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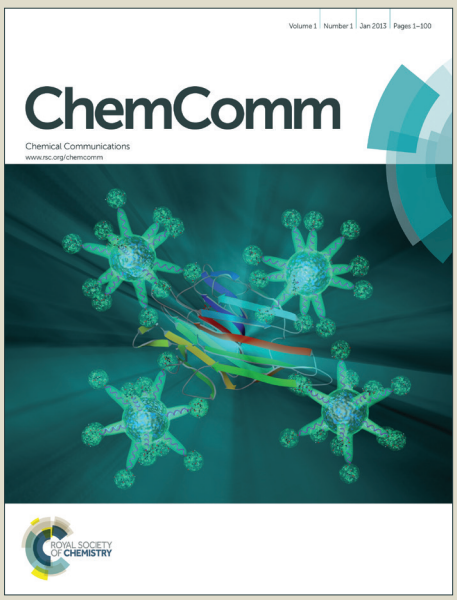

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COMMUNICATION

Ru(II)-Catalyzed Amidation Reactions of 8-Methylquinolines with Azides via C(sp^3)–H Activation†

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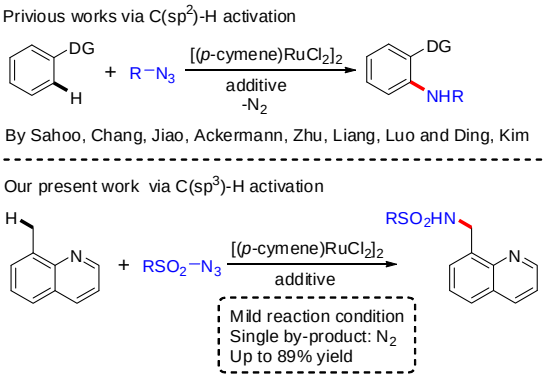
The Ru(II)-catalyzed amidation reactions of 8-methylquinolines with azides have been developed. It is the first example of [(*p*-cymene)RuCl$_2$]$_2$-catalyzed C(sp^3)–H bond intermolecular amidation reaction which give quinolin-8-ylmethanamines under mild reaction conditions in good yields.

Nitrogen widely exists in natural products, bioactive compounds and materials.[1] In the context of synthesis of the compounds with nitrogen atom, much attention has been paid to the exploration of efficient and selective C–N bond forming procedures. In the last decade, with the development of transition-metal catalysis, great efforts have been made to construct C–N bond *via* transition-metal catalyzed direct C–H amination as it alleviates the need for prefunctionalization and is environmental friendly. A variety of transition-metals,[2] such as palladium,[3] rhodium,[4] iridium,[5] and ruthenium[6–8] have been used to catalyze this kind of reactions. During the last decade, following the pioneering works of Oi and Inoue, Ackermann, Darses and Genet, Maseras and Dixneuf, and Li,[9] easy to prepare [(arene)RuCl$_2$]$_2$ catalysts became one of the most hot catalysts in C–H bond functionalizations.[10] Despite many significant achievements include C–C, C–O, and C–X (X = halogen) bond formation have been made, there are only a few works focused on [(*p*-cymene)RuCl$_2$]$_2$-catalyzed direct C–H amination reactions.[6–8] Sahoo, Chang, Jiao, and Ackermann et al have reported some important [(*p*-cymene)RuCl$_2$]$_2$-catalyzed C–H/C–N coupling reactions, in which azides were used as N atom sources for no oxidant would be required and the only byproduct would be environmentally benign N_2 (Scheme 1).[7] However, all the reported examples are limited to C(sp^2)–H bond activation. To the best of our knowledge, there no C–H amination reaction *via* C(sp^3)–H bond activation catalyzed by [(*p*-cymene)RuCl$_2$]$_2$ has been reported up to now. Herein we report the first [(*p*-cymene)RuCl$_2$]$_2$-catalyzed C(sp^3)–H amidation reaction of 8-methylquinolines with azides (Scheme 1).

8-Methylquinolines have been proved to have good cyclometallation ability,[11] many transition-metal catalyzed C(sp^3)–H bond activation of 8-methylquinoline has been reported.[12] But most of these reactions are catalyzed by palladium, little work catalyzed by other metals was reported, and even no report on the use of Ru(II). Our group is continuously interested in Ru(II)-catalyzed C–H bond activation.[13] Meanwhile, we also developed Rh(III)-catalyzed alkenylation and amidation reactions of 8-methylquinolines.[12u,v] Ruthenium is not only much cheaper than rhodium, but also often shows different reactivities from rhodium.[6,10] In this work we have achieved the Ru(II)-catalyzed C(sp^3)–N bond formation reactions of 8-methylquinolines, and higher reactivity and broader substrate scope than the rhodium catalyst were observed.

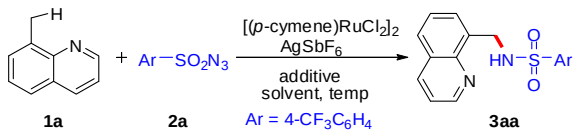


Scheme 1. [(*p*-Cymene)RuCl$_2$]$_2$-catalyzed C–H bond amidation reaction using azides as N atom sources.

At the outset of our study, 8-methylquinoline (**1a**) was chosen as the model substrate. As shown in Table 1, by treating **1a** (0.3 mmol) with 4-(trifluoromethyl)benzenesulfonylazide (**2a**) (0.6 mmol) in the presence of [(*p*-cymene)RuCl$_2$]$_2$ (0.015 mmol, 5 mol %) and $AgSbF_6$ (0.06 mmol) in DCE (2 mL) at 80 °C for 12 h, no desired product was detected (entry 1). Catalytic amount of acetate additive always provided a dramatic improvement in reaction efficiency.[5d,7a–c] Thus various acetate ions were screened (entries 3−6), among which Zn(OAc)$_2$·2H$_2$O was most efficient in leading to good product yield (entry 5). Other solvents were tested in this system giving deficient or negative results (entries 7−9). Raising the reaction temperature was not effective in increasing the product yield (entry 10). The less amount of Zn(OAc)$_2$·2H$_2$O (25 mol%) yielded a poor amount of **3aa** (entry 11). By changing the ratio of **1a**:**2a**, we were pleased to observe that higher yield was obtained with two equivalents of **1a** being used (entries 16–18). Finally, we chose the reaction condition of entry 18 as the standard conditions.

With the optimal reaction conditions in hand, various substituted 8-methylquinolines (**1a**–**p**) were treated with an azide (**2a**) and the corresponding C(sp^3)-amidated products (**3aa**–**na**)

Table 1 Optimization of Reaction Conditions[a]



1a 2a 3aa

Entry	Additive (50%)	Solvent	1a:2a	Yield (%)
1	no additive	DCE	1:1	n.r.
2	no [Ag] and additive	DCE	1:1	n.r.
3	AgOAc	DCE	1:1	16
4	$Cu(OAc)_2·H_2O$	DCE	1:1	16
5	$Zn(OAc)_2·2H_2O$	DCE	1:1	51
6	$Zn(CF_3SO_3)_2$	DCE	1:1	n.r.
7	$Zn(OAc)_2·2H_2O$	CH_2Cl_2	1:1	22
8	$Zn(OAc)_2·2H_2O$	THF	1:1	23
9	$Zn(OAc)_2·2H_2O$	*t*-AmOH	1:1	n.r.
10[b]	$Zn(OAc)_2·2H_2O$	DCE	1:1	44
11	$Zn(OAc)_2·2H_2O$ 25%	DCE	1:1	40
12	$Zn(OAc)_2·2H_2O$ 75%	DCE	1:1	49
13[c]	$Zn(OAc)_2·2H_2O$	DCE	1:1	44
14[d]	$Zn(OAc)_2·2H_2O$	DCE	1:1	46
15[e]	$Zn(OAc)_2·2H_2O$	DCE	1:1	51
16	$Zn(OAc)_2·2H_2O$	DCE	1:2	41
17	$Zn(OAc)_2·2H_2O$	DCE	1.5:1	59
18	**$Zn(OAc)_2·2H_2O$**	**DCE**	**2:1**	**61**
19	$Zn(OAc)_2·2H_2O$	DCE	3:1	61

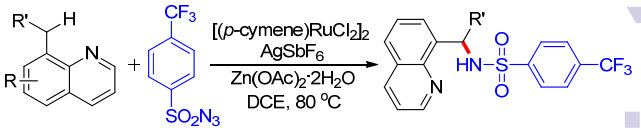
[a]Conditions: **1a** or **2a** (0.3 mmol), $[(p\text{-cymene})RuCl_2]_2$ 5 mol %, $AgSbF_6$ 20 mol %, additive 50 mol %, solvent 2 mL, at 80 °C for 12 h, under Ar, isolated yield. [b]Temp 120 °C. [c]6 h. [d]24 h. [e]Solvent 3 mL.

were obtained in moderate to good yields (Table 2). When 5-substituted or 7-substituted substrates reacted with **2a**, higher yields were obtained with electron-withdrawing groups (**3ea**, **3ka**, and **3na**) than that with electron-donating groups (**3ba** and **3la**). When the substituent groups were located at the 6-position, the electronic effect is not obvious. Both of electron-rich and electron-deficient substrates (**1f–j**) gave moderate to good yields (55–82%). It is noteworthy that 6-OMe substrate (**1g**) and 7-OMe substrate (**1l**) with strong electron-rich group both can give the desired products which are not effective in the Rh(III) system.[12v] The effect of steric hindrance was also investigated. When 8-methylquinoline was replaced by 8-ethylquinoline (**1o**) or quinolin-8-ylmethyl acetate (**1p**), no product was detected probably due to the steric effect of the substrate.

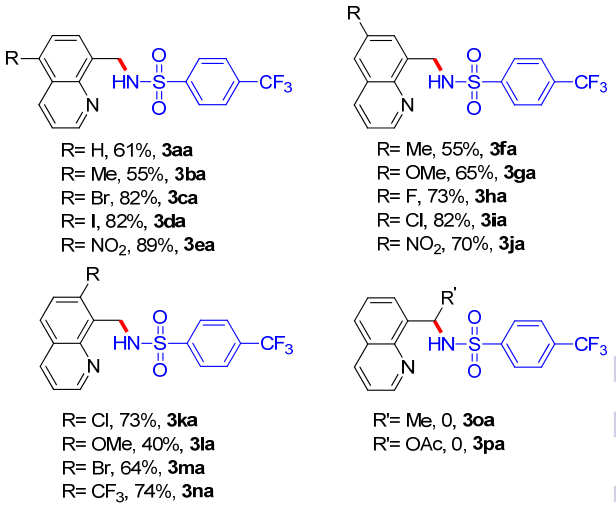
In addition to **2a**, different sulfonyl azides were also tested under the standard reaction conditions (Table 3). All the *para*-, *ortho*-, and *meta*-substituted arenesulfonylazide substrates with electron-withdrawing groups provided good yields (**3ea**, **3ee**, **3ef**, and **3eg**). Compared with the substrates of 8-methylquinolines, azides bearing electron-donating groups also afforded the corresponding products in high yields (**3eb** and **3ec**). Besides the arenesulfonylazides, aliphatic sulfonyl azides (**2h** and **2i**) were also viable to give the desired products in moderate to good yields.

To gain more insight to the mechanism of this reaction, KIE (kinetic isotope effect) experiments were performed in two independent reactions (Scheme 2). The KIE was found to be k_H/k_D = 1.9, indicated that the cleavage of the methyl C−H bond may be involved in the rate-determining step.

Table 2 Substrate Scope of 8-Methylquinolines[a]

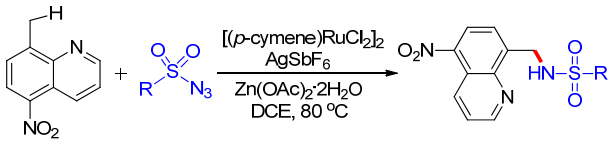


1a-1p 2a 3aa-3pa

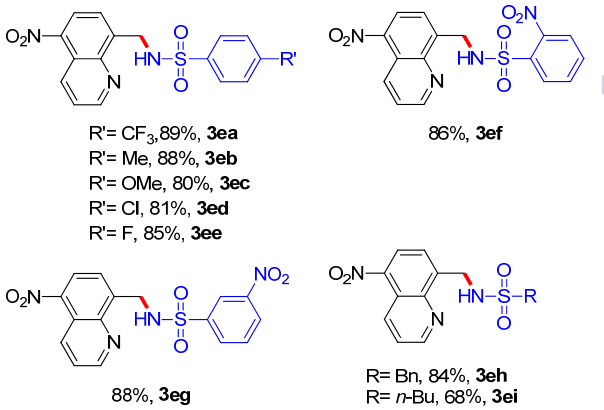


[a]Conditions: **1** (0.6 mmol), **2a** (0.3 mmol), $[(p\text{-cymene})RuCl_2]_2$ 5 mol %, $AgSbF_6$ 20 mol %, $Zn(OAc)_2·2H_2O$ 50 mol %, DCE 2 mL, at 80 °C for 12 h, under Ar, isolated yield.

Table 3 Sulfonyl Azide Scope [a]

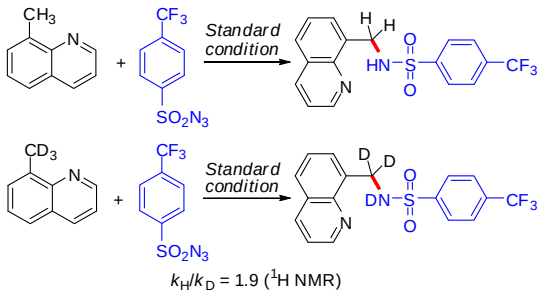


1e 2a-2i 3ea-3ei

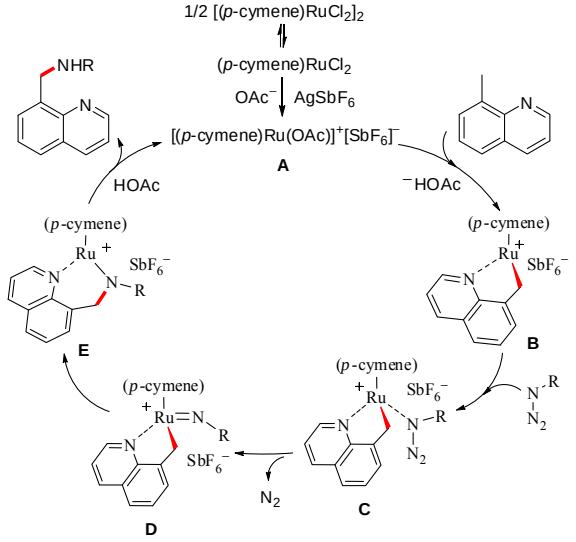


[a]Conditions: **1e** (0.6 mmol), **2** (0.3 mmol), $[(p\text{-cymene})RuCl_2]_2$ 5 mol %, $AgSbF_6$ 20 mol %, $Zn(OAc)_2·2H_2O$ 50 mol %, DCE 2 mL, at 80 °C for 1 h, under Ar, isolated yield.

Based on the known Ru(II)-catalyzed C(sp^2)−H bond amidation reactions,[7] a possible mechanism is proposed for the present catalytic reaction (Scheme 3). The first step is likely to be a C(sp^3)−H activation process affording a five-membered



Scheme 2. The KIE experiments.

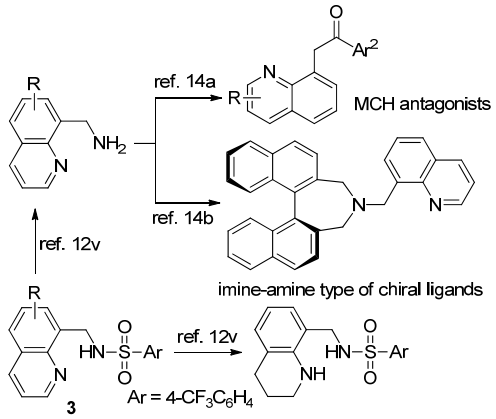


Scheme 3. Proposed mechanistic pathway of the amidation reaction.

intermediate **B**. Coordination of an azide to **B** gives the intermediate **C**. The sulfonamido moiety of intermediate **C** subsequently inserts into the Ru–C bond directly or involving a Ru(IV)−nitrenoid intermediate **D** to form intermediate **E**. Finally, protonolysis of **E** delivers the desired product.

Quinolin-8-ylmethanamine was reported to be a building block in enormous areas involved in medicinal chemistry, organic synthesis, and analytical chemistry.[14] Its derivatives have been studied for their medicinal properties, as exemplified by the potent and selective melanin concentrating hormone (MCH) antagonists.[14a] They are also building blocks in inorganic synthesis like synthesis of imine–amine type of chiral ligands (Scheme 4).[14b] Our work provides a new simple route to synthesize this kind of compounds followed by a simple deprotection process.[12v] To further demonstrate the synthetic utility of the products **3**, one more derivatization reaction was done. The amidation product **3aa** could be reduced selectively by $NaBH_4/NiCl_2{\cdot}6H_2O$, giving the product with exposed amino group (Scheme 4).[15,12v]

In conclusion, we have developed a Ru(II)-catalyzed amidation reaction of 8-methylquionlines with azides to achieve quinolin-8-ylmethanamine derivatives in good yields. This is the first $[(p\text{-cymene})RuCl_2]_2$-catalyzed amidation reaction of C(sp^3)–H bond with azides. Further applications of this method in the synthesis of other targets and a detailed mechanistic investigation are in progress.



Scheme 4. Utility and derivatization reactions of **3**.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Full experimental details, characterization and NMR spectra of the target products are provided. See DOI: 10.1039/b000000x/

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