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METAL-FREE REGIOSELECTIVE SYNTHESIS OF 2-NITRO-3-ARYLIMIDAZO[1,2-*a*]PYRIDINES VIA OXIDATIVE AMINATION UNDER AIR USING SILICA SULFURIC ACID AS AN EFFECTIVE HETEROGENEOUS CATALYST

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Abstract – Metal-free regioselective strategy for the synthesis of 2-nitro-3-arylimidazo[1,2-*a*]pyridines from β-nitrostyrene and 2-aminopyridines under aerobic conditions using silica sulfuric acid (SSA) as heterogeneous catalyst has been developed. The synthetic methodology provides the title compounds with good yields under mild conditions, and complete regioselectivity is observed. Furthermore, SSA was not used previously for this transformation.

Heterocyclic compounds containing imidazo[1,2-*a*]pyridine ring is an important structural moiety in pharmaceutically important compounds such as zolpidem, alpidem, saripidem, necopidem, zolimidine and olprinone[1] (Figure 1). These scaffolds have also shown interesting biological activities such as antiparasitic, antiviral, antitumor, antimicrobial, anti-inflammatory, fungicidal, hypnotic and etc.[2,3]

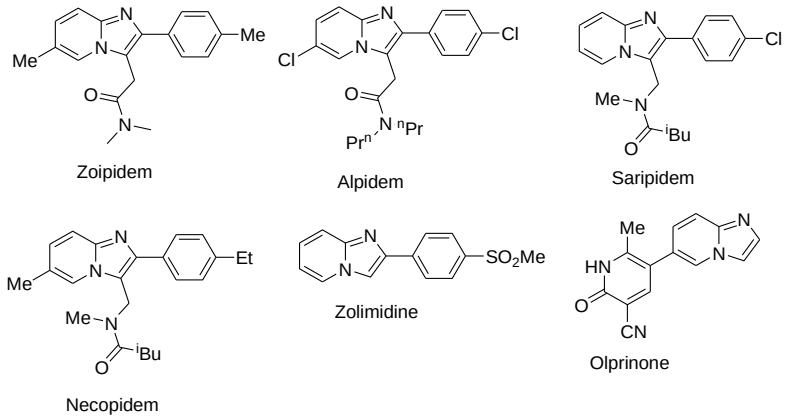
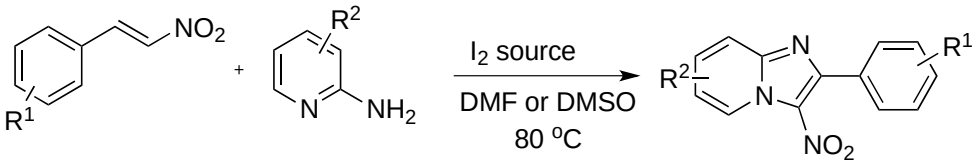


Figure 1. Imidazo[1,2-*a*]pyridine containing drugs

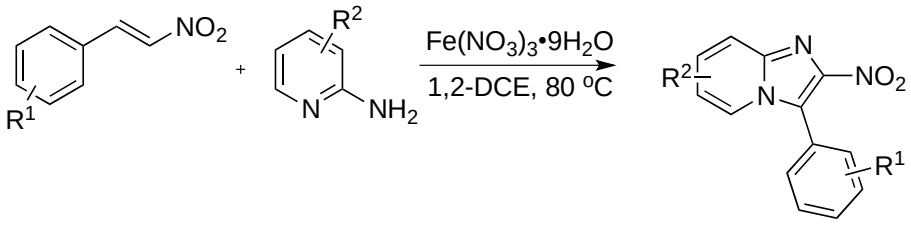
Additionally, these derivatives also work as GABA and benzodiazepine receptor agonists, β-amyloid formation inhibitors, and cardiotonic agents.[4] Moreover, some of them demonstrate excited-state intramolecular proton transfer.[5]

The synthetic strategies involved in the synthesis of imidazo[1,2-*a*]pyridine are based on condensation reactions,[6] oxidative coupling reactions[7-9] and three component coupling,[5,10] intramolecular aminooxygenation,[11] intramolecular C-H amination[12] and oxidative coupling of 2-aminopyridine with ketone[13] / alkyne[14] / diketone[15] / chalcone.[16] Above all, the synthesis of imidazo[1,2-*a*]pyridine using 2-aminopyridine and nitroalkenes[17,18] grabs the attention due to its binucleophilic and bielectrophilic nature of the starting materials respectively. In the reactions, where 2-aminopyridine is used, the nucleophilic attack takes place in two ways which controls the regioselectivity: i) the exocyclic amino group attacks the α-position of β-nitrostyrenes resulting 3-fuctionalized imidazopyridine moieties, ii) the endocyclic pyridinium nitrogen attacks the same position resulting 2-functionalized imidazopyridines and this type reactions have rarely been observed (Scheme 1). Nitroimidazopyridines belong to important class of compounds and are generally employed as key intermediates to synthesize polyfused imidazopyridine derivataives.[19] The synthesis of 3-nitroimidazopyridines is well established[17,20] but the reports corresponding to 2-nitroimidazopyridines are inadequate.[21]

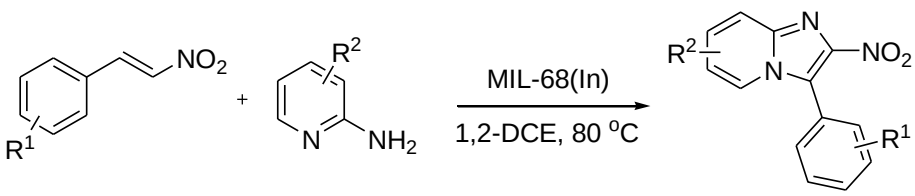
(a) Telvekar and co-workers[20]: 3-nitro-2-arylimidazo[1,2-*a*]pyridines



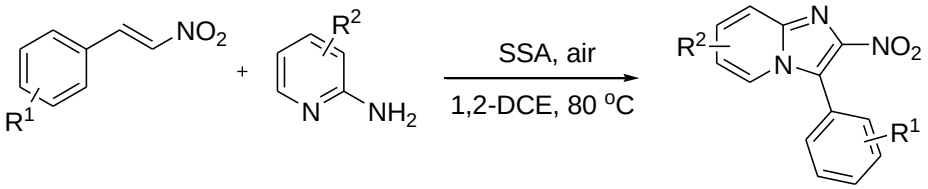
(b) Hajra and co-workers[21]: 2-nitro-3-arylimidazo[1,2-*a*]pyridines



(c) Phan and co-workers[21]: 2-nitro-3-arylimidazo[1,2-*a*]pyridines



This work: 2-nitro-3-arylimidazo[1,2-*a*]pyridines

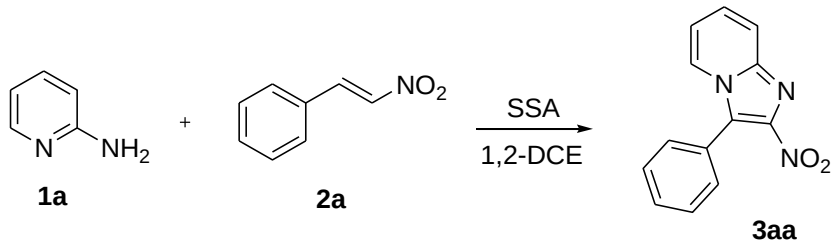


Scheme 1. Synthesis of 2-nitro-3-arylimidazo[1,2-*a*]pyridines from 2-aminopyridines and β-nitrostyrenes

In recent years heterogeneous catalysts grabbed much attention towards synthetic organic chemistry due to environ-economic factors.[22] Among heterogeneous catalysts silica sulfuric acid (SSA) has demonstrated its potentiality as an efficient solid catalyst in various organic transformations.[23] SSA, a product that is easily synthesized from silica gel and chlorosulfonic acid,[24] was observed to improve the reactivity and selectivity in carbon–carbon bond formation reactions,[25a] in cycloaddition reactions,[25b] in protection–deprotection reactions of multistep syntheses[25c] and in syntheses of heterocycles.[25d] In this communication we would like to present the synthesis of 2-nitroimidazo[1,2-*a*]pyridines by reacting 2-aminopyridines with β-nitrostyrenes under aerobic conditions using SSA as heterogeneous catalyst. To the best of our knowledge SSA has not been used for the synthetic transformation of 2-nitroimidazo[1,2-*a*]pyridines.

Looking inside the synthetic strategies[21a,c] for the preparation of 2-nitroimidazo[1,2-*a*]pyridines from 2-aminopyridine and β-nitrostyrene, it was revealed that solvent and temperature play important roles in providing the product in good yield. Particularly, 1,2-dichloroethane (1,2-DCE) serves as both solvent and oxidant.[21c,d] Therefore, in our preliminary experiment we have selected 2-aminopyridine (**1a**) and (*E*)-1-(2-nitrovinyl)benzene (**2a**) as the model substrates and 1,2-dichloroethane as a preferred solvent. Accordingly, the reaction was carried out employing SSA as heterogeneous catalyst (300 mg) in 1,2-dichloroethane as solvent and in the presence of air at refluxing conditions. To our delight, we have isolated the desired product (**3aa**) in 54% yield after 4 h (Table 1, entry 1), and no improvement of the yield was observed even after 6 h (Table 1, entry 2). The reaction product was compared with 2-nitroimidazo[1,2-*a*]pyridine and 3-nitroimidazo[1,2-*a*]pyridine from the literature in order to unmistakably confirm the formation of 2-nitroimidazo[1,2-*a*]pyridine by ^{1}H and ^{13}C NMR.[21c] It must be studied the effect of catalyst loading for the oxidative amination of 2-aminopyridine with *trans*-β-nitrostyrene to generate 2-nitroimidazo[1,2-*a*]pyridine in good yield. Accordingly, we performed the reaction with different amounts of catalyst, separately, and the results were summarized in Table 1.

Table 1. Optimization of the reaction conditions[a]



1a **2a** **3aa**

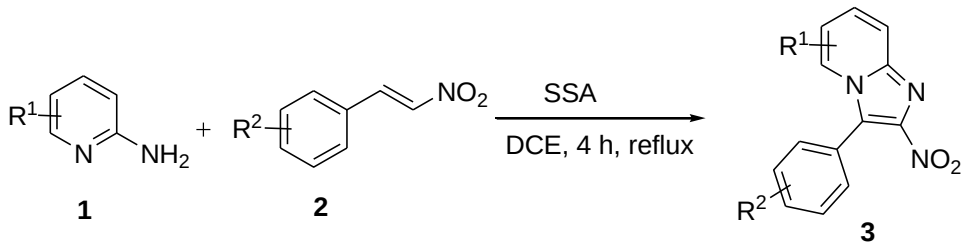
Entry	Catalyst (mg)	Solvent	Reaction time (h)	Temperature (°C)	Yield (%)[b]
1	SSA (300)	1,2-DCE	4	80	54
2	SSA (300)	1,2-DCE	6	80	54
3	**SSA (400)**	**1,2-DCE**	**4**	**80**	**78**
4	SSA (500)	1,2-DCE	4	80	79
5	SSA (400)	1,2-DCE	8	40	10
6	SSA (400)	1,2-DCE	6	60	15
7[c]	SSA (400)	1,2-DCE	6	100	79
8[d]	SSA (400)	DMSO	6	100	<10
9[d]	SSA (400)	DMF	6	100	<10
10[d]	SSA (400)	MeCN	6	80	ND
11	silica gel (500)	1,2-DCE	6	80	35
12	H_2SO_4 (20 mol%)	1,2-DCE	6	80	ND

[a]Reaction conditions: 1 mmol of **1a** and 1 mmol **2a** in the presence of SSA as catalyst in solvent (DCE, 3 mL) unless otherwise stated. [b]Chromatographically isolated yields. [c]Reaction was performed in 10 mL pressurized vial by using 2 mL of 1,2-DCE. [d]Reactions were performed by using 3 mL of respected solvent.

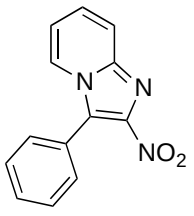
Improvement in the yield of the product **3aa** was noticed by increasing catalyst loading from 300 to 400 mg (Table 1, entry 3). However, further increasing of catalyst loading from 400 to 500 mg did not improve the product yield much (Table 1, entry 4). In order to understand the effect of temperature for the cyclization of *trans*-β-nitrostyrene with 2-aminopyridine in the presence of SSA and 1,2-DCE as solvent to produce 2-nitroimidazo[1,2-*a*]pyridine, a set of reactions at different temperatures have been performed (Table 1, entries 5, 6 and 7). The conversion of 2-aminopyridine with β-nitrostyrene into 2-nitroimidazo[1,2-*a*]pyridine proceeded with difficulty at 40 °C, to produce only 10% yield even after 8 h (Table 1, entry 5). The yield of the 2-nitroimidazo[1,2-*a*]pyridine was not increased much even when the temperature was raised from 40 °C to 60 °C (Table 1, entry 6). It was possible to enhance the yield of the product **3aa** to 78% when the reaction was performed at 80 °C for 4 h (Table 1, entry 3). However, no substantial increase in the yield of the product was observed when the temperature is boosted from 80 °C

to 100 °C (Table 1, entry 7). To probe the effect of solvent, the reaction was conducted at 100 °C under aerobic conditions using SSA as catalyst in DMF, DMSO and MeCN, separately, as the solvents. The reaction provided 2-nitroimidazo[1,2-*a*]pyridine in less than 10% yield in both the solvents (DMF and DMSO) and no product was detected when MeCN used as solvent (Table 1, entries 8, 9 & 10). The reaction continued slowly in DCE in the presence of silica gel as catalyst providing 35% of yield at 80 °C after 6 h (Table 1, entry 11). No product was observed when H_2SO_4 was used as catalyst (Table 1, entry 12). The above observations support that SSA showed higher efficiency for the synthesis of 2-nitroimidazo[1,2-*a*]pyridine starting from 2-aminopyridine and β-nitrostyrene than either silica gel or H_2SO_4.

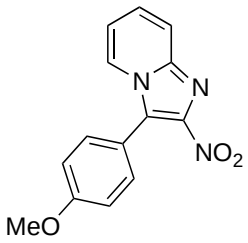
With optimized reaction conditions in hand, we have explored the scope and limitation of the present protocol with substituted 2-aminopyridines. Methyl groups at different positions of 2-aminopyridine reacted well with (*E*)-1-(2-nitrovinyl)benzene (**2a**) to afford 2-nitroimidazo[1,2-*a*]pyridines (Scheme 2, **3ab**, **3ac**) in good yield. The position of the methyl groups on 2-aminopyridine almost had no influence on the yields of the product. The scope of the reaction was further extended by changing both the substituents on 2-aminopyridine and (*E*)-1-(2-nitrovinyl)benzene which offered the corresponding products in good yield (Scheme 2, **3ba**, **3bb**, **3bc**). Oxymethylene group containing β-nitrostyrene (**3c**) also reacted smoothly with 2-aminopyridines (**2a**, **2b**, **2c**) under the reaction conditions to provide the corresponding 2-nitroimidazo[1,2-*a*]pyridines (**3ca**, **3cb**, **3cc**) in good yield.



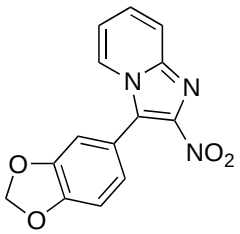
1 **2** **3**



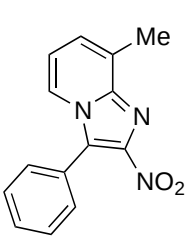
3aa, 78%



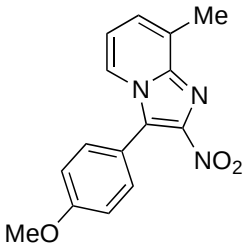
3ba, 66%



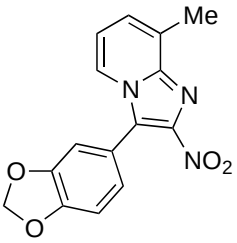
3ca, 76%



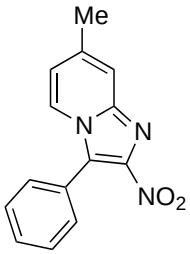
3ab, 81%



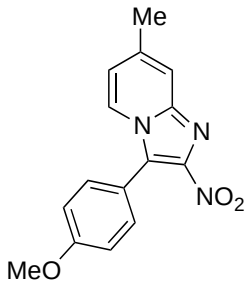
3bb, 69%



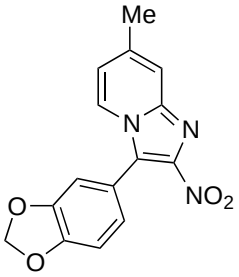
3cb, 74%



3ac, 77%



3bc, 67%



3cc, 73%

Scheme 2. Scope of substrates[a,b]

[a)]All the reactions were carried out with 2-aminopyridine derivative (**1**) 1.0 mmol, β-nitrostyrene (**2**) 1.0 mmol, SSA (400 mg/mmol) in 3 mL of 1,2-DCE [b)] yields of pure and isolated products.

In conclusion we have developed a facile protocol for the regioselective synthesis of 2-nitro-3-arylimidazo[1,2-*a*]pyridine derivatives by oxidative amination of β-nitrostyrenes with 2-aminopyridine in the presence of SSA as heterogeneous catalyst in 1,2-DCE as solvent under aerobic conditions. Easily accessible starting materials, metal-free catalysis, aerobic conditions, tolerance of wide range of functional groups and operational simplicity are the advantages for the present protocol.

EXPERIMENTAL

Reagents were purchased at the highest quality commercially available and used without further purification. Yields refer chromatographically homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out 0.25mm E-Merck silica gel plates (60F-254) using UV light as visualizing agent. Silica gel (100-200mesh) was used for column chromatography. NMR spectra were recorded on Bruker AMX 400 MHz instrument. The following abbreviations were used to explain the multiplets: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad.

General procedure for synthesis of (3aa-cc):

To a mixture of 2-aminopyridine derivative (**2a-c**) (1.0 mmol), β-nitrostyrene (**1a-c**) (1.0 mmol) and SSA (400 mg) was added 3 mL of 1,2-DCE and allowed to heat at reflux (80 ^{o}C) for 4 h. After completion of the reaction as shown by TLC, solvent was evaporated from the reaction mixture. The crude thus obtained was subjected to purification by silica gel column chromatography using 5 to 10% EtOAc in hexanes as eluent, afforded the corresponding products.

2-Nitro-3-phenylimidazo[1,2-*a*]pyridine (3aa): Gummy mass, Yield 78%, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.65-8.60 (m, 1H), 8.27-8.23 (m, 2H), 7.86 (dt, *J* = 6.4, 1.6 Hz, 1H), 7.67-7.62 (m, 1H), 7.59-7.54 (m, 2H), 7.33-7.28 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 111.55, 118.42, 122.99, 128.75, 129.07, 133.39, 133.65, 138.33, 141.16, 148.94, 159.115; Anal Calcd for $C_{13}H_9N_3O_2$: C, 65.27, H, 3.79, N, 17.56; Found: C, 65.32, H, 3.74, N, 17.58%.

3-(4-Methoxyphenyl)-2-nitroimidazo[1,2-*a*]pyridine (3ba): Gummy mass, Yield 66%, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.61-8.56 (m, 1H), 5.21-8.15 (m, 2H), 7.81 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.27-7.20 (m, 2H), 7.05-7.00 (m, 2H), 3.91 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 55.71, 111.68, 114.53, 118.13, 122.53, 126.69, 130.87, 138.27,140.50, 148.95, 159.65, 163.98; Anal Calcd for $C_{14}H_{11}N_3O_3$: C, 62.45, H, 4.12, N, 15.61; Found: C, 62.38, H, 4.18, N, 15.58%.

3-(Benzo[*d*][1,3]dioxol-5-yl)-2-nitroimidazo[1,2-*a*]pyridine (3ca): Gummy mass, Yield 76%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.61-8.55 (m, 1H), 7.84-7.74 (m, 2H), 7.70 (d, *J* = 1.6 Hz, 1H), 7.28-7.19 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.09 (s, 2H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 102.25, 107.14, 108.39, 111.59, 118.29, 122.64, 126.17, 128.59, 138.23, 140.06, 148.75, 148.87, 152.43, 159.29; Anal Calcd for $C_{14}H_9N_3O_4$: C, 59.37, H, 3.20, N, 14.84; Found: C, 59.34, H, 3.18, N, 14.89%.

8-Methyl-2-nitro-3-phenylimidazo[1,2-*a*]pyridine (3ab): Gummy mass, Yield 81%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.41 (dd, *J* = 4.8, 1.2 Hz, 1H), 8.28 -8.23(m, 2H), 7.66-7.59 (m, 2H), 7.58-7.52 (m, 2H), 7.20 (dd, *J* = 7.2, 4.8 Hz, 1H), 2.38 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 17.28, 111.79, 123.34, 128.05, 128.65, 129.02, 133.16, 133.90, 139.13, 140.29, 146.13, 157.512; Anal Calcd for $C_{14}H_{11}N_3O_2$: C, 66.40, H, 4.38, N, 16.59; Found: C, 66.48, H, 4.35, N, 16.54%.

3-(4-Methoxyphenyl)-8-methyl-2-nitroimidazo[1,2-*a*]pyridine (3bb): Gummy mass, Yield 69%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.42-8.36 (m, 1H), 8.23-8.15 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.17 (dd, *J* = 7.6, 4.8 Hz, 1H), 7.02 (d, *J* = 9.2 Hz, 2H), 3.90 (s, 3H), 2.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 17.32, 55.63, 111.90, 114.43, 122.86, 126.90, 127.70, 130.67, 138.99, 139.57, 146.07, 157.89, 163.75; Anal Calcd for $C_{15}H_{13}N_3O_3$; C, 63.60, H,4.63, N, 14.83; Found: C, 63.57, H, 4.69, N, 14.78%.

3-(Benzo[*d*][1,3]dioxol-5-yl)-8-methyl-2-nitroimidazo[1,2-*a*]pyridine (3cb): Gummy mass, Yield 74%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.41-8.35 (m, 1H), 7.77 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.73 (d, *J* = 1.6 Hz, 1H), 7.59 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.18 (dd, *J* = 7.6, 5.2 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H), 2.34

(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 17.29, 102.19, 107.01, 108.34, 111.83, 123.01, 125.94, 127.89, 128.82, 139.01, 139.14, 146.02, 148.67, 152.22, 157.52; Anal Calcd for $C_{15}H_{11}N_3O_4$; C, 60.61, H, 3.73, N, 14.14; Found: C, 60.58, H, 3.68, N, 14.18%.

7-Methyl-2-nitro-3-phenylimidazo[1,2-*a*]pyridine (3ac): Gummy mass, Yield 77%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.44 (d, *J* = 4.8 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.63-7.57 (m, 1H), 7.56-7.49 (m, 2H), 7.12-7.04 (m, 2H), 2.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 21.05, 111.54, 118.85, 124.02, 128.64, 129.01, 133.25, 133.66, 140.99, 148.54, 149.75, 159.29; Anal Calcd for $C_{14}H_{11}N_3O_2$; C, 66.40, H, 4.38, N,16.59; Found: C, 66.45, H, 4.37, N, 16.52%.

3-(4-Methoxyphenyl)-7-methyl-2-nitroimidazo[1,2-*a*]pyridine (3bc): Gummy mass, 67%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.42 (d, *J* = 4.8 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.08-6.98 (m, 4H), 3.89 (s, 3H), 2.41 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** 21.05, 55.63, 111.64, 114.43, 118.53, 123.57, 126.64, 130.70, 140.27, 148.51, 149.63, 159.69, 163.82; Anal Calcd for $C_{15}H_{13}N_3O_3$; C, 63.60, H, 4.63, N, 14.83; Found: C, 63.63, H, 4.59, N, 14.85%.

3-(Benzo[*d*][1,3]dioxol-5-yl)-7-methyl-2-nitroimidazo[1,2-*a*]pyridine (3cc): Gummy mass, Yield 73%, **^{1}H NMR (400 MHz, $CDCl_3$):** 8.41-8.36 (m, 1H), 7.78 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.72 (d, *J* = 1.6 Hz, 1H), 7.60 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.16 (dd, *J* = 7.6, 5.2 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.08 (s, 2H), 2.34 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** 17.24, 102.18, 107.11, 108.38, 111.91, 123.11, 125.89, 127.88, 128.85, 139.04, 139.18, 146.07, 148.71, 152.25, 157.58; Anal Calcd for $C_{15}H_{11}N_3O_4$; C, 60.61, H, 3.73, N, 14.14; Found: C, 60.58, H, 3.74, N, 14.18%.

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