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Ru(II)-catalyzed amidation reactions of 8-methylquinolines with azides *via* C(sp^3)–H activation†

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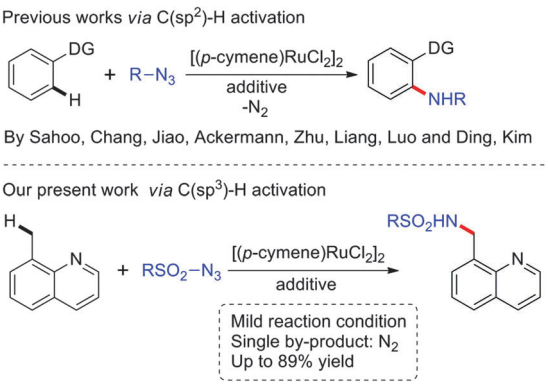
Ru(II)-catalyzed amidation reactions of 8-methylquinolines with azides have been developed. They are the first examples of [(*p*-cymene)-RuCl$_2$]$_2$-catalyzed C(sp^3)–H bond intermolecular amidation reactions which give quinolin-8-ylmethanamines under mild reaction conditions in good yields.

Nitrogen exists widely in natural products, bioactive compounds and materials.[1] In the context of the synthesis of compounds with nitrogen atoms, 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 the C–N bond *via* transition-metal catalyzed direct C–H amination as it alleviates the need for prefunctionalization and is environmentally 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 class of reactions. During the last decade, following the pioneering research work 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 hottest catalysts in C–H bond functionalization reactions.[10] Despite many significant achievements, including the formation of C–C, C–O, and C–X (X = halogen) bonds, having been made, there are only a few reports 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 which 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, 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).



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

8-Methylquinolines have been proved to have good cyclometallation ability,[11] and many transition-metal catalyzed C(sp^3)–H bond activation reactions of 8-methylquinoline have been reported.[12] However, most of these reactions are catalyzed by palladium, little work on reactions catalyzed by other metals has been reported, and there is not even a report on the use of Ru(II). Our group has been continuously interested in Ru(II)-catalyzed C–H bond activation.[13] Meanwhile, we have 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 reactivity 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 those of the rhodium catalyst were observed.

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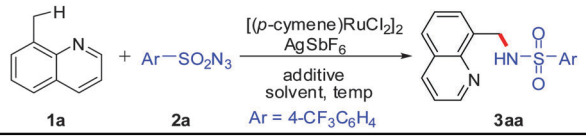
† Electronic supplementary information (ESI) available: Full experimental details, characterization and NMR spectra of the target products are provided. See DOI: 10.1039/c5cc06230f

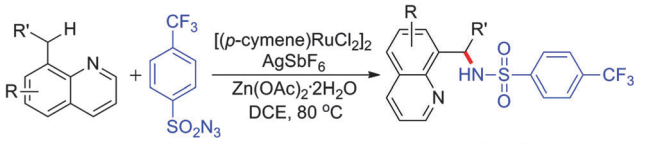
Table 1 Optimization of reaction conditions[a]

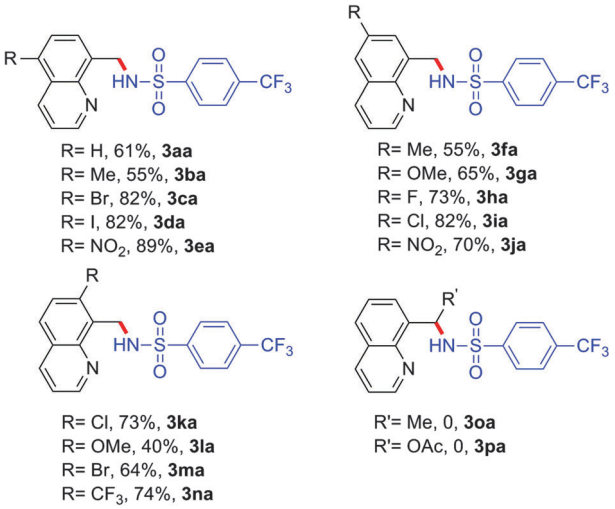


Entry	Additive (50%)	Solvent	1a : 2a	Yield (%)
1	No additive	DCE	1 : 1	n.r.
2	No [Ag] and additive	DCE	1 : 1	n.r.
3	AgOAc	DCE	1 : 1	16
4	$Cu(OAc)_2·H_2O$	DCE	1 : 1	16
5	$Zn(OAc)_2·2H_2O$	DCE	1 : 1	51
6	$Zn(CF_3SO_3)_2$	DCE	1 : 1	n.r.
7	$Zn(OAc)_2·2H_2O$	CH_2Cl_2	1 : 1	22
8	$Zn(OAc)_2·2H_2O$	THF	1 : 1	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.

Table 2 Substrate scope of 8-methylquinolines[a]





[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.

At the outset of our study, 8-methylquinoline (**1a**) was chosen as the model substrate. As shown in Table 1, upon treatment of **1a** (0.3 mmol) with 4-(trifluoromethyl)benzenesulfonylazide (**2a**) (0.6 mmol) in the presence of $[(p\text{-cymene})RuCl_2]_2$ (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). The use of catalytic amounts of the acetate additive always led to a dramatic improvement in the reaction efficiency.[5d,7a–c] Thus various acetate ions were screened (entries 3–6), among which $Zn(OAc)_2·2H_2O$ was the 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). A smaller amount of $Zn(OAc)_2·2H_2O$ (25 mol%) yielded a poor amount of **3aa** (entry 11). By changing the ratio of **1a : 2a**, we were pleased to observe that a higher yield was obtained when two equivalents of **1a** were used (entries 16–18). Finally, we chose the reaction conditions of entry 18 as the standard conditions.

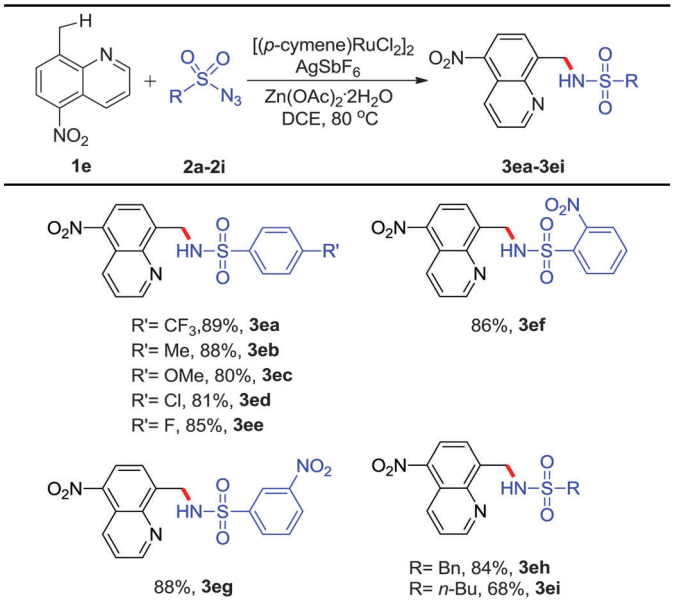
With the optimal reaction conditions in hand, various substituted 8-methylquinolines (**1a–p**) were treated with an azide (**2a**) and the corresponding C(sp^3)-amidated products (**3aa–na**) were obtained in moderate to good yields (Table 2). When 5-substituted or 7-substituted substrates were reacted with **2a**, higher yields were obtained for the electron-withdrawing groups (**3ea**, **3ka**, and **3na**) than for the electron-donating groups (**3ba** and **3la**). When the substituent groups were located at the 6-position, the electronic effect was not obvious. Both of the electron-rich and electron-deficient substrates (**1f–j**) gave moderate to good yields (55–82%). It is noteworthy that both 6-OMe (**1g**) and 7-OMe (**1l**) substrates with strong electron-rich groups 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**). Similarly to 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.

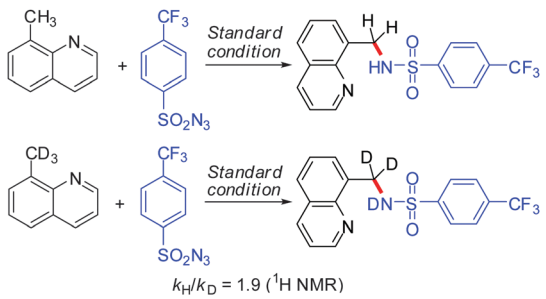
To gain more insight into the mechanism of this reaction, KIE (kinetic isotope effect) experiments were performed in two independent reactions (Scheme 2). The KIE was found to be $k_H/k_D = 1.9$, which indicated that the cleavage of the methyl C–H bond may be involved in the rate-determining step.

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

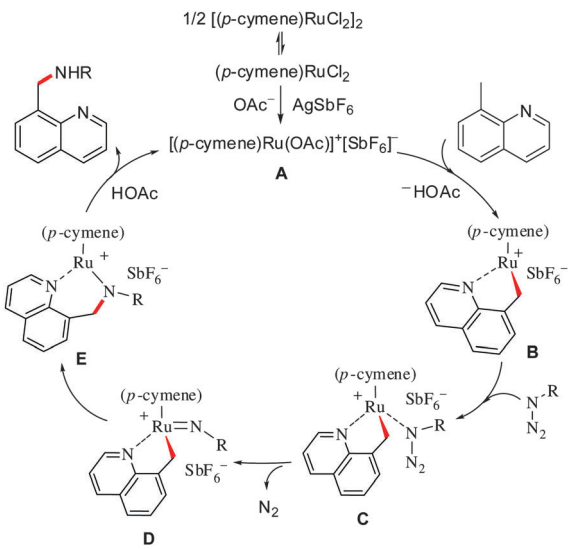
Table 3 Sulfonyl azide scope[a]



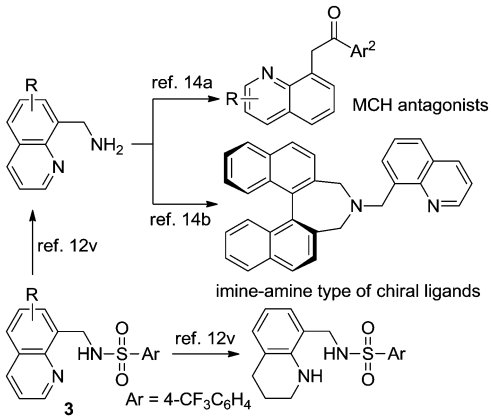
[a] Conditions: **1e** (0.6 mmol), **2** (0.3 mmol), $[(p\text{-cymene})RuCl_2]_2$ 5 mol%, $AgSbF_6$ 20 mol%, $Zn(OAc)_2{\cdot}2H_2O$ 50 mol%, DCE 2 mL, at 80 °C for 12 h, under Ar, isolated yield.



Scheme 2 The KIE experiments.



Scheme 3 Proposed mechanistic pathway of the amidation reaction.



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

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 the synthesis of the imine–amine type of chiral ligands (Scheme 4).[14b] Our work provides a new simple route to synthesize this class of compounds followed by a simple deprotection process.[12v] To further demonstrate the synthetic utility of the products **3**, one more derivatization reaction was carried out. The amidation product **3aa** could be reduced selectively by $NaBH_4/NiCl_2{\cdot}6H_2O$, giving the product with exposed amino groups (Scheme 4).[12v,15]

In conclusion, we have developed a Ru(II)-catalyzed amidation reaction of 8-methylquionlines with azides to obtain 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 application of this method in the synthesis of other targets and a detailed mechanistic investigation are in progress.

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