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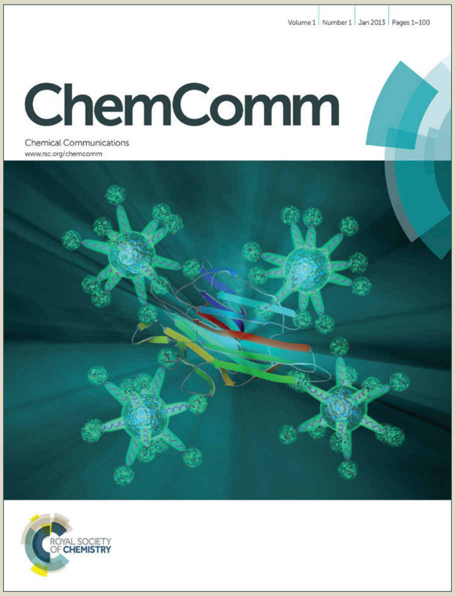

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ARTICLE TYPE

Cobalt(II)/silver relay catalytic isocyanide insertion-cycloaddition cascades: A new access toward pyrrolo[2,3-*b*]indoles

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The combination of Co(acac)$_2$ and AgOTf enables the bimetallic relay catalysis reaction of 2-ethynylanilines and isocyanides, allowing an easy and low-cost access to deliver new densely functionalized pyrrolo[2,3-*b*]indoles. The reaction pathway involves a Co(acac)$_2$-catalyzed double isocyanide insertion and a followed silver-enabled 1,3-dipolar cycloaddition. The synthetic utility of these bicycloaddtion reactions results in subsequent C−C and C−N bond-forming events to rapidly build up molecular complexity.

Natural products with an indole unit occupy a pivotal position in pharmaceutical, medical and organic chemistry because of their unique structures and interesting bioactivities.[1] Among them, the significant pyrrolo[2,3-*b*]indole framework is a key structural motif that exits in the core structure of substantial biologically active alkaloids[1] such as the potent vasodilator amauromine,[2] the insecticidal okaramine C,[3] physostigmine[4], as well as pseudophrynaminol[5], and flustramine C[6] (Figure 1). Therefore, many methodologies for the synthesis of this structural skeleton have been developed. Basically, these methods can be generalized into the following three categories: i) tandem cyclization of tryptophan derivatives;[7-11] ii) copper-catalyzed coupling of iodo-tryptophans;[12] iii) aza-Pauson-Khand cyclocarbonylations.[13] Despite these advances, these developed protocols have some clear limitations, such as the narrow substrate scopes, the prefunctionalization of starting materials, and toxic reagents as well as excess oxidants such as peroxides and NIS, thus suffering from poor atom and/or step efficiency. Accordingly, the exploration of new and general catalytic pathways for the direct formation of pyrrolo[2,3-*b*]indoles, especially through bicycloaddition reactions, has been one of the most attractive but challenging topics.

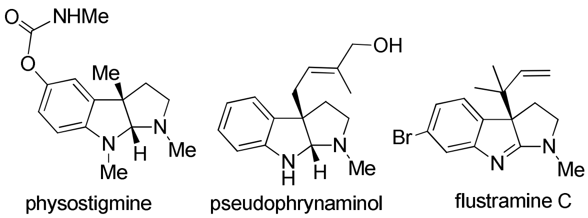
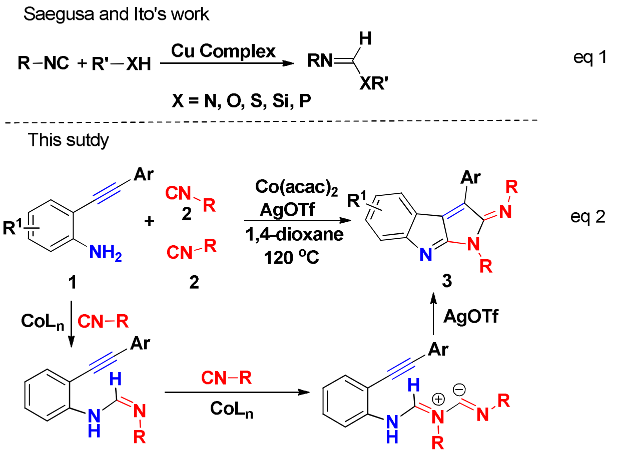


Figure 1 Representative pyrrolo[2,3-*b*]indole-containing heterocycles

Isocyanides have been served as extraordinarily useful synthons for the development of multicomponent reactions,[14] insertion reactions,[15] and oligo-/polymerization processes,[16] owing to their carbene-like reactivity of the divalent carbon atom. Since the pioneering discovery of the copper-catalyzed insertion of isocyanides into alcohols,[17a] thiols,[17b] amines,[17c] silanes,[17d] and phosphines[17e] by Saegusa and Ito[17] (Scheme 1, eq 1), numerous efforts have been devoted to isocyanide insertion reaction, which made it more powerful and applicable. Basically, there are two catalytic systems for isocyanide insertions: through Lewis acid (LA) catalysis[18] or using transition metal.[19] Arguably, the Pd-catalyzed isocyanide insertions have taken a pivotal position.[20] *In sharp contrast, an inexpensive cobalt-enabled process initiated by the electrophilicity of isocyanides and involved double isocyanide insertion is virtually unexplored.* As a continuation of our project on isocyanide-based transformations,[21] we became interested in bimetal relay catalytic cycloadditions between isocyanides and nucleophiles. Considering the beautiful applications of cobalt-catalyzed isocyanide insertion and silver-promoted alkyne-based cycloadditions[22], we envisioned that in the presence of cobalt catalyst, the double insertion of isocyanides into 2-ethynylanilines could yield 1,3-dipole intermediates, followed by a silver-catalyzed intramolecular 1,3-dipolar cycloadditions, thereby transforming into densely functionalized pyrrolo[2,3-*b*]indoles (Scheme 1, eq 2). Herein, we present the realization of this concept, which was achieved through the combination of the cobalt (II) with silver catalysts.

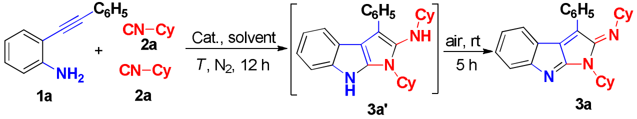


Scheme 1 Insertion reaction of isonitriles

The initial experiments were conducted with 2-(phenylethynyl)aniline (**1a**) and isocyanocyclohexane (**2a**) in a 1:2 mol ratio in the presence of 10 mol % $CoCl_2$ at 100 °C under a nitrogen atmosphere in dry 1,4-dioxane for 12 h. It was observed that the reaction solution turned red from brown under air conditions when the reaction process was monitored by TLC. The further investigation determined by HRMS showed that the in situ generated 1,8-dihydropyrrolo[2,3-*b*]indoles **3a**' was easily converted into the oxidized pyrrolo[2,3-*b*]indoles **3a** under aerobic conditions. Considering the instability of 1,8-dihydropyrrolo[2,3-*b*]indoles **3a**' under air conditions, we plan to synthesize pyrrolo[2,3-*b*]indoles **3a**. After completion of the above operation, the reaction mixture was continuously stirred at room temperature under air conditions for 5 h. This set of conditions afforded the desired product **3a**, albeit in only 10% yield. Other metal catalysts, such as $Cu(OAc)_2$, $Pd(OAc)_2$, $Rh_2(OAc)_4$, were proven ineffective for this transformation (Table 1, entries 2−4). The reaction could be improved by using $Co(acac)_2$ (acac = acetylacetone) as a catalyst, and the product could be obtained in 18% isolated yield. Since silver triflate has been demonstrated as a high-efficient catalyst for activating the alkynes,[22] we decided to utilize AgOTf as an additive to ameliorate this transformation. Gratifyingly, using the combination of $Co(acac)_2$ with 10 mol % AgOTf delivered a 67% yield of **3a** together with some unreacted starting materials (entry 6). The reaction worked efficiently at an elevated temperature (120 °C), giving rise to the corresponding product **3a** in 86% yield with full consumption of the starting materials (entry 7). Lowering or raising the loading of $Co(acac)_2$ or AgOTf (10 mol%) all gave a relatively inferior result under standard reaction conditions (See Table S1). Afterward, the effect of the solvent was investigated (compare entries 7–10). The use of DMF gave the product with a slightly lower yield (entry 8). A moderate yield was isolated when the reaction was conducted by the use of DMSO as the solvent (entry 9).The reaction stumbled in toluene (entry 10). The identical reactions performed under both air and oxygen atmosphere, lowered the yields to 65% and 69%, respectively (compare entries 10–11). Control reactions revealed that the transformation does not proceed in the absence of the $Co(acac)_2$ (entry 13).

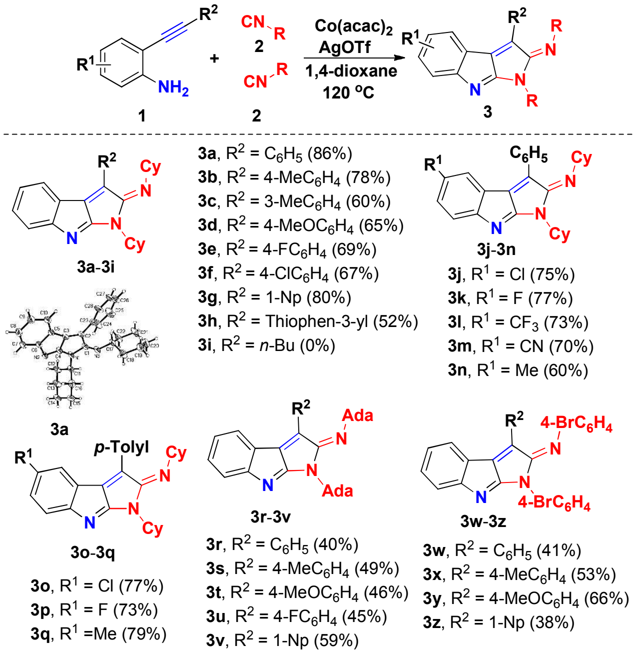
With the optimal reaction conditions for bicycloaddition processes in hand (Table 1, entry 7), we then set out to explore the scope of these transformations; the results are summarized in Scheme 2. Substrates **1** bearing electron-rich, electron-neutral, and electron-poor aromatic groups on the terminal triple bond (R^2) gave the desired products in good yields (**3a**–**3h**). Functional groups like fluoride, chloride, and ester at different positions of aromatic alkyne moieties were well tolerated. Generally, alkyne moieties possessing electron-rich and electron-neutral aryl rings led to better results than those substituted with electron-deficient ones (**3a**-**3b** vs **3e**–**3f**, Scheme 2). More sterically demanding 1-naphthyl (1-Np) substituent (**1g**) can show higher reactivity, generating the corresponding product **3g** in 80% yield. Heterocyclic substituents, such as thiophenes, may transform into the pyrrolo[2,3-*b*]indoles, albeit with lower efficiency. Regrettably, substrates with *n*-butyl substituents at the terminal position of the triple bond (R^2) proved to be unreactive under these conditions (**3i**, Scheme 2). Next, we turned our attention to investigate the electronic properties at the arylamine moiety (R^1). The variation of the electronic properties of R^1 have no significant effect on this transformation, and the corresponding pyrrolo[2,3-*b*]indole products were obtained with comparable efficiency to that observed for **3b**. For instance, functional groups such as nitrile, trifluoromethyl and halogen were well incorporated in these current bicycloadditions (**3j**-**3m**).

Table 1 Optimization of reaction conditions[a]



Entry	Promoter (equiv.)	Solvent	T/ °C	Yield[b] /%
1	$CoCl_2$ (10)	1,4-dioxane	100	10
2	$Cu(OAc)_2$ (10)	1,4-dioxane	100	NR
3	$Pd(OAc)_2$ (10)	1,4-dioxane	100	trace
4	$Rh_2(OAc)_4$ (10)	1,4-dioxane	100	trace
5	$Co(acac)_2$ (10)	1,4-dioxane	100	18
6	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	100	67
7	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	120	86
8	$Co(acac)_2$ (10)/AgOTf (10)	DMF	120	80
9	$Co(acac)_2$ (10)/AgOTf (10)	DMSO	120	62
10	$Co(acac)_2$ (10)/AgOTf (10)	Toluene	120	35
11	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	120	65[c]
12	$Co(acac)_2$ (10)/AgOTf (10)	1,4-dioxane	120	69[d]
13	AgOTf (10)	1,4-dioxane	120	NR

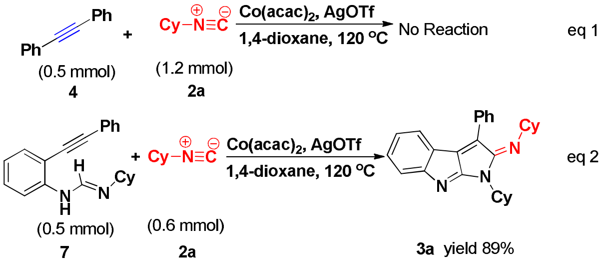
[a]Reaction conditions: 2-(phenylethynyl)aniline (**1a**, 0.5 mmol) and isocyanocyclohexane (**2a**, 1.2 mmol), catalyst (10 mol %), dry solvent (4.0 mL), N_2, 12 h; after completion, all the reaction mixture were stirred at room temperature under air conditions for 5 h. [b] Isolated yield. [c] Isolated yield under air conditions. [d] Isolated yield under O_2 conditions. NR = No Reaction.



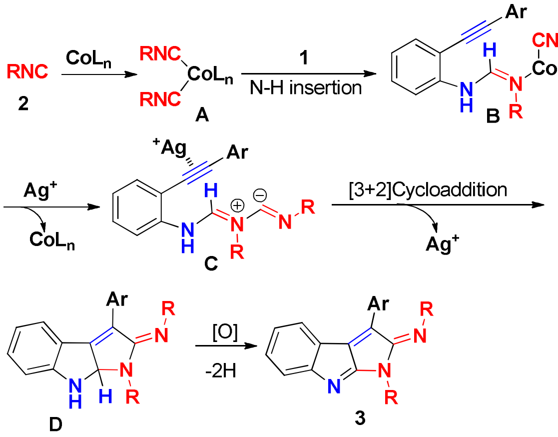
Scheme 2. Scope of the cobalt/silver-co-catalyzed bicycloaddition reaction. Yields of isolated products based on substrate **1** after column chromatography on silica gel are given. **1** (0.5 mmol) and **2** (1.2 mmol), catalyst (10 mol %), dry 1,4-dioxane (4.0 mL), N_2, 12 h; after completion, all the reaction mixture were stirred at room temperature under air conditions for 5 h.

In view of these results, we considered to vary the substituents of the isocyanides and select adamantanyl (Ada) and 4-bromophenyl counterparts as representative isonitriles to explore the feasibility of the reaction. As we expected, adamantanyl isocyanides were subjected with substrates **1** bearing electron-rich, -neutral, or -poor aromatic groups on the alkyne motif, participating in current Co/Ag co-catalyzed bicycloaddition reaction successfully, and the desired pyrrolo[2,3-*b*]indoles **3r**–**3v** were obtained with lower yields (40–59%) owing to its stronger steric hinder. Similarly, 4-bromophenyl isocyanides were also smoothly transformed into the desired products **3w**–**3z** with 38–66% yields and concomitant formation of two new cycles and four σ bonds including two C-N bonds. Note that this is the first reported procedure for the assemble of these new imino-functionalized pyrrolo[2,3-*b*]indoles through Co/Ag-catalyzed double isocyanide insertion/ 1,3-dipolar cycloadditions.

To gain insight into the cycloaddition reaction mechanism, several controlled experiments were conducted (Scheme 3). The reaction between 1,2-diphenylethyne and isocyanocyclohexane did not run under standard conditions, indicating that the amine group is required to fulfill the catalytic cycle (Scheme 3, eq 1). The preformed enyne-imines **7**[23] was treated with isocyanocyclohexane, successfully delivering pyrrolo[2,3-*b*]indoles **3a** in 89% yield (Scheme 3, eq 2). From this observation, it seems that the in situ generated enyne-imines may be a key intermediate to convert into final pyrrolo[2,3-*b*]indoles **3** in this reaction.



Scheme 3. Control experiments



Scheme 4. Mechanistic proposal

Although the mechanism of this bicycloaddition reaction has not been fully elucidated at this point, on the basis of literature reports[17,22] and the above-described observations, a possible reaction pathway for forming pyrrolo[2,3-*b*]indoles **3** is depicted in Scheme 4. The insertion of the ligated isonitrile into N-H bond of arylethynylanilines **1** affords cobalt complexes B[19,24], in which enyne-imine specie **7** was detected by GC-MS. The second migratory insertion allows **B** to form 1,3-dipoles **C**. In the presence of silver triflate, intramolecular 1,3-diplar cycloadditions leads to the thermodynamically stable pyrrolo[2,3-*b*]indoles **3** through dehydrogenation under air conditions. Generally, the divalent carbon atom of isocyanides has pronounced nucleophilicity and is readily served as a nucleophile in addition reactions with electrophiles. During our reaction process, the electrophilicity of isocyanides was initiated in the presence of Co(acac)$_2$ catalyst, which was a key step of this successful transformation involved double isocyanide insertion and 1,3-dipolar cycloaddition.

Conclusions

In summary, an unprecedented cobalt(II)/silver co-catalyzed bicycloaddition of arylethynylanilines with isonitriles has been developed, by which a wide range of functionalized pyrrolo[2,3-*b*]indoles is expediently and stereoselectively synthesized in a convergent manner. The reaction also features Co/Ag bimetallic catalysis, flexible structural modification, reliable scalability and mild reaction conditions. Experimental results indicated that the reaction might be initiated by reductive addition of the arylethynylanilines to the ligated isonitrile, followed by a second-migratory-insertion/1,3-diplar cycloadditions / dehydrogenation sequence.

Acknowledgment

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Notes and references

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