

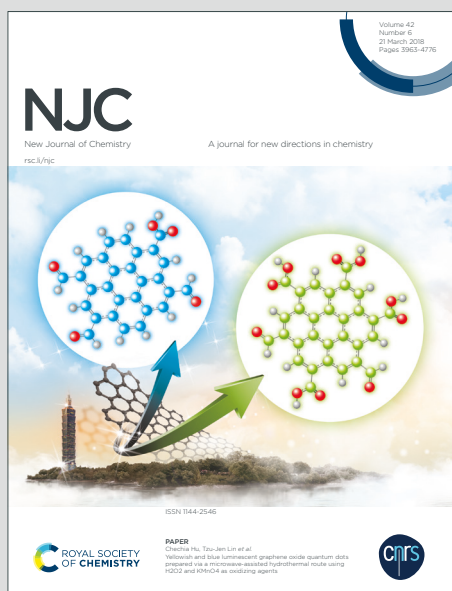
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## COMMUNICATION

## Visible light-emitting diode light-driven one-pot four component synthesis of poly-functionalized imidazoles under catalyst and solvent-free conditions

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Here, we have demonstrated visible LED light promoted synthesis of poly functionalized imidazole derivatives by the four component condensation of 1,2-diphenyl 1,2-diketone, aromatic aldehydes and ammonium acetate and /or amines in excellent yields. The solvent and catalyst-free reaction conditions, excellent isolated yields of the products, shorter reaction time, simple isolation and purification of products have made the present protocol efficient and green alternatives to those of existing protocols.

Naturally occurring five-member imidazole scaffolds have a unique role in heterocyclic chemistry and have their broad spectrum of applications in the field of biochemistry and pharmacology.<sup>1</sup> Multisubstituted imidazole derivatives have exhibited wide range of biological activities such as anti-inflammatory, anti-allergic,<sup>2</sup> analgesic,<sup>3</sup> antibacterial,<sup>4</sup> antitumor,<sup>5</sup> and anticancer/antitubercular/antifungal/anti-HIV<sup>6</sup> activities. Some well known fundamental parts of human organism such as purine, histamine, histidine, biotin, Vitamin-B12 and a component of DNA base have also established by imidazole nucleus as core scaffold.<sup>6</sup> A number of imidazole based commercially available drugs are present in the market such as omeprazole,<sup>7</sup> pimobendan,<sup>8</sup> cimetidine and lansoprazole<sup>9</sup> (Fig 1). Some substituted imidazoles are admitted as convivial inhibitors of P38 kinase.<sup>10</sup> These moieties also used as fungicides, herbicides and plant growth regulators.<sup>11</sup> Recent advances in green chemistry and organometallic catalysis has extended the applications of imidazoles as ionic liquids and *N*-heterocyclic carbenes. As consequences, a number of methods for the synthesis of multi-substituted imidazole derivatives have been developed.

Synthesis of imidazole was first reported in 1858 by Heinrich Debus *via* cyclocondensation of glyoxal, formaldehyde, and ammonia.<sup>12</sup> Later on, various methods have already reported for the synthesis of substituted imidazoles by varying the functional groups on reactants. Traditionally, imidazole derivatives have also been prepared by Ugi reaction and Davidson cyclization<sup>13</sup> or by reaction of imidazolium yelids and lithiated imidazoles.<sup>14</sup>

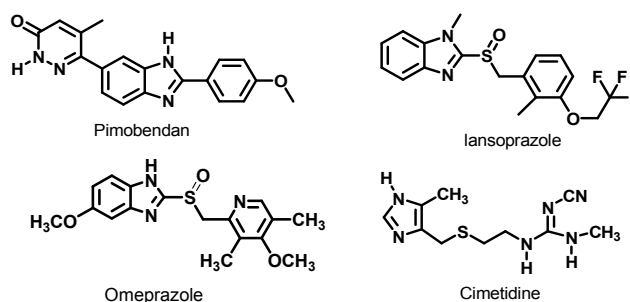


Fig. 1 Structures of few imidazole-based pharmacologically active molecules.

Recently, 2,4,5-substituted and 1,2,4,5-substituted imidazoles have been synthesized by multicomponent reaction by the reactions of 1,2-dicarbonyl compounds, aldehydes, and a nitrogen source using various catalysts such as  $\text{Fe}_3\text{O}_4$ -PEG-Cu,<sup>15</sup>  $\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$ ,<sup>16</sup> PEG-400,<sup>17</sup> DABCO,<sup>18</sup>  $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ ,<sup>19</sup>  $\text{BF}_3/\text{SiO}_2$ ,<sup>20</sup> Silica-bonded propylpiperazine-*N*-sulfamic acid (SBPPSA),<sup>21</sup>  $\text{TiCl}_4$ - $\text{SiO}_2$ ,<sup>22</sup>  $\text{SiO}_2/\text{NaHSO}_4$ ,<sup>23</sup>  $\text{Zr}(\text{acac})_2$ ,<sup>24</sup> Poly phosphoric acid impregnated on silica gel (PPA-SiO<sub>2</sub>),<sup>25</sup>  $[\text{Hbim}]\text{BF}_4$ ,<sup>26</sup> Nano-MgAl<sub>2</sub>O<sub>4</sub>,<sup>27</sup> Polymer-ZnCl<sub>2</sub>,<sup>28</sup> silica sulfuric acid (SSA),<sup>29</sup> CAN,<sup>30</sup> Yb(OTf)<sub>3</sub>,<sup>31</sup> L-proline,<sup>32</sup>  $\text{K}_7\text{Na}_3\text{P}_2\text{W}_{18}\text{Cu}_4\text{O}_{68}$ ,<sup>33</sup>  $\text{H}_2\text{NaPO}_4$ <sup>34</sup> and  $\text{Fe}_3\text{O}_4/\text{SO}_3\text{H}@zeolite-\text{Y}$ .<sup>35</sup> However, use of Lewis acid, costly ionic liquids, and heavy metal as catalyst, tedious work up process, purification, use of volatile and hazardous organic solvents limited their practical applications. Thus, development of novel green synthetic method for synthesis of poly-substituted imidazole derivatives is highly desirable.

Recently, visible light driven organic synthesis has been attracted much attention in the context of green chemistry.<sup>36</sup>

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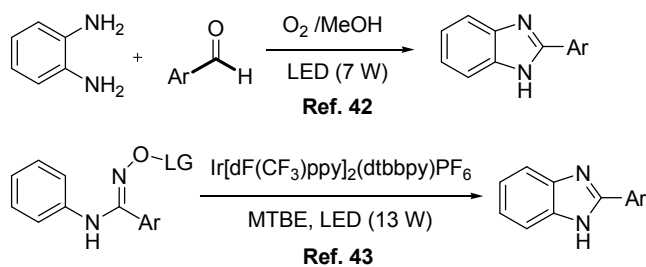
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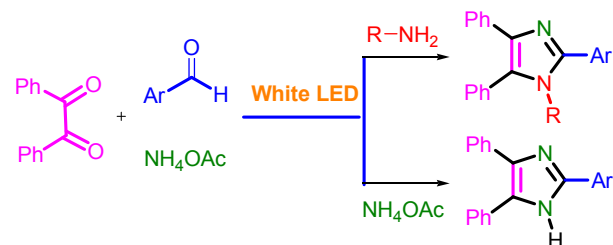
Among other, C–H arylation reactions using aryl diazonium salts under photochemical conditions has widely been investigated.<sup>37–39</sup> Recently, various nitrogen containing molecules have been synthesized under visible LED light. For example, Rueping *et al.*<sup>40</sup> have reported a oxidative three-component reactions for the direct synthesis of  $\alpha$ -amino amides and imides from tertiary amines by using Ir(ppy)<sub>2</sub>(bpy)PF<sub>6</sub> in presence of blue LED *via* the functionalization of C(sp<sup>3</sup>)–H bonds adjacent to nitrogen atoms and aerobic oxidation reactions. A visible-light-induced, Eosin Y catalyzed three-component synthesis of 3-arylsulfonylquinoline derivatives through *N*-propargyl aromatic amines, diaryliodonium salts and sulfur dioxide has been reported.<sup>41</sup> However, most the reported method involves use of photocatalysts. Very recently, Park *et al.*<sup>42</sup> have reported two component syntheses of benzimidazoles under visible light in presence of molecular oxygen (Scheme 1). Wang and his group<sup>43</sup> have reported visible-light-promoted Ir[dF(CF<sub>3</sub>)ppy]<sub>2</sub>(dtbbpy)PF<sub>6</sub>-catalyzed synthesis of 2-substituted benzimidazoles *via* amidinyl radicals (Scheme 1). However, visible light-promoted multicomponent synthesis of highly substituted imidazole derivatives has not been reported in the literature to the best of our knowledge.

As a part of our continuous interest in the development of green synthetic methodologies,<sup>44,45</sup> very recently, we have reported visible LED light promoted aerobic oxidation of alcohols and amines using Cu<sub>x</sub>Fe<sub>1-x</sub>@RCAC.<sup>45</sup> Here, we have reported one-pot four component synthesis of polysubstituted imidazole derivatives using white LED (correlated color temperature 6500 K) under catalyst-and solvent-free reaction conditions (Scheme 1).

#### Previous methods



#### Present method



**Scheme 1** Previous and present method of visible LED light-promoted synthesis of imidazole derivatives.

Initially, we have tested the MCR of benzil, benzaldehyde and aniline and ammonium acetate under visible white LED light

(correlated color temperature 6500 K) in a quartz vessel targeting for the synthesis of 1,2,4,5-tetraphenyl-1H-imidazole (**1a**). Only *N*-benzylidenebenzenamine (**2a**) was isolated in 45% yield along with the other starting materials at room temperature under solvent-free reaction conditions (entry 1, Table 1). When the power of visible white LED light was increased to 20 W, no significant change in the conversion was observed (entry 2, Table 1). However, when the above reaction was performed at 60 °C, the desired product was produced along with the byproduct **2a** in 7:3 ratio. The formation of products was confirmed by the <sup>1</sup>H NMR study (entry 3, Table 1). Next, we have screened the reaction at different temperature. It was observed with increasing temperature conversion as well as proportion of desired product (**1a**) increased (entry 3–6, Table 1) and maximum conversion and yield of **1a** was observed at 100 °C (entry 5, Table 1).

**Table 1** Optimization of reaction conditions<sup>a</sup>

Entry	Conditions	Time (min.)	Conversion (%)	% of 1a: 2a
1.	LED/RT	60	40	0:100
2.	LED <sup>b</sup> /RT	60	45	0:100
3.	LED/60°C	60	42	70:30
4.	LED/80°C	60	75	80:20
5.	LED/100°C	60	95	100:0
6.	LED/120°C	60	95	100:0
7.	Dark/100°C	60	72	0:100
8.	LED/100°C	30	62	100:0
9.	LED/100°C	90	95	100:0
10.	LED <sup>b</sup> /80°C	60	65	100:0

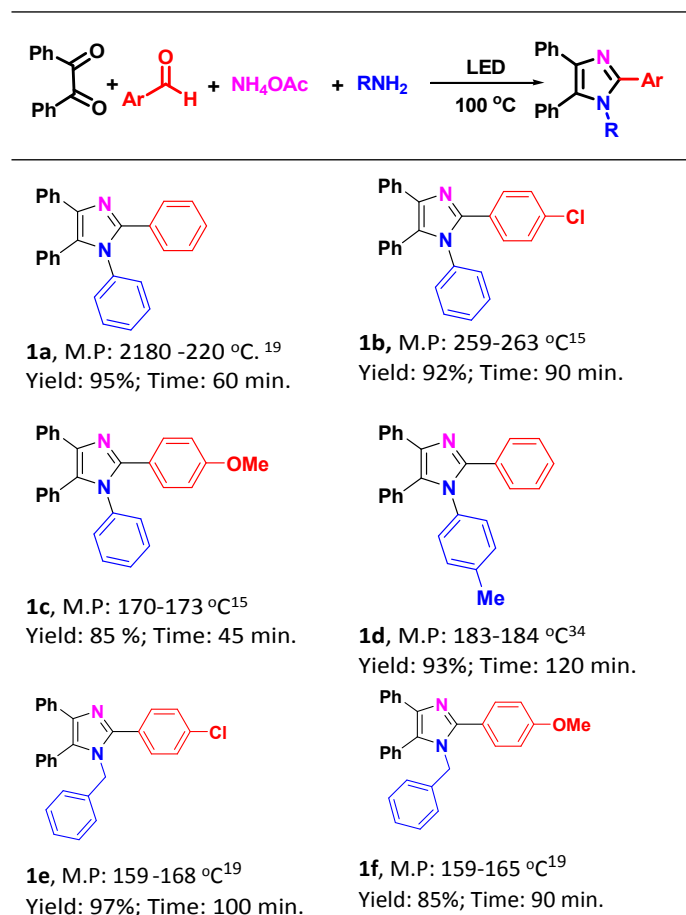
<sup>a</sup>Conditions: Benzil (1.0 mmol), benzaldehyde (1 mmol), ammonium acetate (1 mmol), aniline (1 mmol), neat condition, 10 W white LED bulb and 25 ml quartz round bottom flask. <sup>b</sup> 20 W LED bulb was used.

Interestingly, when model reaction was performed at 100 °C under dark conditions, only **2a** was produced (entry 7, Table 1). Thus, LED plays an important role in the formation of desired 1,2,4,5-tetraphenyl-1H-imidazole (**1a**). On the other hand, with decreasing reaction time yield decreased to 62% (entry 8, Table 1). Thus, a mixture of benzil, benzaldehyde and

aniline and ammonium acetate in (1:1:1:1) under 10 W LED light at 100 °C produced optimized yield (95%) under solvent-free conditions and was considered as optimized reaction conditions (entry 5, Table 1).

Next, using optimized reaction conditions, we have explored the scope of the methodology for the synthesis of polysubstituted imidazole derivatives. In a simple experimental procedure, a mixture of benzil (1.0 mmol), aromatic aldehyde (1 mmol), ammonium acetate (1 mmol) and amine (1 mmol) were heated at 110 °C in presence of LED light (10 W) under neat conditions in a 25 ml quartz round bottom flask till completion of reaction (TLC monitored). After the completion of reaction the reaction mixture was poured into ice-cold water which results the precipitation of imidazole derivatives. The precipitate was filtered, dried in oven and recrystallized from hot ethanol. The pure products were analyzed by their melting point determination and NMR spectroscopic studies.

**Table 2** Product scope of visible LED-driven synthesis of 2-aryl-1,4,5-triphenyl-1H-imidazoles<sup>a</sup>



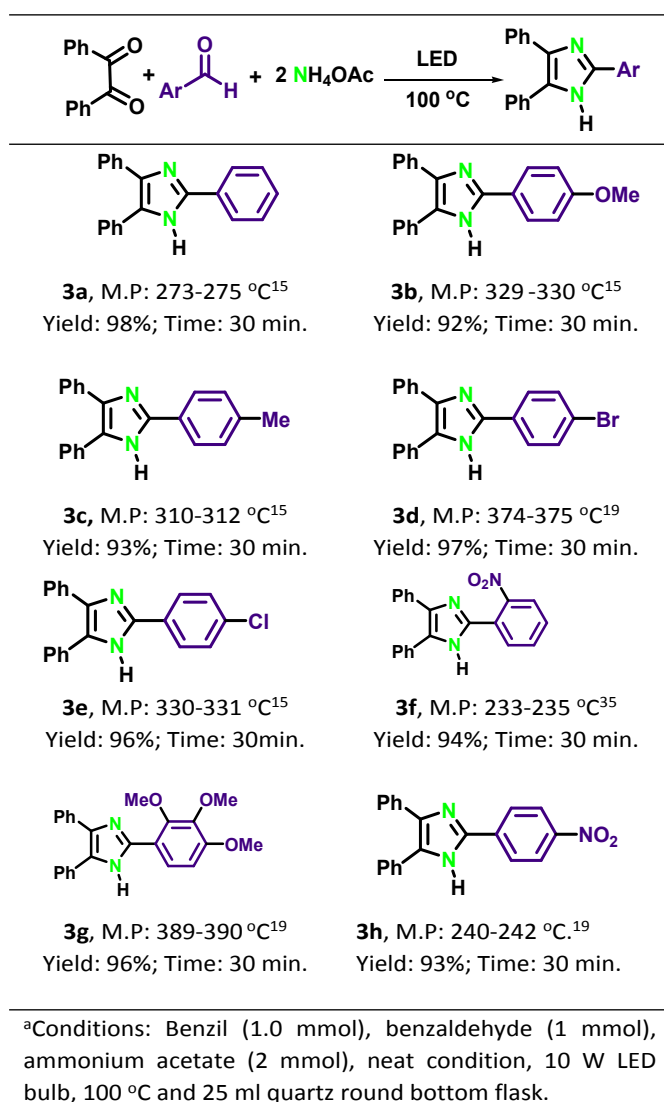
<sup>a</sup>Conditions: Benzil (1.0 mmol), benzaldehyde (1 mmol), ammonium acetate (1 mmol), aniline (1 mmol), neat condition, 10 W LED bulb 100 °C and 25 ml quartz round bottom flask.

A variety of 2-aryl-1,4,5-triphenyl-1H-imidazoles were synthesized by taking various aromatic aldehydes and amines

(1a-f, Table 2). Again, both aromatic and benzyl amines were participated in this present LED promoted MCRs.

Further, when the reaction was carried out in presence of 2 equivalents of ammonium acetate in absence of amine *i.e.* when benzil (1.0 mmol), aromatic aldehyde (1 mmol) and ammonium acetate (2 mmol) were heated at 100 °C in presence of LED light (10 W) under neat conditions 2-aryl-4,5-diphenyl-1H-imidazole derivatives (**3a-h**) were formed in excellent yields (92-98%). The results were summarized in Table 3.

**Table 3** Product scope of visible LED-driven synthesis of 2-aryl-4,5-diphenyl-1H-imidazoles<sup>a</sup>



<sup>a</sup>Conditions: Benzil (1.0 mmol), benzaldehyde (1 mmol), ammonium acetate (2 mmol), neat condition, 10 W LED bulb, 100 °C and 25 ml quartz round bottom flask.

In general all the reactions listed in Table 2 and 3 were very clean and high. The present visible LED promoted synthetic route offered several advantages such as (i) metal and other catalyst-free reaction, (ii) reactions were performed under neat conditions and no hazardous organic solvents were used, (iii) shorter reaction time (60 min.) and high percentage of yields yielding (85-97 %), (iv) no byproduct formation, (v) simple isolation from water and purification from hot ethanol

and thus avoid of tedious work up and purification process. Thus, the present method is better alternative green protocol to these of existing protocols.

Finally, a comparison of our present LED promoted method to those of reported methods<sup>15-35</sup> for the synthesis of imidazole *via* MCR of benzil, aldehydes, ammonium acetate and amines has been presented in Table 4. The comparison clearly demonstrated that present methods are more efficient, economic and eco-friendly in nature compared to reported methods.

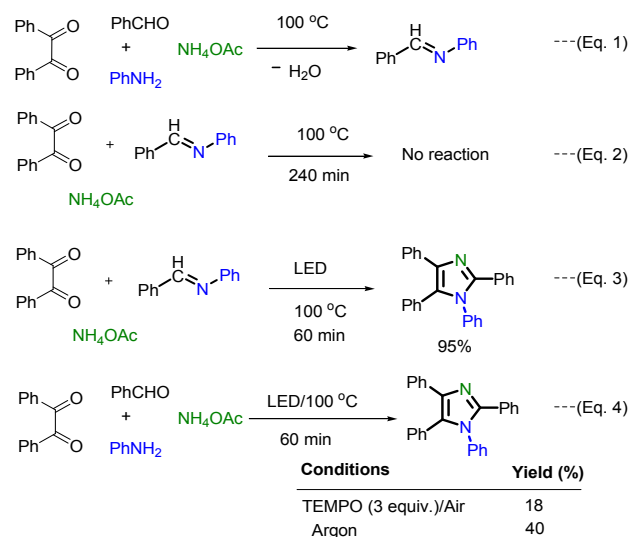
**Table 4** Comparison of present method to those of reported methods for the synthesis of 2-aryl-4,5-diphenyl-1H-imidazole derivatives.

Entry	Catalyst/Conditions	Time	Yield (%)	Ref.
1	LED/100 °C	30-55 min.	88-98	This work
2	Fe <sub>3</sub> O <sub>4</sub> -PEG-Cu/110 °C	30-55 min.	88-98	15
3	K <sub>3</sub> CoW <sub>12</sub> O <sub>40</sub> .3H <sub>2</sub> O	2-2.5 h	80-93	16
4	PEG-400	1.5-2 h	89-96	17
5	DABCO	12-15 h	92	18
6	InCl <sub>3</sub> .3H <sub>2</sub> O	6-9 h	47-84	19
7	BF <sub>3</sub> /SiO <sub>2</sub>	2 h	80-96	20
8	SBPPSA	1-2.5 h	85-90	21
9	TiCl <sub>4</sub> .SiO <sub>2</sub>	2.5 h	60-91	22
10	SiO <sub>2</sub> /NaHSO <sub>4</sub>	120 min	85-92	23
11	Zr(acac) <sub>2</sub>	20-40 min.	87-96	24
12	PPA-SiO <sub>2</sub>	12-20 min.	87-97	25
13	[Hbim]BF <sub>4</sub>	2-2.5 h	85-95	26
14	Nano-MgAl <sub>2</sub> O <sub>4</sub>	15 min	89-96	27
15	Polymer-ZnCl <sub>2</sub>	240	31-96	28
16	SSA	4-8 h	59-73	29
17	CAN	3-6 h	65-85	30
18	Yb(OTf) <sub>3</sub>	3-6 h	17-92	31

19	L-proline	8.5-10 h	78-88	32
20	K <sub>7</sub> Na <sub>3</sub> P <sub>2</sub> W <sub>18</sub> Cu <sub>4</sub> O <sub>68</sub>	1.5-2 h		33
21	H <sub>2</sub> NaPO <sub>4</sub>	25-40 min.	80-92	34
22	Fe <sub>3</sub> O <sub>4</sub> /SO <sub>3</sub> H@zeolite-Y/ 120 °C	20-65 min.	85-98	35

The present protocol is also effective in large scale synthesis of 2-aryl-,4,5-diphenyl-1H-imidazoles and good yield (82%) of **3a** was obtained after 5 fold scaled-up (5 mmol scale) under the optimized reaction conditions.

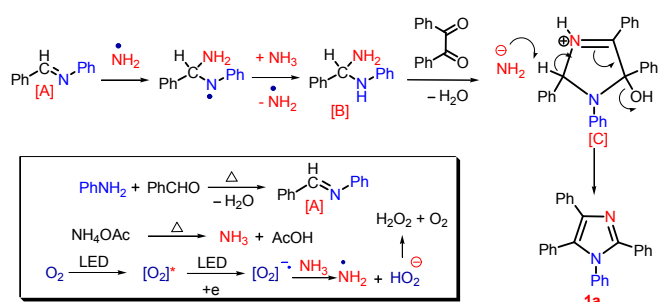
Next we have investigated the mechanism of LED light promoted synthesis of imidazoles by performing few control experiments as given in Scheme 3. When benzil, benzaldehyde, ammonium acetate and amiline are heated at 100 °C under dark conditions, *N*-benzylidenebenzenamine was formed as only product (Eq. 1, Scheme 2). Further, when imine was heated at 110 °C with benzil and ammonium acetate, no desired product was formed and starting materials were isolated (Eq. 2, Scheme 2). Interesting, when the above reaction was performed in presence of LED light desired product was formed in 95% yields (Eq. 3, Scheme 2). Thus, LED plays a crucial role in the formation of imidazole (**1a**). This reaction also proved that imine is formed as intermediate. Finally, a significant decrease in yield of **1a** was observed when the optimized reaction was performed in presence of a radical quencher, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) (Eq. 4, Scheme 2). This indicates that the reaction proceeds *via* radical pathway. Again, doing reaction in argon atmosphere, the yield of the product decreased to 40%. Thus, aerial oxygen also plays a significant role in the process (Eq. 4, Scheme 2).



**Scheme 2** Few control experiments to study the mechanism. Based on the following observation, a plausible mechanism of visible LED light and heat promoted synthesis of imidazole derivative (**1a**) under catalyst and solvent-free conditions has



been depicted in Scheme 3. The reaction initiated *via* the formation of imine intermediate (**A**) by eliminating of water molecule from benzaldehyde and aniline and decomposition of ammonium acetate results the formation of acetic acid and ammonia. The oxygen in air has been photo-excited to superoxide radical ( $O_2^{\cdot-}$ ),<sup>46</sup> which further reacts with ammonia to produce amino radical ( $NH_2^{\cdot}$ ). It is well known that superoxide radical abstract hydrogen atom from the protic reagents.<sup>47</sup> The formation of  $NH_2^{\cdot}$  radical was also reported by the reaction of ammonia and hydroxyl radical.<sup>48</sup> The  $NH_2^{\cdot}$  radical was then added to imine followed by the reaction with fresh ammonia to form diamine [**B**]. In the next step, condensation of diamine with 1,2-benzil followed by dehydration through the imino intermediate [**C**] yielded the desired product **1a**.



**Scheme 3** Proposed mechanism for the visible LED light promoted formation of 1,2,4,5-tetraphenyl imidazole (**1a**).

## Conclusions

In summary, we have demonstrated an efficient and environmentally friendly visible LED light-heat promoted protocol for the synthesis of 2,4,5-substituted and 1,2,4,5-substituted imidazoles by the multicomponent condensation of 1,2-diphenyl 1,2-diphenyl 1,2-diketone, aromatic aldehydes and ammonium acetate and /or amines in excellent yields. The present method offered several advantages such as (i) solvent and catalyst-free reaction conditions, (ii) excellent isolated yields of the products (85-98%), (iii) shorter reaction time (60 min.), (iv) simple and economic isolation from ice cold water, (v) purification of products by recrystallization from ethanol and thus avoiding any volatile and hazardous organic solvents. Thus, the present visible LED light/heat-promoted multicomponent synthesis is better green alternatives to those of existing protocols.

## Acknowledgment

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

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- L. Zhang, X. M. Peng, G. L. Damu, R. X. Geng and S. H. Zhou, *Med. Res. Rev.* 2014, **34**, 340–437. (b) D. I. Ma Gee, M. Bahramnejad and M. Dabiri, *Tetrahedron Lett.* 2013, **54**, 2591–2594. (c) A. Keivanloo, M. Bakherad, E. Imanifar and M. Mirzaee, *Appl. Catal.* 2013, **467**, 291–300.
- Black, J. W.; Durant, G. J.; Emmett, J. C.; Ganellin, C. R. *Nature*, 1974, **248**, 65–67.
- U. Ucucu, N. G. Karaburun, I. Iskdag, *Farmaco* 2001, **56**, 285–290.
- M. Antolini A. Bozzoli, C. Ghiron, G. Kennedy, T. Rossi, A. Ursini, *Bioorg. Med. Chem. Lett.* 1999, **9**, 1023–1028.
- L. Wang, K. Woods, W. Li, Q. Barr, K. J. McCroskey, R. W. Hannick, S. M.; Gherke, L. Credo, R. B. Hui, Y.H. Marsh, K. Warner, R. Lee, J. Y. Zielinsky-Mozng, N. Frost, D. Rosenberg, S. H. Sham, H. L. Potent, *J. Med. Chem.* 2002, **45**, 1697–1711.
- A. Verma, S. Joshi, D. Singh *Journal of Chemistry* Volume 2013, Article ID 329412, 12 pages <http://dx.doi.org/10.1155/2013/329412>
- P. Lindberg, P. Nordberg, T. Alminger, A. Brandstom, B. Wallmark, *J. Med. Chem.* 1986, **29**, 1327–1329.
- R. Mannhold, B.F. Mirjalili, A.H. Bamoniri, L.Zamani, *Drugs Future* 2012, **10**, 570.
- W.H. Beggs, F.A Andrews, G.A. Sarosi, *Life Sci.*, 1981, **28**, 111–118. J. Delgado, N. Remers, W.A., 1998. *Textbook of Organic Medicinal and Pharmaceutical Chemistry*. Lippincott-Raven, Philadelphia, New York
- J. Lee, C. Laydon, J. T. McDonnell, P. C. Gallagher, T. F. Kumar, S. Green, D. McNully, D. Blumenthal, M. Heys, J. R. Landvatter, S. W. Strickler, J. E. McLauhlin, M. M. Siemens, I. R. Fisher, S. M. Livi, J. P. White, J. R. Adams, J. L. Young, *Nature*, 1994, **372**, 739–746. ,
- R. Schmierer, H. Mildenerger, H. Buerstell, *German Patent*, 361464 *Chem. Abst.*, 1988, **108**, 37838.
- H. Debus, *Ann. Chem. Phar.* 1858, **107**, 199–208.
- K. Sung, S.H. Wu, P. I. Chen. *Tetrahedron Lett.* 2002, **58**, 5599. (b) R. Torregrosa, I. M. Pastor M. Yus, *Tetrahedron Lett.* 2005, **61**, 11148 (c) A.V. Gulevich, E.S. Balenkova, V.G. Nenajdenko, *J. Org. Chem.* 2007, **72**.
- C.A. Zifcsak, D.J. Hlasta, *Tetrahedron Lett.* 2005, **46**, 4789.(b) R. Torregrosa, I.M. Pastor, M. Yus, *Tetrahedron Lett.*, 2005, **61**, 11148.
- Z. Zarnegar and J. Safari *New J. Chem.* 2014, **38**, 4555.
- L. Nagarapu, S. Apuri and S. Kantevari, *J. Mol. Catal. A: Chem.* 2007, **266**, 104–108.
- X.C. Wang, H. P. Gong, Z. J. Quan, L. Li and H. L. Ye, *Chin. Chem. Lett.* 2009, **20**, 44–47.
- S. N. Murthy, B. Madhav and Y. V. D. Nageswar, *Tetrahedron Lett.*, 2010, **51**, 5252–5257.
- S. D. Sharma, P. Hazarika and D. Konwar, *Tetrahedron Lett.* 2008, **49**, 2216–2220.
- B. Sadeghi, B. F. Mirjalili and M. M. Hashemi, *Tetrahedron Lett.* 2008, **49**, 2575–2577.
- K. Niknam, A. Deris, F. Naeimi and F. Majleci, *Tetrahedron Lett.* 2011, **52**, 4642–4645.
- B. F. Mirjalili, A. Bamoniri and M. A. Mirhoseini, *Sci. Iran.* 2013, **20**, 587–591.
- A. R. Karimi, Z. Alimohammadi, J. Azizian, A. A. Mohammadi and M. R. Mohammadzadeh, *Catal. Commun.* 2006, **7**, 728–732.
- A. R. Khosropour, *Ultrason. Sonochem.* 2008, **15**, 659–664.
- N. Montazeri, K. Pourshamsian, M. Khoddadi, K. Khoddadi, *Orient. J. Chem.* 2011, **27(3)**, 1023–1027.
- S. A. Siddiqui, U. C. Narkhede, S. S. Palimkar, T. Daniel, R. J.

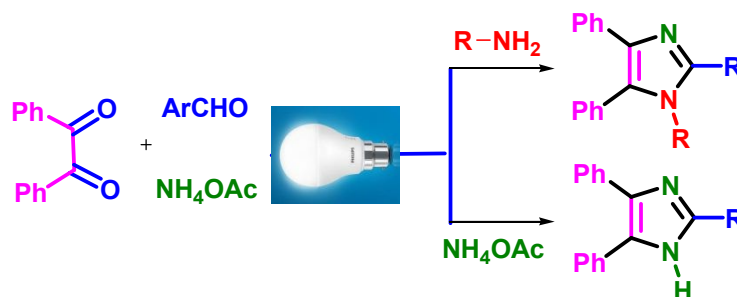
## COMMUNICATION

Journal Name

- Lahoti and K. V. Srinivasan, *Tetrahedron*, 2005, **61**, 3539–3546.
- 27 J. Safari, S. Gandomi-Ravandi, Z. Akbari, *J. Adv. Res.* 2003, **4**, 509–514.
- 28 L. Wang and C. Cai, *Monatsh. Chem.* 2009, **140**, 541–546.
- 29 A. Shaabani and A. Rahmati, *J. Mol. Catal. A: Chem.*, 2006, **249**, 246–248.
- 30 A. Shaabani, A. Maleki and M. Behnam, *Synth. Commun.* 2009, **39**, 102–110.
- 31 L. Min, Y. H. Wang, H. Tian, Y. F. Yao, J. H. Shao and B. Liu, *J. Fluorine Chem.* 2006, **127**, 1570–1573.
- 32 S. Samai, G. Ch. Nandi, P. Singh and M. S. Singh, *Tetrahedron*, 2009, **65**, 10155–10161.
- 33 N. M. Kalkhorani and M. M. Heravi, *Journal of Chemistry*, 2013, **2013**, Article ID 645801, 5 pages.
- 34 Z. Karimi-Jaberi and M. Barekat. *Chinese Chem. Lett.* 2010, **21**, 1183–1186.
- 35 M. Kalthor and Z. Zarnegar, *RSC Adv.* 2019, **9**, 19333–19334.
- 36 (a) J. M. R Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* 2011, **40**, 102–113. (b) C. K Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, **113**, 5322–5363. (c) K. L.; Skubi, Blum, T. R.; Yoon, T. P. *Chem. Rev.* 2016, **116**, 10035–10074. (d) C.S. Wang, P. H. Dixneuf, J.-F. Soulé, *Chem. Rev.*, 2018, **118**, 7532–7585.
- 37 (a) D. P Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* 2012, **134**, 2958–2961. (b) D. P. Hari, B. König, *Angew. Chem., Int. Ed.* 2013, **52**, 4734–4743. (c) W. Guo, L.-Q. Lu, Y. Wang, Y.-N Wang, Chen, J.-R. Xiao, W. J. *Angew. Chem., Int. Ed.* 2015, **54**, 2265–2269. (d) J. Jiang, W.-M. Zhang, J.-J. Dai, J. Xu, H.-J. Xu, *J. Org. Chem.* 2017, **82**, 3622–3630.
- 38 J. Lee, B. Hong, A. J. Le, *Org. Chem.* 2019, **84**, 9297–9306.
- 39 L. Buglioni, P. Riente, E. Palomares, A. Miquel Pericàs, *Eur. J. Org. Chem.* 2017, 6986–6990.
- 40 M. Rueping and C. Vila, *Org. Lett.* 2013, **15** (9), 2092–2095.
- 41 D. Sun, K. Yin, R. Zhang, *Chem. Commun.* 2018, **54**, 1335–1338.
- 42 S. Park, J. Jung, E. J. Cho, *Eur. J. Org. Chem.* 2014, 4148–4154.
- 43 G. Li, R. He, Q. Liu, Z. Wang, Y. Liu, and Q. Wang, *J. Org. Chem.* **2019**, **84**, 8646–8660.
- 44 (a) S. Banerjee, V. Balasanthiran, R. Koodali and G. Sereda, *Org. Biomol. Chem.* 2010, **8**, 4316; (b) S. Banerjee and A. Saha, *New J. Chem.* 2013, **37**, 4170; (c) S. Banerjee, S. Payra, A. Saha and G. Sereda, *Tetrahedron Lett.* 2014, **55**, 5515; (d) A. Saha, S. Payra and S. Banerjee, *Green Chem.* 2015, **17**, 2859; (e) A. Saha, S. Payra, S. K. Verma, M. Mandal, S. Thareja and S. Banerjee, *RSC Adv.* 2015, **5**, 100978; (f) S. Payra, A. Saha, S. Guchhait and S. Banerjee, *RSC Adv.* 2016, **6**, 33462; (g) S. Payra, A. Saha and S. Banerjee, *RSC Adv.* 2016, **6**, 52495; (h) S. Payra, A. Saha, C. M. Wu, B. Selvaratnam, T. Dramstad, L. Mahoney, S. K. Verma, S. Thareja, R. Koodali and S. Banerjee, *New J. Chem.* 2016, **40**, 9753; (i) A. Saha, S. Payra, B. Selvaratnam, S. Bhattacharya, S. Pal, R. Koodali, S. Banerjee, *ACS Sustainable Chem. Eng.* 2018, **6**, 11345; (j) A Saha, S Payra, S Banerjee, *New J. Chem.* 2017, **41**, 1337; (k) A. R. Patel, A. Asatkar, G. Patel, S. Banerjee, *ChemistrySelect*, 2019, **4**, 5577; (l) S. Payra, A. Saha and S. Banerjee, *ChemCatChem*. 2018, **10**, 5468; (m) S. Payra, S. Banerjee, *ChemistrySelect*, 2019, **4**, 9556; (n) P. R. Verma, S. Payra, F. Khan, S. Penta and S. Banerjee, *ChemistrySelect*, 2020, **4**, 1950.
- 45 A. R. Patel, G. Patel, S. Banerjee, *ACS Omega*, 2019, **4**, 22445.
- 46 M. Hayyan, M. A. Hashim, I. M. AlNashef, *Chem. Rev.* 2016, **116**(5), 3029.
- 47 C. P. Andrieux, P. Hapiot, J. M. Saveant, *J. Am. Chem. Soc.* 1987, **109** (12), 3768–3775.
- 48 P. Neta, P. Maruthamuthu, P. M. Carton and R. W. Fessenden, *J. Phys. Chem.* 1978, **82** (17), 1875–1878.

## Graphical Abstract

Visible light-emitting diode light-driven one-pot four component synthesis of poly-functionalized imidazoles under catalyst and solvent-free conditions



- VisibleLED light promoted MCRs
- Metal and acid catalyst-free conditions
- Solvent-free reactions
- Excellent yields of products (85-98%)

Visible light-emitting diode light-driven green and sustainable protocol has been demonstrated for the one-pot four component synthesis of poly-functionalized imidazoles under catalyst and solvent-free conditions.