An Efficient Synthesis of Bis (Indolyl) Methanes Under Solvent Free Condition Using Silica Supported Polyphosphoric Acid (PPA-SiO_2) as Recyclable Catalyst

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Abstract

Silica supported poly-phosphoric acid (PPA-SiO_2) has been utilized as an efficient and an environmentally friendly heterogeneous, reusable catalyst for the synthesis of bis(indolyl)methanes under solvent free condition. The significances of this protocol are mild reaction condition, excellent yield and simple work up procedure.

Keywords: Bis (indolyl) Methanes, Polyphosphoric Acid, Silica, Solvent Free, Recyclable Catalyst

1. Introduction

Indoles and their derivatives have been widely present in bioactive metabolites of both terrestrial and marine origin. The importance of indoles and its derivatives are well recognized by synthetic as well as biological chemists[1]. It has been identified in over 3000 natural isolates and known to possess broad spectrum of biological and pharmaceutical activities[2–3]. Particularly bis(indolyl)methanes are known to enhance estrogen metabolism in humans and is likely to be drug of choice for breast cancer preventive and antibacterial agent. Because of these interesting biological activities and other uses, development of protocols for the synthesis of bis(indolyl)methanes is of current interest. The electrophilic substitution reaction of indoles with carbonyl compounds to produce bis(indolyl) alkane is an acid catalyzed reaction, and both protic (e.g., HCl, H_2SO_4) [4,5] as well as Lewis acids like $AlCl_3$, BF_3.Et_2O [6–7] are known to promote this reaction. A variety of reagents such as acetic acid [8], sulphamic acid [9], $InCl_3$ [10], $ZrCl_4$ [11], $In(OTf)_3$ [11], $Ln(OT)_3$ [12], InF_3.H_2O [13], $LiClO_4$ [14], $FeCl_3$[15], I_2[16–17], NBS [18], $KHSO_4$ [19], $Zn(HSO_4)_3$ [20], PPh_3•$HClO_4$ (TPP)[21], H_2NSO_3H[22], zeolites [23,24], clay [25,26], CAN [27], Amberlyst-15 [28], $ZrOCl_2$.$8H_2O$ [29], SSA [30], Boric acid [31], trichloro-1,3,5-triazine[32], sodium dodecyl sulfate (SDS)[33], PEG supported sulfonic acid[34] etc. have been employed to accomplish this transformation. Generally, traditional Lewis acids catalysts are moisture sensitive and are easily decomposed or deactivated in presence of water while in some cases [35,36] more amounts of Lewis acids are required because these can be trapped by nitrogen containing reactants. Although numerous methods have been employed for the preparation of bis(indolyl)methanes, but there are still some drawbacks in these catalytic systems, such as the requirement for a large quantity of catalyst, long reaction times, poor yield of products, drastic conditions for catalyst preparation, or tedious workup that leads to the generation of large amounts of toxic waste.

Recently, several reports have been published on the use of solid acids such as $HClO_4$–SiO_2 [37], $ZrOCl_2$–SiO_2 [38], H_2SO_4–SiO_2 [39, 40], $NaHSO_4$–SiO_2 [41], as catalyst for the synthesis of bis(indolyl)methanes. The high catalytic activity, low toxicity, moisture, air tolerance, ease of handling, their recyclability and particularly low price make the use of solid supported reagents attractive alternatives to conventional Lewis acids [42]. Although the catalytic applications of solid supported reagents for organic synthesis have been well established, there is no report on the use of silica supported polyphosphoric acid (PPA-SiO_2) for the synthesis of bis(indolyl)methanes. In particular, performing a reaction under heterogeneous condition is more promising as it involves the facile recovery and reuse of the catalyst.

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In continuation of our work in synthesis of heterocyclic compounds [43-45], herein we wish to report silica supported poly-phosphoric acid (PPA-SiO_2) as reusable catalyst, Figure 1, represents the synthetic protocol.

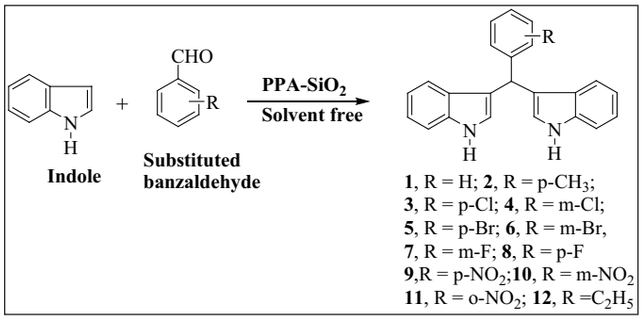

Fig. 1: Synthesis of Bis(Indolyl)Methanes Using Silica Supported Poly-Phosphoric Acid (PPA-SiO_2) as Reusable Catalyst

2. Experimental

Indole, carbonyl compounds, poly-phosphoric acid were purchased from Aldrich and Merck. All the chemicals were of analytical grade. Thin layer chromatography (Merck Kiesel 60 F254, 0.2 mm thickness) was used to monitor the progress of the reactions. The ^{1}H NMR and ^{13}C NMR spectrum were recorded on Jeol ECX spectrospin instrument at 400 and 100 MHz, respectively using TMS as internal standard. The chemical shift values have been expressed on δ scale and the coupling constant (J) in Hz. FT-IR of all the synthesized bis(indolyl)methanes were recorded on a spectrometer Perkin Elmer Spectrum BX II from range 4000-400 cm^{-1} by making sample pallets with KBr. The melting points of synthesized compounds were determined on a Thomas Hoover Unimelt capillary melting point apparatus.

2.1. Preparation of the Catalyst (PPA-SiO_2)

PPA (2.1 g) was added to a suspension of silica gel SiO_2 (400 mesh, 4.9 g) in chloroform (100 mL). The mixture was stirred at 50 °C for 1h and then concentrated in rotary evaporator. The residue dried under vacuum at 100 °C for 3hrs to afford PPA-SiO_2 as a free flowing powder.

2.2. General Procedure for Condensation of Indole with Benzaldehyde in the Presence of PPA-SiO_2

To a mixture of indole (0.002 mol) and benzaldehyde (0.001 mol), PPA-SiO_2 (5 mol%) was added. The resulting mixture was stirred at 70 °C for 10 minutes. After completion of the reaction, as indicated by TLC, the reaction mixture has been diluted with chloroform (10 mL) and the catalyst was allowed to settle. The chloroform layer was decanted off and the catalyst washed with chloroform (5 mL) and the combined chloroform layers were concentrated under reduced pressure to afford almost pure product, which was further purified by recrystallization from petroleum ether.

2.3. Spectroscopic Data of the Synthesized Compounds

3,3'-Bis(indolyl)-phenylmethane (1): IR(KBr, cm^{-1}): 3397, 3051, 1457, 1335, 1217, 1092, 1008, 745; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.87 (s, 1H), 6.64(s, 2H), 6.96-7.00 (t, 2H, J=8.05 Hz), 7.14-7.20(m, 2H,), 7.25-7.27 (m, 4H),7.32-7.38(m, 5H), 7.90 (br, 2H, NH).13C NMR ($CDCl_3$, 100 MHz):40.15, 110.97, 119.28, 119.97, 121.85, 123.56, 126.10, 127.19,

128.15, 128.68, 136.22, 144.25.

3,3'-Bis(indolyl)-3-flurophenylmethane (2): IR(KBr, cm^{-1}): 3402, 3051, 1606, 1459, 1338, 1220, 1095, 1011, 745; ^{1}H NMR (CDCl3, 400 MHz) δ: 5.82 (s, 1H), 6.61-6.63 (m, 2H), 6.97 (t, 2H, J=8.05 Hz), 7.03 (t, 2H, J=8.05 Hz),

7.14-7.18 (m, 3H),7.26-7.29 (m, 2H), 7.31-7.35 (m, 4H), 7.82 (br, 2H, NH);^{13}C NMR ($CDCl_3$, 100 MHz): 39.41, 102.54, 111.15, 114.88, 119.29, 119.81, 122.06, 123.53, 124.82, 129.91, 130.16, 131.45, 135.89, 136.64, 139.56, 143.56.

3,3'-Bis(indolyl)-4-flurophenylmethane (3): IR(KBr, cm^{-1}): 3404, 3053, 1601, 1455, 1335, 1215, 1092, 1009, 741;

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.86 (s, 1H), 6.61- 6.62 (m, 2H), 6.92 (t, 2H, J=8.05 Hz), 6.99 (t, 2H, J=8.05 Hz), 7.14-

7.19 (m, 2H),7.26-7.29 (m, 2H), 7.33-7.37 (m, 4H), 7.80 (br, 2H, NH);^{13}C NMR ($CDCl_3$ 100 MHz): 39.42, 102.59, 111.05, 114.82, 119.27, 119.82, 122.00, 123.51, 129.99, 136.65, 139.64, 143.84.

3,3'-Bis(indolyl)-3-chlorophenylmethane (4): IR(KBr, cm^{-1}):3406, 3020, 2927, 1687, 1582, 1419 1215, 1194,

1093, 741;^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.86 (s, 1H), 6.65(s, 2H), 7.01 (t, 2H, J=8.05 Hz), 7.16-7.19 (m 3H), 7.20-7.22 (m, 2H,) 7.34 (d, 2H, J=7.32 Hz), 7.37(d, 2H, J=7.32 Hz), 7.92 (br, 2H, NH).^{13}C NMR (CDCl3, 100 MHz): 39.92, 110.63, 114.49, 118.88, 119.27, 119.87, 120.12, 122.90, 123.71, 124.32, 126.83, 130.57, 131.64, 133.61, 136.61, 146.14.

3,3'-Bis(indolyl)-4-chlorophenylmethane (5): IR(KBr, cm^{-1}): 3404, 3052, 1594, 1455, 1215, 1089, 1011, 742.^{1}H NMR (CDCl3, 400 MHz) δ: 5.87 (s, 1H), 6.66 (s, 2H), 7.02 (t, 2H, J=8.05 Hz), 7.15(t, 2H, J= 8.05 Hz), 7.22-7.24 (m, 2H), 7.26-7.29 (m, 2H), 7.34(d, 2H, J=7.32 Hz), 7.36 (d, 2H, J=7.32 Hz), 7.92 (br, 2H, NH).^{13}C NMR ($CDCl_3$, 100 MHz): 39.58, 102.59, 110.98, 111.08, 119.15, 119.32, 119.79, 122.05, 123.56, 126.84, 128.33, 130.04, 131.75, 136.64, 142.52.

3,3'-Bis(indolyl)-3-bromophenylmethane (6): IR(KBr, cm^{-1}): 3407, 3052, 1585, 1455, 1336, 1214, 1091, 1009, 741; ^{1}H NMR (CDCl3, 400 MHz) δ: 5.84 (s, 1H), 6.61-6.62 (br, 2H), 7.01 (t, 2H, J=8.05 Hz), 7.12 (t, 2H, J=8.05 Hz), 7.17 (d, 2H, J=7.32 Hz),7.26 (d, 1H, J=7.32 Hz), 7.32-7.37 (m, 4H), 7.48-7.49 (m, 1H), 7.89 (br, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz): 39.90, 111.08, 118.89, 119.35, 119.71, 119.92, 122.36, 123.63, 124.34, 126.81, 127.34, 129.33, 129.80, 131.66, 136.62, 146.44.

3,3'-Bis(indolyl)-4-bromophenylmethane (7): IR(KBr, cm^{-1}): 3408, 3055, 1490, 1455, 1335, 1216, 1092, 1009, 743; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.87 (s, 1H), 6.63-6.64 (br, 2H), 6.98 (t, 2H, J=8.05 Hz), 7.15 (t, 2H, J=8.05 Hz), 7.19 (d, 1H, J=7.32 Hz),7.27 (d, 1H, J=7.32 Hz), 7.33 (d, 4H, J=7.32 Hz), 7.37(d, 2H, J=7.32 Hz), 7.88 (br, 2H, NH); ^{13}C NMR ($CDCl_3$ 100 MHz): 40.01, 110.99, 119.19, 119.67, 119.90, 121.88, 123.57, 126.10, 127.03, 128.18, 128.68, 136.63, 143.95.

3,3'-Bis(indolyl)-2-nitrophenylmethane (8): IR (KBr, cm^{-1}): 3403, 3058, 1620, 1531, 1457, 1420, 1222, 1082, 1001, 746, 690. ^{1}H NMR (CDCl3, 400 MHz) δ: 5.94 (s, 1H), 6.61 (s, 2H), 7.02 (t, 2H, J = 8.05 Hz), 7.22 (t, 2H, J = 8.05), 7.41 (t, 4H, J =8.05 Hz) 7.43 (t, 1H, J = 8.05 Hz), 7.68 (d, 1H, J =7.32 Hz), 7.99 (br, 2H, NH), 8.04 (d, 1H, J= 7.32 Hz), 8.23 (s, 1H).^{13}C NMR ($CDCl_3$ 100 MHz): 39.17, 110.23, 111.25, 118.29, 119.67, 119.78, 121.49, 122.18, 123.67, 123.89, 124.14, 126.89, 129.18, 134.57, 136.78, 137.98, 146.79.

3,3'-Bis(indolyl)-3-nitrophenylmethane (9): IR (KBr, cm^{-1}): 3404, 3052, 1616, 1521, 1453, 1415, 1218, 1092, 1006, 741, 692. ^{1}H NMR (CDCl3, 400 MHz) δ: 5.93 (s, 1H), 6.61 (s, 2H), 7.05 (t, 2H, J = 8.05 Hz), 7.14 (t, 2H, J = 8.05 Hz), 7.31 (t, 4H, J = 8.05 Hz) 7.40 (t, 1H, J = 8.05 Hz), 7.60 (d, 1H, J =7.32 Hz), 7.91 (br, 2H, NH), 8.04 (d, 1H, J = 7.32 Hz), 8.15 (s, 1H).^{13}C NMR ($CDCl_3$ 100 MHz): 39.47, 111.11, 118.21, 119.56, 119.89, 121.22, 122.59, 123.60, 123.68, 124.71, 126.84, 129.34, 130.98, 134.93, 136.71, 146.33.

3,3'-Bis(indolyl)-4-nitrophenylmethane (10): IR(KBr, cm^{-1}): 3404, 3052, 1521, 1346, 1212, 1093, 742; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 5.97 (s, 1H), 6.66-6.68(m, 2H), 6.98-7.02 (t, 2H, J=8.05 Hz), 7.16-7.20 (m, 2H), 7.30-7.38 (m, 4H), 7.42-7.49 (m, 2H), 7.99 (br, 2H, NH), 8.10-8.13 (m, 2H);^{13}C NMR ($CDCl_3$ 100 MHz): 39.88, 111.25, 117.44, 119.58, 119.68, 122.35, 123.64, 126.66, 129.57, 136.55, 146.44.

3,3'-Bis(indolyl)-4-methylphenylmethane (11): IR(KBr, cm^{-1}): 3413, 3044, 1457, 1339, 1213, 1092, 1008, 738; 1H NMR (CDCl3, 400 MHz) δ: 2.32 (s, 3H), 5.84 (s, 1H), 6.62-6.63 (s, 2H), 6.98 (t, 2H, J=8.05 Hz), 7.08 (d, 2H, J=7.32

Hz), 7.16(t, 2H, J=8.05 Hz), 7.22 (d, 2H, J=7.32 Hz), 7.33(d, 2H, J=7.32 Hz), 7.40 (d, 2H, J=7.32 Hz), 7.84 (br, 2H, NH);^{13}C NMR ($CDCl_3$ 100 MHz): 21.05, 39.71, 110.98, 119.13, 119.81, 119.91, 121.82, 123.51, 127.04, 128.52, 128.87, 135.45, 136.61, 140.93.

3,3'-Bis(indolyl)-4-ethylphenylmethane (12): IR(KBr, cm^{-1}): 3404, 3051, 1480, 1453, 1211, 1095, 1010, 740; ^{1}H

NMR (CDCl3, 400 MHz) δ: 1.30 (t, 3H), 2.39 (q, 2H), 5.82 (s, 1H), 6.61 (s, 2H), 7.01 (t, 2H, J=8.05 Hz), 7.09 (d, 2H, J=7.32 Hz), 7.17 (t, 2H, J=8.05 Hz), 7.24 (d, 2H, J=7.32 Hz), 7.36 (d, 2H, J=7.32 Hz), 7.40 (d, 2H, J=7.32 Hz), 7.81 (br,

2H, NH);^{13}C NMR (CDCl3 100 MHz): 16.11, 26.05, 39.70, 110.92, 119.15, 119.84, 119.95, 121.86, 123.54, 127.08, 128.54, 128.88, 135.46, 136.66, 140.97.

3. Results and Discussion

Effect of solvent, such as $CHCl_3$, MeOH, DMF and THF, was evaluated for the model reaction between indole and benzaldehyde as shown in Table 1. The desired product was obtained in 40-60% yields after the prolonged reaction time 60-90 minutes, whereas solvent free condition afforded the product in excellent 94% yield within very short time 10 minutes.

Table 1. Effect of Various Solvents for Synthesis of Bis (Indolyl) Methanes

Entry	*Solvent*	*Time(mins)*	*Yield(%)*
1	$CHCl_3$	60	50
2	MeOH	65	45
3	DMF	80	52
4	THF	40	60
5	H_2O	90	40
6	Neat	10	94

The FESEM image of pure Silicon dioxide and silica supported polyphosphoric acid depicts the surface morphology of silica before and after immobilizing polyphosphoric acid. It can be observe that surface of silica becomes more rough as compare to bare silica which is the contributing factor in enhancement of the surface area for catalyzing our reaction.

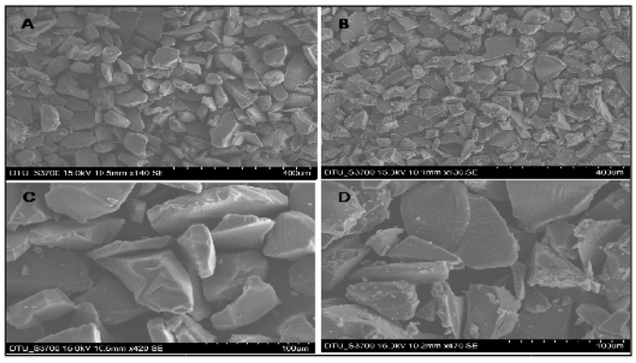

Fig. 2: FESEM Image of Pure Silicon Dioxide (A and C) and Silica Supported Polyphosphoric Acid (B and D).

Appropriate concentration of the catalyst PPA-SiO_2, were investigated using the model reaction at different concentrations of catalyst like 1, 2, 5 and 10 mol %. The product formed in 75, 88, 94 and 94% yield respectively, as shown in Table 2. After considering the reaction time and yield of product we opt for 5 mol % of PPA-SiO_2 as the optimum amount of the catalyst to obtain best result.

Table 2. Effect of the Amount of Catalyst for Synthesis of Bis (Indolyl) Methanes for 10 Minutes

Entry	*Catalyst mol (%)*	*Time(mins)*	*Yield(%)*
1	1	10	75
2	2	10	88
3	5	10	94
4	10	10	94
5	20	10	93

Further, we have also screened a variety of aromatic aldehydes with indoles to obtain the corresponding products. The results are summarized in Table 3. It has been observed that substituents in the aromatic ring of aldehydes have an effect on the rate of the reaction. Aromatic aldehydes with electron-withdrawing groups reacted faster than those with electron-donating groups.

Table 3. Silica Supported Poly-Phosphoric Acid (PPA-SiO_2) Synthesis of Bis (Indolyl) Methane Derivatives

Entry	*R*	*Time (mins)*	*Yield (%)*	*Mp (°C)*	
				Found	*Lit.*
1	H	10	94	123-125	125-126
2	4-CH_3	12	86	97-99	95-97
3	4-Cl	15	91	76-77	77-81
4	3-Cl	18	89	80-82	78-80
5	4-Br	15	92	109-112	110-112
6	3-Br	15	90	113-115	115-117
7	3-F	14	88	80-82	82-83
8	4-F	12	90	79-80	80-82
9	4-NO_2	20	96	217-221	220-221
10	3-NO_2	20	94	220-222	218-220
11	2-NO_2	25	89	140-142	140-141
12	4-C_2H_5	30	82	178-181	179-181

The recovered catalyst was activated by heating at 70°C under vacuum for 1 h. and reused for the synthesis of bis(indolyl)methane from fresh benzaldehyde (1 mmol) and indole (2 mmol). The recovered catalyst, after activation, was reused for synthesis of bis(indolyl)

methane from fresh benzaldehyde (1 mmol) and indole (2 mmol) affording 92%, 89%, 85% and 81% yields, respectively, in 15, 25, 40 and 60 minutes. These results are summarized in Figure 3.

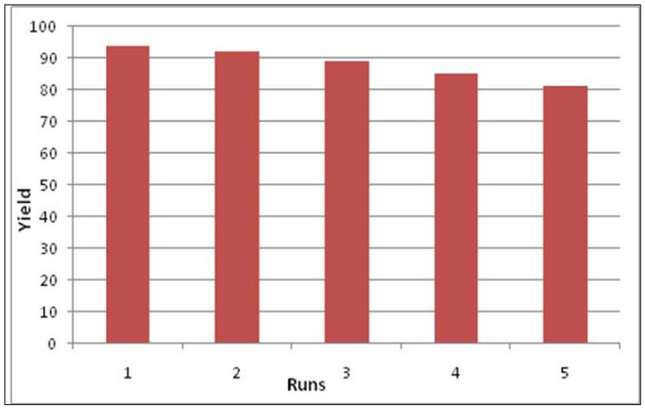

Fig. 3: Results Showing Recyclability of the Catalyst

4. Conclusions

In conclusion, we have developed a simple, novel and efficient synthetic protocol for the synthesis of bis(indolyl)methanes using silica supported poly-phosphoric acid (PPA-SiO_2) as catalyst under solvent free conditions at room temperature. This procedure offers several advantages such as easy catalyst separation from the reaction medium, a simple workup procedure, catalyst reusability, short reaction time, and good to excellent product yields. In addition, the use of environmentally benign catalysts and avoidance of hazardous organic solvents are important features of this method.

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References

1. Sundberg, R. J. (1996). *The Chemistry of Indoles.* Academic press: New York.
2. Bell, R., Carmeli, S., and Sar, N. (1994). *Journal of Natural Products*, 57, 1587.
3. Fukuyama, T., and Chen, X. (1994). *Journal of the American Chemical Society,* 116, 3125-3126.
4. Gregorovich, B. V., Liang, K., Clugston, M., and Macdonald, S. (1968). *Can J Chem*., 46, 3291.
5. Roomi, M., and MacDonald, S. (1970). *Can. J. Chem*., 48, 139.
6. Yadav, J. S., Reddy, B. V. S., and Sunitha, S. (2003). *Adv. Synth. Catal*., 345, 349.
7. Banerji, J., Chatterji, A., Manna, S., Pascard, C., Prange, T., and Shoolery, J. (1981). *Heterocycles,* 15, 325.
8. Kamal, A., and Qureshi, A. A. (1963). *Tetrahedron*, 19, 513.
9. Li, W. J., Lin, X. F., Wang, J., Li, G. L., and Wang, Y. G. (2005). *Synth. Commun*., 35, 2765.
10. Babu, G., and Sridhar, N., and *Perumal, P. T.* (2000). *Synth. Commun,* 30, 1609.
11. Nagawade, R. R., and Shinde, D. B. (2005). *Bull. Korean Chem. Soc*., 26, 1962.
12. Chen, D., Yu, L., and Wang, P. G. (1996). *Tetrahedron Letters,* 37, 4467.
13. Bandgar, B. P., and Shaikh, K. A. (2004). *J Chem Res*., 34.
14. Yadav, J. S., Reddy, B. V. S., Murthy, V. S. R., Kumar, G. M., and Madan, C. (2001). *Synthesis*, 5, 783.
15. Xia, M., Wang, S. B., and Yuan, W. B. (2004). *Synth. Commun*., 34, 3175.
16. Bandgar, B. P., and Shaikh, K. A. (2003). *Tetrahedron Letters,* 44, 1959.
17. Ji, S. J., Wang, S. Y., Zhang, Y., and Loh, T. P. (2004). *Tetrahedron*, 60, 2051.
18. Koshima, H., and Matsuaka, W. J. (2002). *Heterocyclic Chem*., 39, 1089.
19. Nagarajan, R., and Perumal, P. T. (2004), *Chemistry Letters*, 33, 288.
20. Niknam, K., Zolfigol, M. A., Sadabadi, T., and Nejati, A. (2006). *J. Iranian Chem. Soc*., 3, 318.
21. Nagarajan, R., and Perumal, P. T. (2002). *Synth. Commun*., 32, 105.
22. Li, J. T., Dai, H. G., Xu, W. Z., and Li, T. S. (2006), *Ultrasonics Sonochem*., 13, 24.
23. Karthik, M., Tripathi, A. K., Gupta, N. M., Palanichamy, M., and Murugesan, V. (2004). *Catalysis Communication,* 5, 371.

24. Reddy, A. V., Ravinder, R., Reddy, V. L. N., Goud, T. V., Ravikanth, V., and Venkateseswarlu, Y. (2003). *Synthetic Communication,* 33, 3687.
25. Chakrabarty, M., Gosh, N., Basak, R., and Harigaya, Y. (2002). *Tetrahedron Letters,* 43, 4075.
26. Penieres-Carrillo, G., Garcia-Estrada, J. G., Gutierrez-Ramirez, J. L., Alvarez-Toledano, C., (2003). *Green Chem*., 5, 337.
27. Zeng, X. F., Ji, S. J., and Wang, S. Y. (2005). *Tetrahedron*, 61, 10235.
28. Chimmani, R., Banerjee, J., Pal, R., and Das, B. (2003). *Adv Synth Catal.,* 345, 557.
29. Firouzabadi, H., Iranpoor, N., Jafarpoor, M., and Ghaderi, A. (2006). *J Mol Catal A: Chem.*, 253, 249.
30. Pore, D. M., Desai, U. V., Thopate, T. S., and Wadgaonkar, P. P. (2006). *Arkivoc.,* 12, 75.
31. Yadav, J. S., Gupta, M. K., Nagendra, R. J., Yadav, N., and Reddy, B. V. S. (2010). *Monatsh. Chem.*, 141, 1001.
32. Sharma, G. V. M., Reddy, J. J., Lakshmi, P. S., and Krishna, P. R. A. (2004). *Tetrahedron Letters,* 45, 7729.
33. Deb, M. L., and Bhuyan, P. J. (2005). *Tetrahedron Letters,* 47, 1441.
34. Shou, R. S., Qiu-Ying, W., Yan, D., Xiao-Ling, L., and Ming-Zhong, C. (2009). *Catal. Lett*., 128, 418.
35. He, X., Hu, S., Liu, K., Guo, Y., Xu, J., and Shao, S. (2006). *Org. Lett*., 8, 333.
36. Fahy, E., Potts, B. C. M., Faulkner, D. J., and Smith, K. (1991). *J Nat Prod*., 54, 564.
37. Kamble, V. T., Kadam, K. R., Joshi, N. S., and Muley, D. B. (2007). *Catal. Commun.*, 8, 498.
38. Zolfigol, M. A., Salehi, P., Shiri, M., Sayadi, A., Abdoli, A., Keypour, H., Rezaeivala, M., Niknam, K., and Kolvari, E. (2008). *Mol Divers,* 12, 203.
39. Ramesh, C., Banerjee, J., Pala, R., and Das, B. (2003), *Adv. Synth. Catal*., 345, 557.
40. Salehi, P., Dabiri, M., Zolfigol, M., and Fard, M. B. A. (2003). *Tetrahedron Letters,* 44, 2889.
41. Shimizu, K., Hayashi, E., Hatamachi, T., Kodama, T., and Kitayama, Y. (2004). *Tetrahedron Lett*ers, 45, 5135.
42. Hajipour, A. R., Abidi, H., and Ruoho, A. E. (2003). *Journal of Organic Chemistry,* 68, 4553.
43. Kirti, S., and Masram, D. T. (2013). *J Advances Chem*., 1, 575.
44. Kirti, S., and Masram, D. T. (2013). Chemistry and *Biology Interface*, 6, 375.
45. Kirti, S., Masram, D. T., and Singh, R. (2013). *Organic Chemistry*: *An Indian Journal*., 10, 56.