

## RICE HUSK IS AN INEXPENSIVE, EFFICIENT AND MILD CATALYST FOR THE SYNTHESIS OF BIOLOGICALLY ACTIVE 2,4,5-TRIARYL-1H-IMIDAZOLES

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**Abstract:** Rice Husk was found to be an efficient catalyst for the green synthesis of biologically active 2,4,5-Triaryl-1H-Imidazoles by the coupling of Benzil/Benzoin, aldehyde and ammonium acetate under ultrasound-irradiation at ambient temperature for appropriate time to furnish the desired product in good to excellent yield. The catalyst provides clean conversion; greater selectivity and easy workup make this protocol practical and economically attractive.

**Keywords:** 2,4,5-Triaryl-1H-Imidazoles; Benzil/Benzoin; Aldehyde; Ultrasound-irradiation, Rice Husk.

**Introduction:** Nitrogen containing heterocyclic compounds have a great interest within the field of pharmaceutical chemistry and drug industry due to their strong and selective hydrogen bonds with protein/enzyme moieties, which are responsible for important biological activities.<sup>1-3</sup> Imidazole moieties are privileged structures in today's medicinal chemistry. Also, multisubstituted imidazoles exhibit good pharmaceutical properties such as antibacterial<sup>4</sup>, antioxidant,<sup>5</sup> anticancer,<sup>3</sup> antifungal,<sup>5</sup> p38 $\alpha$  MAP kinase inhibitor,<sup>6</sup> B-Raf kinase inhibitor<sup>7</sup> etc.<sup>8-11</sup> In addition, imidazole derivatives are used as ionic liquids which are nonvolatile and clean solvents in green chemistry, and materials for energy-based areas.<sup>12</sup> Some APIs such as losartan, eprosartan, and olmesartan are well-known substituted imidazoles, which are used, in the treatment of especially u<sub>21</sub>b<sub>4</sub> (hypertension), indirectly diabetic kidney disease and heart failure and also trifenagrel drug uses, as arachidonate cyclooxygenase inhibitor.<sup>1,13-15</sup>

The three component condensation of benzil/benzoin, aldehydes and ammonium acetate in a variety of catalysts, such as ionic liquid,<sup>16</sup> iodine,<sup>17</sup> zeolite HY/silica gel,<sup>18</sup> ZrCl<sub>4</sub>,<sup>19</sup> acidic Al<sub>2</sub>O<sub>3</sub>,<sup>20</sup> AcOH,<sup>21</sup> NH<sub>4</sub>OAc,<sup>22</sup> Yb(OTf)<sub>3</sub>,<sup>23</sup> scolecite,<sup>24</sup> PEG-400,<sup>25</sup> L-proline,<sup>26</sup> boric acid<sup>27</sup> and CAN.<sup>28</sup> However many of these procedures suffer from one or more disadvantages such as harsh reaction conditions, prolonged time period, poor yields, use of hazardous and expensive catalysts. So the development of clean, high-yielding and environmentally friendly approaches is still desirable and much in demand.

In recent years, the use of green reagents in organic reactions has attracted the attention of many organic chemists. This attention can be attributed to the reduction of environmental pollution and the cost of the applied methods.

Rice husk, as a thin but abrasive skin in nature, which covers the edible rice kernel, contains cellulose, hemicellulose, lignin, silica, solubles, and moisture.<sup>29,30</sup> The worldwide annual rice husk output is about 80 million tons and over 97% of the husk is generated in developing countries.<sup>31</sup> In the course of decades, rice husk has found different applications in chemistry and industry. For example, unmodified rice husk has been evaluated for its ability to bind zinc(II) and other metal ions.<sup>32,33</sup> On the other hand, various modifications have been done on rice husk in order to enhance its sorption capacities for metal ions and other pollutants.<sup>34,35</sup> In addition, both rice husk and rice husk ash are used as potential raw materials in ceramics, cements and silica-based industries.<sup>36</sup>

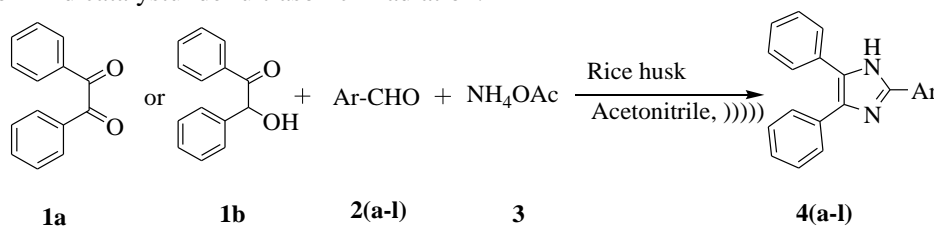
Chemistry is study of interaction of energy and matter. Energy is required for chemical reactions, in one form or another. Chemical reactions ceases as the temperature approaches absolute zero. One has only partial control over the nature of this interaction. The properties of a specific energy source determines the course of a chemical reaction. Ultrasound irradiation differs from conventional energy sources (such as heat, light, or ionizing radiation) in time, pressure, and energy per molecule. Ultrasound is a unique technique used for interaction of matter and energy. Ultrasound enhances chemical and physical changes in a liquid medium through the generation and subsequent destruction of cavitation bubbles<sup>37</sup>.

The use of ultrasound irradiation technique for activating various reactions is well documented in the literature such as Saponification,<sup>38</sup> Reformatsky reaction,<sup>39</sup> Pinacol-pinacolone reaction,<sup>40</sup> Ullmann condensation<sup>41</sup> and Suzuki cross-coupling.<sup>42</sup>

As part of continuing effort in our laboratory<sup>43-45</sup> toward the development of new methods in organic synthesis, we became interested in the possibility of developing synthesis of 2,4,5- triaryl-1H-imidazoles using catalyst by rice husk.

## Results & Discussion

In continuation of our research work of developing methods in various organic transformations,<sup>40-42</sup> we have developed a methodology for the synthesis of 2,4,5-triaryl-1*H*-imidazoles using rice husk, which makes use of mild catalyst under ultrasonic-irradiation.



The reaction of benzoin **1a** and benzaldehyde **2a** and ammonium acetate **3** using 10 mol% rice husk under ultrasonic-irradiation, has been considered as a standard model reaction.

Initially, we have screened a number of different catalysts on the model reaction. When the reaction was carried out in the presence of Silica Sulphuric acid, *p*-TsOH, Dowex 50, Sulphamic acid, amberlyst15 under ultrasonic-irradiation it gave lower yield of product even after prolonged reaction time. However, when the same reaction was conducted under ultrasonic-irradiation using rice husk as a catalyst it gave excellent yields of product in short reaction time (Table 1, entry 5).

We also studied the solvent effect for the synthesis of **4a** as a model reaction by reacting benzoin **1a** and benzaldehyde **2a** and ammonium acetate **3** using 10 mol% rice husk as a catalyst in different solvents. From Table 2 we observed that the reaction in DMF, H<sub>2</sub>O, DMSO, Ethanol, Methanol afforded the product in lower yield. The observation revealed that in all the solvents the yields of the products were found to be low but in case of acetonitrile we got the excellent yield of products as compared to other solvents (Table 2, entry 6).

After optimizing the conditions, we have carried out the same cyclocondensation reaction with various aromatic/heteroaromatic aldehydes containing electron donating or electron withdrawing functional groups at different positions worked well and did not show remarkable differences in the yields of product and reaction time and the results are shown in Table 3. Under similar reaction conditions, we have carried out the cyclocondensation of benzoin **1b** with aromatic/heteroaromatic aldehydes and ammonium acetate in presence of rice husk resulted into the corresponding triarylimidazoles in good yields but the reaction requires more time as compared to benzoin (Table 3). The formation of triarylimidazoles have been confirmed by physical and spectroscopic data and is in full agreement with reported data. Also, the present method was found to be effective for benzoin compared to benzoin in terms of time and yield.

### Anti-microbiological Assay of the Compounds:

In literature, the antimicrobial activity of pyrazoles, chromones, pyrazolines, chalcones, Schiff bases,  $\beta$ -lactams, thiazolidinone etc. have shown that many of them are useful as bactericides and fungicides against various gram positive and gram negative bacteria and fungi.<sup>43-45</sup>

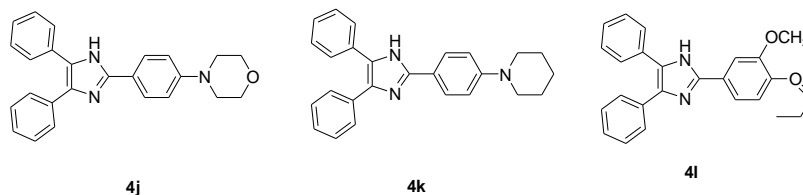
Some of the synthesized compounds were screened for in vitro antibacterial activities against gram +ve and gram -ve bacteria. In gram +ve bacteria, *Staphylococcus aureus* (*S. aureus*) and *Bacillus subtilis* (*B. subtilis*) were used and in gram -ve *Escherichia coli* (*E. coli*) and *Salmonella typhi* (*S. typhi*) were used against standard Tetracyclin and Ampicillin.

The antibacterial activities were carried out on nutrient agar with following composition and by standard procedure of paper disc method.<sup>46</sup>

1. Peptone: 5 gm
2. Beef extract: 3 gm
3. Sodium chloride: 8 gm
4. Agar-agar powder: 15 gm
5. Distilled water: 1000 mL

Petri dishes and necessary glasswares were sterilized in hot air oven (190°C, 45min). The nutrient agar and saline (0.82% NaCl) were sterilized in autoclave (121 °C, 15psi, 20min). Inoculum was prepared in sterile saline and optical density of all pathogens was adjusted to 0.10 at 625nm on ChemitoSpectrscan UV 2600 Spectrophotometer which is equivalent to 0.5 McFarland standards. The nutrient agar plates were prepared by pour plate method.<sup>47</sup> The sensitivity of the compounds was tested by disc diffusion method (paper disc method). All the bacterial cells were cultured in nutrient plates and the compounds to be tested were dissolved in DMSO solvent and were soaked on paper disc. The discs were placed into the plates and

incubated at 37 °C for 24h. The diameter in mm of zone of inhibition around each disc was measured by scale and results were recorded in **Table 5**



**Conclusions:**-In conclusion, we have demonstrated that Rice Husk is an excellent catalyst for the synthesis of 2,4,5-Triaryl-1H-Imidazoles. The catalyst has high activity and can be handled very easily in large scale synthesis. The procedure has the advantages of mild reaction conditions, higher yield of the products, short reaction time & ease of product isolation. We believe that this method is a useful addition to the present methodology for the synthesis of 2,4,5-Triaryl-1H-Imidazoles.

**Experimental:**-Melting points were determined in open capillaries in a paraffin bath and are uncorrected. IR spectra were recorded on a Bruker spectrophotometer using KBr discs, and the absorption bands are expressed in  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  spectra were recorded on a Varian AS 400 MHz spectrometer in  $\text{CDCl}_3/\text{DMSO-d}_6$ , chemical shifts ( $\delta$ ) are in ppm relative to TMS, and coupling constants (J) are expressed in Hertz (Hz). Mass spectra were taken on a Macro mass spectrometer (Waters) by electro-spray method (ES). Bandelin Sonorex (with a frequency of 35 KHz and a nominal power 200 W) ultrasonic bath was used for ultrasonic irradiation. Built-in heating, 30-80°C thermostatically adjustable. The reaction vessel placed in side the ultrasonic bath containing water.

**A typical experimental procedure:**-A mixture of aldehydes **2** (1 mmol), Benzil **1a** or Benzion **1b**, (1 mmol) and ammonium acetate **3** (1.5 mmol) and rice husk (10 mol%) in acetonitrile (500 ml) was irradiated under ultrasound irradiation for an appropriate time. The reaction progress was monitored by TLC (EtOAc:Hexane, 10-25% mixture in Hexane) and HPLC, respectively. After complete conversion the heterogeneous mass was filtered and the resin was washed with acetonitrile. The solvent was removed in a rotary evaporator under reduced pressure. To the crude reaction mass heptanes (500 mL) was added and distilled off the heptane in a rotary evaporator under reduced pressure to result off solid product. To this solid again added 200 mL of heptanes and stirred for 15-20 minutes at room temperature. The solid was filtered and dried in an oven in vacuum to afford the pure product (Yield: 94%).

#### Spectroscopic data

**(4a)** Mp 277–278°C IR ( $\text{KBr, cm}^{-1}$ ): 7126, 3040, 1480, 1460, 1130, 695.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.73 (brs, 1H, NH), 8.10 (d, 2H,  $J = 7.6$  Hz, ArH), 7.40–7.50 (m, 13H, ArH). MS (EI):  $m/z$  (%) = 296 (46) [ $\text{M}^+$ ]. Anal. calcd. for  $\text{C}_{21}\text{H}_{16}\text{N}_2$ : C, 85.11; H, 5.44; N, 9.45. Found: C, 85.07; H, 5.41; N, 9.52.

**(4b)** Mp 261-262°C IR ( $\text{KBr, cm}^{-1}$ ): 3060, 1605, 1455, 1090, 763, 695.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.85 (brs, 1H, NH), 8.12 (d, 2H,  $J = 8.4$  Hz, ArH), 7.22–7.55 (m, 12H, ArH). MS (EI):  $m/z$  (%) = 330 (36), 332 (12) [ $\text{M}^+$ ]. Anal. calcd. for  $\text{C}_{21}\text{H}_{15}\text{C}_1\text{N}_2$ : C, 76.24; H, 4.57; N, 8.47. Found: C, 76.20; H, 4.55; N, 8.51.

**(4c)** Mp 195-197°C IR ( $\text{KBr, cm}^{-1}$ ): 3430, 3065, 1630, 1505, 1498.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.45 (brs, 1H, NH), 7.25–7.55 (m, 14H, ArH). MS (EI):  $m/z$  (%) = 330 (36), 332 (12) [ $\text{M}^+$ ]. Anal. calcd. for  $\text{C}_{21}\text{H}_{15}\text{C}_1\text{N}_2$ : C, 76.24; H, 4.57; N, 8.47. Found: C, 76.20; H, 4.55; N, 8.51.

**(4d)** Mp 228-229°C IR ( $\text{KBr, cm}^{-1}$ ): 3030, 1610, 1490, 1250, 1030, 695.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.55 (brs, 1H, NH), 8.00 (d, 2H,  $J = 8.0$  Hz, ArH), 7.52 (d, 4H,  $J = 6.8$  Hz, ArH), 7.30–7.37 (m, 6H, ArH), 7.05 (d, 2H,  $J = 7.6$  Hz, ArH), 3.82 (s, 3H,  $\text{CH}_3$ ). MS (EI):  $m/z$  (%) = 326 (36) [ $\text{M}^+$ ]. Anal. calcd. for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ : C, 80.96; H, 5.56; N, 8.58. Found: C, 80.94; H, 5.53; N, 8.63.

**(4e)** Mp 231-232°C IR ( $\text{KBr, cm}^{-1}$ ): 3425, 3086, 1590, 1500, 1335, 1105.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.67 (s, NH), 8.05 (d,  $^3J = 7.5$  Hz,  $\text{C}_6\text{H}_4\text{NO}_2$ ), 7.08–7.62 (m,  $2\text{C}_6\text{H}_5$ ), 6.65 (d,  $^3J = 7.4$  Hz,  $\text{C}_6\text{H}_4\text{NO}_2$ ). MS (EI):  $m/z$  (%) = 297 (60), 269 (20), 165 (100), 105 (25), 77 (50). Anal. calcd. for  $\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}_2$ : C, 73.90; H, 4.39; N, 12.31. Found: C, 73.83; H, 4.32; N, 12.39.

**(4f)** Mp 187-189°C IR ( $\text{KBr, cm}^{-1}$ ): 3025, 1495, 1230, 837, 765, 695.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 12.71 (brs, 1H, NH), 8.13 (d, 2H,  $J = 4.2$  Hz, ArH), 7.57 (d, 4H,  $J = 5.6$  Hz, ArH), 7.25–7.40 (m, 8H, ArH). MS (EI):  $m/z$  (%) = 314 (44) [ $\text{M}^+$ ]. Anal. calcd. for  $\text{C}_{21}\text{H}_{15}\text{FN}_2$ : C, 80.24; H, 4.81; N, 8.91. Found: C, 80.27; H, 4.79; N, 8.86.

**(4h)** Mp 199-200°C IR ( $\text{KBr, cm}^{-1}$ ): 3322, 2987, 2470, 1660, 1210, 1170, 875, 717, 637.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ,  $\delta$  ppm): 7.95–8.02 (m, 6H, Ar), 7.60–7.70 (m, 3H, Ar), 7.46–7.58 (m, 4H, Ar), 7.20 (m,

1H, NH). MS (EI) (m/z, %) = 286 (29) [M<sup>+</sup>]. Anal. calcd. for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O: C, 79.70;H, 4.93; N,9.78. Found: C, 79.66;H, 4.91; N, 9.74.

(4i) Mp 271-272°C IR (KBr,cm<sup>-1</sup>): 3282, 3055, 1700, 1609, 1494, 696. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub> δ ppm): 12.42 (s, 1H, NH), 9.71 (s, 1H, OH), 7.90 (d, 2H, J = 8.4 Hz, ArH), 7.54 (d, 2H, J = 7.6 Hz, ArH), 7.50 (d, 2H, J = 7.2 Hz, ArH), 7.44 (t, 2H, J = 7.6 Hz, ArH), 7.35 (t, 1H, J = 7.6 Hz, ArH), 7.30 (t, 2H, J = 7.6 Hz, ArH), 7.25 (t, 1H, J = 7.2 Hz, ArH), 6.85 (d, 2H, J = 8.4 Hz, ArH). MS (EI): m/z (%) = 312 (40) [M<sup>+</sup>]. Anal. calcd. for C<sub>21</sub>H<sub>16</sub>N<sub>2</sub>O: C, 80.75;H, 5.16; N, 8.97. Found: C, 80.70; H, 5.18; N, 8.93.

**Table 1. Screening of catalysts on the model reaction<sup>a</sup>**

Entry	Catalysts	Time (min)	Yield <sup>b</sup> (%)
1	Silica Sulphuric acid	10	64
2	p-TsOH	10	55
3	Dowex 50	10	68
4	Sulphamic acid	10	47
5	Amberlyst-15	10	71
6	Rice Husk	10	95

Reaction of benzil, benzaldehyde and ammonium acetate in presence of rice husk under ultrasonic irradiation.<sup>b</sup> Isolated yield.

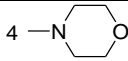
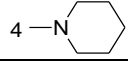
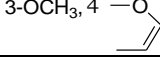
**Table 2. Screening of Solvents<sup>a</sup>**

Entry	Solvent	Time	Yield (%) <sup>b</sup>
1	DMF	10 (h)	75
2	H <sub>2</sub> O	12 (h)	30
3	DMSO	1 (h)	90
4	MeOH	2 (h)	90
5	EtOH	45 (min)	91
6	Acetonitrile	10 (min)	95

<sup>a</sup>Reaction Conditions: **1** (1 mmol), **2a** (1 mmol), 3(1.5 mmol) rice husk (10 mol%), solvent (10 mL)

<sup>b</sup>Isolated yields without ultrasound irradiation. <sup>c</sup>Isolated yields with ultrasound irradiation.

**Table 3. Synthesis of 2,4,5-Triaryl-1H-Imidazoles 4(a-l) Using rice husk as a catalyst<sup>a</sup>**

Entry	Comp	R	1	Time (min)	Yield (%) <sup>b</sup>	m.p (°C)
1	4a	H	Benzil	10	95	277-278
2	4b	4-Cl	Benzil	15	92	261-262
3	4c	2-Cl	Benzil	15	90	195-197
2	4d	4-OMe	Benzil	15	92	228-229
5	4e	4-NO <sub>2</sub>	Benzil	18	90	231-232
6	4f	4-F	Benzil	18	92	187-189
7	4g	2-Thienyl	Benzil	18	89	260-262
8	4h	2-Furyl	Benzil	20	92	199-200
9	4i	4-OH	Benzil	17	88	271-272
10	4j		Benzil	25	75	280-282
11	4k		Benzil	25	79	272-273
12	4l		Benzil	27	70	291-293
13	4a	H	Benzoin	30	90	—
14	4b	4-Cl	Benzoin	30	89	—
15	4h	2-Furyl	Benzoin	30	87	—
16	4d	4-OMe	Benzoin	30	88	—
17	4g	2-Thienyl	Benzoin	30	85	—

<sup>a</sup>Reaction conditions: benzil/benzoin (1 mmol), aldehydes (1 mmol), ammonium acetate (1.5 mmol), rice husk (10 mol%) under ultrasonic irradiation. <sup>c</sup>Isolated yields.

**Table 4. In-vitro Antibacterial Activity of 2,4,5-Triaryl-1H-Imidazoles Derivatives**

Entry	Zone of inhibition (mm)			
	Gram positive		Gram negative	
	<i>B. subtilis</i> (ATCC No. 6633)	<i>S. aureus</i> (ATCC No. 25923)	<i>S. typhi</i> (ATCC No. 23564)	<i>P. aeruginosa</i> (ATCC No. 27853)
4j	8	6	----	----
4k	23	20	15	14
4l	----	5	8	9
Streptomycin	20	19	22	24
Ampicillin	24	23	25	25

**References:**

1. E. Vitaku, D.T. Smith, J.T. Njardarson, *Journal of Medicinal Chemistry*, **2014**, *57*, 10257.
2. L. M. Wang, Y. H. Wang, H. Tian, Y. F. Yao, J. H. Shao, *Journal of Fluorine Chemistry* .**2006**, *127*, 1570.
3. G. V. M Sharma, A. Ramesh, A. Singh, G. Srikanth, G.V. Jayaram, *Medicinal Chemistry Communications* **2014**, *5*, 1751.
4. Y. Fang, R. Yuan, W. Ge, Y. G. Wang Liu, *Synthesis and biological evaluation of 1*, **2017**, *43*, 5.
5. R. Ghorbani-Vaghei, V. Izadkhah, J. Mahmoodi, R. Karamian, M. A. Khoei, *Monatshefte für Chemie-Chemical Monthly*, **2018**, *149*, 1447.
6. M. Mader, A. De Dios, C. Shih, R. Bonjouklian *Imidazolylbenzimidazoles and imidazo*, **2008**, *8*, 5.
7. A. K. Takle, M. J. Brown, S. Davies, D. K. Dean, G. Francis, *Bioorganic & Medicinal Chemistry Letters*, **2006**, *16*, 378.
8. R. Rossi, G. Angelici, G. Casotti, C. Manzini, M. Lessi, *Catalytic synthesis of 1*, **2019**, *361*, 2737.
9. M. Esmaeilpour, J. Javidi, M. Zandi, *New Journal of Chemistry* .**2015**, *39*, 3388.
10. K. Bahrami, M. Khodaei, *Catalytic synthesis of 1*, **2011**, *142*, 5.
11. D. Kumar, D.N. Kommi, N. Bollineni, A. R. Patel, A. K. Chakraborti, *Green Chemistry* .**2012**, *14*, 2038.
12. M. D. Green, T. E. Long, *Polymer Reviews* **2009**; *49*, 291.
13. A. R. Moosavi-Zare, Z. Asgari, A. Zare, M. A. Zolfigol, M. Shekouhy, *RSC advances*, **2014**, *4*, 60636.
14. S. L. Abrahams, R. J. Hazen, A. G. Batson, A. P. Phillips, *Journal of Pharmacology and Experimental Therapeutics* **1989** *249*, 359.
15. N. L. Higuera, D. Peña-Solórzano, C. Ochoa-Puentes, *Synlett*. **2019**, *30*, 225.
16. (a) S. A. Siddiqui, U. C. Narkhede, S. S. Palimkar, T. Daniel, R. J. Lahoti, K. V. Srinivasan, *Tetrahedron* **2005**, *61*, 3539; (b) A. Shaabani, B. Rahmati, J. Aghaaliakbari, G. Safaei, *Synth. Commun.* **2006**, *36*, 65.
17. M. Kidwai, P. Mothsra, V. Bansal, R. Goyal, *Mont. Fur. Chem.* **2006**, *137*, 1189.
18. S. Balalaie, A. Arabanian, M. S. Hashtroudi, *Mont. Fur. Chem.* **2000**, *131*, 945.
19. G. V. M. Sharma, Y. Jyothi, P. S. Lakshmi, *Synth. Commun.* **2006**, *36*, 2991.
20. A. Y. Usyatinsky, Y. L. Khmel'nitsky, *Tetrahedron Lett.* **2000**, *41*, 5031.
21. S. E. Wolkenberg, D. D. Winoski, W. H. Leister, Y. Wang, Z. Zhao, C. W. Lindsley, *Org. Lett.* **2004**, *6*, 1453.
22. M. Kidwai, S. Saxena, S. Rastogi, *Bull. Korean Chem. Soc.* **2005**, *26*, 2051.
23. L. M. Wang, Y. H. Wang, T. He, Y. F. Yao, J. H. Shao, B. Liu, *J. Fluorine Chem.* **2006**, *127*, 1570.
24. L. S. Gadekar, S. R. Mane, S. S. Katkar, B. R. Arbad, M. K. Lande, *Central Eur. J. Chem.* **2009**, *7*, 550.
25. X. C. Wang, H. P. Gong, Z. J. Quan, L. Li, H. L. Ye, *Chin. Chem. Lett.* **2009**, *20*, 44.
26. N. V. Shitole, K. F. Shelke, S. S. Sonar, S. A. Sadaphal, B. B. Shingate, M. S. Shingare, *Bull. Korean Chem. Soc.* **2009**, *30*, 1963.
27. K. F. Shelke, S. B. Sapakal, S. S. Sonar, B. R. Madje, B. B. Shingate, M. S. Shingare, *Bull. Korean Chem. Soc.* **2009**, *30*, 1057.
28. E. Rajender, K. R. Murthy, N. N. Reddy, *Ind. J. Org. Chem.*, **2011**, *50B*, 926.
29. F. Adam, I.A. Rahman, M.I. Saleh R. Othman (Ed.), *Seramik Nusantara*, U. S. M. Penang, Malaysia (1990), p. 261 Google Scholar
30. M.A. Hamad *J. Chem. Biotechnol.*, *31* (1981), p. 624 View PDF CrossRef View Record in Scopus

31. L. Armesto, A. Bahillo, K. Veijonen, A. Cabanillas J. Otero., 23 (2002), p. 171 ArticleDownload PDFView Record in Scopus
32. D. Roy, P.N. Greenla, B.S. Shane J. Environ. Sci. Health. A, 28 (1993), p. 37 View PDFCrossRef
33. E. Munaf, R. Zein Technol., 18 (1997), p. 359 View PDFCrossRefView Record in Scopus
34. R. Suemitsu, R. Uenishi, I. Akashi, M. Nakano J. Appl. Polym. Sci., 31 (1986), p. 75 View Record in Scopus
35. K.K. Krishnani, X. Meng, C. Christodoulatos, V.M. Boddue. Hazard. Mater., 153 (2008), p. 1222 ArticleDownload PDFView Record in Scopus
36. I.A. Rahman, J. Ismail, H. Osman J. Mater. Chem., 7 (1997), p. 1505 View Record in Scopus
37. S. Puri, B.Kaur, A.Parmar, H. Kumar, *Current Organic Chemistry*, **2013**, 17, 1790.
38. V. K. Ahluwalia, M. Kidwai, *New Trends in Green Chemistry*, **2004**.
39. V. Singh, V. Sapehiya, G. L Kad, *Synthesis* **2003**, 198.
40. (a) K.S. Niralwad, I. B. Ghorade, *World J. of Pharm. and Pharmaceut. Sci.* **2015**, 4, 704. (b) N. V. Shitole, K. S. Niralwad, B. B. Shingate, M. S. Shingare, *Arabian Journal of Chemistry*, **2016**, 9, S858. (c) K. S. Niralwad, I. B. Ghorade, P. R. Pande, *current Global Reviewer- Special Issue* (Ugc Approved Sr.No.-64310, Issn 2319-8648).
41. (a) K. S. Niralwad, B. B. Shingate, M. S. Shingare, *Ultrasonics Sonochemistry*, **2010**, 17, 760 (b) K. S. Niralwad, B. B. Shingate, M. S. Shingare, *Tetrahedron Letters*, **2010**, 51, 3616 (c) K. S. Niralwad, B. B. Shingate, M. S. Shingare, *Chinese Chemical Letters*, **2011**, 22, 551.
42. (a) K. S. Niralwad, B. B. Shingate, M. S. Shingare, *Journal of the Chinese Chemical Society*, **2010**, 57, 89. (b) K. S. Niralwad, B. B. Shingate, M. S. Shingare, *J. Heterocyclic Chem*, **2011**, 48, 742. (c) K. S. Niralwad, I. B. Ghorade, *European Academic Research*, **2014**, 2, 4112.
43. N. S Joshi, Ph D, Thesis, University of Pune, **2004**.
44. S. B Pawar, Ph D, Thesis, University of Pune, **2006**.
45. S, S, Argade Ph D, Thesis, University of Pune, **2008**
46. P B, Godkar In Text Book of Medical Laboratory Technology, Bhalani Publishing House, Bombay, India, **1996**.