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A TRANSITION METAL-FREE SYSTEM FOR C3-H NITROSATION OF IMIDAZO[1,2-*a*]PYRIDINE USING SODIUM NITRITE AT ROOM TEMPERATURE

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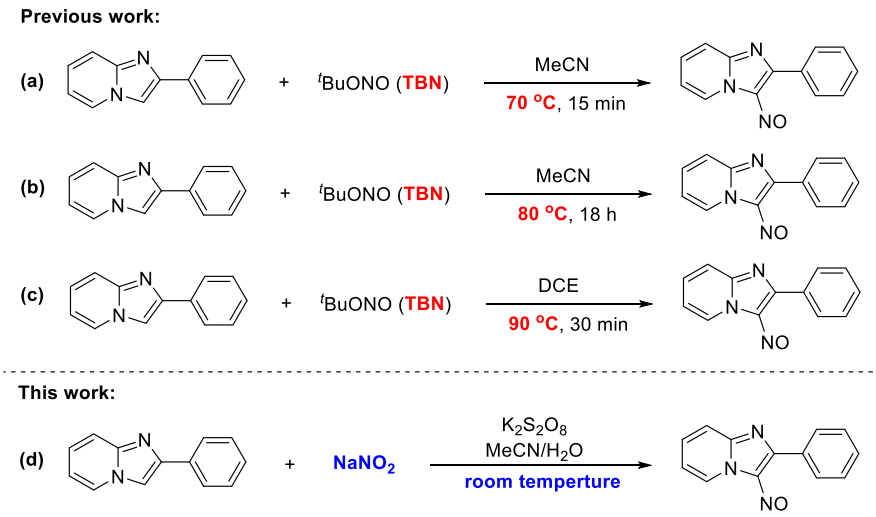
Abstract – Most current strategies for the direct nitrosations (nitrosylations) of imidazo[1,2-*a*]pyridines employ $NaNO_2$/AcOH system, which generally need low temperatures to ensure safety and suffer acidic conditions, or flammable, explosive *tert*-butyl nitrite, which releases toxic gases when heated, as the NO source. Therefore, a novel strategy to prepare these 3-nitrosoimidazo[1,2-*a*]pyridines is necessary. Here, a transition metal-free C3–H nitrosation of imidazo[1,2-*a*]pyridine was developed using low-cost, stable $NaNO_2$ as the nitrosylation source in the presence of $K_2S_2O_8$ at room temperature under an air atmosphere. Imidazo[1,2-*a*]pyridine derivatives with different substituents were efficiently converted to their respective nitrosylation products in moderate-to-good yields under mild conditions *via* ion processes. Moreover, the successful gram-scale reaction and post-synthetic transformations reveal the potential of this strategy for application in industrial production, drug synthesis, and other fields.

INTRODUCTION

Imidazo[1,2-*a*]pyridine derivatives are the core frameworks of numerous bioactive molecules and pharmaceutical intermediates. Numerous synthetic procedures have been developed to functionalize imidazo[1,2-*a*]pyridine.[1,2] Compared with other positions on the imidazole ring, the C3 position is

nucleophilic, and thus, reactions with free radicals or electrophiles could form carbon-carbon or carbon-heteroatom bonds.[1] C3-Functionalized imidazo[1,2-*a*]pyridines, in particular, exhibit various pharmacological activities, such as antiviral, anti-bacterial, anti-cytotoxic, and anti-inflammatory activities.[3,4] Developing novel strategies to synthesize C3-functionalized imidazo[1,2-*a*]pyridine derivatives with good flexibility, high efficiency, and strong practicability consistently attracts attention in the field of organic synthetic chemistry.

C-Nitroso compounds are critical in various biological metabolic processes. As two key subsets of these compounds, the chemical properties of nitrosoalkanes and -arenes are the focus of research.[5] Among imidazo[1,2-*a*]pyridine derivatives, 3-nitrosoimidazo[1,2-*a*]pyridine attracts extensive attention because of its antiretroviral activity.[6,7] Currently, there are numerous studies regarding the direct nitrosylation of imidazo[1,2-*a*]pyridine,[8,9] but most of them employ $NaNO_2$/AcOH system, which generally need low temperatures to ensure safety and suffer acidic conditions. To overcome this limitation and satisfy the increasing demand for 3-nitrosoimidazo[1,2-*a*]pyridines, developing novel synthetic methods towards these compounds is an urgent challenge.



Scheme 1. The protocols for the preparation of 3-nitrosoimidazo[1,2-*a*]pyridine

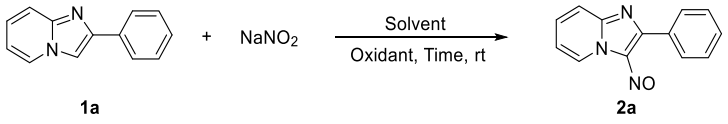
C–H Activation resulted in numerous pioneering studies since its discovery, although this research field is not saturated.[10] C–H Activation was realized under transition-metal catalysis and even transition metal-free conditions.[11] The extensive revival of transition metal-mediated C–H activation, in particular, changed the field of organic synthesis, providing effective synthetic methods in retrosynthetic analyses of complex molecules and improving the overall efficiencies of the required transformations.[12] Currently, various transition-metal catalysts (Pd, Rh, Co, Cu, Fe, Ag, Ni, Ir, etc.) have been developed for use in functionalizing C–H bonds to produce alcohol, amine, and alkyl/aryl halide and borane products.[13] Undoubtedly, in order to make the synthesis protocol more green, harmless and benign, the development of transition metal-free C–H activation is still one of the goals pursued by researchers. The methods of

transition metal-free C−H functionalization of imidazo[1,2-*a*]pyridine have clearly developed,[14] including the C3–H nitrosylation of imidazo[1,2-*a*]pyridine, e.g., in 2015, Hajra et al.[15] reported a direct, straightforward method of regioselectively synthesizing 3-nitrosoimidazo[1,2-*a*]pyridine *via* C(sp^2)–H bond functionalization, employing *tert*-butyl nitrite (TBN) with no additives or catalysts. Furthermore, two other effective methods of the C3–H nitrosylation of imidazo[1,2-*a*]pyridine in metal-free systems were developed in 2016 by Wang et al.[16] and Song et al.,[17] respectively. Both methods employ TBN as the source of nitrosylation, but the solvents and reaction times differ. Undeniably, they all generate the corresponding 3-nitrosoimidazo[1,2-*a*]pyridine derivatives in good yields. However, as an organic reagent, TBN is flammable, explosive, decomposes easily and releases toxic gases when heated, and requires harsh storage conditions. Unfortunately, all of these methods require heat, which may increase the danger of the scaled-up reactions. In 2019, Zou and co-workers developed an efficient approach to 3-nitrosoindoles under a $NaNO_2/K_2S_2O_8$ system in a neutral solvent at 80 °C, which showed $NaNO_2$ was also an outstanding nitroso source.[18]

We aim to demonstrate simple, mild, efficient reaction patterns of the C3−H functionalization of imidazo[1,2-*a*]pyridine.[19] Herein, we designed a direct, economical, safe strategy for the C3–H nitrosylation of imidazo[1,2-*a*]pyridine, which employs $NaNO_2$ as the nitrosylation source at room temperature (Scheme 1d).

RESULTS AND DISCUSSION

Table 1. Screening of optimal conditions[a]



1a 2a

Entry	Solvent	Oxidant	Time	Yield(%)[b]
1	1,2-DCE	$K_2S_2O_8$	9 h	15
2	MeCN	$K_2S_2O_8$	9 h	trace
3	toluene	$K_2S_2O_8$	9 h	trace
4	THF	$K_2S_2O_8$	9 h	trace
5	DMF	$K_2S_2O_8$	9 h	trace
6	DMSO	$K_2S_2O_8$	9 h	trace
7	EtOH	$K_2S_2O_8$	9 h	trace
8	EA	$K_2S_2O_8$	9 h	trace
9	1,2-DCE/H_2O (1:1)	$K_2S_2O_8$	9 h	48
10	**MeCN/H_2O (1:1)**	**$K_2S_2O_8$**	**9 h**	**93**
11	toluene/H_2O (1:1)	$K_2S_2O_8$	9 h	65
12	THF/H_2O (1:1)	$K_2S_2O_8$	9 h	trace

13	DMF/H_2O (1:1)	$K_2S_2O_8$	9 h	trace
14	DMSO/H_2O (1:1)	$K_2S_2O_8$	9 h	trace
15	EtOH/H_2O (1:1)	$K_2S_2O_8$	9 h	trace
16	EA/H_2O (1:1)	$K_2S_2O_8$	9 h	30
17	H_2O	$K_2S_2O_8$	9 h	10
18	MeCN/H_2O (1:1)	$Na_2S_2O_8$	9 h	88
19	MeCN/H_2O (1:1)	$(NH_4)_2S_2O_8$	9 h	85
20	MeCN/H_2O (1:1)	KHS_2O_8	9 h	11
21	MeCN/H_2O (1:1)	BPO	9 h	trace
22	MeCN/H_2O (1:1)	$PhI(OAc)_2$	9 h	trace
23	MeCN/H_2O (1:1)	H_2O_2	9 h	trace
24	MeCN/H_2O (1:1)	TBHP	9 h	trace
25	MeCN/H_2O (1:1)	DTBP	9 h	trace
26	MeCN/H_2O (1:1)	-	9 h	trace
27	MeCN/H_2O (1:1)	$K_2S_2O_8$	8 h	90
28	MeCN/H_2O (1:1)	$K_2S_2O_8$	10 h	93

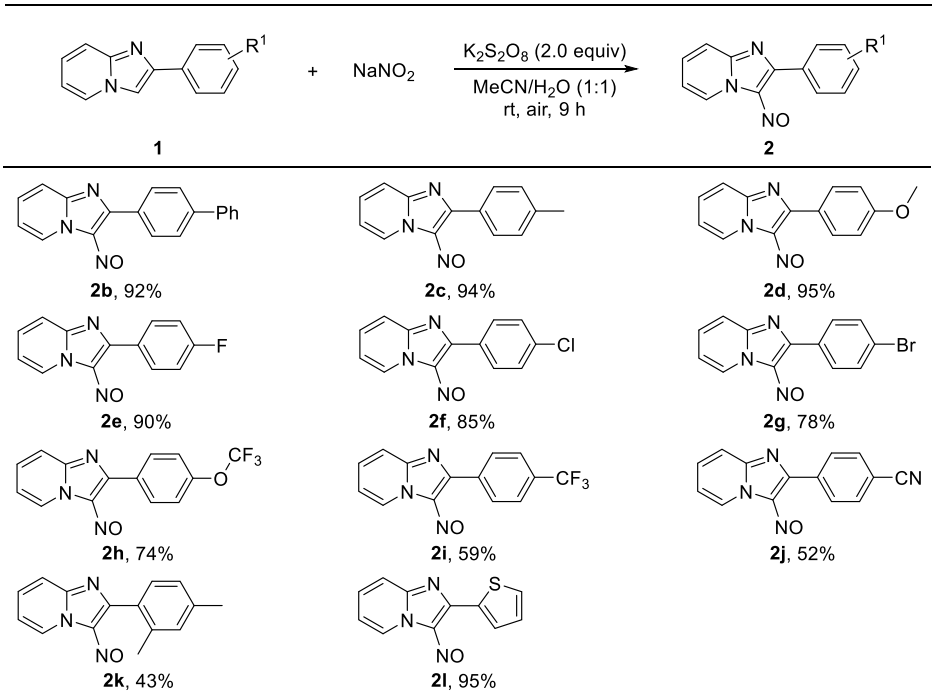
[a]Reaction conditions: **1a** (0.2 mmol, 39 mg), $NaNO_2$ (0.8 mmol, 55 mg), oxidant (0.4 mmol), solvent (2.0 mL), at room temperature under air; [b]Isolated yield.

Firstly, 2-phenylimidazo[1,2-*a*]pyridine (**1a**) was used as the model substrate to optimize the reaction conditions (Tables 1). When $NaNO_2$ (4.0 equiv.), $K_2S_2O_8$ (2.0 equiv.), and 1,2-dichloroethane (1,2-DCE) were used as the nitrosylation reagent, oxidant, and solvent, respectively, and the reaction was conducted at room temperature for 9 h, the target product **2a**, could be obtained in a yield of 15% (Entry 1, Table 1). Other conventional solvents were then used, such as MeCN, toluene, tetrahydrofuran (THF) and so on (Entries 2–8, Table 1), with unsatisfactory results. As the nitrosylation reagent and oxidant are inorganic salts, we added H_2O to the reaction system.[20] Gratifyingly, **2a** is obtained in a 48% yield when 1,2-DCE/H_2O is used as the solvent. Other solvent mixtures were also examined (Entries 10–16, Table 1), and MeCN/H_2O (v:v = 1:1) is the optimal solvent (Entry 10, Table 1). When only H_2O is used as the solvent, the reaction displays little progress (Entry 17, Table 1). This result indicates that a small amount of water may promote this reaction due to the improvements of solubility of inorganic salts $NaNO_2$ and $K_2S_2O_8$, while an excess amount will inhibit the reaction because of the presence of organic reactant. And even in some cases, selecting H_2O and organic solvents synchronously as the solvents for the heterogeneous reaction systems could make relevant for the reactions to achieve the target products with high yields.[20] As a result, the organic solvent is also needed in this nitrosylation reaction except for H_2O, which is served as the good reaction medium for organic reactant. Several oxidants were examined (e.g., $Na_2S_2O_8$, $(NH_4)_2S_2O_8$, KHS_2O_8, benzoyl peroxide, $PhI(OAc)_2$, H_2O_2, *tert*-butyl hydroperoxide, and di-*tert*-butyl peroxide), and none of them could match the reactivity of $K_2S_2O_8$ (Entries 18–25, Table 1 *vs*

Entry 10, Table 1); however, no desired product observed in the absence of an oxidant (Entry 26, Table 1). After 9 h of reaction, the highest yield is observed, which does not change after a prolonged reaction time (Entries 27, 28, Table 1). As above, we have obtained the optimal reaction conditions for the C3–H nitrosylation of imidazo[1,2-*a*]pyridine with the $NaNO_2/K_2S_2O_8$ system (Entry 10, Table 1). Because $NaNO_2$ is usually added in small portions with cooling in the $NaNO_2$/AcOH system in order to prevent the reaction from being too violent,[8,9] our reaction conditions are simpler, more convenient and safer.

Based on the optimized reaction conditions, we explored the generality of the reaction system by examining a series of imidazo[1,2-*a*]pyridine derivatives. As shown in Table 2, substrates with electron-neutral or -donating groups on the benzene rings of their 2-phenylimidazo[1,2-*a*]pyridine moieties generate the nitroso products in excellent yields (**2b–2d**, 92%–95%). Substrates bearing halogens (e.g., F, Cl, and Br) could also be tolerated well in this reaction system (**2e–2g**, 78%–90%), and those with other electron-withdrawing groups, such as $-OCF_3$, $-CF_3$, and -CN, generate the respective products in yields of 52%–74% (**2h–2j**). However, simultaneous methyl substitution at the *ortho* and *para* positions of the benzene ring may retard the reaction, with only a 43% yield of **2k** obtained, which may mainly be attributed to the steric hindrance of the methyl group at *ortho* position. A thiophen-2-yl group at the C2 position of imidazo[1,2-*a*]pyridine is also stable in this oxidized system, generating the target product in a 94% yield (**2l**).

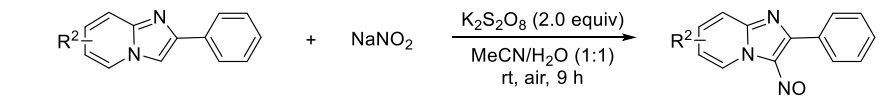
Table 2. Substrate scope of imidazo[1,2-*a*]pyridine derivatives[a,b]



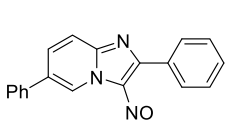
[a]Reaction conditions: **1** (0.2 mmol), $NaNO_2$ (0.8 mmol, 55 mg), $K_2S_2O_8$ (0.4 mmol, 108 mg), $MeCN/H_2O$ (v:v = 1:1, 2.0 mL), at room temperature under air for 9 h; [b]Isolated yield.

Subsequently, a wide range of 2-phenylimidazo[1,2-*a*]pyridine derivatives with substituents on their pyridine rings were also explored. As shown in Table 3, electron effects clearly influence this reaction, e.g., imidazopyridines with substituents such as -Ph, -Me, and -OMe react to furnish the corresponding products in satisfactory yields (**2m–2r**, 91%–96%). Halogen (such as F, Cl, or Br)-substituted imidazopyridines generate the respective products in moderate-to-good yields (**2s–2v**, 50%–88%), but the strongly electron-withdrawing group -CN restrains nitrosylation (**2w**). Moreover, the disubstituted substrate is also suitable in this reaction system (**2x**, 77%). Compared with the data shown in Table 2, the inhibitory effects of electron-withdrawing groups on the pyridine rings of 2-phenylimidazo[1,2-*a*]pyridine derivatives are stronger than those of electron-withdrawing groups on their benzene rings.

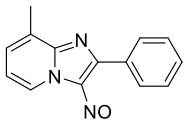
Table 3. Substrate scope of other imidazo[1,2-*a*]pyridine derivatives[a,b]



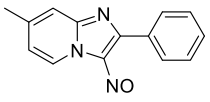
1 **2**



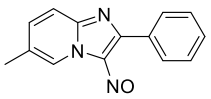
2m, 91%



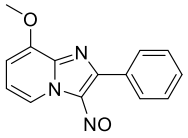
2n, 94%



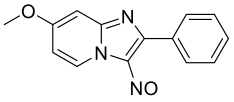
2o, 95%



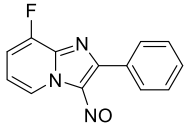
2p, 93%



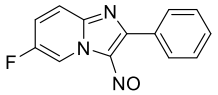
2q, 94%



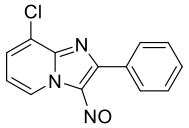
2r, 96%



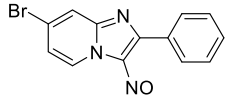
2s, 88%



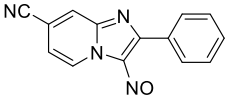
2t, 90%



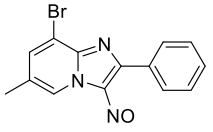
2u, 74%



2v, 50%



2w, trace

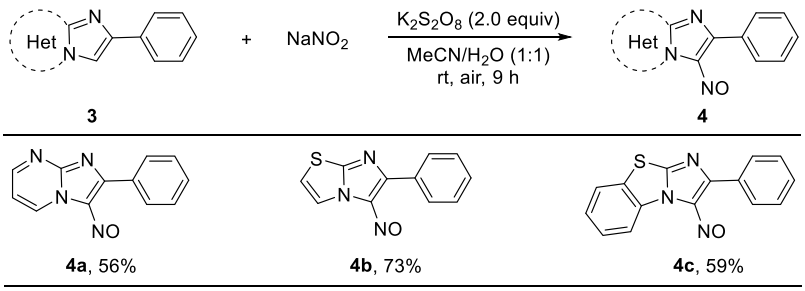


2x, 77%

[a]Reaction conditions: **1** (0.2 mmol), $NaNO_2$ (0.8 mmol, 55 mg), $K_2S_2O_8$ (0.4 mmol, 108 mg), MeCN/H_2O (v:v = 1:1, 2.0 mL), at room temperature under air for 9 h; [b]Isolated yield.

Other imidazoheterocycles were then also evaluated to extend the scope of the method. Gratifyingly, 2-phenylimidazo[1,2-*a*]pyrimidine (**3a**), 6-phenylimidazo[2,1-*b*]thiazole (**3b**), and 2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole (**3c**) react similarly, providing the nitrosylation products in yields of 56%–73% (Table 4).

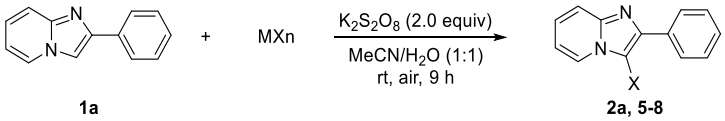
Table 4. Substrate scope of imidazoheterocycles[a,b]

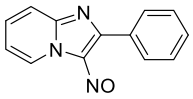
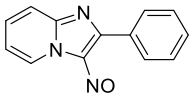
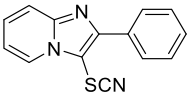
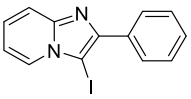
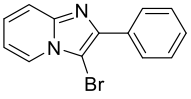


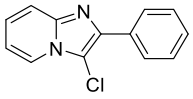
[a]Reaction conditions: **3** (0.2 mmol), $NaNO_2$ (0.8 mmol, 55 mg), $K_2S_2O_8$ (0.4 mmol, 108 mg), MeCN/H_2O (v:v = 1:1, 2.0 mL), at room temperature under air for 9 h; [b]Isolated yield.

Finally, other inorganic salts were also used under the standard conditions. As shown in Table 5, employing KNO_2 or $Ca(NO_2)_2$ generates the corresponding 3-nitroso-2-phenylimidazo[1,2-*a*]pyridine in an excellent yield (Entries 1, 2, Table 5). Gratifyingly, the reaction is facile with KSCN and 2-phenylimidazo[1,2-*a*]pyridine, affording the thiocyanation product in a good yield (Entry 3, Table 5). Remarkably, halogenations with halide salts are also successful, e.g., employing NaI and NaBr generate the target products in excellent yields under similar reaction conditions, albeit employing NaCl generates a much lower yield (Entries 4–6, Table 5). However, the C3-H thiocyanation and halogenation of 2-phenylimidazo[1,2-*a*]pyridine could not occur at all without $K_2S_2O_8$, so $K_2S_2O_8$ is necessary for those reactions.

Table 5. Substrate scope of other inorganic salts[a]

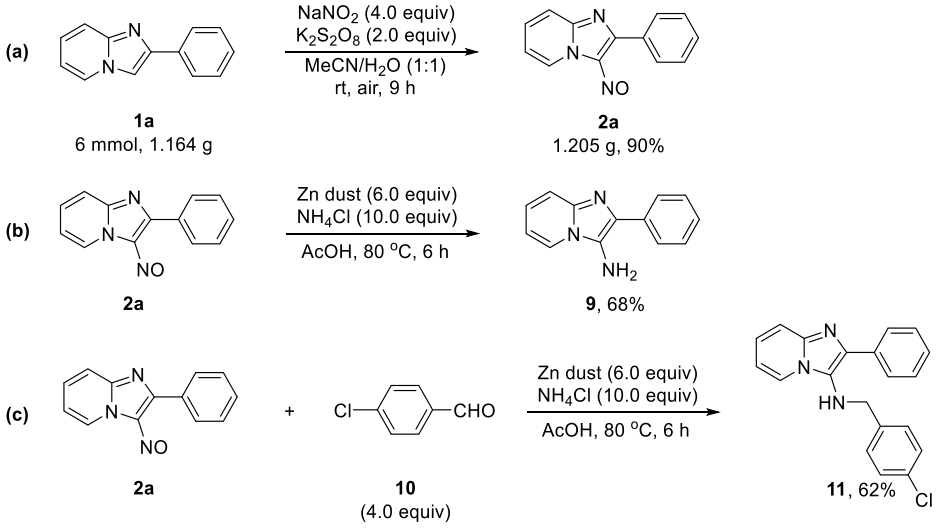


Entry	MX_n	Products	Yield(%)[b]
1	KNO_2	 **2a**	91%
2[c]	$Ca(NO_2)_2$	 **2a**	90%
3	KSCN	 **5**	85% (trace)[e]
4	NaI	 **6**	96% (trace)[e]
5[d]	NaBr	 **7**	90% (trace)[e]

6[d]	NaCl	 **8**	33% (trace)[e]

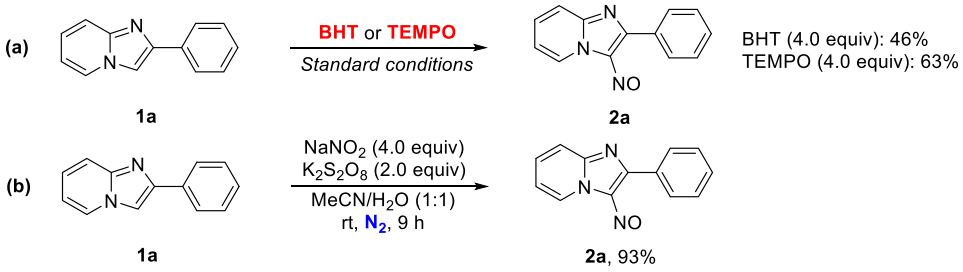
[a]Reaction conditions: **1a** (0.2 mmol, 39 mg), MX_n (0.8 mmol), $K_2S_2O_8$ (0.4 mmol, 108 mg), MeCN/H_2O (v:v = 1:1, 2.0 mL), at room temperature under air for 9 h; [b]Isolated yield; [c]$Ca(NO_2)_2$ (0.4 mmol); [d]1,2-DCE/H_2O (v:v = 1:1, 2.0 mL); [e] Without $K_2S_2O_8$.

A gram-scale reaction was also investigated using this method, and the yield of this reaction does not decrease significantly (Scheme 2a), indicating the potential of this protocol in the syntheses of C3-substituted imidazopyridines. Applying common reductive methods, the nitroso product **2a** could be easily converted to critical amino intermediates **3** and **5** in yields of 68% and 62%, respectively (Scheme 2b and 2c).

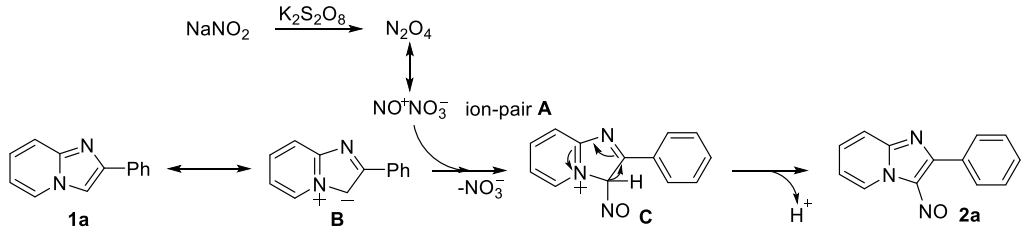


Scheme 2. Synthetic utility of products

The reported C–H nitrosylation reactions generally occur *via* a free-radical or an ion process. The nitrosylation may occur successfully despite the addition of the free radical inhibitor 2,6-diisopropyl-4-methylphenol (BHT) or 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) under standard conditions, and thus, the reaction does not occur *via* a radical process (Scheme 3a). Furthermore, the reaction proceeds well in the absence of oxygen, indicating that oxygen does not participate in the process (Scheme 3b).



Scheme 3. Control experiments



Scheme 4. Plausible mechanism

Based on these results and those of previous studies,[17b,18] a plausible mechanism of this nitrosylation is shown in Scheme 4. First, $NaNO_2$ may undergo oxidation to yield N_2O_4. Whereas N_2O_4 exhibits an ion-pair resonant structure **A**, which nucleophilically attacks imidazo[1,2-*a*]pyridine (at the electron-rich C3 position) subsequently, forming an intermediate **C**. Finally, proton translocation and the restoration of the conjugation of **C** provides the desired product **2a**.

In conclusion, we developed a protocol for the transition metal-free oxidative C3–H nitrosylation of imidazo[1,2-*a*]pyridine. Low-cost, stable $NaNO_2$ served as the nitroso source, and the reaction could proceed perfectly at room temperature, providing a facile, convenient, effective route to synthesize C3-nitroso-substituted imidazo[1,2-*a*]pyridine derivatives. Various functional groups and inorganic salts were well-tolerated in this reaction system, producing the target products in satisfactory yields. As this was a nucleophilic substitution, an electron-withdrawing substituent was not conducive to the reaction, and that on the pyridine ring displayed a clearer effect. Additionally, this mild, efficient method of synthesizing nitrosoimidazopyridines exhibits synthetic potential in the field of pharmaceutical synthesis.

EXPERIMENTAL

1. General Information

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. Mass spectra were measured on an LC-MSD-Trap-XCT instrument. Elemental analysis was determined by Elementar Vario EL. All solvents were used directly without further purification. Dichloromethane (DCM), petroleum ether (PE) and ethyl acetate (EA) were used for column chromatography. The commercials were obtained from commercial sources and used as-received without further purification unless otherwise noted.

2. Typical Procedure for the Products

(a) A 10 mL reaction tube was equipped with a magnetic stir bar and charged with imidazo[1,2-*a*]pyridine derivatives **1** (0.2 mmol), $NaNO_2$ (0.8 mmol, 55 mg), $K_2S_2O_8$ (0.4 mmol, 108 mg), MeCN/H_2O (v:v = 1:1, 2 mL). The resulting mixture was stirred under air at room temperature for 9 h. Upon completion, DCM

(20 mL) was added to the reaction system, which was extracted with H_2O (20 mL), and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using DCM-EA as an eluent to afford the pure product **2**.

3-Nitroso-2-phenylimidazo[1,2-*a*]pyridine (2a) (Known compound)[17]: Obtained as a green solid in 93% yield (41.5 mg) (DCM/EA, 10:1); Mp 162-163 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (d, J = 6.7 Hz, 1H), 8.68 (dd, J = 1.4 Hz, 8.0 Hz, 2H), 7.88-7.82 (m, 2H), 7.62-7.54 (m, 3H), 7.29-7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.07, 153.38, 145.71, 136.10, 131.59, 131.55, 130.84, 128.85, 126.51, 119.53, 117.51.

2-([1,1'-Biphenyl]-4-yl)-3-nitrosoimidazo[1,2-*a*]pyridine (2b): Obtained as a green solid in 92% yield (55.0 mg) (DCM/EA, 10:1); Mp 167-168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (d, J = 6.7 Hz, 1H), 8.77 (d, J = 8.5 Hz, 2H), 7.87-7.78 (m, 4H), 7.70 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.8 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 7.27-7.24 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.62, 153.44, 145.86, 144.27, 140.18, 136.14, 131.29, 130.50, 128.93, 128.03, 127.52, 127.22, 126.56, 119.47, 117.50. MS (ESI+) $[M+H]^+$ *m/z*: 300.1. Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.38; N, 14.04. Found: C, 76.28; H, 4.33; N, 14.07.

3-Nitroso-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (2c) (Known compound)[17]: Obtained as a green solid in 94% yield (44.6 mg) (DCM/EA, 10:1); Mp 195-196 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (d, J = 6.7 Hz, 1H), 8.58 (d, J = 8.2 Hz, 2H), 7.84-7.79 (m, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.25-7.21 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.14, 153.34, 145.88, 142.30, 136.12, 130.79, 129.68, 128.84, 126.57, 119.53, 117.39, 21.65.

2-(4-Methoxyphenyl)-3-nitrosoimidazo[1,2-*a*]pyridine (2d) (Known compound)[17]: Obtained as a green solid in 95% yield (48.1 mg) (DCM/EA, 10:1); Mp 239-240 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (d, J = 5.1 Hz, 1H), 8.68 (d, J = 7.6 Hz, 2H), 7.81 (s, 2H), 7.22 (s, 1H), 7.29-7.25 (m, 1H), 7.07 (d, J = 7.4 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.91, 159.91, 153.25, 146.24, 136.23, 132.64, 126.69, 124.24, 119.00, 117.23, 114.46, 55.48.

2-(4-Fluorophenyl)-3-nitrosoimidazo[1,2-*a*]pyridine (2e) (Known compound)[17]: Obtained as a green solid in 90% yield (43.4 mg) (DCM/EA, 10:1); Mp 232-233 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H), 8.72 (s, 2H), 7.85 (s, 2H), 7.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.38 (d, J = 254.7 Hz), 158.88, 153.21, 145.72, 136.25, 133.00 (d, J = 9.3 Hz), 127.90, 126.54, 119.59, 117.47, 116.10 (d, J = 22.0 Hz).

2-(4-Chlorophenyl)-3-nitrosoimidazo[1,2-*a*]pyridine (2f) (Known compound)[17]: Obtained as a green solid in 85% yield (43.7 mg) (DCM/EA, 10:1); Mp 220-221 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (d, J = 6.7 Hz, 1H), 8.64 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 4.0 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.29-7.26 (m,

1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.60, 153.25, 145.64, 138.29, 136.21, 131.97, 130.06, 129.18, 126.49, 119.73, 117.54.

2-(4-Bromophenyl)-3-nitrosoimidazo[1,2-*a*]pyridine (2g) (Known compound)[17]: Obtained as a green solid in 78% yield (47.0 mg) (DCM/EA, 10:1); Mp 220-221 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.92 (d, J = 6.7 Hz, 1H), 8.58 (d, J = 8.5 Hz, 2H), 7.85 (d, J = 4.0 Hz, 2H), 7.70 (d, J = 8.5 Hz, 2H), 7.30-7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.69, 153.29, 145.64, 136.23, 132.16, 130.49, 126.96, 126.51, 119.77, 117.56.

3-Nitroso-2-(4-(trifluoromethoxy)phenyl)imidazo[1,2-*a*]pyridine (2h): Obtained as a green solid in 74% yield (45.4 mg) (DCM/EA, 10:1); Mp 162-164 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.91 (d, J = 6.7 Hz, 1H), 8.74 (d, J = 8.8 Hz, 2H), 7.86-7.52 (m, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.32-7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.30, 153.27, 151.90, 145.59, 136.19, 132.43, 130.08, 126.46, 120.86, 120.43 (q, J = 256.7 Hz), 119.79, 117.57. MS (ESI+) $[M+H]^+$ *m/z*: 308.0. Anal. Calcd for $C_{14}H_8F_3N_3O_2$: C, 54.73; H, 2.62; N, 13.68. Found: C, 54.80; H, 2.64; N, 13.61.

3-Nitroso-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (2i) (Known compound)[17]: Obtained as a green solid in 59% yield (34.3 mg) (DCM/EA, 10:1); Mp 203-204 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (d, J = 6.7 Hz, 1H), 8.81 (d, J = 8.2 Hz, 2H), 7.90-7.85 (m, 2H), 7.81 (d, J = 8.3 Hz, 3H), 7.33-7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.97, 153.35, 145.42, 136.21, 134.86, 132.84 (q, J = 28.5 Hz), 130.99, 126.40, 125.65 (q, J = 3.7 Hz), 124.02 (q, J = 269.87 Hz), 120.15, 117.74.

4-(3-Nitrosoimidazo[1,2-*a*]pyridin-2-yl)benzonitrile (2j) (Known compound)[15]: Obtained as a green solid in 52% yield (25.8 mg) (DCM/EA, 10:1); Mp 247-248 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (d, J = 6.6 Hz, 1H), 8.84 (d, J = 8.4 Hz, 2H), 7.91-7.84 (m, 4H), 7.36-7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.19, 153.33, 145.34, 136.27, 135.72, 132.43, 131.11, 126.39, 120.40, 118.49, 117.83, 114.73.

2-(2,4-Dimethylphenyl)-3-nitrosoimidazo[1,2-*a*]pyridine (2k): Obtained as a green solid in 43% yield (21.6 mg) (DCM/EA, 10:1); Mp 166-168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.89 (d, J = 6.6 Hz, 1H), 8.84 (d, J = 8.4 Hz, 2H), 7.91-7.84 (m, 4H), 7.36-7.33 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.81, 153.85, 145.39, 140.62, 138.44, 135.71, 133.44, 132.07, 127.97, 126.58, 126.25, 119.35, 117.58, 24.40, 21.04. MS (ESI+) $[M+H]^+$ *m/z*: 252.1. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, C, 71.72; H, 5.26; N, 16.70.

3-Nitroso-2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (2l) (Known compound)[17]: Obtained as a green solid in 95% yield (43.5 mg) (DCM/EA, 10:1); Mp 197-198 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.87 (d, J = 6.5 Hz, 1H), 8.47 (d, J = 3.8 Hz, 1H), 7.82-7.77 (m, 2H), 7.73 (d, J = 5.0 Hz, 1H), 7.27-7.25 (m, 1H), 7.23-7.20 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.73, 151.48, 146.33, 136.39, 134.28, 133.24, 132.92, 129.08, 126.50, 119.16, 117.19.

3-Nitroso-2,6-diphenylimidazo[1,2-*a*]pyridine (2m): Obtained as a green solid in 91% yield (54.4 mg) (DCM/EA, 10:1); Mp 209-210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.19 (d, J = 0.8 Hz, 1H), 8.68 (d, J = 8.6 Hz, 2H), 8.07-8.05 (m, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.60-7.44 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 160.16, 153.47, 144.76, 135.82, 135.44, 134.34, 131.63, 131.58, 130.81, 129.42, 128.99, 128.86, 127.14, 123.81, 117.23. MS (ESI+) $[M+H]^+$ *m/z*: 300.3. Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.38; N, 14.04. Found: C, 76.20; H, 4.35; N, 14.11.

8-Methyl-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2n) (Known compound)[15]: Obtained as a green solid in 94% yield (44.6 mg) (DCM/EA, 10:1); Mp 130-131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.79 (d, J = 6.6 Hz, 1H), 8.69-8.67 (m, 2H), 7.62-7.52 (m, 4H), 7.13 (t, J = 7.0 Hz, 1H), 2.74 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.33, 153.77, 145.59, 135.45, 131.86, 131.34, 130.84, 128.76, 127.93, 124.24, 119.44, 16.52.

7-Methyl-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2o) (Known compound)[17]: Obtained as a green solid in 95% yield (45.0 mg) (DCM/EA, 10:1); Mp 195-196 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.81 (d, J = 6.9 Hz, 1H), 8.67-8.64 (m, 2H), 7.60-7.50 (m, 4H), 7.06 (dd, J = 1.4 Hz, 7.1 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.32, 153.25, 148.93, 146.64, 131.64, 131.53, 130.78, 128.79, 126.08, 121.36 116.48, 22.29.

6-Methyl-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2p) (Known compound)[21]: Obtained as a green solid in 93% yield (44.1 mg) (DCM/EA, 10:1); Mp 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.82 (d, J = 0.7 Hz, 1H), 8.64 (d, J = 8.0 Hz, 2H), 7.74-7.65 (m, 2H), 7.59-7.52 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.76, 153.27, 144.66, 138.56, 131.69, 131.40, 130.71, 130.34, 128.78, 124.78, 116.69, 18.34.

8-Methoxy-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2q): Obtained as a green solid in 94% yield (47.6 mg) (DCM/EA, 10:1); Mp 190-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.49 (d, J = 6.3 Hz, 1H), 8.71-8.69 (m, 2H), 7.60-7.51 (m, 3H), 7.19-7.12 (m, 2H), 4.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 158.71, 154.01, 148.23, 139.16, 131.61, 131.37, 130.94, 128.69, 119.73, 118.95, 113.71, 56.81. MS (ESI+) $[M+H]^+$ *m/z*: 253.2. Anal. Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40; H, 4.38; N, 16.59. Found: C, 66.45; H, 4.41; N, 16.55.

7-Methoxy-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2r) (Known compound)[17]: Obtained as a green solid in 96% yield (48.6 mg) (DCM/EA, 10:1); Mp 197-199 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (d, J = 7.5 Hz, 1H), 8.65 (dd, J = 1.2 Hz, 8.2 Hz, 2H), 7.60-7.51 (m, 3H), 7.09 (d, J = 2.5 Hz, 1H), 6.81 (dd, J = 2.5 Hz, 7.5 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.33, 160.88, 149.37, 131.64, 131.53, 130.78, 128.79, 128.62, 110.97, 96.66, 56.37.

8-Fluoro-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2s): Obtained as a green solid in 88% yield (42.4 mg) (DCM/EA, 10:1); Mp 201-203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 6.7 Hz, 1H),

8.73-8.70 (m, 2H), 7.88-7.82 (m, 2H), 7.64-7.53 (m, 4H), 7.20-7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.51, 153.89, 150.56 (d, J = 258.4 Hz), 131.86, 131.26, 130.98, 128.91, 122.60 (d, J = 5.8 Hz), 119.50 (d, J = 15.9 Hz), 119.04 (d, J = 5.4 Hz). MS (ESI+) $[M+H]^+$ *m/z*: 242.4. Anal. Calcd for $C_{13}H_8FN_3O$: C, 64.73; H, 3.34; N, 17.42. Found: C, 64.80; H, 3.36; N, 17.35.

6-Fluoro-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2t) (Known compound)[17]: Obtained as a green solid in 90% yield (43.4 mg) (DCM/EA, 10:1); Mp 214-215 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98-9.96 (m, 1H), 8.66-8.64 (m, 2H), 7.85-7.81 (m, 1H), 7.74-7.69 (m, 1H), 7.62-7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.99, 157.13 (d, J = 243.4 Hz), 153.95, 142.96, 131.67, 131.40, 130.67, 128.93, 126.28 (d, J = 23.8 Hz), 117.91 (d, J = 8.5 Hz), 114.01 (d, J = 42.9 Hz).

8-Chloro-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2u): Obtained as a green solid in 74% yield (38.0 mg) (DCM/EA, 10:1); Mp 218-219 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (d, J = 6.7 Hz, 1H), 8.73-8.70 (m, 2H), 7.88-7.82 (m, 2H), 7.64-7.53 (m, 4H), 7.20-7.16 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.76, 153.15, 143.79, 136.61, 131.80, 131.27, 130.79, 128.93, 127.43, 124.39, 117.76. MS (ESI+) $[M+H]^+$ *m/z*: 257.9. Anal. Calcd for $C_{13}H_8ClN_3O$: C, 60.60; H, 3.13; N, 16.31. Found: C, 60.65; H, 3.18; N, 16.24.

7-Bromo-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2v): Obtained as a green solid in 50% yield (30.1 mg) (DCM/EA, 10:1); Mp 227-228 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.75 (dd, J = 0.5, 7.1 Hz, 1H), 8.68-8.65 (m, 2H), 8.02 (dd, J = 0.5 Hz, 1.9 Hz, 1H), 7.61-7.54 (m, 3H), 7.34 (dd, J = 2.0 Hz, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.37, 153.09, 145.94, 131.93, 131.24, 130.95, 129.96, 128.93, 126.40, 122.97, 120.20. MS (ESI+) $[M+H]^+$ *m/z*: 302.1. Anal. Calcd for $C_{13}H_8BrN_3O$: C, 51.68; H, 2.67; N, 13.91. Found: C, 51.66; H, 2.63; N, 13.88.

8-Bromo-6-methyl-3-nitroso-2-phenylimidazo[1,2-*a*]pyridine (2x) (Known compound)[21]: Obtained as a green solid in 77% yield (48.5 mg) (DCM/EA, 10:1); Mp 184-185 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.74 (s, 1H), 8.69-8.67 (m, 2H), 7.89-7.88 (m, 1H), 7.60-7.52 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.65, 153.79, 142.61, 140.45, 131.64, 131.43, 130.98, 130.64, 128.80, 123.50, 111.62, 18.12.

3-Nitroso-2-phenylimidazo[1,2-*a*]pyrimidine (4a): Obtained as a green solid in 56% yield (25.1 mg) (DCM/EA, 10:1); Mp 172-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.95 (d, J = 6.7 Hz, 1H), 8.68 (dd, J = 1.4 Hz, 8.0 Hz, 2H), 7.88-7.82 (m, 2H), 7.62-7.54 (m, 3H), 7.29-7.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.69, 158.42, 151.77, 147.87, 133.77, 132.41, 131.40, 131.05, 129.01, 115.29. MS (ESI+) $[M+H]^+$ *m/z*: 224.1. Anal. Calcd for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 24.99. Found: C, 64.31; H, 5.08; N, 10.69.

5-Nitroso-6-phenylimidazo[2,1-*b*]thiazole (4b) (Known compound)[15]: Obtained as a green solid in 73% yield (60.2 mg) (PE/EA, 10:1); Mp 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66-8.64 (m, 2H), 8.42

(d, *J* = 4.3 Hz, 1H), 7.60-7.51 (m, 3H), 7.07 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 159.04, 158.93, 156.86, 131.70, 131.55, 130.21, 128.97, 121.85, 116.79.

3-Nitroso-2-phenylbenzo[*d*]imidazo[2,1-*b*]thiazole (4c) (Known compound)[15]: Obtained as a green solid in 59% yield (60.2 mg) (PE/EA, 10:1); Mp 119-121 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.95 (d, *J* = 8.5 Hz, 1H), 8.58 (d, *J* = 6.8 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.58-7.52 (m, 4H), 7.46 (t, *J* = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.24, 158.47, 157.31, 132.83, 131.87, 131.47, 130.98, 130.04, 128.85, 126.72, 123.28, 118.88.

(b) A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **1a** (0.2 mmol), MX_n (0.8 mmol), $K_2S_2O_8$ (0.4 mmol, 108 mg), MeCN/H_2O (v:v = 1:1, 2 mL). The resulting mixture was stirred under air at room temperature for 9 h. Upon completion, DCM (20 mL) was added to the reaction system, which was extracted with H_2O (20 mL), and the aqueous layer was extracted with DCM (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using DCM-EA as an eluent to afford the pure products **2a** and **5**-**8**.

2-Phenyl-3-thiocyanatoimidazo[1,2-*a*]pyridine (5) (Known compound)[22]: Obtained as a white solid in 85% yield (42.7 mg) (DCM/EA, 10:1); Mp 122-123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.46 (d, *J* = 6.8 Hz, 1H), 8.07-8.05 (m, 2H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.56-7.46 (m, 4H), 7.14 (t, *J* = 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 153.14, 148.01, 131.98, 129.48, 128.84, 128.76, 128.00, 124.41, 118.31, 114.43, 108.06, 94.73.

3-Iodo-2-phenylimidazo[1,2-*a*]pyridine (6) (Known compound)[23]: Obtained as a white solid in 96% yield (61.4 mg) (DCM/EA, 10:1); Mp 159-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.20 (d, *J* = 6.9 Hz, 1H), 8.08-8.06 (m, 2H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.42-7.38 (m, 1H), 7.26-7.22 (m, 1H), 6.95-6.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 148.14, 148.08, 133.60, 128.55, 128.37, 126.54, 125.56, 117.61, 113.18, 59.51.

3-Bromo-2-phenylimidazo[1,2-*a*]pyridine (7) (Known compound)[23]: Obtained as a white solid in 90% yield (49.0 mg) (DCM/EA, 10:1); Mp 82-83 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.19-8.12 (m, 3H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.28-7.24 (m, 1H), 6.95-6.91 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.49, 142.72, 132.88, 128.48, 128.32, 127.92, 125.11, 123.98, 117.65, 113.07, 91.73.

3-Chloro-2-phenylimidazo[1,2-*a*]pyridine (8) (Known compound)[23]: Obtained as a white solid in 33% yield (15.0 mg) (DCM/EA, 10:1); Mp 121-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.15-8.09 (m, 3H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.50-7.46 (m, 2H), 7.40-7.36 (m, 1H), 7.26-7.21 (m, 1H), 6.94-6.90 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 143.74, 139.83, 132.55, 128.56, 128.26, 127.51, 124.84, 122.70, 117.68, 112.91, 105.70.

(c) For the gram scale reaction: A 100 mL reaction tube was equipped with a magnetic stir bar and charged with **1a** (6.0 mmol, 1.164 g), $NaNO_2$ (24.0 mmol, 1.656 g), $K_2S_2O_8$ (12.0 mmol, 3.244 g), MeCN/H_2O (v:v = 1:1, 60 mL). The resulting mixture was stirred under air at room temperature for 9 h. Upon completion, DCM (50 mL) was added to the reaction system, which was extracted with H_2O (50 mL), and the aqueous layer was extracted with DCM (2 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using DCM-EA as an eluent to afford the pure product **2a** (1.205 g, 90% yield).

(d) A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **2a** (0.2 mmol, 45 mg), Zn dust (1.2 mmol, 76 mg), NH_4Cl (2.0 mmol, 108 mg), and AcOH (2 mL). The resulting mixture was stirred under air at 80 ^oC for 6 h. Upon completion, the mixture was neutralized with saturated solution of $NaHCO_3$ and was extracted with DCM (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using hexane-EtOAc (DCM/EA, 10:1) as an eluent to afford the pure product **9**.

2-Phenylimidazo[1,2-*a*]pyridin-3-amine (9) (Known compound)[15]: Obtained as a gray solid in 68% yield (28.4 mg) (DCM/EA, 10:1); Mp 117-118 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 8.04-7.98 (m, 3H), 7.58-7.55 (m, 1H), 7.51-7.47 (m, 2H), 7.37-7.33 (m, 1H), 7.16-7.11 (m, 1H), 6.85-6.82 (m, 1H), 3.44 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.00, 134.45, 133.12, 128.72, 127.16, 123.18, 122.63, 121.82, 117.37, 111.71.

(e) A 10 mL reaction tube was equipped with a magnetic stir bar and charged with **2a** (0.2 mmol, 45 mg), **10** (0.8 mmol, 112 mg), Zn dust (1.2 mmol, 76 mg), NH_4Cl (2.0 mmol, 108 mg), and AcOH (2 mL). The resulting mixture was stirred under air at 80 ^oC for 6 h. Upon completion, the mixture was neutralized with saturated solution of $NaHCO_3$ and was extracted with DCM (3 × 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and filtered. After evaporation of the solvent under vacuum, the residue was purified by column chromatography on silica gel (200–300 mesh) using hexane-EtOAc (DCM/EA, 10:1) as an eluent to afford the pure product **11**.

N-(4-Chlorobenzyl)-2-phenylimidazo[1,2-*a*]pyridin-3-amine (11): Obtained as a gray solid in 62% yield (41.3 mg) (DCM/EA, 10:1); Mp 162-163 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.97-7.93 (m, 3H), 7.55-7.53 (m, 1H), 7.47-7.43 (m, 2H), 7.37-7.32 (m, 1H), 7.28-7.23 (m, 4H), 7.16-7.11 (m, 1H), 6.77-6.73 (m, 1H), 4.14 (d, J = 6.2 Hz, 2H), 3.54 (t, J = 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.65, 137.43, 136.55, 134.18, 133.46, 129.50, 128.77, 128.68, 127.52, 127.11, 125.23, 124.07, 122.23, 117.57, 111.80, 51.74. MS (ESI+) $[M+H]^+$ *m/z*: 334.1. Anal. Calcd for $C_{20}H_{16}ClN_3$: C, 71.96; H, 4.83; N, 12.59. Found: C, 72.00; H, 4.80; N, 12.54.

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