Title

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Multi-Component Synthesis of Imidazo[1,2-*a*]pyridines: Aerobic Oxidative Formation of C-N and C-S Bonds by Flavin–Iodine-Coupled Organocatalysis

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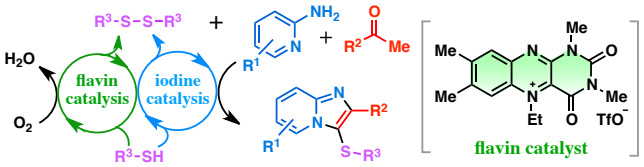
Supporting Information Placeholder



ABSTRACT: Herein, we report an aerobic oxidative C-N bond-forming process that enables the facile synthesis of imidazo[1,2-*a*]pyridines and takes advantage of a coupled organocatalytic system that uses flavin and iodine. Furthermore, the dual catalytic system can be applied to the one-pot three-step synthesis of 3-thioimidazo[1,2-*a*]pyridines from aminopyridines, ketones, and thiols.

The development of green and atom-economical aerobic oxidation systems for diverse organic transformations is a central theme of modern organic chemistry.[1] Molecular oxygen is recognized to be an ideal terminal oxidant because of its sustainable abundance, safety, cost-effectiveness, atom-economy, and minimally polluting nature. However, aerobic oxidation is generally kinetically unfavourable and often suffers from narrow substrate scope and poor selectivity, which make it difficult to develop multi-step and multi-component reactions using aerobic process, despite such reactions providing atom- and step-economical syntheses that fulfil the strong demands of green and sustainable chemistry.[2] On the other hand, living cells apply well-designed multiple catalytic systems to synthesize diverse complex molecules through multistep reactions that use molecular oxygen under mild conditions. The construction of biomimetic multiple catalytic systems is among the most promising approaches for designing efficient multi-step organic syntheses.[3] Flavin catalysts have evolved because they mimic the enzymatic function of flavin monooxygenase, which promotes selective aerobic oxygen-atom-transfer reactions in the presence of reductive coenzyme NAD(P)H,[4] and, as a result, catalyzes a diverse range of aerobic oxygenations that require reducing agents to activate molecular oxygen.[5,6] As evidenced by the diverse range of flavin-containing enzymatic systems in nature,[7] flavin catalysis, with its modest and versatile oxidizing ability, is expected to be suitable for constructing multiple catalytic systems.[8,9]

Imidazo[1,2-*a*]pyridine is a privileged heterocyclic structure that is found in numerous biologically active pharmaceuticals and natural products.[10] Many commercially available drugs, such as alpidem,[11] zolpidem,[11] nicopidem,[12] saripidem (anxiolytic agents),[12] zolimidine (a gastroprotective agent),[13] olprinone (a cardiotonic agent),[14] and rifaximin (an antibiotic),[15] as well as potential medicinal candidates[16] contain this scaffold (Figure 1). Due to their importance not only to medicinal chemistry, but also to materials science,[17] a range of methods for the synthesis of imidazo[1,2-*a*]pyridines has been developed.[18,19] Among them, aerobic oxidative cyclizations from simple and readily available 2-aminopyridines **1** and ketones **2** is recognized to be an atom-economical and straightforward way that generates environmentally benign water as the only by-product, and the copper-catalyzed systems that use zinc, indium, and boron as a cocatalyst have been reported (Figure 2A).[20] However, the examples have been limited to the copper-catalyzed method, and the development of other approaches is required to increase options. In this article, we report the first metal-free aerobic system for the synthesis of imidazo[1,2-*a*]pyridines **3** that uses a coupled flavin–iodine (**4•TfO**/I_2) catalyst (Figure 2B). The flavin–iodine-coupled organocatalytic system was recently

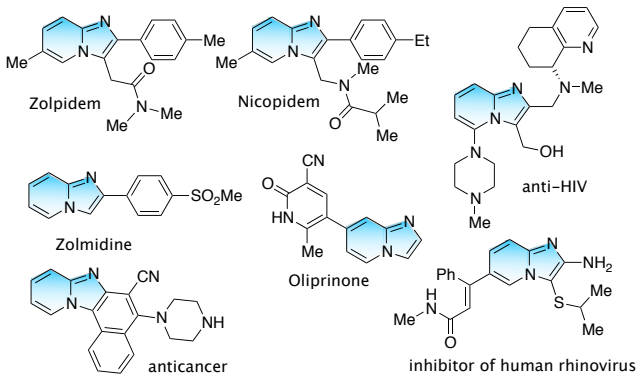


Figure 1. Structures of biologically important imidazo[1,2-*a*]pyridines.

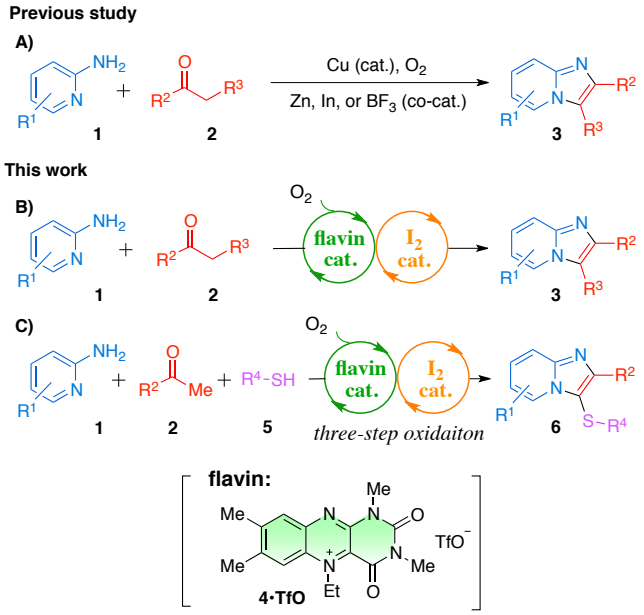


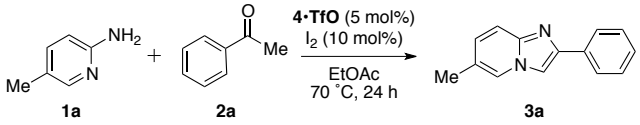
Figure 2. (A, B) Methods for the synthesis of **3** by the aerobic oxidative cyclization of **1** and **2**. (C) One-pot synthesis of **6** through the three-step oxidation of **1**, **2**, and **5**.

developed for the oxidative formation of C-S bonds, in which the biomimetic flavin catalyst activates molecular oxygen through electron transfer from the coupled iodine catalyst,[21] thereby providing a green oxidative transformation, with molecular oxygen (1 atm or air) as the only sacrificial reagent and no other oxidizing or reducing agent required.[22] While successful examples have been limited to the oxidative formation of C-S bonds,[22,23] here we demonstrate the first example of oxidative C-N bond formation. Furthermore, we combined the present C-N bond-formation chemistry with that previously reported for C-S bond formation, to synthesize 3-thioimidazo[1,2-*a*]pyridines **6** from **1**, **2**, and thiols **5** in a one-pot three-component process that involves three oxidation steps, namely, aerobic oxidative C-N, S-S, and C-S bond formations (Figure 2C).

We began our study by examining the reaction of 2-amino-5-methylpyridine (**1a**) and acetophenone (**2a**) in an atmosphere of molecular oxygen (1 atm, balloon). We investigated the effects of the flavin catalyst, iodine source, and solvent (Tables S1 and S2, ESI), which revealed that the corresponding imidazo[1,2-*a*]pyridine **3a** was successfully obtained in 87% yield when the alloxazinium-type flavin catalyst **4•TfO** (5 mol%), which was synthesized from commercially available riboflavin (vitamin B_2),[24] was used in the presence of iodine (10 mol%) in EtOAc at 70 °C (entry 1, Table 1). In sharp contrast, the desired product was hardly produced in the absence of **4•TfO**, iodine, or molecular oxygen (entries 2–4), suggested that the reaction is promoted by aerobic oxidation catalyzed by the flavin and iodine. The use of air afforded 17% yield, revealed that the rate of the present reaction depended on the concentration of molecular oxygen (entry 5). It is noteworthy that the use of a stoichiometric amount of I_2 (120 mol%) afforded a poor yield under these conditions (entry 6) probably due to the effect of the *in-situ* generated H^+ which decreased the nucleophilic reactivity of **1** through the protonation. This result highlights the apparent merit of the present dual catalytic system.

With the optimized conditions in hand, we investigated the substrate scope of the present imidazo[1,2-*a*]pyridine synthesis method (Scheme 1). 2-Aminopyridines bearing both electron-donating and electron-withdrawing substituents gave the desired

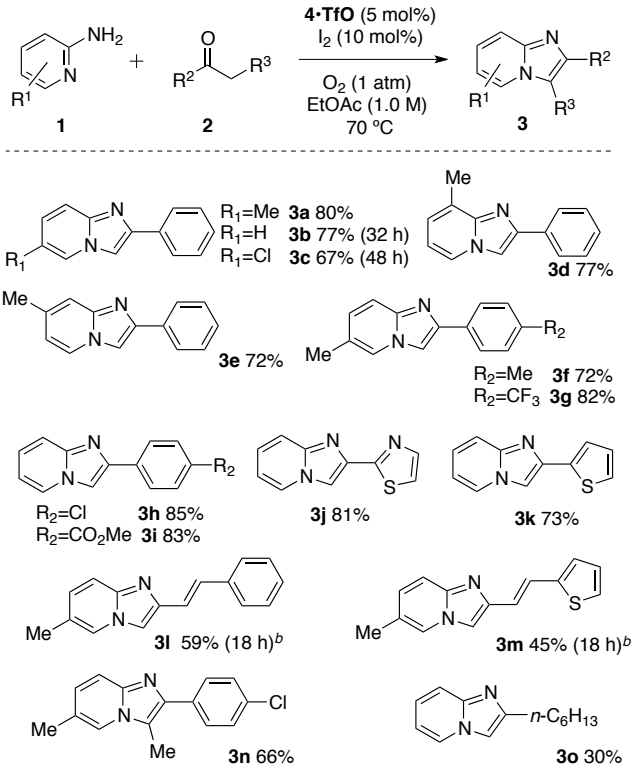
Table 1. Flavin–Iodine-catalyzed synthesis of 3a from 1a and 2a[a]



entry	flavin (mol%)	I_2 (mol%)	atmosphere	yield (%)
1	**4•TfO** (5)	I_2 (10)	O_2	87
2	none	I_2 (10)	O_2	7
3	**4•TfO** (5)	none	O_2	none
4	**4•TfO** (5)	I_2 (10)	N_2	8
5	**4•TfO** (5)	I_2 (10)	air	17
6	none	I_2 (120)	N_2	6

[a]Conditions: **1a** (1.0 M), **2a** (1.5 M), flavin, I_2, and EtOAc under O_2, N_2, or air (1 atm, balloon) at 70 °C. Yield was determined by ^{1}H NMR or GC measurements with 1,1,2,2-tetrachloroethane or triethylene glycol dimethyl ether as an internal standard.

Scheme 1. Scope of the Flavin–Iodine-Catalyzed Synthesis of 3[a]

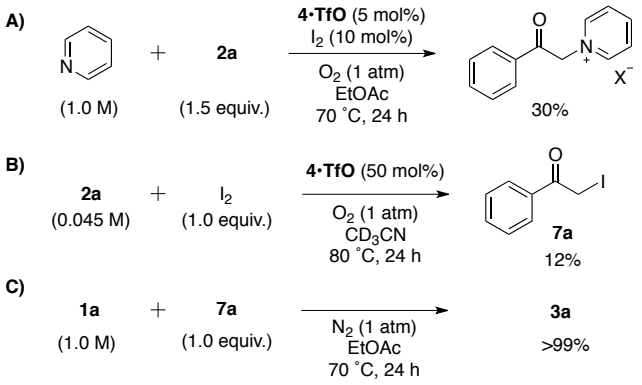


[a]Conditions: **1** (1 M), **2** (1.5 M), **4•TfO** (5 mol%), I_2 (10 mol%), and EtOAc under O_2 (1 atm, balloon) at 70 °C for 24 h. [b]3 equiv. of **2** were used.

products **3a-c**, although electron-deficient substrates required somewhat longer reaction times, and 3- and 4-substitued aminopyridines afforded the corresponding imidazo[1,2-*a*]pyridines **3d** and **3e** without any loss of yield. The reactions of variously substituted acetophenones proceeded smoothly to give **3f-i** in good yields, with chloro and ester functionalities tolerated, while thiazolyl and thiophenyl ketones could be used in this reaction to produce **3j** and **3k**. Furthermore, the present reaction is amenable to α,β–unsaturated ketones, affording alkenyl imizadopyridines **3l** and **3m** in yields of 59% and 45%, respectively. When propiophenone was used instead of an acetophenone, the corresponding 3-methylimidazo[1,2-*a*]pyridine **3n** was obtained in 66% yield. The reaction with aliphatic ketone was relatively difficult, and the desired product **3o** was given in 30% yield.

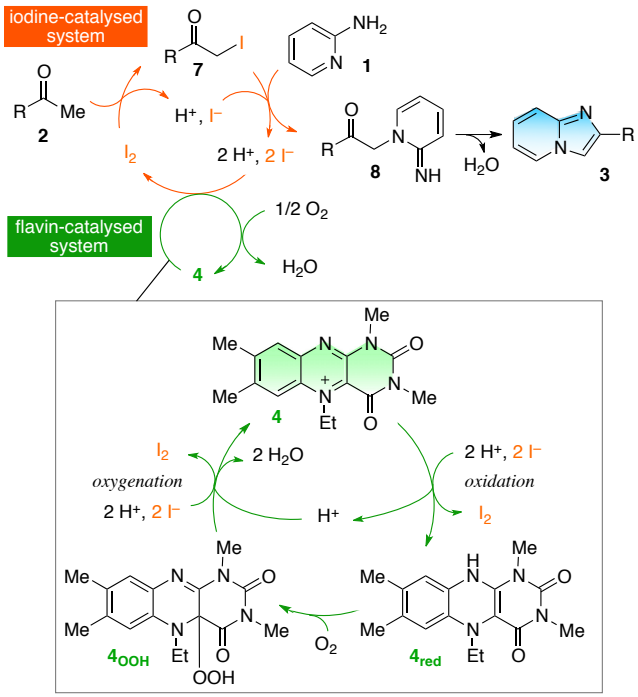
We performed control experiments to gain insight into the reaction mechanism, as shown in Scheme 2. The pyridinium adduct was formed through the reaction with **2a** when pyridine was used instead of **1a**, suggesting that the formation of the C-N bond plays an important role in the present imidazo[1,2-*a*]pyridine synthesis (Scheme 2A). In the presence of stoichiometric amount of I_2, the formation of phenacyl iodide (**7a**) from **2a** was displayed by the ^{1}H NMR measurement in CD_3CN (Scheme 2B). Furthermore, the uncatalyzed reaction of **1a** and **7a** under nitrogen provided **3a** (Scheme 2C). Based on these experimental results and previous reports, we propose a plausible mechanism for the flavin–iodine-catalyzed reaction of **1** and **2** (Scheme 3). In this system, **1a** reacts with I_2 to produce the corresponding iodide **7**, which undergoes nucleophilic substitution by **2** to form adduct **8**, and then cyclodehydrates to form the desired imidazo[1,2-*a*]pyridine **3**. The generated I^- and H^+ are converted to I_2 and H_2O in this flavin-catalyzed system, in which the aerobic oxidation of HI proceeds efficiently through oxidation and oxygenation steps.[22] The consumption of H^+ is also the advantageous feature of the present system, and it could be the reason why the catalytic imidazopyridine formation smoothly occurred in contrast to the result using a stoichiometric I_2 (entry 5, Table 1). Consequently, this imidazopyridine synthesis is driven by molecular oxygen and generates environmentally benign water as the sole by-product.

Scheme 2. Control Experiments

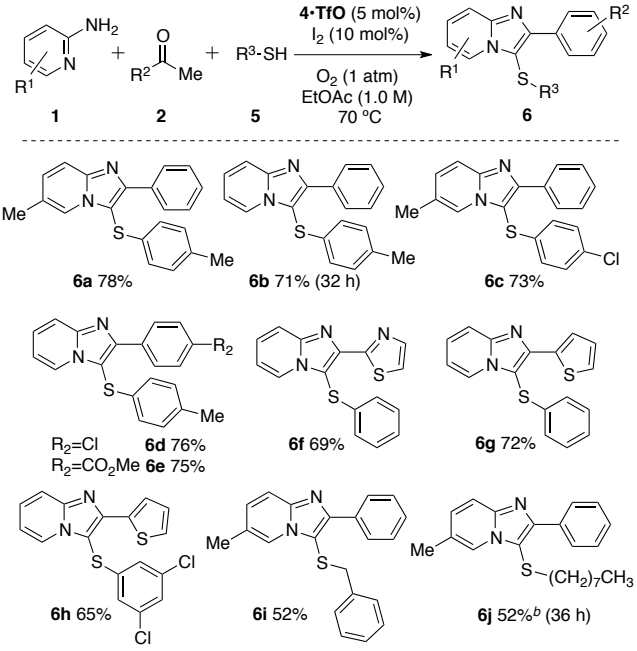


In a further set of experiments, we investigated the one-pot three-component synthesis of sulfenylimidazo[1,2-a]pyridines **6** (Figure 2C). Due to the pharmacological interest in sunfenylimidazo[1,2-a]pyridines bearing various thio functionalities, various methods for the sulfenylation of **3** have been developed.[25] Recently, we reported that the flavin-iodine coupled catalysis promoted the aerobic oxidative sulfenylation of indole analogues including **3**s with thiols.[23a,b] Based on this result, we anticipated that the catalytic sulfenylation of **3** with a

Scheme 3. Proposed Mechanism for the Catalytic Synthesis of 3



Scheme 4. One-pot Three-Component Synthesis of 6[a]

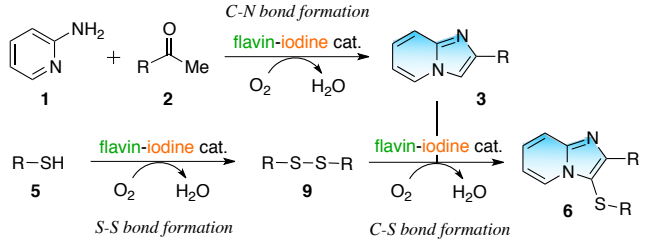


[a]Conditions: **1** (1 M), **2** (1.5 M), **5** (1.2 M), **4•TfO** (5 mol%), I_2 (10 mol%), and EtOAc under O_2 (1 atm, balloon) at 70 °C for 24 h. [b]2.5 equiv. of **5** were used.

thiol would accompany the present imidazo[1,2-*a*]pyridine synthesis catalyzed by flavin and iodine. To our delight, the 3-sulfenylated imidazo[1,2-a]pyridine **6a** was obtained in 78% yield when *p*-toluenethiol was reacted with **1a** and **2a** in the present reaction system; **6a** was formed by sequential C-N and C-S bond formation (Scheme 4). A series of 2-aminopyridines, ketones, and thiols bearing a variety of substituents were compatible with this one-pot synthesis protocol to produce the desired products **6a-6e** in good yields. Although **4•TfO** was not the best flavin catalyst for the simple sulfenylation of **6**,[23b] the sulfenylation in the present three-component synthesis was almost quantitatively promoted for 24 h. Thiazolyl and thiophenyl ketones were smoothly transformed into the corresponding products **6g-6h.** In addition to the benzenethiols having electro-donating and withdrawing substituents, phenylmethanethiol and alkanethiol were applied to this reaction to afford the corresponding 3-thioimidazo[1,2-*a*]pyridines **6i** and **6j** in yields of 52%.

The one-pot three-component synthesis of **6** by flavin–iodine-coupled catalysis proceeds through three aerobic oxidative transformations, namely the formation of C-N, S-S, and C-S bonds (Scheme 5). In addition to the oxidation of I^- to I_2, this dual catalysis promotes the aerobic oxidative coupling of thiols **5** to form the S-S bonds in the corresponding disulfides **9.**[23a,b] In the presence of I_2, **9** is then converted into the sufenyliodide (RSI), which then undergoes nucleophilic attack by **3** to form the C-S bond in **6**. These oxidative transformations are enabled by the flavin and iodine catalysts, thereby providing a green multi-step synthesis driven by molecular oxygen. To the best of our knowledge, these are the first examples of the one-pot syntheses of compounds **6** from **1**, **2**, and **5**.

Scheme 5. The Sequential Three Aerobic Oxidative Transformations Involved in the Catalytic Synthesis of 6



In conclusion, we successfully synthesized **3** from **1** and **2** in a flavin–iodine-catalyzed system, which represents the first aerobic synthesis carried out under metal-free conditions. Gentle O_2 activation catalyzed by the flavin was further used to enable a multi-step transformation driven by molecular oxygen, with flavin–iodine-coupled catalysis promoting the three-component synthesis of **6** from **1**, **2**, and **5** in a transformation that proceeding through the aerobic oxidative formations of C-N, S-S, and C-S bonds. The present findings provide novel green organocatalytic methodology for the multi-step synthesis of complex organic molecules, including aerobic oxidative transformations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization data for known and new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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