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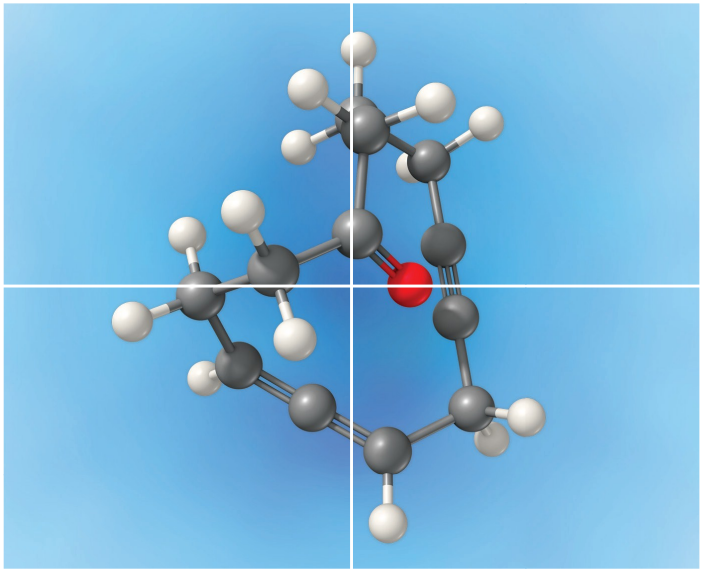

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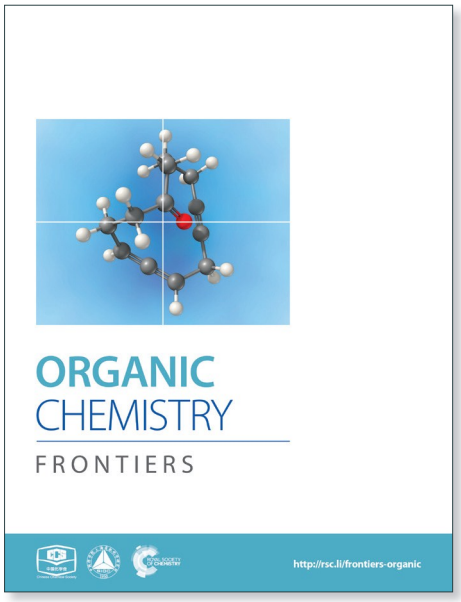

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Copper-Mediated C(sp^3)-H Amination in a Multiple C-N Bond-Forming Strategy for the Synthesis of *N*-Heterocycles

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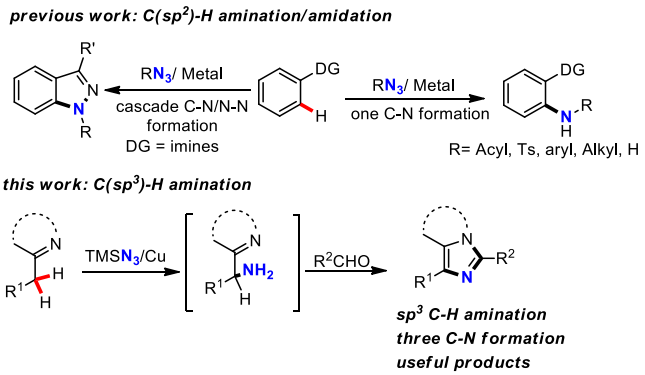
An efficient construction of imidazo[1,5-*a*]pyridines, through a three-component reaction involving benzyl substituted pyridines, aldehydes, and $TMSN_3$, has been developed. Three C-N bonds were formed in one pot. Copper-promoted amination of the benzylic C(sp^3)-H bond was a key step of this multiple C-N bond-forming sequence.

Carbon-nitrogen bond formation is one of the major topics of organic synthesis due to the great importance of nitrogen-containing compounds in natural products, pharmaceuticals, and agrochemicals as well as functional chemicals.[1] In recent years, transition-metal-catalyzed amination/amidation of C-H bonds has emerged as an atom-economic and efficient alternative to traditional C-N bond-forming methods using prefunctionalized substrates.[2-4] Organic azides have been utilized increasingly as amino sources recently, since the method normally requires no extra oxidant and only N_2 gas is released as a byproduct.[5] Additionally, structurally diversified organic azides are readily available. As a result, a variety of transition-metal-based catalytic systems have successfully been exploited in directed intermolecular C-H amination/amidation with organic azides.[6-11] Although great success has been achieved in this filed, some challenges still exist: 1) process involving multiple C-N bond formation is uncommon; 2) the use of directing group limits the application of this strategy; 3) intermolecular amidation/amination of C(sp^3)-H bond is still rare.[12] Recently, a cascade intermolecular C(sp^2)-H amidation and intramolecular N-N bond-forming strategy using organic azides was applied in the synthesis of indazoles.[13, 14] Herein, we report a new synthesis of imidazo[1,5-*a*]pyridines via amination of a sp^3 hybridized C-H bond as a key C-N bond-forming step with $TMSN_3$ as an amino source promoted by Cu(II) (Scheme 1). In this three-component reaction involving benzyl substituted N-heterocycles, aldehydes, and $TMSN_3$, imidazo[1,5-*a*]pyridines and related more complicated fused heterocycles were constructed with sequential three C-N bonds formation. Besides, the heterocyclic nitrogen functionalized as both a direction group and an intramolecular nucleophile in this process.

The scaffold of imidazo[1,5-*a*]pyridine[15] exists in many natural products and pharmaceutical agents with broad biological activities, such as antimicrobial, anti-neoplastic, anti-anxiety, and anti-inflammatory and consequently, much attention has been paid to its synthesis. Methods for the synthesis of imidazo[1,5-*a*]pyridines are mainly limited to 1,2,3-triazolo[1,5-*a*]pyridine-derived carbene insertion into nitriles, and Vilsmeier-type dehydrative cyclization of *N*-2-pyridylmethylamides and oxidative cyclization of 2-pyridinyl imine or amine derivatives.[16] However, most of the starting materials applied in these methods require multiple-step preparations. The general procedure reported here starts from readily available substrates with C(sp^3)-H amination as a key step.

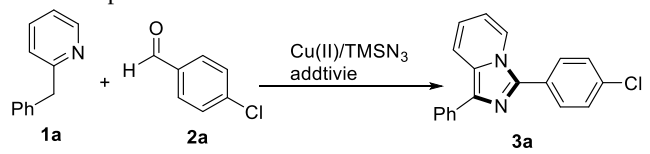


Scheme 1. C-H amination/amidation for the construction of *N*-heterocycles.

We initiated the study with a reaction between 2-benzylpyridine **1a**, *p*-chlorobenzaldehyde **2a**, and $TMSN_3$ under the reaction conditions we reported recently.[10a] The desired product, 3-(4-chlorophenyl)-1-phenylimidazo[1,5-*a*]pyridine **3a**, was isolated in 14% yield. Then, different acids in place of PivOH were tested. PivOH was proved to be the additive of choice (entries 1-5, Table 1). DCB (*o*-dichlorobenzene) was a better solvent than others screened (entries 6-8). Investigation of copper salts indicated that $Cu(TFA)_2xH_2O$ was optimal. When the reaction was subjected to catalytic amount of $Cu(TFA)_2XH_2O$ (0.2 equiv) with oxidants such as TBHP and dioxygen, the corresponding oxidation by-product, phenyl(pyridin-2-yl)methanone, was obtained and only trace amount of the desired product **3a** was detected. During the optimization, we found that 2-

benzylpyridine was partially oxidized to the corresponding ketone. The yield of **3a** was improved to 28% when the amount of **1a** was doubled (entry 11). Addition of $TMSN_3$ in two portions and increasing the loading of $Cu(TFA)_2$ to 1.2 equiv were helpful for product formation (entries 12-13). Finally, the yield was maximized to 72% when the reaction was performed in higher concentration and a total 4.0 equivalents of $TMSN_3$ (3 + 1) was applied (entries 14-15).

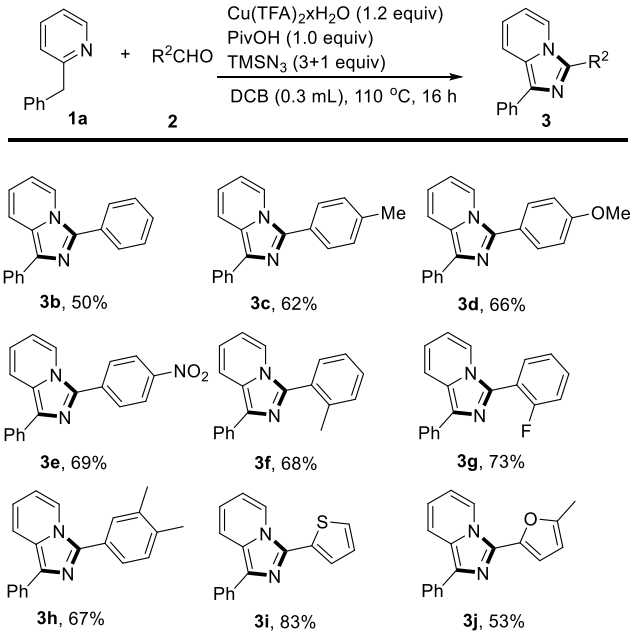
Table 1. Optimization of the reaction conditions[a]



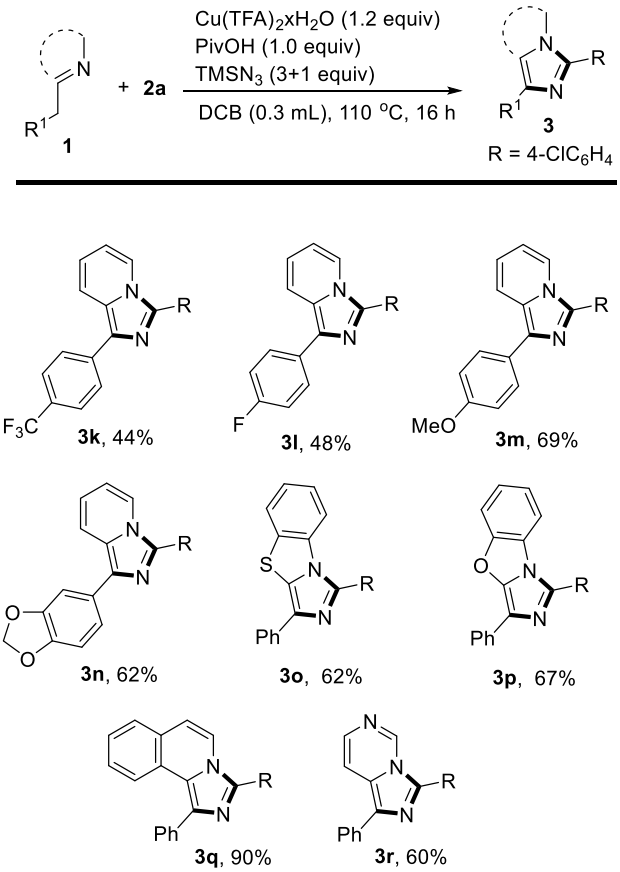
entry	copper (equiv)	additive (1 equiv)	solvent (mL)	yield (%)
1	$Cu(TFA)_2$ (1.0)	PivOH	DCB (2)	14
2	$Cu(TFA)_2$ (1.0)	TFA	DCB (2)	n.d.
3	$Cu(TFA)_2$ (1.0)	TsOH	DCB (2)	trace
4	$Cu(TFA)_2$ (1.0)	HOTf	DCB (2)	n.d.
5	$Cu(TFA)_2$ (1.0)	-	DCB (2)	10
6	$Cu(TFA)_2$ (1.0)	PivOH	toluene (2)	trace
7	$Cu(TFA)_2$ (1.0)	PivOH	DMF (2)	trace
8	$Cu(TFA)_2$ (1.0)	PivOH	DCE (2)	trace
9	$Cu(OAc)_2$ (1.0)	PivOH	DCB (2)	<5
10	$CuCl_2$ (1.0)	PivOH	DCB (2)	<5
11[b]	$Cu(TFA)_2$ (1.0)	PivOH	DCB (2)	28
12[b,c]	$Cu(TFA)_2$ (1.0)	PivOH	DCB (2)	32
13[b,c]	$Cu(TFA)_2$ (1.2)	PivOH	DCB (2)	47
14[b,c]	$Cu(TFA)_2$ (1.2)	PivOH	DCB (0.3)	60
15[b,d]	**$Cu(TFA)_2$ (1.2)**	**PivOH**	**DCB (0.3)**	**72**

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), copper salt, additive (1.0 equiv), $TMSN_3$ (3.0 equiv), solvent, in Ar, 110 °C. [b]**1a** (0.4 mmol), **2a** (0.2 mmol). [c]Addition of $TMSN_3$ (2.0 equiv) at the beginning of the reaction, and the second portion of $TMSN_3$ (1.0 equiv) was added after 8 h. [d]Addition of $TMSN_3$ (3.0 equiv) at the beginning of the reaction, and the second portion of $TMSN_3$ (1.0 equiv) was added after 8 h. DCB = *o*-dichlorobenzene, PivOH = pivalic acid, TFA = trifluoroacetic acid, TsOH = *p*-toluenesulfonic acid, HOTf = trifluoromethanesulfonic acid.

With the optimal conditions in hand, we started to exam the generality of aldehydes applicable to this three-component reaction (Scheme 2). Benzaldehydes substituted at the *para* position with either electron-donating OMe, Me or electron-withdrawing NO_2 groups reacted smoothly with **1a** and $TMSN_3$ to give the corresponding products in 62% to 69% yield (**3c**-**3e**), demonstrating that the electronic density of the aromatic aldehydes had little effect on the product formation. Benzaldehydes bearing *ortho* substituents (Me, F) also gave the desired products (**3f**, **3g**) in comparable yields. Furthermore, thiophene-2-carbaldehyde and furyl aldehyde afforded the corresponding heterocycle substituted products (**3i**, **3j**) in 83% and 53% yield, respectively. Unfortunately, aliphatic aldehydes failed to deliver the corresponding products with the method. It was notable that in these cases, no by-product, derived from either Schmidt reaction[17] or Jiao's reaction[18] through C-C bond cleavage, was detected.



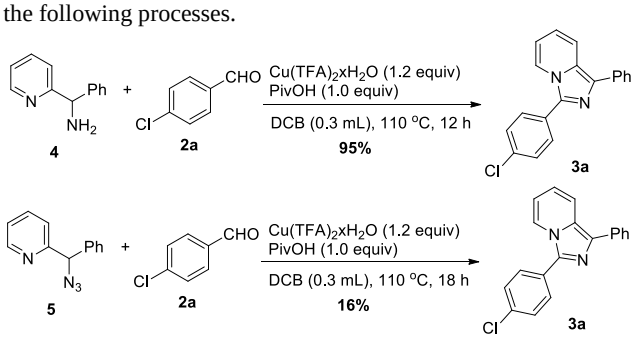
Scheme 2. The scope of aldehydes. Reaction conditions: **1a** (0.4 mmol, 2.0 equiv), **2** (0.2 mmol, 1.0 equiv), PivOH (0.2 mmol, 1.0 equiv), $Cu(TFA)_2xH_2O$ (0.24 mmol, 1.2 equiv), DCB (0.3 mL), $TMSN_3$ (0.6 mmol, 3.0 equiv, 8 h, then 0.2 mmol, 1.0 equiv, 8 h), 110 °C, in Ar.



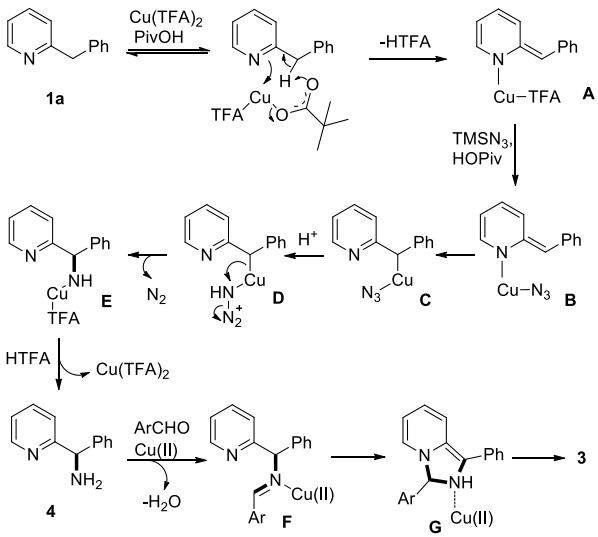
Scheme 3. The scope of *N*-heterocyles. Reaction conditions: **1** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv), PivOH (0.2 mmol, 1.0 equiv), $Cu(TFA)_2xH_2O$ (0.24 mmol, 1.2 equiv), DCB (0.3 mL), $TMSN_3$ (0.6 mmol, 3.0 equiv, 8 h, then 0.2 mmol, 1.0 equiv, 8 h), 110 °C, in Ar.

Then, the scope of substituents on the phenyl ring of 2-benzylpyridine was studied (Scheme 3). Electron-rich 2-benzylpyridines afforded the corresponding products in higher yields than those substituted with electron-withdrawing CF_3 or F groups in reactions with *p*-chlorobenzaldehyde **2a** (**3m**, **3n** vs. **3k**, **3l**). Besides pyridine, other *N*-heterocycles could also be used to build fused heterocyclic systems. For example, 2-benzylbenzothiazole and 2-benzylbenzoxazole reacted smoothly with **2a** to afford the more complicated tricyclic scaffolds **3o** and **3p** in good yields. Isoquinoline is an excellent directing group in this highly efficient C-N bond-forming reaction, delivering **3q** in 90% yield. Substituted imidazo[1,5-*a*]pyrimidine derivative **3r** could also be obtained in 60% yield by applying this method.

In order to gain insights into the reaction mechanism, some possible reaction intermediates derived from benzaldehyde, such as benzonitrile, benzoic acid and benzamide, reacted with **1a** and TMN_3 under the standard conditions. No trace amount of the desired product was detected in these cases. Phenyl(pyridin-2-yl)methanone, the oxidation byproduct of **1a**, also failed to give **3a** in a reaction with **2a** and $TMSN_3$. Then, azidation or amination of one of the benzylic C-H bonds was proposed as the initial step of this multiple C-N forming sequence. Therefore, corresponding amino and azido substituted derivatives **4** and **5** were synthesized and tested (Scheme 4). Both **4** and **5** could react with **2a** in the absence of $TMSN_3$ to give the desired product **3a** in 95% and 16% yield, respectively. However, the amino intermediate was not detected even in the absence of aldehyde, probably due to its instability under the reaction conditions. We proposed that amination of the C(sp^3)-H bond in **1a** rather than azidation was likely the first step triggering the following processes.



Scheme 4. Reactions of possible intermediates.



Scheme 5. Proposed mechanism.

Although the exact mechanism of this reaction is not completely clear at this stage, a plausible mechanism was proposed (Scheme 5).[10a, 12b] Initially, coordination of Cu(II) with the pyridinyl nitrogen facilitates the deprotonation by pivaloate anion to give intermediate **A**. Subsequently, the azido anion derived from HOPiv and $TMSN_3$ may replace TFA in **A** to form intermediate **B**. Carbon-copper bond may be formed in intermediate **C** via 1, 3-migration. With the assistance of acid, the first C-N bond was formed with the release of N_2 as a driving force, delivering the aminated intermediate **5** via intermediates **D** and **E**.[19] Then, condensation of **5** with aldehyde followed by cycloaddition generates intermediate **G**. Finally, oxidative aromatization by Cu(II) gives the desired product **3**.[16d]

Conclusions

In conclusion, we have developed an efficient method for the synthesis of fused heterocycles containing imidazole moiety starting from benzyl substituted N-heterocycles and aldehydes using $TMSN_3$ as a nitrogen source. Copper-mediated amination of the sp^3 hybridized C-H bond is the initial step for this multiple C-N bond-forming sequence. This methodology not only provides a useful approach for synthesis of imidazo[1,5-*a*]pyridines and related fused heterocycles, but also offers a new strategy for retro-synthetic analysis of certain *N*-heterocycles, in which multiple C-N bonds could be disconnected around aromatic nitrogen to yield simple and readily available feedstock chemicals as synthetic starting materials.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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