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Arkivoc **2021**, part viii, 0-0

Meldrum's acid as an excellent catalyst for the facile, efficient and one-pot synthesis of *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines

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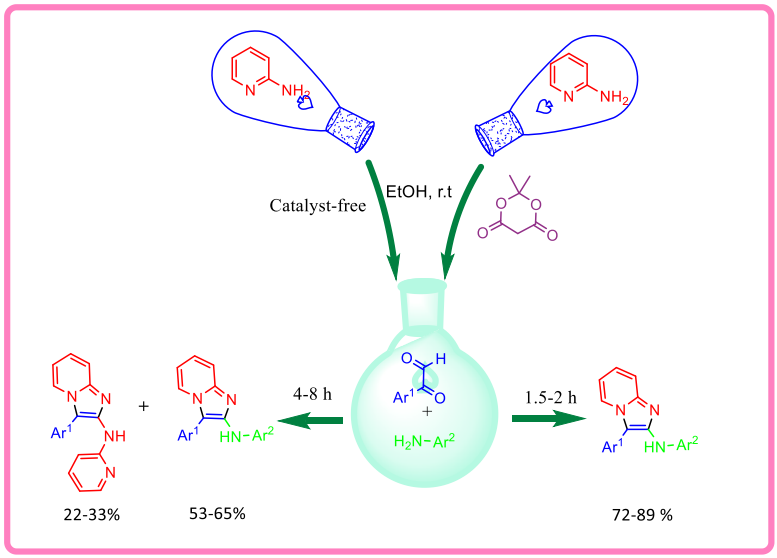
Received 07-23-2021 **Accepted Manuscript** 09-06-2021 **Published on line** 09-19-2021

Abstract

Using the three-component reaction between aryl glyoxals, arylamines, and 2-aminopyridine were synthesized *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines and 3-aryl-*N*-(pyridine-2-*yl*)imidazo[1,2-*a*]pyridin-2-amines under catalyst-free conditions. Using these starting materials under the same conditions and in the presence of Meldrum's acid as catalyst gave only *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines. It was observed for the synthesis of these products, Meldrum's acid as catalyst gave 72-89% yields in 1.5-2 hours as against 4-8 hours required to get 53-65 % yields under catalyst-free conditions.



Keywords: One-pot synthesis, *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines, aryl glyoxals, arylamines, 2-aminopyridine, Meldrum's acid

Introduction

Bicyclic heterocycles, especially imidazo[1,2-*a*]pyridines, which have an amine group on the imidazole ring, are biologically and pharmacologically important.[1-5] In recent years, there has been a strong interest in building a fused imidazole framework.[6] *N*,3-Diarylimidazo[1,2-*a*]pyridin-2-amines have attracted the attention of the synthetic community due to their wide range of applications such as in agrochemistry, materials, polymer science,[7] and medicinal chemistry.[1,8] These compounds have a wide range of properties, including anti-virus,[2] anti-tumor,[3] anti-proliferative,[4] and smooth antagonistic activity.[5] Also, there are several imidazo[1,2-*a*]pyridine-2-amine containing drugs available on the market e.g., zolpidem,[9] zolimidine,[10] and soraprazan.[11]

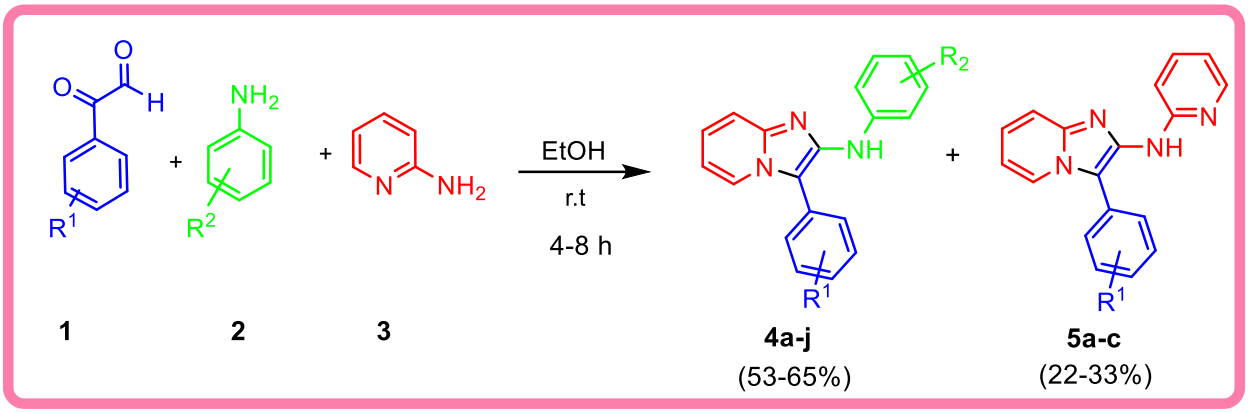
Accordingly, considering the wide range of applications of imidazo[1,2-*a*]pyridine-2-amines, the synthesis of this group of compounds has been considered by chemical and medical researchers. Being highly efficient processes, multicomponent reactions (MCRs)[12] have become very common and have inspired a range of synthetic methods for the formation of *N*,3-diphenylimidazo[1,2-*a*]pyridin-2-amines.[13] In recent years, several effective initiatives have been reported in the field of intramolecular cyclization, tandem reactions, *via* radical addition/cyclization reactions,[14] oxidative couplings with the hypervalent iodine(III) reagents,[15] *via* imidazo[1,2-*a*]pyridin-2-yl triflate through a Suzuki cross-coupling reaction followed by a direct arylation,[16] two-component cyclization of substituted 2-aminopyridines and substituted phenacyl bromides catalysed by DBU,[17] and multistep approaches.[18,19] Also, these compounds can be prepared by one-pot Groebke–Blackburn–Bienayme multicomponent reactions,[20-23] using metallic or non-metallic catalysts[7,24-26] and MW-assisted.[27,28] No doubt, the existing methods are useful but also possess certain limitations like long reaction times, special apparatus, high temperature, expensive catalysts, toxic solvents and tedious workup process. There is always scope to overcome certain limitations.

In this regard, and in continuation of our previous work on the development of multicomponent reactions for the synthesis of imidazole compounds,[29] we herein describe a facile and efficient strategy for the synthesis of *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines *via* the one-pot, three-component reaction of aryl glyoxals, arylamines, and 2-aminopyridine in the presence of Meldrum's acid in ethanol at room temperature.

Results and Discussion

To initiate our study, a mixture of an aryl glyoxal (**1**, 1.0 mmol), an arylamine (**2**, 1.0 mmol), and 2-aminopyridine (**3**, 1.0 mmol) were reacted together in EtOH, from which products *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amine **4a-j** and 3-aryl-*N*-(pyridin-2-*yl*)imidazo[1,2-*a*]pyridin-2-amine **5a-c** were isolated and purified (Table 1).

Table1. Synthesis of *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amine **4a-j** and 3-aryl-*N*-(pyridin-2-*yl*)imidazo[1,2-*a*]pyridin-2-amine **5a-c**



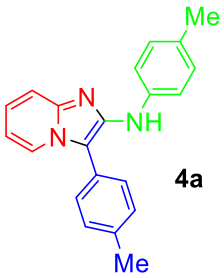
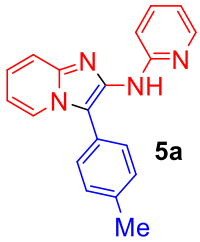
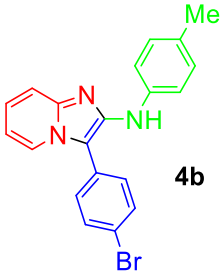
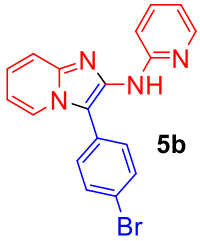
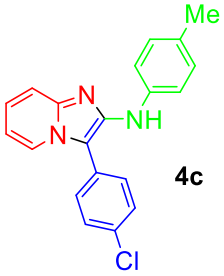
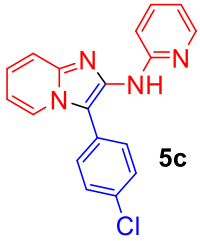
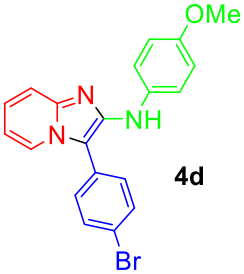
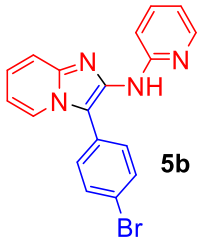
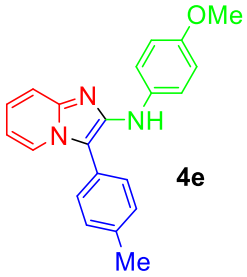
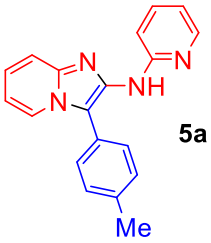
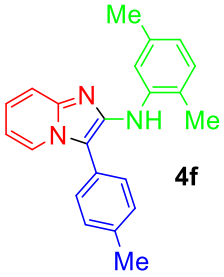
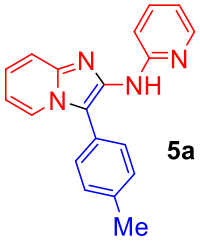
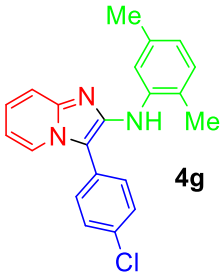
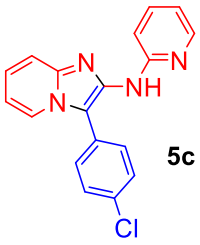
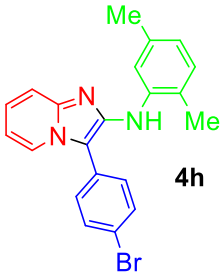
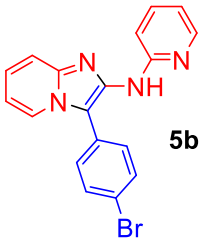
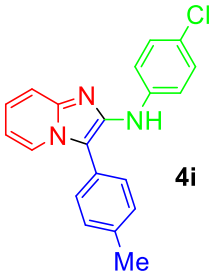
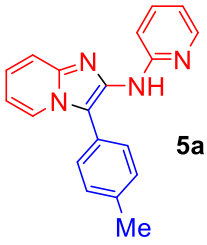
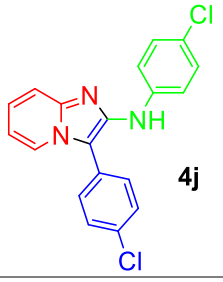
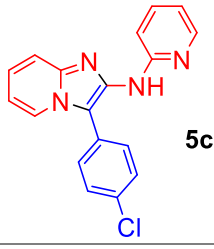
Entry	R^1	R^2	Product (**4**)	Product (**5**)	Time (h)	Yield (%)[a]	
1	4-Me	4-Me	 **4a**	 **5a**	5	**4a** (53)	**5a** (33)
2	4-Br	4-Me	 **4b**	 **5b**	6	**4b** (55)	**5b** (31)
3	4-Cl	4-Me	 **4c**	 **5c**	4	**4c** (58)	**5c** (30)
4	4-Br	4-OMe	 **4d**	 **5b**	7	**4d** (60)	**5b** (25)

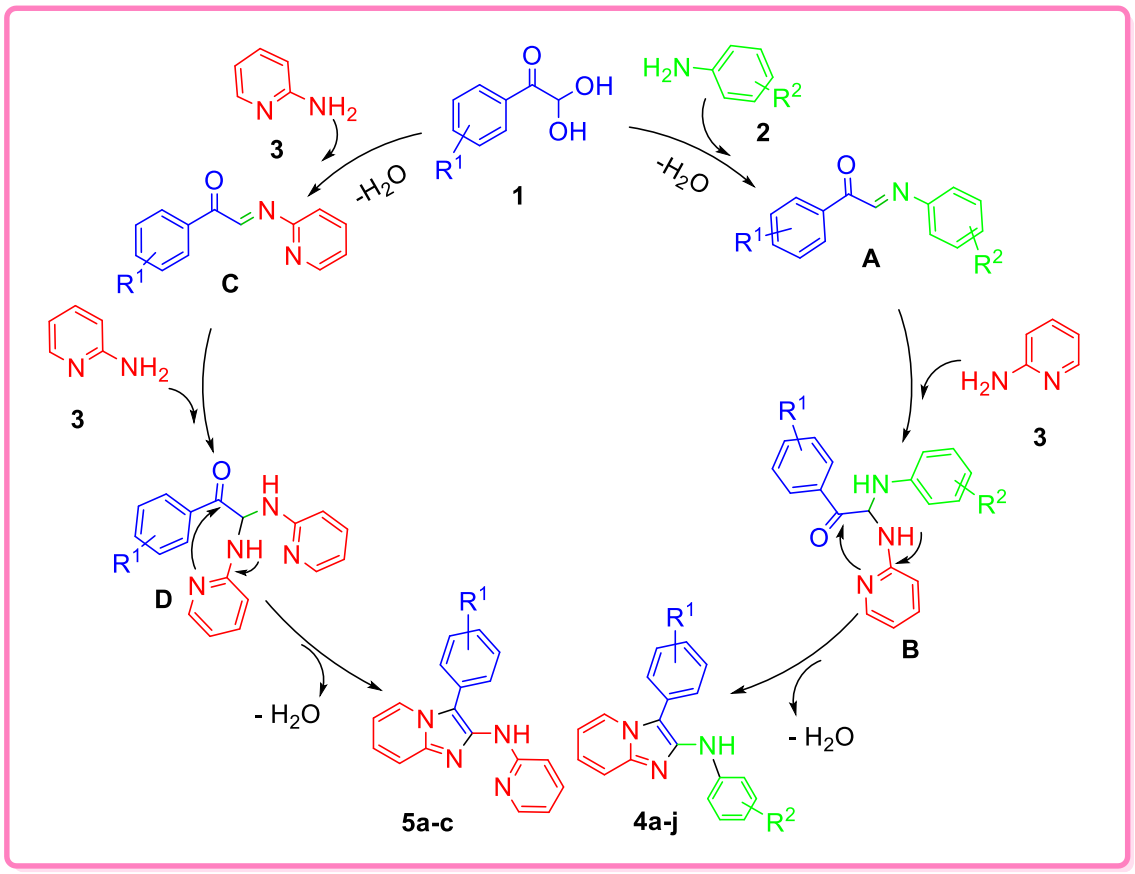
Table 1. Contined

Entry	R^1	R^2	Product (**4**)	Product (**5**)	Time (h)	Yield (%)[a]
5	4-Me	4-OMe	 **4e**	 **5a**	5	**4e** (56) **5a** (32)
6	4-Me	2,5-$(Me)_2$	 **4f**	 **5a**	4	**4f** (59) **5a**(26)
7	4-Cl	2,5-$(Me)_2$	 **4g**	 **5c**	6	**4g** (65) **5c** (22)
8	4-Br	2,5-$(Me)_2$	 **4h**	 **5b**	8	**4h** (65) **5b** (25)
9	4-Me	4-Cl	 **4i**	 **5a**	7	**4i** (57) **5a** (23)
10	4-Cl	4-Cl	 **4j**	 **5c**	6	**4j** (56) **5c** (22)

[a] Isolated yields

To the best of our knowledge, all the synthesized compounds are unknown and were characterized by ^{1}H and ^{13}C NMR, IR, CHN analysis, and melting points. The detailed spectroscopic data, presented in the Experimental, are in agreement with the assigned structures.

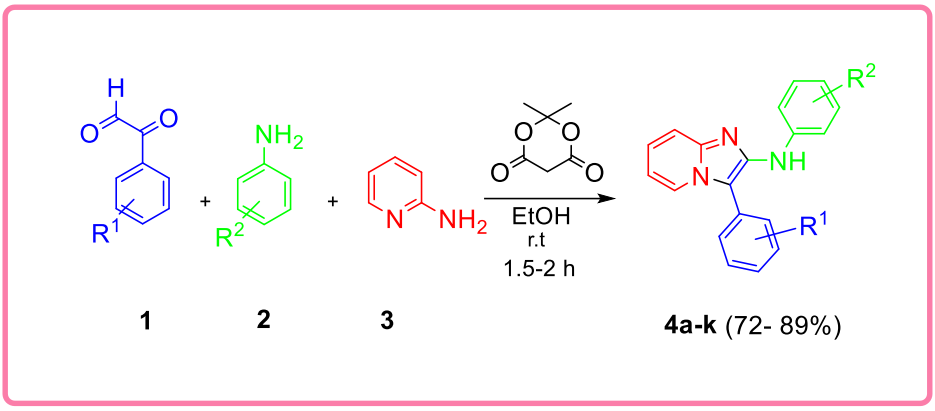
A proposed mechanism for the formation of compounds **4a-j** and **5a-c** is shown in Scheme 1. The compounds **4a-j** are formed in three steps. Initially, an intermediate **A** is prepared from the condensation of aryl glyoxal **1** and arylamine **2**. Subsequently, compound **B** is produced through nucleophilic addition of 2-aminopyridine **3** to the intermediate **A**. In continuation, compounds **4a-j** result from intramolecular cyclization the pyridine ring nitrogen to the carbonyl group and elimination of water. To explain the formation of **5a-c**, it is suggested that firstly, condensation occurs between aryl glyoxal and 2-aminopyridine, and intermediate **C** is formed. Then, a second molecule of 2-aminopyridine, instead of arylamine, adds to **C**, leading to the intermediate **D**. Then, an intramolecular cyclization occurs, as in the formation of compounds **4**, and **5a-c** are obtained with the elimination of water.



Scheme 1. Proposed mechanism for the preparation of compounds **4a-j** and **5a-c**

Further studies showed that Meldrum's acid is an excellent catalyst for the formation of only product *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines **4** in the above reaction. For this purpose, a mixture of aryl glyoxal (**1**, 1.0 mmol), arylamine (**2**, 1.0 mmol), and 2-aminopyridine (**3**, 1.0 mmol) in the presence of Meldrum's acid (0.3 mmol) in EtOH (5.0 mL) were reacted at room temperature, when only the products **4** were obtained (Table 2).

Table 2. Synthesis of *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines **4a-k**



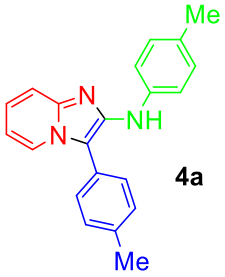
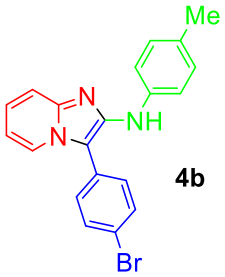
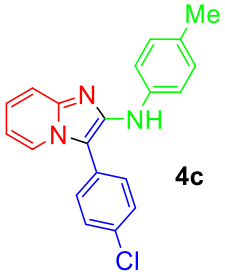
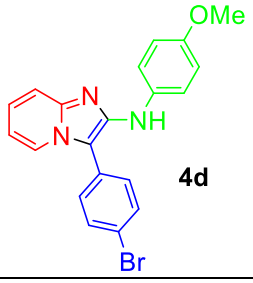
Entry	R^1	R^2	Product (**4**)	Time (h)	Yield (%)[a]
1	4-Me	4-Me	 **4a**	2	72
2	4-Br	4-Me	 **4b**	1.5	76
3	4-Cl	4-Me	 **4c**	1.5	80
4	4-Br	4-OMe	 **4d**	2	86

Table 2. Continued

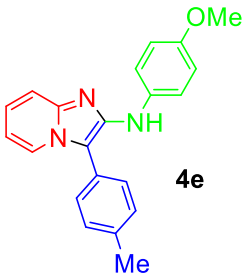
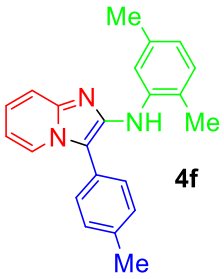
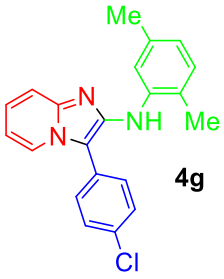
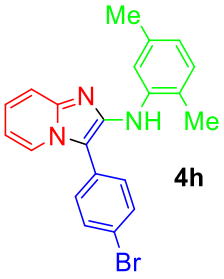
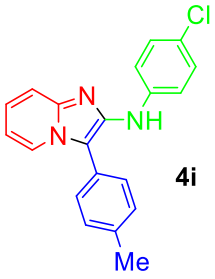
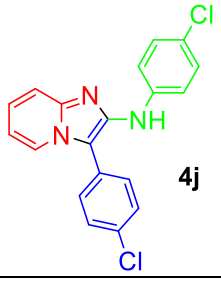
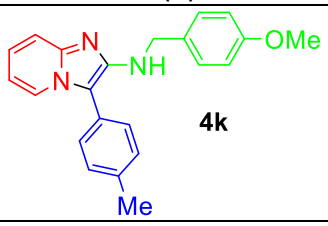
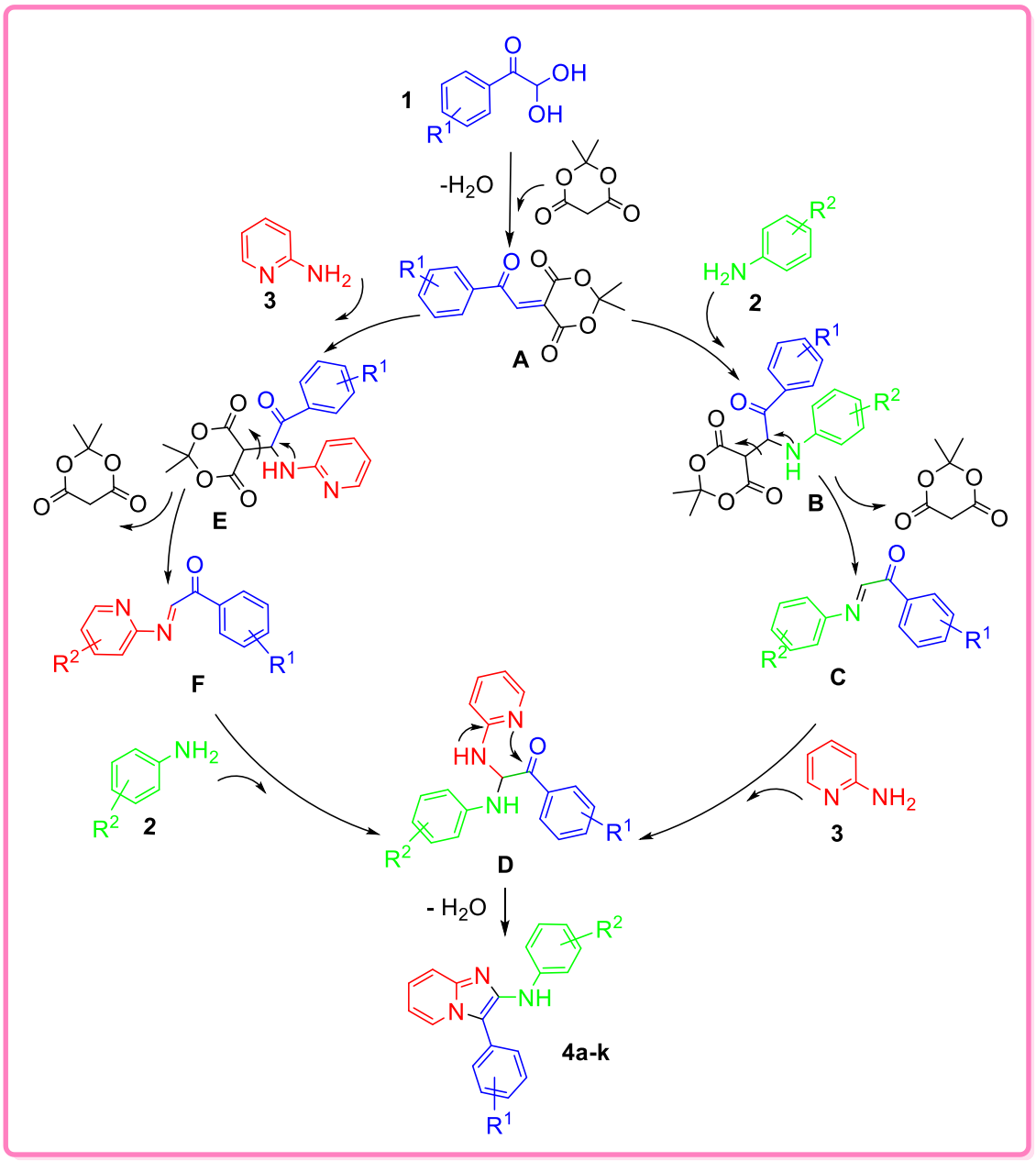
Entry	R^1	R^2	Product (**4**)	Time (h)	Yield (%)[a]
5	4-Me	4-OMe	 **4e**	2	83
6	4-Me	2,5-$(Me)_2$	 **4f**	2	79
7	4-Cl	2,5-$(Me)_2$	 **4g**	1.5	89
8	4-Br	2,5-$(Me)_2$	 **4h**	1.5	88
9	4-Me	4-Cl	 **4i**	1.5	81
10	4Cl	4-Cl	 **4j**	2	80

Table 2. Continued

Entry	R1	R2	Product (4)	Time (h)	Yield (%)a
11	4-Me	4-OMe-Bn	 **4k**	2	80

[a] Isolated yields

When Meldrum's acid is used as a catalyst for the above reaction, it is proposed that there are two pathways, shown in Scheme 2, for the formation of *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines **4a-k**.



Scheme 2. Proposed mechanism of the formation of **4a-k** in the presence of Meldrum's acid as catalyst

In the sequence shown on the right, **4a-k** are formed in five steps. Initially, an intermediate **A** is formed from the Knoevenagel condensation of the aryl glyoxal **1** with Meldrum's acid. Subsequently, nucleophilic addition of arylamine **2** to the intermediate **A** leads to compound **B**. In continuation, with the help of nitrogen nonbonding pair, the Meldrum's acid group is removed and an intermediate of **C** is obtained. Then, compound **D** is obtained by Michael's addition of 2-aminopyridine to intermediate **C**, and finally, intramolecular cyclization and elimination of water leads to compounds **4a-k**. Alternatively, as shown on the left in Scheme 2, initially intermediate **A** is formed as before. Subsequently, compound **E** is formed through nucleophilic addition of 2-aminopyridine **3** to the intermediate **A**. In continuation, with the help of the nitrogen nonbonding pair, the Meldrum's acid group is removed and intermediate **F** is obtained. Next, by Michael's addition of arylamine to intermediate **F**, compound **D** is obtained. In the final stage, intramolecular cyclization, followed by the removal of a molecule of H_2O, leads to compounds (Scheme 2).

A comparison of the data presented in Tables 1 and 2 clearly shows that the use of Meldrum's acid has (i) considerably enhanced the yields of the products (from 53-65% to 72-89%) and (ii) reduced the reaction time from 4-8 h to 1.5-2 h. Also, no by-product (**5**) was formed in the method using Meldrum's acid.

Conclusions

We have successfully prepared new *N*,3-diarylimidazo[1,2-*a*]pyridin-2-amines, which were synthesized by the one-pot, three-component reaction of aryl glyoxals, arylamines, and 2-aminopyridine in the presence of Meldrum's acid as a catalyst. The advantages of the reaction are the simple reaction conditions, using cheap and readily available starting materials, high yields, and short reaction times. Moreover, the participation of Meldrum's acid makes this process highly efficient.

Experimental Section

General. All chemicals were purchased from Aldrich and Merck with high-grade quality and used without any purification. All products were obtained by reaction at room temperature in ethanol as solvent. All melting points were obtained by Barnstead Electro thermal 9200 apparatus and are uncorrected. IR spectra were recorded on a Bruker FT-IR Equinax-55 spectrophotometer in KBr with absorption in cm^{-1}. The NMR spectra were recorded on a Varian model UNITY Inova 500 MHz spectrometer (^1H: 500, ^{13}C: 125 MHz) in $CDCl_3$ using TMS as an internal standard. Elemental analyses were performed using a Carlo Erba EA 1108 instrument. All products were characterized by their spectral and physical data.

Synthesis of compounds 4a-j and 5a-c in catalyst-free conditions

A mixture of aryl glyoxal (**1**, 1.0 mmol), arylamine (**2**, 1.0 mmol), and 2-aminopyridine (**3**, 1.0 mmol) was stirred in ethanol (5.0 mL) at rt for 4-8 h. After the completion of the reaction (TLC), the solvent was removed under reduced pressure and the crude product was purified by plate chromatography (20×20 cm) using *n*-hexane/EtOAc (1:2) as eluent to give the pure compounds **4a-j** (53-65%) and **5a-c** (22-33%).

Synthesis of compounds 4a-k in presence of Meldrum's acid as catalyst

A mixture of aryl glyoxal (**1**, 1.0 mmol), arylamine (**2**, 1.0 mmol), and 2-aminopyridine (**3**, 1.0 mmol) in presence of Meldrum's acid (0.3 mmol) as catalyst was stirred in ethanol (5.0 mL) at rt for 1.5-2 h. After

completion of the reaction (TLC), the solvent was removed under reduced pressure and the crude product was purified by plate chromatography, as above, to give the pure compounds **4a-k** (72-89%).

***N*,3-Di-*p*-tolylimidazo[1,2-*a*]pyridin-2-amine (4a)**. Yellow solid; yield 72%; mp 213-215 °C. IR: 3168, 3001, 1686, 1579 cm^{-1}. ^1H NMR: δ 2.27 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 5.49 (s, 1H, NH), 6.50 (d, *J* 8.4 Hz, 2H, ArH), 6.75 (t, *J* 6.7 Hz, 1H, ArH), 7.01 (d, *J* 8.2 Hz, 2H, ArH), 7.18 (d, *J* 8.1 Hz, 2H, ArH), 7.21 (t, *J* 8.0 Hz, 1H, ArH), 7.63 (d, *J* 9.0 Hz, 1H, ArH), 7.81 (d, *J* 6.8 Hz, 1H, ArH), 7.89 (d, *J* 8.2 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 20.4, 21.2, 112.0, 113.4, 117.4, 118.1, 122.7, 124.8, 126.9, 129.1, 129.2, 130.2, 137.6, 139.2, 142.3, 142.5, 144.5 ppm. Anal. Calcd for $C_{21}H_{19}N_3$ (313.40): C, 80.48; H, 6.11; N, 13.41. Found: C, 80.12; H, 6.06; N, 13.48 %.

3-(4-Bromophenyl)-*N*-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (4b). Yellow solid; yield 76%; mp 218-220 °C. IR: 3228, 3098, 1670, 1597 cm^{-1}. ^1H NMR: δ 1.95 (s, 3H, CH_3), 6.21 (d, *J* 8.3 Hz, 2H, ArH), 6.49 (t, *J* 6.8 Hz, 1H, ArH), 6.68 (d, *J* 8.1 Hz, 2H, ArH), 6.88 (s, 1H, NH), 6.95 (t, *J* 5.4 Hz, 1H, ArH), 7.17 (d, *J* 8.5 Hz, 2H, ArH), 7.29 (d, *J* 9.0 Hz, 1H, ArH), 7.58 (d, *J* 7.6 Hz, 1H, ArH),7.68 (d, *J* 8.6 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 20.2, 111.8, 113.1, 117.2, 119.4, 121.1, 122.9, 124.8, 128.0, 128.4, 129.8, 131.2, 132.7, 137.2, 142.2, 142.4 ppm. Anal. Calcd for $C_{20}H_{16}BrN_3$ (378.27): C, 63.50; H, 4.26; N, 11.11. Found: C, 63.72; H, 4.31; N, 11.02 %.

3-(4-Chlorophenyl)-*N*-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (4c). Yellow solid; yield 80%; mp 236-238 °C. IR: 3221, 3027, 1672, 1576 cm^{-1}. ^1H NMR: δ 2.26 (s, 3H, CH_3), 5.49 (s, 1H, NH), 6.49 (d, *J* 7.9 Hz, 2H, ArH), 6.76 (t, *J* 6.8 Hz, 1H, ArH), 7.02 (d, *J* 7.9 Hz, 2H, ArH), 7.23 (t, *J* 10.4 Hz, 1H, ArH), 7.32 (d, *J* 7.7 Hz, 2H, ArH), 7.62 (d, *J* 10.3 Hz, 1H, ArH), 7.82 (d, *J* 5.4 Hz, 1H, ArH), 7.95 (d, *J* 9.0 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 20.4, 112.2, 113.4, 117.7, 118.5, 122.7, 125.1, 128.3, 128.7, 129.4, 130.3, 131.9, 133.7, 134.2, 141.9, 142.7 ppm. Anal. Calcd for $C_{20}H_{16}ClN_3$ (333.82): C, 71.96; H, 4.83; N, 12.59. Found: C, 72.24; H, 4.86; N, 12.47 %.

3-(4-Bromophenyl)-*N*-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-2-amine (4d). Yellow solid; yield 86%; mp 219-221 °C. IR: 3213, 3001, 1672, 1593 cm^{-1}. ^1H NMR: δ 3.75 (s, 3H, OCH_3), 5.38 (s, 1H, NH), 6.54 (d, *J* 8.9 Hz, 2H, ArH), 6.78 (t, *J* 8.6 Hz, 1H, ArH), 6.88 (d, *J* 10.0Hz, 1H, ArH), 7.24 (t, *J* 6.0 Hz, 1H, ArH), 7.48 (d, *J* 8.5 Hz, 2H, ArH), 7.62 (d, *J* 9.0 Hz, 1H, ArH), 7.84 (d, *J* 6.6 Hz, 2H, ArH), 7.89 (d, *J* 8.5 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 55.6, 112.2, 114.5, 115.4, 117.7, 121.8, 122.7, 125.1, 125.9, 128.5, 131.7, 133.0, 138.0, 145.3, 148.5, 153.7 ppm. Anal. Calcd for $C_{20}H_{16}BrN_3O$ (394.27): C, 60.93; H, 4.09; N, 10.66. Found: C, 61.14; H, 4.13; N, 10.79 %.

***N*-(4-Methoxyphenyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (4e).** Yellow solid; yield 83%; mp 218-220 °C. IR: 3216, 3086, 1674, 1578 cm^{-1}. ^1H NMR: δ 2.34 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 5.44 (s, 1H, NH), 6.53 (d, *J* 8.9 Hz, 2H, ArH), 6.74 (t, *J* 6.8 Hz, 1H, ArH), 6.77 (d, *J* 8.9 Hz, 2H, ArH), 7.17 (d, *J* 7.9 Hz, 2H, ArH), 7.20 (m, 1H, ArH), 7.62 (d, *J* 6.7 Hz, 1H, ArH), 7.81 (d, *J* 9.2 Hz, 2H, ArH), 7.89 (d, *J* 8.2 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 21.2, 55.6, 111.8, 114.5, 115.3, 117.5, 118.6, 122.6, 124.6, 126.9, 129.2, 130.7, 137.5, 138.5, 139.3, 142.5, 153.6 ppm. Anal. Calcd for $C_{21}H_{19}N_3O$ (329.40): C, 76.57; H, 5.81; N, 12.76. Found: C, 76.44; H, 5.86; N, 12.52 %.

***N*-(2,5-Dimethylphenyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (4f).** Yellow solid; yield 79%; mp 226-228 °C. IR: 3403, 3072, 1685, 1576 cm^{-1}. ^1H NMR: δ 2.07 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 5.37 (s, 1H, NH), 5.98 (s, 1H, ArH), 6.62 (d, *J* 9.3 Hz, 1H, ArH), 6.73 (t, *J* 6.8 Hz, 1H, ArH), 7.09 (d, *J* 7.5, 1H, ArH), 7.16 (d, *J* 7.8 Hz, 2H, ArH), 7.20 (t, *J* 7.7 Hz, 1H, ArH), 7.65 (d, *J* 9.1 Hz, 1H, ArH), 7.71 (d, *J* 6.8 Hz, 1H, ArH), 7.87 (d, *J* 8.2 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 17.1, 21.1, 21.2, 111.9, 112.5, 115.6, 117.5, 118.0, 119.3, 120.4, 122.6, 124.6, 126.7, 129.3, 130.7, 137.4, 137.5, 139.2, 142.3, 142.6 ppm. Anal. Calcd for $C_{22}H_{21}N_3$ (327.43): C, 80.70; H, 6.46; N, 12.83. Found: C, 80.27; H, 6.38; N, 12.70 %.

3-(4-Chlorophenyl)-*N*-(2,5-dimethylphenyl)imidazo[1,2-*a*]pyridin-2-amine (4g). Yellow solid; yield 89%; mp 239-241 °C. IR: 3183, 3001, 1686, 1580 cm^{-1}. ^1H NMR: δ 2.07 (s, 3H, CH_3), 2.38(s, 3H, CH_3), 5.38 (s, 1H, NH), 5.96 (s, 1H, ArH), 6.63 (d, *J* 7.6 Hz, 1H, ArH), 6.76 (t, *J* 6.7 Hz, 1H, ArH), 7.10 (d, *J* 7.5, 1H, ArH), 7.24 (t, *J* 6.8 Hz, 1H, ArH), 7.30 (d, *J* 7.8 Hz, 2H, ArH), 7.63 (d, *J* 9.0 Hz, 1H, ArH), 7.72 (d, *J* 6.1 Hz, 1H, ArH), 7.89 (d, *J* 8.1 Hz, 2H,

ArH) ppm. ^{13}C NMR: δ 17.1, 21.1, 112.3, 112.4, 117.6, 118.3, 119.3, 120.6, 122.7, 125.2, 128.1, 128.7, 130.8, 131.9, 133.6, 137.5, 138.2, 142.0, 142.7 ppm. Anal. Calcd for $C_{21}H_{18}ClN_3$ (347.85): C, 72.51; H, 5.22; N, 12.08. Found: C, 72.86; H, 5.35; N, 12.03 %.

3-(4-Bromophenyl)-*N*-(2,5-dimethylphenyl)imidazo[1,2-*a*]pyridin-2-amine (4h). Yellow solid; yield 88%; mp 222-224 °C. IR: 3184, 3001, 1686, 1579 cm^{-1}. ^{1}H NMR: δ 2.07 (s, 3H, CH_3), 2.38(s, 3H, CH_3), 5.37 (s, 1H, NH), 5.96 (s, 1H, ArH), 6.63 (d, *J* 8.2 Hz, H, ArH), 6.77 (t, *J* 6.8 Hz, 1H, ArH), 7.09 (d, *J* 7.5 Hz, 1H, ArH), 7.23 (t, *J* 8.3 Hz, 1H, ArH), 7.45 (d, *J* 8.5 Hz, 2H, ArH), 7.63 (d, *J* 9.1 Hz, 1H, ArH), 7.72 (d, *J* 6.7 Hz, 1H, ArH), 7.83 (d, *J* 8.6 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 17.1, 21.1, 112.3, 112.4, 117.6, 118.5, 119.3, 120.7, 121.9, 122.7, 125.2, 128.4, 130.8, 131.7, 132.4, 137.5, 138.2, 142.0, 142.7 ppm. Anal. Calcd for $C_{21}H_{18}BrN_3$ (392.30): C, 64.30; H, 4.63; N, 10.71. Found: C, 64.28; H, 4.71; N, 10.58 %.

***N*-(4-Chlorophenyl)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (4i).** Yellow solid; yield 81%; mp 235-237 °C. IR: 3239, 3080, 1673, 1595 cm^{-1}. ^{1}H NMR: δ 2.33 (s, 3H, CH_3), 5.74 (s, 1H, NH), 6.49 (d, *J* 8.9 Hz, 2H, ArH), 6.75 (t, *J* 6.7 Hz, 1H, ArH), 7.13 (d, *J* 4.3, 2H, ArH), 7.15 (d, *J* 3.5 Hz, 2H, ArH), 7.20 (t, *J* 8.1 Hz, 1H, ArH), 7.59 (d, *J* 9.0 Hz, 1H, ArH), 7.75 (d, *J* 6.8 Hz, 1H, ArH), 7.82 (d, *J* 8.2 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 21.2, 112.2, 114.5, 117.2, 117.5, 122.4, 124.5, 125.0, 126.8, 129.3, 129.7, 130.2, 137.8, 139.6, 142.7, 143.4 ppm. Anal. Calcd for $C_{20}H_{16}ClN_3$ (333.82): C, 71.96; H, 4.83; N, 12.59. Found: C, 72.14; H, 4.78; N, 12.50 %.

***N*,3-Bis(4-chlorophenyl)imidazo[1,2-*a*]pyridin-2-amine (4j).** Yellow solid; yield 80%; mp 265-267 °C. IR: 3239, 3050, 1675, 1595 cm^{-1}. ^{1}H NMR: δ 5.77 (s, 1H, NH), 6.49 (d, *J* 8.8 Hz, 2H, ArH), 6.78 (t, *J* 6.7 Hz, 1H, ArH), 7.15 (d, *J* 8.8 Hz, 2H, ArH), 7.23 (t, *J* 7.4 Hz, 1H, ArH), 7.27 (d, *J* 8.6 Hz, 2H, ArH), 7.59 (d, *J* 9.0 Hz, 1H, ArH), 7.76 (d, *J* 6.8 Hz, 1H, ArH), 7.86(d, *J* 8.6 Hz, 2H, ArH) ppm. ^{13}C NMR: δ 112.5, 114.5, 117.7, 122.5, 124.9, 125.4, 128.1, 128.7, 129.8, 131.6, 133.8, 138.5, 142.6, 142.8,143.0 ppm. Anal. Calcd for $C_{19}H_{13}Cl_2N_3$ (354.23): C, 64.42; H, 3.70; N, 11.86. Found: C, 64.81; H, 3.79; N, 11.73 %.

4-Methyl-*N*-((3-(*p*-methoxy)imidazo[1,2-*a*]pyridin-2-*yl*)methyl)aniline(4k). Yellow solid; yield 80%; mp 223-225 °C. IR: 3443, 3010, 1671, 1572 cm^{-1}. ^{1}H NMR: δ 2.44 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 4.57 (d, j 5.5 Hz, 2H, CH_2), 6.24 (broad, 1H, NH), 6.84 (d, *J* 8.7 Hz, 2H, ArH), 6.88 (d, *J* 12.1 Hz, 2H, ArH), 7.10 (d, *J* 8.5 Hz, 2H, ArH), 7.21-7.30 (m, 2H, ArH), 7.32 (d, *J* 7.6 Hz, 2H, ArH), 7.67 (d, *J* 8.0 Hz, 1H, ArH), 7.83 (d, *J* 8.0 Hz, 1H, ArH) ppm. Anal. Calcd for $C_{22}H_{21}N_3O$ (343.43): C, 76.94; H, 6.16; N, 12.24. Found: C, 76.77; H, 6.04; N, 12.08 %.

***N*-(Pyridin-2-*yl*)-3-(*p*-tolyl)imidazo[1,2-*a*]pyridin-2-amine (5a).** Yellow solid; yield 23-33 %; mp 196-198 °C. IR: 3443, 3005, 1630, 1597 cm^{-1}. ^{1}H NMR: δ 2.34 (s, 1H, CH_3), 6.11 (d, *j* 8.6 Hz, 1H, ArH), 6.75-6.81 (m, 2H, ArH), 6.86 (s, 1H, NH), 7.18 (d, *j* 7.9 Hz, 2H, ArH), 7.24 (t, *j* 8.0 Hz, 2H, ArH), 7.39 (t, *j* 7.2 Hz, 1H, ArH), 7.67 (d, *j* 7.9 Hz, 2H, ArH), 7.24 9 (t, *j* 8.0 Hz, 2H, ArH), 7.39 9 (t, *j* 7.2 Hz, 1H, ArH), 7.67 (d, *j* 10.2 Hz, 1H, ArH), 7.88 (d, *j* 6.8 Hz, 1H, ArH), 7.95 (d, *j* 8.2 Hz, 2H, ArH), 8.20 (d, *j* 5.0 Hz, 1H, ArH).) ppm. ^{13}C NMR: δ 21.2, 106.4, 112.2, 115.1, 117.1, 121.9, 125.0, 126.2, 129.8, 136.7, 138.6, 142.8, 143.0, 149.0, 157.4, 169.1 ppm Anal. Calcd for $C_{19}H_{16}N_4$ (300.37): C, 75.98; H, 5.37; N, 18.65. Found: C, 76.64; H, 5.34; N, 18.51 %.

3-(4-Bromophenyl)-*N*-(pyridin-2-*yl*)imidazo[1,2-*a*]pyridin-2-amine (5b). Yellow solid; yield 25-31 %; mp 220-222 °C. IR: 3446, 3001, 1655, 1600 cm^{-1}. ^{1}H NMR: δ 6.12 (d, *j* 8.2 Hz, 1H, ArH), 6.55 (s, 1H, NH), 6.79-6.84 (m, 2H, ArH), 7.27 (t, *j* 6.7 Hz, 1H, ArH), 7.42 (t, *j* 7.2 Hz, 1H, ArH), 7.50 (d, *j* 8.5 Hz, 1H, ArH), 7.66 (d, *j* 9.1 Hz, 1H, ArH), 7.89 (d, *j* 5.7 Hz, 1H, ArH), 7.95 (d, *j* 8.6 Hz, 1H, ArH), 8.24 9 (d, *j* 3.5 Hz, 1H, ArH) ppm. ^{13}C NMR: δ 107.0, 112.3, 115.4, 122.5, 125.4, 128.6, 131.7, 135.8, 139.3, 143.6, 145.4, 148.3, 154.5, 161.5 ppm. Anal. Calcd for $C_{18}H_{13}BrN_4$ (365.23): C, 59.19; H, 3.59; N, 15.34. Found: C, 59.32; H, 4.06; N, 15.25 %.

3-(4-Chlorophenyl)-*N*-(pyridin-2-*yl*)imidazo[1,2-*a*]pyridin-2-amine (5c). Yellow solid; yield 22-30 %; mp 230-232 °C. IR: 3443, 3010, 1680, 1596 cm^{-1}. ^{1}H NMR: δ 6.11 (d, *j* 8.3 Hz, 1H, ArH), 6.76 (t, *j* 7.2 Hz, 1H, ArH), 6.81 (t, *j* 6.7 Hz, 1H, ArH), 7.24-7.27 (m, 2H, NH, ArH), 7.31 (d, *j* 8.6 Hz, 2H, ArH), 7.39 (t, *j* 8.8 Hz, 1H, ArH), 7.66 (d, *j* 9.0 Hz, 1H, ArH), 7.88 (d, *j* 7.3 Hz, 1H, ArH), 7.99 (d, *j* 4.9 Hz, 2H, ArH), 8.16 (d, *j* 3.3 Hz, 1H, ArH) ppm. ^{13}C NMR: δ

106.4, 112.5, 115.8, 116.6, 117.8, 122.5, 125.4, 128.4, 128.7, 131.6, 132.9, 133.7, 138.8, 143.0, 148.5, 156.7 ppm. Anal. Calcd for $C_{18}H_{13}ClN_4$ (320.78): C, 67.40; H, 4.09; N, 17.47. Found: C, 67.61; H, 4.14; N, 17.36 %.

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