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Rh(III)-Catalyzed Amide-Directed Cross-Dehydrogenative Heteroarylation of Pyridines

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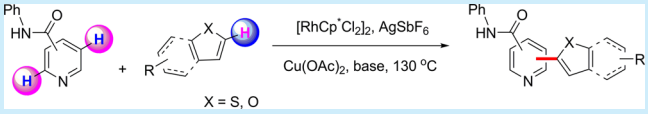
Supporting Information

ABSTRACT: A new catalytic methodology has been developed for the synthesis of heteroaryled pyridines via a rhodium(III)-catalyzed dehydrogenative cross-coupling reaction. This protocol features a good substrate scope with a broad range of functional group tolerance and high regioselectivity of the pyridyl C−H activation.



The structural motif of (hetero)arylated pyridine appears in a large number of natural products and bioactive compounds, as well as in pharmaceuticals and functional materials.[1] Consequently, synthetic organic chemists have made great efforts to develop more efficient and versatile methods for the direct (hetero)arylation of pyridines. However, unlike various reliable means for the C−H arylation of other (hetero)arenes,[2] the methods for installing heteroarene groups into pyridine rings through pyridyl C−H decoration raises substantial challenges. The following difficulties were initially envisaged to consider: (1) the relatively low reactivity of pyridines due to their poor electron density; (2) strong coordination of pyridines with transition metal centers; and (3) levels of regioselectivity of pyridines.

Previously reported approaches for the heteroarylation of pyridines mostly proceed by means of the transition-metal-catalyzed cross-coupling of pyridyl halides or pseudohalides with other heteroaryl organometallic reagents.[3] These methods suffer from tedious preparation procedures for organometallic reagents and the generation of stoichiometric metal halide salts as waste after the reaction finished. From the viewpoint of step and atom economy, the development of oxidative C−H/C−H cross-coupling of pyridines with heterocycles is highly desirable, as this transformation would provide a more efficient and straightforward access to the pyridine-containing biheteroaryls.[4] In this context, Bergman, Ellman,[4a−c] Chatani,[4d] Hiyama,[4e,f] Baran,[4g] and other groups[4h−j] reported C-2/C-4 arylation or alkylation of unmodified pyridines by utilizing rhodium, nickel, or silver catalysts. Very recently, the Yu group successfully established palladium-catalyzed C-3 arylation and unprotected pyridines or nicotinic/isonicotinic acid derivatives.[5] At the same time, the Sames group developed a novel protocol for selective arylation of pyridines bearing various electron-withdrawing groups.[6]

Furthermore, the Chang group achieved rhodium-catalyzed C-8 arylation of quinolines.[7] Later on, the palladium-catalyzed direct C-2 heteroarylation of pyridines was achieved by employing a large excess of pyridines as the substrate and solvent, which represented considerable progress in achieving the C-2 heteroarylation of pyridines in an atom-economic fashion.[8] Nevertheless, the use of a large quantity of pyridines as solvent rendered this reaction less appealing. Therefore, developing more efficient methods for the direct heteroarylation of pyridines, especially with varied selectivity, would be highly desirable.

Additionally, although previous studies emphasized the important role of palladium catalysts in biaryls formation through oxidative C−H/C-H cross-couplings,[9] the recently developed rhodium(III)-catalyzed 2-fold C−H functionalization reactions also proved to be an excellent means for generating biaryl molecules.[10,11] The Glorius group has achieved a dehydrogenative cross-coupling reaction of benzamide with simple arenes and heterocycles.[12] Subsequently, the same group reported the synthesis of 2,2′-bi(heteroaryl) compounds by dehydrogenative cross-coupling of electron-rich heterocycles, such as furans, thiophenes, indoles, and pyrroles.[13] The You group also succeeded in the oxidative cross-coupling of various nitrogen-containing heteroarenes with other heteroarenes by 2-fold C−H functionalization.[14] In spite of these achievements, the rhodium(III)-catalyzed direct reactions of heterocycles with pyridines has remained untouched. Herein, we report a rhodium(III)-catalyzed amide-directed cross-dehydrogenative heteroarylation of pyridines. Notably, this is the first example of Rh-catalyzed C−H/C−H cross-coupling between directing-group-assisted pyridines and heterocycles.

Initially, we began our investigation by evaluating the reaction between *N*-phenyl isonicotiamide (**1a**) and 2-methylthiophene (**2a**) in detail (Table 1).[15] In light of the previous contributions from Miura,[11f] Glorius,[11a] Fagnou,[16a,b] and other groups, the traditional conditions of $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10%), $Cu(OAc)_2$ (2.0 equiv), and dioxane (2.0 mL) at 130 °C were used (Table1, entries 1−4). We were pleased to obtain the desired product **3a** in 6%

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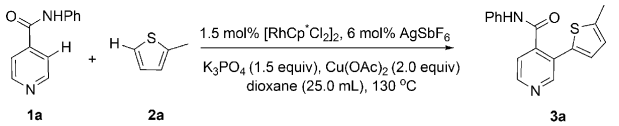
Table 1. Selected Screening Results for Reacion Conditions[a]



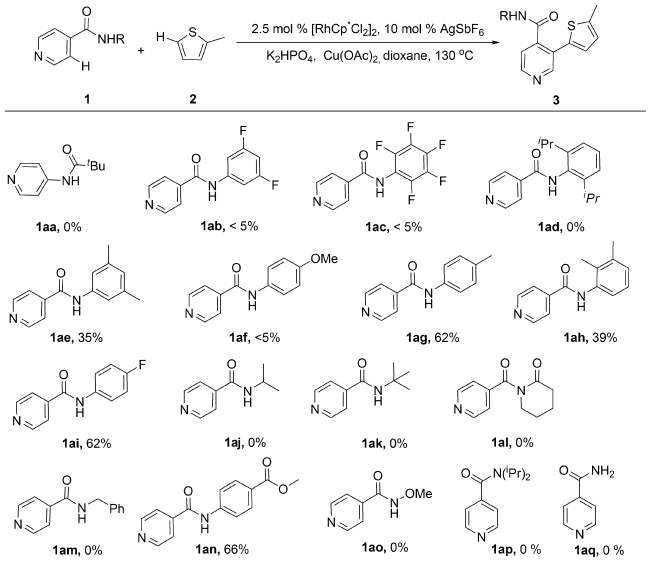
1a 5 mmol + **2a** 15 mmol → **3a** 49 % isolated yield

entry	base	oxidant	solvent	yield (%)[b]
1[c]	PivOCs	$Cu(OAc)_2$	toulene	<5
2[c]	PivOCs	$Cu(OAc)_2$	*t*-AmOH	n.d.[d]
3[c]	PivOCs	$Cu(OAc)_2$	DMF	n.d.
4[c]	PivOCs	$Cu(OAc)_2$	dioxane	6
5	K_2CO_3	$Cu(OAc)_2$	dioxane	<5
6	Na_2CO_3	$Cu(OAc)_2$	dioxane	<5
7	PivONa	$Cu(OAc)_2$	dioxane	<5
8	KOAc	$Cu(OAc)_2$	dioxane	35
9	K_3PO_4	$Cu(OAc)_2$	dioxane	52
10	K_2HPO_4	$Cu(OAc)_2$	dioxane	61
11	Na_3PO_4	$Cu(OAc)_2$	dioxane	23
12	K_2HPO_4	$Cu(OAc)_2$	DCE	<5
13	K_2HPO_4	$Cu(OAc)_2$	PhCl	n.d.
14	K_2HPO_4	Ag_2CO_3	dioxane	<5
15	K_2HPO_4	$Cu(OAc)_2$	dioxane	65[e]
16	**K_2HPO_4**	**$Cu(OAc)_2$**	**dioxane**	**70**[f]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), oxidant (2.0 equiv), base (1.5 equiv), $AgSbF_6$ (10 mol %), solvent (2.0 mL), 130 °C, 24 h, N_2. [b]Isolated yield. [c]PivOCs (1.0 equive). [d]The formation of product was not detected. [e]Dioxane (1.0 mL). [f]$[Cp^*RhCl_2]_2$ (1.5 mol %), $AgSbF_6$ (6.0 mol %), dioxane (1.0 mL).

isolated yield. After screening various bases, the results revealed K_2HPO_4 (1.5 equiv) was the most effective base, affording the desired product **3a** in 61% isolated yield (Table 1, entry 10). Then, the effect of solvent was investigated, yet there was no significant improvement in the product yield (Table 1, entries 12−13). When Ag_2CO_3 was used in place of $Cu(OAc)_2$, unfortunately, only a trace of the desired product was obtained (Table 1, entry 14). In addition, using $[RhCp^*(MeCN)_3](SbF_6)_2$ as the catalyst, the desired product was just obtained in 26% yield.[15] An attempt to increase the concentration of substrates led to a slight increase in yield to 65% (Table 1, entry 15). Encouraged by these results, we further examined the influence of the directing groups (Scheme 1). However, the results showed us that electron-withdrawing *N*-polyfluorophenyl amides (**1ab, 1ac**), steric *N*-2,6-diisopropylphenyl amide (**1ad**), *N*-alkyl amides (**1aj, 1ak**), *N*-dialkyl amide (**1ap**), isonicotinamide (**1aq**), *N*-benzyl amide (**1am**), *N*-piv amide (**1aa**), *N*-disubstituted amide (**1al**), *N*-methoxyl amide (**1ao**), and *N*-4-methoxyphenyl amide (**1af**) gave only a trace of the corresponding cross-coupling product. Although *N*-4-methylphenyl amide (**1ag**), *N*-4-fluorophenyl amide (**1ai**), *N*-4-methoxycarbony amide (**1an**), *N*-3,5-dimethylphenyl amide (**1ae**), and *N*-2,3-dimethylphenyl amide (**1ah**) afforded the target products in moderate yields, there was no obvious improvement in the reaction outcomes. To our delight, decreasing the catalyst loading to 1.5 mol % improved the yield to 70% (Table 1, entry 16). Remarkably, this procedure exhibited high selectivity for the monosubstituted product. In order to demonstrate the utility of the present method, the reaction was conducted in 5.0 mmol scale, under the optimized conditions of *N*-phenyl isonicotiamide (**1a**) and 2-methylthiophene (**2a**) for the one-step synthesis of the desired product (**3a**) in 49% isolated yield (Scheme 4).

Scheme 1. Influence of the Directing Groups[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $Cu(OAc)_2$ (2.0 equiv), K_2HPO_4 (1.5 equiv), dioxane (1.0 mL), 130 °C, 24 h, N_2, isolated yield.

With the optimized conditions in hand, the substrate scope of the reaction was initially expanded with respect to heterocycles. As shown in Scheme 2, this reaction was applicable to a variety of substituted thiophenes and furans, affording the corresponding products with excellent selectivity. A range of diverse functional substituents were compatible under our conditions, including both electron-rich (**3b, 3f, 3g**) and electron-withdrawing groups (**3d, 3e**). Moreover, 3-substituted thiophenes (**3c, 3j**) also provided corresponding products. Additionally, electron-rich benzothiophene (**3l**) and benzofuran (**3n**) furnished the product in moderate yields. Notably, the bromo-containing substrates (**3k, 3m**) also participated in this cross-coupling reaction smoothly. For other heterocycles, 2-methythiazole (**3p**) was suitable for this reaction system to afford a low yield.

The generality of the *N*-phenyl isonicotinamide substrate was subsequently evaluated (Scheme 3). Both electron-deficient (**4a, 4c**) and electron-rich (**4b**) group substituted *N*-phenyl isonicotinamides provided monosubstituted heteroarylation products. Substitution at the *ortho* position (**4i, 4j, 4k**) was also well tolerated. Furthermore, *N*-phenyl quinoline-4-carboxamide (**4d**) and *N*-phenyl quinoline-3-carboxamide (**4e**) both provided the expected products, respectively, in moderate to excellent yields. In addition, unsubstituted thiophene (**4h**) not only was compatible but also gave a monoheteroarylated product.

Based on the above results and previous research,[16] the following mechanism was proposed. Initially the coordination of the rhodium(III) species with *N*-phenyl amide (**1a**) activated the *ortho* C−H bond via a five-membered ring transition[17] to form an aryl-rhodium(III) intermediate, followed by a reaction with 2-methythiophene (**2a**) to form a complex. Subsequently, reductive elimination from the rhodium(III) center generated the final product (**3a**) and a rhodium(I) species. Finally, the catalytic cycle was completed when rhodium(III) was regenerated by oxidation of the copper salt.

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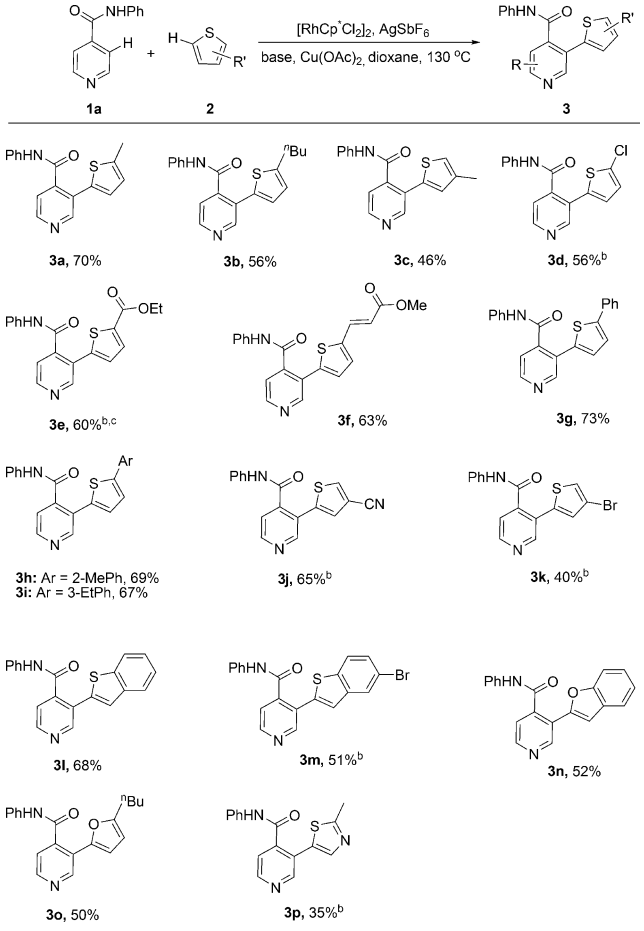
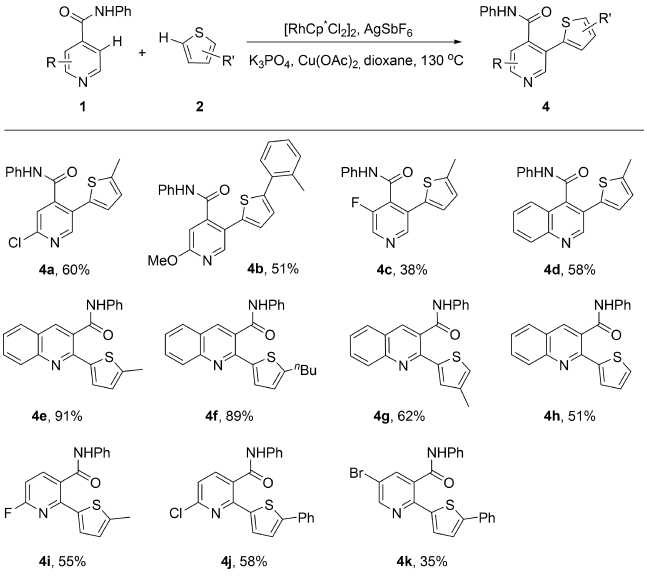
Scheme 2. Scope of Heterocycles[a]



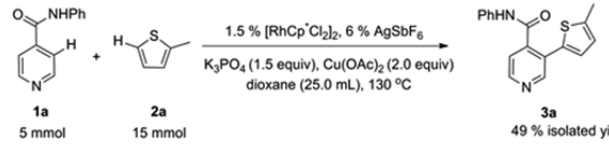
[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), $[RhCp^*Cl_2]_2$ (1.5 mol %), $Cu(OAc)_2$ (2.0 equiv), K_2HPO_4 (1.5 equiv), dioxane (1.0 mL), 130 °C, 24 h, N_2, isolated yield. [b] K_3PO_4 (1.0 equiv) was used instead of K_2HPO_4. [c] Carried out at 150 °C.

Scheme 3. Scope of the *N*-Phenyl Isonicotinamide[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), $[RhCp^*Cl_2]_2$ (1.5 mol %), $Cu(OAc)_2$ (2.0 equiv), K_3PO_4 (1.0 equiv), dioxane (1.0 mL), 130 °C, 24 h, N_2, isolated yield.

Scheme 4. Application for the Synthesis of 3-Heteroarylation of Pyridine 3a



In summary, a novel method for the heteroarylation of pyridines has been developed based on a rhodium(III)-catalyzed dehydrogenative cross-coupling reaction of aromatic heterocycles with amide-directed pyridines for the first time. This protocol features a good substrate scope with respect to a broad range of functional group tolerance. Additionally, the research offers high regioselectivity of the pyridyl C−H bond cleavage. This catalytic system can provide a new methodology for the direct synthesis of heteroarylated pyridines through dual C−H bond cleavage. Further studies to uncover the comprehensive reaction mechanism and to expand the scope of simple arenes as coupling partners are underway.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization of new compounds. This 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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