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Cooperative Co(III)/Cu(II)-Catalyzed C−N/N−N Coupling of Imidates with Anthranils: Access to 1*H*-Indazoles via C−H Activation

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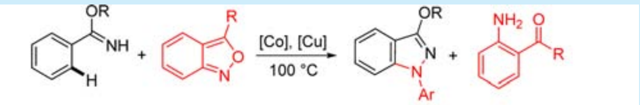
Supporting Information

ABSTRACT: Cooperative cobalt- and copper-catalyzed C−H activation of imidate esters and oxidative coupling with anthranils allowed efficient synthesis of 1*H*-indazoles in the absence of metal oxidants. The anthranil acts as a convenient aminating reagent as well as an organic oxidant in this transformation. The copper catalyst likely functions at the stage of N−N formation.

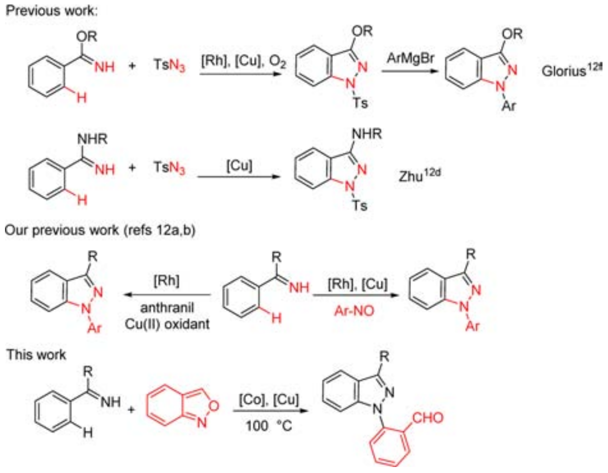


- Co/Cu Cooperative Catalysis
- One-Pot to Indazoles via C-N/N-N Formations
- Aminating Reagent as Organic Oxidant
- Readily Available Substrate and Broad Scope

Transition-metal-catalyzed direct C−H functionalization of arenes has been extensively employed over the past decades as a powerful strategy in organic synthesis[1] owing to high atom- and step-economy.[2,3] Despite the high activity of various second- and third-row transition-metal catalysts, applications of cost-effective, earth-abundant, and functionally unique first-row metal catalysts are highly desirable. Pioneered by Kanai and Matsunaga,[4] the higher Lewis acidity and catalytic activity of stable Cp*Co(III) complexes have allowed the development of new catalytic systems of C−H activation. This was made possible by the enhanced metal−ligand corporation in the catalytic cycle. Afterward, the groups of Glorius,[5] Ackermann,[6] Ellman,[7] Daugulis,[8] Chang,[9] and others[10] have made progress in cobalt-catalyzed C−H activation. These catalytic systems can stay complementary to those enabled by the rhodium(III) congeners in terms of substrate scope, activity, and selectivity.

1*H*-Indazoles are known as an important skeleton that has shown a wide range of pharmacological activities,[11] including anti-inflammatory, antiviral, antimicrobial, and anticancer activities. Therefore, the development of inexpensive and efficient methods to access 1*H*-indazoles in a green and step-economic fashion is highly desirable. In this regard, the strategy of transition-metal-catalyzed C−H bond activation/functionalization has exhibited significant potentials in indazole synthesis.[12] For example, Glorius reported a Rh(III)-catalyzed oxidative annulation between imidates and sulfonyl azides to deliver 1*H*-indzaoles.[12f] Subsequently, copper-catalyzed 1*H*-indzaole synthesis via C−N/N−N bond formations has been disclosed by the group of Zhu.[12d] We recently developed two distinctive methods to construct indazoles via Rh(III)-catalyzed C−H activation of imidates under both oxidative and redox-neutral conditions (Scheme 1).[12a,b] While we have briefly applied anthranil as an aminating reagent in one report, both expensive rhodium(III) catalysts and a stoichiometric amount of Cu(II) oxidant were necessary.[12a] Thus, direct access to these synthetically useful substituted indazoles via base metal catalysis needs further exploration. We now reported synergistic cobalt- and copper-catalyzed synthesis of 1*H*-indazoles via C−H activation and C−N/N−N bond formations, where anthranils[13] act as both an aminating reagent and an organic oxidant.[12d]

Scheme 1. Intermolecular Synthesis of 1*H*-Indazoles



We commenced our investigation with the screening of reaction parameters for the coupling between imidates (**1a**) and 5-chloro-3-phenylbenzo[*c*]isoxazole (**2a**, Table 1). Using $[Cp^*Co(CO)I_2]$ (10 mol %)/$AgSbF_6$ (20 mol %) as a catalyst, a coupling occurred and the desired indazole product **3aa** was isolated in 60% yield in the presence of $Cu(OAc)_2$ (2.1 equiv, entry 1). Switching the catalyst to $[Cp^*Co(MeCN)_3](SbF_6)_2$ slightly improved the yield (entry 2). When the amount of **2a** was increased from 1.5 to 3.0 equiv, the yield of **3aa** was improved to 92% (entry 3), but lowering the catalyst loading resulted in diminished yields (entries 4 and 5). We noted that in some cases anthranil decomposed to a 2-aminobenzophenone in rhodium-catalyzed reactions, so we reasoned that it might act as an organic oxidant. Indeed, the reaction proceeded

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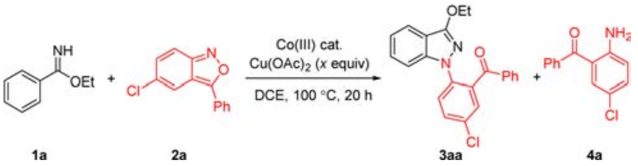
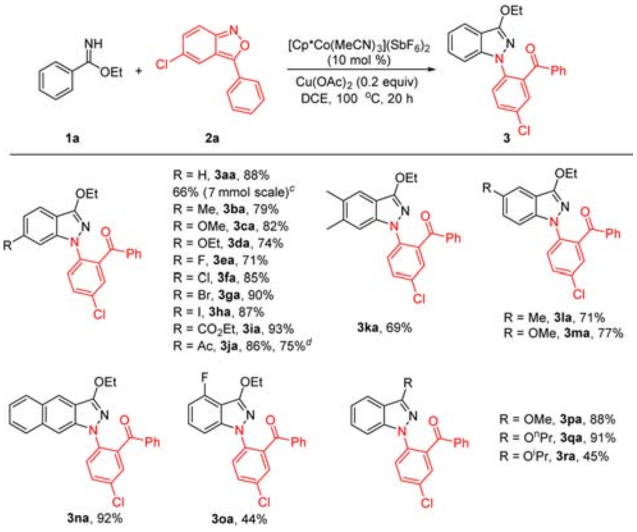
Table 1. Optimization of the Reaction Conditions[a]



entry	cat. (mol %)	x	yield[b] (%)
1	$[Cp^*Co(Co)I_2]_2$(10)/$AgSbF_6$ (20)	2.1	60[c]
2	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	2.1	66[c]
3	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	2.1	92
4	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (8)	2.1	85
5	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (5)	2.1	60
6	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	2.1	56[d]
7	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	0.2	88
8	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	0.2	56[e]
9	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	0.2	81[f]
10	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	0.2	84[g]
11	$[Cp^*Co(MeCN)_3](SbF_6)_2$ (10)	0	ND
12		0.2	ND

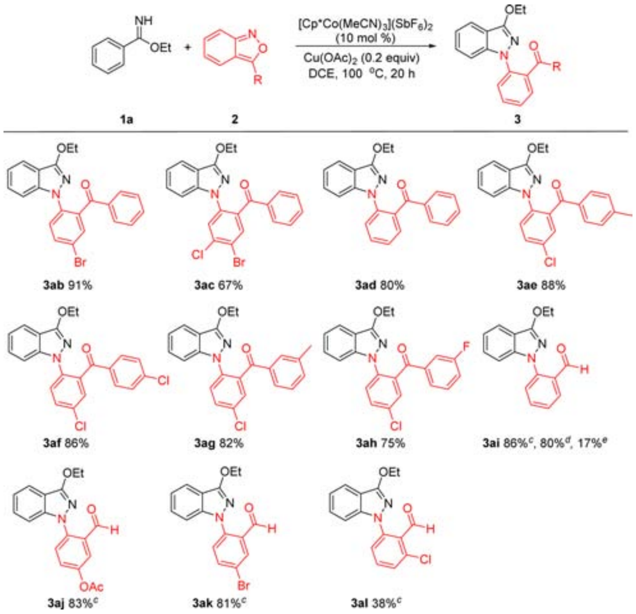
[a] The reaction was carried out using imidate ester **1a** (0.2 mmol), **2a** (0.6 mmol), Co catalyst, and $Cu(OAc)_2$ in DCE (3 mL) at 100 °C (sealed tube) under N_2. [b] Isolated yield after column chromatography. [c] **2a** (0.3 mmol). [d] 80 °C. [e] Reaction was performed with **2a** (0.3 mmol) under 1 atm of O_2. [f] **2a** (0.4 mmol). [g] **2a** (0.5 mmol).

Scheme 2. Substrate Scope of Imidates[a,b]



[a] The reaction was carried out using imidate ester (0.2 mmol), **2a** (0.6 mmol), the cobalt catalyst (0.02 mmol), and $Cu(OAc)_2$ (0.04 mmol) in DCE (3 mL) at 100 °C (sealed tube) under N_2. [b] Isolated yield after column chromatography. [c] Reaction was performed with 7 mmol of **1a**. [d] **2a** (0.5 mmol).

Scheme 3. Scope of Anthranils in Indazole Synthesis[a,b]



[a] The reaction was carried out using **1a** (0.2 mmol), anthranil (0.6 mmol), the Co catalyst (0.02 mmol), and $Cu(OAc)_2$ (0.04 mmol) in DCE (3 mL) at 100 °C (sealed tube) under N_2 for 20 h. [b] Isolated yield after column chromatography. [c] PivOH (0.2 mmol). [d] PivOH (0.2 mmol) and anthranil (0.5 mmol). [e] Reaction was performed with 2-azidobenzaldehyde.

with comparable efficiency (88% yield) in the presence of 20 mol % of $Cu(OAc)_2$ (entry 7), and the reduced coproduct **4a** was isolated yield (45% based on **2a** and 130% based on **1a**). However, further decreasing the amount of **2a** gave inferior results even in the presence of O_2 (entry 8). It was found that 3.0 equiv of **2a** was the optimal loading (entries 7, 9, and 10). Control experiments indicated that no desired reaction occurred when either the Co(III) catalyst or $Cu(OAc)_2$ was omitted (entries 11 and 12).

With the optimized reaction conditions in hand, the scope and generality with respect to imidates were next examined in the coupling of **2a** (Scheme 2). Thus, imidates bearing both electron-donating and -withdrawing groups at the *para* position of the phenyl ring all coupled in good to excellent yields (**3aa**–**ja**). It was observed that the electronic properties of imidates had no apparent effect on the reaction. In addition, *meta*-substituted or disubstituted imidates (**3ka**–**na**) coupled in moderate to excellent yields in high site selectivity, where C–H functionalization occurred at the less hindered site. Introduction of an *o*-fluoro group was also tolerated, delivering **3oa** in 44% yield. Besides the ethyl ester, other alkyl esters also coupled smoothly in excellent yields (**3pa**,**qa**), although the isopropyl imidate reacted with diminished efficiency (**3ra**).

We next examined the scope of the anthranil substrate. As given in Scheme 3, introduction of functional groups such as halogens (**3ab**,**ac**) and phenyl (**3ad**) to different positions of the anthranil ring was compatible. In addition, introduction of a substituted phenyl group into the 3-position of the anthranil ring was fully tolerated (**3ae**–**ah**). However, when the nonsubstituted anthranil was applied under the standard conditions, the reaction became sluggish. To our delight, further introduction of PivOH regained the coupling efficiency (**3ai**), which likely facilitated the C–H activation process. In comparison, a poor result was observed when the aminating reagent was replaced by 2-azidobenzaldehyde, indicating the intrinsic reactivity of anthranils. Thus, several substituted anthranils coupled smoothly in high yields (**3aj**,**ak**) in the presence of PivOH, although introduction of a 4-chloro group reduced the reaction efficiency likely due to steric effects (**3al**).

To access a functionalized product, a derivatization reaction was carried out (eq 1). Using TsN_3 as an amidating reagent, product **5** was isolated in moderate yield via a Ru(II)-catalyzed C–H amidation process.[14] Reduction of **3aa** with $NaBH_4$ afforded alcohol **6** in 83% yield (eq 2). Moreover, acid

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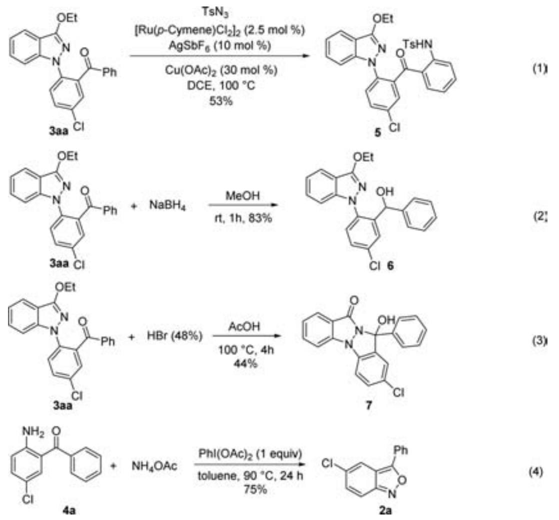
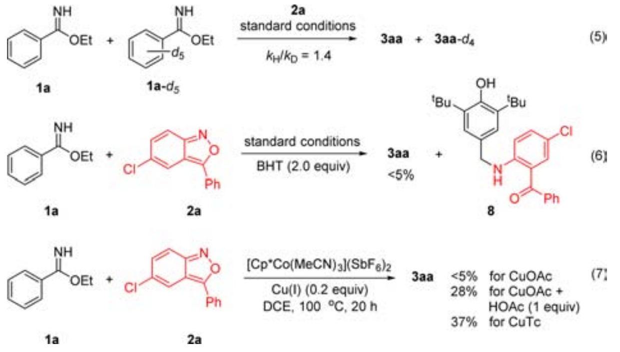


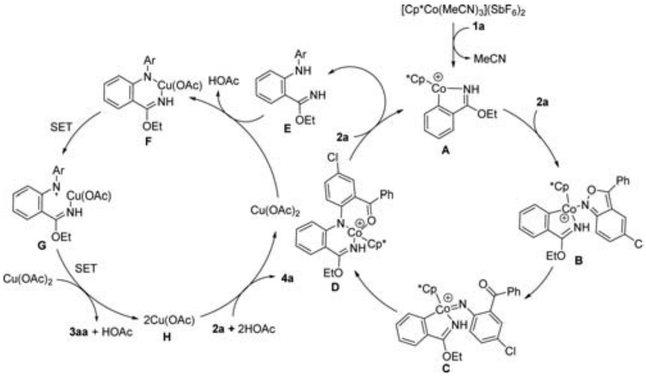
treatment of **3aa** led to deprotection of the ether[12f] followed by intramolecular nucleophilic addition to give hemiaminal **7** in 44% yield (eq 3). Recycling of coproduct **4a** has been briefly explored.[15] Satisfyingly, when a stoichiometric amount of $PhI(OAc)_2$ was used as an oxidant, the anthranil **2a** was isolated in 75% yield (eq 4).

To gain mechanistic insight into the catalytic system, two side-by-side parallel reactions were carried out for coupling of **1a** and **1a**-d_5 with anthranil **2a** at a low conversion. A small value of $k_H/k_D = 1.4$ was obtained on the basis of ^1H NMR analysis (eq 5), indicating that C−H bond cleavage is likely not involved in the turnover-limiting step. To explore the intermediacy of radical species and hence the possibility of single-electron transfer in N−N bond formation,[12f] the amination reaction was performed in the presence of 2,6-di-*tert*-butyl-4-methylphenol (BHT, eq 6). The reaction was inhibited, but an amine (**8**) was isolated in 30% yield, suggesting that a radical pathway is probably involved in this reaction. To further probe the formation of N−N bond, the $Cu(OAc)_2$ was replaced by CuOAc for the coupling of **1a** and **2a**, and **3aa** was isolated in 28% yield in the presence of AcOH (eq 7). Switching to CuTc (0.2 equiv) gave rise to **3aa** in 37% yield, thus indicating that a Cu(I) species might be involved in the N−N formation process.



On the basis of our preliminary results and relevant reports,[12a,b,d,f] a plausible catalytic cycle is proposed in Scheme 4 (see the SI for alternative mechanisms). The reaction is initiated by cyclometalation of the imidate to furnish a five-membered metallacyclic intermediate **A** to which anthranil coordinates to afford intermediate **B**, which undergoes intramolecular N−O bond cleavage to deliver a nitrene intermediate **C**. Migratory insertion of the Co−aryl bond into the nitrene gives a tripodal intermediate **D**. Coordination of an imidate to **D** and subsequent C−H activation releases the aminated intermediate **E** with the regeneration of cobalt(III) **A**. In a sequential copper-catalyzed cycle, coordination of $Cu(OAc)_2$ to **E** with extrusion of HOAc gives a Cu(II) species **F**, which undergoes double single-electron transfer to generate indazole **3aa** and Cu(I) intermediate **H**. This interemdiate could be oxidized by another molecule of **2a** in the presence of AcOH to regenerate the $Cu(OAc)_2$. In this process, reductive opening of the anthranil ring generates a nitrogen radical that is trappable by BHT. However, an alternative Cu(II)−Cu(0)−Cu(II) pathway remains possible in which intermediate **F** reductively eliminates the product **3aa** and HOAc to give a Cu(0). Oxidation of Cu(0) by anthranil to Cu(II) then regenerates the active copper catalyst.

Scheme 4. Proposed Mechanism



In summary, we have developed a synergistic Co/Cu-catalyzed system to construct substituted 1*H*-indazoles from easily available imidates and anthranils via a C−H activation pathway where anthranils also serve as an organic oxidant. This catalytic system tolerates a wide range of substrates with high reaction efficiency. Meanwhile, mechanistic studies indicated that the N−N formation likely involved nitrogen radical species. Moreover, the reduced coproduct could be recycled to the anthranil substrate under oxidative conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01716.

Experimental procedures, characterization data, alternative mechanism, and ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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