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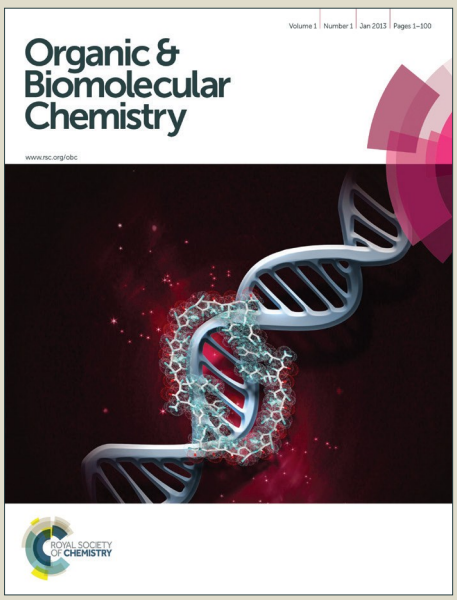

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ARTICLE TYPE

Palladium-catalyzed intermolecular oxidative cyclization of *N*-aryl enamines with isocyanides through double sp^2 C-H bonds cleavage: facile synthesis of 4-aminoquinoline derivatives

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An efficient method for the synthesis of 4-aminoquinolines via palladium-catalyzed intermolecular oxidative cyclization of *N*-aryl enamines and isocyanides through double sp^2 C-H bonds cleavage has been developed.

Quinoline nucleus is one of the most important structural motifs because of its ubiquity in natural compounds and pharmaceuticals with a broad range of bioactivities.[1] For instance, mefloquine, chloroquine, and amodiaquine are well-known antimalarial drugs (Figure 1).[2] Therefore, substantial synthetic methods for the preparation of these "privileged scaffolds" have been reported since more than a century ago.[3] In addition, introducing fluorine atoms into a privileged scaffold sometimes play a pivotal role in its physical, chemical, and biological properties. Great progress has been made in the synthesis of versatile CF_3-containing building blocks.[4] In view of the importance of quinoline derivatives, the development of facile synthetic methods to access functionalized quinolines is critical to pharmaceutical and fine chemical industries. Herein we designed a series of target molecules having the similar structure to mefloquine and chloroquine, 2-trifluoromethyl quinoline-containing skeleton (Figure 1).

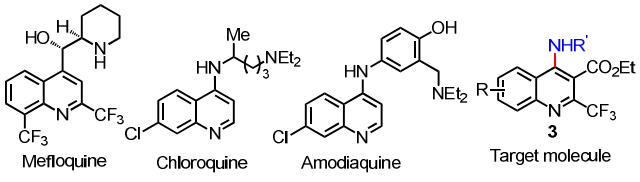
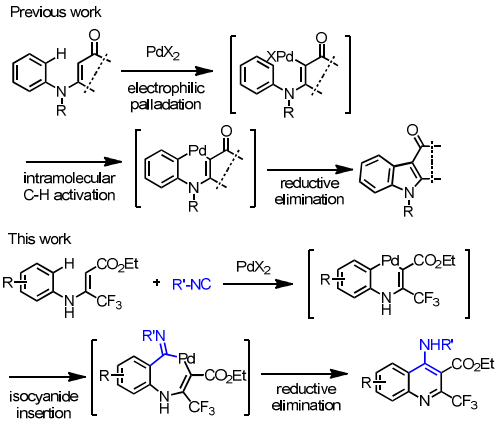


Fig. 1 Examples of Quinoline-based Drugs and Our Target Molecule.

Recently, transition-metal-catalyzed oxidative cyclization has become particularly attractive strategy for the synthesis of various privileged heterocycles, such as indole,[5] pyrrole,[6] carbazole,[7] benzofuran,[8] oxazole,[9] benzothiophene,[10] and some other fused heterocycles.[11] In 2008, Glorius and co-workers reported a novel palladium-catalyzed oxidative cyclization of *N*-aryl enamines to synthesize substituted indoles.[5a] In 2012, palladium-catalyzed aerobic oxidative cyclization of *N*-aryl imines for the synthesis of indoles has been developed by Yoshikai and co-worker.[5d] Recently, Guan and co-workers also developed an efficient palladium-catalyzed oxidative cyclization of tertiary enamines for the synthesis of 1,3,4-trisubstituted pyrroles and 1,3-disubstituted

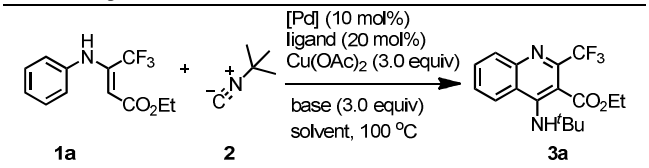


Scheme 1 Csp^2-H Activation of *N*-Aryl enamines.

indoles.[5g] According to their proposed mechanism, we anticipated that palladium-catalyzed cascade oxidative cyclization of enamines and isocyanides insertion may provide a direct approach to 4-aminoquinoline derivatives (Scheme 1).

In fact, isocyanides as versatile C1 building blocks have attracted great attentions in organic, medicinal, and combinatorial chemistry.[12] During the past decade, a vast number of methods for the efficient construction of various heterocycles based on transition-metal-catalyzed C-H bond activation and isocyanide insertion have been investigated.[13]

Table 1 Optimization of the Reaction Conditions[a]



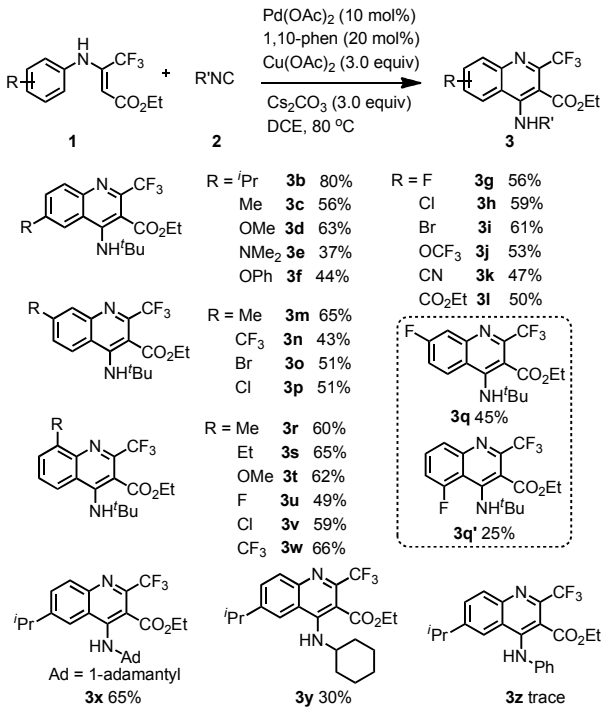
Entry	[Pd]	Ligand	Base	Solvent	Yield (%)[a]
1	$Pd(OAc)_2$	-	K_2CO_3	Toluene	30
2	$Pd(OAc)_2$	-	DBU	Toluene	NR
3	$Pd(OAc)_2$	-	Cs_2CO_3	Toluene	37
4	$Pd(OAc)_2$	-	NaO^tBu	Toluene	Trace
5	$Pd(OAc)_2$	-	K_2HPO_4	Toluene	NR
6	$Pd(OAc)_2$	PCy_3	Cs_2CO_3	Toluene	35
7	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	Toluene	37
8	$Pd(OAc)_2$	Ad_2P^nBu	Cs_2CO_3	Toluene	40
9	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	Toluene	35
10	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	Toluene	57
11	$Pd(TFA)_2$	1,10-phen	Cs_2CO_3	Toluene	42
12	$Pd_2(dba)_3$	1,10-phen	Cs_2CO_3	Toluene	Trace
13	$PdCl_2(MeCN)_2$	1,10-phen	Cs_2CO_3	Toluene	41
14	$PdCl_2(PCy_3)_2$	1,10-phen	Cs_2CO_3	Toluene	Trace
15	$PdCl_2(PhCN)_2$	1,10-phen	Cs_2CO_3	Toluene	48
16	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	PhCl	32
17	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	Dioxane	Trace
18	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DMF	Trace
19	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DCE	42
20	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DMSO	trace
21	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	THF	22
22	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	MeCN	33
23	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DCE	61
24[c]	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DCE	65
25[c,d]	$Pd(OAc)_2$	1,10-phen	Cs_2CO_3	DCE	71

[a] Reaction conditions: all reaction were performed with *N*-phenyl enamine **1a** (0.2 mmol), *tert*-butyl isocyanide **2a** (3.0 equiv), [Pd] (10 mol%), ligand (20 mol%), $Cu(OAc)_2$ (3.0 equiv), base (3.0 equiv), solvent (2.0 mL), at 100 °C for 16 h, at the atmosphere of N_2; [b] Isolated yield based on enamine **1a**, NR = no reaction; [c] At 80 °C; [d] *tert*-Butyl isocyanide was injected for three times with equal amount (at the first, second, and third hour).

In 2011, Zhu and co-workers reported the palladium-catalyzed intramolecular C-H amidination reaction by isocyanides insertion.[13a] Recently, Yu group reported an aerobic C-H activation and isocyanide insertion of arenes or heterocycles containing *N*-methoxy amide group, affording various functionalized heterocyles in good to excellent yields.[13i] Herein we describe an efficient palladium-catalyzed oxidative cyclization and isocyanide insertion into sp^2 C-H bond of *N*-aryl enamines to give 4-aminoquinolines in one pot.

Based on previous works,[5,13] our preliminary investigation focused on the reaction of *N*-phenyl enamine **1a** with *tert*-butyl isocyanide **2a** to give **3a** in 30% yield in the presence of 10 mol% $Pd(OAc)_2$, $Cu(OAc)_2$ as the oxidant, and K_2CO_3 as the base at 100 °C in toluene (Table 1, entry 1). When $CuCl_2$, 1,4-benzoquinone, $K_2S_2O_8$, and Ag_2CO_3 were employed as the oxidant individually, no better results were observed (see supporting information). The reaction could not be detected in the absence of K_2CO_3, which shows that the base has an important effect on this transformation. Among bases

Scheme 2 The Scope of Substrates[a,b]



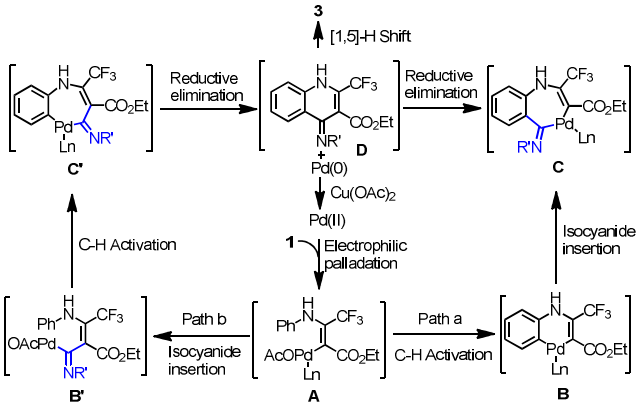
[a] Reaction conditions: *N*-aryl enamine **1** (0.3 mmol), *tert*-butyl isocyanide **2a** (3.0 equiv), $Pd(OAc)_2$ (10 mol%), 1,10-phen (20 mol%), $Cu(OAc)_2$ (3.0 equiv), Cs_2CO_3 (3.0 equiv), DCE (2.5 mL), 80 °C, at the atmosphere of N_2; [b] Isolated yield based on **1**.

examined, Cs_2CO_3 proved to be the best one (Table 1, entry 3). Subsequently, some commercially available mono- and bidentate *P*- or *N*-ligands were added in this transformation in order to improve the yield. To our delight, the yield was improved to 57% when 1,10-phen was used (Table 1, entry 10). However, some other modified 1,10-phen ligands couldn't improve yield further (see supporting information). Inferior results were obtained when other palladium sources such as $Pd(TFA)_2$, $Pd_2(dba)_3$, $PdCl_2(MeCN)_2$, $PdCl_2(PCy_3)_2$, and $PdCl_2(PhCN)_2$ were employed (Table 1, entries 11-15). Further solvent screening revealed that DCE appeared to be the best solvent and the yield was increased to 61% (Table 1, entry 23). Gratifyingly, lowering the temperature or changing the injection mode of isocyanide improved the efficiency of this catalytic system with 71% yield (Table 1, entry 25).

The scope of *N*-aryl enamines was investigated first under the optimized conditions [$Pd(OAc)_2$ (10 mol%), 1,10-phen (20 mol%), $Cu(OAc)_2$ (3.0 equiv), Cs_2CO_3 (3.0 equiv), DCE , 80 °C, N_2] (Scheme 2). The *para* position substituted *N*-aryl enamines **1** bearing a variety of electron-donating [such as alkyl (methyl and isoproyl), methoxy, and *N,N*-dimethyl] or withdrawing groups [halogen (fluoro, chloro, and bromo), cyano, ester, triflormethyl, and trifluoromethoxy] gave the desired products **3b-l** in moderate to good yields. For instance, substrate **1b** with an isopropyl group reacted with *tert*-butyl isocyanide **2a** affording the corresponding product **3b** in 80% yield. The presence of trifluoromethoxy group on the phenyl ring of substrate **1j** resulted in the desired product **3j** in 53% yield. *Meta*-substituted substrates containing a variety of

functional groups, such as Me, CF_3, Br, and Cl, were compatible with the reaction conditions (**3m-p**), and the cyclization/isocyanide insertion took place exclusively at the *ortho*-position with less steric hindrance. Only when *N*-3-fluorophenyl enamine was applied to the reaction, a mixture of the two isomers **3q** and **3q'** in the ratio of 2:1 was obtained probably due to the less steric hindrance of F atom. The presence of an *ortho*-substitutent on the phenyl ring of substrate also could proceed well, resulting in products **3r-w** in good yields. Subsequently, we also investigated the scope of isocyanides **2** under the standard conditions. Several other isocyanides **2**, such as 1-adamantyl, cyclohexyl, *n*-butyl, and phenyl isocyanides, were examined with substrate **1b**. The results showed that only sterically hindered 1-adamantylisocyanide **2b** was a suitable substrate, leading to the corresponding product **3x** with 65% isolated yield. While other isocyanides, such as *n*-butylisocyanide and phenylisocyanide showed poor reactivity.

A plausible mechanism of the palladium-catalyzed oxidative cyclization/isocyanide insertion of *N*-aryl enamines is depicted in Scheme 3. On the basis of previous reports,[5,13] we proposed the catalytic cycle involving a Pd(II)/Pd(0) redox process. Vinylpalladium intermediate **A** was generated via electrophilic palladation of **1** with $Pd(OAc)_2$ through C-H activation of the vinyl proton in the presence of 1,10-phen as ligand and Cs_2CO_3 as base.[5a, 5d, and 5g] Then the intermediate **A** may undergo two pathways. Path a: Intramolecular electrophilic aromatic palladation through C-H activation of the aromatic hydrogen, to form a six-membered palladacycle intermediate **B**, [5a,5d,and 5g] which undergoes migratory insertion of isocyanide providing cyclic palladium species **C**.[13] Finally, reductive elimination of intermediate **C** generate Pd(0) and the product **3** upon [1,5]-H shift of intermediate **D**. Alternatively, the intermediate **A** may undergo isocyanide insertion prior to C-H bond activation (path b). The Pd(0) species is reoxidized to Pd(II) by $Cu(OAc)_2$. For the time being, pathway a might be the more likely reaction mechanism because trace of indole by-product from the reductive elimination of intermediate **B** was detected in some reactions.



Scheme 3 Possible Reaction Mechanism.

In conclusion, we have developed an efficient Pd-catalyzed intermolecular oxidative cyclization of readily available *N*-aryl enamines and isocyanides through double sp^2 C-H bonds cleavage. The method tolerates a series of functional groups, such as alkyl (methyl, ethyl, and isoproyl), methoxy, trifluoromethoxy, halogen (fluoro, chloro, and bromo), cyano, ester, trifluoromethyl, and *N,N*-dimethyl. Thus, it provides a facile pathway for straightforward synthesis of valuable 4-aminomethylquinoline derivatives[11b] from easy available *N*-aryl enamines and isocyanides under mild conditions.

Acknowledgements

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† Electronic Supplementary Information (ESI) available: [Experimental procedure, characterization data, ^1H, ^{13}C, and ^{19}F NMR spectra of compounds **3**]. See DOI: 10.1039/b000000x/

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