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Cobalt-Catalyzed Oxidative Isocyanide Insertion to Amine-Based Bisnucleophiles: Diverse Synthesis of Substituted 2-Aminobenzimidazoles, 2-Aminobenzothiazoles, and 2-Aminobenzoxazoles

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2-Aminobenzoxazoles, 2-aminobenzothiazoles, and 2-aminobenzimidazoles are privileged heteroaromatic scaffolds in biologically active compounds and natural products (Figure 1). For example, the core scaffold of the selective inhibitor of the human $P2Y_1$ receptor **I**[1] and the drug for treating insomnia **II**[2] is 2-aminobenzoxazole. The core structure of the anti-HIV agent **III**[3] and the phosphodiesterase 10 inhibitor **IV**[4] is 2-aminobenzothiazole. The histamine H1-receptor **V**, named astemizloe,[5] and bioactive compounds **VI** and **VI'**[6] all contain the 2-aminobenzimidazole skeleton.

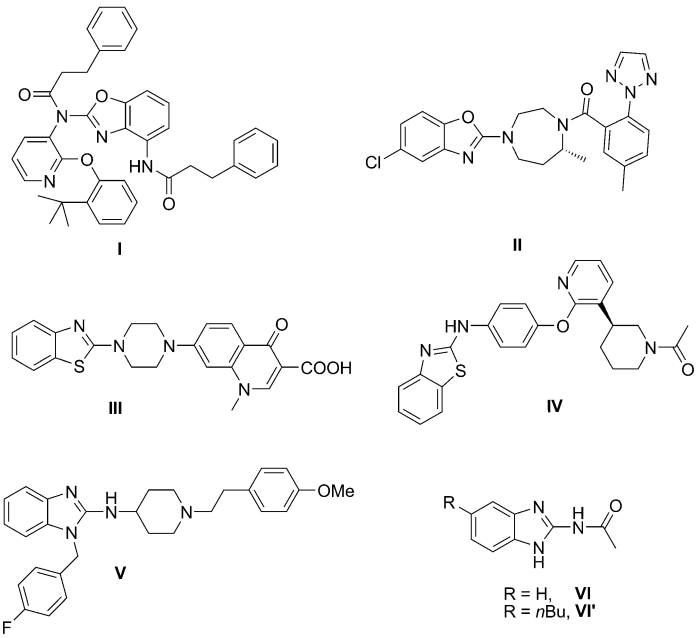
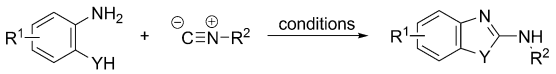


Figure 1. Selected biologically active compounds.

There are several reported approaches to these scaffolds: 1) The addition of amines to isothiocyanates or CS_2 followed by intramolecular condensation,[7,8] 2) the cross-coupling reaction of bisnucleophiles with cyanogen bromide,[9] 3) intramolecular cyclization by C–H activation,[10] and 4) passing through the intermediate formation of isocyanide dibromides.[11] All these procedures suffer from the use of unenviromental, toxic, and/or dangerous reagents and poor step efficiency. Thus, the development of a new, general, and atom-economic method to obtain these compounds remains great challenge to chemists.

Recently, reactions using isocyanide insertion (similar to carbon monoxide) have been developed for the synthesis of N-heterocycles.[12] As a continuation of our work on the insertion of isocyanide into an active N–H bond,[13] we hope to apply this insertion strategy to the reaction of isocyanide with –SH,[14] –OH,[15] and $-NH_2$[16] based bisnucleophilic reagents, such as *o*-aminophenols, *o*-aminobenzenethiol, and *o*-aminoanilines, for the synthesis of 2-aminobenzimidazoles, 2-aminobenzothiazoles, and 2-aminobenzoxazoles, respectively (Scheme 1). Moreover, since the pioneering work of Kharasch[17] on the metal-catalyzed homocoupling reaction of aromatic Grignard reagents in the middle of the 20th century, cobalt-catalyzed cross-coupling reactions have received particular attention.[18] Herein, we report a safe and efficient cobalt-catalyzed C–N, C–O(S,N) bond formation by isocyanide insertion to *o*-diaminobenzene, 2-aminobenzenethiol, and 2-aminophenol derivatives. Whilst we were preparing this paper, Orru and Maes's group reported a palladium-catalyzed isocyanide insertion to bisnucleophiles.[19]



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Scheme 1. Direct strategy for the synthesis of 2-aminobenzimidazoles, 2-aminobenzothiazoles, and 2-aminobenzoxazoles by isocyanide insertion.

We initiated our study by investigating isocyanide insertion reactions involving 2-aminophenol **1a** and *tert*-butyl isocyanide **2a**. When the model reaction was performed in the presence of nano-Co_3O_4, the desired product *N*-*tert*-butyl-

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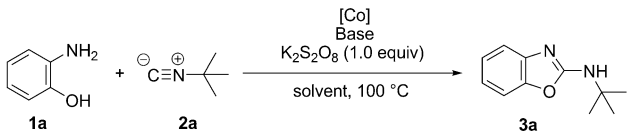
benzo[*d*]oxazol-2-amine (**3a**) was obtained in 33% LC yield (Table 1, entry 2). After optimization of the reaction conditions (see the Supporting Information and Table 1 for details), it was found that the optimal reaction conditions involved $Co(OAc)_2{\cdot}4H_2O$(10 mol%), NaOAc (2 equiv), and $K_2S_2O_8$ (1 equiv) in 1,4-dioxane at 100°C (Table 1, entry 15).

Table 1. Cobalt-catalyzed insertion reactions with 2-amino phenol **1a** of *tert*-butyl isocyanide **2a**.[a]



1a 2a 3a

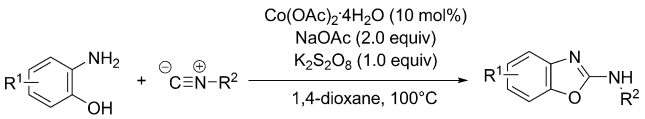
Entry	[Co]	Base	Solvent	Yield [%][b]
1	–	–	THF	0
2	nano-Co_3O_4	Na_2CO_3	THF	33
3	$Co(OAc)_2{\cdot}4H_2O$	Na_2CO_3	THF	55
4	$[Co(acac)_2]$	Na_2CO_3	THF	23
5	$[Co(acac)_3]$	Na_2CO_3	THF	trace
6	$CoCl_2{\cdot}6H_2O$	Na_2CO_3	THF	14
7	$CoSO_4$	Na_2CO_3	THF	trace
8	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	THF	80
9	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	1,4-dioxane	93
10	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	DME[c]	83
11	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	toluene	50
12	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	DMF[d]	90
13	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	DMSO[e]	85
14[f]	$Co(OAc)_2{\cdot}4H_2O$	NaOAc	1,4-dioxane	82
15[g]	**$Co(OAc)_2{\cdot}4H_2O$**	**NaOAc**	**1,4-dioxane**	**96**

[a] Reaction Conditions: 2-aminophenol **1a** (0.5 mmol), *tert*-butyl isocyanide **2a** (0.6 mmol), cobalt catalyst (20 mol%), base (2 equiv), oxidant $K_2S_2O_8$ (1 equiv), solvent (3 mL), 100°C, 18 h. [b] Yield was determined by LC analysis with biphenyl as the internal standard. [c] DME: dimethoxyethane. [d] DMF. [e] DMSO. [f] 5 mol% cobalt catalysts is used. [g] The dosage of cobalt catalyst is 10 mol%.

With the optimized conditions in hand, the scope of this reaction was investigated and the results are summarized in Table 2. The substituted 2-aminophenols (**1b–g**) reacted well with *tert*-butyl isocyanide (**2a**) (Table 2, entries 2–7) to give the desired products **3b–g** in moderate to excellent yields. It is noteworthy that 2-aminophenols bearing electron-donating groups (Me or OMe), or electron-withdrawing groups (NO_2) could afford the desired products in good yields. In addition, relatively bulky substrate **1d** also efficiently underwent the transformation, generating the desired products **3d** in 95 (Table 2, entry 2). Then, several structurally varied isocyanides were also investigated. When other aliphatic and aromatic isocyanides (**2b–e**) were applied to the reaction, the reactions also proceeded smoothly in moderate yields (67–81%) under slightly modified conditions (DMF was used as the solvent instead of 1,4-dioxane) (Table 2, entries 8–11). However, when 2-aminoethanol (**1h**) was subjected to this reaction, no desired product was observed (Table 2, entry 12).

To evaluate the general performance of our method, we further tested other amine-based bisnucleophiles, such as *o*-

Table 2. Cobalt-catalyzed isocyanide insertion reactions with 2-aminophenols **1a–h**.[a]



1a–h 2 3a–l

Entry	1	2	Product	Yield [%][b]
1	R^1=H (**1a**)	R^2=*t*Bu (**2a**)	**3a**	87
2	R^1=5-NO_2 (**1b**)	R^2=*t*Bu (**2a**)	**3b**	92
3	R^1=4-NO_2 (**1c**)	R^2=*t*Bu (**2a**)	**3c**	85
4	R^1=3-NO_2 (**1d**)	R^2=*t*Bu (**2a**)	**3d**	95
5	R^1=4-Cl (**1e**)	R^2=*t*Bu (**2a**)	**3e**	83
6	R^1=5-CH_3 (**1f**)	R^2=*t*Bu (**2a**)	**3f**	89
7	R^1=4-OCH_3 (**1g**)	R^2=*t*Bu (**2a**)	**3g**	81
8[c]	R^1=H (**1a**)	R^2=Cy (**2b**)	**3h**	67
9[c]	R^1=H (**1a**)	R^2=*n*Bu (**2c**)	**3i**	81
10[c]	R^1=H (**1a**)	R^2=2,6-$Me_2C_6H_3$ (**2d**)	**3j**	68
11[c]	R^1=H (**1a**)	R^2=Bn (**2e**)	**3k**	71
12		R^2=*t*Bu (**2a**)	**3l**	trace

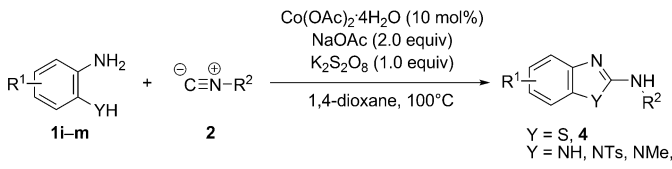
[a] Reaction Conditions: 2-aminophenol **1a–h** (0.5 mmol), isocyanide **2** (0.6 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol%), NaOAc (2 equiv), $K_2S_2O_8$ (1 equiv), 1,4-dioxane (3 mL), 100°C, 18 h. [b] Isolated yield. [c] DMF instead of 1,4-dioxane was used as the reaction solvent.

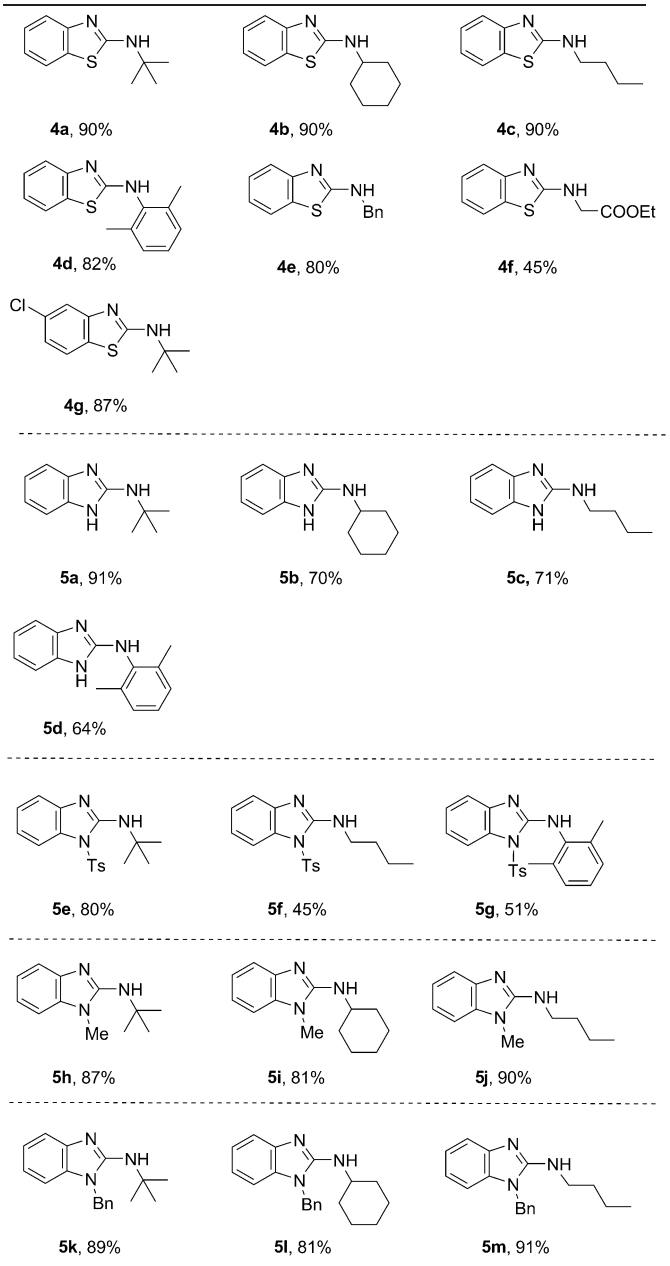
aminobenzenethiol (**1i**) and *o*-aminoanilines (**1j–m**), under the optimal conditions. The results are listed in Table 3. The reactions of 2-aminobenzenethiol (**1i**) with different isocyanides furnished the corresponding products **4a–f** in up to 90% yields (Table 3). Introducing a Cl group at the *para*-position of the aromatic ring maintained a high yield (**4g**, 87% yield).

Based on the above results, we believed that this insertion reaction would enable concise syntheses of *o*-aminobenzimidazoles by using *o*-aminoanilines instead of *o*-aminobenzenethiol as the substrate. When the reaction utilizing bisnucleophiles *o*-aminoanilines was applied to the optimized conditions, the cobalt-catalyzed isocyanide insertion reactions also proceeded well to afford the desired products in yields ranging from 45 to 91%. It was observed that the use of Ts-substituted *o*-aminoaniline **1k** gave the desired products in relatively lower yields than when Me-substituted *o*-aminoaniline **1l** or Bn-substituted *o*-aminoaniline **1k** were used (Table 3).

In conclusion, a novel and practical $Co(OAc)_2{\cdot}4H_2O$-catalyzed direct insertion reaction of isocyanides into active N–H, O(S, NR)–H bonds has been developed. This method not only expands the scope of the cobalt-catalyzed cross-coupling reaction but also provides a general, reliable, and diverse approach leading to the valuable substituted 2-aminobenzimidazole, 2-aminobenzothiazole, and 2-aminobenzoxazole frameworks. Further studies to understand the cobalt-catalyzed insertion reaction mechanism and extending this strategy to synthetic applications are ongoing in our laboratory.

Table 3. Cobalt-catalyzed isocyanide insertion reactions with other bisnucleophiles **1i–m**.[a]





[a] Conditions: bisnucleophilic reagent **1i–m** (0.5 mmol), isocyanide **2** (0.6 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol%), NaOAc (2 equiv), $K_2S_2O_8$ (1 equiv), 1,4-dioxane (3 mL), 100°C, 18 h, isolated yields.

Experimental Section

General procedure: 1,4-Dioxane or DMF (3 mL) was added to a mixture of amino compound (0.5 mmol), isocyanide (0.6 mmol), $Co(OAc)_2{\cdot}4H_2O$ (10 mol%), NaOAc (2 equiv), and $K_2S_2O_8$ (1 equiv). The mixture was stirred by magnetic stirrer in an appropriate time at 100°C until the amino compound was completely consumed (checked by TLC analysis). Then, the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as the eluents to afford pure product.

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Keywords: cobalt · cross-coupling · diversity · heterocycles · isocyanide insertion

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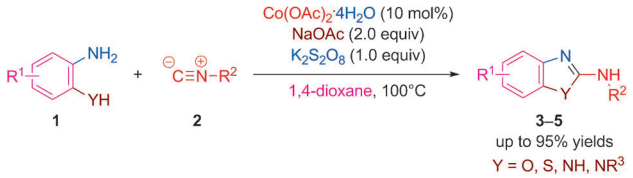

Cobalt catalysis: Synthesis of substituted 2-aminobenzimidazoles, 2-aminobenzothiazoles, and 2-aminobenzoxazoles was achieved by using cobalt(II) acetate catalyzed isocyanide insertion to *o*-diaminobenzene, 2-aminobenzenethiol, and 2-aminophenol derivatives in 1,4-dioxane (see scheme). It was found that the reaction proceeded efficiently to give the desired products in up to 95% isolated yields by C–N and C–S (O, N) formation in a single step.

Heterocycles