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Indole Synthesis via Cobalt(III)-Catalyzed Oxidative Coupling of *N*-Arylureas and Internal Alkynes

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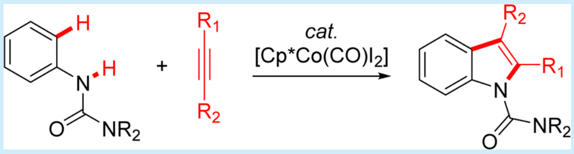
Supporting Information

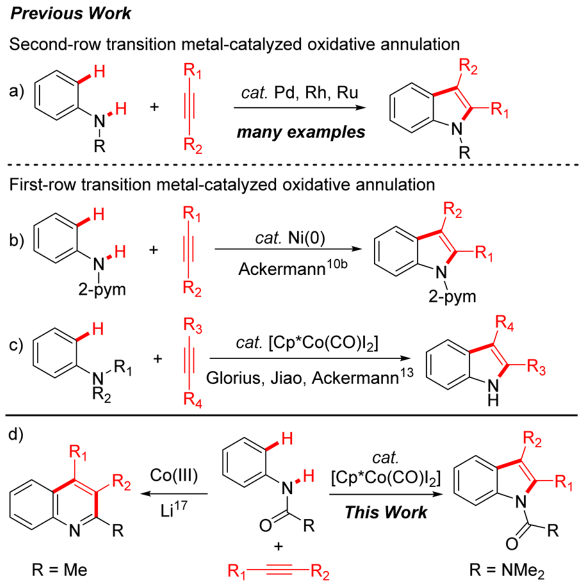
ABSTRACT: A mild Co(III)-catalyzed oxidative annulation of *N*-arylureas and internal alkynes has been developed. The use of less electrophilic ureas other than acetamides as directing groups is crucial for the reaction. A broad range of synthetically useful functional groups are compatible with this reaction, thus providing a new opportunity for the synthesis of diverse indoles.



The indole nucleus is prevalent in natural products, biologically active molecules, and pharmaceuticals.[1] Consequently, interest in the synthesis and modification of this privileged structural motif has constantly grown,[2] after Emil Fischer's landmark achievement of indole synthesis over a century ago.[3] One of the most powerful synthetic methods to access these compounds is Larock's indole synthesis via Pd-catalyzed coupling of *ortho*-haloanilines with alkynes.[4] More recently, a wealth of research has been directed toward the synthesis of indoles via transition-metal-catalyzed C−H functionalization, and many elegant methods have been developed.[2c,d] Particularly, the oxidative annulation of anilines or their derivatives with alkynes have received tremendous attention, due to the ready availability of each coupling partner. In 2008, Fagnou and co-workers reported the first Rh(III)-catalyzed indole synthesis via the reaction of acetanilides with internal alkynes.[5] Shortly after, Jiao reported a Pd-catalyzed oxidative coupling of *N*-nonsubstituted and *N*-alkyl monosubstituted anilines with electron-deficient alkynes.[6] Ever since then, indole synthesis via the oxidative annulation of alkynes with various *N*-substituted or *N*-nonsubstituted anilines catalyzed by second-row transition metal catalysts, such as Rh(III), Pd(II), or Ru(II), have been well investigated by Li,[7] Glorius,[8] Lu,[9] Ackermann,[10a] Huang,[11] and others (Scheme 1a).[12] In contrast, indole synthesis via C−H activation catalyzed by more sustainable and cost-effective first-row transition metals is very rare. Ackermann reported a Ni(0)-catalyzed annulation of *N*-(2-pyrimidyl)indoles with internal alkynes.[10b] During the preparation of this work, Glorius, Jiao, and Ackermann independently reported the Co(III)-catalyzed redox-neutral synthesis of indoles using Boc-protected hydrazines, *N*-nitroso, or nitrone as oxidizing directing groups.[13]

Recently, cobalt-catalyzed C−H functionalization has received increased attention due to its abundance and inexpensiveness.[14,15] As part of our ongoing studies on first-row transition-metal-catalyzed C−H functionalization,[16] we had found that a cationic high valent Cp*Co(III) complex efficiently catalyzed the C2-selective C−H alkynylation of indoles.[15m] To expand the utility of the Cp*Co(III) catalysis further, we herein report the Co(III)-catalyzed oxidative annulation of *N*-arylureas and internal alkynes to access diverse indoles. The method features high functional group tolerance, broad substrate scope, high yields, and the use of a cost-effective, first-row transition metal catalyst. It was noteworthy that this indole synthesis via oxidative annulation was enabled by the fine-tuning of the electrophilicity of the directing groups, which was mechanistically complementary to the synthesis of quinolines via nucleophilic addition/dehydration recently reported by Li (Scheme 1d).[17]

Scheme 1. Indole Synthesis via Transition-Metal-Catalyzed Oxidative Annulation of Anilines with Alkynes



Although the oxidative indole synthesis has been well studied in Rh(III) catalysis using acetanilides and alkynes,[5] we failed to achieve the Co(III) version of this reaction under the same

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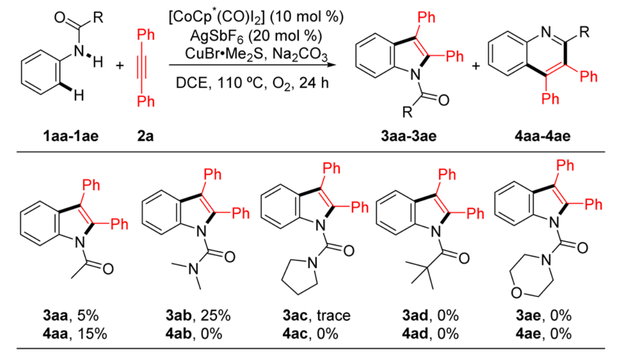
reaction conditions by treatment of acetanilide **1aa** with diphenylacetylene **2a**. After extensively screening various oxidants and additives, the desired oxidative annulation product **3aa** was only obtained in 5% yield when a copper salt was used, with the nucleophilic addition/dehydration product **4aa** produced predominantly (**4aa**, 15%, Scheme 2).

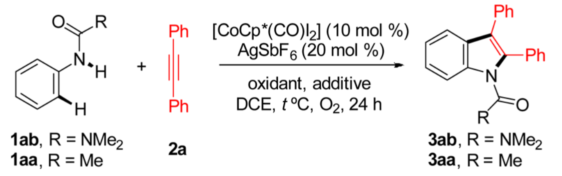
Scheme 2. Effect of Directing Groups



This is likely ascribable to the intrinsic property of cationic Co(III) complexes in activating the carbonyl group toward nucleophilic attack of organocobalt species.[15b,e,17] We reasoned that lowering the electrophilicity might shift the selectivity to indole formation. Consistent with this hypothesis, we were pleased to find that switching acetanilide to an *N*-phenylurea (**3a**) resulted in the isolation of the indole product (**3ab**) in 25% yield under our previous conditions. Other commonly used directing groups gave unsatisfactory results (Scheme 2).

Inspired by this promising result, we next sought to improve the efficiency using 1,1-dimethyl-3-phenylurea **1a** and diphenylacetylene **2a** as coupling partners (Table 1). The screening of oxidants revealed that the yield could be increased to 35% by using $AgBF_4$ (entries 1−3). A slight improvement in yield was observed when the amount of Na_2CO_3 was increased from 0.4 to 1.0 equiv (entry 4). NaH_2PO_4 was found to be the optimal additive, giving indole **3ab** in 44% yield (entry 5). Next, we increased the quantity of the $AgBF_4$ from 40 to 100 mol %, and a significant improvement was achieved (entry 6). Further tuning the amount of oxidants and additives revealed that the reaction proceeded better in the presence of 2 equiv of NaH_2PO_4 and 1.2 equiv of Ag_2CO_3 (entries 7−9). In addition, the reaction temperature was also examined, and the yield could be improved to 84% at 130 °C (entry 10). Finally, the indole product **3ab** could be obtained in 94% isolated yield by changing the ratio of **1ab** and **2a** (entry 11). As expected, when switching an *N*-phenylurea to the acetanilide as a substrate under these coupling conditions, indole **3aa** was obtained in a reduced yield (29%) along with the nucleophilic addition/dehydration product **4aa** (entry 12).

Table 1. Optimization of the Reaction Conditions[a]



entry	R	oxidant (equiv)	additive (equiv)	*t* (°C)	yield (%)[b]
1	NMe_2	Ag_2O (0.4)	Na_2CO_3 (0.4)	110	19
2	NMe_2	Ag_2CO_3 (0.4)	Na_2CO_3 (0.4)	110	28
3	NMe_2	$AgBF_4$ (0.4)	Na_2CO_3 (0.4)	110	35
4	NMe_2	$AgBF_4$ (0.4)	Na_2CO_3 (1)	110	40
5	NMe_2	$AgBF_4$ (0.4)	NaH_2PO_4 (1)	110	44
6	NMe_2	$AgBF_4$ (1)	NaH_2PO_4 (1)	110	65
7	NMe_2	Ag_2CO_3 (1)	NaH_2PO_4 (1)	110	70
8	NMe_2	Ag_2CO_3 (1)	NaH_2PO_4 (2)	110	76
9	NMe_2	Ag_2CO_3 (1.2)	NaH_2PO_4 (2)	110	80
10	NMe_2	Ag_2CO_3 (1.2)	NaH_2PO_4 (2)	130	84
11[c]	NMe_2	Ag_2CO_3 (1.2)	NaH_2PO_4 (2)	130	94[d]
12[c]	Me	Ag_2CO_3 (1.2)	NaH_2PO_4 (2)	130	3aa, 29[d] 4aa, 16[d]

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), [CoCp*(CO)I_2] (10 mol %), $AgSbF_6$ (20 mol %) in DCE (1 mL). [b] ^1H NMR yield using 1,3,5-trimethoxybenzene as the internal standard. [c] **1a** (0.15 mmol), **2a** (0.10 mmol). [d] Isolated yield.

With the optimal reaction conditions in hand, we next tested the scope of the *N*-arylureas using diphenylacetylene **2a** as the annulation partner (Figure 1). In general, indoles were successfully obtained from a broad range of substrates in moderate to high yields with *ortho*-regioselectivity. Both electron-donating and -withdrawing substituents were tolerated. A number of synthetically useful functional groups, such as fluoro (**3ba**), bromo (**3ca**), methoxycarbonyl (**3da** and **3fa**), and methoxy (**3ha**), were compatible with this reaction. The tolerance of halides was particularly important, since such substituents could be further transformed to other functional groups via a traditional cross-coupling reaction. We also found that this protocol tolerates the presence of *ortho* substituents well. As demonstrated, *N*-arylureas bearing methyl and methoxyl in the *ortho* position reacted smoothly to give the desired indole products **3ga** and **3ha**. Furthermore, the annulation of disubstitued substrate **1ia** could also afford the desired product **3ia** in moderate yield. Moreover, the reaction is not limited to the *N*,*N*-dimethyl ureas. When *N*-pyrrolyl urea

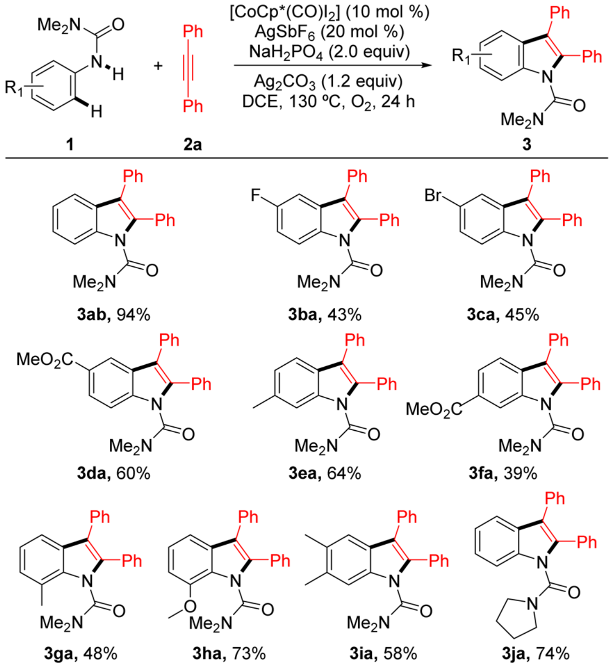


Figure 1. Scope of *N*-arylureas.

1ja was reacted with diphenylacetylene **2a**, indole **3ja** was obtained in 74% yield.

Subsequently, we evaluated the substrate scope with respect to internal alkynes (Figure 2). The reaction was compatible with electron-donating substituents at the *para*-position on the benzene rings of internal alkynes, such as Me-, MeO-, ^{n}Bu-, and ^{t}Bu-groups (**5a**−**5d**), providing the corresponding indoles in generally good yields (42%−75%). In addition, halogen-substituted benzene rings of internal alkynes proceeded to give the desired product in moderate yields (**5e**, 63% and **5f**, 48%). Furthermore, a heterocyclic thiophene motif also served as a suitable substrate as exemplified by the synthesis of **5g**. In addition, 1-phenyl-1-propyne coupled in high regioselectivity, and only one single regioisomer was detected (**5h**). Unfortunately, terminal alkynes were not compatible with this protocol.

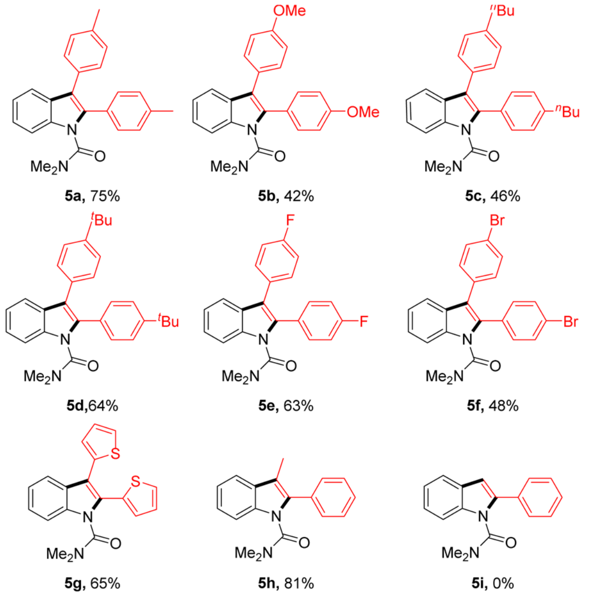
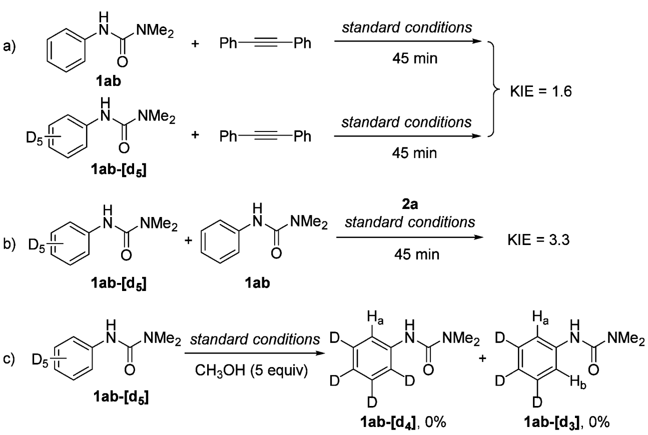


Figure 2. Scope of alkynes.

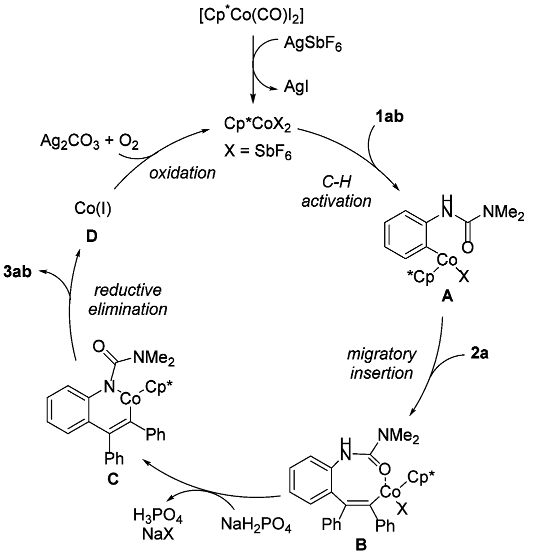
To gain some insight into the mechanism, a series of deterium labeling experiments were carried out (Scheme 3). Two separate experiments using **1ab** and **1ab**-[**d**$_5$] were carried out, from which a k_H/k_D value of 1.6 was found on the basis of ^{1}H NMR (Scheme 3a). Further, a 1:1 mixture of **1ab** and **1ab**-[**d**$_5$] was then treated and gave a consistent value of k_H/k_D = 3.3 (Scheme 3b), indicating that C−H activation is likely turnover-limiting in coupling systems. To check the reversibility of the C−H activation step, **1ab**-[**d**$_5$] was heating in MeOH under the oxidative coupling conditions in the absence of diphenylacetylene, and H/D scrambling was not observed here (Scheme 3c). This suggested irreversibility of C−H activation. This observation is in sharp contrast to Glorius and Jiao's observations.[13a,b]

Scheme 3. Mechanism Studies



On the basis of our mechanistic experiments and previous reports,[5b,12d,15i] a plausible catalytic cycle is depicted in Scheme 4. First, an active cationic Co(III) catalyst is generated upon treatment of [Cp*Co(CO)I$_2$] with AgSbF$_6$. Cobalt-mediated irreversible C−H bond activation of *N*-arylurea affords a six-membered metallacyclic intermediate **A**.[15i] Alkyne coordination and migratory insertion of the aryl group generates a Co(III) alkenyl species **B**. Intermediate **C** is formed via base-assisted elimination of HX. C−N bond reductive elimination delivers indole **3aa** along with a Co(I) species **D**. The catalytic cycle is completed when Co(I) is reoxidized to Co(III) via Ag$_2$CO$_3$ and O$_2$. When acetanilide **1aa** was used as a substrate, quinolone **4aa** was generated via nucleophilic addition of metallacyclic **B** followed by dehydration.[17]

Scheme 4. Proposed Reaction Mechanism



In conclusion, we have developed the Cp*Co(III)-catalyzed oxidative annulation of *N*-arylureas and internal alkynes for the construction of indoles. The use of less electrophilic ureas other than acetamides as directing groups is crucial for the reaction. This reaction proceeds under mild conditions and tolerates a wide range of functional groups, providing a straightforward access to diverse indoles. In addition, when unsymmetrical internal alkynes were employed, the annulation adducts were obtained with high regioselectivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00494.

Experimental details and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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