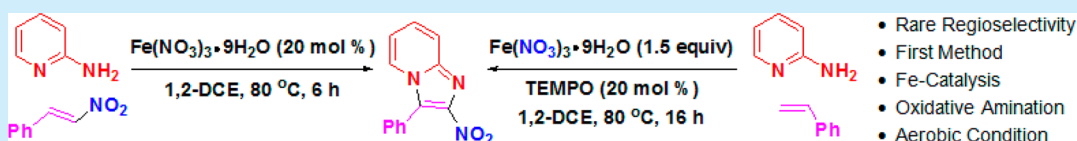


Unprecedented Catalytic Activity of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: Regioselective Synthesis of 2-Nitroimidazopyridines via Oxidative Amination

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S Supporting Information



ABSTRACT: A unique iron-catalyzed oxidative diamination of nitroalkene with 2-aminopyridine for the synthesis of 2-nitro-3-aryl-imidazo[1,2-*a*]pyridines with complete regioselectivity has been achieved under mild and aerobic reaction conditions. This is the first method for the synthesis of 2-nitroimidazo[1,2-*a*]pyridines. These scaffolds were also synthesized directly from styrenes.

Imidazopyridine, an important class of nitrogen containing heterocycles, shows a wide range of biological activities such as antitumor, antiparasitic, antiviral, antimicrobial, fungicidal, anti-inflammatory, hypnotic, etc.¹ These derivatives are also GABA and benzodiazepine receptor agonists, β -amyloid formation inhibitors, and cardiostonic agents.² In addition, this motif is the core structure of some marketed drugs such as necopidem, saripidem, zolimidine, olprinone, zolpidem, and alpidem.³ Furthermore, a few of them exhibit excited-state intramolecular proton transfer.⁴

Accordingly, a variety of synthetic strategies have been developed for the construction of imidazo[1,2-*a*]pyridine scaffolds. These methods include three-component coupling of 2-aminopyridine, aldehyde, and alkyne⁵/isonitrile⁶/nitroalkane,⁷ condensation of aminopyridine and α -haloketone,⁸ and oxidative coupling of 2-aminopyridine with ketone⁹/ alkyne¹⁰/diketone¹¹/chalcone.¹² Additionally intramolecular aminooxygenation¹³ and intramolecular C–H amination¹⁴ are also important strategies for the synthesis of these derivatives. Furthermore, the coupling between 2-aminopyridine and nitroolefins^{15,16} is an attractive way to synthesize these scaffolds. It is interesting to note that in most of the cases the 2-aminopyridine has been employed as the starting material due to its commercial availability and binucleophilic nature. In this context, the reaction of 2-aminopyridine proceeds through initial nucleophilic addition in two ways which controls the regioselectivity: by either the exocyclic amino group (Path a, Figure 1) or endocyclic pyridinium nitrogen (Path b, Figure 1). Generally in the presence of metal catalysts the exocyclic N-atom of the 2-aminopyridine moiety first reacts with the coupling partner. As a consequence the 3-functionalized imidazopyridine moieties are obtained in most of the cases. However, the methodologies for the synthesis of 2-functionalized imidazopyridines are limited.^{8c,d,10b,11}

The pharmacological activity of imidazopyridine derivatives is shown to be dependent on the nature of substituents at different positions. There is continuous effort toward the

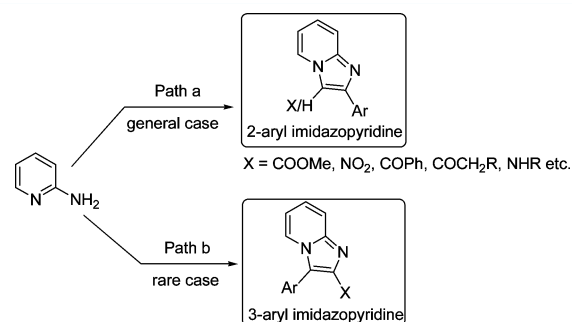


Figure 1. Regioselectivity in synthesis of imidazo[1,2-*a*]pyridine scaffolds.

development of new methods for the synthesis of this class of compounds with a variety of substituents at the 2 and 3 positions. Nitroimidazopyridines are important derivatives and are generally used as a key intermediate to synthesize polyfused imidazopyridine derivatives.¹⁷ Recently nitroalkenes have been used as a coupling partner with 2-aminopyridines for the synthesis of 3-nitroimidazopyridines.¹⁵ However, there is no such method for the synthesis of the 2-nitroimidazopyridines. Therefore, we became interested in whether we can change the substituent selectivity on the imidazo[1,2-*a*]pyridine moiety by the reaction between 2-aminopyridine and nitroalkene under suitable reaction conditions.

In recent times much attention has been drawn to the exploration of the catalytic properties of the iron salts in organic transformations from the aspect of pure science as well as sustainable chemistry.¹⁸ Iron is the second most abundant metal in the earth; in addition, it is inexpensive, safe, and environmentally benign.¹⁹ Various types of reactions, such as oxidation, Michael addition, hydrosilylation, hydrogenation,

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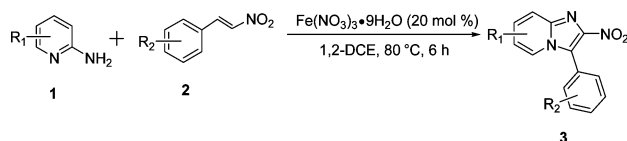
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cross-coupling reaction, cycloaddition, isomerization, rearrangement, etc. have been efficiently catalyzed by the iron catalysts.²⁰

On the other hand, the direct C–H amination is a challenging field of synthetic organic chemistry as there is no need to prefunctionalize the starting materials.²¹ Transition metals such as Pd-, Cu-, Rh-, and Ru-catalysts have been extensively utilized for this purpose.²² Various terminal oxidants are required to carry out these transformations among which molecular oxygen is the most preferable one, as it only produces water as the byproduct.²³ However, the application of iron salts for the direct C–H amination employing molecular oxygen as the terminal oxidant has not been extensively explored so far.²⁴

In continuation of our research to develop newer methodologies for the construction of functionalized imidazo[1,2-*a*]pyridine derivatives,^{9a,12,16} herein we are demonstrating a unique $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -catalyzed one-step synthesis of 2-nitro-3-arylimidazo[1,2-*a*]pyridine derivatives with rare selectivity via C–H amination in ambient air (Scheme 1).

Scheme 1. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -Catalyzed Synthesis of 2-Nitro-3-arylimidazo[1,2-*a*]pyridines



First 2-aminopyridine and (*E*)-1-(2-nitrovinyl)benzene were selected as the model substrates to find suitable reaction conditions by using various metal catalysts and solvents. The results are summarized in Table 1. Initially the reaction was carried out employing 20 mol % $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the

Table 1. Optimization of the Reaction Conditions^a

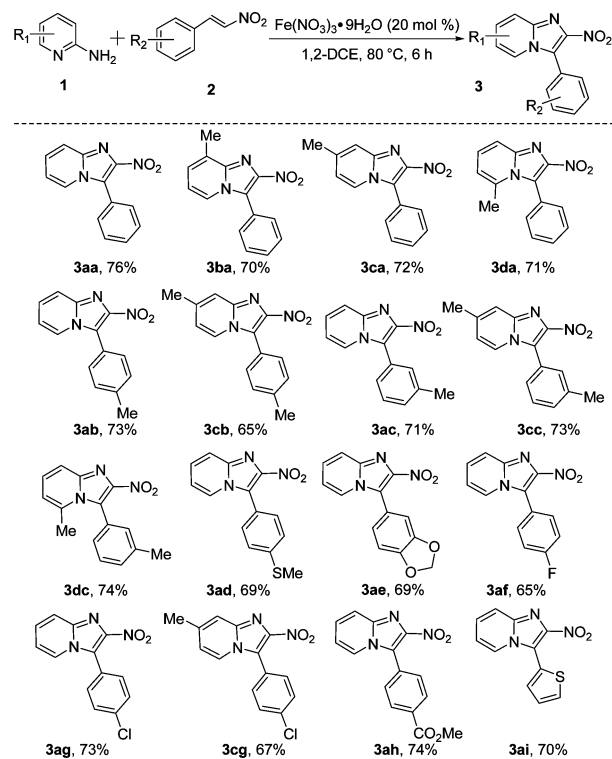
entry	catalyst (mol %)	solvent	yield (%) ^b
1	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	1,2-DCB	10
2	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	DMF	ND
3	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	1,2-DCE	76
4	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	DMSO	<10
5	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	CH_3CN	<10
6	FeCl_3 (20)	1,2-DCE	ND
7	FeBr_3 (20)	1,2-DCE	ND
8	$\text{Fe}(\text{OTf})_3$ (20)	1,2-DCE	ND
9	CuI (20)	1,2-DCE	ND
10	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (20)	1,2-DCE	ND
11	AgNO_2 (20)	1,2-DCE	ND ^c
12	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (10)	1,2-DCE	51
13	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (30)	1,2-DCE	74
14	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	1,2-DCE	74 ^d
15	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (20)	1,2-DCE	64 ^e
16	–	1,2-DCE	ND ^c

^aReaction conditions: 1 mmol of **1a** and 1 mmol of **2a** in the presence of catalyst in solvent (2 mL) at 80 °C for 6 h. ^bIsolated yields. ND: Not detected in TLC. ^cMichael adduct was obtained. ^dReaction carried out at 100 °C. ^eReaction carried out at 60 °C for 10 h.

catalyst in 1,2-dichlorobenzene (1,2-DCB) solvent at 80 °C under aerobic reaction conditions (Table 1, entry 1). The desired product was obtained only in 10% isolated yield after 6 h, and no improvement of the yield was observed even after 12 h. Inspired by this result, the effects of different solvents such as 1,2-dichloroethane (1,2-DCE), DMSO, DMF, and acetonitrile were tested, and the best result was achieved in 1,2-DCE at 80 °C affording a 76% isolated yield (Table 1, entries 2–5). 1,2-DCE may act as both solvent and oxidant for this reaction.^{19d} FeCl_3 , FeBr_3 , and $\text{Fe}(\text{OTf})_3$ were totally ineffective for this transformation (Table 1, entries 6–8). Other metal salts such as CuI , $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and AgNO_2 also were not capable of producing the desired product (Table 1, entries 9–11). The effect of the catalyst loading was also screened. No improvement in the yield was observed by increasing the catalyst loading whereas decreasing the catalyst loading decreased the yield (Table 1, entries 12–13). No substantial increase in the yield was observed by increasing the temperature, and a lower yield was obtained at 60 °C even after 10 h (Table 1, entries 14–15). No product was formed in the absence of any catalyst, but only the Michael product was obtained through the addition of endocyclic pyridinium nitrogen. Finally, the optimized reaction conditions were obtained using 20 mol % $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1,2-DCE at 80 °C for 6 h under aerobic conditions (Table 1, entry 3).

With optimized reaction conditions in hand, we then turned our attention toward the scope of the reaction, and the results are shown in Scheme 2. A wide range of substituted nitroalkenes and aminopyridines were subjected to proof the general applicability of our present procedure. 2-Aminopyridines substituted with a methyl group at different positions

Scheme 2. Substrate Scopes^{a,b}

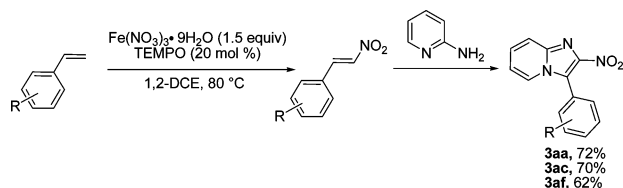


^aReaction conditions: 1 mmol of **1** and 1 mmol of **2** in the presence of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 1,2-DCE at 80 °C for 6 h. ^bIsolated yield.

efficiently react with nitroalkenes to afford the corresponding products with good yields (**3ba**, **3ca**, **3da**). The position of the substituent on 2-aminopyridines almost had no influence on the chemical yields. 2-Aminopyridines with a methyl substituent at the 3, 4, and 6 positions afforded the products with comparable yields under the present reaction conditions. Nitroalkenes bearing several functionalities such as $-\text{Me}$, $-\text{SMe}$, $-\text{Cl}$, and even $-\text{F}$ are unaffected under the present reaction conditions (**3ab**, **3cb**, **3ac**, **3cc**, **3dc**, **3ad**, **3af**, **3ag**, **3cg**). Acid sensitive groups such as $-\text{COOMe}$ and oxymethylene containing nitroalkenes were also successfully employed to produce the desired products (**3ae** and **3ah**) with good yields. Moreover, heteroaryl nitroalkene gave the corresponding product with good yield (**3ai**). However, aliphatic nitroalkenes such as 3-methyl-1-nitrobut-1-ene and (2-nitrovinyl)cyclohexane did not afford the desired products.

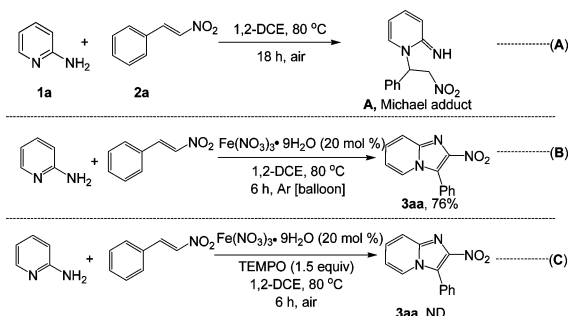
To make our present methodology more convenient and practical, we started the reaction from styrene by the *in situ* formation of nitrostyrene employing a recent methodology by Maiti et al.^{20c} Comparable yields were obtained in this one-pot procedure also (Scheme 3). Furthermore, 2-nitro-3-phenylimidazopyridine (**3aa**) was easily converted to a 2-amino derivative (**4aa**) by simple reduction (see Supporting Information).

Scheme 3. One-Pot Synthesis of Imidazopyridines from Styrenes



To prove the mechanistic pathway, we studied the reaction under different reaction conditions. Initially the reaction was carried out without any catalyst under optimized reaction conditions, and no desired product was obtained; only the Michael product (**A**) was isolated even after 18 h in 48% yield (Scheme 4, eq A). The same Michael adduct was also obtained

Scheme 4. Additional Experiments

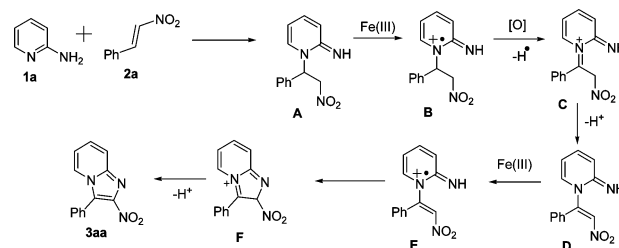


in the presence of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ within 2 h under the optimized reaction conditions. Now to demonstrate the oxidative coupling we applied the optimized reaction conditions to the Michael product, and the corresponding imidazo[1,2-*a*]pyridine was obtained in quantitative yield. When the reaction between **1a** and **2a** was carried out with 20 mol % $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ under an argon atmosphere, the desired

product was obtained in 76% yield (Scheme 4, eq B). This result indicates that probably 1,2-dichloroethane acts as the solvent as well as the oxidant to complete the catalytic cycle for this reaction.^{19d} The reaction was also carried out in the presence of 1.5 equiv of TEMPO under the same reaction conditions; no desired product was observed which favors the formation of imidazo[1,2-*a*]pyridine through the radical mechanistic pathway (Scheme 4, eq C).

A plausible mechanism of the reaction is represented in Scheme 5. The first step is the Michael addition of 2-

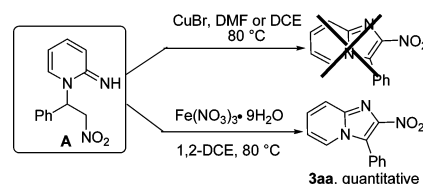
Scheme 5. Probable Mechanism



aminopyridine to the nitroalkene by the endocyclic nitrogen which forms the Michael adduct (**A**). Subsequently oxidation occurred by $\text{Fe}(\text{NO}_3)_3$ through SET which was followed by the intramolecular cyclization to form the intermediate **F**. The intermediate **F** afforded the desired product (**3aa**) through deprotonation.

It is noteworthy to mention that the isolated Michael adduct (**A**) did not undergo cyclization in the presence of CuBr (Scheme 6).¹⁵ Other Fe-salts except $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are not also effective for this oxidative amination. This indicates that $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plays a unique role for this cyclization.

Scheme 6. Specific of Role of $\text{Fe}(\text{NO}_3)_3$ in Oxidative Cyclization



In summary, we have developed an $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ catalyzed oxidative amination of nitroalkenes with 2-aminopyridines for the regioselective synthesis of 2-nitro-3-aryl-imidazo[1,2-*a*]pyridine derivatives. To the best of our knowledge this is the first report on the synthesis of 2-nitroimidazo[1,2-*a*]pyridines. The reaction proceeds through regioselective Michael addition following a unique $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ catalyzed oxidative intramolecular amination. These derivatives were directly synthesized from styrenes also employing this strategy. Easily available basic chemicals as the starting materials, a less expensive metal catalyst, aerobic reaction conditions, tolerance of a wide range of functional groups, and operational simplicity are the notable advantages of this present protocol. These advantages render this protocol facile and suitable to create a diversified library of 2-nitro-3-aryl-imidazo[1,2-*a*]pyridine derivatives.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional data, spectral data of all compounds, and scanned spectra of new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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