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Authors: Weiguang Kong, Yao Zhou, and Qiuling Song

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Lewis-acid Promoted Chemoselective Condensation of 2-Aminobenzimidazoles or 3-Aminoindazoles with 3-Ethoxycyclobutanones to Construct Fused Nitrogen heterocycles

Weiguang Kong,[a,b] Yao Zhou,[a,b] Qiuling Song[a,*]

[a] Institute of Next Generation Matter Transformation, College of Chemical Engineering at Huaqiao University, 668 Jimei Blvd, Xiamen, Fujian, 361021, P. R. China

[b] W. Kong and Y. Zhou contributed equally to this work.
fax:(+86)-592-6162990; email: qsong@hqu.edu.cn

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Abstract: A Lewis-acid promoted chemoselective condensation of 2-aminobenzimidazoles or 3-aminoindazoles with 3-ethoxycyclobutanones is presented. Diverse fused heterocycles benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives were obtained in moderate to high yields under mild conditions, the reaction mechanism of which was in sharp contrast to previous [3+3] annulation reaction of 3-ethoxycyclobutanones.

Keywords: chemoselective condensation; benzo[4,5]-imidazo[1,2-*a*]pyrimidine; pyrimido[1,2-*b*]-indazole; 3-ethoxycyclobutanones; [3+3] annulation

Due to the important biological activity and therapeutic effect, fused nitrogen heterocyclic skeletons are present in a broad range of natural products and synthetic molecules.[1] Among them, benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives have emerged as two frequent scaffolds. As shown in Figure 1, compound **A** (T808) can work as a specific PET tracer for imaging of Tau Pathologies.[2] Compound **B** displays good antiinflammatory activity against IL-6

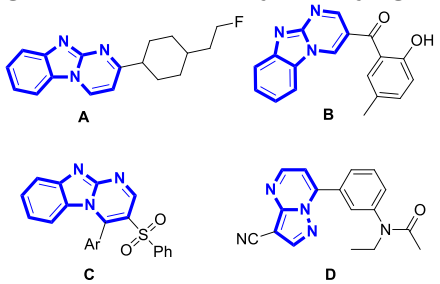
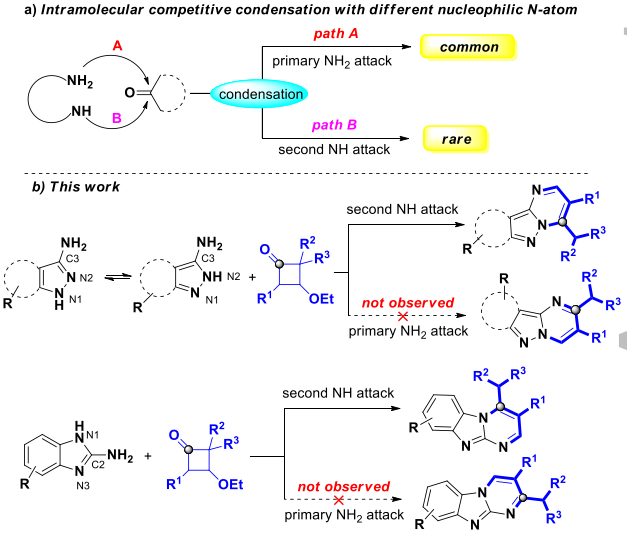


Figure 1. Some representatively bioactive compounds.

and TNF-α,[3] and compound **C** exhibits decent biological properties, such as anticancer and analgesic/anti-inflammatory activities.[4] Compound **D** is a commercial drug—Zaleplon, which has the hypnotic and sedative effects for the therapy of insomnia.[5] These important benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole[7] derivatives could be achieved from 2-aminobenzimidazoles and 3-aminoindazoles, which are two families of the most important classes of heterocycles for drug and material development purposes. In recent years, condensation of 2-aminobenzimidazoles and 3-aminoindazoles with carbonyl compounds is the frequent and effective tactic for the construction of benzo[4,5]-imidazo[1,2-a]pyrimidine[6] and pyrimido[1,2-*b*]-indazole derivatives.[7] However, all the three adjacent



Scheme 1. Chemoselective condensation of 2-aminobenzimidazoles or 3-aminoindazoles

nucleophilic nitrogens in 2-aminobenzimidazoles and 3-aminoindazoles could attack and condense the carbonyl group, leading to the inseparable regioisomers, which might limit the application of 2-

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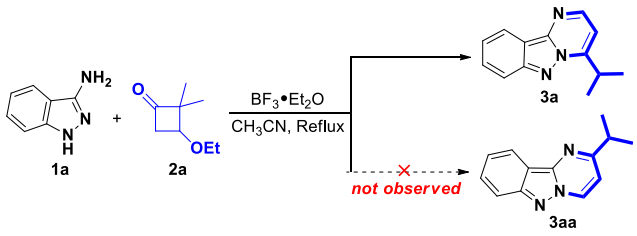
aminobenzimidazoles and 3-aminoindazoles to construct fused N-heterocycles. Therefore, the development of an efficient and facile method to accomplish the chemoselective reaction of these three nucleophilic nitrogens is highly desirable and poses a significant challenge. In generally, when 2-aminobenzimidazoles and 3-aminoindazoles were used to access N-heterocycles, the free primary NH_2 group condensed of the carbonyl compounds preferentially and then other annulation reactions occurred (Scheme 1a Path A). The publications in which efficient cyclization reactions stem from the N1 or N2 in 3-aminoindazoles and N1 or N3 in 2-aminobenzimidazoles are relatively rare (Scheme 1a Path B).[6k]

In recent years, 3-ethoxycyclobutanones has emerged as a fruitful synthon to build N-heterocycles.[8] For example, Matsuo's group developed the [4+2] cycloaddition reactions[9] and Rao's group discovered the [3+3] annulation reactions[10] by employing 3-ethoxycyclobutanones as annulation partners. Very recently, our group also demonstrated a [3+3] annulation reaction between 3-ethoxycyclobutanones and enamines or amidines towards substituted pyrimidine and pyridine derivatives.[11] Although 3-ethoxycyclobutanones have been used for preparation of various nitrogen heterocycles, the 3-ethoxycyclobutanones have never been employed to construct the important benzo[4,5]-imidazo[1,2-a]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives. As part of our ongoing interest in activation of cyclobutanones,[11,12] we herein report transition-metal free synthesis of benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives via chemoselective condensation of 2-aminobenzimidazoles and 3-aminoindazoles with 3-ethoxycyclobutanones, in which the heteroatomic nitrogen rather than the free primary NH_2 of 2-aminobenzimidazoles or 3-aminoindazoles condensed 3-ethoxycyclobutanones preferentially (Scheme 1b).

At the outset of our investigation, commercial 1*H*-indazol-3-amine (**1a**) and 2,2-dimethyl-3-ethoxycyclobutanone (**2a**) condensed in the presence of BF_3•Et_2O in CH_3CN at reflux temperature for 12 h. As expected, a white solid was obtained after column

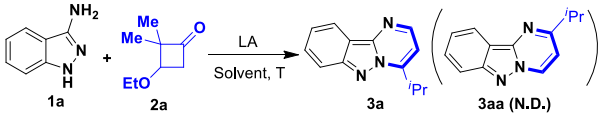


Scheme 2. Condensation of 1*H*-indazol-3-amine **1a** with 2,2-dimethyl-3-ethoxycyclobutanone (**2a**)

chromatography. However, the accurate structure of the product was unambiguously for the fact that the three adjacent nucleophilic nitrogens in 1*H*-indazol-3-amine (**1a**) could attack and condense the 2,2-dimethyl-3-ethoxycyclobutanone (**2a**), which might ferment different reaction pathways to render various products (Scheme 2). The exact structure of the product was confirmed by the X-ray crystallographic analysis,[13] which revealed that the product we obtained was **3a** rather than **3aa**.

Having identified the product structure, we then turned our attention to optimize the reaction conditions for this chemoselective condensation (Table 1). When the reaction was performed using BF_3•Et_2O as Lewis-acid in MeCN at 80 °C, 89% yield of **3a** was gained (Table 1, entry 1). Subsequently, we tested other Lewis-acids (Table 1, entries 2-5). Among the Lewis-acids investigated, BF_3•Et_2O still demonstrated the optimal efficiency. We also screened the solvent effects on this transformation and it turned out DCM was the best choice (Table 1, entry 6). The attempt to reduce the reaction temperature slightly decreased the yield of **3a** (Table 1 entries 12-13). Disappointingly, only marginal improvements were acquired when we changed the loading of BF_3•Et_2O (Table 1, entries 14-15). To our delight, the yield of **3a** has no distinct influence when we shorten the reaction time to 6 h (Table 1, entry 16).

Table 1. Screening of the reaction conditions



Entry[a]	LA	Solvent	Temperature	Yield of 3a[b]
1	BF_3•Et_2O	CH_3CN	80 °C	(89%)[c]
2	$B(C_6F_5)_3$	CH_3CN	80 °C	N.D.
3	$Sc(OTf)_3$	CH_3CN	80 °C	26%
4	$Yb(OTf)_3$	CH_3CN	80 °C	<10%
5	$SnCl_4$	CH_3CN	80 °C	N.D.
6	BF_3•Et_2O	DCM	80 °C	(92%)[c]
7	BF_3•Et_2O	DCE	80 °C	76%
8	BF_3•Et_2O	DMF	80 °C	N.D.
9	BF_3•Et_2O	DMSO	80 °C	N.D.
10	BF_3•Et_2O	Dioxane	80 °C	28%
11	BF_3•Et_2O	EtOAc	80 °C	31%
12	BF_3•Et_2O	DCM	50 °C	79%
13	BF_3•Et_2O	DCM	RT	77%
14[d]	BF_3•Et_2O	DCM	80 °C	82%
15[e]	BF_3•Et_2O	DCM	80 °C	52%
16[f]	BF_3•Et_2O	DCM	80 °C	91%

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), BF_3•Et_2O (0.2 mmol) DCM (1 mL), 80 °C, Air, 12 h. [b] GC yields. [c] Isolated yields. [d] BF_3•Et_2O (1.5 eq). [e] BF_3•Et_2O (0.5 eq). [f] 6 h.

Having established the optimal reaction conditions, the substrate scope of this chemoselective condensation of 3-aminoindazoles with 3-ethoxycyclobutanones was examined firstly (Scheme 3). A series of 3-ethoxycyclobutanones (**2a-2g**) proved to be efficient annulation partners and

Scheme 3. Substrate scope for the synthesis of various pyrimido[1,2-*b*]-indazoles

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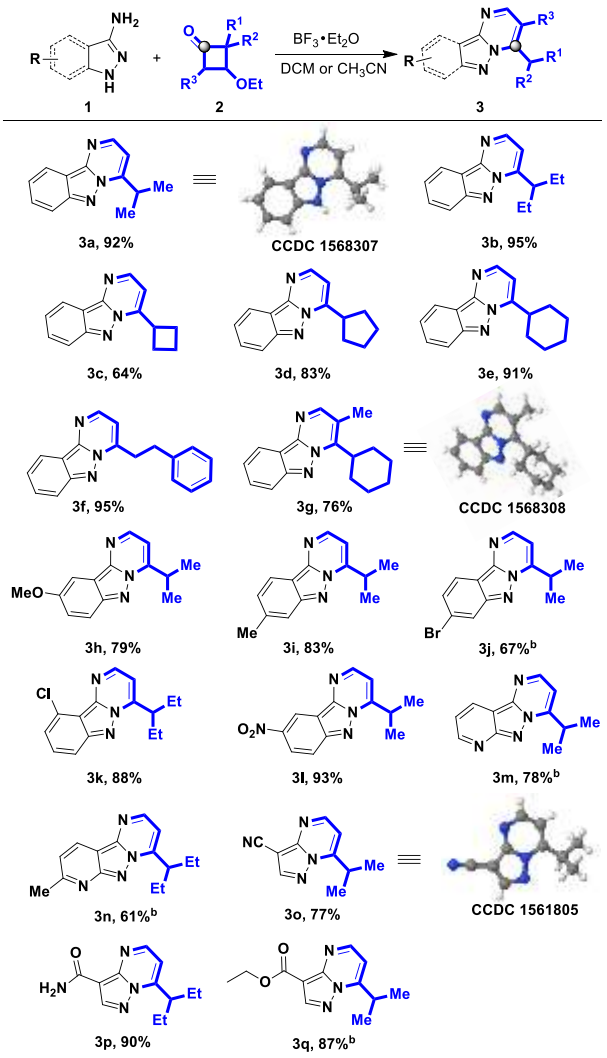
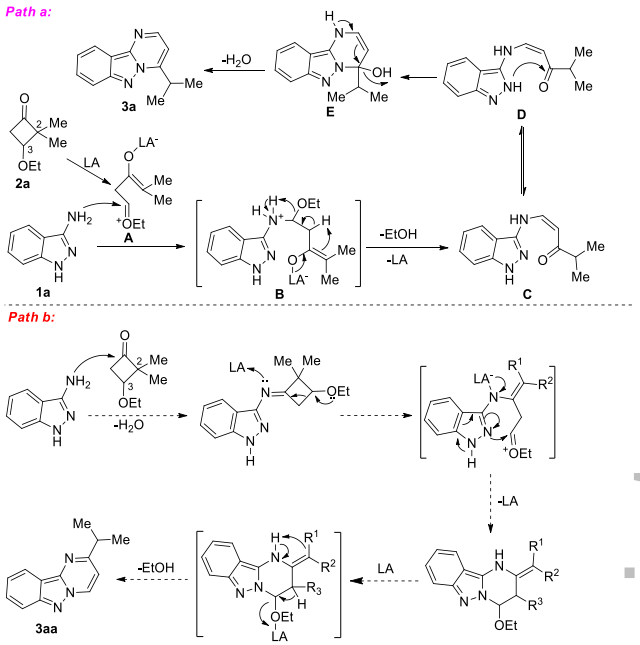


[a] Unless otherwise noted, the reactions were run with **1** (0.3 mmol), **2** (0.45 mmol) and BF_3•Et_2O (0.3 mmol) in DCM (1 mL) at 80 °C for 6-12 h. [b] CH_3CN as the solvent.

delivered the desired products (**3a**-**3g**) in good to excellent yields. Similarly smooth transformations were also achieved for 3-aminoindazoles bearing various groups at different positions of the phenyl ring. For instance, electron-donating groups substituted 3-aminoindazoles **1h** and **1i** were good candidates in this transformation, delivering the corresponding pyrimido[1,2-*b*]-indazoles in 79% and 83% yield, respectively. Electron-withdrawing groups substituted 3-aminoindazoles **1j**-**1l** were amenable to this transformation as well, rendering the expected products **3j**-**3l** in good to high yields. To our delight, heteroaromatic 3-aminoindazoles **1m** and **1n** could work smoothly under standard conditions as well, giving the desired products **3m** and **3n** in good yields. In addition to 3-aminoindazoles, 3-aminopyrazoles such as **1o**-**1q** were also good substrates in this transformation and produced the targeted products **3o**-**3q** in 77%, 90% and 87% yields, respectively.

As depicted in Scheme 4, when 3-aminoindazoles reacted with 3-ethoxycyclobutanones, there are two possible pathways for condensation and annulation to



Scheme 4. Proposed Reaction Mechanism

deliver the products. To understand the reaction mechanism, we cultivated several crystals and the X- ray crystallographic analysis of **3a**, **3g** and **3o** confirmed the accurate position of the isopropyl, which was in sharp contrast to previous documents. Based on the reaction mechanism of previous reports,[10,11] when anilines, hydrazines, enamine and amidines reacted with 3-ethoxycyclobutanones, the free primary NH_2 group condensed of the carbonyl group preferentially and then other intramolecular annulation reactions occurred. If so, the product in this transformation should be **3aa** in which the isopropyl was adjacent to nitrogen-atom of the free primary NH_2 group (path b in Scheme 4). However, the product we acquired was **3a**, which implied the presence of unique reaction mechanism of this transformations and it might undergo the path a in Scheme 4 to give the product **3a**. Firstly, BF_3•Et_2O activates cyclobutanone **2a** via cleaving the more substituted C2–C3 bond to form the zwitterionic intermediate **A**,[8-11,14] which further was attacked by 3-aminoindazole **1a** to generate the intermediate **B**. Elimination of Lewis-acids and one molecule of EtOH from intermediate **B** provides intermediate **C**. Subsequently, intramolecular attack the carbonyl group by the N2 in 3-aminoindazoles renders intermediate **E**, which undergoes elimination of one molecule of H_2O to furnish the product **3a**.

Inspired by the successful synthesis of various pyrimido[1,2-*b*]-indazoles via chemoselective condensation of 3-aminoindazoles and 3-ethoxycyclobutanones. Next we focused on the scope for the reaction of 2-aminobenzimidazoles and 3-ethoxycyclobutanones. As summarized in Scheme 5, a series of benzo[4,5]-imidazo[1,2-*a*]pyrimidine derivatives were synthesized by the

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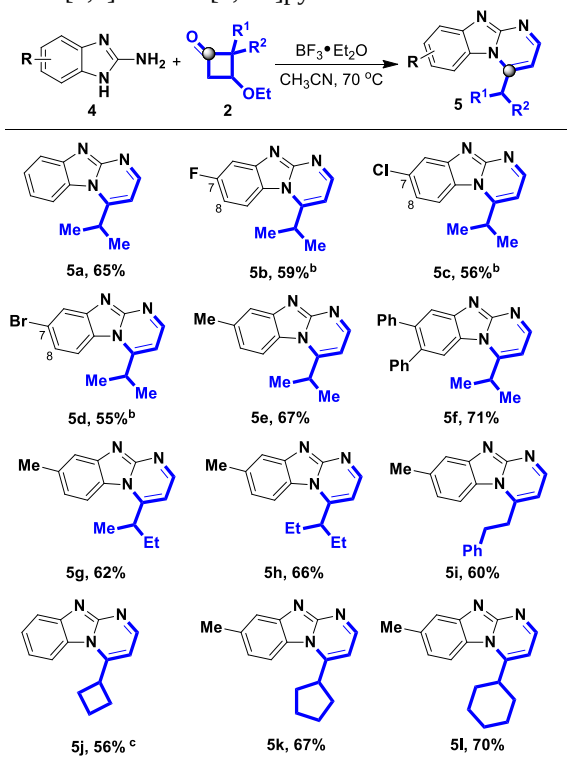
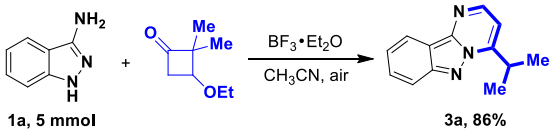
Sheme 5. Substrate scope for the synthesis of various Benzo[4,5]-imidazo[1,2-*a*]pyrimidines



Unless otherwise noted, the reactions were run with **4** (0.3 mmol), **2** (1.8 eq) and BF_3 Et_2O (0.3 mmol) in CH_3CN (1 mL) at 70 °C for 18 h. [b] the ratio at C7 and C8 was 1:1. [c] **2** (2 eq)

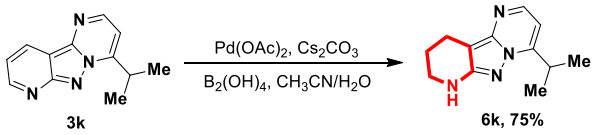
reaction of differently substituted 2-aminobenzimidazoles **4** and 3-ethoxycyclobutanones **2**. Halo-substituted 1*H*-benzo[d]imidazol-2-amines such as fluorine, chlorine and bromine were well compatible in this transformation, affording the desired benzo[4,5]-imidazo[1,2-*a*]pyrimidines (**5b**-**5d**) in moderate yields. Although the isomers were observed when mono-substituted 2-aminobenzimidazoles (**4b**-**4d**) were employed, a single configuration was obtained when electron-donating groups were installed on 2-aminobenzimidazoles. For instance, 5-methyl-1*H*-benzo[d]imidazol-2-amine **4e** produced the corresponding product **5e** in 69% yield and no isomer was detected from ^{1}H-NMR. In addtion to the mono-substituted 2-aminobenzimidazoles, the bis-substituted 2-aminobenzimidazole **4f** was also good candidate for this [3+3] annulation and delivered the targeted product **5f** in 71% yield. Subsequently, a variety of 3-ethoxycyclobutanones were investigated under standard conditions, which turned out that they were both amenable to this transformation and provided the corresponding benzo[4,5]-imidazo[1,2-*a*]pyrimidines (**5g**-**5l**) in moderate to good yields.



(eq 1)

We also explored the scalability of this chemoselective condensation of 3-aminoindazoles with 3-ethoxycyclobutanones. When current protocol was performed with 5 mmol of **1a**, the desired product **3a** was obtained in good yield without loss of efficiency (eq 1).

Recently, our group disclosed an effective palladium-catalyzed reduction of N-heterocyclic compounds via diboron-assisted transfer hydrogenation of water.[15] We were inquisitive whether the benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives of current protocol could be reduced. To our delight, when 4-isopropylpyrido[2',3':3,4]pyrazolo[1,5-*a*]pyrimidine **3k** was subjected to the hydrogenation reactions, the selective reduction of this fused N-heterocycles did occur and delivered the product **6k** in good yield (Scheme 6).



Scheme 6. Selective reduction of 3k

In summary, a facile and one-pot method has been developed for the synthesis of benzo[4,5]-imidazo[1,2-*a*]pyrimidine and pyrimido[1,2-*b*]-indazole derivatives in moderate to high yields. The desired fused nitrogen heterocycles were obtained via Lewis-acid promoted chemoselective condensation of 2-aminobenzimidazoles or 3-aminoindazoles with 3-ethoxycyclobutanones, the reaction mechanism of which was in sharp contrast to previous [3+3] annulation reaction of 3-ethoxycyclobutanones. It is noteworthy that the current protocol could be readily scaled up without loss of the efficiency.

Experimental Section

General process for the synthesis of 3:

BF_3•Et_2O (42.6 mg, 0.3 mmol, 1.0 equiv) was added to a mixture of 1*H*-indazol-3-amine **1** (0.3 mmol, 1 equiv), cyclobutanones **2** (0.3 mmol, 1.5 equiv) in DCM or CH_3CN (1 mL). Then the sealed tube was stirred at 80 °C for 6~12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the desired product **3**.

General process for the synthesis of 5:

BF_3•Et_2O (42.6 mg, 0.3 mmol, 1.0 equiv) was added to a mixture of 1H-benzo[d]imidazol-2-amine **4** (0.3 mmol, 1 equiv), cyclobutanones **2** (0.3 mmol, 1.5 equiv) in CH_3CN (1 mL). Then the sealed tube was stirred at 80 °C for 18 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, MeOH:EtOAc = 1:100, v/v) to give the desired product **5**.

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