Synthesis, characterization, and catalytic application of PbS nanoparticles for the synthesis of amidoalkyl naphthols under solvent-free conditions

Ashok V. Borhade · Bhagwat K. Uphade · Dipak R. Tope

Abstract A simple one-pot synthesis has been developed for the synthesis of amidoalkyl naphthols using an efficient and recyclable nanocrystalline PbS catalyst under solvent-free condition. Using this nanocrystalline solid catalyst, the reactions could be carried out under mild reaction conditions with very good yield (85–95 %). This catalyst could be recycled very easily, which makes this methodology environmentally benign. The biologically active drug-like molecule 1-aminomethyl-2-naphthol derivatives can be easily obtained from 1-amidomethyl-2-naphthol by amide hydrolysis reaction in the presence of PbS nanoparticles. Characterization of the catalyst was performed by X-ray diffraction, transmission electron microscopy, and adsorption/desorption analysis (BET).

Keywords Lead sulfide nanoparticles · Amidoalkyl naphthols · Multicomponent reaction · Recyclable catalyst

Introduction

The multicomponent coupling reactions are emerging as useful sources for accessing small drug-like molecules with several levels of structural diversity. The multicomponent reaction has attracted the great attention of research groups working in medicinal chemistry, drug discovery, and material science. In organic synthesis, heterogeneous catalysts have much more importance due to economic and environmental considerations [1]. Multicomponent reactions are used to produce the target products in a single operation which reduce reaction times and energy [2]. The solvent-free reactions have attracted attention due to environmental problems

A. V. Borhade (✉) · B. K. Uphade · D. R. Tope
Research Centre, Department of Chemistry, HPT Arts and RYK Science College,
Nasik 422005, India
e-mail: ashokborhade2007@yahoo.co.in

[3]. The biologically active 1-amino methyl-2-naphthol derivatives can be obtained from 1-amido methyl-2-naphthols by amide hydrolysis reaction, which have activities like hypotensive and brady cardiac effects [4–6]. This 1-aminoalkyl alcohol type ligand is used as a catalyst and in asymmetric synthesis [7, 8]. 1, 3-oxazine derivatives can be obtained from 1-Amidoalkyl-2-naphthol which has different biological activities [9–11].

1-amidoalkyl-2-naphthol can be prepared by condensation of aryl aldehydes, 2-naphthol, and amide in the presence of silica sulfuric acid [12], $FeCl_3 \bullet SiO_2$ [13], $NaHSO_4 \bullet H_2O$ [14], $HClO_4$–SiO_2 [15, 16], P_2O_5 [17], ionic liquid [18], thiamine hydrochloride [19], Yb (OTf)$_3$ [20], $NaHSO_4 \bullet SiO_2$ [21], $InCl_3$ [22], zwitterionic-type molten salt [23], TBBDA [24], silica gel-supported dual acidic ionic liquid [25], $H_4SiW_{12}O_{40}$ [26], copper p-toluenesulfonate [27], PEG-based dicationic acidic ionic liquids [28], hexanesulfonic acid sodium salt [29], Zeolite H-BEA [30], $KHSO_4$ [31], nano-sulfated zirconia [32], Al (HSO$_4$)$_3$ [33], silica gel-supported-SO_3H functionalized benzimidazolium-based ionic liquid [34], $ZrOCl_2.8H_2O$ [35], and phosphoric acid supported on alumina [36]. However, many of these methods suffer from the drawbacks of green chemistry [37, 38], long reaction times, low yields, expensive and poorly available catalysts, and harsh conditions which limit their use. Therefore, the eco-friendly, heterogeneous, clean process and green catalysts which can be recycled are under permanent attention.

Nowdays, transition metal nanoparticles are used as efficient catalysts for synthetic organic transformations due to their high surface area to volume ratio and co-ordination sites which are mainly responsible for their catalytic activity [39, 40]. Metal oxide nanoparticles used as a catalyst and viable alternative to conventional materials in various fields of chemistry have attracted the interest of chemists. Metal oxide nanoparticles are known to be promising material for the rising heterogeneous catalyst in a variety of organic transformations [41]. Nanoparticles have the potential for improving the efficiency, selectivity, and yield of catalytic processes. Therefore, the attempt was made to use PbS as a catalyst in a multicomponent reaction. The demand for a environmentally benign procedure with a heterogeneous and reusable catalyst prompted us to develop a safe alternate method for the synthesis of amidoalkyl naphthols. In view of the importance of PbS nanoparticles as a catalyst in organic synthesis, we report here a simple solvent-free synthesis of 1-amidoalkyl-2-naphthol derivatives via multicomponent reactions in the presence of PbS nanoparticles as a reusable catalyst under solvent-free conditions.

Experimental

All chemicals were purchased from Aldrich Chemical and were used without further purification. X-ray diffraction (XRD) pattern was recorded using Philips-1710 diffractometer with Cu-kα radiation ($\lambda = 1.54$ Å). The surface area was recorded with help of a Quantachrome Autosorb Automated Gas Sorption System. Transmission electron microscopy (TEM) was recorded with SAED using a CM-200 Philips Microscope. Melting points reported were determined by a melting point apparatus with open capillary tubes and are uncorrected. FTIR

spectra of different products were recorded on a Schimadzu 8400 S spectrometer using KBr pellets. ^{1}H NMR spectra were recorded with a Bruker Advance II 400 MHz spectrometer in DMSO-d_6 with TMS as an internal standard. Mass spectra were determined on a Varian–Saturn GS/MS instrument.

Preparation of PbS nanoparticles

PbS nanoparticles were synthesized by a simple precipitation method, in which a solution of analytical grade with high purity was made of $Pb(NO_3)_2$ (lead nitrate), a source of Pb^{++} ions, and Na_2S (sodium sulfide), one mole of each. In this solution, Triton X-100 and sodium hydroxide (0.1 N) was slowly added and solution was stirred for 2 h. The solution was filtered and the nanocrystalline lead sulfide material was dried in an oven at 110 °C. The lead sulfide nanocrystal was further calcinized at 400 °C for 2 h.

Synthesis of amidoalkyl naphthols

A mixture of 2-naphthol (1 mol), aldehyde (1 mol), acetamide (1.2 mol) and PbS nanoparticles was heated at 120 °C in an oil bath for few minutes under solvent-free condition. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to room temperature. The solid residue was dissolved in hot ethanol to separate the PbS catalyst. The recovered catalyst was washed, dried, and reused further in successive reactions. The isolated catalyst can be recycled without considerable loss of its activity. By recrystallization from aqueous ethyl alcohol (15 %), pure products were obtained. The compounds obtained are known and were characterized by comparison of their spectroscopic (IR, ^{1}HNMR and MS) and physical data (mp) with those reported in the literature.

Spectral data of some compounds

N-[Phenyl-(2-hydroxynapthalen-1-yl)-methyl]-acetamide

IR (KBr) υ: 3,406, 3,243, 3,067, 1,642, 1,587, 1,511, 1,374, 1,067, 804, 746, 697 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.04 (*s*, 3H), 7.17-7.21 (*m*, 9H), 7.63 (*d*, *J* = 8.5 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.83 (*s*, 1H) 8.42 (*d*, *J* = 8.5 Hz, 1H), 9.98 (*s*, 1H). MS m/z: 292 (M + H)$^{+}$.

N-[(4-Methoxy-Phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide

IR (KBr) υ: 3,393, 3,065, 2,965, 2,830, 2,782, 2,701, 2,611, 1,622, 1,584, 1,511, 1,434, 1,374, 1,274, 1,175, 1,083, 984, 884, 743 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1·96 (*s*, 3H), 2·52 (*s*, 3H), 5.34 (*s*, 1H), 7·03-7·05 (*m*, 6H), 7·74-7·81 (*m*, 4H), 8·41 (*d*, *J* = 8.6 Hz, 1H), 10 (*s*, 1H). MS m/z: 322 (M + H)$^{+}$.
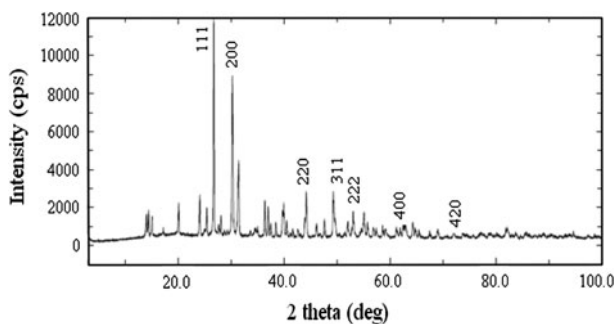
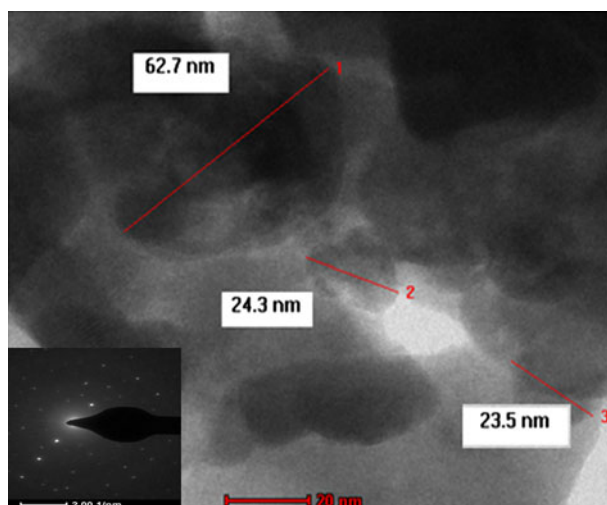**Fig. 1** XRD pattern of PbS nanomaterial

Fig. 2 TEM and SAED of PbS prepared by the precipitation method

N-[(3-Nitro-Phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide

IR (KBr) υ: 3,373, 3,224, 2,921, 1,647, 1,573, 1,438, 1,374, 1,312, 1,201, 1,167, 1,064, 1,039, 1,002, 924, 809, 745, 713 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 2·07 (*s*, 3H), 7·16-7·20 (*m*, 5H), 7·64 (*d, J = 7.8 Hz,* 1H), 7·77-7·79 (*m*, 5H), 8·54 (*d, J = 8.1 Hz,* 1H), 10·11 (*s*, 1H). MS *m/z*: 337 (M + H)$^+$.

N-[(2-Chloro-Phenyl)-(2-hydroxy-napthalen-1-yl)-methyl]-acetamide

IR (KBr) υ: 3,427, 3,062, 1,647, 1,513, 1,438, 1,267, 809, 745, 504 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ 1.92 (*s*, 3H), 7·07-7·54 (*m*, 8H), 7·71 (*d, J = 7.6 Hz,* 1H), 7·77 (*d, J = 6.1 Hz,* 1H), 8·00 (t, *J = 7.0 Hz,* 1H), 8.50 (*s*, 1H), 9.77 (*s*, 1H). MS m/z: 325 (M + H)$^+$.
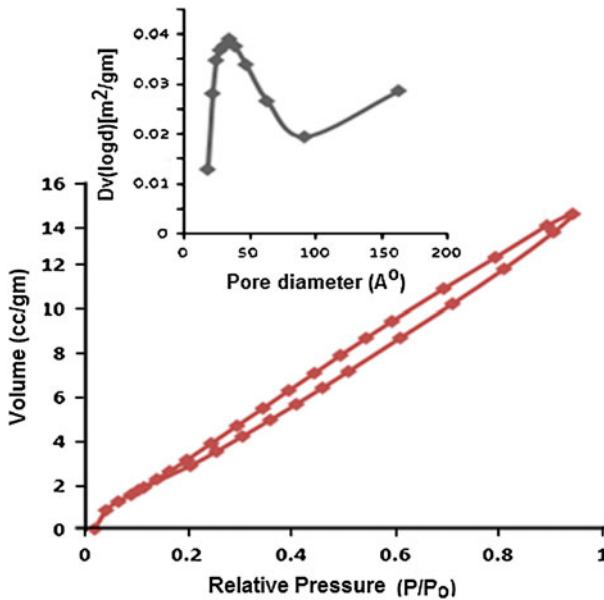
Fig. 3 BET surface area of PbS nanoparticles

Table 1 Optimization of catalyst concentration

| Entry	Amount of catalyst (gm)	Times (min)	Yield[a] (%)
1.	0.020	9	81
2.	0.030	8	89
3.	0.040	6	95
4.	0.050	6	91
5.	0.060	6	88

[a] Isolated yield

Results and discussion

Figure 1 depicts the XRD pattern of PbS prepared by the precipitation method using Triton X-100. Further, there were no additional peaks observed, indicating the phase purity of the PbS. The XRD patterns of the lead sulfide nanoparticles have fundamental peaks due to diffraction of the lead sulfide on the plane 111, 200, 220, 311, 222, 400, and 420, which is in good agreement with the reported values [42]. The XRD pattern of synthesized lead sulfide nanoparticles shows only a single phase system. The crystalline size was calculated from FWHM using Scherrer's formula and was observed to be 31 nm. The XRD pattern is in agreement with the cubic structure of the lead sulfide sample (JCPDS Card No. 78-1057) with a space group Fm3 m (225).

Figure 2 shows TEM and SAED images of PbS synthesized by the precipitation method. The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponds to PbS nanomaterial. TEM reveals the highly crystalline cubic structure of PbS. Triton X-100 acts as a surfactant as well as

Table 2 Preparation of 1-amidoalkyl-2-naphthol under various conditions

Solvent	Time/condition	Yield (%)
CHCl$_3$	24 h/reflux	71
CH$_2$Cl$_2$	24 h/reflux	75
MeOH	24 h/reflux	60
EtOH	24 h/reflux	56
DMF	24 h/reflux	15
1,4-Dioxane	24 h/reflux	65
THF	24 h/reflux	61
Solvent-free	7 min/110 °C	88
Solvent-free	6 min/120 °C	95
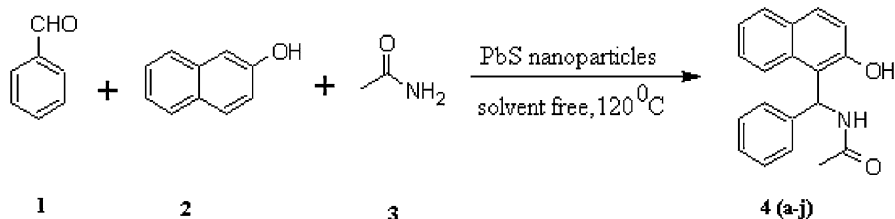
Scheme 1 Synthesis of 1-amidoalkyl-2-naphthol using PbS nanoparticles

a reaction medium which control the crystal growth. The dark spot in the TEM micrograph can be alluded to synthesized PbS nanoparticles as the SAED pattern. Such a spot reveals the occurrence of cubic PbS in total agreement with the XRD data. The average size of the PbS nanocrystallites obtained by TEM was found to be 31 nm.

The N$_2$ adsorption–desorption isotherms and BJH pore size distribution of PbS nanoparticles reveal that the samples have a typical IV curve of the N$_2$ adsorption–desorption isotherm (Fig. 3) with H$_1$ hysteresis, which indicates that the samples have cylindrical mesopores. The BJH pore size distribution demonstrates that all the samples have a narrow pore diameter range. Based on the N$_2$ adsorption–desorption isotherms, the specific surface area (S$_{BET}$) of PbS nanoparticles obtained from the BET method is 15.65 m^2/g, and the average pore volume (V$_P$) and pore diameter (dp) were 0.02649 cc/g and 24.80 Å, respectively (Fig. 3).

Catalytic results

In continuation of our research on the synthesis of heterocyclic molecules using nanoparticles for cyclization and condensation reactions [43, 44], the choice of an appropriate medium is important for successful synthesis. Initially, the three-component reaction of 2-naphthol (1 mol), benzaldehyde (1 mol), acetamide (1.2 mol), and PbS nanoparticles was used as the model reaction to optimize the amount of the catalyst. Generally, the reaction rate and yield increased with the amount of the catalyst. It was found that 0.040 g of catalyst was the appropriate

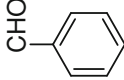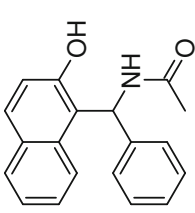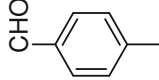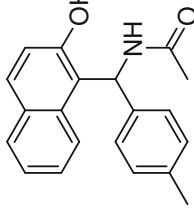**Table 3** Synthesis of amidoalkyl naphthols in the presence of PbS nanoparticles
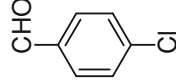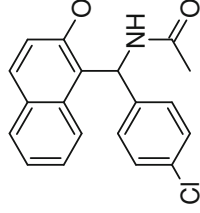
Entry	Aldehydes	Time (min)	Products	Yields[a,b] (%)	M.P (°C) [Lit] Ref
4a	CHO (phenyl)	6	(naphthol amide, phenyl)	95	244 [241–243] [21]
4b	CHO (4-methylphenyl)	8	(naphthol amide, 4-methylphenyl)	90	223 [222–223] [26]
4c	CHO (4-chlorophenyl)	5	(naphthol amide, 4-chlorophenyl)	92	224 [224–227] [21]

Table 3 continued
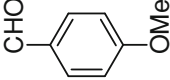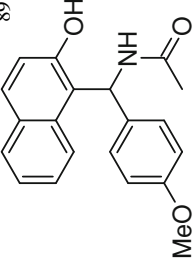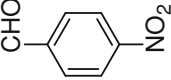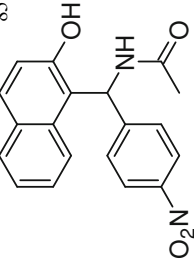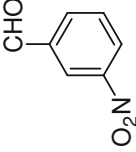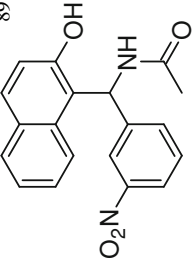
Entry	Aldehydes	Time (min)	Products	Yields[a,b] (%)	M.P (°C)[Lit]Ref
4d	CHO—⟨ ⟩—OMe	8		89	185 [184–186] [21]
4e	CHO—⟨ ⟩—NO$_2$	4		85	249 [248–250] [26]
4f	CHO—⟨ ⟩ (O$_2$N, meta)	5		89	242 [241–242] [26]

Table 3 continued
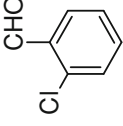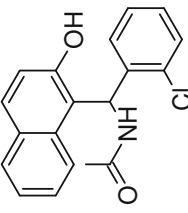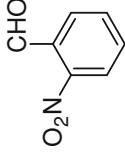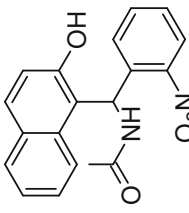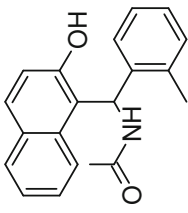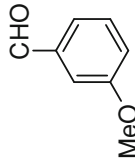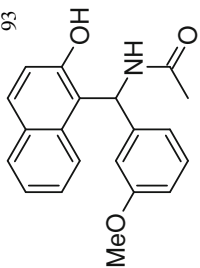
Entry	Aldehydes	Time (min)	Products	Yields[a,b] (%)	M.P (°C)[Lit]Ref
4 g		7		87	214 [213–215] [26]
4 h		9		86	181 [180–182] [21]
4i		9		89	201 [200–202] [13]

Table 3 continued

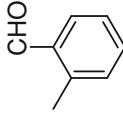| Entry	Aldehydes	Time (min)	Products	Yields[a,b] (%)	M.P (°C)[Lit]Ref
4j		9		93	202 [203–205] [12]

[a] Isolated yield

[b] All the products were characterized by IR, ^{1}H NMR, and MS spectral data and were compared with the reference compounds [15, 16, 26, 30, 35]

Table 4 Reusability of catalyst	Cycles	Yields (%)
	Initial	90
	1	90
	2	90
	3	89
	4	88
	5	86

amount for the reaction (Table 1). Smaller amounts gave a low yield even after a long reaction time, and larger amounts did not cause an obvious increase in the yield of the product. Hence, the optimal amount of catalyst chosen for the subsequent reactions was 0.040 g.

To demonstrate the scope of the solvent-free condition and PbS nanoparticle catalyst, the condensation of 2-naphthol with benzaldehyde and acetamide was examined in the presence of PbS nanoparticles (0.040 g) at 120 °C under solvent-free condition. The corresponding results are displayed in Table 4. As can be seen, the reactions were carried out efficiently within 6 min and the desired products were produced in good to high yields. Thus, PbS nanoparticles are an efficient and recyclable catalyst for the preparation of 1-amidoalkyl-2-naphthols (Table 2).

After optimizing the reaction conditions, a variety of aromatic aldehydes with 2-naphthol and acetamide were employed under reaction conditions to evaluate the scope of this reaction. The results obtained are shown in Scheme 1. The reactions proceeds smoothly and no undesirable side reactions were observed. A series of amidoalkyl naphthol derivatives were prepared by using PbS nanoparticles as a catalyst (Table 3) with an excellent yield (85–95 %). Ortho-substituted aromatic aldehydes decrease the yield of the reaction due to the steric effect, though meta- and para-substituted aromatic aldehydes gave good results. In all the cases, aromatic aldehydes with electron-withdrawing groups or electron-donating groups reacted successfully and gave the products in high yields. It was shown that the aromatic aldehydes with electron-withdrawing groups reacted faster than the aromatic aldehydes with electron-releasing groups.

In order to study the possibility of reusability, the catalyst was centrifuged and filtered after completion of the reaction, washed with ethanol, and then calcined at 200 °C in an oven for 2 h. The reusability of the catalyst was checked for several successive runs under identical reaction conditions. The catalyst was found to be stable and reusable even after five cycles without significant loss in activity (Table 4).

Conclusion

In conclusion, we report for the first time a new application of lead sulfide nanoparticles for the synthesis of amidoalkyl naphthol derivatives, biologically active drug-like molecules using three-component reactions of 2-naphthol,

benzaldehyde, and acetamide. A series of amidoalkyl naphthols were obtained under thermal, solvent-free conditions. We demonstrated a green procedure which offers advantages, such as simple work-up, shorter reaction times, excellent yields, environmentally benign, reusability of catalyst, and cost-effective recovery. The repeated use of the catalyst shows that the catalyst was highly active after successive five runs. Consequently, this one-pot synthesis offers the synthetic utility of the lead sulfide nanoparticles as versatile reagents in organic chemistry.

References

1. V.R.A. Santen, M. Neurock, *Molecular Heterogeneous Catalysis: A Conceptual and Computational Approach* (Wiley-VCH, Weinheim, 2006)
2. A. Domling, I. Ugi, Angew. Chem. Int. Ed. **39**(18), 3168 (2000)
3. A. Corma, H. Garcia, Chem. Rev. **103**, 4307 (2003)
4. A.Y. Shen, C.T. Tsai, C.L. Chen, Eur. J. Med. Chem. **34**, 877 (1999)
5. T. Dinermann, D. Steinhiller, G. Folkers, *Molecular Biology in Medicinal Chemistry* (Wiley-VCH, Weinheim, 2004)
6. A.Y. Shen, C.L. Chen, C.I. Lin, Chin. J. Physiol. **35**, 45 (1992)
7. R. Hulst, H. Heves, N.C.M.W. Peper, R.M. Kellogg, Tetra. Asymm. **7**, 1373 (1996)
8. X. Li, C.H. Yeung, A.S.C. Chan, T.K. Yang, Tetra. Asymm. **10**, 759 (1999)
9. F. Benedini, G. Bertolini, R. Cereda, G. Doná, G. Gromo, S. Levi, J. Mizrahi, A. Sala, J. Med. Chem. **38**, 130 (1995)
10. H. Matsuoka, N. Ohi, M. Mihara, H. Suzuki, K. Miyamoto, N. Maruyama, K. Tsuji, N. Kato, T. Akimoto, Y. Takeda, K. Yano, T. Kuroki, J. Med. Chem. **40**, 105 (1997)
11. H. Ren, S. Grady, D. Gamenara, H. Heinzen, P. Moyna, S. L. Croft, S. L. H Kendrick, V. Yardley, G. Moyna, Bioorg. Med. Chem. Lett. **11**, 1851(2001)
12. G. Srihari, M. Nagaraju, M.M. Murthy, Helv. Chim. Acta **90**, 1497 (2007)
13. H.R. Shaterian, H. Yarahmadi, Tetrahedron Lett. **49**, 1297 (2008)
14. H.R. Shaterian, H. Yarahmadi, M. Ghashang, Tetrahedron Lett. **64**, 1263 (2008)
15. H.R. Shaterian, H. Yarahmadi, Arkivoc **vii**, 105 (2008)
16. G.H. Mahdavinia, M.A. Bigdeli, M.M. Heravi, Chin. Chem. Lett. **19**, 1171 (2008)
17. G.C. Nandi, S. Samai, R. Kumar, M.S. Singh, Tetrahedron Lett. **50**, 7220 (2009)
18. A.R. Hajipour, Y. Ghayeb, N. Sheikhan, A.E. Ruoho, Tetrahedron Lett. **50**, 5649 (2009)
19. M. Lei, L. Ma, L.H. Hu, Tetrahedron Lett. **50**, 6393 (2009)
20. A. Kumar, M. Sudershan Rao, I. Ahmad, B. Khungar, Can. J. Chem. **87**(6), 714 (2009)
21. H.R. Shaterian, H. Yarahmadi, M. Ghashang, Turk. J. Chem. **33**, 449 (2009)
22. N.L. Chavan, P.N. Naik, S.K. Nayak, R.S. Kusurkar, Synth. Commun. **40**(19), 2941 (2010)
23. D. Kundu, A. Majee, A. Hajra, Catal. Commun. **11**(14), 1157 (2010)
24. R.G. Vaghei, S.M. Malaekehpour, Cent. Eur. J. Chem. **8**(5), 1086 (2010)
25. Q. Zhang, Y. Luo, Y. Wei, Green Chem. **12**, 2246 (2010)
26. A.R. Supale, G.S. Gokavi, J. Chem. Sci. **122**(2), 189 (2010)
27. M. Wang, Y. Liang, Monatsh. Chem. **142**(2), 153 (2011)
28. J. Luo, Q. Zhang, Monatsh. Chem. **142**(9), 923 (2011)
29. K.S. Niralwad, B.B. Shingate, M.S. Shingare, Chin. Chem. Lett. **22**(5), 551 (2011)
30. S.R. Mistry, R.S. Joshi, K.C. Maheria, J. Chem. Sci. **123**(4), 427 (2011)
31. X. Cai, H. Guo, B. Xie, Jordan J. Chem. **6**(1), 17 (2011)
32. A. Zali, A. Shokrolahi, Chin. Chem. Lett. **23**(3), 269 (2012)
33. H.R. Shaterian, M. Ghashang, M. Asadi, N.T. Riki, J. Iranian Chem. Soc. **9**(1), 1 (2012)
34. D.A. Kotadia, S.S. Soni, J. Mol. Catal. A: Chem. **353**, 44 (2012)

35. S.S. Mansoor, K. Aswin, K. Logaiya, S.P.N. Sudhan, J. Saudi Chem. Soc. (2012). doi:10.1016/j.jscs.2012.06.003
36. H.R. Shaterian, K. Azizi, N. Fahimi, Arab. J. Chem. (2012). doi:10.1016/j.arabjc.2012.07.006
37. P.T. Anastas, *Green Chemistry Theory and Practice* (Oxford University Press, New York, 2000)
38. J.H. Clark, Green Chem. **1**, 1 (1999)
39. Y. Jiang, S. Decker, C. Mohs, K.J. Klabunde, J. Catal. **180**(1), 24 (1998)
40. R. Schlogl, S.B. Abd Hamid, Angew Chem. Int. Ed. **43**(13), 1628 (2004)
41. B. Vinay Kumar, H.S. Bhoiya Naik, D. Girija, B. Vijaya Kumar, J. Chem. Sci. **123**(5), 615 (2011)
42. K.J. Mispa, P. Subramanium, R. Murugesan, Chalcogenide Lett. **7**(5), 335 (2010)
43. A.V. Borhade, D.R. Tope, D.R. Patil, Res. Chem. Intermed. (2012). doi:10.1007/s11164-012-0693-8
44. A.V. Borhade, D.R. Tope, D.R. Patil, J. Chem. Pharm. Res. **4**(5), 2501 (2012)