

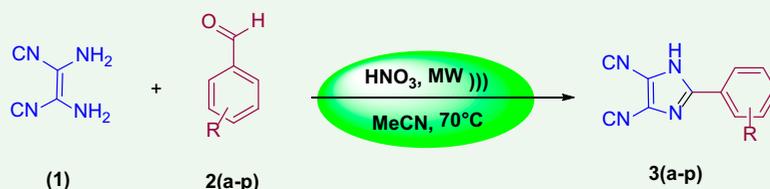
## Microwave-assisted one-step rapid synthesis of dicyano imidazoles by HNO<sub>3</sub> as a high efficient promoter

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### ABSTRACT

Microwave-activated synthesis is a special and remarkable technique in modern synthetic organic chemistry. In the current research, it is described the microwave-assisted synthesis of 2-aryl-4,5-dicarbonitrile imidazole derivatives *via* a one-step reaction between aromatic aldehydes and 2,3-diaminomaleonitrile (DAMN) using HNO<sub>3</sub> as a metal-free catalyst and a strong oxidizing agent. The present methodology has significant advantages as like as one-step synthesis, shorter reaction times, available starting materials, and higher yields of products with easy purification process, cleaner reaction than the previously reported processes. The valuable benefits of this method have provided a promising prospect for easier, greener, and faster synthesis of dicyano imidazoles.



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### KEYWORDS

Microwave-assisted synthesis; dicyano imidazole; nitric acid; metal-free oxidation catalyst; one-step reaction

## Introduction

The synthesis of *N*-heterocycles with various functional groups is an important research domain in organic synthesis and medicinal chemistry, because the scope and applicability of such post-functionalized compounds may be increased (1). Imidazole, as one of the most important *N*-heterocycles, plays a significant role in pharmaceutical chemistry. The imidazole ring with diverse functional groups can have biological activities (2–4). Drugs based on functionalized imidazole skeleton are presented in Figure 1. Therefore, the development of efficient procedures for the synthesis of those privileged scaffolds is an active ongoing research area for chemists (5–7).

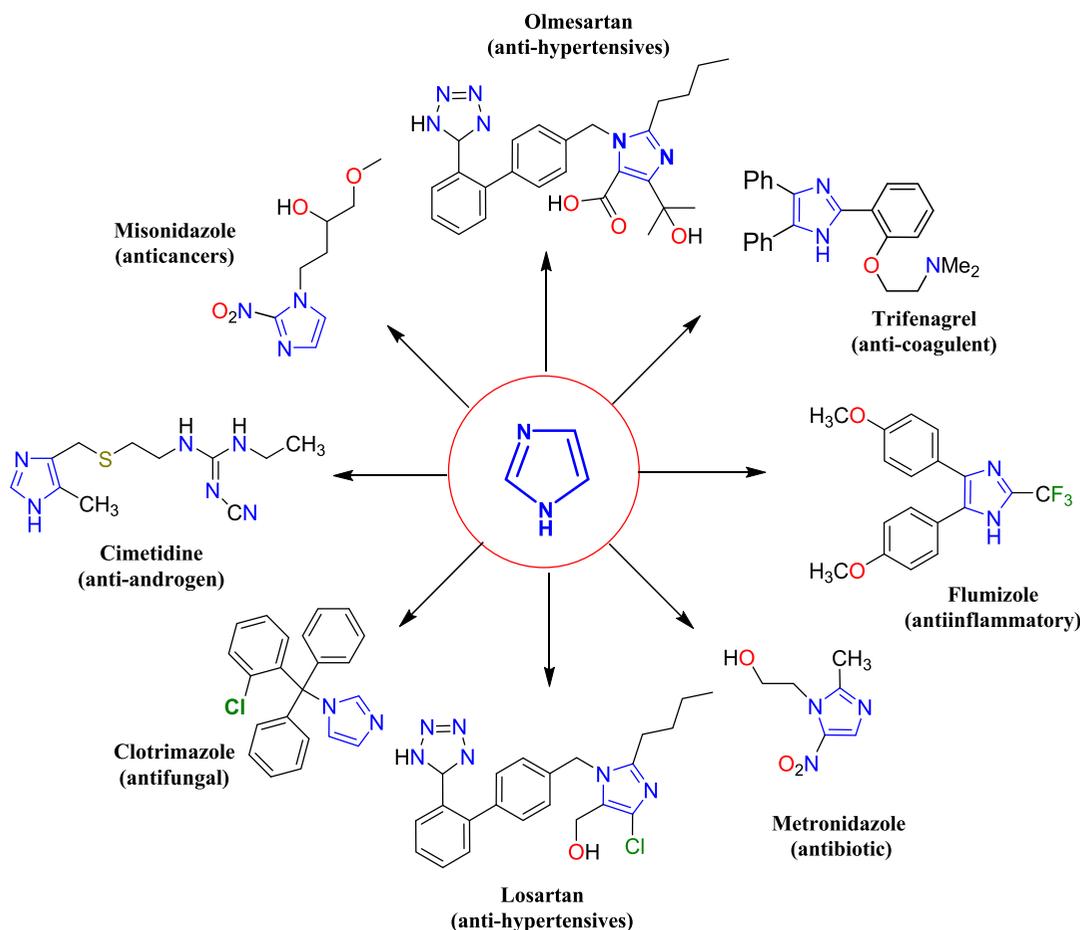
Cyano-containing imidazoles especially 2-aryl-4,5-dicarbonitrile imidazoles are considered an important class of organic heterocycles due to their pharmacological activities. These substituted imidazoles are used in the synthesis of new promising acceptor moieties (8,9). The first report for the synthesis of 4,5-dicyanoimidazole was presented in 1950 by Woodward (10). Although a great deal of chemistry on 4,5-dicyanoimidazoles has

been described in the literature, there are few references about the synthesis of 2-aryl-4,5-dicarbonitriles. Among the reported methods (so far, four methods), the reaction between Schiff bases and oxidizing reagents such as 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or diiminosuccinonitrile (DISY) (11), *N*-chlorosuccinimide (NCS) (12), iodine, and sodium acetate (13), and Pb(OAc)<sub>4</sub> (14) have been used for the preparation of these heterocyclic compounds. Recently, we have reported a better pathway for the synthesis of these compounds via a one-pot transformation of aldehydes and 2,3-diaminomaleonitrile using cerium(IV) ammonium nitrate (CAN) (15). But the usage of excess CAN reagent, long reaction time, the use of transition metal, and two-step reaction were the limitations of this approach. Also in another report, we were able to reduce a small amount of CAN as a catalyst and the reaction was performed under solvent or solvent-free conditions (16,17). All the reported methods have some disadvantages as like as hazardous reaction conditions, long reaction times, unsatisfactory yields, the use of stoichiometric amounts of toxic reagents and transition

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**Figure 1.** Drugs based on functionalized imidazole ring.

metals, high temperature, complex work-up procedures, and tedious purification steps. Therefore, the development of a simple, efficient, rapid, and high-yield and environmentally benign approach is required for the synthesis of this type of heterocyclic compounds.

In recent years, the development of new synthetic methods and straightforward protocol such as microwave-assisted synthesis using new and more efficient reagents for the synthesis of functionalized heterocycles is becoming more attractive. Microwave-assisted organic synthesis is a sustainable and economically acceptable synthetic tool for the preparation of functionalized *N*-heterocycles (18–23), Application of microwave technology in synthetic chemistry helps to the reduction in reaction time, increased in product yields, cleaner reaction, milder conditions, and suppression of unwanted byproducts formation (19).

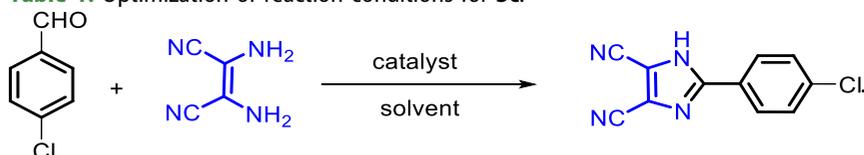
On the other hand, nitric acid is a key starting material in organic synthesis and analytical chemistry such as a precursor for nitration of organic compounds (24), a strong oxidizing agent (25), and an effective catalyst in catalytic processes (26,27). Also, it is an analytical reagent for determining metal trace in solutions (28),

the production of fertilizers, helping to boost the arability and yield of farmland (29). Moreover,  $\text{HNO}_3$  is used as a cleaning agent such as etching in printmaking, pickling stainless steel or cleaning silicon wafers in electronics (30). However,  $\text{HNO}_3$  has not yet been used as a catalyst in the oxidative production of heterocycles under microwave irradiations.

By considering these facts and in our further research efforts for planning on easy synthesis of heterocyclic compounds (31,32), we now report  $\text{HNO}_3$ -catalyzed, efficient and time-saving one-pot protocol for the synthesis of 2-aryl-4,5-dicarbonitrile imidazoles from aromatic aldehydes and 2,3-diaminomaleonitrile using microwave heating technique.

## Result and discussion

In the present work, we have reported a simple and rapid  $\text{HNO}_3$ -catalyzed and microwave-assisted synthesis of 2-aryl-4,5-dicarbonitriles. To optimize this procedure, *p*-chlorobenzaldehyde and 2,3-diaminomaleonitrile were selected as a model reaction. Different reaction conditions were evaluated and the results are

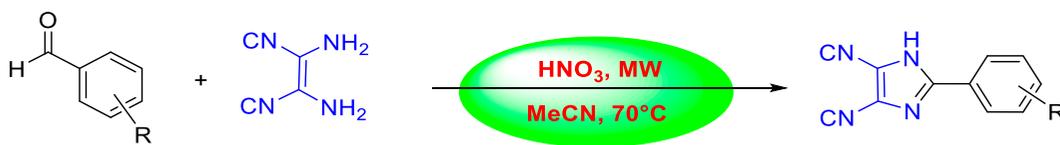
**Table 1.** Optimization of reaction conditions for **3c**.

Entry	Catalyst loading(equiv.)		Solvent	Temperature (°C)	Power (W)	Time (min)	Yield (%) <sup>a</sup>
	HNO <sub>3</sub>	CAN					
1	–	0.4	CH <sub>3</sub> CN	70	600	20	– <sup>b</sup>
2	1	0.1	CH <sub>3</sub> CN	70	600	7	90
3	1	0.05	CH <sub>3</sub> CN	70	600	5	78
4	1	0.05	CH <sub>3</sub> CN	70	600	7	90
5	1	0.03	CH <sub>3</sub> CN	70	600	7	53
6	1	0.05	–	70	600	7	47
7	0.5	0.05	CH <sub>3</sub> CN	70	600	7	73
8	APS (0.1) <sup>c</sup>	0.05	CH <sub>3</sub> CN	70	600	20	–
9	H <sub>2</sub> O <sub>2</sub> (1)	0.05	CH <sub>3</sub> CN	70	600	20	–
10	H <sub>2</sub> O <sub>2</sub> (1)	–	CH <sub>3</sub> CN	90	600	20	–
11	1	–	CH <sub>3</sub> CN	70	600	7	89
12	2	–	CH <sub>3</sub> CN	70	600	7	57
13	1.5	–	CH <sub>3</sub> CN	70	600	7	65
14	0.5	–	CH <sub>3</sub> CN	70	600	7	70
15	1	–	CH <sub>3</sub> CN	70	600	7	89
16	1	–	CH <sub>3</sub> CN	70	600	7	75
17	<b>1</b>	–	<b>CH<sub>3</sub>CN</b>	<b>70</b>	<b>500</b>	<b>5</b>	<b>89</b>
18	1	–	CH <sub>3</sub> CN	70	400	5	78
19	1	–	CH <sub>3</sub> CN	60	500	5	80
20	1	–	CH <sub>3</sub> CN	80	500	5	89
21	1	–	EtOH	70	500	5	–
22	1	0.05	EtOH	70	500	20	–
23	1	–	CH <sub>3</sub> CN	90	–	30	– <sup>d</sup>
24	1	–	CH <sub>3</sub> CN	80	–	60	–

<sup>a</sup>Isolated yield.<sup>b</sup>The product was Schiff base<sup>c</sup>Ammonium per sulfate<sup>d</sup>The reaction was performed under refluxing, but no pure product was obtained.

summarized in Table 1. For the first step, according to the results obtained in previous research (15), we examined the effect of CAN as a catalyst on the progress of the reaction at 70°C under microwave heating (600 W) and in MeCN solvent. But the isolated product was Schiff base in one-step reaction and imidazole was not produced (Table 1, entry 1). It was considered the necessity of using an oxidant in the presence of CAN for the synthesis of imidazole. Therefore, different amounts of HNO<sub>3</sub>/CAN were investigated under similar condition and 1/0.05 eq. of catalyst led to the expected product **3c** in 90% yield in 7 min' (Table 1, entry 4). When the model reaction was carried out with H<sub>2</sub>O<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, the catalytic process was not successful (Table 1, entries 8–10). Interestingly, the reaction showed admirable results in the presence of nitric acid without CAN under similar condition, because 89% yield of the product was obtained during 7 min (Table 1, entry 15). The removal of CAN (as a transition metal containing compound) compared to the previously reported method (15), was an effective step in the application of the principles of green chemistry for the preparation of dicyano imidazoles. Microwave technique could be another

important goal of this research towards the goals of green chemistry. Because it was a key stage to reduce the reaction time and increase the yield. In order to show the effect of the power of microwave irradiation, the model reaction was conducted using different powers. According to the results, 500 W was chosen as the optimized power for the synthesis of substituted imidazole derivatives in 5 min (Table 1, entry 17). We continued our studies by examining the effect of temperature on the product yield in the model reaction using microwave irradiation. At 70°C the yield of the product increased while reaction time decreased (Table 1, entry 17). The reaction was not successful in ethanol solvent (Table 1, entries 21 and 22). To investigate the effect of using microwave irradiation as the source of energy on this chemical transformation, the model reaction was carried out in conventional heating under optimized reaction condition. But no pure product was obtained (Table 1, entry 23). The possibility of employing milder and less toxic reagents offers a further advantage of using this heating technology. Therefore, preparation of the **3c** imidazole with microwave heating was technically faster, simpler, and higher in yield than previous routes.



**Figure 2.** HNO<sub>3</sub> catalyzed synthesis of dicyano imidazoles under microwave irradiation.

To generalize the current method for the synthesis of dicyano midazoles, we evaluated the reaction of a series of aldehydes with diaminomaleonitrile in presence of microwave irradiation under optimal conditions (Figure 2).

The obtained results are summarized in Table 2. The reaction proceeded smoothly for a wide spectrum of aromatic aldehydes bearing substituent with varied electronic nature and the dicyano midazoles were obtained in moderate to excellent yields with high purity.

A plausible mechanism for the synthesis of dicyano imidazoles catalyzed by HNO<sub>3</sub> under microwave irradiation is suggested in Figure 3. HNO<sub>3</sub> is an oxidant as well as Brønsted acid catalyst in the synthesis of Schiff base. Furthermore, HNO<sub>3</sub> can act as a highly active oxidant in an oxidative process for closing the imidazole ring (33). The current method had been previously reported in a one-pot, two-step reaction with an excess CAN (0.45 equiv.) as the reagent (15). But microwave metal-free activated procedure has been carried out successfully using HNO<sub>3</sub> as an oxidant by one-step approach.

All synthesized compounds have been known and were identified using FT-IR, NMR, and Mass spectroscopy and by comparison with their authentic samples (8,12,13,15,16). In the <sup>1</sup>H NMR spectra of compounds **3a-p**, the absence of the –NH<sub>2</sub> resonance and the appearance of a broad singlet in the 12.44–14.62 ppm regions, related to the resonance of the imidazole ring –NH group, supports the formation of the product. However, the proton (NH) on the position of the imidazole ring was not observed in the spectrum of some synthesized imidazoles, probably due to the effect of exchange of this acidic proton with the deuterium of small amounts of D<sub>2</sub>O, which is present in DMSO-*d*<sub>6</sub>, used as a solvent (34). The other spectral data appeared in regions expected, which confirm the predicted structures of the products.

Table 3 summarizes a comparison of reaction conditions, substrates used, and percentage yields of all previous methods with the results in the present work. A glancing look at the table reveals that the present synthetic method, compared to previous methods, has outstanding advantages such as a very short reaction time and high yield with microwave technique. Therefore, it can be the best synthetic green approach for the synthesis of 2-aryl dicyano

imidazoles, which have been obtained so far under other difficult conditions.

## Experimental

### Materials and apparatus

All chemical reagents in high purity (commercial grade) were purchased from the Merck Chemical Company. Melting points were determined in open capillaries using an electro-thermal digital melting point apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker spectrometer (400 or 500 MHz). NMR spectra were obtained in DMSO-*d*<sub>6</sub> solution and are reported as parts per million (ppm) downfield from Me<sub>4</sub>Si as internal standard. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm<sup>-1</sup> with a JASCO 4200-A spectrometer. A mass spectrum was recorded by an Agilent model: 5975C VL MSD with a Triple-Axis detector spectrometer at 70 eV. The reaction was performed in a microwave oven (FlexiWAVE, Milestone) equipped with a temperature controller.

### Microwave-assisted synthesis of dicyano imidazoles

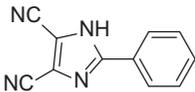
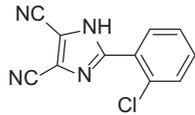
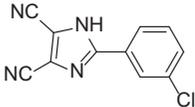
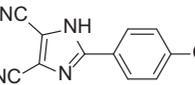
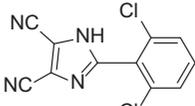
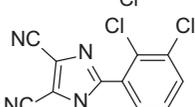
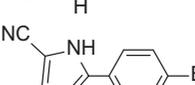
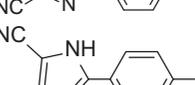
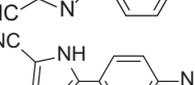
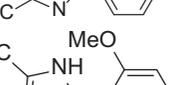
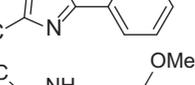
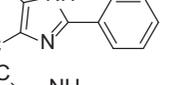
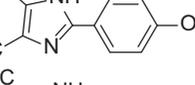
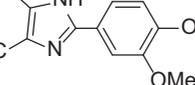
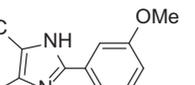
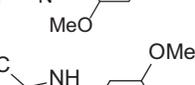
Aromatic aldehyde (0.5 mmol), 2,3-diaminomaleonitrile (0.5 mmol), and HNO<sub>3</sub> (1 equiv.) and acetonitrile (2 mL) were combined into a 50 mL round-bottomed flask and contents were irradiated under microwave for 5–8 min at 70°C and 500 W (Table 2). After completion of the reaction (monitored by TLC; ethyl acetate/*n*-hexane, 2:1), the organic solvent was removed and the crude product was purified by adding the minimum amounts of ethanol and water. Most of the dicyano imidazole products were known and characterized by comparison of their physical (Mp) and spectral data (IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR) with those of authentic samples.

### Spectral data for the derivatives of dicyano imidazoles

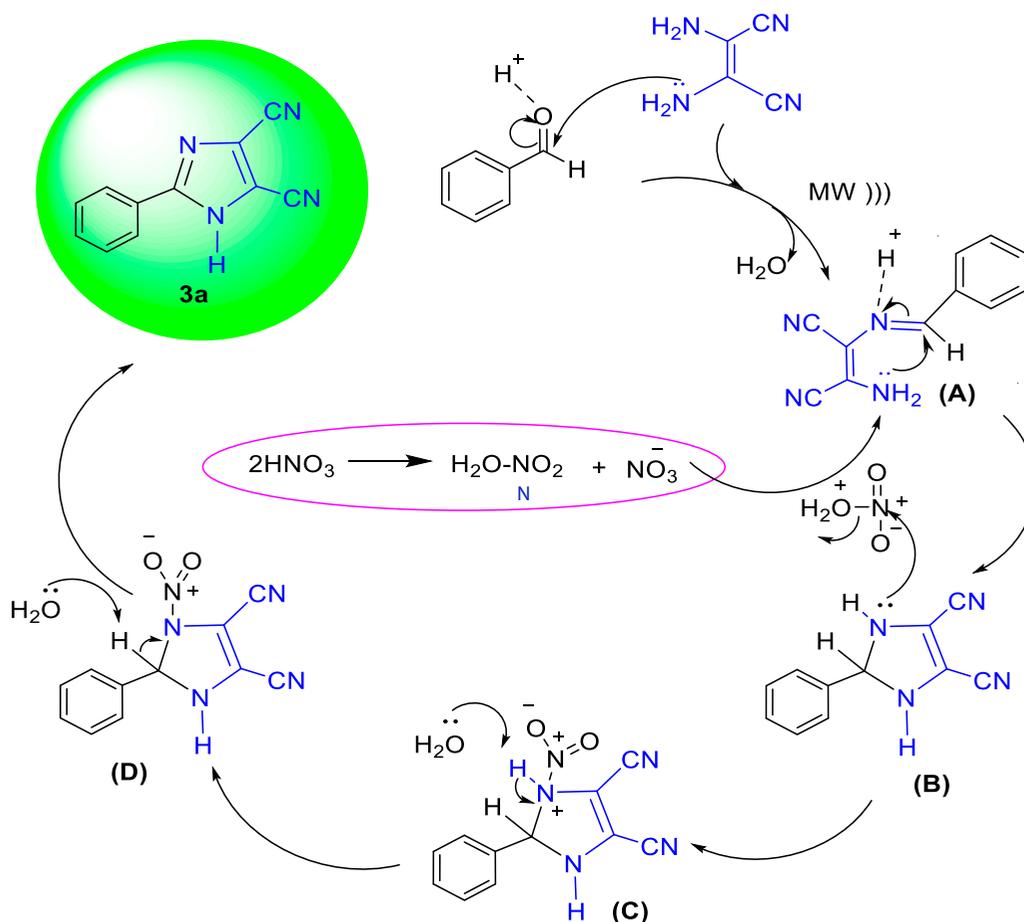
2-Phenyl-1*H*-imidazole-4,5-dicarbonitrile (3a).

FT-IR (KBr) ( $\nu_{\max}$ ): 3430 (N–H), 2237 (C≡N), 1637 (C=N), 1458, 1291 (C=C), 1113, 1029, 715 cm<sup>-1</sup>; <sup>1</sup>H NMR

**Table 2.** Synthesis of dicyano imidazoles catalyzed with HNO<sub>3</sub> under microwave irradiation.

No.	Product	Mp (°C) <sup>b</sup>	Time (min)	Yield (%) <sup>a</sup>
3a		240–242 (220–222)	8	80
3b		203–206 (202–204)	5	85
3c		218–220 (227–228)	8	89
3d		290–292 (288–290)	5	92
3e		232–235 (233–235)	5	88
3f		242–245 (242–245)	5	87
3g		319–321 (316–321)	5	90
3h		213–216 (211–212)	5	85
3i		254 (252–254)	5	92
3j		220–222 (223–225)	5	88
3k		180–182 (173–177)	5	80
3l		230–232 (230–232)	5	90
3m		240 (238–241)	5	80
3n		245–247 (245–248)	5	88
3o		243–245 (243–246)	5	90
3p		228–231 (229–231)	8	80

<sup>a</sup>Isolated yields<sup>b</sup>Melting points in parentheses are reported in the literature [8, 12, 13, 15, 16]



**Figure 3.** Suggested mechanism for the synthesis of dicyano imidazole by HNO<sub>3</sub>.

(400 MHz, DMSO-*d*<sub>6</sub>):  $\delta_H$  7.54 (s br, 3H, H-ph), 7.97 (s br, 2H, H-ph) (NH of the imidazole ring was not observed that probably due to the effect of the exchange of this acidic proton with deuterium in small amounts of D<sub>2</sub>O, which is present in DMSO-*d*<sub>6</sub>) ppm.

**Table 3.** Comparison of conditions used for the synthesis of dicyano imidazole **3c**.

Entry	Starting materials	Conditions	Yield (%) <sup>a</sup> (Ref.)
1	Schiff base <sup>a</sup>	DDQ <sup>b</sup> , MeCN, Reflux for 4 days	33 (10)
2	Schiff base	NCS <sup>c</sup> , nicotinamide DMF, 40°C, 3h	64 <sup>d</sup> (11)
3	Schiff base	I <sub>2</sub> , AcONa and 1-methyl pyrrolidin-2-one, 100 °C, 24h	59 (12)
4	Schiff base	Pb(OAc) <sub>4</sub> , Benzene, 5–10 °C, overnight	55 (13)
5	DAMN, aldehyde	CAN (0.40 eq.), MeCN, 50 °C, 40 min, two-step	84 (14)
6	DAMN, aldehyde	CAN/ HNO <sub>3</sub> , solvent-free, 120 °C, 15 min, one-step	88 (16)
7	DAMN, aldehyde	CAN/HNO <sub>3</sub> (0.05/0.4), MeCN, 70°C, 25 min, one-step	82 (17)
8	<b>DAMN, aldehyde</b>	<b>HNO<sub>3</sub> (1 eq.), MWI, MeCN, 70°C, 5 min, one-step</b>	<b>89 (This work)</b>

<sup>a</sup>Schiff bases from condensation of DAMN with aldehydes

<sup>b</sup>2,3-dichloro-5,6-dicyano-1,4-benzoquinone

<sup>c</sup>*N*-chloro-succinimide

<sup>d</sup>The yield of **3b**

2-(2-Chlorophenyl)-1*H*-imidazole-4,5-dicarbonitrile (3b).

FT-IR (KBr) ( $\nu_{\max}$ ): 3288 (N–H), 2240 (C≡N), 1655 (C=N), 1223 (C=C), 1121, 786 (C–Cl), 686 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta_H$  7.52 (t, *J* = 7.55 Hz, 1H, H-Ar), 7.58 (t, *J* = 7.95 Hz, 1H, H-Ar), 7.66 (d, *J* = 8.05 Hz, 1H, H-Ar), 7.76 (d, *J* = 7.70 Hz, 1H, H-Ar), (NH of the imidazole ring was not observed that probably due to the effect of exchange of this acidic proton with deuterium in small amounts of D<sub>2</sub>O, which is present in DMSO-*d*<sub>6</sub>) ppm; EIMS (*m/z*, %): 228 (M<sup>+</sup>, 100), 201 (7), 193 (12), 149 (15), 123 (18), 114 (25), 102 (20), 75 (21), 53 (24).

2-(3-Chlorophenyl)-1*H*-imidazole-4,5-dicarbonitrile (3c).

FT-IR (KBr) ( $\nu_{\max}$ ): 3436, 3179 (N–H), 3090 (C–H), 2261, 2234 (C≡N), 1644 (C=N), 1466 (C=C), 1120, 799 (C–Cl), 725 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta_H$  7.57 (d, *J* = 7.55 Hz, 2H, H-Ar), 7.91 (d, *J* = 6.85 Hz, 1H, H-Ar), 7.98 (s, <sup>1</sup>H, H-Ar), (NH of the imidazole ring was not observed that probably due to the effect of the exchange of this acidic proton with deuterium in small amounts of D<sub>2</sub>O, which is present in DMSO-*d*<sub>6</sub>) ppm.

2-(4-Chlorophenyl)-1*H*-imidazole-4,5-dicarbonitrile (3d).

FT-IR (KBr) ( $\nu_{\max}$ ): 3447, 3176 (N-H), 3098 (C-H), 2260, 2232 (C≡N), 1606 (C=N), 1481, 1092, 843 (C-Cl)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  7.61 (d,  $J = 8.00$  Hz, 2H, H-Ar), 7.95 (d,  $J = 8.00$  Hz, 2H, H-Ar) ppm.

2-(2,6-Dichlorophenyl)-1H-imidazole-4,5-dicarbonitrile (3e).

FT-IR (KBr) ( $\nu_{\max}$ ): 3220 (N-H), 3097 (C-H), 2252, 2236 (C≡N), 1585 (C=N), 1434, 1383, 1196 (C=C), 701 (C-Cl)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  7.61 (m, 3H, H-Ar) ppm.

2-(2,3-Dichlorophenyl)-1H-imidazole-4,5-dicarbonitrile (3f).

FT-IR (KBr) ( $\nu_{\max}$ ): 3289 (N-H), 2240 (C≡N), 1651 (C=N), 1541, 1506, 1446, 1417, 1308, 1237 (C=C), 1193, 1156, 1135, 1083, 1055, 975, 804 (C-Cl), 710, 500  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  7.54 (t,  $J = 7.92$  Hz, 1H, H-Ar), 7.72 (d,  $J = 7.65$  Hz, 1H, H-Ar), 7.86 (d,  $J = 8.00$  Hz, 1H, H-Ar) ppm, (NH of the imidazole ring was exchanged with  $\text{D}_2\text{O}$ );  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  111.1, 115.8, 128.6, 129.4, 130.1, 130.7, 132.7, 133.0, 148.1 ppm; EIMS ( $m/z$ , %): 263 ( $\text{M}^+$ , 80), 262 (100), 227 (22), 192 (12), 183, 157 (15), 148 (20), 87 (18), 53 (28).

2-(4-Bromophenyl)-1H-imidazole-4,5-dicarbonitrile (3g).

FT-IR (KBr) ( $\nu_{\max}$ ): 3442, 3171 (N-H), 3093 (C-H), 2258, 2234 (C≡N), 1600 (C=N), 1557, 1540, 1473, 1424 (C=C), 1010, 832 (C-Br), 728, 577  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  7.77 (d,  $J = 8.40$  Hz, 2H, H-Ar), 7.92 (d,  $J = 8.40$  Hz, 2H, H-Ar) ppm, (NH of the imidazole ring was exchanged with  $\text{D}_2\text{O}$ ).

2-(4-Fluorophenyl)-1H-imidazole-4,5-dicarbonitrile (3h).

FT-IR (KBr) ( $\nu_{\max}$ ): 3433, 3196 (N-H), 3117 (C-H), 2256, 2225 (C≡N), 1610 (C=N), 1487, 1433, 1398, 1237 (C=C), 1161 (C-N), 1108 (C-F), 960, 844, 735, 529  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  7.38 (t,  $J = 8.78$  Hz, 2H, H-Ar), 8.00 (dd,  $J_1 = 5.39$  Hz,  $J_2 = 3.19$  Hz, 2H, H-Ar) ppm, (NH of the imidazole ring was exchanged with  $\text{D}_2\text{O}$ ).

2-(4-Nitrophenyl)-1H-imidazole-4,5-dicarbonitrile (3i).

FT-IR (KBr) ( $\nu_{\max}$ ): 3447 (N-H), 2232 (C≡N), 1605 (C=N), 1518, 1348 ( $\text{NO}_2$ ), 1475 (C=C), 1112, 860, 716  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  8.20 (d,  $J = 8.40$  Hz, 2H, H-Ar), 8.33 (d,  $J = 8.40$  Hz, 2H, H-Ar) ppm; EIMS ( $m/z$ , %): 239 ( $\text{M}^+$ , 100), 209 (44), 181 (54), 139, 102 (19), 75 (15), 50 (25).

2-(2-Methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3j).

FT-IR (KBr) ( $\nu_{\max}$ ): 3276 (N-H), 2238 (C≡N), 1603 (C=N), 1475 (C=C), 1247 (C-O), 1209 (C-O), 1091, 1021, 749  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.25 (s, 3H, OMe), 7.08 (t,  $J = 4.40$  Hz, 1H, H-Ar), 7.22 (d,  $J = 5.20$  Hz, 1H, H-Ar), 7.50 (d,  $J = 5.60$  Hz, 1H, H-Ar), 8.04 (d,  $J = 6.00$  Hz, 1H, H-Ar), 13.72 (br, 1H, NH), ppm;  $^{13}\text{C}$  NMR

(100 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  55.7 (OMe), 111.1, 112.1, 115.3, 119.1, 121.0, 129.4, 132.6, 147.9 (C=N), 156.5 (C-O) ppm.

2-(3-Methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3k).

FT-IR (KBr) ( $\nu_{\max}$ ): 3546 (N-H), 2243 (C≡N), 1585 (C=N), 1237, 1046 (C-O), 739  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.38 (s, 3H, OMe), 7.07 (s, 1H, H-Ar), 7.26-7.95 (m, 3H, H-Ar) ppm.

2-(4-Methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3l).

FT-IR (KBr) ( $\nu_{\max}$ ): 3186 (N-H), 3114, 2938 (C-H), 2260, 2226 (C≡N), 1613 (C=N), 1490, 1440, 1398, 1303 (C=C), 1257, 1180 (C-O), 1028, 840, 739  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  3.88 (s, 3H, OMe), 6.99 (d,  $J = 8.40$  Hz, 2H, H-Ar), 7.88 (d,  $J = 8.40$  Hz, 2H, H-Ar), 12.44 (s, 1H, NH) ppm;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.81 (s, 3H, OMe), 7.08 (d,  $J = 8.40$  Hz, 2H, H-Ar), 7.90 (d,  $J = 8.40$  Hz, 2H, H-Ar) ppm.

2-(3,4-Dimethoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3m).

FT-IR (KBr) ( $\nu_{\max}$ ): 3546, 3199 (N-H), 2240 (C≡N), 1607 (C=N), 1498, 1447, 1406 (C=C), 1261, 1132, 1017 (C-O), 844, 733  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.75 (s, 3H, OMe), 3.81 (s, 3H, OMe), 7.10 (m, 1H, H-Ar), 7.52 (d br, 2H, H-Ar), 14.62 (br, 1H, NH) ppm; EIMS ( $m/z$ , %): 254.3 ( $\text{M}^+$ , 100), 238.2 (26), 211.2 (42), 168.2 (23), 103.1 (6), 63.1 (12).

2-(2,5-Dimethoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3n).

FT-IR (KBr) ( $\nu_{\max}$ ): 3277 (N-H), 2234 (C≡N), 1591 (C=N), 1543, 1490, 1438, 1307 (C=C), 1281, 1196 (C-O), 1171, 1146 (O-Me), 1084, 1042, 1018, 811, 743  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.78 (s, 3H, OMe), 3.92 (s, 3H, OMe), 7.10 (dd,  $J_1 = 2.90$  Hz,  $J_2 = 6.15$  Hz, 1H, H-Ar), 7.17 (d,  $J = 9.05$  Hz, 1H, H-Ar), 7.56 (d,  $J = 2.80$  Hz, 1H, H-Ar), 13.72 (br, 1H, NH) ppm;  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  55.6, 56.0 (OMe), 111.3 (2C), 113.3, 115.6, 118.5 (2C), 147.9, 150.9, 153.1 ppm; EIMS ( $m/z$ , %): 254 ( $\text{M}^+$ , 100), 239 (45), 236 (90), 221 (35), 211 (25), 202 (18), 181 (21), 168 (27), 142 (14), 53 (10).

2-(3,4,5-Tri methoxyphenyl)-1H-imidazole-4,5-dicarbonitrile (3o).

FT-IR (KBr) ( $\nu_{\max}$ ): 3462, 3297 (N-H), 2940 (C-H), 2230, 2208 (C≡N), 1614 (C=N), 1585, 1508, 1382, 1330 (C=C), 1242, 1128 (C-O), 989  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta_{\text{H}}$  3.71 (s, 3H, OMe), 3.83 (s, 6H, OMe), 7.25 (d,  $J = 1.58$  Hz, 2H, H-Ar), ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta_{\text{C}}$  56.0, 60.2 (OMe), 103.6, 111.2, 122.5, 139.6, 145.4, 150.6, 153.3 (C-O) ppm.

2-(4-Methylthiophen-2-yl)-1H-imidazole-4,5-dicarbonitrile (3p).

FT-IR (KBr) ( $\nu_{\max}$ ): 3462, 3187, 3156 (NH), 3118, 2925 (C-H), 2260, 2226 (C≡N), 1601 (C=N), 1513, 1446, 1309

(C=C), 1088 (C-S), 925, 807, 716  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ):  $\delta_H$  2.49 (s, 3H, Me), 6.92 (s, 1H, H-Ar), 7.52 (d,  $J$  = 3.20 Hz, 1H, H-Ar) ppm; EIMS ( $m/z$ , %): 214.1 ( $M^+$ , 100), 169.1 (24), 122.1 (12), 69.1 (16).

## Conclusion

In summary, we developed a general and green microwave-assisted synthesis of dicyano imidazoles promoted by  $\text{HNO}_3$  as a high efficient promoter and a robust metal-free catalyst under mild conditions. The higher environmental sustainability and compatibility factors such as very short reaction time, the use of microwave irradiation, the economy of steps, transition metal-free conditions, available starting materials, and easy isolation and purification of the product along with satisfactory yields make the present methodology a greener process for the synthesis of dicyano imidazoles compared to previously reported methods. The use of this green method opens the window to unique opportunities for the synthesis of heterocyclic compounds with diverse applications, which is not easily achievable *via* other synthesis techniques.

## Supporting information

Supporting Information is available on the publisher's website along with the article.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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