

# Calcined eggshell (CES): An efficient natural catalyst for Knoevenagel condensation under aqueous condition

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**Abstract.** A convenient, eco-friendly and economic method for Knoevenagel condensation of aromatic aldehydes with active methylene compounds using calcined eggshell (CES) as an efficient natural catalyst in aqueous medium has been reported. CES is a new, ecologically safe and inexpensive green catalyst obtained from renewable resources.

**Keywords.** Natural catalyst; CES; Knoevenagel condensation; green catalyst; renewable resources.

## 1. Introduction

Knoevenagel condensation of aldehydes with active methylene compounds is an important method used for the synthesis of different pharmaceutically important organic compounds.<sup>1</sup> Formation of carbon–carbon bond in organic syntheses has attracted attention of many researchers. Knoevenagel condensation is one of the important reactions to achieve carbon–carbon bond formation in organic syntheses. Some eco-friendly methods for Knoevenagel condensation have been reported using green catalysts and under solvent-free-conditions. However, completion of reaction with high yield has been achieved by maintaining high reaction temperature and long reaction time. Some newly reported methods employ catalysts such as sulphated zirconia,<sup>2</sup> diazabicyclo[5.4.0]undec-7-ene (DBU),<sup>3</sup> silica supported ammonium acetate,<sup>4</sup> guanidine,<sup>5</sup> with different reaction conditions. The Knoevenagel condensation is carried out using catalysts such as polymeric sulphonate of piperazine,<sup>6</sup> thiourea,<sup>7</sup> MgO/ZrO<sub>2</sub>,<sup>8</sup> ion-exchange resin,<sup>9</sup> potassium sorbate,<sup>10</sup> and also in the presence of various solvents.<sup>11</sup>

The Knoevenagel condensation is also performed using Lewis acids such as LaCl<sub>3</sub>·7H<sub>2</sub>O,<sup>12</sup> ZnCl<sub>2</sub>,<sup>13</sup> I<sub>2</sub>/K<sub>2</sub>CO<sub>3</sub>,<sup>14</sup> and CuCl<sub>2</sub>.<sup>15</sup> At the same time some base catalysts such as alumina,<sup>16</sup> ethylene diamine,<sup>17</sup> dimethyl amino pyridine,<sup>18</sup> alkaline earth oxides,<sup>19</sup> have been reported which work efficiently for Knoevenagel condensation. Recently, alumina-supported

MOF<sup>20</sup> eggshell as porous superhydrophobic material is reported for Knoevenagel condensation. However, many reported methods have various drawbacks such as prolonged reaction time, toxicity and use of harmful organic solvents. Introduction of clean procedures utilizing eco-friendly green catalysts have attracted great attention of workers.

Recently, we have developed calcined eggshell (CES) as a natural catalyst and we found that it works efficiently for Knoevenagel condensation between aromatic and hetero aromatic aldehydes and active methylene compounds.

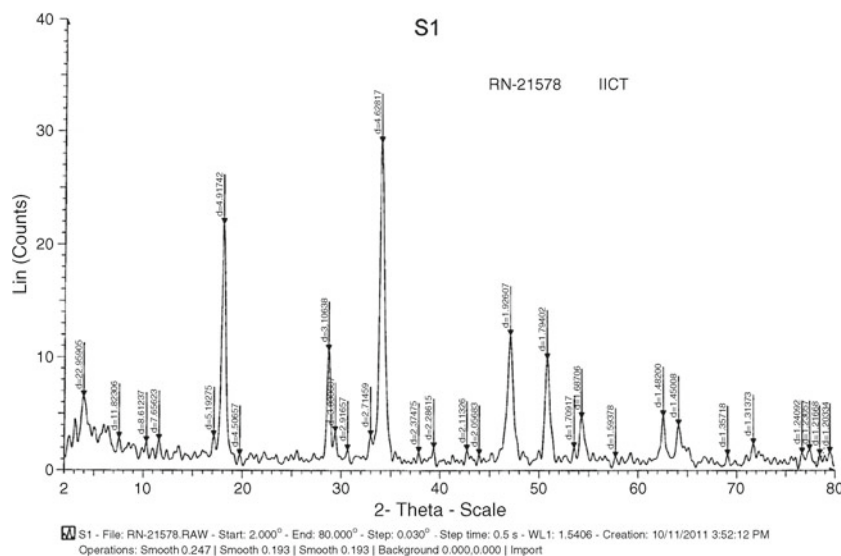
CES has been developed from processing of waste eggshells. Eggshell material mainly consists of high percentage of calcium carbonate, nearly about 94%.<sup>21</sup> Waste eggshells have been utilized as humidity adsorbent,<sup>22</sup> as an adsorbent in the removal of chromium from its aqueous solution,<sup>23</sup> and also as a low cost solid catalyst for biodiesel production,<sup>24</sup> as a catalyst for lactose isomerization to lactulose.<sup>25</sup> Being a natural source of calcium, eggshell powder can serve as a good calcium supplement in prevention and treatment of osteoporosis.<sup>26</sup>

## 2. Experimental

### 2.1 Materials and methods

All the chemicals used were of commercial reagent grade. The carbonyl compounds and active methylene compounds were purified by standard procedures and

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**Figure 1.** X-ray diffraction pattern of CES.

purity was determined by thin-layer chromatography (TLC). The  $^1\text{H}$  NMR spectra were measured with Avance-300 NMR spectrophotometer. IR spectra were obtained using potassium bromide pallets on Bruker ALPHA FT-IR Spectrometer. Melting points were measured on open capillary method on DBK-programmable melting point apparatus. Purity of the substrates and completion of reactions were checked by TLC using Merck silicagel 60 F<sub>254</sub> plates.

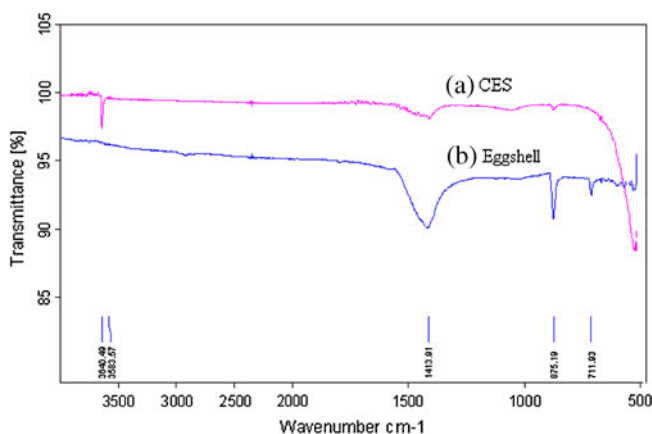
**2.1a Preparation of catalyst CES:** The waste eggshells were collected, cleaned and dried in an oven at 100°C. After crushing, the raw eggshell powder was calcined at heating rate 2°C/min in Muffle furnace up to 900°C and this temperature was maintained for 3 h. After thermal treatment, most of the organic materials were burnt out and the eggshell got transformed

into white soft powder, which was denominated as CES.

**2.1b Characterization of catalyst:** Aqueous 1% CES solution was checked on pH meter and it was found that aqueous CES is strongly alkaline with pH 13.9.

Formation of suitable active phase of CES was found by X-ray diffraction (XRD) and confirmed by FT-IR spectra. The X-ray powder diffraction analysis (XRD) of CES sample (figure 1) shows characteristic peaks of CaO at  $2\theta = 32.97, 37.85, 53.57$ , peaks of  $\text{Ca}(\text{OH})_2$  at  $2\theta = 17.06, 28.71, 34.08, 47.14, 50.8$  and at  $2\theta = 29.37, 39.38$  characteristics peaks of  $\text{CaCO}_3$ .

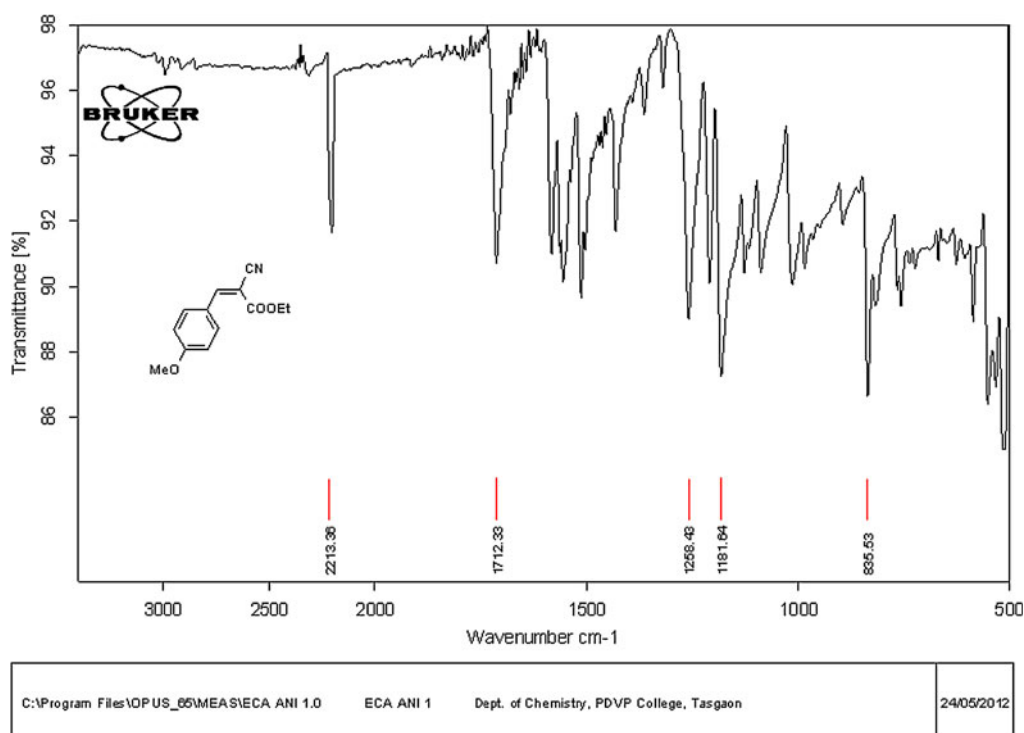
The IR spectra of CES (figure 2a) shows a sharp band at  $3640.49\text{ cm}^{-1}$  due to active phase  $\text{Ca}(\text{OH})_2$ , which supports for adsorption of water on CaO and disappearance of broad band at  $1413.91\text{ cm}^{-1}$ , sharp



**Figure 2.** IR spectra of (a) CES and (b) Eggshell powder.



**Figure 3.** Product formation during reactions for entries 2, 3, 11, 14 (table 1).

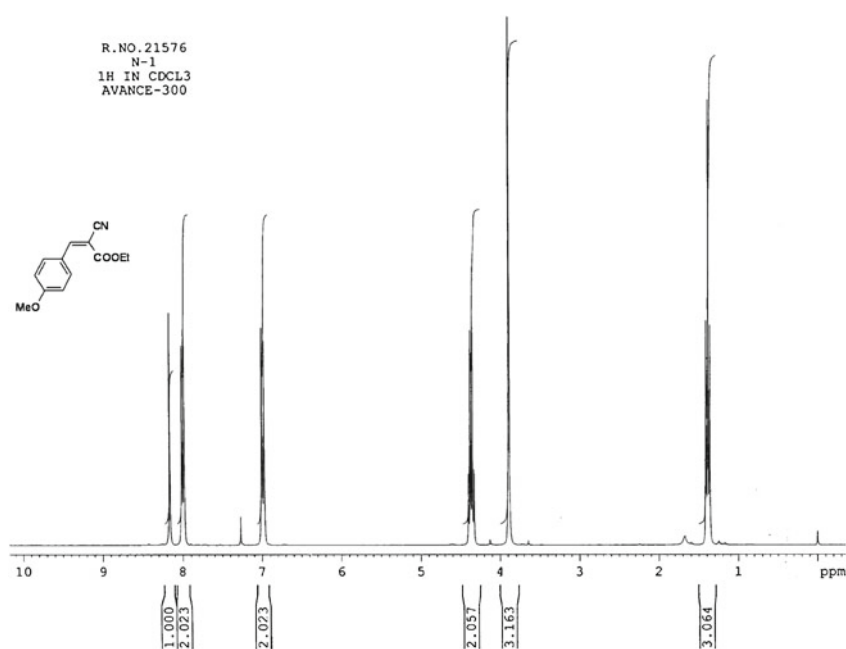


**Figure 4.** IR spectra of ethyl-2-cyano-3-(4-methoxyphenyl) prop-2-enoate (table 1, entry 2).

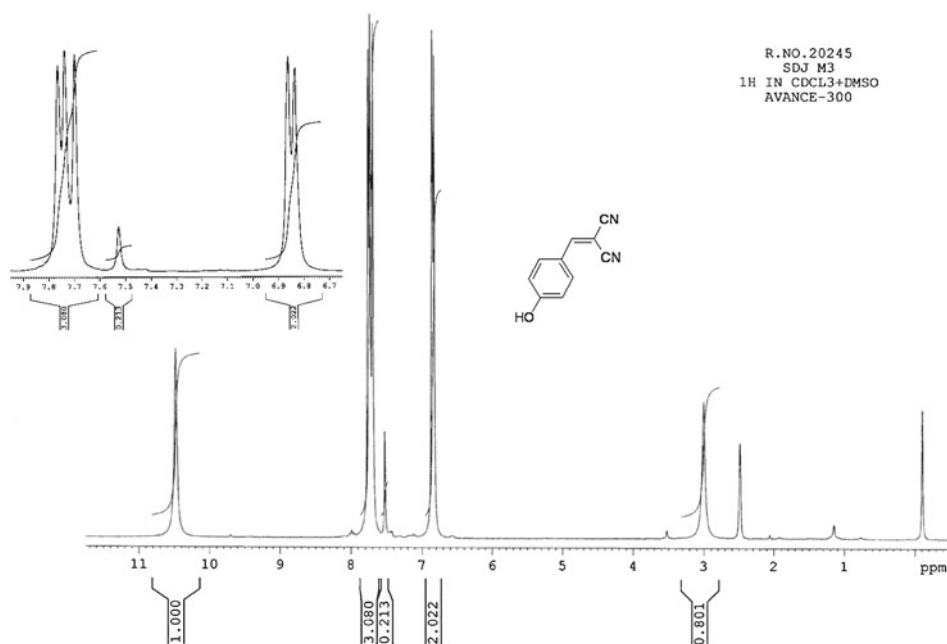
bands at 875.19, 711.93  $\text{cm}^{-1}$  which are characteristics of  $\text{CaCO}_3$  observed in IR spectra of eggshell powder (figure 2b).

**2.1c General method for synthesis of (2-Nitrobenzylidene)propanedinitrile (14):** To the mixture of 2-nitrobenzaldehyde (1.51 g, 10 mmol)

and malononitrile (0.66 g, 10 mmol) in 2 mL water, 2.5 wt% of CES catalyst (catalyst to solvent weight ratio) was added with constant stirring at room temperature. Progress of the reaction was monitored by TLC. After completion of the reaction (checked by TLC), 5 ml water was added and the reaction mixture was extracted with ethyl acetate. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and ethyl acetate was removed



**Figure 5.** NMR spectra of ethyl-2-cyano-3-(4-methoxyphenyl)prop-2-enoate (table 1, entry 2).



**Figure 6.** NMR spectra of (4-hydroxybenzylidene)propanedinitrile (table 1, entry 15).

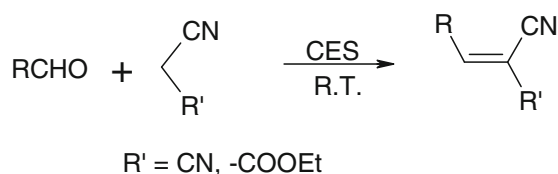
under reduced pressure to get crude product. Recrystallization of crude product with ethanol produces orange crystalline product. All Knoevenagel products (1–19) were synthesized by following the same procedure and the products formed (figure 3) were confirmed by IR and NMR spectral analysis (figures 4–6).

### 3. Result and discussion

Knoevenagel condensation is basically reported as base catalysed reaction. In literature we found both acid as well as base catalysts reported efficiently for this condensation. As a part of our research work, we have reported the Knoevenagel condensation using lemon juice as a natural acid catalyst.<sup>27</sup>

In continuation with our research program concerning the development of natural catalysts, we are reporting here CES as an efficient natural base catalyst for Knoevenagel condensation of aromatic aldehydes and active methylene compounds (scheme 1).

To optimize the reaction conditions, initially we have decided to estimate the effect of solvent on the



**Scheme 1.** CES catalysed Knoevenagel condensation.

CES catalysed Knoevenagel condensation in different organic solvents as well as in aqueous medium. For this study, the reaction between 4-nitrobenzaldehyde and malononitrile was chosen as model reaction. When the reaction was examined in different solvents such as water, ethanol, acetone, tetrahydrofuran (THF), toluene, acetonitrile, dichloromethane and chloroform, we found that the reaction proceeds smoothly at room temperature in water (table 1, entry 1) with 97% yield of product in 15 min. While, in the presence of organic solvents, reaction proceeds comparatively with low yield (table 1, entries 2 to 8) taking more time. Hence, water can be used as best solvent due to high yield and shorter reaction time. Moreover, using water as the


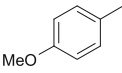
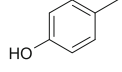
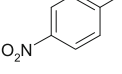
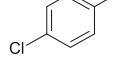
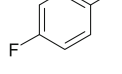
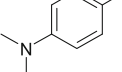
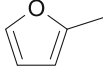
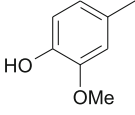

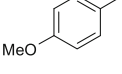
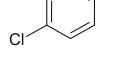
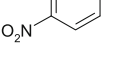

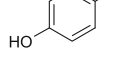
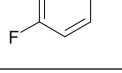
**Table 1.** Optimization of reaction conditions using various solvents.<sup>a</sup>

Sr. No.	Solvent	Time <sup>b</sup> (min)	Yield
1	Water	05	97
2	Ethanol	30	87
3	Acetone	35	84
4	Toluene	60	90
5	THF	120	82
6	Acetonitrile	75	85
7	Dichloromethane	110	84
8	Chloroform	150	82

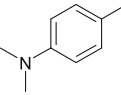
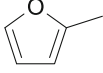
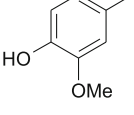
<sup>a</sup>The reactions were carried out at ambient temperature using 4-nitro benzaldehyde (10 mmol) and malononitrile (10 mmol), 2.5 wt% CES in corresponding solvent.

<sup>b</sup>Time reported in min monitored by TLC.

**Table 2.** Knoevenagel condensation of aromatic aldehydes with active methylene compounds.<sup>a</sup>

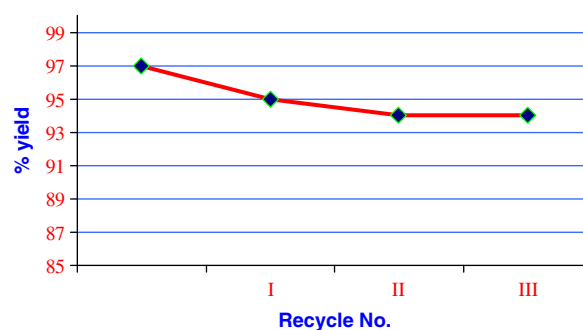
Entry	Aldehydes	R'	Time <sup>b</sup> (min)	Yield
1		COOEt	40	91
2		COOEt	30	95
3		COOEt	45	92
4		COOEt	15	98
5		COOEt	25	91
6		COOEt	35	90
7		COOEt	55	94
8		COOEt	40	90
9		COOEt	65	89
10		CN	15	92
11		CN	12	94
12		CN	05	89
13		CN	05	97
14		CN	10	92
15		CN	10	92
16		CN	10	89

**Table 2.** (continued).

Entry	Aldehydes	R'	Time <sup>b</sup> (min)	Yield
17		CN	45	89
18		CN	30	90
19		CN	50	92

<sup>a</sup>Reactions are carried out at ambient temperature in aqueous medium using 2.5 wt% (0.050 gm) CES.

<sup>b</sup>Time reported in min monitored by TLC.

**Figure 7.** Efficiency of CES after recycling.

reaction medium made the separation process much easier than using other solvents. For example, with water as a solvent, the product could be obtained with high purity through simple filtration and washing with a little amount of water.

These observations indicate that, water increases the catalytic activity of CES effectively as compared to other organic solvents.

After optimization we subsequently examined the extent and feasibility of CES catalysed Knoevenagel condensation between different aromatic aldehydes and active methylene compounds, malononitrile and ethylcyanoacetate using 2.5 wt% of CES in aqueous medium. The results for all synthesized compounds are reported in table 2.

A very small quantity of catalyst is sufficient for completion of reaction and for getting better yields. After completion of reaction the catalyst can be recollected easily from the reaction mixture.

CES catalyst gave good results when it was recycled. The reaction between 4-nitrobenzaldehyde (10 mmol)



**Table 3.** Comparison of different catalysts used for synthesis of compound (10) Benzylidenepropanedinitrile (R = C<sub>6</sub>H<sub>5</sub>).

Sr. No.	Catalyst	Solvent	Time	Condition	Yield (%)
1	SO <sub>4</sub> <sup>2-</sup> & ZrO <sub>2</sub>	–	180 min	Stirred in N <sub>2</sub> atm. & reflux	89
2	Guanidine <sup>5</sup>	DCM	4 h	RT	89.8
3	Thiourea <sup>7</sup>	–	2 min	MW	82
4	Ionic liquid supported proline <sup>28</sup>	acetonitrile	24 h	Stirred 80°C	98
5	SiO <sub>2</sub> -NH <sub>4</sub> OAc <sup>29</sup>	DCM	7 h	Refluxed 60°C	87
6	USY Zeolite <sup>30</sup>	Benzene	12 h	Reflux	92
7	AlPO <sub>4</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>31</sup>	–	¼ h	Stirred at RT	80
8	CTMAB <sup>32</sup>	Water	1.5 h	Stirred at RT	90.6
9	TEBA <sup>33</sup>	–	10 min	Grinding at RT	90
10	NH <sub>4</sub> OAc-Basic Al <sub>2</sub> O <sub>3</sub> <sup>34</sup>	–	6 min	MW (850 W)	80
11	MgBr <sub>2</sub> .OEt <sub>2</sub> <sup>35</sup>	TEA, THF	1–2 h	Stirred at RT	98
12	K <sub>2</sub> CO <sub>3</sub> PEG 400 <sup>36</sup>	–	60 min	Stirred at 90°C	89
13	–	H <sub>2</sub> O	2 min	MW Irradiation <sup>37</sup>	89
14	CES	Water	15 min	Stirred at RT	92
15	CaO (without calcination)	Water	15 min	Stirred at RT	91
16	CaO (calcined 900°C for 2 h)	Water	15 min	Stirred at RT	91

and malononitrile (10 mmol) was chosen for this purpose as model reaction to study the effectiveness of catalyst on recycling. The model reaction was carried out in the presence of 2.5 wt% of CES in water medium. The reaction mixture was stirred for appropriate time. After extraction of the product with ethylacetate, the aqueous phase containing CES was collected separately. The recovered aqueous solution containing CES was used as the reaction medium for the next cycle. The recycling was repeated for three times using similar amount of 4-nitrobenzaldehyde and malononitrile (figure 7). The catalyst was found to be efficient even after recycling.

Comparison of the results using CES catalyst with some other reported catalysts for Knoevenagel condensation (table 3) shows the efficiency of this catalyst. It furnishes high reaction yield, takes shorter reaction time, and small quantity of this inexpensive and readily available catalyst is sufficient to get good yield of expected products.

In order to compare the activity of CES with pure CaO, the catalytic activity of CaO was also investigated for the model reaction. The results indicate that, CES and CaO (table 3, entries 14 to 16) have comparable catalytic performance. Since both have similar catalytic performance, we recommend here CES as best catalyst as it is derived from renewable resources, waste eggshell.

This natural CES catalyst helps to prevent use of hazardous chemicals as catalyst for this reaction. Use of easily available waste eggshells from renewable source as precursor of CES reduces cost of the process. The reaction is conducted using water as green

solvent, which highlights the method as green method for Knoevenagel condensation.

#### 4. Conclusion

The highly efficient green method is reported for the Knoevenagel condensation using CES as a natural catalyst resulting in good yields. Use of CES obtained from renewable natural source, mild reaction conditions, simple workup without involvement of any hazardous material quantify this method as an environmentally benign approach for Knoevenagel condensation. This work adds new catalyst in organic transformations and CES has been proved to be a potential alternative to soluble bases.

#### References

1. Jones G 1967 *Organic reactions* (New York: Wiley) vol. 15, p. 204
2. Reddy B M, Patil M K, Rao K N and Reddy G K 2006 *J. Mol. Catal. A: Chem.* **258** 302
3. Ware M, Madje B, Pokalwar R, Kakade G and Shingare M 2007 *Bull. Catal. Soc. India* **6** 104
4. Gupta R, Gupta M, Paul S and Gupta R 2009 *Bull. Korean Chem. Soc.* **30(10)** 2419
5. Han J, Xu Y, Su Y, She X and Pan X 2008 *Catal. Commun.* **9** 2077
6. Wen X 2006 *Indian J. Chem. Sect. B* **45b** 762
7. Li J P, Qiu J K, Li H J and Zhang G S 2011 *J. Chin. Chem. Soc.* **58** 268
8. Gawande M B and Jayaram R V 2006 *Catal. Commun.* **7(12)** 931

9. Hein R W, Astle M J and Shelton J R 1961 *J. Org. Chem.* **26(12)** 4874
10. Liu Q, Ai H and Li Z 2011 *Ultrason. Sonochem.* **18(2)** 477
11. Hangarge R V, Sonwane S A, Jarikote D V and Shingare M S 2001 *Green Chem.* **3** 310
12. Narsaiaha A V and Nagaiah K 2003 *Synth. Commun.* **33** 3825
13. Rao P S and Ratnam R V 1991 *Tetrahedron Lett.* **32** 5821
14. Ren Y M and Cai C 2007 *Synth. Commun.* **37** 2209
15. Attanasi O, Fillippone P and Mei A 1983 *Synth. Commun.* **13** 1203
16. Kwon P S, Kim Y M, Kang C J, Kwon T W, Chung S K and Chang Y T 1997 *Synth. Commun.* **27** 4091
17. (a) Cardillo G, Fabbri S, Gentilucci L, Gianotti M and Tolomelli A 2003 *Synth. Commun.* **33** 1587; (b) Acker D S and Hertler W R 1962 *J. Am. Chem. Soc.* **84** 3370
18. Narsaiah A V, Basak A K, Visali B and Nagaiah K 2004 *Synth. Commun.* **34** 2893
19. Moison H, Texier-Boullet F and Foucaud A 1987 *Tetrahedron* **43** 537
20. Aguado S, Canivet J, Schuurman Y and Farrusseng D 2011 *J. Catal.* **284** 207
21. Tsai W T, Yang J M, Lai C W, Cheng Y H, Lin C C and Yeh C W 2006 *Bioresour. Technol.* **97** 488
22. Pongtonglor P, Hoonnivathana E, Limsuwan P, Limsuwan S and Naemchanthara K 2011 *J. Appl. Sci.* **11(21)** 3659
23. Rajendran A and Mansiya C 2011 *Br. J. Environ. Climate Change* **1(2)** 44
24. Wei Z, Xu C and Li B 2009 *Bioresour. Technol.* **100(11)** 2883
25. Montilla A, Castillo M D D, Sanz M L and Olano A 2005 *Food Chem.* **90(4)** 883
26. Rovensky J, Stancíková M, Masaryk P, Svík K and Istok R 2003 *Int. J. Clin. Pharmacol. Res.* **23(2-3)** 83
27. Deshmukh M B, Patil S S, Jadhav S D and Pawar P B 2012 *Synth. Commun.* **42** 1177
28. Zhuo C, Xian D, Wei W J and Hui X 2011 *International Scholarly Research Network ISRN Organic Chemistry*, Vol. Article Id 676789, 5 Pages
29. Gupta R, Gupta M, Paul S and Gupta R 2009 *Bull. Korean Chem. Soc.* **30(10)** 2419
30. Wang Q L, Ma Y D and Zuo B J 1997 *Synth. Commun.* **27** 4107
31. Cabello J A, Campelo J M, Garcia A, Luna D and Marianis J M 1984 *J. Org. Chem.* **49** 5195
32. Wang S, Ren Z, Cao W and Tong W 2001 *Synth. Commun.* **31(5)** 673
33. Rong L, Li X, Wang H, Shi D, Tu S and Zhuang Q 2006 *Synth. Commun.* **36** 2407
34. Balalaie S and Nemati N 2000 *Synth. Commun.* **30** 869
35. Abaee M S, Mojtahedi M M, Zahedi M M and Khanalizadeh G 2006 *Arkivoc* **15** 48
36. Cao Y Q, Dai Z, Zhang R and Chen B H 2004 *Synth. Commun.* **34(16)** 2965
37. El-Rahman N M A, El-Kateb A A and Mady M F 2007 *Synth. Commun.* **37** 3961