



King Saud University
Journal of Saudi Chemical Society

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Nanocrystalline $MgAl_2O_4$ as an efficient catalyst for one-pot synthesis of multisubstituted imidazoles under solvent-free conditions

Javad Safari *, Zahra Akbari, Simin Naseh

Laboratory of Organic Chemistry Research, Department of Organic Chemistry, College of Chemistry, University of Kashan, 87317-51167 Kashan, Islamic Republic of Iran

Received 28 July 2012; accepted 27 October 2012

KEYWORDS

Nanocrystalline magnesium aluminate;
Multi-component reactions;
Solvent-free;
2,4,5-Trisubstituted imidazoles;
1,2,4,5-Tetrasubstituted imidazoles

Abstract An efficient and eco-friendly procedure has been developed using nanocrystalline $MgAl_2O_4$ with specific surface area as catalyst for rapid and an improved synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles under solvent-free conditions in excellent yields. The method has several benefits, such as shorter reaction time, recyclable catalyst and excellent yields.

© 2012 King Saud University. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

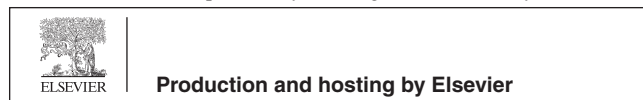
Multi-component reactions (MCRs) have an outstanding status in medicinal chemistry and modern organic synthesis because they are one-pot processes that assemble three or more components. The known multi-component reactions and improving of new MCRs are an area of important current interest (Sadeghi et al., 2008). Over a century multi-substituted imidazoles are current go-between in many compounds of remarkable biological activity and have absorbed the attention of synthetic chemists (Frutos et al., 2005). The imidazole ring

system and its derivatives are the most considerable structures found in medicinal active compounds such as histamine, biotin, and histidine and a large number of natural products (Safari et al., 2010), because of their possibility of hydrogen bond formation and not-shared electron pair of nitrogen atom of the imidazole cycle (Wang et al., 2006). They also are well known as inhibitors of P38 map kinase (Xia and Lu, 2007), herbicides and fungicides (Siddiqui et al., 2005), plant growth regulators (Joshi et al., 2010), pesticides (Sharma et al., 2008), and used as organic materials, such as to resist composition on textile, electroluminescent materials, optical materials, photographic materials and fluorescent whiteners on textile (Safari et al., 2010). Recently, various methods have been reported for the synthesis of trisubstituted and tetrasubstituted imidazoles. Generally trisubstituted imidazoles are synthesized by the condensation of 1,2-diketones, an aldehyde and ammonium acetate by using microwave and ionic liquids (Xia and Lu, 2007), $InCl_3 \cdot 3H_2O$ (Sharma et al., 2008), $Yb(OTf)_3$ Wang et al. (2006), TBAB (Chary et al., 2008), HOAc (Shaabani and

* Corresponding author. Tel.: +98 3615912320.

E-mail address: Safari@kashanu.ac.ir (J. Safari).

Peer review under responsibility of King Saud University.



Rahmati, 2006) and tetrasubstituted imidazoles are synthesized by the condensation of 1,2-diketones, an aldehyde, ammonium acetate and primary amine in the presence of heteropolyacids (Nagarapu et al., 2007; Heravi et al., 2007), ionic liquids (Zang et al., 2010; Hasaninejad et al., 2010), I_2 (Kidwai et al., 2007), $Zr(acac)_4$ Khosropour (2008), DABCO (Narayana Murthy et al., 2010), and PEG-200 (Wang et al., 2009). Though they are potentially beneficial, most of these synthetic methods suffer from harsh conditions, high temperature, low yields and side reactions leading to mixture of products. In the present work, we have reported an appropriate, mild and easy method for the multi-component, one-pot synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles in high yields by using nanocrystalline magnesium aluminate under solvent-free conditions. $MgAl_2O_4$ is magnesium and aluminum mixed oxide whose physical properties lie between those of magnesium oxide and aluminum oxide (Trjero and Ibarra, 1993) and it has been widely used in industrial applications. It has this applicability because of its unique properties such as high mechanical, high thermal shock resistance, strength, chemical inertness, good resistance to both acids and bases and catalytic properties (Meshkani and Rezaei, 2009; Navaei Alvar et al., 2010). It has wide applications in many industrial areas, e.g. humidity sensors, transparent ceramics and refractory materials (Navaei Alvar et al., 2010; Bai et al., 2011). Nanoscale supports create catalysts with more edges and corners, which can lead to higher performance of the catalyst. Nanocrystalline $MgAl_2O_4$ with high specific surface area is an efficient and novel catalyst. The crystallite sizes of the Magnesium aluminate determined by TEM analysis were at 700 °C between 3 and 10 nm and increased to 4–12 nm at 800 °C (Fig. 1). The pore volume, pore diameter and pore size were also calculated from the N_2 adsorption/desorption isotherm result; the pore volume was approximately $1.10 \text{ cm}^3 \text{ g}^{-1}$, the pore diameter 20.68 nm and the pore size approximately 5.3 nm. In addition to these the surface area was approximately $201 \text{ m}^2 \text{ g}^{-1}$ (Trjero and Ibarra, 1993).

Magnesium aluminate with large specific surface area is a potential catalyst support for various reactions and a promising sorbent for chemisorptions and destructive adsorption of a variety of pollutants. In the field of catalysis, $MgAl_2O_4$ has strong basic properties, which are associated with catalysis by bases in many organic reactions. Nanoscale supports create

catalysts with more edges and corners, which can lead to higher performance of the catalyst.

2. Experimental

2.1. Materials and apparatus

Chemical reagents of high purity were purchased from the Merck Chemical Company. All materials were of commercial reagent grade.

Melting points were determined in an open capillary using an Electrothermal Mk3 apparatus. ^1H NMR and ^{13}C NMR spectra were recorded in $\text{DMSO-}d_6$ using a Bruker DRX-400 spectrometer at 400 and 100 MHz, respectively. Infrared (IR) spectra were recorded using a Perkin-Elmer FTIR 550 spectrometer. The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer carried out on a Perkin-Elmer 240c analyzer.

2.1.1. Preparation of nanocrystalline $MgAl_2O_4$

In a typical preparation, stoichiometric amounts of magnesium nitrate and aluminum nitrate and a desired amount of CTAB were added to well stirring deionized water. After that, ammonia solution was added dropwise to the well stirring slurry for adjusting pH value around 9. After precipitation, the slurry was stirred for another 30 min and then refluxed at 80 °C for 24 h under continuous stirring. The mixture then was cooled to room temperature and filtered. The final product was dried at 100 °C for 24 h under flowing air and calcined at different temperatures (Meshkani and Rezaei, 2009).

2.1.2. Preparation of 2,4,5-trisubstituted imidazoles by use of nanocrystalline $MgAl_2O_4$

In a 50 mL round bottom flask a mixture of 1,2-diketone (1 mmol), ammonium acetate (2 mmol), aldehyde (1 mmol), and nanocrystalline magnesium aluminate (0.05 g) was stirred at 120 °C for 30 min. The progress of the reaction was monitored by TLC (petroleum ether–ethyl acetate 7:3). After cooling, the reaction mixture was dissolved in acetone and filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure and the solid product obtained was washed with water and recrystallized from acetone–water 9:1 (v/v). Pure products were obtained in excellent yields.

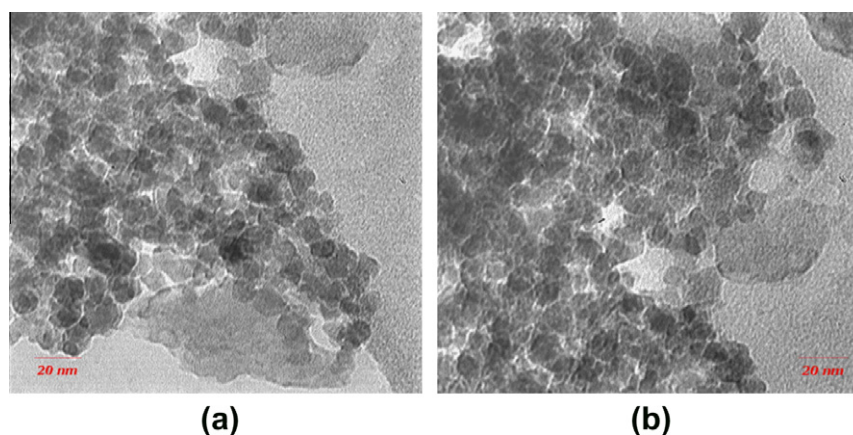


Figure 1 TEM images of the sample with $[\text{CTAB}]/[\text{M}] = 0.3$ calcined at (a) 700 °C and (b) 800 °C.

2.1.3. Preparation of 1,2,4,5-tetrasubstituted imidazoles by use of nanocrystalline MgAl₂O₄

In a 50 mL round bottom flask a mixture of 1,2-diketone (1 mmol), ammonium acetate (4 mmol), aldehyde (1 mmol), primary amine (4 mmol) was taken and in the presence of nanocrystalline magnesium aluminate (0.05 g) was stirred at 120 °C for 30 min. The progress of the reaction was monitored by TLC. After cooling, the reaction mixture was dissolved in acetone and filtered. The filtrate was concentrated on a rotary evaporator under reduced pressure and the solid product obtained was washed with water and recrystallized from acetone–water. Pure products were obtained in excellent yields.

2.1.4. Spectral data for new compounds

2.1.4.1. 2-(3,4-Dimethoxyphenyl)-1,4,5-triphenyl-1H-imidazole (5d). White powdery crystals, mp 178–180 °C; UV–vis (EtOH) λ_{\max} : 311 nm; ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.61 (s, 6H, 2CH₃), 6.85 (d, *J* = 8.8 Hz, 2H, H-Ar), 7.15–7.33 (m, 15H, H-Ar), 7.48 (d, *J* = 7.2 Hz, 1H, H-Ar) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ 55.57, 55.60, 115.18, 124.55, 127.18, 128.53, 128.61, 129.09, 129.19, 129.20, 129.36, 130.10, 131.15, 132.30, 132.48, 136.50, 136.55, 136.61, 140.49, 145.29 ppm; IR (KBr) (ν_{\max} , cm⁻¹): 3045 (C–H aromatic), 1617 (C=C aromatic), 1578 (C=N), 1154 (C–O-Ar) cm⁻¹; MS (70 eV) *m/z* (%): 432 (M⁺, 55), 417 (50), 402 (44), 77 (32); Anal. Calcd for C₂₉H₂₄N₂O₂: C, 80.53; H, 5.60; N, 6.48%. Found: C, 80.52; H, 5.59; N, 6.47%.

2.1.4.2. 2-(2-Fluorophenyl)-1,4,5-triphenyl-1H-imidazole (5f). Yellow powder, mp 165–168 °C; UV–vis (EtOH) λ_{\max} : 302 nm; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.11–7.30 (m, 15H, H-Ar), 7.41 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.46 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.53 (t, *J* = 8.0 Hz, 1H, H-Ar) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ 129.82, 129.94, 130.51, 130.55, 130.64, 131.60, 132.75, 132.81, 133.65, 136.61, 136.82, 138.50, 140.50, 143.13, 144.90, 148.02 ppm; IR (KBr) (ν_{\max} , cm⁻¹): 3050 (C–H aromatic), 1509 (C=C), 1095 (C=N), 1095 (C–F) cm⁻¹; MS (70 eV) *m/z* (%): 390 (M⁺, 55), 371 (50), 295 (48); Anal. Calcd for C₂₇H₁₉FN₂: C, 83.06; H, 4.9; N, 7.17%. Found: C, 83.5; H, 4.93; N, 7.018%.

2.1.4.3. 2-(3,5-Dimethoxyphenyl)-1,4,5-triphenyl-1H-imidazole (5h). Yellow needles; mp 163–165 °C, UV–vis (EtOH) λ_{\max} : 296 nm; ¹H NMR (400 MHz, DMSO-*d*₆): δ 3.55 (s, 6H, 3CH₃), 6.43 (s, 1H, H-Ar), 6.55 (d, 2H, H-Ar), 7.15–7.57 (m, 15H, H-Ar) ppm; ¹³C NMR (100 MHz, DMSO-*d*₆): δ 53.55, 58.64, 124.11, 125.65, 126.11, 127.52, 128.64, 130.07, 130.16, 130.25, 130.32, 130.45, 132.12, 132.24, 133.45, 137.55, 137.67, 137.80, 140.19, 142.78 ppm; IR (KBr) (ν_{\max} , cm⁻¹): 3057 (C–H aromatic), 1597 (C=C aromatic), 1154 (C–O-Ar) cm⁻¹; MS (70 eV) *m/z* (%): 432 (M⁺, 62), 401 (55), 370 (53), 295 (44); Anal. Calcd for C₂₉H₂₄N₂O₂: C 80.51, H 5.61, N 6.45%. Found: C 80.53, H 5.59, N 6.48%.

2.1.4.4. 2,4,5-Triphenyl-1-propyl-1H-imidazole (5i). Yellow needles; mp 87–89 °C; UV–vis (EtOH) λ_{\max} : 284 nm; ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.51 (t, *J* = 6.8 Hz, 3H, CH₃), 1.32 (m, *J* = 6.8 Hz, 2H, CH₂), 3.81 (t, *J* = 7.2 Hz, 2H, CH₂), 7.10–7.55 (m, 13H, H-Ar), 7.7 (d, *J* = 6.8 Hz, 2H, H-Ar); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 11.07, 23.56, 46.32, 126.55, 128.50, 129.12, 129.17, 129.33, 129.62, 130.27,

131.30, 131.56, 131.78, 135.17, 137.0, 147.20 ppm; IR (KBr) (ν_{\max} , cm⁻¹): 3025 (C–H aromatic), 1597 (C=C aromatic), 1479 (C=N) cm⁻¹; MS (70 eV) *m/z* (%): 338 (M⁺, 68), 323 (65), 309 (57), 295 (43), 15 (40); Anal. Calcd for C₂₄H₂₂N₂: C 85.17, H 6.55, N 8.28%. Found: C 85.14, H 6.56, N 8.30%.

2.1.4.5. 2-(4-Chlorophenyl)-4,5-diphenyl-1-propyl-1H-imidazole (5j). Yellow crystals; mp 85–87 °C; UV–vis (EtOH) λ_{\max} : 294 nm; ¹H NMR (400 MHz, DMSO-*d*₆): δ 0.51 (t, *J* = 6.8 Hz, 3H, CH₃), 1.34 (m, *J* = 6.8 Hz, 2H, CH₂), 3.81 (t, *J* = 7.2 Hz, 2H, CH₂), 7.15–7.30 (m, 12H, H-Ar), 7.34 (d, *J* = 7.2 Hz, 2H, H-Ar); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 11.08, 23.54, 46.39, 126.55, 126.66, 128.53, 129.24, 129.43, 129.65, 130.52, 130.65, 130.89, 131.29, 133.30, 134.96, 136.15, 146.98 ppm; IR (KBr) (ν_{\max} , cm⁻¹): 3025 (C–H aromatic), 1645 (C=C aromatic), 1489 (C=N), 1011 (C–Cl) cm⁻¹; MS (70 eV) *m/z* (%): 435 (M⁺, 55), 432 (53), 417 (50), 402 (44), 77 (32); Anal. Calcd for C₂₄H₂₂ClN₂: C 77.30, H 5.68, N 7.51%. Found: C 77.32, H 5.69, N 7.48%.

3. Results and discussion

In an initial study, for examination of the catalytic activity of different catalysts such as AlCl₃, SbCl₃ and nanocrystalline MgAl₂O₄ in the condensation reaction, benzaldehyde first reacted with benzil, primary amine and ammonium acetate in the presence of each catalyst (0.05 g) separately. In this study we found that nanocrystalline MgAl₂O₄ was the most effective catalyst in terms of the yield of tetraarylimidazole (90%) while other catalysts formed the product with the yields of 20–43%. In the absence of catalyst, the yield of the product was found to be very low. Therefore, we decided to use nanocrystalline MgAl₂O₄ with a high specific surface area a catalyst with higher activity and better controlled selectivity.

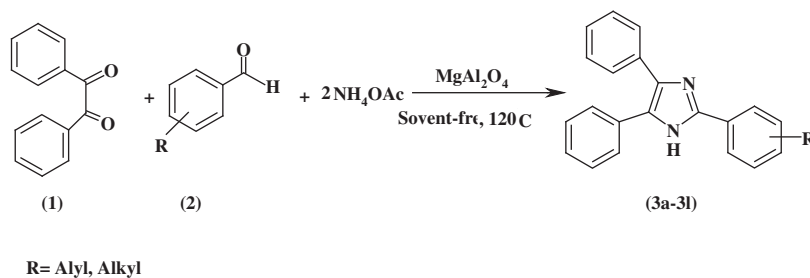
Subsequent efforts were focused on optimizing conditions for the formation of trisubstituted imidazoles by using different amounts of nanocrystalline MgAl₂O₄ and different temperatures to determine their effects on the reaction (Table 1).

We reported the reaction of benzil, with various aromatic aldehydes carrying either electron-releasing or electron-withdrawing substituent in different positions and ammonium acetate at 120 °C under solvent-free conditions to afford trisubstituted imidazoles (Scheme 1). But aliphatic aldehydes produced imidazoles under these conditions.

Results from the condensation reaction of benzil with different aromatic aldehydes, ammonium acetate and nanocrystalline MgAl₂O₄ are given in Table 2.

Table 1 Optimization of reaction conditions for the preparation of 2,4,5-trisubstituted imidazole.

Entry	Catalyst (g)	Time (min)	Temp (°C)	Yield (%)
1	2	15	90	15
2	3	15	90	36
3	5	15	90	43
4	7	15	90	40
5	2	30	120	60
6	3	30	120	85
7	5	30	120	95
8	7	30	120	87



Scheme 1

Table 2 Nanocrystalline $MgAl_2O_4$ catalyzed synthesis of trisubstituted imidazoles at 120 °C under solvent-free conditions.

Entry	R	Product	Yield (%)	Mp (°C)
1	H	3a	93	272–273 Safari et al. (2010)
2	4-Me	3b	96	226–227 Safari et al. (2010)
3	4-MeO	3c	94	227–228 Safari et al. (2010)
4	4-Cl	3d	92	259–261 Safari et al. (2010)
5	3- Cl	3e	95	282–284 Safari et al. (2010)
6	2-MeO	3f	98	260–261 Safari et al. (2010)
7	3-NO ₂	3g	91	269–271 Safari et al. (2010)
8	2-OH	3h	94	203–205 Safari et al. (2010)
9	4-OH	3i	92	260–261 Safari et al. (2010)
10	3,5-(MeO) ₂	3j	97	255–256 Safari et al. (2010)
11	4-Br	3k	95	261–263 Safari et al. (2010)
12	4-N(Me) ₂	3l	96	255–256 Safari et al. (2010)

In order to probe the applicability of this method, the same reaction conditions were applied for the synthesis of tetrasubstituted imidazoles via benzil, aldehyde, ammonium acetate, primary amine and $MgAl_2O_4$ at temperature 120 °C (Scheme 2) and the results obtained are given in Table 3.

The successful results of magnesium aluminate catalyzed synthesis of tetrasubstituted imidazoles in the absence of solvent are given in Table 4.

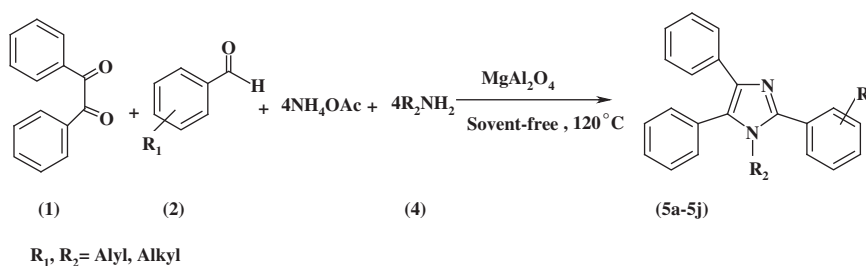
The high efficiency of the nanoparticle is caused not only by its high surface area but also by the high concentration of low-coordinated sites and structural defects on its surface. As the particle size is scaled down to a few nanometers, the constituting atoms have highly defective coordination environments. Most of the atoms have unsatisfied valencies and reside at the surface.

We have not established an exact mechanism in case of 1,2,4,5-tetrasubstituted imidazoles, however, a reasonable possibility is shown in Scheme 3. A plausible mechanism for these

Table 3 Optimization of reaction conditions for the preparation of 1,2,4,5-tetrasubstituted imidazole.

Entry	Catalyst (g)	Time (min)	Temp (°C)	Yield (%)
1	2	15	90	20
2	3	15	90	39
3	5	15	90	66
4	7	15	90	55
5	2	30	120	38
6	3	30	120	60
7	5	30	120	95
8	7	30	120	87

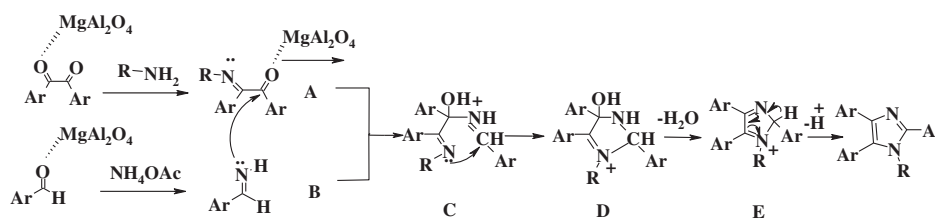
reactions is that aldehyde and 1,2-diketone are first activated by $MgAl_2O_4$ to afford A and B, respectively. $MgAl_2O_4$ catalyzes the reaction as a mild Lewis acid. This catalyst is



Scheme 2

Table 4 Nanocrystalline MgAl₂O₄ catalyzed synthesis of trisubstituted imidazoles at 120 °C under solvent-free conditions.

Entry	R ₁	R ₂	Product	Yield (%)	Mp (°C)
1	H	Ph	5a	91	216–218 Sharma et al. (2008)
2	<i>p</i> -Me	Ph	5b	95	186–188 Sharma et al. (2008)
3	<i>p</i> -MeO	Ph	5c	93	253–254 Sharma et al. (2008)
4	3,4-(OMe) ₂	Ph	5d	90	178–180
5	<i>p</i> -Cl	Ph	5e	96	152–154 Sharma et al. (2008)
6	<i>o</i> -F	Ph	5f	93	165–168
7	<i>o</i> -OH	Ph	5g	90	253–255 Sharma et al. (2008)
8	3,5-(OMe) ₂	Ph	5h	97	163–165
9	H	<i>n</i> -Pr	5i	96	87–89
10	4-Cl	<i>n</i> -Pr	5j	94	85–87

**Scheme 3**

capable of bonding with the carbonyl oxygen increasing the reactivity of the parent carbonyl compounds. Then, imine intermediate (A), condenses further with the carbonyl carbon of 1,2 diketone imine (B) and the formation of carbocation (C) followed by the attack of imine nitrogen at the positive center and dehydration to afford the iso-imidazole (E), which rearranges via (Varma, 1999) sigmatropic shift to the required imidazole (Scheme 3).

In accordance with this mechanism, intermediates that are made from aliphatic aldehydes cannot stabilize the ring. Aliphatics cannot help to stabilize the positive charge in ring.

4. Conclusions

An environmentally friendly and mild method has been developed for the preparation of trisubstituted and tetrasubstituted imidazoles catalyzed by (0.035) mol% nanocrystalline magnesium aluminate. This protocol provides a very fast, good yield, low pollution, green and low cost procedure for the synthesis of these products.

Acknowledgment

This work was financially supported by a Grant (No.159198/XIII) from research foundation of the University of Kashan.

References

Sadeghi, B., Mirjalili, B.B.F., Hashemi, M.N., 2008. BF₃·SiO₂: an efficient heterogeneous alternative for region-chemo and stereoselective Claisen–Schmidt condensation. *Tetrahedron Lett.* 49, 2575–2577.

- Frutos, R.P., Gallou, I., Reeves, D., Xu, Y., Krishnamurthy, D., Senayake, C.H., 2005. Expedient synthesis of substituted imidazoles from nitriles. *Tetrahedron Lett.* 46, 8369–8372.
- Safari, J., Dehghan Khalili, S., Rezaei, M., Banitaba, S.H., Meshkani, F., 2010. Nanocrystalline magnesium oxide: a novel and efficient catalyst for facile synthesis of 2,4,5-trisubstituted imidazole derivatives. *Monatsh. Chem.* 141, 1339–1345.
- Wang, L.M., Wang, Y.H., Tian, H., Yao, Y.M., Shao, J.H., Liu, B., 2006. Ytterbium triflate as an efficient catalyst for one-pot synthesis of substituted imidazoles through three-component condensation of benzyl, aldehydes and ammonium acetate. *J. Fluorine Chem.* 127, 1570–1573.
- Xia, M., Lu, Y., 2007. A novel neutral ionic liquid-catalyzed solvent-free synthesis of 2,4,5-trisubstituted imidazoles under microwave irradiation. *J. Mol. Catal. A: Chem.* 265, 205–208.
- Siddiqui, S.A., Narkhede, U.C., Palimkar, S.S., Daniel, T., Lahoti, R.J., Srinivasan, K.V., 2005. Room temperature ionic liquid promoted improved and rapid synthesis of 2,4,5-triaryl imidazoles from arylaldehydes and 1,2-diketones or α -hydroxyketone. *Tetrahedron* 61, 3539–3549.
- Joshi, R.S., Mandhane, P.G., Shaikh, M.U., Kale, R.P., Gill, C.H., 2010. Potassium dihydrogen phosphate catalyzed one-pot synthesis of 2,4,5-triaryl-1*H*-imidazoles. *Chin. Chem. Lett.* 21, 429–432.
- Sharma, S.D., Hazarika, P., Konwar, D., 2008. An efficient and one-pot synthesis of 2,4,5-trisubstituted and 1,2,4,5-tetrasubstituted imidazoles catalyzed by InCl₃·3H₂O. *Tetrahedron Lett.* 49, 2216–2220.
- Safari, J., Dehghan Khalili, S., Rezaei, M., Banitaba, S.H., 2010. A novel and an efficient catalyst for one-pot synthesis of 2,4,5-trisubstituted imidazoles by using microwave irradiation under solvent-free condition. *J. Chem. Sci.* 122, 437–441.
- Chary, M.V., Keerthysri, N.C., Vupallapati, S.V.N., Lingaiah, N., Kantevari, S., 2008. Tetrabutylammonium bromide (TBAB) in isopropanol: can efficient, novel, neutral and recyclable catalytic system for the synthesis of 2,4,5-trisubstituted imidazoles. *Catal. Commun.* 9, 2013–2217.

- Shaabani, A., Rahmati, A., 2006. Silica sulfuric acid as an efficient and recoverable catalyst for the synthesis of trisubstituted imidazoles. *J. Mol. Catal. A: Chem.* 249, 246–248.
- Nagarapu, L., Apuri, S., Kantevari, S., 2007. Highly efficient, four-component one-pot synthesis of tetrasubstituted imidazoles using Keggin-type heteropolyacids as green and reusable catalysts. *J. Mol. Catal. A: Chem.* 266, 104–108.
- Heravi, M.M., Derikvand, F., Bamoharram, F.F., 2007. Synthesis of 2,4,5-triaryl-imidazoles catalyst by $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ under heterogeneous system. *J. Mol. Catal. A: Chem.* 263, 112–114.
- Zang, H., Su, Q., Mo, Y., Cheng, B.W., Jun, S., 2010. Ionic liquid [EMIM] under ultrasonic irradiation towards the first synthesis of trisubstituted imidazoles. *Ultrason. Sonochem.* 17, 749–751.
- Hasaninejad, A., Zare, A., Shekouhy, M., Ameri Rad, J., 2010. Catalyst-free one-pot four component synthesis of polysubstituted imidazoles in neutral ionic liquid 1-butyl-3-methylimidazolium bromide. *J. Comb. Chem.* 12, 844–849.
- Kidwai, M., Mothsra, P., Bansal, V., Somvanshi, R.K., Ethayathulla, A.S., Dey, S., Singh, T.P., 2007. One-pot synthesis of highly substituted imidazoles using molecular iodine: a versatile catalyst. *J. Mol. Catal. A: Chem.* 265, 177–182.
- Khosropour, A.R., 2008. Ultrasound-promoted greener synthesis of 2,4,5-trisubstituted imidazoles catalyzed by $\text{Zr}(\text{acac})_4$ under ambient conditions. *Ultrason. Sonochem.* 15, 659–664.
- Narayana Murthy, S., Madhav, B., Nageswar, Y.V.D., 2010. DABCO as a mild and efficient catalytic system for the synthesis of highly substituted imidazoles via multi-component condensation strategy. *Tetrahedron Lett.* 51, 5252–5257.
- Wang, X.C., Gong, H.P., Quan, Z.J., Li, L., Ye, H.L., 2009. PEG-200 as an efficient reaction medium for the synthesis of 2,4,5-triaryl-1*H*-imidazoles and 1,2,4,5-tetraaryl-1*H*-imidazoles. *Chin. Chem. Lett.* 20, 44–47.
- Trjero, J.M., Ibarra, A., 1993. Use of luminescence of Mn^{2+} and Cr^{3+} in probing the disordering process in MgAl_2O_4 . *J. Phys. Chem. Solids* 54, 203–207.
- Meshkani, F., Rezaei, M., 2009. *Powder Technol.* 196, 85–88.
- Navaei Alvar, E., Rezaei, M., Navaei Alvar, H., 2010. Synthesis of mesoporous nanocrystalline MgAl_2O_4 spinel via surfactant assisted precipitation route. *Powder Technol.* 198, 275–278.
- Bai, J., Liu, J., Li, C., Li, G., Du, Q., 2011. Mixture of fuels approach for solution combustion synthesis of nanoscale MgAl_2O_4 powders. *Adv. Powder Technol.* 22, 72–76.
- Varma, R.S., 1999. Solvent-free organic syntheses: using supported reagents and microwave irradiation. *Green Chem.* 1, 43–55.