3.0 mmol), $Pd(OAc)_2$ (0.0125 mmol, 2.5 mol %), AgOAc (0.75 mmol, 1.5 equiv), TFA (1 mL), TFEtOH (1 mL), 10 min at rt, then heated at 100 °C with stirring for 12 h; isolated yields based on biphenylamine **1**; (b) **1a** (10 mmol), iodobenzene **2a** (60 mmol), $Pd(OAc)_2$ (0.25 mmol), AgOAc (15 mmol), TFA (10 mL), TFEtOH (10 mL), 10 min at rt, then heated at 100 °C with stirring for 12 h.

lower yields than those obtained with electron-withdrawing groups (**4d**−**4h**). *Meta*-substituted aryl iodides participated smoothly in the reaction to give the diarylated products in moderate yields (**4i** and **4j**). This diarylation reaction also displayed good functional group tolerance toward 5- and 4′-substituted biphenylamines (**4k**−**4o** and **4p**−**4q**). Again, electron-rich biphenylamines (**4k** and **4l**) show higher efficiency than electron-deficient ones (**4m**, **4n**, and **4o**).

The six-membered palladacycle complex **A** was prepared according to the method previously described in the literature.[7e] Subjecting the palladacycle complex **A** to the reaction with iodobenzene (**2a**) resulted in the arylated product with excellent yield under standard reaction conditions in the absence of AgOAc (Scheme 1).

A plausible reaction mechanism has been proposed in Scheme 2. The intermediate **B** is formed through the oxidative addition of Pd(0) to aryl iodide. The electrophilic palladation of arylamine generates the palladacycle intermediate **A**, which undergoes the transmetalation with palladium intermediate **B** to give intermediate **C**[15]and Pd(II). The subsequent reductive elimination of **C** affords

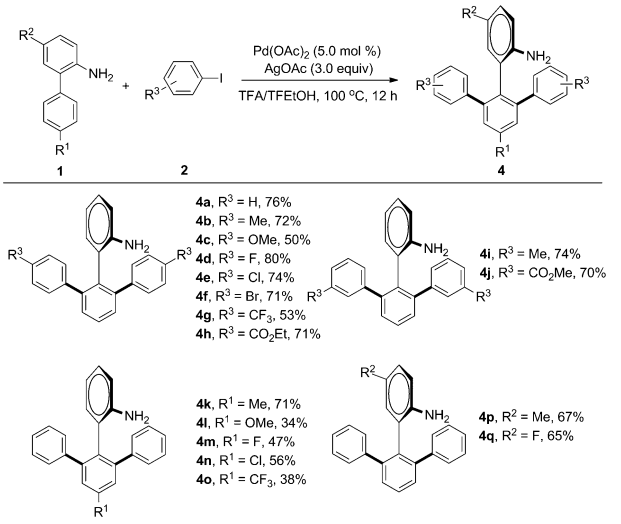
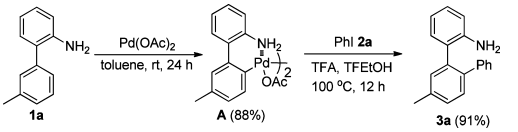


Figure 2. Diarylation of biphenylamine. Reaction conditions: biphenylamine **1** (0.5 mmol), aryl iodide **2** (5.0 mmol), $Pd(OAc)_2$ (0.025 mmol, 5 mol %), AgOAc (1.5 mmol, 3.0 equiv), TFA (1 mL), TFEtOH (1 mL), 10 min at rt, then heated at 100 °C with stirring for 12 h; isolated yields based on biphenylamine **1**.

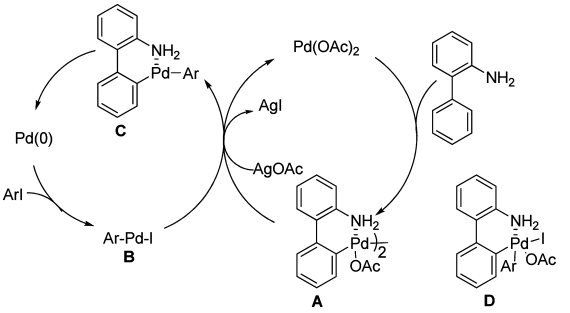
the arylation product and liberates Pd(0). Silver salt may act as a halide scavenger to improve the reaction.[5a,12b,16] Another possible pathway for this transformation is the oxidative addition of intermediate **A** to aryl iodide to give a Pd(IV) intermediate **D**, which undergoes the reductive elimination to afford the arylated product and Pd(II) (a Pd(II)/Pd(IV) mechanism).

In conclusion, we have developed an efficient method for Pd(II)-catalyzed arylation of the C(sp^2)–H bond directed by a free-amine group. Biaryl-2-amines react with various aryl iodides to give the corresponding *ortho*-monoarylated or diarylated products with exclusive regioselectivity. Detailed mechanistic studies of this arylation reaction are ongoing in our laboratory.

Scheme 1. Direct Arylation of Palladacycle Complex **A**



Scheme 2. A Plausible Mechanism



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Supporting Information Available. Experimental procedures, characterization data (^{1}H NMR, ^{13}C NMR, MS, HRMS, and IR). This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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