Advanced Synthesis & Catalysis

Accepted Article

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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201800040

Link to VoR: http://dx.doi.org/10.1002/adsc.201800040

10.1002/adsc.201800040

COMMUNICATION

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Cu(I)-Catalyzed Site Selective Acyloxylation of Indoline Using O_2 as the Sole Oxidant

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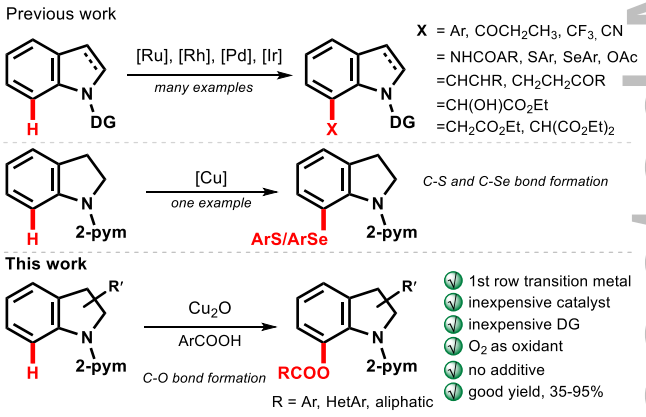
Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201

Abstract. A Cu(I)-catalyzed regioselective cross-dehydrogenative coupling of indoline with a variety aryl and alkyl carboxylic acids is described. The divergent process for the oxygenation was achieved in satisfactory yields under additive free conditions, which provides an efficient strategy for the regioselective C7 functionalization of indolines using inexpensive copper catalyst. Oxygen as the sole oxidant is required in this protocol. The method is tolerated by a wide range of functional groups. Preliminary mechanistic study provided support for a reversible C–H bond metallation step.

Keywords: indole, C–H functionalization, copper catalysis, acyloxylation, cross-dehydrogenative coupling

Indole and indoline motifs are considered as privileged scaffolds by reason of their omnipresence in numerous biologically active natural products and pharmaceuticals.[1] Thus, functionalization of indole and indoline derivatives is in great demand. Numerous methods for the C–H functionalization of indole have been reported largely at the C2 and C3 positions because of the inherent reactivity of the pyrrole ring.[2] However, regioselective C–H functionalization on the benzenoid ring is relatively less explored.[3] In particular, despite the pharmacological significance of C7 functionalized indoline derivatives,[4] only few protocols for the regioselective C7 functionalization of indoline have been reported.[5-9] For examples, second (Ru,[5] Rh,[6] and Pd[7]) and third row transition (Ir[8]) metal-catalyzed reactions were reported for arylation,[7b,g,h,l-n] acylation,[5a,d,7a,d,f] alkylation,[5c,6e,k,p,7c,k,8d-e] allylation,[6r-s] alkenylation,[6a,h,i,m-o,t,u,7e,i,j,8b,c] amination,[5b,f,g,6d,f,g,j,8a,f] thioarylation,[6l] selenoarylation,[6l] cyanation,[6q] trifluoromethylation[6c], and acetoxylation[5e,6b] at the C7 position of indolines (Scheme 1). However, these methods mostly deal with the formation of C–C and C–N bonds besides the use of expensive and environmentally toxic metal complexes. On the contrary, methods for the corresponding C–O bond formation is less reported.[6b] During the ongoing process of our protocol, a rhodium catalyzed method for C7 acetoxylation of few indoline derivatives was reported by Deb et al.[6b] However, no other coupling partner was used except acetic anhydride. Satoh and Miura also reported a rhodium-catalyzed protocol for the acetoxylation on the benzenoid moiety of carbazole and 2-substituted indole derivatives.[5e] The first use of copper catalyst for the C7 functionalization of indoline has been reported very recently by Ackermann et al.[9]



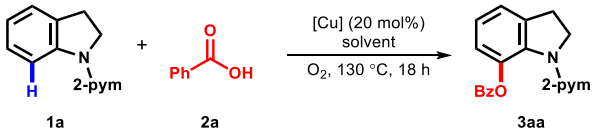
Scheme 1. C7 functionalization of indoline/indole.

As a part of our research interest,[10] we argued, chelation-assisted direct acyloxylation[11] of indoline with various carboxylic acids would offer two fold benefits. Firstly, it would illustrate a method for the direct acyloxylation at the C7 position. Secondly, an indirect method for the synthesis of C7–OH would be established. In addition, if the cross-dehydrogenative coupling could be executed through copper catalysis,[12] a practical and environmentally benign method for C7 functionalization would be obtained. To the best of our knowledge, no copper-catalyzed

10.1002/adsc.201800040

hydroxylation/acyloxylation method for the C7 functionalization of indoline has been reported. Herein, we describe a first ever method for the C7 acyloxylation to indoline via copper catalysis.

Table 1. Screening of acyloxylation conditions[a].



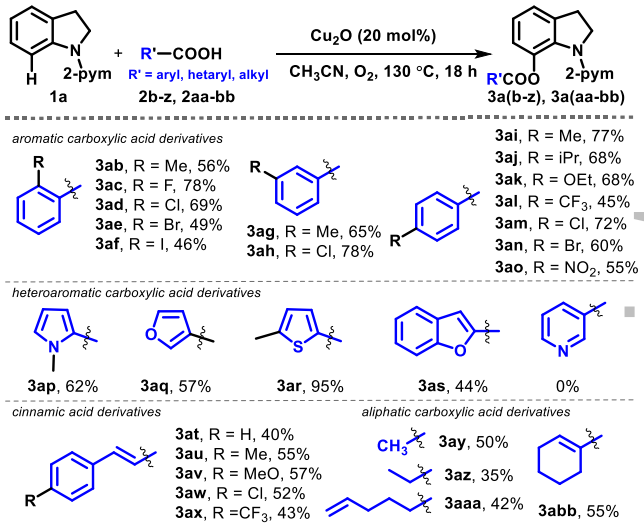
1a 2a 3aa

entry	catalyst	solvent	Additives (equiv)	2a (equiv)	Yield[b] (%)
1[c]	$Cu(OAc)_2$	CH_3CN	---	2.0	traces
2	$Cu(OAc)_2$	CH_3CN	---	2.0	58
3	$Cu(OAc)_2$	CH_3CN	---	---	12[d]
4	$CuCl_2$	CH_3CN	---	2.0	---
5	$CuBr_2$	CH_3CN	---	2.0	---
6	$Cu(acac)_2$	CH_3CN	---	2.0	39
7	CuO	CH_3CN	---	2.0	trace
8	Cu_2O	CH_3CN	---	2.0	84
9	CuCl	CH_3CN	---	2.0	51
10	CuBr	CH_3CN	---	2.0	---
11	CuOAc	CH_3CN	---	2.0	trace
12	Cu_2O	PhCN	---	2.0	16
13	Cu_2O	DMF	---	2.0	25
14	Cu_2O	DCE	---	2.0	65
15	Cu_2O	CH_3CN	Na_2CO_3 (2.0)	2.0	---
16	Cu_2O	CH_3CN	PivOH (0.2)	2.0	72
17	Cu_2O	CH_3CN	Ag_2O (2.0)	2.0	26
18	Cu_2O	CH_3CN	NaOBz (2.0)	---	---
19	Cu_2O	CH_3CN	---	3.0	62
20	Cu_2O	CH_3CN	---	2.5	70
21	Cu_2O	CH_3CN	---	1.7	71

[a]Reactions conditions: 0.25 mmol of **1a**, 2.0 equiv. of **2a**, 2 mL of solvent, O_2, 130 ºC. [b]Isolated yield. [c]in the presence of air. [d]acetoxylated product.

In the model reaction, a mixture of indoline pyrimidine (**1a**), benzoic acid (**2a**) and $Cu(OAc)_2$ in CH_3CN was heated at 130 °C (Table 1). Only traces amount of product was detected in the presence of air (entry 1), while in the presence of oxygen the desired product **3aa** was isolated in 58% yield (entry 2). Notably, no acetoxylated product was observed. However, 12% of acetoxylated product was isolated in the absence of benzoic acid (entry 3). We then screened various Cu(II) catalysts. However, none of the catalysts provided better yield. (entries 4–7). Therefore, various Cu(I) catalysts were screened (entries 8–11). Cu_2O was found to be the best and yielded **3aa** in 84% yield (entry 8). Other solvents like benzonitrile (entry 12), DMF (entry 13), 1,2-dichloroethane (entry 14) were less productive. Addition of Na_2CO_3 as basic additive completely stopped the reaction (entry 15). Although acidic additive (pivalic acid, 20 mol%) yielded **3aa**, a detrimental effect on the yield was observed (entry 16). External oxidant also led to lower reaction yield (entry 17). When **2a** was replaced by sodium benzoate, no product was isolated (entry 18). The yield could not be further improved by either increasing or decreasing the amount of benzoic acid (entries 19–21).

Table 2. Scope of the acyloxylation reaction[a]



[a]Reactions conditions: 0.25 mmol of **1a**, 2.0 equiv. of **2b-z, 2aa-bb**, 2 mL of solvent, O_2, 130 ºC, isolated yields.

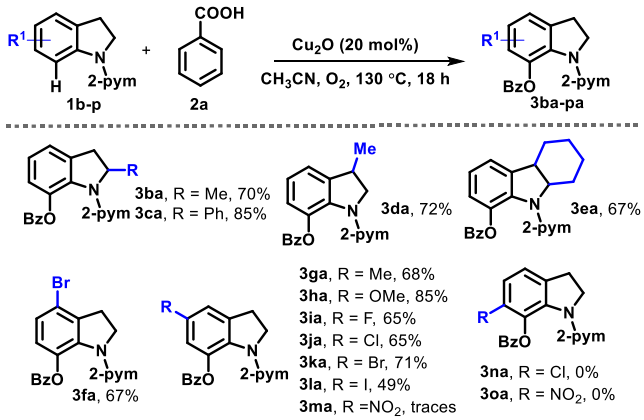
The structure of **3aa** was unambiguously confirmed by X-ray analysis.

Figure 1: ORTEP diagram with 30% ellipsoid probability for non-H atoms of the crystal structure of **3aa**

With the optimized reaction conditions in hand, the scope and limitation of the protocol were tested with respect to benzoic acid derivatives (Scheme 2). To our delight, a wide range of benzoic acids containing different functional groups (alkyl, fluoro, chloro, bromo, iodo, ethoxy, nitro) were well tolerated in this transformastion. Yields of the *para*-substituted derivatives (**3ai**, **3am**, **3an**) were better than the corresponding o*rtho*-substituted derivatives (**3ab**, **3ad**, **3ae**). Benzoic acids bearing electron-donating groups (methyl, isopropyl, ethoxyl) yielded the products in good yields (**3ab**, **3aj**, **3ak**). Good yields were obtained for the benzoic acids (**3ac**–**3af, 3ah, 3al**–**3an**) having halogen substituents (fluoro, chloro, bromo, iodo, trofluoromethyl). However, 4-nitrobenzoic acid furnished the product (**3ao**) in moderate yield. We next examined various heteroaromatic carboxylic acids as coupling partner (Scheme 2). Delightfully, pyrrole- (**3ap**), furan- (**3aq**),

benzofuran- (**3as**) and thiophene- (**3ar**) derived carboxylic acids were very well tolerated. Unfortunately, pyridine derived carboxylic acid derivatives (2-picolinic acid, nicotinic acid and isonicotinic acid) did not furnish any desired product (data not shown). Possibly, due to the preferable coordination of copper with the pyridyl group and formation of a stable copper-pyridine complex does not further allow copper to coordinate with the nitrogen of pyrimidine ring. We also tested various cinnamic acid derivatives (**3at**–**3ax**), which furnished the products with moderate yields. Various aliphatic carboxylic acids also reacted, but the desired products (**3ay**, **3az**, **3aaa**, **3abb**) were obtained in moderate yields (35–55%) in general. Neither prolonged heating, nor the increase in equivalence of carboxylic acid derivatives improved the yields. Most of the cases, the unreacted starting material (**1a**) was recovered.

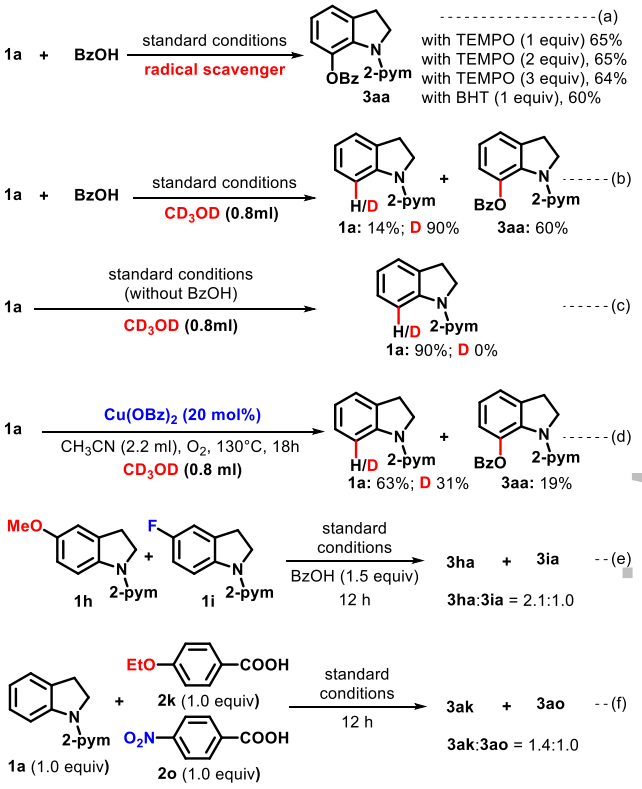
Table 3. Scope of the acyloxylation reaction[a]



[a]Reactions conditions: 0.25 mmol of **1b-p**, 2.0 equiv. of **2a**, 2 mL of solvent, O_2, 130 °C, isolated yields.

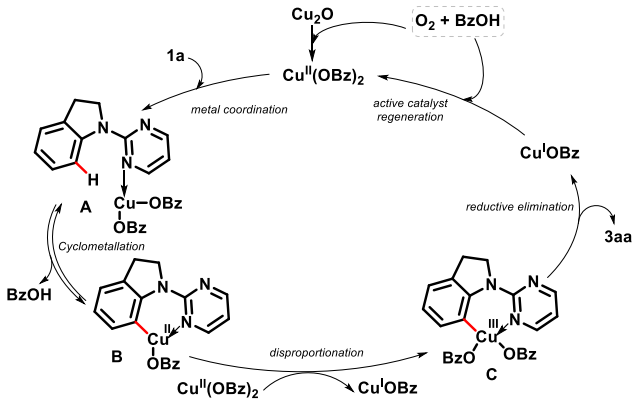
Next various indolines were tested (Scheme 3). While the benzenoid ring bearing electron donating substituents furnished the desired products (**3ga** and **3ha**) in very good yields, no products were obtained in case of strong electron withdrawing substituents (**3ma** and **3oa**). Gratifyingly, alkyl (**3ba**, **3da**, **3ea**) and aryl (**3ca**) substituted indolines afforded the products in very good yields. Fluoro (**3ia**), chloro (**3ja**), bromo (**3fa, 3ka**) and iodo (**3la**) substituted indolines also furnished the desired products in very good yields. This opens for the possibility of further functionalization of the indoline derivatives. Unfortunately, C6 substituted derivatives (**3na**, **3oa**) did not furnish any product.

Table 4. Control experiments for mechanistic aspect



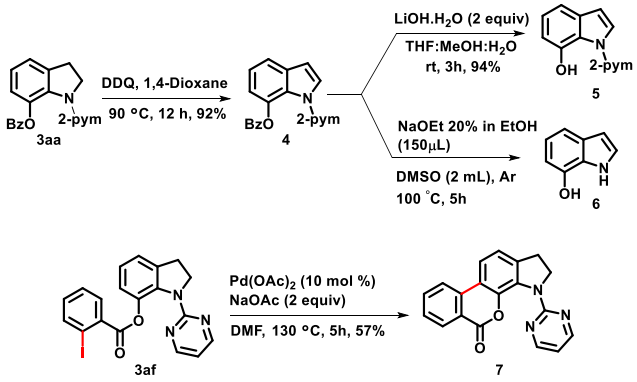
Various control experiments were conducted to understand the mechanistic pathway (Scheme 4). Under the typical radical scavenger experiment (Scheme 4a), **3aa** was isolated in 65% (with 1 equiv of TEMPO), 65% (with 2 equiv of TEMPO), 64% (with 3 equiv of TEMPO), and 60 % (with 1 equiv of BHT) yields, suggesting a non-radical mediated reaction pathway. Significant deuterium incorporation (90%) was observed at the C7 position when CD_3OD was used as a co-solvent (Scheme 4b), indicating an involvement of reversible C–H bond cleavage.[9] In sharp contrast, no deuterium incorporation was observed in the absence of benzoic acid (Scheme 4c), suggesting the requirement of carboxylate as a suitable ligand for the facile C–H activation. Thus, without benzoic acid, 20 mol% of $Cu(OBz)_2$ could catalyze the H-D isotope scrambling process (Scheme 4d). Competitive Control experiments (Scheme 4e and 4f) revealed that formation of the products from electronically rich indolines and benzoic acids are kinetically favoured than the electronically poor substrates.

Based on the preliminary experimental data and literature,[9,11c,12] we propose a plausible reaction pathway for the developed protocol (Scheme 2). First, the active catalyst generated by the oxidation of Cu_2O coordinates with **1a** to form intermediate **A** which subsequently facilitates reversible C–H bond cleavage for the generation of cyclometalated Cu(II) intermediate **B.** A typical disproportionation reaction of Cu(II) ion generates highly active Cu(III) intermediate **C** which follows a reductive elimination process to liberate the product **3aa** and Cu(I)OBz. Subsequently, regeneration of active catalyst occurs via oxidation of Cu(I)OBz by oxygen.



Scheme 2. Proposed reaction pathway

We next demonstrated the usefulness of the developed C–H acyloxylation process (Scheme 3). Indoline **(3aa)** was very easily oxidized to indole in 92% yield. Further, the 7-hydroxy indole (**5** and **6**) was obtained in excellent yield. Finally, an intramolecular Heck reaction[13] was conducted to convert **3af** into indoloisochromenone scaffold.



Scheme 3. Synthetic application

In conclusion, an operationally simple protocol for the C7 acyloxylation of indolines was achieved via cross-dehydrogenative coupling of indoline with carboxylic acid using inexpensive copper catalyst. A wide variety of both indolines and carboxylic acids having diverse functionality were tolerated by the method, indicating the robustness of the protocol. The additive free method required oxygen as the sole oxidant. The method has been applied for the construction of complex polycyclic scaffold.

Experimental Section

To a solution of indoline pyrimidine (0.25 mmol) in acetonitrile (2 mL), Cu_2O (7.25 mg, 20 mol%) and carboxylic acid (0.50 mmol, 2 equiv.) was added in sealed tube vial and O_2 was purged in the solution for 30 min. And the reaction mixture was kept at a pre-heated oil-bath (130 ˚C) for 18 hours. After completion of the reaction, the reaction mixture was quenched with saturated solution of sodium bicarbonate. 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 anhydrous Na_2SO_4. The organic layer was evaporated via rotavapor and crude mixture was purified by silica gel column chromatography to yield the corresponding acyloxylated product.

CCDC-1587464 contains the supplementary crystallographic data for compound **3aa** reported in this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Financial support from DST-SERB (EMR/2016/000613), CSIR-New Delhi (A. A., H. S. D.), and UGC-New Delhi (B. K.) is gratefully acknowledged. We thank Dr. Tejender S. Thakur, MSB division, CSIR-CDRI, for supervising the X-ray data collection and structure determination. We thank the CDRI SAIF division for analytical support. CDRI Communication No. xxxx.

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10.1002/adsc.201800040

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Cu(I)-Catalyzed Site Selective Acyloxylation of Indoline Using O_2 as the Sole Oxidant

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