Organic LETTERS

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Rh(III)-Catalyzed Cascade Oxidative Olefination/Cyclization of Picolinamides and Alkenes via C−H Activation

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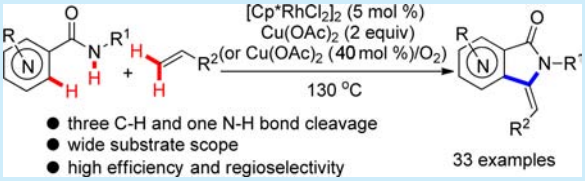
Supporting Information

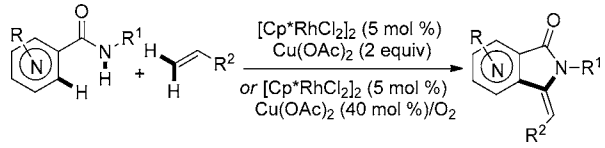
ABSTRACT: Rh(III)-catalyzed cascade oxidative alkenylation/cyclization of picolinamides and alkenes to furnish pyrido pyrrolone derivatives is described, in which three C−H bonds and one N−H bond broke, while one C−C bond and one C−N bond formed. The reaction proceeded with high yield and high regioselectivity and stereoselectivity. Moreover, copper acetate can also be used in catalytic amounts with O_2 serving as the terminal oxidant.



Pyridine derivatives are common structural motifs in pharmaceuticals, natural products, and optical materials.[1,2] Consequently, the functionalization of the pyridine ring is an important transformation for the synthesis of pyridine derivatives. However, due to the low reactivity of the pyridine nucleus toward an aromatic electrophilic substitution reaction such as the Friedel−Crafts reaction, prefunctionalization including halogenation and metalation are usually required to install substituents in a pyridine ring.[3] Accordingly, the development of efficient routes for the preparation of pyridine-containing compounds through a pyridine C−H functionalization strategy has gained significant attention but remains challenging to date.

During the past decade, several research groups have made considerable progress in the transition-metal-catalyzed direct C−H functionalization of pyridine.[4−6] Among them, a number of transition-metal-catalyzed pyridine C−H conversions have been realized by employing pyridine *N*-oxides or *N*-iminopyridinium ylides to yield 2-functionalized pyridines,[5] while additional steps are needed for the preparation and reduction of *N*-oxides from a viewpoint of organic synthesis. In this protocol, the enhanced reactivity of pyridine *N*-oxides,[5a−f] compared with that of parent pyridine, is apparently attributed to the electron-deficient nitrogen that activates the C(2)−-H bond. Recently, a strategy of utilization of directing group has been widely exploited in transition-metal-catalyzed C−H functionalization of arenes.[7,8] Nonetheless, extension of this strategy to pyridines has been only partially successful.[9] Yu's group first reported a regioselective C−H arylation of pyridines using a simple amide as a directing group.[9a] Subsequently, Li's and Glorius's groups also reported oxidative annulation of nicotinamide with alkyne or allene to give a mixtutre of two isomers at the 2- and 4-positions.[9b,c] Herein, we report a rhodium(III)-catalyzed cascade alkenylation/annulation of picolinamides with activated alkenes to generate pyridopyrrolones via C−H activation with high regioselectivity and stereoselectivity (Scheme 1). In this reaction, amide is used not only as a directing group for regioselective olefination of pyridine but also as a strong electron-withdrawing group to activate the C−H bond on pyridine. Moreover, the amide group possesses a potential to cyclize with alkene to construct fused pyridine rings. This reaction involves three C−H bonds and one N−H bond cleavage with one C−C bond and one C−N bond formation in one pot.

Scheme 1. Rh(III)-Catalyzed Oxidative Olefination/Cyclization between Picolinamides and Alkenes



Olefination of arenes through direct C−H bond activation has been demonstrated to be an effective and efficient synthetic protocol for introducing an alkene moiety.[8] A diverse number of arene C−H olefinations catalyzed by different transition metals has been reported.[5h,10] Recently, Glorius[8h] and Li[8i] have successfully reported Rh(III)-catalyzed oxidative olefination of benzamide with olefins. Inspired by these works and our ongoing project for the efficient synthesis of heterocycles,[11] we want to develop a new method to access pyridine-containing heterocycles via a C−H functionalization strategy. Initially, we tested the reaction of readily available 2-picolinamide **1a** and *n*-butyl acrylate **2a** with loading 1 mol % of $(Cp^*RhCl_2)_2$ as catalyst and 2 equiv of $Cu(OAc)_2$ as oxidant in toluene at 130 °C. The product **3aa** was detected in trace amounts by GC−MS (Table 1, entry 1). When the catalyst loading was increased to 3 and 5 mol %, the product **3aa** was obtained in 65% and 94% yield, respectively, and the ratio of *E*/*Z* isomer was in 99/1 (based on

Received: May 5, 2014
Published: May 21, 2014

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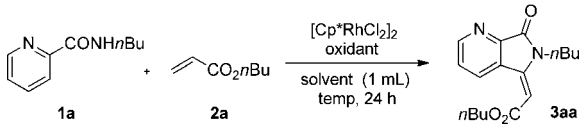
Table 1. Screening Conditions for the Rh(III)-Catalyzed Reaction of Picolinamide and Butyl Acrylate[a]



entry	$[Cp^*RhCl_2]_2$	oxidant	solvent	temp (°C)	GC-yield (%)
1	1%	$Cu(OAc)_2$ (2 equiv)	Toluene	130	trace
2	3%	$Cu(OAc)_2$ (2 equiv)	Toluene	130	65[b]
3	5%	$Cu(OAc)_2$ (2 equiv)	Toluene	130	94[b]/92[c]
4	5%	AgOAc (4 equiv)	Toluene	130	NR
5	5%	Ag_2CO_3 (2 equiv)	Toluene	130	NR
6	5%	BQ (2 equiv)	Toluene	130	NR
7	5%	$Cu(OAc)_2$ (2 equiv)	DMSO	130	NR
8	5%	$Cu(OAc)_2$ (2 equiv)	1,4-dioxane	130	55[d]
9	5%	$Cu(OAc)_2$ (2 equiv)	DCE	130	93[b]
10	5%	$Cu(OAc)_2$ (2 equiv)	Toluene	100	89[b]
11	5%	$Cu(OAc)_2$ (2 equiv)	Toluene	70	37[b]
12	5%	$Cu(OAc)_2$ (40 mol %)/O_2	Toluene	130	< 5
13	5%	$Cu(OAc)_2$ (40 mol %)/O_2	DCE	130	93[b]
14	5%	$Cu(OAc)_2$ (30 mol %)/O_2	DCE	130	88[e]
15	5%	$Cu(OAc)_2$ (20 mol %)/O_2	DCE	130	86[f]
16	5%	O_2	DCE	130	NR
17	-	$Cu(OAc)_2$ (2 equiv)	DCE	130	NR

[a]Reaction conditions: 2-picolinamide **1a** (0.2 mmol), alkene **2a** (0.22 mmol). [b]Ratio of isomer: *E*:*Z* = 99:1. [c]Isolated yield. [d]Ratio of isomer: *E*:*Z* = 18:1. [e]Ratio of isomer: *E*:*Z* = 45:1. [f]Ratio of isomer: *E*:*Z* = 20:1.

GC−MS analysis) (entries 2 and 3). When AgOAc, Ag_2CO_3, and 1,4-benzoquinone were employed as the oxidant individually, no product was observed and starting materials remained (entries 4−6). After solvent screening (entries 3, 7−9), we were pleased to find that the reaction could proceed smoothly in toluene and 1,2-dichloroethane (DCE) (entry 3 and entry 9). The yield of this reaction was found to decline with the decrease of the reaction temperature (entries 10 and 11). To make the process more ecofriendly and economical, we further investigated the possibility of using $Cu(OAc)_2$ in catalytic amount and O_2 as the oxidant.[12,13] First, the reaction was treated using 5 mol % of $[Cp^*RhCl_2]_2$ and 40 mol % of $Cu(OAc)_2$ in toluene at 130 °C under an atmosphere of O_2, and only a trace amount of **3aa** was detected (entry 12). To our delight, when the reaction was treated using 5 mol % of $[Cp^*RhCl_2]_2$ and 40 mol % of $Cu(OAc)_2$ in DCE at 130 °C under an atmosphere of O_2, the reaction proceeded well and a similar yield of **3aa** was obtained (entry 13). Lower loading of Cu catalyst still could give an advisibly useful yield (entries 14 and 15). Control experiments confirmed that no reaction occurred without using Rh catalyst or $Cu(OAc)_2$ (entries 16 and 17), indicating the importance of combination of these two catalysts.

With these results in hand, the scope and limitation of this reaction were next explored and representative results are shown in Figure 1. Picolinamides **1** bearing both electron-donating and electron-withdrawing groups at different positions of the pyridine ring afforded pyrido pyrrolone (*E*)-**3** in high isolated yields (**3aa**−**ga**). When 3-picolinamide was used, the reaction occurred exclusively at the 2-position to afford product (*E*)-**3ha** in 58% yield. When the 2-position was occupied by a substitutent, such as **1i**, the reaction occurred at the 4-position with the formation of (*E*)-**3ia** in 83% yield accompanied by compound **4ia** and (*Z*)-**3ia** in 7% and 5% isolated yield,

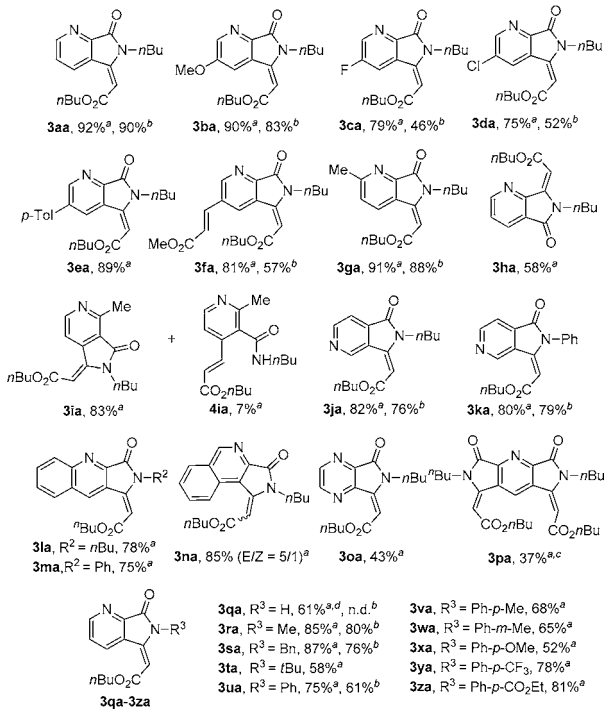


Figure 1. Scope with respect to the picolinamide component. (a) Conditions A: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.4 mmol), toluene (1 mL), 130 °C, 24 h, N_2. (b) Conditions B: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.08 mmol), DCE (1 mL), 130 °C, 24 h, O_2. The yields are of the isolated products. (c) 2.2 equiv of **2a**, 4 equiv of $Cu(OAc)_2$. (d) Determined as *Z*-isomer.

respectively. When 4-picolinamides were employed in the reaction, the desired products were also afforded in high yields (**3ja**−**ka**). In these cases, only mono-olefinated product was detected, indicating that the amide functionality in the cyclized product could not function as an efficient directing group to achieve further *ortho* C−H activation. Notably, the presented method was able to selectively address C(2)−H, C(3)−H, and C(4)−H positions of pyridine ring. Exception of picolinamides, this reaction also proceeded smoothly with polycyclic pyridine carboxamides, such as quinoline-2-carboxamide and isoquinoline-3-carboxamide, and the corresponding products were formed in good yields (**3la**−**3na**). Quinoline-2-carboxamide performed in good stereoselectivity (*E*/*Z* = 99/1), while isoquinoline-3-carboxamide resulted in a 5/1(*E*/*Z*) isomers, which may be attributed to steric bulk in aryl group. Reaction of pyrazine-2-carboxamide with **2a** furnished the cyclized product (**3oa**) in 43% yield with high stereoselectivity. Furthermore, utilization of pyridine-2,6-dicarboxamide afforded product (**3pa**) in 37% yield, in which the reaction underwent dual cascade olefination/cyclization involving six C−H bonds and two N−H bonds cleavage, and meanwhile two C−C bonds and two C−N bonds formation in one pot.

We also investigated the effects of different *N*-substituted picolinamides. To our surprise, when primary 2-picolinamide was treated with reaction conditions A, the product was determined as the *Z*-isomer, which was probably attributed to the intramolecular hydrogen bond[8h] (see the Supporting Information). Alkyl *N*-substituted picolinamides also reacted with olefin to give the corresponding products (**3ra** and **3sa**) in satisfacgtory yields. When steric bulk alkyl *N*-substituted picolinamide was used in the reaction, the product (**3ta**) was

dx.doi.org/10.1021/ol501275r | *Org. Lett.* 2014, 16, 3142−3145

formed in 58% yield. To our delight, colorless single crystals of **3ra** suitable for X-ray diffraction analysis were obtained by recrystallization. The structure of **3ra** in Figure 2 clearly showed

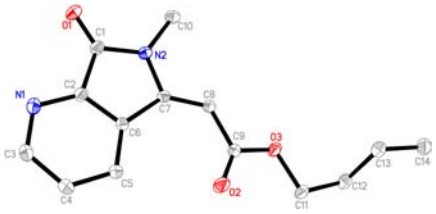


Figure 2. Crystal structure of **3ra** (ORTEP drawing of $C_{14}H_{16}N_2O_3$ with 30% probability ellipsoids, with the omission of hydrogen atoms for clarity).

the formation of pyrido pyrrolone skeleton with *E*-stereoismer. Aryl *N*-substituted picolinamides were also good substrates in the reaction, and the electron-poor aryl *N*-substituted substrates gave higher yields than electron-rich aryl *N*-substituted substrates (**3ua-3za**). Reaction of *N*-(pivaloyloxy)picolinamide and **2a** afforded the product (**3qa**) in 48% yield with the release of OPiv group under conditions A.

Next, reactions of **1a** with various olefins **2** were carried out under the optimized conditions to further determine the scope and limitations of the present method (Figure 3). Various

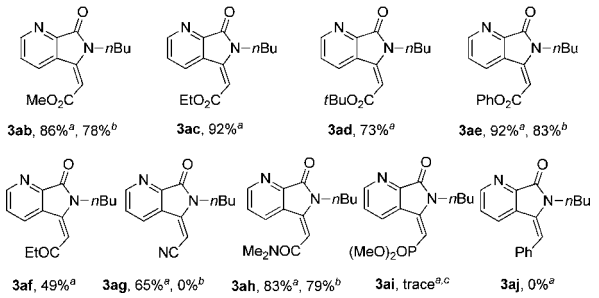
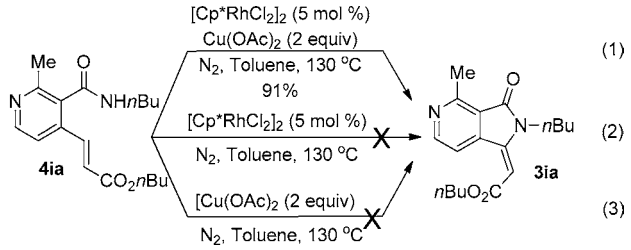


Figure 3. Scope with respect to the alkene component. (a) Conditions A: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.4 mmol), toluene (1 mL), 130 °C, 24 h, N_2. (b) Condition B: **1** (0.2 mmol), **2** (0.22 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $Cu(OAc)_2$ (0.08 mmol), DCE (1 mL), 130 °C, 24 h, O_2. The yields are of the isolated products. (c) Detected by GC–MS.

electron-deficient alkenes could be successfully employed. Alkyl acrylate reacted with **1a** to furnish the corresponding product in high isolated yields (**3aa–ad**) (for the crystal structure of **3ac**, see the Supporting Information). When phenyl acrylate was used in this reaction the corresponding product (**3ae**) was formed in 92% yield. Ethyl vinyl ketone worked to give product (**3af**) in 49% yield. When **1a** was subjected to acrylonitrile, the cyclized product (**3ag**) was isolated in 65% yield. *N,N*-Dimethylacrylamide was used in this reaction, and the corresponding product (**3ah**) was obtained in 83% yield. However, vinyl phosphonate was used in this reaction, and the desired product was observed in trace amounts. Furthermore, unreactive alkene, such as styrene, failed to yield the desired product and starting materials remained.

Additional experiments were performed to gain insights for the reaction mechanism. Compound **4ia**, isolated from the reaction of **1i** and **2a**, was treated with standard conditions to afford **3ia** in 91% isolated yield (eq 1). This result demonstrated that the oxidative olefination product should be the intermediate leading

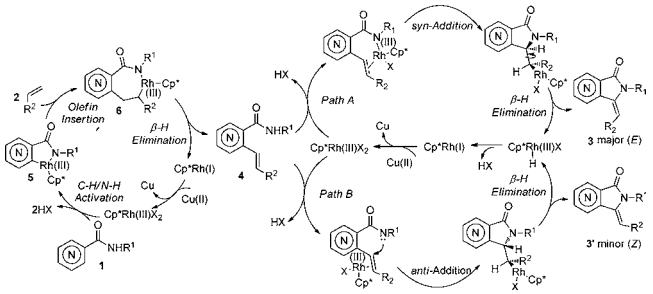


to the cyclized product. When **4ia** was treated with $[Cp^*RhCl_2]_2$ (5 mol %) and N_2 in toluene at 130 °C, the reaction did not proceed (eq 2) and **4ia** remained. In addition, **4ia** was treated with $Cu(OAc)_2$ (2 equiv) in toluene at 130 °C, and the reaction did also not proceed (eq 3). These results indicate that cyclization needs both Rh catalyst and Cu catalyst.

In addition, during the course of the reactions, red precipitate was obtained as copper metal after workup, which was confirmed by the XPS analysis (see the Supporting Information).

Based on the aforementioned results, a plausible reaction mechanism is proposed and shown in Scheme 2. Rhodation of

Scheme 2. Plausible Catalytic Pathway for the Oxidative Olefination/Cyclization



picolinamide **1** with $[Cp^*RhCl_2]_2$ produces the five-membered rhodacycle **5**, followed by olefin insertion to generate the seven-membered ring **6**, which undergoes β-hydride elimination to give the *ortho*-olefinated intermediate **4**. The oxidative cyclization reaction proceeds through electrophilic activation of olefin followed by C–N bond formation and subsequent β-hydride elimination. Cp*Rh(I) is then reoxidized to Cp*Rh(III) by $Cu(OAc)_2$. The rhodation of intermediate **4** can occur via either *syn*- or *anti*-addition. *syn*-Addition (path A) leads to *E*-isomer, and *anti*-addition (path B) leads to *Z*-isomer. The obtained products support that the *syn*-addition is major and the *anti*-addition is minor.

In summary, we have achieved Rh(III)-catalyzed intermolecular oxidative alkenylation/cyclization of picolinamides and alkenes with high regio- and stereoselectivity to furnish pyrido pyrrolone derivatives in good to excellent yields. This process features the cleavage of three C–H bonds and one N–H bond, while new C–C and C–N bonds formed in one pot. This approach provides an efficient route for the construction of pyridine-fused heterocycles without prefunctionality.

■ ASSOCIATED CONTENT

Supporting Information

Text and figures giving experimental procedures, full characterization data, including ^1H, ^{13}C NMR data and spectra for all new compounds, XPS measurements and analysis, and X-ray data for

dx.doi.org/10.1021/ol501275r | Org. Lett. 2014, 16, 3142–3145

compounds **3ra** and **3ac** (CIF). 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.

ACKNOWLEDGMENTS

This work was supported by the National Key Basic Research Program of China (973 program) (2012CB933402) and the National Natural Science Foundation of China (Nos. 21272132 and 21032004).

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