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Rh(III)-Catalyzed C−H Amidation with *N*-Hydroxycarbamates: A New Entry to *N*-Carbamate-Protected Arylamines

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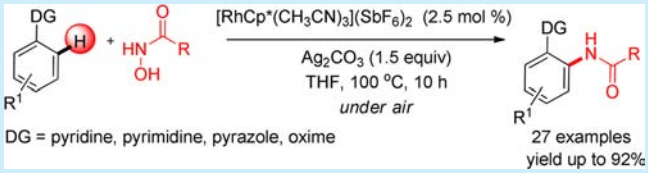
Supporting Information

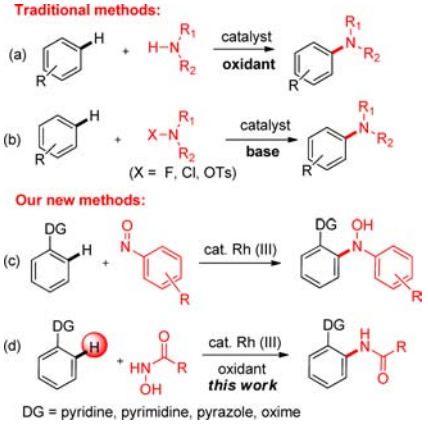
ABSTRACT: An unprecedented Rh(III)-catalyzed direct intermolecular C−H amidation with *N*-hydroxycarbamates has been developed. Different directing groups, such as pyridine, pyrimidine, pyrazole, and *N*-OMe oxime, can be employed in this C−H amidation process, providing valuable *N*-carbamate-protected arylamines (e.g., Cbz, Moz, Ac, Boc, and Fmoc). More importantly, this process may afford a new avenue for intermolecular C−H amidation where readily available *N*-hydroxycarbamates can be used as the nitrogen source



The arylamine functionality is a common motif in biologically active natural products, pharmaceuticals, and functional materials.[1] To date, the most reliable and practical methods to attach amine groups to aromatic rings are represented by Buchwald−Hartwig- and Ullman-type cross couplings.[2] However, these approaches need preactivated aryl (pseudo)halides as the substrates. With the continuous advancement in catalytic C−H bond activation,[3] extensive research has been devoted to metal-catalyzed direct C−H amination reactions.[4]

To date, two strategies can be employed in metal-catalyzed intermolecular (hetero)arene C−H amination. The first strategy is direct C−H amination of activated arenes[5] and few chelate group containing arenes[6] with amines or amides under oxidative conditions (Scheme 1a). Alternatively, the use of preactivated amino precursors (*O*-acylhydroxylamines, chloroamines, NFSI, azides) has been demonstrated in redox-neutral amination reactions (Scheme 1b).[7,8] Despite these advances, owing to the abundance and structural diversity of arylamines, further development of novel catalytic amination reactions (particularly ones employing other readily available amino source) is still highly desirable.

Scheme 1. C−N Bond Formation via C−H Activation



Recently, Rh(III) complexes have been employed as a promising catalyst for addition of aryl C−H bonds to polar C═N or C═O groups.[9] Very recently, we reported a mild Rh(III)-catalyzed addition of aryl C−H bonds to nitrosobenzenes (N═O bonds) to give *N*,*N*-diarylhydroxylamines (Scheme 1c).[10] Inspired by these works,[11−14] herein we report the first example of Rh(III)-catalyzed aryl C−H amidation with *N*-hydroxycarbamates giving access to *N*-carbamate protected arylamines (Scheme 1d). Notably, this is the first example of employing readily available *N*-hydroxycarbamates as the amino source in the catalytic C−H amidation reaction, thus affording a new direction for intermolecular amidation of C−H bonds with *N*-hydroxycarbamates.

Our initial studies focused on the reaction of 2-phenylpyridine (**1a**) and carbobenzyloxy (Cbz)-protected hydroxylamine (**2a**). As shown in Table 1, heating a mixture of **1a** with **2a**, $Cu(OAc)_2$, and catalyst $[RhCp^*Cl_2]_2$ (2.5 mol %) in the presence fo $AgSbF_6$ (10 mol %) at 100 °C in DCE led to product **3a** in 30% yield. Interestingly, no hydroxylamine product **4a** was observed, presumably because **4a** is unstable and spontaneously decomposes to give **3a** via nitroxide radical intermediate.[15] The structure of the amidation product **3a** was confirmed by single-crystal X-ray crystallography.[16] The prepared catalyst $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.5 mol %) afforded a higher yield (entry 2). Next, other oxidants were screened (entries 3−7), and Ag_2CO_3 was found to be the ideal oxidant for the reaction (entry 7). A screen of the solvents gave THF as an optimal one (entry 10). A decrease of yield was observed when raising or lowering the reaction temperature (entries 11 and 12). A control experiment showed that the Rh catalyst was necessary for the reaction (entry 13), and both

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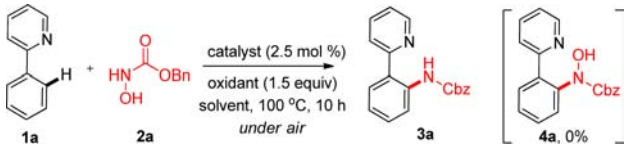
Table 1. Optimization of the Rh-Catalyzed Amidation Reaction[a]



entry	catalyst	oxidant	solvent	3a (%)
1	$(Cp^*RhCl_2)_2/AgSbF_6$	$Cu(OAc)_2$	DCE	30
2	$Cp^*Rh(MeCN)_3(SbF_6)_2$	$Cu(OAc)_2$	DCE	57
3	$Cp^*Rh(MeCN)_3(SbF_6)_2$	MnO_2	DCE	20
4	$Cp^*Rh(MeCN)_3(SbF_6)_2$	*t*-BuOOH	DCE	15
5	$Cp^*Rh(MeCN)_3(SbF_6)_2$	AgOAc	DCE	60
6	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2O	DCE	60
7	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	DCE	70
8	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	PhMe	65
9	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	1,4-dioxane	55
10	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	THF	77
11[b]	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	THF	70
12[c]	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	THF	67
13		Ag_2CO_3	THF	0
14[d]	$Cp^*Rh(MeCN)_3(SbF_6)_2$	Ag_2CO_3	THF	70
15	$Cp^*Rh(MeCN)_3(SbF_6)_2$		THF	25

[a]**1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (0.005 mmol), oxidant (0.3 mmol), and solvent (1 mL) at 100 °C for 10 h. Yield of isolated product. [b]Reaction temperature = 120 °C. [c]Reaction temperature = 80 °C. [d]The reaction was carried out under Ar.

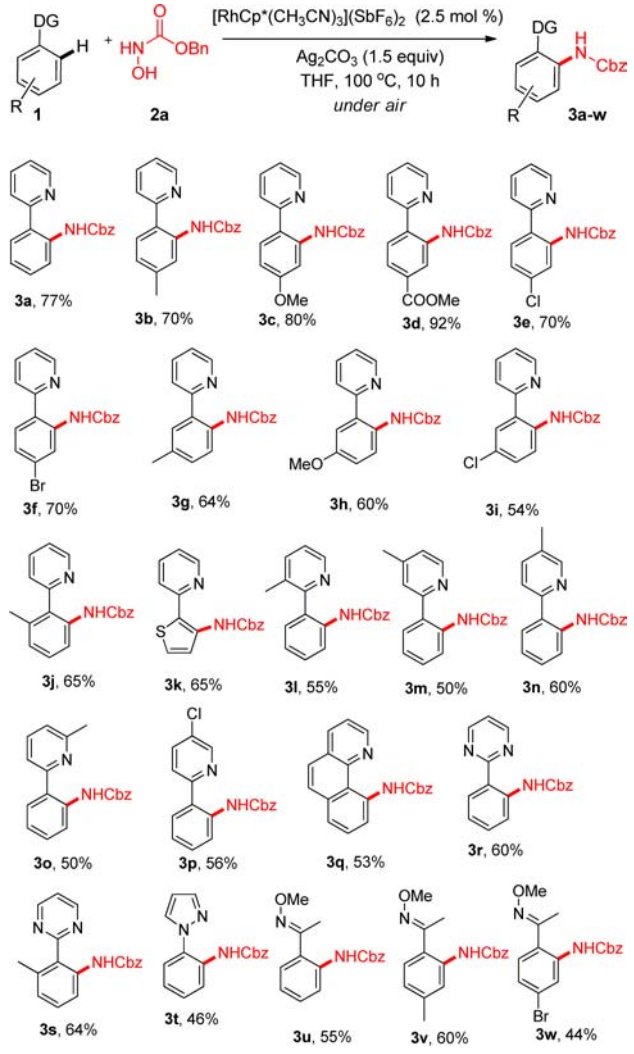
Ag_2CO_3 and oxygen could promote this transformation as an oxidant (entries 14 and 15)

With the optimized reaction conditions in hand, we next surveyed the scope of the reaction (Scheme 2). Both electron-donating (**3b**, **3c**, **3g**, **3h**) and -withdrawing (**3d**) groups on the phenyl ring were well tolerated, as were halogen-substituted substrates (**3e**, **3f**, **3i**). *Meta*-substituted derivatives showed high regioselectivity in favor of the sterically more accessible C−H bond (**3g**−**i**). In particular, the *o*-Me derivative is also a productive substrate (**3j**), thus indicating high steric tolerance of this system. Notably, the ester (**3d**) and halogen groups (**3e**, **3f**) were well tolerated, making further functionalization possible. In addition, this catalyst system also allowed for the use of a heterocyclic system (**3k**).

In addition to the simple pyridine group, other directing groups were also investigated (Scheme 2). First, a variety of pyridinyl directing groups were evaluated, and we were delighted to find that pyridines with electron-donating (**3l**−**o**) and -withdrawing (**3p**) groups also participated in this amidation reaction. Encouragingly, pyridine rings functionalized with a methyl group at the 3- to 6-positions (**3l**−**o**) were well tolerated, thus indicating high steric tolerance. Tricyclic benzo[*h*]quinolone (**3q**) could also be amidated by this method. In addition to pyridines, other *N*-based heterocycles, such as pyrimidine (**3r**, **3s**) and pyrazole (**3t**), could also serve as effective directing groups for this amidation reaction. Next, we investigated the replacement of the *N*-based heterocycles with a more common and synthetically useful moiety. Thus *O*-Me oxime have been shown to be an effective directing group, giving the corresponding amidation products in moderate to good yields (**3u**−**w**). Notably, only monoamidation product was observed in all cases.

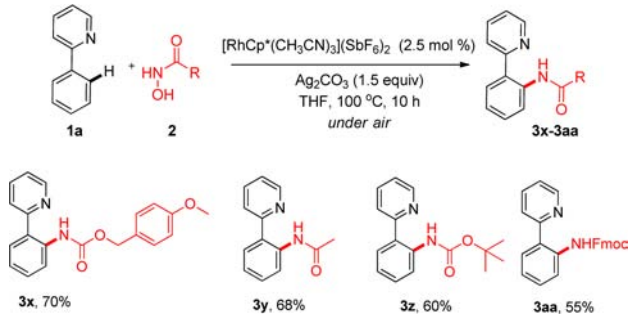
Next, different *N*-substituted hydroxylamines were examined for the catalytic reaction conditions (Scheme 3). To our

Scheme 2. Scope of Arene Substrates[a]



[a]Isolated yields. See the Supporting Information for details.

Scheme 3. Scope of Different *N*-Protecting Groups[a]



[a]Isolated yields. See the Supporting Information for details.

delight, in addition to the *N*-Cbz group, other common *N*-protecting groups (i.e., Moz (**3x**), Ac (**3y**), Boc (**3z**), and even Fmoc (**3aa**)) could also be installed by this amidation reaction.

To shed light on the mechanism of amidation, the following experiments were conducted. First, a cyclometalated Rh(III) complex **5** could be used as a catalyst precursor and catalyzed the amination of **1a** to provide the desired product **3a** in good yield under the same catalytic conditions, thus indicating the

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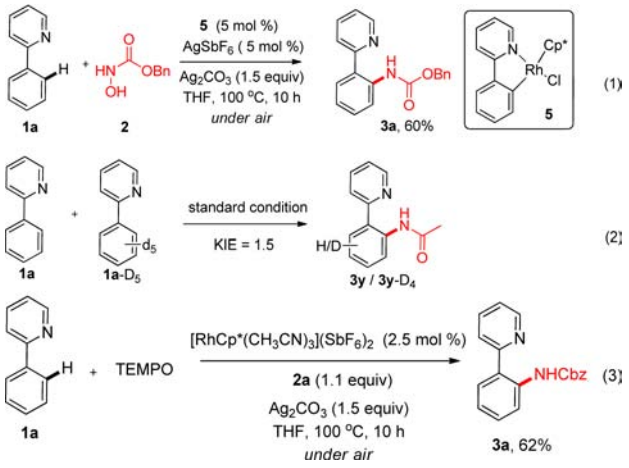
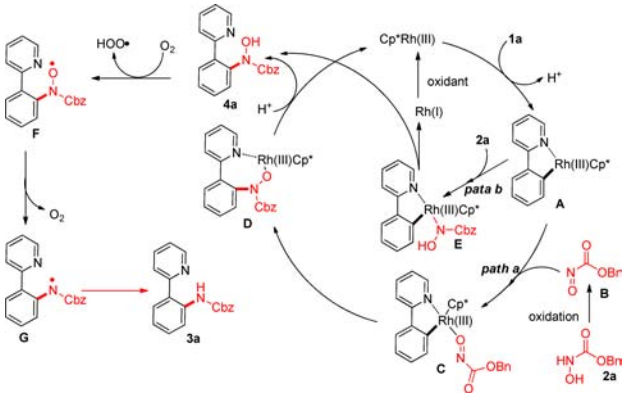
relevancy of C−H activation (eq 1). On the other hand, a kinetic isotopic effect (KIE) of 1.5 in an intermolecular



competition experiment was observed, indicating that the C−H bond cleavage might be not involved in the rate-limiting step (eq 2).[17] Futhermore, the addition of TEMPO (2 equiv) to the reaction as a radical scavenger caused a slight decrease of the yield (eq 3).

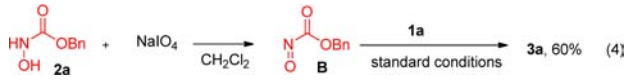
On the basis of the above observations, a possible mechanism is proposed (Scheme 4). First, the five-membered rhadacycle **A**

Scheme 4. Proposed Mechanism



is formed through the coordination of 2-phenylpyridine to the rhodium center and a subsequent *ortho* C−H bond activation.[18] Coordination of **B**, generated from oxidation of **2a** in situ, to **A** gives **C**, which was transformed into seven-membered rhodacycle **D** by migratory insertion or nucleophilic addition. **D** is protonated to give the hydroxylamine intermediate **4a**, and the Rh(III) catalyst is regenerated (path a). Alternatively, **2a** could react with the Rh(III) center directly, giving the intermediate **E** which undergoes reductive elimination to deliver the intermediate **4a** and Rh(I) catalyst (path b). Then oxidation of the Rh(I) intermediate with Ag(I) slat regenerates the Rh(III) catalyst. Oxidation of **4a** with silver slat or air gives the nitroxide **F**, which was transformed into aminyl radicals **G** via dimerization and subsequent fragmentation, similarly to the dimerization of peroxyl radicals. Finally, hydrogen abstraction from solvents or **4a** affords the prodcuct **3a**.

We next carried out an experiment to probe the reaction pathway. When the freshly prepared **B** was used as the reagent under the standard conditions, **3a** was obtained in 60% yield, suggesting that pathway a should be more reliable (eq 4).



In summary, a novel Rh(III)-catalyzed arene C−H amidation has been described for the first time, which employed the readily available *N*-hydroxycarbamates as an nitrogen source. A variety of *N*-carbamate protecting groups, such as Cbz, Moz, Ac, Bocs and even Fmoc, could also be installed by this amidation reaction, affording a complement to previous amidation methods. More importantly, this process may provide a new avenue for intermolecular arene C−H amidation involving the use of *N*-hydroxycarbamates as the nitrogen source.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization of products, and copies of ^{1}H and ^{13}C NMR spectra. The material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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