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Copper(II)/Iron(III) Co-catalyzed Intermolecular Diamination of Alkynes: Facile Synthesis of Imidazopyridines

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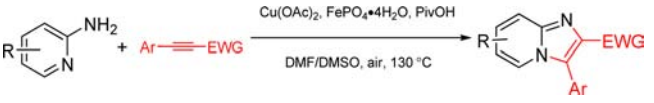
ABSTRACT



A facile synthesis of imidazo[1,2-α]pyridines has been achieved by copper(II) and iron(III) co-catalyzed C−N bond formation. This reaction involves an intermolecular oxidative diamination of alkynes with high chemoselectivity and regioselectivity.

The imidazo[1,2-α]pyridine skeleton is a privileged structure widely found in many pharmacologically important compounds.[1] Accompanied by an extensive range of bioactivities such as antiviral, antibacterial, fungicidal, and anti-inflammatory properties,[2] the significance of the imidazo[1,2-α]pyridine scaffold in the drug discovery sector is well appreciated. Because of such appealing benefits, many commercially available drugs featuring this scaffold have been developed. Common imidazo[1,2-α]pyridine-derived drugs (Figure 1) include alpidem[3] and zolpidem,[4] which are used to treat anxiety and insomnia, necopidem and saripidem,[5] which possess sedative and anxiolytic effects, and the optically active GSK812397, which is a candidate for the treatment of HIV infection.[6] The ubiquitous emergence of such compounds in the pharmaceutical industry signals huge potential for molecules of this class, resulting in an ever-growing interest in the synthesis of imidazo[1,2-α]pyridines.

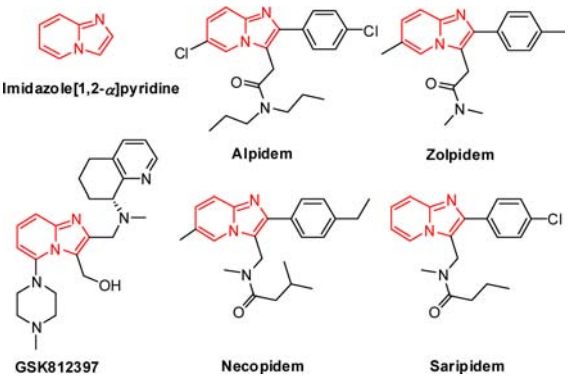


Figure 1. Imidazo[1,2-α]pyridine-based drugs.

Although various synthetic methods have been developed to prepare imidazo[1,2-α]pyridine heterocyclic scaffolds,[7] the utility of these methods is often limited by the numerous steps required to obtain the precursors and their narrow

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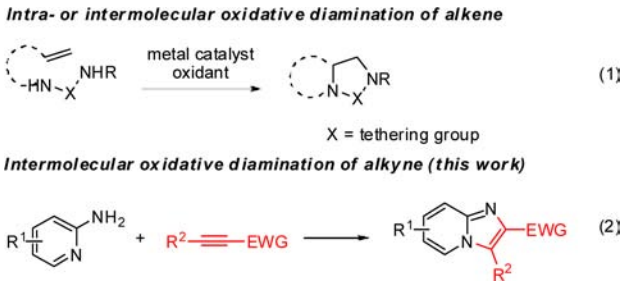


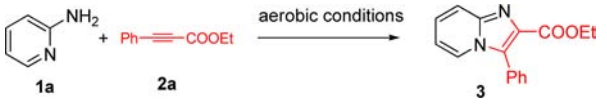
Figure 2. Intra- and intermolecular diamination of alkenes and alkynes.

substrate scope. Recently, several elegant methods have been reported for the synthesis of imidazo[1,2-α]pyridines, including a copper-catalyzed three-component coupling reaction,[8] copper-catalyzed intramolecular C−H amination,[9] dehydrogenative amino oxygenation,[10] asymmetric organocatalytic [3 + 2]-annulation,[2] etc. The dearth of methods means that the continuation of research in this area is imperative.

Oxidative olefin diamination is rapidly becoming an active area of research. It provides a powerful entry to vicinal diamines which exhibit wide utilities in drug discovery, materials, and catalysis.[11] To date, olefin diamination has been largely explored using stoichiometric or catalytic amounts of palladium,[12] nickel,[13] gold,[14] and copper[15] in an intra- or intermolecular manner (Figure 2, eq 1).[16] However, reports about the intermolecular diamination of alkynes remain surprisingly limited.[17] In continuation of our interest in the development of novel methodology for the synthesis of heterocyclic compounds,[18] we envisaged that intermolecular diamination of internal alkynes with 2-aminopyridines might provide a versatile and an efficient way to synthesize imidazo[1,2-α]pyridines (Figure 2, eq 2). The successful implementation of this strategy would imply developing a novel route that bypasses the difficulties associated with previous methods, providing an alternative route to imidazopyridines.

We commenced our study by investigating the reaction of 2-aminopyridine **1a** (1.0 equiv) with ethyl phenylpropiolate **2a** (1.5 equiv) in the presence of $Pd(OAc)_2$ (0.1 equiv) and $Cu(OAc)_2$ (0.2 equiv) in DMF at 110 °C under O_2 atmosphere (Table 1, entry 1). Unfortunately, the reaction did not proceed under basic conditions, but when PivOH was

Table 1. Optimization of Oxidative Diamination Reaction[a]



entry	catalyst (equiv)	additive (equiv)	yield[b] (%)
1	$Pd(OAc)_2$ (0.1), $Cu(OAc)_2$ (0.2)	K_2CO_3 (2)	
2	$Pd(OAc)_2$ (0.1), $Cu(OAc)_2$ (0.2)	PivOH (2)	21
3	$Cu(OAc)_2$ (0.2), PivOH (2)		20
4	$Cu(OAc)_2$ (0.5), PivOH (2)		30
5	$Cu(OAc)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	49
6	$Cu(acac)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	31
7	$Cu(nd)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	32
8	$Cu(TFA)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	34
9	$CuCl_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	
10	CuBr (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	
11[c]	$Cu(OAc)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	55
12[d]	$Cu(OAc)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	41
13[e]	$Cu(OAc)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	67
14[f]	$Cu(OAc)_2$ (0.1), $FePO_4 \cdot 4H_2O$ (0.1)	PivOH (2)	72
15[f]	$Cu(OAc)_2$ (0.1), $Fe(acac)_3$ (0.1)	PivOH (2)	68
16[f]	$Cu(OAc)_2$ (0.1), $Fe(OAc)_2$ (0.1)	PivOH (2)	54
17[f]	$Cu(OAc)_2$ (0.2)	PivOH (2)	55
18[f]	$FePO_4 \cdot 4H_2O$ (0.5)	PivOH (2)	

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.2 mmol, 1 equiv) and **2a** (0.3 mmol, 1.5 equiv) with catalyst and additive in DMF (2 mL) at 110 °C under O_2 atmosphere for 24 h. [b] Isolated yields of **4a**. [c] Reaction was carried out in DMF and DMSO (10:1, 2 mL). [d] Reaction was carried out in DMSO (2 mL). [e] Reaction was carried out using **2a** (0.2 mmol, 1 equiv), **1a** (0.3 mmol, 1.5 equiv) in DMF, and DMSO (10:1, 2 mL) at 110 °C under O_2 atmosphere. [f] Reaction was carried out using **2a** (0.2 mmol, 1 equiv), **1a** (0.3 mmol, 1.5 equiv) in DMF, and DMSO (10:1, 2 mL) at 130 °C under air. $Cu(acac)_2$ = copper(II) acetylacetonate; $Cu(nd)_2$ = copper(II) neodecanoate; PivOH = pivalic acid; $Cu(TFA)_2$ = copper(II) trifluoroacetate.

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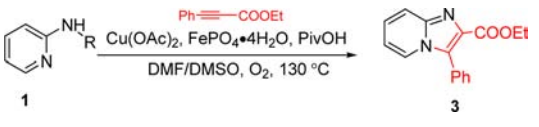
used as an additive instead of K_2CO_3 (Table 1, entry 2), the desired product **3** was obtained in 21% yield (see the Supporting Information). Interestingly, with only $Cu(OAc)_2$ as catalyst, the reaction still proceeded to afford the desired product, and 0.5 equiv of $Cu(OAc)_2$ was able to achieve a higher yield as compared to 0.2 equiv (Table 1, entries 3 and 4). Recent reports on copper/iron co-catalyzed C−H activation and C−H amination[10,19] prompted us to employ iron in this reaction system. To our delight, the combination of $Cu(OAc)_2$ and $FePO_4 \cdot 4H_2O$ increased the yield to 49% (Table 1, entry 5). Among the tested copper salts, $Cu(acac)_2$ and $Cu(nd)_2$ produced lower yields, while $Cu(TFA)_2$, despite shortening the reaction time, decreased the yield because of an increased amount of byproduct (Table 1, entries 6−8). In addition, copper halogenides such as $CuCl_2$ and CuBr were found to be totally inefficient (Table 1, entries 9 and 10). In the investigation of solvents, we utilized a 10:1 mixture of DMF and DMSO as solvent to further increase the yield to 55% (Table 1, entry 11). Interestingly, DMSO alone did not promote the reaction (Table 1, entry 12). When excess of **1a** was added to the reaction mixture (Table 1, entry 13), the yield of **3** was improved to 67%. The reaction temperature was increased to 130 °C to further improve the yield to 72% (Table 1, entry 14). In this case, air could be used as terminal oxidant. Further investigation on a number of iron salts revealed that $Fe(acac)_3$ gave a slightly lower yield (Table 1, entry 15). The Fe(II) compound $Fe(OAc)_2$ gave lower yields even though it might be oxidized to Fe(III) in the reaction system (Table 1, entry16).When the reaction was carried out without iron(III) catalyst (Table 1, entry 17), only 55% of product was obtained. However, a complex mixture was observed and no desired product was isolated when the reaction was carried out with only an iron(III) catalyst (Table 1, entry 18).

The reactivity of *N*-protected aminopyridine was also investigated using the optimized conditions above under an O_2 atmosphere (Table 2). It was observed that with methyl- or *tert*-butyl-protected aminopyridine, no product was formed. This could be due to the stabilizing and steric effects of the protecting groups. On the other hand, the reaction with acetyl-protected substrates gave the desired product in 28% yield, along with recovered starting material, whereas for Boc- or COOEt-protected aminopyridines, better yields were observed as compared to other protecting groups, but yields were still lower than 50%. Consolidating the observations on the optimization studies, we concluded that the best yields was obtained when the reaction was conducted with 1.5 equiva of unprotected 2-aminopyridine, 1 equiv of alkyne, 0.1 equiv of $Cu(OAc)_2$ and $FePO_4 \cdot 4H_2O$, and 2 equiv of PivOH in DMF and DMSO (10:1) at 130 °C under an air atmosphere.

Table 2. Optimization of Various *N*-Protected Aminopyridines[a]



1 3

entry	R	yield[b] (%)	entry	R	yield[b] (%)
1	**1b**, R = Me		4	**1e**, R = Boc	34
2	**1c**, R = *tert*-Butyl		5	**1f**, R = COOEt	42
3	**1d**, R = Ac	28			

[a] Unless otherwise specified, all reactions were carried out using **1** (0.2 mmol, 1 equiv), **2a** (0.3 mmol, 1.5 equiv), $Cu(OAc)_2$ (0.02 mmol, 0.1 equiv.) and $FeSO_4 \bullet 4H_2O$ (0.02 mmol, 0.1 equiv) in DMF and DMSO (10:1, 2 mL) at 130 °C under O_2 for 24 h. [b] Isolated yields.

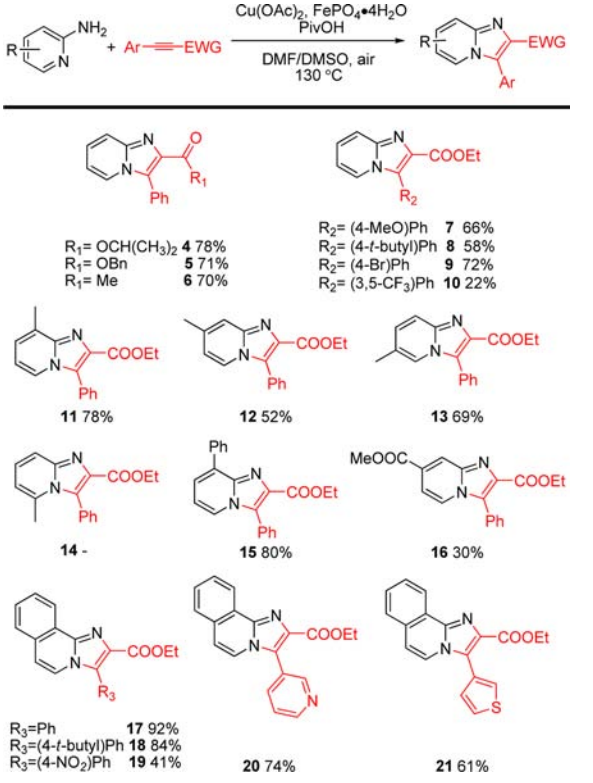


Figure 3. Substrate scope of the diamination reaction.

With this optimized set of conditions in hand, we further investigated the substrate scope (Figure 3). Good yields were obtained when 2-aminopyridine was reacted with isopropyl or benzyl phenylpropiolate (**4** and **5**). Smooth progress was also observed for ynone affording **6** in a reasonable yield. Ethyl phenylpropiolates substituted with electron-donating groups proceeded well under the optimized reaction conditions, and acceptable yields were observed (**7**−**9**). However, the reaction with (3,5-bistrifluoromethyl)phenylpropiolate gave the resulting product **10** in poor yield. Unfortunately, the reaction with unactivated alkynes such as diphenylacetylene did not proceed to give the desired products under the current reaction conditions.

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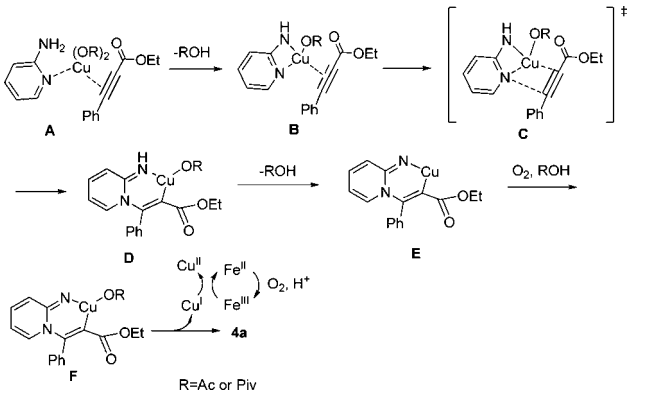
2-Aminopyridines substituted at the 3-, 4-, and 5-positions also underwent this oxidative cyclization reaction to form the corresponding products (Figure 3). Notably, the reactions with 3- and 5-methyl substrates (**11**, **13**) gave much higher yields than that of the 4-methyl substrate (**12**). Conversely, even with higher temperature and longer reaction times (140 °C, 48 h), 2-amino-6-methylpyridine did not afford the expected product (**14**). This could be due to the steric hindrance of the 6-methyl group. In addition, electron-withdrawing groups exerted a negative effect on the reactivity of 2-aminopyridine, as exemplified when methoxy carboxylate was placed at the 4-position of 2-aminopyridine (**16**), which resulted in a lower yield. Interestingly, when 1-amino-2-isoquinoline was reacted with ethyl phenylpropiolate or ethyl (4-tertbutyl) phenylpropiolate, the reactions were able to produce the corresponding products in good to excellent yields (**17** and **18**). The reaction with ethyl (4-nitro)phenylpropiolate also generated the desired product **19** in an acceptable yield. Heterocyclic substituted propiolates performed very well, affording the respective imidazo[1,2-*a*]isoquinoline in a reasonable yield (**20** and **21**).

Although detailed experimental evidence is still pending, a plausible mechanism for this reaction is outlined in Scheme 1. It is suggested that copper will coordinate with the endocyclic nitrogen atom of 2-aminopyridine as depicted in **A**.[20] and *cis*-aminocupration[21] will occur (might through transition state **C**) to produce Cu(II) intermediate **D**. Deprotonation would give intermediate **E** which can further be oxidized to a reactive Cu(III) intermediate **F**.[22] Reductive elimination then can take place to deliver the product **4a**,[23] with concurrent formation of Cu(I). In the reaction system, Fe(III) is suggested to oxidize Cu(I) to Cu(II). Finally, Fe(II) is oxidized to Fe(III) by O_2 to close the catalytic cycle.

Scheme 1. Proposed Reaction Mechanism



In summary, we have documented, for the first time, a Cu(II) and Fe(III) co-catalyzed diamination of 2-aminopyridines and 2-aminoisoquinolines with readily available alkynes. The strategy allows for the direct synthesis of imidazo[1,2-*a*]pyridines and imidazo[1,2-*a*]isoquinolines in yields of up to 92%. These structures are ubiquitously found in a large variety of compounds which possess important pharmacological properties that are essential to the biopharmaceutical and chemical sectors. Our discovery provides simple, facile, and straightforward access to an extensive array of compounds and synergizes the well-explored intramolecular diamination of alkenes to alkynes in an intermolecular manner. For aminopyridines and aminoquinolines, the high levels of chemoselectivity and regioselectivity of the two nitrogens were demonstrated for a range of compounds, demonstrating the flexibility and good reactivity of this strategy. Further studies into the application of this unique and efficient methodology to unactivated alkynes and investigations on the mechanism are currently underway in our laboratory.

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Supporting Information Available. Experimental procedure, characterization of all of the products, and X-ray data for compounds **3** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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