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Cu-Catalyzed Directed C7–H Imidation of Indolines via Cross-Dehydrogenative Coupling

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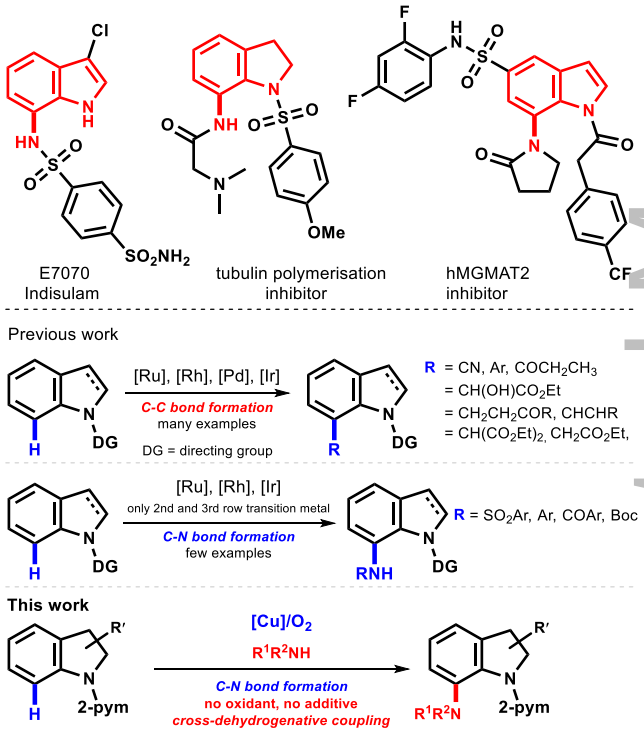
Abstract: Cu(I)-catalyzed C7–H imidation of indolines via cross-dehydrogenative coupling is developed. The reaction involves C–H activation of indolines via six-membered metallacycle and various imides were coupled with indolines, with a broad substrate scope, and functional groups tolerance. Only oxygen is required for the catalytic process. A reversible C–H bond metalation process has been observed in the preliminary mechanistic interrogation.
Keywords: indole, C–H functionalization, copper-catalysis, imidation, cross-dehydrogenative coupling

Amine is undoubtedly the most versatile group that plays diverse functional roles when present in active pharmaceutical ingredients (API) and drug molecules.[1] In addition, the prevalence of amines in materials, catalysts and agrochemicals makes them valuable synthetic target. Over the years, numerous protocols have been developed for the synthesis of aromatic amines that include reduction of nitro aromatics, nucleophilic amination, electrophilic amination, etc.[2] Perhaps, the most noteworthy development in the history of amination has been the transition metal-catalyzed cross-coupling reaction of amines with aryl- or alkenyl halides, especially, the palladium catalyzed Buchwald-Hartwig amination that is widely used for the academic and industrial synthesis of many aminated substrates.[3] Yet, despite these notable advancements, the requirement of pre-functionalized expensive halide (or pseudohalide) precursors and formation of stoichiometric amounts of halide salts as by-products serve as the major restraints for the economic and environmentally benign synthesis of amines.[3i-k] Therefore, although extremely challenging, thermodynamically and kinetically disfavoured direct C–H amination of hydrocarbons using transition-metal catalysts has been the latest effort to obviate these stark impediments, offering straightforward synthesis of amines with high atom economy. In this endeavor, not only various transition metal-catalyzed[4] and metal-free[5] conditions have been established, but also a number of nonprefunctionalized and prefunctionalized aminating reagents were developed to overcome the high activation energy barrier.



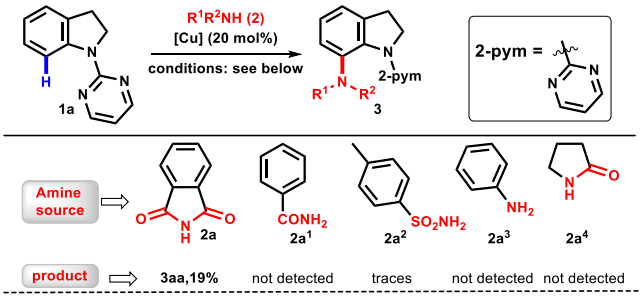
Scheme 1. C7 functionalized bioactive indole derivatives.

Indole and indoline scaffolds have been of great importance in recent years because of their frequent appearances in bioactive compounds.[6] In particular, the C7-substituted amino variants exhibiting diverse bioactivity profiles have received much attention (Figure 1A). While a number of reports have demonstrated direct C7 functionalization of indolines largely for the construction of C–C bond via transition metal catalyzed chelation-assisted C–H activation,[7] only a handful number of reports on C–

O[8]/S[9]/Se[9] and C–N[10] bond formation are known (Figure 1B). Zhu et al for the first time disclosed a ruthenium-catalyzed method for the formation of C–N bond at the C7 of indolines using organic sulfonyl azides that have previously been used by Chang and other groups as C–H amidating reagent to various other scaffolds.[10a] Subsequently, Chang et al disclosed a better variant of this protocol using not only with the sulfonyl azides, but also with aryl, and alkyl azides, albeit using Ir-catalyst.[10b,c] Importantly, the reaction occurred at room temperature, delivering products with excellent yields even with the substrates that contain readily removable *N*-protecting groups. Zhou and Li et al documented almost simultaneously a very closely related work to Chang's report using same metal catalyst.[10d] In the quest of developing novel aminating sources, the Chang group further disclosed a protocol for the indoline C7 amidation using phosphoryl azides and azidocarbamates, albeit again via iridium catalysis.[10e.f] Dioxazolones[10g,j,m] and anthranils[10i,k,l] have also been explored as alternative aminating reagents for the indoline amidation. However, these protocols essentially require expensive and environmentally toxic second- and third-row transition metal catalysts. In addition, despite the importance of imide as final product or common synthetic intermediate that can easily be exploited for a variety of functional group transformation chemistry, none of these methods demonstrate indoline C7–H imidation protocol. Herein, we report copper catalyzed C7–H imidation of indolines via cross-dehydrogenative coupling (CDC).

We have recently demonstrated that C7-H of indoline could be acyloxylated by carboxylic acid derivatives using first-row transition metal-catalyst (copper).[11] This finding encouraged us to investigate the possibility of developing a copper-catalyzed protocol for the C−H amination at the C7 position of indolines. Our experiment began with indoline **1a** as the model substrate having 2-pyrimidine as the directing group. A quick survey of various amine sources like phthalimide (**2a**), benzamide (**2a^1**), sulfonamide (**2a^2**), aniline (**2a^3**), and pyrrolidin-2-one (**2a^4**) revealed that phthalimide could be a potential amine source for the envisioned C–H amination. Interestingly, in 2014, Shen et al. also reported a method for the C–H imidation of indoles directed by 2-pyrimidine auxiliary.[12] In this case, imidation occurred exclusively at the C2 position because of the preferred five-membered cyclometallation and innate reactivity of the C(2)=N bond. However, imidation at the C7 position involving 6-membered metallacycle was not reported. Therefore, we turned our attention for optimizing the direct C–H imidation of indolines via cross-dehydrogenative coupling. After a brief survey of various copper catalysts (entries 1–10), it turned out that Cu(I)OAc was the best and the product **3aa** was isolated in 81% yield. Screening of solvents showed that 1,2-dichlorobenzene (DCB) was the most effective solvent (entries 12–17). The reaction was completely shut down in the presence of basic additives, as observed previously by us[11] (entries 19–20). Neither acids (pivalic acid, TFA) nor additional oxidant (Ag_2O) improved the efficacy of the transformation (entries 18, 21). Use of oxygen was inevitable as the yields were reduced when the reactions were carried out either using air or nitrogen atmosphere (entries 22–23) under otherwise standard conditions. Changing the directing group from 2-pyrimidine to 2-pyridine did not favour to increase the yield (entry 24).

Table 1. Screening of imidation conditions[a]



entry	catalyst	solvent	Additives (equiv)	**2a** (equiv)	Yield[b] **3aa**(%)
1	Cu_2O	DCB	---	1.0	19
2	$Cu(OAc)_2$	DCB	---	1.0	64
3	$Cu(OBz)_2$	DCB	---	1.0	50
4	$Cu(TFA)_2$	DCB	---	1.0	35
5	CuOAc	DCB	---	1.0	70
6	Cu(I)Tc	DCB	---	1.0	65
7	CuCl	DCB	---	1.0	11
8	CuBr	DCB	---	1.0	24
9	CuI	DCB	---	1.0	12
10	**CuOAc**	**DCB**	**---**	**1.3**	**81**
11	CuOAc	DCB	---	2.0	57
12	CuOAc	DCE	---	1.3	63
13	CuOAc	toluene	---	1.3	53
14	CuOAc	acetonitrile	---	1.3	12
15	CuOAc	DMSO	---	1.3	trace
16	CuOAc	DMF	---	1.3	trace
17	CuOAc	dioxane	---	1.3	13
18	CuOAc	DCB	PivOH (0.2)	1.3	42
19	CuOAc	DCB	K_2CO_3	1.3	trace
20	CuOAc	DCB	Na_2CO_3	1.3	trace
21	CuOAc	DCB	Ag_2O	1.3	14
22[c]	CuOAc	DCB	---	1.3	61
23[d]	CuOAc	DCB	---	1.3	19
24[e]	CuOAc	DCB	---	1.3	47

[a]Reactions conditions: 0.25 mmol of **1a**, 2 mL of solvent, O_2, 130 °C, time 30 h. [b]Isolated yield. [c]in the presence of air. [d]in the presence of nitrogen. [e]using 2-pyridine as directing group. Tc= Thiophene 2-carboxylate. DCB = 1,2 dichlorobenzene.

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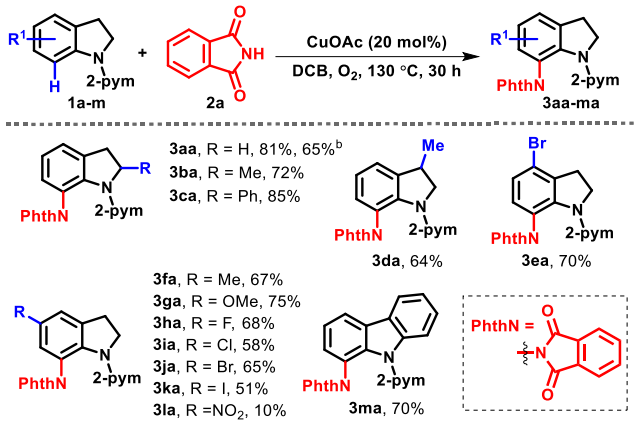
Scheme 2. Scope of indolines[a]

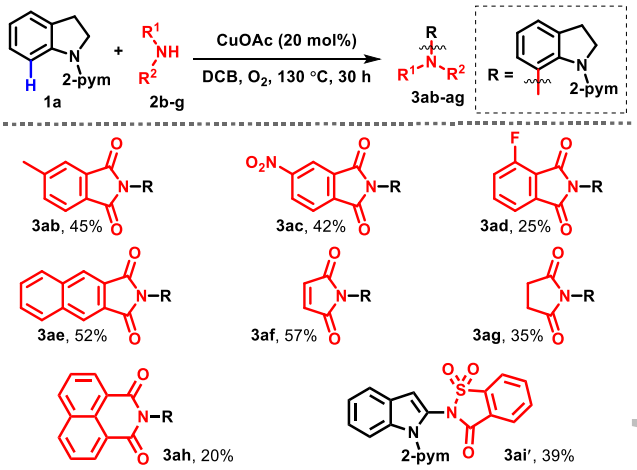


[a]Reactions conditions: 0.25 mmol of **1a–1m**, 1.3 equiv. of **2a**, 2 mL of solvent, O_2, 130 °C, isolated yields. [b] yield corresponds to scale up reaction.

With an optimized protocol in hand, the scope and limitation of the title reaction was explored (Scheme 2). With respect to the various indoline derivatives, the reaction was found quite general and tolerated by various functional groups. For instance, alkyl and aryl substituted indolines were coupled with phthalimde to furnish the imidated products (**3ba**, **3ca**, **3da**, **3fa**) in good to very good yields (64–85%). Under the optimized conditions, halogenated indolines were also imidated uneventfully and the fluoro (**3ha**), chloro (**3ia**), bromo (**3ea, 3ja**) and iodo (**3ka**) derivatives were obtained in good yields (51–70%). Electronically rich indoline furnished better yield (**3ga**, 75%) than their electronically deficient counterpart (**3la**, 10%). Carbazole derivative also furnished the desired product (**3ma**) in 70% yield. On a preparative scale reaction set up, **1a** (1.0 gm) furnished **3aa** in 65% yield.

Next various imides were tested (Scheme 3). To our delight imides bearing alkyl, electron withdrawing, and halogen substituents were coupled with **3a** to furnish the corresponding C7 substituted products (**3ab, 3ac**, **3ad**) in moderate yields (25–45%). Naphthalimide coupled product (**3ae**) was also obtained in 52% yield. Succinimide and maleimide were also successfully coupled in moderate yields (**3af**–**3ag,** 35–57%). 1H-benzo[de]isoquinoline-1,3(2H)-dione was also coupled with **1a** to furnish **3ah**, albeit in low yield. Unfortunately, saccharine as aminitaing source furnished only C2 functionalized indole **3ai** in 39% yield.

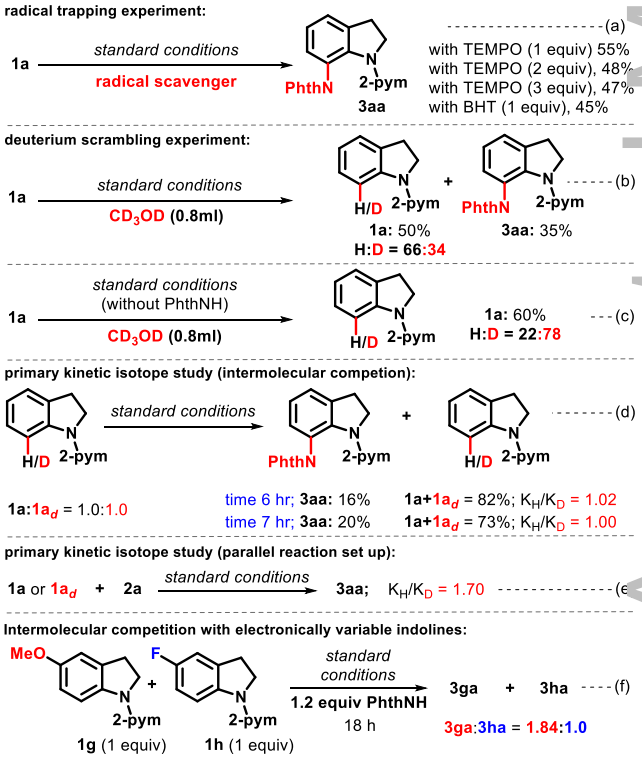
Scheme 3. Scope of imides[a]



[a]Reactions conditions: 0.25 mmol of **1a**, 1.3 equiv. of **2b–g**, 2 mL of solvent, O_2, 130 °C, isolated yields.

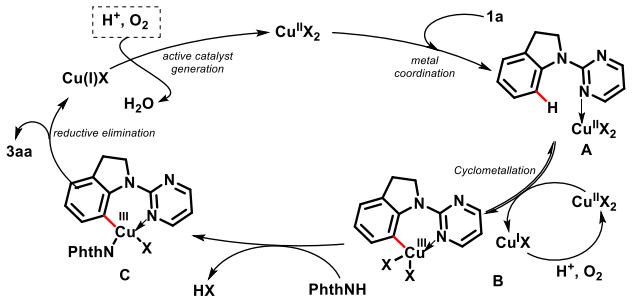
We performed various control experiments to elucidate the mechanistic pathway (Scheme 4). Under the radical trapping experiment with 1, 2 and 3 equiv of TEMPO (Scheme 4a), **3aa** was isolated in 55%, 48% and 47% respectively. With 1 equiv of BHT, 45% of **3aa** was obtained. These results suggest that the reaction does not operate under radical mediated pathway.

Scheme 4. Control experiments for mechanistic aspect



Formation of deuterium incorporated starting material (Scheme 4b, 4c) under deuterium scrambling experiment with CD_3OD implies that there might be the involvement of a reversible C–H bond cleavage.[9]

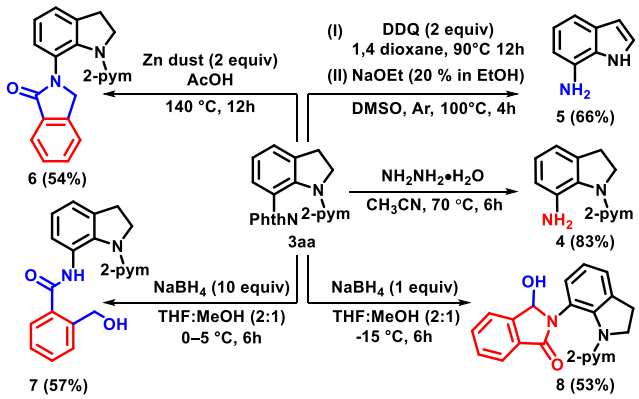
The result of the primary kinetic isotope effect studies (intermolecular and parallel, Scheme 4d, 4e) indicated that the C–H bond cleavage step was not the rate determining. We also found (Scheme 4f) that the electronically rich indolines are more reactive than the electronically poor substrates.



Scheme 5. Proposed reaction pathway

Based on the literature[9b,11,12,13] and our experimental data, a plausible reaction pathway is outlined in Scheme 5. The first step is likely the oxygen mediated oxidation of Cu(I) catalyst, generating the active Cu(II) species. Next, the pyrimidyl group of **1a** coordinates with copper to form species **A**. Subsequently, **A** takes part in disproportionative C–H functionalization reaction and generates cyclometalated aryl-Cu(III)[14] intermediate **B**. Next, ligand exchange of **B** with phthalimide generates species **C** which undergoes reductive elimination to furnish **3aa** and Cu(I) salt, which is again oxidized by oxygen to regenerate the active catalyst. Similar disproportionative reaction generating aryl-Cu(III) intermediate has been described in the literature as an alternative of single electron transfer (SET) pathway.[14] However, the possibility of a SET pathway cannot be completely ignored.[15]

Scheme 6. Synthetic application



To investigate the synthetic utility of the imidated products, several transformations were carried out (Scheme 6). First, 7-amino indoline derivative **4** was obtained in excellent yield. Further, oxidation followed by global deprotection of **3aa** furnished the 7-aminoindole **5** in 66% overall yields. Imide **3aa** was also reduced to amide **6** in 54% yields. Ring opening via reduction of **3aa** provided hydroxymethyl functionalized amide derivative **7**. A selective reduction of imide of **3aa** yielded highly reactive hydroxylactam derivative **8,** thereby expanding the possibilities of further functionalization.

In conclusion, we have developed a copper catalyzed regioselective cross-dehydrogenative coupling of indoline with phthalimide for the indoline C7 amination. The developed amination was successfully applied to a broad range of indoline as well as imide derivatives. Notably, the protocol is environmentally benign as only molecular oxygen is used for catalyst regeneration.

Experimental Section

To a solution of indoline pyrimidine **1a** (0.25 mmol) in *o*-dichlorobenzene (2 mL), CuOAc (6.17 mg, 20 mol%) and Phthalimide (0.32 mmol, 1.3 equiv.) were added in sealed tube vial and O_2 was purged in the solution for 30 min and the reaction mixture was kept at 130 ˚C for 30 hours. After completion of the reaction, the reaction mixture was quenched with 10% aqueous solution of sodium hydroxide. The reaction mixture was extracted with ethyl acetate (2 x 15 mL) and the organic layer was washed with brine solution followed by drying over Na_2SO_4. The organic layer was evaporated via rotavapor and crude mixture was purified by silica gel column chromatography to yield the corresponding imidated product **3aa** (81%). The structure of **3aa** (CCDC 1854894)[16] was unambiguously confirmed by X-ray analysis.

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