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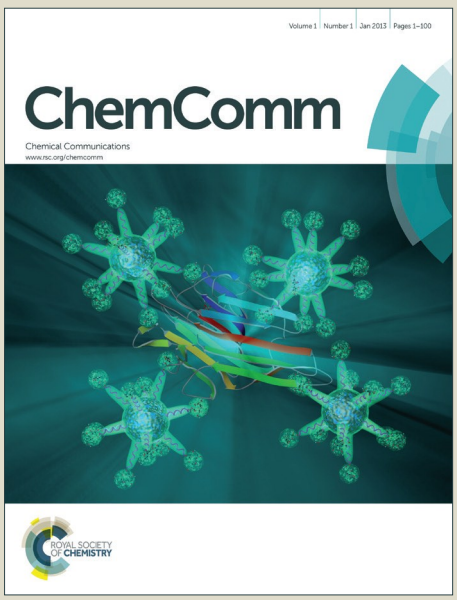

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COMMUNICATION

Palladium-Catalyzed Oxidative Carbamoylation of Isoquinoline *N*-Oxides with Formylamides by Means of Dual C-H Oxidative Coupling

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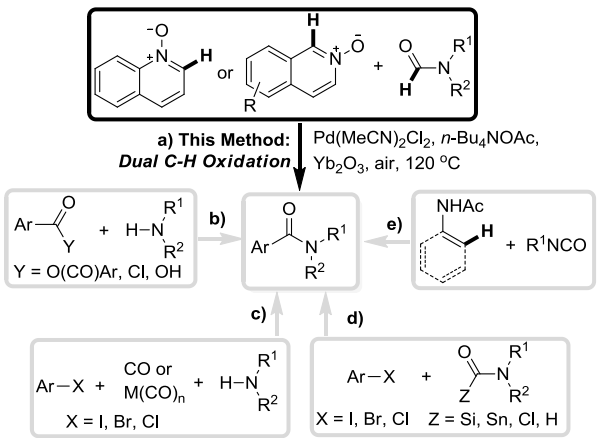
A new palladium-catalyzed oxidative carbamoylation of isoquinoline *N*-oxides with formylamides for the synthesis of isoquinoline-1-carboxamides is established. The method represents the first example of the carbamoylation of isoquinoline *N*-oxides with formylamides to furnish arylamides using the dual C-H oxidation strategy.

Amides, including arylamides, are a class of fundamental chemicals in organic synthesis and chemical industries.[1] Consequentially, many useful methods have been developed for amides synthesis, and the most important method for arylamides synthesis is the reaction of activated acid derivatives (acyl chlorides and anhydrides) with amines (Method b in Scheme 1).[2] However, this method is restricted to both labile substrates and a multistep process resulting in large amounts of unwanted by-products. To avoid these disadvantages, considerable efforts were devoted to the development of some more direct approaches.[3-6] Among these, transition metal-catalyzed cross-coupling reactions display particular efficiency, and include two common types of transformations:[4,5] one is the carbonylation of aryl halides with CO (or inorganic metal carbonyls) and amines (Method c),[4] and the other involves carbamoylation of aryl halides with formylamides, carbamoylsilanes, carbamoylstannanes or carbamoyl chlorides (Method d).[5] However, high toxic and/or expensive substrates limit this approach's applications. Although lower toxic and inexpensive formylamides were employed for these purposes, high expensive aryl halides as well as the presence of halide anions make this reaction unfavorable in both environment and applications (Method d). Recently, Bergman and Ellman described a novel Rh-catalyzed C-H functionalization method that aryl and vinyl C-H bonds could replace the reported aryl C-X bond (X = I, Br, Cl) for the carbamoylation reaction using the *N*-acyl amino directing strategy, but higher toxic and unavailable isocyanates were employed as the carbamoyl sources (Method e).[6] In light of these above results, we envision that the development of a new route employing both an aryl C-H bond and a formylamide C-H bond as the reaction partners for the carbamoylation reaction to construct a new carbon-carbon bond is highly interesting.

We herein report the first example of furnishing arylamides by Pd-catalyzed dual C-H oxidation/cross-coupling of isoquinoline *N*-oxides or quinoline *N*-oxides with formylamides using air as the terminal oxidant.[7] This new method allows the practical synthesis of isoquinoline-1-carboxamides and quinoline-2-carboxamides, which are also a common feature in approved drugs and drug candidates.[8]



Scheme 1. Synthesis of Arylamides

As shown in Table 1, our initial examinations focused on the identification of a suitable catalyst and reaction conditions for the carbamoylation between the sp^2 C-H bond in 3-phenylisoquinoline 2-oxide (**1a**) and the acyl C-H bond in *N*,*N*-dimethylformamide (DMF, **2a**) to furnish arylamide **3**. In the presence of $Pd(MeCN)_2Cl_2$ and ZnO, the reaction between substrate **1a** and 75 equiv DMF afforded the target *N*,*N*-dimethylisoquinoline-1-carboxamide **3** in 4% yield after 24 h, and most of substrate **1a** were recovered (entry 1). These results encouraged us to optimize the other reaction conditions. After a series of trials, we were pleased to find that PTC (phase-transfer catalyst) could improve the reaction, and *n*-Bu_4NOAc was the most effective. The reaction afforded product **3** in 52% yield in the presence of *n*-Bu_4NOAc, while the yield of **3** was enhanced slightly in *n*-Bu_4NBr, *n*-Bu_4NCl or *n*-Bu_4NF (entries 2-5). These results suggest that *n*-Bu_4NOAc might play a reductant role to facilitate the reaction besides as PTC. Notably, treatment of substrate **1a** with amide **2a**, $Pd(MeCN)_2Cl_2$ and *n*-Bu_4NOAc could offer product **3** in 62% yield without the aid of the additional ZnO base, although the longer reaction time was required (entry 6). To understand the effect of the additional bases, a number of other bases, including Yb_2O_3, MgO, CuO, Ag_2O, Fe_2O_3, Al_2O_3, Bu_3N and LiOAc, were subsequently investigated (entries 7-14). The results demonstrated that all the

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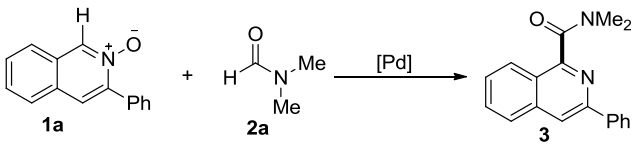
bases affected the reaction (entries 8-14), and only Yb_2O_3 favored the reaction (entry 7): In the presence of $Pd(MeCN)_2Cl_2$, *n*-Bu_4NOAc and Yb_2O_3, the reaction of substrate **1a** with amide **2a** afforded the desired product **3** in 67% yield. Among the Pd catalysts examined, it turned out that the other Pd catalyst, such as $PdCl_2$, $Pd(OAc)_2$ or $Pd(PPh_3)_2Cl_2$, were inferior to $Pd(MeCN)_2Cl_2$ (entries 7 and 15-17). Screening revealed that the oxidant, air, played an important role in the reaction: the reaction could not take place under argon atmosphere (entry 18), and the yield was lowered using O_2 instead of air due to the generation of some unidentified products (entry 19). Using 10 equiv *N*,*N*-dimethylformamide (**2a**), the yield was lowered to 47% (entry 20). Two solvents, *N*,*N*-dimethylacetamide (DMA) and toluene, were tested and it was found that the reaction using 75 equiv DMF in toluene provided the better yield (entries 21-23). Notably, the desired product **3** could not be formed in the absence of Pd catalysts, but a N-O bond reduction product, 3-phenylisoquinoline (**4**), was isolated in 60% yield (entry 24).

Table 1. Screening Optimal Conditions [a]

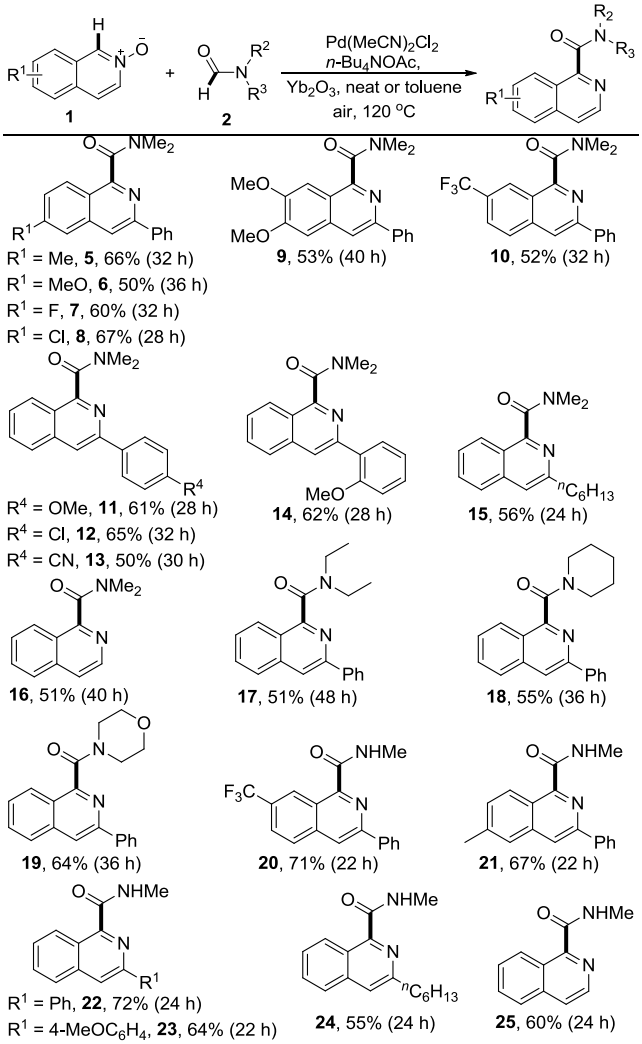


Entry	[Pd]	Additive	Base	Yield [%]
1	$Pd(MeCN)_2Cl_2$	—	ZnO	4
2	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NBr	ZnO	12
3	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NCl	ZnO	11
4	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NF	ZnO	9
5	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	ZnO	52
6[b]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	—	62
7	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	67
8	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	MgO	35
9	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	CuO	29
10	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Ag_2O	40
11	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Fe_2O_3	47
12	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Al_2O_3	26
13	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Bu_3N	37
14	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	LiOAc	27
15	$PdCl_2$	*n*-Bu_4NOAc	Yb_2O_3	30
16	$Pd(OAc)_2$	*n*-Bu_4NOAc	Yb_2O_3	5
17	$Pd(PPh_3)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	7
18[c]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	trace
19[d]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	31
20[e]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	47
21[f]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	56
22[g]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	70
23[h]	$Pd(MeCN)_2Cl_2$	*n*-Bu_4NOAc	Yb_2O_3	55
24[i]	—	*n*-Bu_4NOAc	Yb_2O_3	0

[a] Reaction conditions: **1a** (0.5 mmol), DMF (**2a**) (75 equiv), [Pd] (10 mol%), additive (2 equiv) and base (2 equiv) at 120 °C for 24 h under air atmosphere, isolated yields. [b] For 48 h. [c] Under argon atmosphere. [d] Under O_2 (1 atm). Some unidentified products were observed by GC-MS analysis. [e] DMF (**2a**) (10 equiv) was added. [f] DMF (**2a**) (75 equiv) in *N*,*N*-dimethylacetamide (DMA, 1 mL). [g] DMF (**2a**) (75 equiv) in toluene (1 mL). [h] DMF (**2a**) (50 equiv) in toluene (1 mL). [i] A reductive product, 3-phenylisoquinoline (**4**), was isolated in 60% yield.

The scope of both isoquinoline *N*-oxides **1** and formylamides **2** was explored under the optimal reaction conditions, and the results are summarized in Table 2. Initially, the reactions between a variety of isoquinoline *N*-oxides **1** and N,N-dimethylformamide (**2a**) were investigated under standard conditions (Products **5**-**16**). The results demonstrated that the reaction had high substituents compatibility: several substituents, such as Me, MeO, F, Cl, aryl and *n*-hexyl groups, on the isoquinoline moiety were tolerated well. 6-Methylisoquinoline 2-oxide, for instance, was treated with amide **2a** smoothly to provide the desired product **5** in 66% yield. It was found that 6-MeO-substituted substrate could produce the desired product **6** in 50% yield. Gratifyingly, substituents, Cl and F, were compatible with the optimal conditions, thereby facilitating additional modifications at the halogenated positions (Products **7** and **8**). It is worth noting that substrate bearing two MeO groups only afforded product **9** in moderate yield. Using electron-deficient substrate, a moderate yield was still achieved

Table 2. $Pd(MeCN)_2Cl_2$-Catalyzed Oxidative Carbamoylation of Isoquinoline N-Oxides with Formylamides [a]



[a] Reaction conditions: **1** (0.5 mmol), **2a** (75 equiv), $Pd(MeCN)_2Cl_2$ (10 mol%), *n*-Bu_4NOAc (2 equiv), Yb_2O_3 (2 equiv) and toluene (1 mL) at 120 °C under air atmosphere. The isolated yield is average yield of two runs that carried out under neat or toluene condition.

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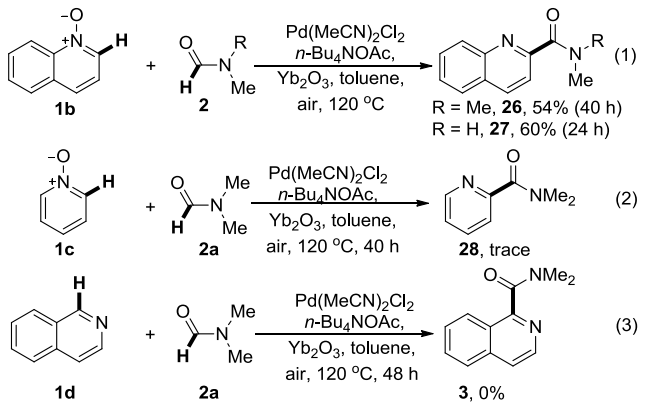
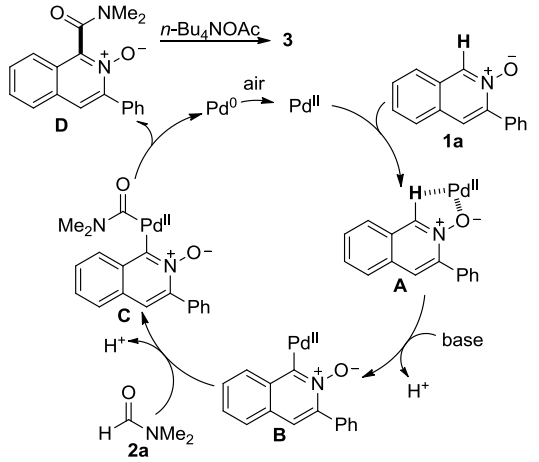
(Product **10**). Screening revealed that substrates, bearing either aryl or alkyl groups, on the 3-postion of the isoquinoline moiety were suitable for the C-H oxidation reaction (Products **11**-**15**). Notably, the reaction was high regioselective: only *N*,*N*-dimethylisoquinoline-1-carboxamide (**16**) was isolated when isoquinoline 2-oxide was employed to react with amide **2a**. In light of the above results, the scope of formylamides **2** was also examined under standard conditions. The reaction disclosed that the other *N*,*N*-disubstituted amides, *N*,*N*-diethylformamide, piperidine-1-carbaldehyde and morpholine-4-carbaldehyde, were successful for the reaction to give products **17**-**19** in 51-64% yields. Interestingly, a *N*-monosubstituted amide, *N*-methylformamide, was also compatible with the optimal conditions (Products **20**-**25**). For example, *N*-methylformamide could undergo the reaction with 3-phenyl-7-(trifluoromethyl)-isoquinoline 2-oxide to furnish the desired product **20** in good yield. It is noteworthy that a regioselective product **25** was obtained from the reaction of isoquinoline 2-oxide with *N*-methylformamide. However, 3-position carbamoylated product could not be detected when 1-phenyl-isoquinoline-N-oxide was treated with DMF under standard conditions.

The oxidative carbamoylation of quinoline 1-oxide (**1b**) or pyridine 1-oxide (**1c**) with formylamides **2** was also tested under standard conditions (Scheme 2). In the presence of $Pd(MeCN)_2Cl_2$, *n*-Bu_4NOAc, Yb_2O_3 and air, substrate **1b** (0.5 mmol) was successfully reacted with 75 equiv of either *N*,*N*-dimethylformamide or N-methylformamide, providing the corresponding products **26** and **27** in moderate yield (eq 1). However, both pyridine 1-oxide (**1c**) and isoquinoline (**1d**) were unsuitable substrates under the optimal reaction (eqs 2 and 3). The results of eq 3 imply that the N-O bond plays an important role in the coupling reaction.



Scheme 2. Oxidative Carbamoylation of Other Substrates

Consequently, a possible mechanism as outlined in Scheme 3 is proposed.[5-7,9] Initially, complexation of the active Pd^{II} species with 3-phenylisoquinoline 2-oxide (**1a**) takes place to furnish intermediate **A**,[5-7,9] followed by insertion into the *ortho*-C-H bond of the N-O group affords intermediate **B**. The reaction of intermediate **B** with amide **2a** offers intermediate **C**.[6] Reductive elimination of intermediate **C** gives rise to intermediate **D** and the Pd^0 species with the aid of bases.[9] Finally, the N-O reduction of intermediate **D** in the presence of *n*-Bu_4OAc affords the desired product **3**.[10] The active Pd^{II} species can be regenerated by the oxidation of the Pd^0 species with air.



Scheme 3. Possible Mechanism.

In summary, we have described a new route to the synthesis of isoquinoline-1-carboxamides by palladium-catalyzed oxidative carbamoylation of isoquinoline N-oxides with formylamides. This method enables two C-H bond oxidation/cross-coupling to construct a new carbon-carbon bond. Moreover, quinoline N-oxide is also compatible for this oxidative coupling reaction. Applications of this palladium-catalyzed oxidative transformation in organic synthesis are currently underway in our laboratory.

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Notes and references

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