Organic LETTERS

Letter

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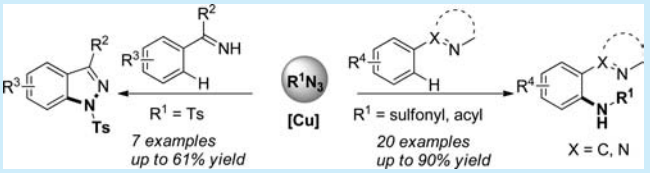
Copper-Catalyzed C(sp^2)−H Amidation with Azides as Amino Sources

Jiangling Peng, Zeqiang Xie, Ming Chen, Jian Wang, and Qiang Zhu*

State Key Laboratory of Respiratory Disease, Guangzhou Institutes of Biomedicine and Health, Chinese Academy of Sciences, 190 Kaiyuan Avenue, Guangzhou 510530, China

Supporting Information

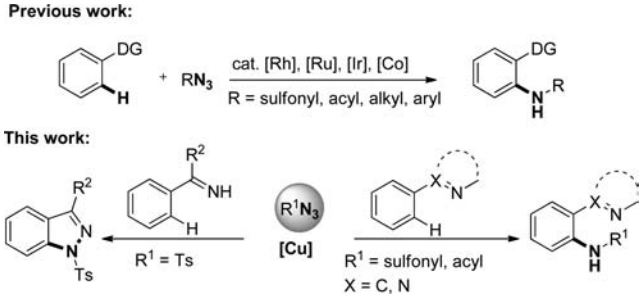
ABSTRACT: A copper-catalyzed C−H amidation process, with azides as amino sources under oxidant-free conditions, has been developed. When *N*-heterocycles were employed as directing groups, sulfonylazide and benzoylazide could be used as amidating reagents to provide corresponding *N*-arylamides. When amidines or imine were used, tandem C−N/N−N bond formation occurred to afford indazole derivatives in one pot.



Aromatic C−N bond formation is one of the most important research topics in organic synthesis due to the ubiquity of aniline derivatives in numerous molecules of biological importance.[1] Buchwald−Hartwig[2] and Ullmann-type[3] aminations are among the most reliable and widely used methods for its formation, which require prefunctionalized reactants. Therefore, extensive efforts have been devoted to transition-metal-catalyzed direct C(sp^2)−H amination/amidation reactions with higher step-efficiency and atom-economy. In general, there are two major strategies for C(sp^2)−H activation/C−N bond formation.[4] One employs neutral amines/amides in the presence of external oxidants,[5] while the other uses preactivated amino sources, such as *N*-chloroamines,[6] *N*-hydroxycarbamates,[7] *O*-acylhydroxylamines,[8] nitrosobenzenes,[9] and NFSI,[10] under oxidant-free conditions. However, in most of these processes, generation of stoichiometric byproducts derived from either oxidants or preactivated amino reagents cannot be avoided.

In recent years, azides have emerged as powerful amino sources in transition-metal-catalyzed direct amination/amidation of aromatic C−H bonds due to the readily availability, structural diversity of azides, and environmental benignity of the reaction byproduct, gaseous N_2.[11] In 2007, Driver reported a seminal rhodium-catalyzed intramolecular C−H amination reaction with vinylazides to construct *N*-heterocycles.[12] Later, the same group applied a similar catalytic system in cycloamination of C−H bonds starting from arylazides for carbozole and indole synthesis.[13] In 2012, a breakthrough in intermolecular C−H amination/amidation with sulfonylazides[14] and arylazides[15] was realized by Chang and co-workers using cationic Cp*Rh as a catalyst assisted by a directing group. Shortly after, they extended the reaction to benzyl- and alkylazides[16] as coupling partners. Very recently, the work by Chang demonstrated the power of azides as amino sources in amination of sp^2 as well as sp^3 hybridized C−H bonds in the presence of Cp*Ir under mild conditions.[17] Many other groups including Ackermann, Sahoo, and Jiao reported their contributions in C−H amination/amidation with azides using Ru-based catalytic systems.[18] A recent work by Kanai showed that Cp*Co was also capable of catalyzing sulfonylamidation of indoles with corresponding sulfonylazides (Scheme 1).[19]

Scheme 1. C(sp^2)−H Amination/Amidation with Azides



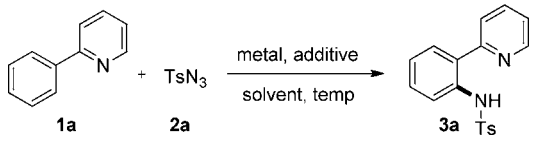
Copper catalysts have been widely employed in selective C−H functionalization.[20] Given cost and sustainability concerns, the development of related processes employing less toxic and inexpensive copper catalysts as surrogates of other transition-metal catalysts, such as Pd, Rh, and Ir, is still attractive. As a result, copper mediated/catalyzed dehydrogenative cross-coupling of amines/amides with aromatic C−H bonds has emerged as a straightforward strategy for the synthesis of aniline derivatives.[21] For example, Shen and co-workers recently reported a copper catalyzed C−H amidation with phthalimide as an amino source.[22] Herein, we would like to report the capability of inexpensive copper salt in catalyzing C(sp^2)−H amidation with azides as amino sources.[23] *N*-Arylamides are accessible by using *N*-heterocycles as directing groups, while indazole derivatives are obtained by applying acyclic N−H-containing amidines or imine as directing groups via tandem C−N/N−N bond formation (Scheme 1). In this process, a Cu(III) rather than a copper-nitrenoid[24] intermediate is proposed. Acid played an important role in this catalytic transformation.

Received: July 9, 2014
Published: September 5, 2014

dx.doi.org/10.1021/ol502010g | *Org. Lett.* 2014, 16, 4702−4705

We initiated the study by reacting 2-phenylpyridine **1a** with TsN_3 **2a** in the presence of various copper salts (entries 1–4, Table 1). To our delight, the desired amidated product **3a** was

Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3a

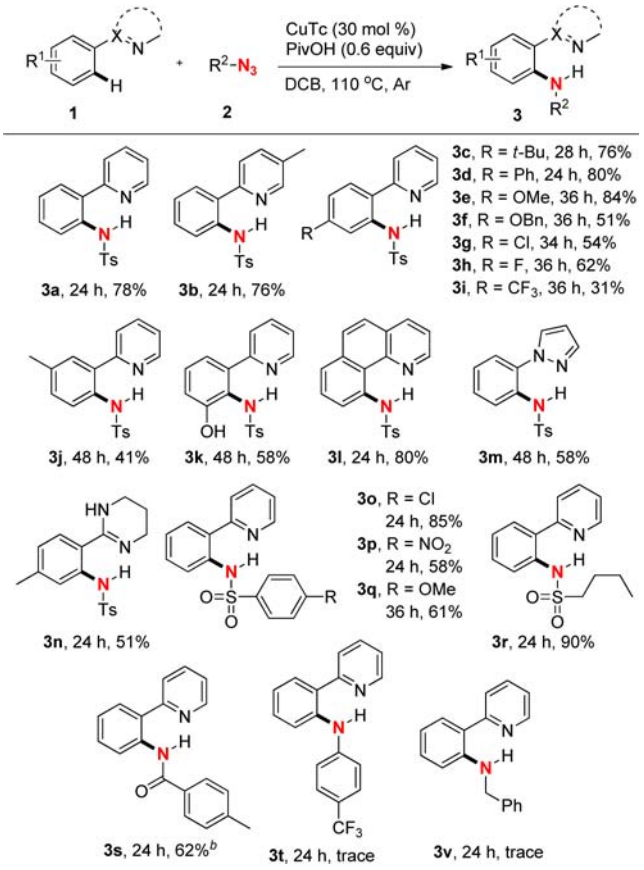
entry	catalyst (equiv)	additive (equiv)	solvent	time (h)	yield (%)[b]
1	$Cu(TFA)_2$ (0.2)		DCB	30	36%
2	$Cu(OAc)_2$ (0.2)		DCB	30	nr
3	CuTc (0.2)		DCB	30	27
4	$CuCl_2$ (0.2)		DCB	30	nr
5	$Cu(TFA)_2$ (0.2)	PivOH (0.4)	DCB	30	42
6	$CuCl_2$ (0.5)	PivOH (0.4)	DCB	30	38
7	CuCl (0.5)	PivOH (0.4)	DCB	30	52
8	CuTc (0.2)	PivOH (0.4)	DCB	48	69
9	CuTc (0.2)	PivOH (0.4)	DCE	48	54
10	CuTc (0.2)	PivOH (0.4)	DMSO	48	nr
11	CuTc (0.3)	PivOH (0.4)	DCB	28	76
12	**CuTc (0.3)**	**PivOH (0.6)**	**DCB**	**24**	**78**

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.4 mmol), copper salt, additive, solvent (1 mL), Ar, sealed tube, 110 °C. [b]Yield of isolated **3a**, DCB = 1,2-dichlorobenzene. DCE = 1,2-dichloroethane. CuTc = copper(I) thiophene-2-carboxylate.

obtained in 36% yield by using $Cu(TFA)_2 \cdot xH_2O$ (20 mol %) as a catalyst in 1,2-dichlorobenzene under Ar atmosphere at 110 °C. The presence of PivOH as an additive can improve the yield slightly to 42% (entry 5). It was further confirmed that PivOH played an essential role in this amidation process in the case of $CuCl_2$ as a catalyst (entries 4 and 6). Screening of various cuprous species in the presence of PivOH revealed that CuTc was superior to other Cu catalysts, delivering **3a** in 69% yield (entries 5–8). Then, a number of solvents, including DCE, 1,4-dioxane, MeOH, DMF, and DMSO, were screened, and no better results were obtained than DCB (entry 9, and the Supporting Information). Increasing the loading of CuTc to 30 mol % and PivOH to 0.6 equiv further improved the yield of **3a** to 78% in a shorter reaction time (24 h, entry 12).

With the optimized reaction conditions in hand, the scope of substituents on both the phenyl and the pyridyl rings of 2-arylpyridines **1** was investigated in reactions with TsN_3 (Scheme 2). A methyl group on the C5 of the pyridyl moiety had little influence on the tosylamidation reaction, providing tosylamide **3b** in 76% yield. Substituents with varied electronic properties located at the para-position of the phenyl ring were studied. In general, electron-donating groups, such as *t*-Bu (**3c**), Ph (**3d**), and MeO (**3e**), were preferable to electron-withdrawing ones including Cl (**3g**), F (**3h**), and CF_3 (**3i**) in terms of isolated yields. When 2-(*m*-tolyl)pyridine was subjected to the reaction, the less sterically hindered C–H bond was amidated selectively to deliver **3j** as the sole regioisomer. On the contrary, the reacting site was switched to the more steric hindered C–H bond exclusively in the case of 3-(pyridin-2-yl)phenol as a substrate, giving **3k** in 58% yield. The regioselectivity was probably due to the coordination of the phenolic OH with the copper catalyst.[25] Benzo[*h*]quinoline reacted smoothly with TsN_3 to give the corresponding product **3l** in good yield. Other heterocycles

Scheme 2. Scope of C–H Amidation with Azides[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.3 mmol), CuTc (30 mol %), PivOH (0.6 equiv), DCB (1.0 mL), Ar, sealed tube, 110 °C, yield of isolated **3**. [b]One equiv of $Cu(TFA)_2$ was used.

including pyrazole and cyclic amidine could also act as directing groups in this Cu-catalyzed C–H amidation reaction, furnishing **3m** and **3n** in 58% and 51% yields, respectively. The scope of arylsulfonylazide was then briefly tested. Similar yields were obtained for NO_2 (**3p**) and OMe (**3q**) substituted arylsulfonylazides, suggesting that a broad range of arylsulfonylazides could be used as amino sources in the current tosylamidation reaction. It was notable that alkylsulfonylazide was an excellent class of sulfonylamidating reagent, as exemplified by the high-yielding formation of **3r**. Other organic azides were also tested. Optimized yield (62%) of 4-methyl-*N*-(2-(pyridin-2-yl)phenyl)-benzamide **3s** was obtained by reacting 4-methylbenzoyl azide with **1a** under modified conditions. However, phenylazide and benylazide failed to deliver the corresponding amination products (**3t** and **3v**).

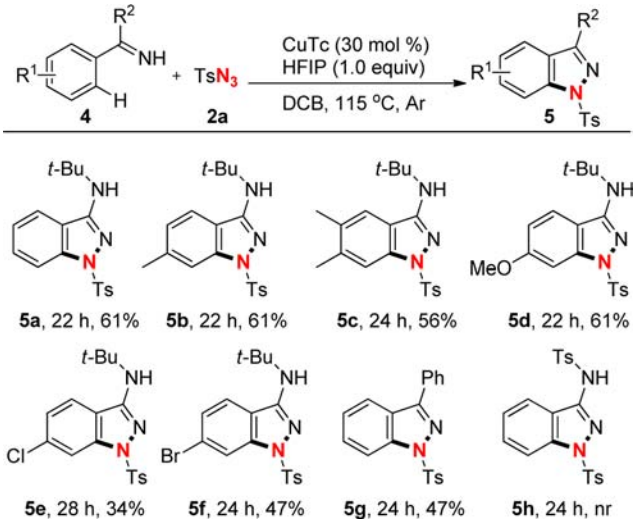
Cu-catalyzed oxidative coupling of two NH groups to form a new N–N bond, either intermolecularly or intramolecularly, has been well documented.[26] It is hypothesized that when N–H-containing moieties replace *N*-heterocycles as directing groups in the aforementioned C–H amidation reactions with azides, the preexisted NH will couple with the introduced NH intramolecularly in the presence of copper catalyst. During this process, new C–N and N–N bonds will be formed sequentially in one pot starting from simple substrates, providing an efficient approach to *N*-heterocycles. To test the hypothesis, a one-pot reaction between *N*-(*tert*-butyl)benzimidamide **4a** and tosylazide **2a** was studied. Satisfyingly, the desired heterocyclic product, *N*-

dx.doi.org/10.1021/ol502010g | Org. Lett. 2014, 16, 4702–4705

(*tert*-butyl)-1-tosyl-1*H*-indazol-3-amine **5a**, was generated in 61% yield under slightly modified conditions (CuTc (30 mol %), HFIP (1.0 equiv) in DCB at 115 °C under argon) (for details, see the Supporting Information). In this case, HFIP acted as a superior acidic additive to PivOH. Recently, Glorius and Jiao reported one-pot tandem C−N/N−N bond-forming reactions for the synthesis of 1*H*-indazoles and pyrido[1,2-*b*]indazoles, respectively.[27]

Next, the generality of this Cu-catalyzed tandem C−N/N−N bond-forming method was tested (Scheme 3). *N*-*tert*-Butylarylamidine substrates **4** bearing Me, MeO, Cl, or Br reacted well with TsN_3 to provide corresponding *N*-*tert*-butyl-3-aminoindazoles **5b**−**5f** in 34−61% yields. Unfortunately, both tosyl-protected and free benzimidamide did not produce the desired product under the current conditions. 3-Phenylated 1*H*-indazole **5g** was obtained in a synthetically useful yield with diphenylmethanimine as the substrate. It was notable that increasing the amount of TsN_3 to 2.0 equiv deteriorated the yield of **5**, probably due to decomposition of the amidine substrates by the reaction byproduct, $TsNH_2$.

Scheme 3. Cu-Catalyzed Synthesis of 1*H*-Indazoles with TsN_3[a]

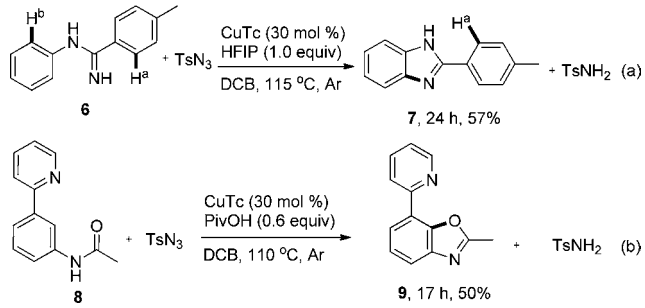


[a]Reaction conditions: **4** (0.2 mmol), TsN_3 (0.3 mmol), CuTc (30 mol %), HFIP (1.0 equiv), DCB (1.5 mL), Ar, sealed tube, 115 °C, yield of isolated **5**. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol. nr = no reaction.

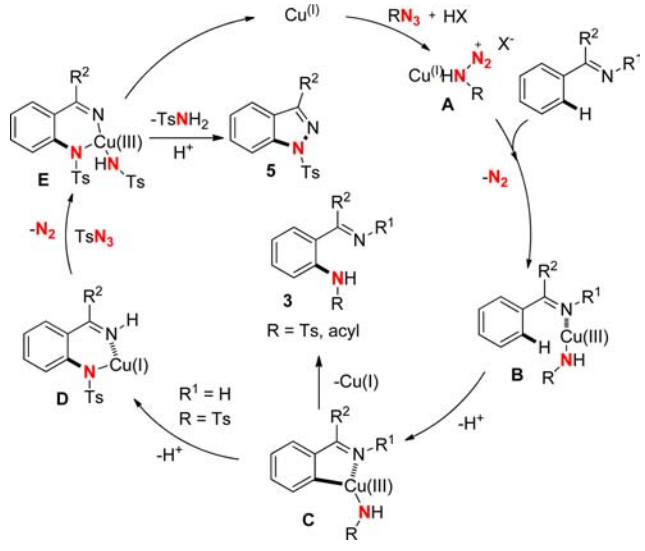
In the process of exploring the scope for the synthesis of 1*H*-indazoles, an unexpected formation of 2-(*p*-tolyl)-1*H*-benzo[*d*]-imidazole **7** was observed by employing 4-methyl-*N*-phenylbenzimidamide **6** as a substrate in inert atmosphere (a, Scheme 4). Furthermore, when *N*-(3-(pyridin-2-yl)phenyl)acetamide **8** was subjected to the standard reaction conditions, 2-methyl-7-(pyridin-2-yl)benzo[*d*]oxazole **9** was formed without any formation of the desired tosylamidated product. The preferred intramolecular C−N or C−O bond formation suggested that a $Cu^{(III)}$ species rather than a reactive copper-nitrenoid intermediate might be involved in these processes.[28] TsN_3 probably acted as an oxidant of $Cu^{(I)}$ in the presence of acid, and $TsNH_2$ was isolated as a byproduct in both cases.

On the basis of mechanistic studies and literature reports,[29] a possible reaction mechanism was proposed in Scheme 5. First, in the presence of acid, a higher valent $Cu^{(III)}$ intermediate **B** is generated through two electrons transfering from $Cu^{(I)}$ to

Scheme 4. Mechanistic Studies



Scheme 5. Plausible Mechanism



protonated azide with concurrent releasing of N_2. The following C−H bond activation and C−Cu bond formation yields a $Cu^{(III)}$ intermediate **C**. When *N*-heterocycles are used as directing groups, the corresponding amidated products **3** and $Cu^{(I)}$ are generated upon reductive elimination. In the case of R^1 = H, intermediate **D** chelated with $Cu^{(I)}$ can be oxidized again by another molecule of TsN_3 in the presence of acid. Reductive elimination of the $Cu^{(III)}$ intermediate **E** delivers 1*H*-indazole **5** and $Cu^{(I)}$ as a result of intramolecular NH/NH oxidative coupling.

In summary, we have developed a Cu-based reaction system for the conversion of aromatic C−H to C−N bonds with azides as amino sources in the presence of acid. Several *N*-heterocycles can act as chelation groups to assist the key C−H activation step with sulfonylazides or acylazide, forming secondary anilides containing an *ortho*-*N*-heterocycle under oxidant-free conditions. The synthesis of substituted 1*H*-indazoles from easily available arylimidines/imines with tosylazide via Cu-catalyzed tandem C−N and N−N bond formation is also developed. A plausible reaction mechanism involving oxidation of $Cu^{(I)}$ to $Cu^{(III)}$ by azide in the presence of acid is also proposed. The exploration of related transformations and detailed mechanistic studies are currently underway in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and full analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/ol502010g | *Org. Lett.* 2014, 16, 4702−4705

AUTHOR INFORMATION

Corresponding Author

*(Q.Z.) E-mail: zhu_qiang@gibh.ac.cn

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the National Science Foundation of China (21202167) for financial support of this work.

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