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Co(II)/Cu(II)-cocatalyzed oxidative C–H/N–H functionalization of benzamides with ketones: a facile route to isoindolin-1-ones

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A cobalt and copper catalyzed reaction protocol has been developed to achieve the oxidative C–H/N–H annulation of benzamides containing 8-aminoquinoline moiety as the directing group with ketones. Structurally diverse isoindolin-1-ones were furnished by the reaction of various substituent benzamides with ketones.

Isoindolin-1-one is an essential heterocyclic structural unit which is widely discovered in various natural and bioactive compounds (Figure 1).1 Therefore, the synthesis of organic compounds containing the structural moiety is to encourage synthetic chemists' efforts. Conventionally, the intramolecular lactamization of ortho-aminomethyl benzoic acids is a wellknown approach.² However, this transformation usually is achieved with prefunctionalized substrates under harsh conditions, and suffers from more waste by-products. In the past decades, transition-metal catalyzed C-H functionalization strategies as the straightforward, atom-economic and powerful synthesis protocol has been proverbially applied to constructing important targets.³ For example, the welldeveloped transition-metal catalyzed C-H carbonylation was applied to the construction of isoindolin-1-ones, whereas this transformation usually requests the participant of the toxic CO gas.⁴ Thus it can be seen that transition-metal catalyzed C-H functionalization was also proved to be powerful tools for the synthesis of isoindolin-1-ones.⁵ Owing to their high catalytic activity and functional group compatibility, Rh(III) complexes were widely utilized to synthesize isoindolin-1-ones by the reaction of benzoic amide derivatives with alkenes.⁶ But rhodium as a precious and rare transition metal is not an ideal catalyst due to the economic considerations. Thus the earthabundant and inexpensive cobalt catalysts attract more

attention by taking advantage of their cheap availability and outstanding catalytic efficiency,⁷ cobalt complexes were also exploited to catalyze the oxidative annulation of electrondeficient olefins with benzamides by Ackermann and Jeganmohan.⁸ But alkenes usually accompany some sidereactions such as self-polymerization and isomerization in reactions. To overcome the limitation, other reagents were explored to applying to the synthesis of different isoindolin-1ones. We noticed that diazo compounds,⁹ and alkynes ¹⁰ could afford the corresponding target products.

On the other hand, the strategy for forming alkenes in situ was adopted to enlarge the application of alkenes. Recently, efforts to achieve transition-metal more catalvzed dehydrogenative desaturation of various compounds generating olefins have been made.¹¹ For example, saturated ketones could be utilized to provide the desired alkenes with the aid of transition-metal catalysts.¹² Su's group contributed more interesting works on transition-metal catalyzing dehydrogenation of saturated ketones and then olefin reaction sequence, including Pd or Rh/Cu catalyzed β-arylation of ketones with benzoic acids or (hetero)arenes as arylating reagents,¹³ and Cu catalyzed β - functionalization of saturated ketones with different nucleophiles.14 As for the facile methods for the construction of β -arylated ketones, Dong and Li have developed the Pd-catalyzed dehydrogenative desaturation of ketones and successive *β*-arylation reaction with various aromatic sources.¹⁵ Recently, Dong has realized the Pd-catalyzed β -alkylation of ketones with simple alkyl bromides.¹⁶ We were encouraged by the versatility of ketones as the efficient precursor of alkene and anticipated to employ ketones to accessing isoindolin-1-one derivatives. Herein, we describe a novel approach to the synthesis of substituted isoindolin-1-ones via manipulating copper-catalyzed dehydrogenation of ketones and cobalt-catalyzed oxidative C-H/N-H annulation of aromatic amides.

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Fig. 1 Two biologically active molecules containing isoindolinone moiety

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Me	Me Ref + Et + Co(OAc) ₂ (15 m0%) (20(OAc) ₂ (5 m0%) PPh ₃ (5 m0%) Me Ag ₂ CO ₃ (2.5 equiv.) TEMPO (1.0 equiv.)	↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓
1a	a 2a DCB, 110 °C, 21 h standard conditions	3a
Entry	Variations of standard conditions	Yield (%) ^b
1	none	76
2	without Co(OAc) ₂	0
3	without Cu(OAc) ₂	36
4	Co(acac) ₂	39
5	Co(OAc) ₂ (10 mol%)	57
6	Co(OAc) ₂ (20 mol%)	70
7	AgOAc (5 equiv.)	30
8	Ag ₂ O (2.5 equiv.)	38
9	Ag_2CO_3 (3.0 equiv.)	75
10	Cu(OAc) ₂ (10 mol%)	46
11	PPh₃ (10 mol%)	42
12	without PPh₃	53
13	PhCl instead of DCB	56
14	DCE instead of DCB	30
15	TFE instead of DCB	0
16	100 °C	52
17	120 °C	57
18	2a (3 equiv.)	63
19	air atmosphere	58

^{*a*}Unless otherwise noted, all the reactions were run with **1a** (0.15 mmol) and **2a** (3.5 equiv.) in DCB (0.75 mL) for 21 h, 110 °C, N₂ atmosphere. TEMPO = 2,2,6,6-Tetramethylpiperidine-1-oxyl, DCB = 1,2-Dichlorobenzene, DCE = 1,2-Dichloroethane, TFE = 2,2,2-Trifluoroethanol. ^{*b*}Isolated yield.

Given the reported copper-catalyzed dehydrogenation of ketones12d, 14 and cobalt catalyzed N, N'-bidentate directing group-assisted C–H bond functionalization reactions,^{7d, 17} we selected the easily available copper and cobalt compounds as co-catalysts and the reaction of amide 1a and ketone 2a as a model reaction to examine the practicability of this method for the synthesis of isoindolin-1-ones. And we noted that 8aminoquinoline as the directing group was chosen to assist C-H activation by Daugulis in 2005.18 The reaction, where $Co(OAc)_2/Cu(OAc)_2$ was employed as catalysts and Ag₂CO₃/TEMPO was utilized as oxidants, gratifyingly, furnished the desired product 3a in 76% yield (Table 1, entry1). Then a series of control experiments was conducted to investigate influence factors of this reaction (Table 1 and SI). At first, there was no desired product detected when cobalt acetate was ignored, indicating that the cobalt salt as a catalyst is vital to accomplish the reaction (entry 2). Then the absence of copper acetate in the reaction resulted in a dramatical decrease in the product yield, suggesting that copper catalyst is also essential to achieve the better conversion (entry 3). There was no improvement in the product yield when different cobalt salts and the diverse amount of cobalt acetate were employed in the reaction (entries 4-6). Silver salts were also evaluated and silver carbonate was demonstrated to furnish the better result (entries 6 and 7). Increasing the dosage of Ag₂CO₃, there was no obvious influence on the reaction (entry 9). We subsequently adjusted the amount of copper acetate and PPh₃ and found that the yield clearly decreased and the amide 1a was (entries 10-12). The effect of PPh₃ was obvious to the reaction but the exact role of PPh₃ is unclear $n_{QWArtiVariaWs}$ solvents and reaction temperature were also investigated and DCB was certified to be the better solvent for the present reaction, at 110 °C (entries 13-17). Reducing the amount of ketone **2a**, the yield decreased to 63%, revealing that a higher concentration of **2a** appears to be necessary to improve this transformation (entry 18). Finally, the reaction was performed under air and led to a lower yield of product (entry 19). Consequently, the reaction was carried out under inert atmosphere in order to obtain a better conversion.

The scope with respect to amide substrates was first evaluated with ketones under optimal conditions or modified standard conditions as shown in Scheme 1. The reaction of unsubstituted benzamide with 4'-methylpropiophenone or 4'fluoropropiophenone could generate the corresponding product in a moderate yield whether PPh₃ exists or not (3b and 3c). The structure of 3b was further confirmed by the X-ray crystallography (CCDC 1904901). Aromatic amides containing one or two methyl groups at different position provided the desired products in fair to good yields (3d-3i). The intramolecular competition reaction of meta-methyl substituted benzamides gave the preferential isomer of 3e as the major product, due to the steric hindrance of methyl group. Notably, chloro as an electron-withdrawing group at different position of benzamides led to moderate conversion (3k-3n). The reaction of 1n gave the desired product 3n as the major isomer, which was similar with the reaction of 1e. The reactivity of substrates bearing a trifluoromethyl group delivered the desired products in moderate to good yields (3o-3p). We also scaled up the reaction of 1p to 1.5 mmol and obtained the product **3p** in 58% isolated yield. The transformation of naphthyl amide also occurred in 58% yield (3r). We also examined the heteroaryl such as thienyl amide in this catalytic system, but the reaction could not furnish the



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corresponding product and further research is in progress.

To investigate the reactivity of various ketones, we selected amide 1a as one reactant after exploring the compatibility of amides (Scheme 2). Propiophenone gave the expected product in 63% yield (4a) when 3.0 equivalents of silver carbonate were used in the catalytic system. This protocol is also applicable to a series of ketones bearing either electrondonating or -withdrawing substituents on the benzene ring of propiophenones. Notably, propiophenones containing a methyl or methoxy group on different positions of benzene rings could furnish the desired isoindolin-1-one derivatives in moderate to good yields (4b-4d). We noted that the propiophenones containing F, Cl and Br at different positions of benzene rings also delivered the desired product under modified reaction conditions by removing PPh₃ or increasing $\mathsf{Ag}_2\mathsf{CO}_3$ (4e-4k). Remarkably, the compatibility of halogen groups on the benzene ring provides a feasible chance for further transformation to synthesize other compounds. Unfortunately, a trifluoromethyl substituent on 4-position of benzene in propiophenone only provided the desired product in only 35% yield (41). Other reaction conditions were also tried but there was no demonstrable improvement on this reaction 4'-(trifluoromethyl)propiophenone. of Additionally. heteroaromatic ketones such as 2-propionylthiophene and 2methyl-5-propionylfuran were demonstrated to undergo this reaction (4m and 4n). Interestingly, aliphatic ketone, namely 3pentanone, could be transformed to the corresponding product in 37% yield (4o). 8-Amino-5-methoxyquinoline benzamide (1s) reacted with 2a to give the product 4p in 75% yield. The auxiliary group can be removed affording heterocycle 5 in 60% yield (Scheme 3).

To gain some primary insight to the mechanism of this reaction, some related experiments were carried out (Scheme 4 and ESI). Control experiments about the desaturation of ketone **2b** were performed and the results indicate that $Cu(OAc)_2$ and TEMPO are crucial to form the olefin and Ag_2CO_3 could improve the formation of the olefin (Scheme 4a). Then the reaction of **2b'** with **1a** afforded **4a** in 52% yield under the



Scheme 2 Scope of ketone substrates. "Reaction conditions: 1a (0.15 mmol), 2 (3.5 equiv.), DCB (0.75 mL), 21 h, 110 °C, N₂, isolated yield. "In the absence of PPh₃. cAg₂CO₃ (3.0 equiv.). "Reaction temperature: 120 °C.



Scheme 3 Removal of the directing group.



standard conditions (Scheme 4b). Subsequently, isotope labelling experiments were also performed and the results suggest that the C–H cleavage of phenyl amides is nearly irreversible under the reaction conditions. And the one-pot competitive kinetic isotope effect (KIE) value (1.43) and the parallel KIE value (1.17) were observed, and the results suggest the C–H cleavage in this reaction was unlikely involved in the rate-limiting step (see ESI).¹⁹

On the basis of the above experiments and the reported cobalt catalyzed C-H bond functionalization^{8, 17, 20} and coppercatalyzed the dehydrogenation of saturated ketones,¹⁴ a plausible mechanism for the Co/Cu catalyzed oxidative C-H/N-H functionalization was proposed in Scheme 5. The Co(II) species I is generated from cationic Co(II) coordinating to the nitrogen of substrate amide 1, and then is oxidized to Co(III) complex by Ag(I). Subsequently, the Co(III) species activates the C-H bond to deliver a cyclometalated intermediate II through an ortho-C-H cleavage of benzamide.²⁰ The olefin which derives from the dehydrogenation of ketone catalyzed by Cu/TEMPO/Ag₂CO₃ inserts into C-Co bond leading to the formation of intermediate III that undergoes β -hydrogen elimination and reduction elimination producing IV and Co(I) species. And then the cobalt (I) species is oxidized to Co(II) by silver salt in the catalytic system, and intermediate IV undergoes the intramolecular Michael addition to afford the product 3.



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In summary, we have first developed an efficient protocol for cobalt/copper-catalyzed oxidative C–H/N–H annulation of various amides with different saturated ketones, hence providing a step-economical access to isoindolin-1-one derivatives. This protocol is to possess a broad scope of substrates and good functional group compatibility. In this transformation, inexpensive and easily available cobalt and copper compounds were utilized as catalysts, and TEMPO and silver carbonate were employed as oxidants. Further efforts will be devoted to expanding the ketones and amides scope and exploring the application of this protocol.

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Conflicts of interest

There are no conflicts to declare.

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