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Poly(*N*-vinylimidazole) as an efficient catalyst for acetylation of alcohols, phenols, thiols and amines under solvent-free conditions

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Nader Ghaffari Khaligh*

Poly(*N*-vinylimidazole) is able to promote instantaneous quantitative acetylation of a variety of functionalized alcohols, phenols, thiols and amines with acetic anhydride at room temperature under solvent-free conditions. This new method consistently has excellent yields and the catalyst can be reused and recovered several times. Furthermore, the reaction can even be carried out on a larger scale.

1. Introduction

Organic bases are catalysts for a wide range of reactions.[1–5] The development of heterogeneous catalysts has become a major area of research in synthetic organic chemistry due to some potential advantages of these materials over homogeneous systems, such as simplified recovery, reusability, enhanced selectivity and reactivity, easy product isolation and incorporation in continuous reactors and microreactors.[6]

The imidazole ring is a structural fragment of the side chain in most amino acids (*i.e.*, histamine, histidine, *etc.*), which constitutes a part of almost all enzymes and is partly responsible for their catalytic activity. Imidazole is known to catalyze a number of biochemical reactions,[7,8] therefore, the catalytic behaviors of monomeric[9] and polymeric[10] imidazole was extensively studied while simulating some biological processes.[11,12] Imidazole-containing macromolecules catalyze the hydrolysis of *p*-nitrophenyl acetate,[11] Michael addition of thiols to electron-deficient alkenes[13] and *aza*-Michael reaction in water[14] acting as base catalysts.

Poly(*N*-vinylimidazole) (PVIm) is a weak base ($pK_{BH^+} = 5–6$).[15] Its peculiar features in comparison with aliphatic amines are negligible protonation within the neutral pH range and a high capacity for hydrogen bonding.[16,17] Poly(*N*-vinylimidazole) is known to form complexes with such metal ions as Cu(II),[10] Zn(II),[18] Cd(II),[19] Ag(I)[10] and Hg(II).[20] The synthesized poly(*N*-vinylimidazole) with trimethoxysilyl terminal groups was chemically anchored (grafted) on magnetic nanoparticles that were to be used for the removal and recovery of heavy metals from industrial effluents.[21a] The practical applications of PVIm are numerous, ranging from dyestuffs, catalysts, corrosion inhibitors, ion exchange resins to their utility in quenching media and metal ion complexations.[21b]

It is worth noting that in several cases, the use of solvent-free conditions is necessary for the success of the process that can be dramatically slow or practically unfeasible using an organic solvent.[22,23]

The protection of alcohols, phenols, thiols and amines by the formation of esters and amides is one of the most important and widely used transformations in organic chemistry.[24] The protection of such functional groups is often necessary during the course of various transformations in a synthetic sequence, especially in the construction of polyfunctional molecules, such as nucleosides, carbohydrates, steroids and natural products.[25,26] A variety of procedures are routinely performed for the preparation of acetyl derivatives, including homogeneous or heterogeneous catalysts, such as DMAP and 4- pyrrolidinopyridine,[27] TMEDA,[28] Bu_3P,[29] iodine,[30] *p*-toluenesulfonic acid,[31] alumina,[32] montmorillonite K-10 and KSF,[33] zeolite HSZ-360,[34] zirconium sulfophenyl phosphonate,[35] phosphomolybdic acid (PMA),[36] acetonyltriphenylphosphonium bromide,[37] $Sc(OTf)_3$,[38] trimethylsilyl trifluoromethanesulfonate (TMSOTf),[39] $Cu(OTf)_2$,[40] copper(II) tetrafluoroborate,[41a] $Mg(NTf_2)_2$,[41b] $In(OTf)_3$,[42] $Ce(OTf)_3$,[43] silver triflate,[44] magnesium bromide,[45] bismuth(III) salts,[46] $Mg(ClO_4)_2$,[47a] $HClO_4–SiO_2$,[47b] $HBF_4–SiO_2$,[47c] $BiOClO_4·xH_2O$,[47d] ferric perchlorate adsorbed on silica gel,[48] zinc chloride,[49] cobalt chloride,[50] $RuCl_3$,[51] $InCl_3$,[52] $ZrCl_4$,[53] $TaCl_5$,[54] Cp_2ZrCl_2[55] and cerium polyoxometalate.[56] However, some of the reported methods for the acetylation suffer from one or more of the disadvantages, such as drastic reaction conditions, expensive catalysts, hygroscopicity and thermal instability of the catalysts, use of halogen-containing solvents and catalysts, long reaction times and low yields. Therefore, the introduction of new methods and catalysts for the preparation of esters and amides is still in demand.

It is clear that green chemistry not only requires the use of environmentally benign reagents and solvents, but also the recovery and reuse of the catalyst. One way to overcome the problem of recyclability of the traditional reagents is to chemically anchor the reactive center onto a large surface

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Department of Chemistry, College of Science, University of Guilan, Rasht, 41335-19141, Iran. E-mail: ngkhaligh@guilan.ac.ir; ngkhaligh@gmail.com; Fax: +982166934046; Tel: +982166431738

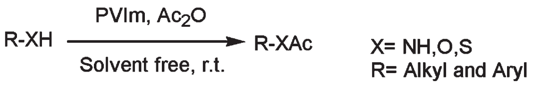
area solid carrier.[57] In these types of solids, the reactive centers are highly mobile, similar to homogeneous reagents, and at the same time these species have the advantage of being recyclable in the same fashion as heterogeneous reagents. Functional polymers have the potential advantages of small molecules with the same functional groups.[58]

Following our current interest based on the use of solid catalysts under solvent-free conditions,[59] in this paper, we are describing our work on the successful use of non-toxic, environmentally benign and inexpensive poly(*N*-vinylimidazole) (PVIm) as a solid nucleophile catalyst for the acetylation of alcohols, phenols, thiols and amines with acetic anhydride at room temperature under solvent-free conditions. The novelty of this work is the use for the first time of PVIm for the acetylation of alcohols, phenols, thiols and amines with acetic anhydride. The results could be useful in finding new applications for this polymer.

2. Results and discussion

In continuation of our ongoing research program on the development of new catalysts and methods for organic transformations,[59–61] here we wish to report the environmentally benign synthesis of poly(*N*-vinylimidazole) (PVIm) for acetylation of alcohols, phenols, thiols and amines at room temperature under solvent-free conditions (Scheme 1). PVIm was synthesized using a standard free-radical polymerization, as reported earlier.[62,63]

To begin with, a comparative study with imidazole (Im) and *N*-methylimidazole (MIm), instead of poly(*N*-vinylimidazole) (PVIm) was carried out. The acetylation of 4-chlorobenzyl alcohol by Ac_2O with equivalent ratio was carried out in the presence of monomeric and polymeric acetylating agents at room temperature under solvent-free conditions (Table 1). As shown, after stirring for 6 h at room temperature in the absence of acetylating agents, the reaction did not proceed as monitored by TLC (Table 1, entry 1). On the other hand, in the presence of a certain amount of the Im, MIm and PVIm acetylating agents at room temperature, the reaction was completed with 100% conversion in 10, 5 and 5 min, respectively. When the acetylating agent was changed from imidazole to *N*-methylimidazole, the reaction time was improved (Table 1, entries 2, 3), however, when replacing *N*-methylimidazole with poly(*N*-vinylimidazole), no significant improvement was observed in the reaction time (Table 1, entries 3, 4). According to the results in Table 1, it can be concluded that both acetylating agents were effective for the acetylation of benzyl alcohol at room temperature, but PVIm is a heterogeneous catalyst, also as compared to *N*-methylimidazole and imidazole, poly(*N*-vinylimidazole) is highly stable and easy to handle.



Scheme 1 Acetylation of alcohols, phenols, thiols and amines at room temperature under solvent-free conditions.

Table 1 Reaction of 4-chlorobenzyl alcohol and Ac_2O in the presence of Im, MIm and PVIm at room temperature under solvent-free conditions[a]

Entry	Catalyst	Amount (mg)	Time (min)	Yield (%)[b]
1	—	—	6 h	N. R.
2	Imidazole	50	10	92
3	*N*-methylimidazole	50	5	94
4	Poly(*N*-vinylimidazole)	50	5	94

[a] Reaction conditions: substrate, 1.0 mmol; Ac_2O, 1.0 mmol. [b] GC-MS yield.

In order to standardize the reaction, different amounts of PVIm were used to get 4-chlorobenzyl acetate from 4-chlorobenzyl alcohol and acetic anhydride at room temperature under solvent-free conditions, and the results are summarized in Table 2. It was clear that the reaction can be carried out in the presence of a catalytic amount of PVIm and the yields were excellent. It was found that the reaction was not possible without catalyst.

After these preliminary experiments, a catalytic amount of PVIm (20 mg) was used to convert a variety of functionalized alcohols, phenols, thiols and amines with acetic anhydride into respective esters and amides at room temperature under solvent-free conditions, and the results are presented in Table 3.

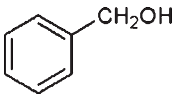
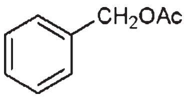
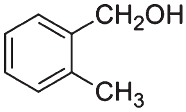
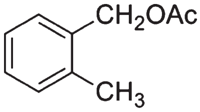
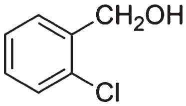
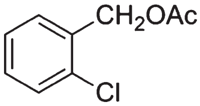
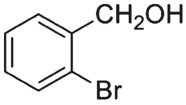
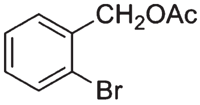
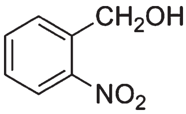
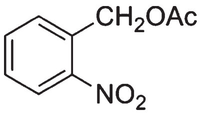
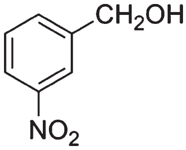
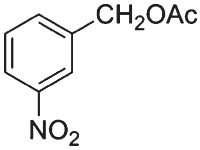
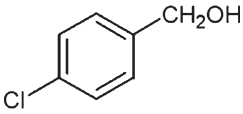
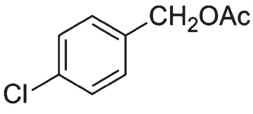
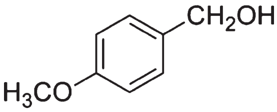
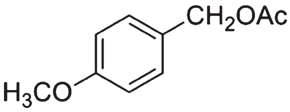
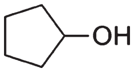
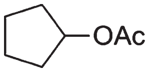
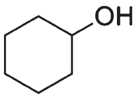
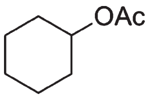
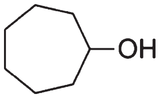
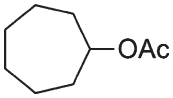
The results incorporated in Table 3 demonstrate the generality and scope of PVIm during the acetylation of structurally diverse alcohols and phenols. The reaction could be carried out with 1 equiv. of Ac_2O at room temperature in 5–35 min. The compounds containing both electron withdrawing and electron donating groups reacted equally efficiently under the standard reaction conditions to give the acetylated products in excellent yields. The reaction conditions were mild enough not to induce any damage to moieties like the methoxyl group (Table 3, entry 9), which often underwent cleavage in the presence of strong acids or certain Lewis acids. Sterically hindered and electron deficient alcohols (Table 3, entries 5, 6 and 13–16) were efficiently acetylated under solvent-free conditions. Excellent selectivity was observed in that secondary and tertiary alcohols did not experience any competitive dehydration (Table 3, entries 9–16). In order to

Table 2 Reaction of 4-chlorobenzyl alcohol and Ac_2O in the presence of different amounts of PVIm at room temperature under solvent-free conditions

Entry	Amount of PVIm (mg)	Time (min)	Yield (%)[a]
1	—	6 h	N. R.
2	2	30	36
3	5	25	42
4	10	10	78
5	20	5	94
6	30	5	95

[a] GC-MS yield.

Table 3 PVIm catalyzed acetylation of alcohols, phenols, thiols and amines[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1			5	98
2			5	96
3			5	95
4			5	94
5			30	88
6			35	83
7			5	94
8			8	95
9			8	92
10			8	92
11			8	94

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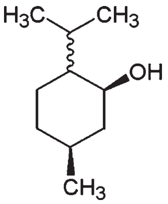
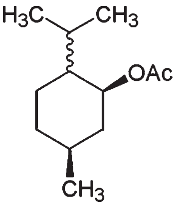
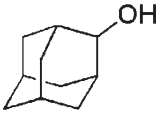
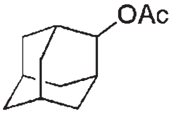
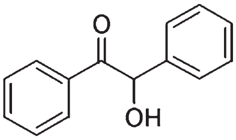
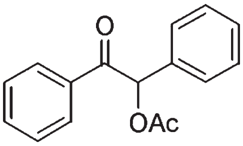
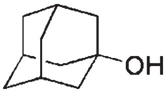
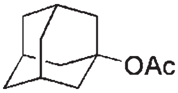
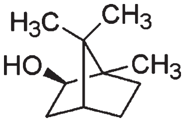
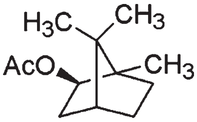
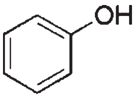
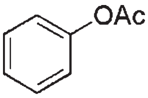
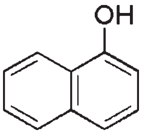
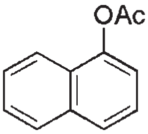
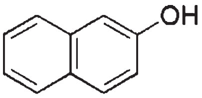
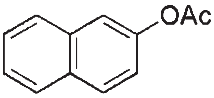
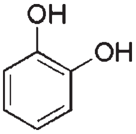
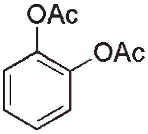
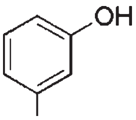
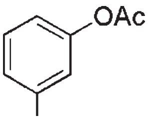
12			25	86
13			28	88
14			20	96
15			20	89
16			12	95
17			18	94
18			25	90
19			20	90
20			30	84[c]
21			20	87[c]

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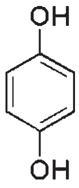
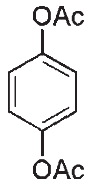
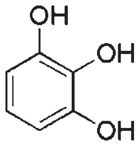
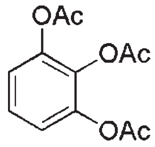
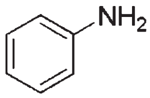
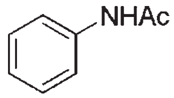
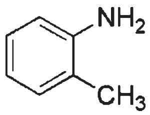
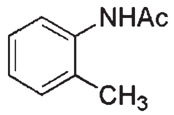
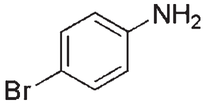
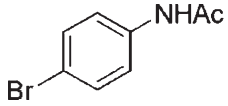
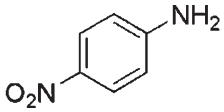
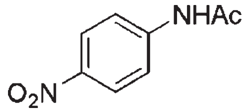
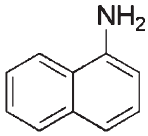
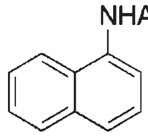
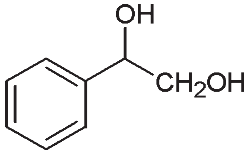
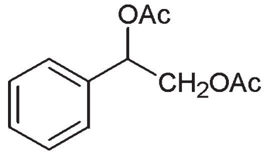
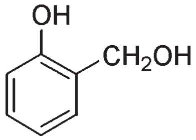
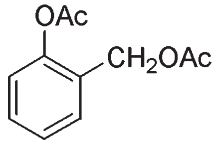
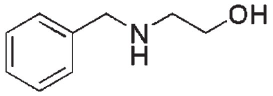
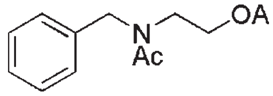
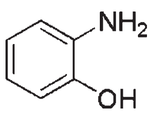
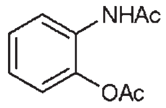
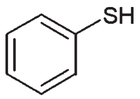
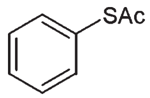
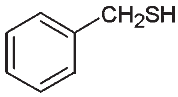
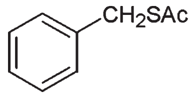
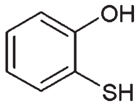
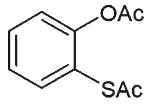
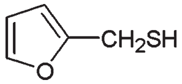
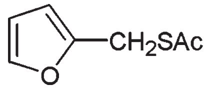
22			5	93[c]
23			45	92[d]
24			2	90
25			4	96
26			4	86
27			2	93
28			4	90
29			20	93[c]
30			8	98[c]
31			15	98[c]

Table 3 (*Continued*)

32			4	98[c]
33			10	94
34			8	96
35			10	96[c]
36			6	88

[a] Reaction conditions: substrate, 1.0 mmol; Ac_2O, 1.0 mmol; catalyst, 20 mg. [b] Isolated yield of the corresponding acetylated product. [c] Ac_2O, 2.0 equiv.; isolated yield of the di-acetate. [d] Ac_2O, 3.0 equiv.; isolated yield of the tri-acetate.

elucidate the mildness and stereospecificity of the PVIm catalyzed acetylation of alcohols, the reaction of optically active l(−)-Menthol and *R*(+)-Borneol were studied (Table 3, entries 12 and 16). We observed that l(−)-Menthol ($[\alpha]_D$= −49.0°, c = 10 in 95% ethanol, 99% e.e.) and *R*(+)-Borneol ($[\alpha]_D$= +37.9°, *c* = 5 in ethanol, 99% e.e.) react enantioselectivity with retention of the configuration on the benzylic center to provide l(−)-Menthyl acetate ($[\alpha]_D$ = −73.0°, neat, 98% e.e.) and (+)-Bornyl acetate ($[\alpha]_D$ = +41.5°, neat, 96% e.e.). The highest optical purity was obtained in an enantiopure form in high yield and under high regioselectivity using PVIm at room temperature under solvent-free conditions. The optical rotation of the product was determined and compared with that reported from Aldrich.

Also, we extended the use of PVIm for direct acetylation of amines (Table 3, entries 24–28) and thiols (Table 3, entries 33–36) with Ac_2O. The superiority of PVIm was further established by the fact that direct acetylation of amines and thiols with 1.0 equiv. Ac_2O could be achieved in 2–12 min at room temperature (86–96% yields) under the catalytic influence of 20 mg PVIm. Our protocol has some advantage because the two groups were acetylated during the reaction conditions (Table 3, entries 29–32, 35) and furyl mercaptane was transformed smoothly to the corresponding acetate derivative (Table 3, entry 36).

We have compared the obtained results in the acetylation of benzyl alcohol with acetic anhydride catalyzed by PVIm, with some heterogeneous and homogeneous catalysts, as reported in the literature (Table 4). It is clear that based on Table 4, some methods are superior in terms of reaction time, catalyst amount, or product yield. However, here we describe one or more of the limitations of the existing protocols, such as the use of halogenated catalysts, use of hazardous materials and use of costly catalysts (*e.g.* the triflates). Although the triflates, in general, are claimed as the most effective catalysts, they lead to competitive side reactions (*e.g.* dehydration and rearrangement *etc.*) for acid sensitive substrates.

We are currently engaged in mechanistic studies to understand the precise role of PVIm. Although the actual mechanism of the reaction was not clear, based on the literature[64–66] and FTIR spectra of PVIm (bottom) and the initial reaction of PVIm with acetic anhydride to generate an intermediate PVIm–Ac (top), the mechanism shown in Scheme 2 was selected as the most probable one.

The acetic anhydride-imidazole and acetic anhydride-*N*-methylimidazole systems proceed entirely by a nucleophilic and general base catalysis, respectively.[66] It seems that the acetic anhydride-poly(*N*-vinylimidazole) system also reacts entirely *via* a nucleophilic route, with the intermediate formation of the acetylimidazolinium-anion ion-pair intermediate (I). This was followed by an essentially irreversible attack of an alcohol, phenol, thiol or amine to the intermediate (I) to generate an ester, thioester or amide product and to regenerate PVIm. PVIm can be used in high enough amounts to serve as both the proton scavenger (III) and the catalyst (I).

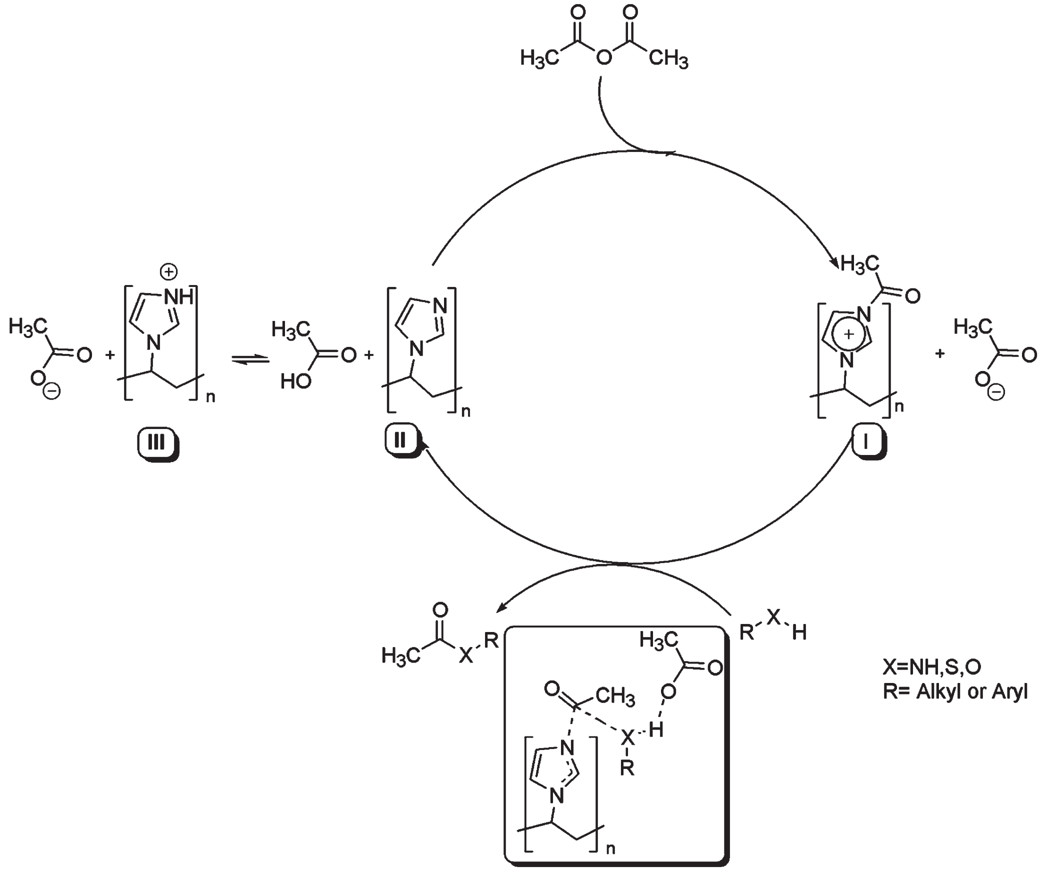
Table 4 Comparison of PVIm with other catalysts for the acetylation of benzyl alcohol at room temperature

Entry	Catalyst	Solvent	Catalyst (mol%)	Time (min)	Yield (%)[a]	Ref.
1	I_2	Neat	10	1	99	30
2	montmorillonite KSF	Neat	20 mg	60	90	33
3	zeolite HSZ-360	Neat	20 mg	60	84	34[b]
4	$Cu(OTf)_2$	CH_2Cl_2	2.5	30	97	40
5	$Ce(OTf)_3$	CH_3CN	1	12	98	43
6	$Mg(ClO_4)_2$	Neat	1	15	100	47
7	$CoCl_2$	Neat	0.5	240	98	50
8	$RuCl_3$	CH_3CN	5	60	96	51
9	$InCl_3$	Neat	0.1	30	85	52
10	Cp_2ZrCl_2	Neat	1	600	93	55
11	PVIm	Neat	20 mg	5	98	This work

[a] Isolated yield. [b] Temperature 60 °C.

In the acetic anhydride-poly(*N*-vinylimidazole) system the spectral evidence for intermediate formation was seen (Fig. 1). PVIm (20 mg) was treated with Ac_2O (1.0 mmol) in the absence of a substrate at room temperature under solvent-free conditions and magnetic stirring. After 5 min, the mixture was diluted with Et_2O (25 ml) and the catalyst allowed to settle down. The supernatant ethereal solution was decanted off, the catalyst washed with Et_2O (2 × 10 ml) and dried at room temperature under a vacuum for 2 h. The FTIR spectra of the acetylimidazolinium-anion ion-pair intermediate (top), was compared with FTIR spectra of PVIm (bottom).

The PVIm spectrum contains bands of stretching vibrations of imidazole rings (1516, 1422, 1285 and 1233 cm^{-1}), stretching vibrations of azole C–H (1080 cm^{-1}) and bending vibrations of heterocycles (914, 825 and 747 cm^{-1}).[67] The most important distinction between these two spectra was the development of a band at 1714 cm^{-1} following the functionalization of imidazole groups of PVIm with acetyl groups upon reaction with acetic anhydride. The imidazole units of PVIm corresponding to the ring deformation suffered a shift towards a higher wave number, (1013, 877, 761 cm^{-1}) when the imidazole ring was acetylated with acetic anhydride. This



Scheme 2 The plausible mechanism.

interaction increased the stiffness of the associated ring and consequently more energy was required to deform the aromatic cycle, reflected in a higher wave number value. Additionally, the intensity of the band at about 1555 cm^{-1}, as shown in Fig. 1, corresponded to positively charged nitrogen atoms. Combining the obvious and strong OH bands at 2595 and 1966 cm^{-1} in Fig. 1, we can infer that hydrogen bonding formed between the PVIm and acetic acid at equilibrium (Scheme 2). Furthermore, there was change of positions of the absorption peaks from 1670–1284 cm^{-1} for PVIm–Ac (top) in comparison with PVIm (bottom) in Fig. 1, which implies that the acetyl groups of PVIm–Ac were ionized.

In addition, we also checked the chemoselectivity of this protocol. In Table 5, we demonstrate the inter-chemoselective acetylation of benzyl alcohol, phenol, thiophenol and aniline together. The results showed that aniline was acetylated selectively in the presence of benzyl alcohol, phenol and thiophenol (Table 5, entries 1, 2, 3). It was evident that only aniline was acetylated to acetanilide, while almost all of the starting benzyl alcohol, phenol and thiophenol were recovered at the end of the reaction. This may be considered as a useful practical achievement in the acetylation of amines in the presence of alcohols, phenols and thiols. Also benzyl alcohol was acetylated in the presence of phenol and thiophenol in 85 : 15% and 84 : 16% yields, respectively (Table 5, entry 4, 5). Lastly, phenol was acetylated in the presence of thiophenol in 62 : 38% yield (Table 5, entry 6). On the other hand, the intra-chemoselective acetylation is shown in Table 3 (Entries 29–32). Results showed that the phenol, primary and secondary alcohol, and amine and aniline moiety were acetylated with together.

3. Experimental

3.1. General remarks

Chemicals were purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. *N*-vinylimidazole was obtained from Aldrich Chemical Co. and

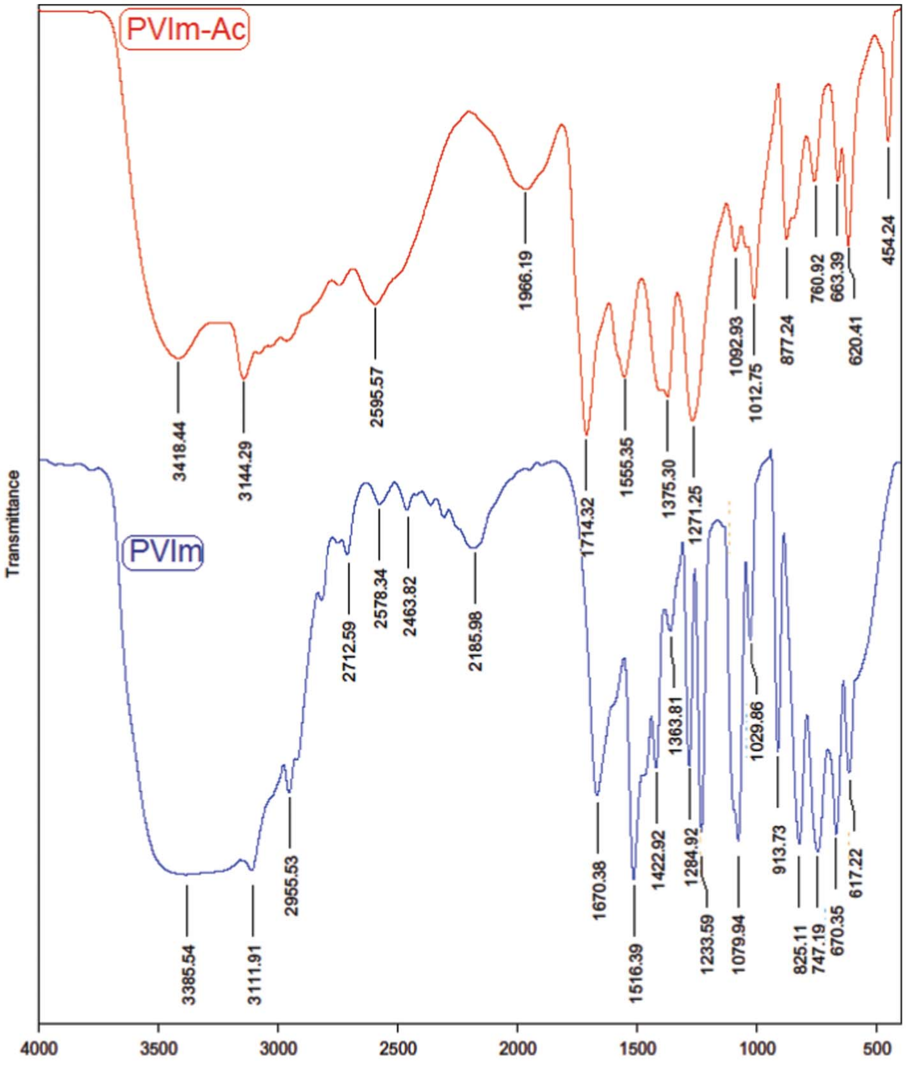
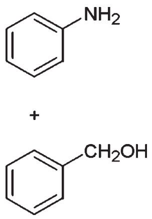
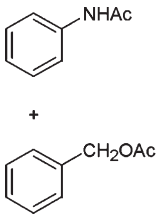
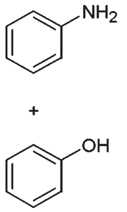
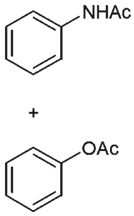
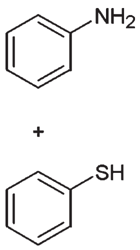
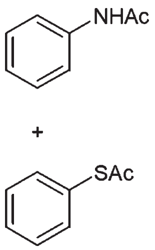
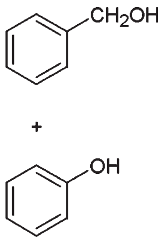
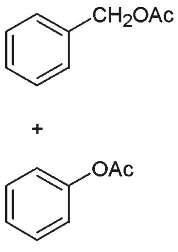
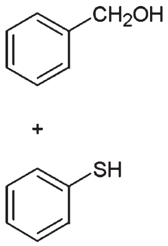
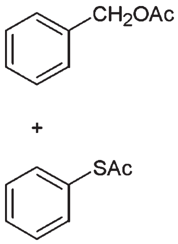
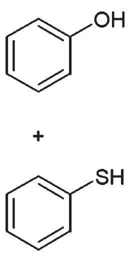
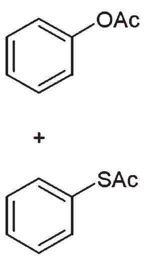


Fig. 1 FTIR spectra for PVIm (bottom) and PVIm–Ac (top).

Table 5 Competitive acetylation of benzyl alcohol, phenol and aniline catalyzed by PVIm[a]

Entry	Substrate	Product	Time (min)	Yield (%)[b]
1			5	100 0
2			5	100 0
3			5	100 0
4			5	85 15
5			5	84 16
6			5	62 38

[a] Reaction conditions: substrate, 1.0 mmol; Ac_2O, 1.0 mmol; catalyst, 20 mg. [b] Determined by GC-MS of the corresponding acetylated product.

was distilled under reduced pressure at 55 °C just prior to use. Azoisobutyronitrile (AIBN; BDH) (Fluka) was recrystallized from ethanol just before use. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. The MS were measured under GC (70 eV) conditions. The IR spectra were recorded on a Perkin Elmer 781 and Bruker Vector 22 Spectrophotometer. In all of the cases the ^{1}H NMR spectra were recorded with a Bruker Avance 400 or 300 MHz instrument. Chemical shifts are reported in parts per million in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR data were collected on a Bruker Avance 100 or 75 MHz instrument.

3.2. Typical procedure of acetylation

The substrate (alcohol, phenol, thiol or amine; 1.0 mmol) was treated with Ac_2O (1.0 mmol) in the presence of PVIm (20 mg) at room temperature under solvent-free conditions and magnetic stirring. After completion of the reaction, as indicated by TLC, the mixture was diluted with Et_2O (25 ml) and the catalyst allowed to settle down. The supernatant ethereal solution was decanted off, the catalyst washed with Et_2O (2 ml) and the combined ethereal solution concentrated under a vacuum to afford the product identical (mp, IR, 1H and ^{13}C NMR and GCMS) to an authentic sample of acetylated product. An important advantage of polymeric catalysts is that they can readily be separated from the products due to a considerable difference in the properties of high- and low-molecular compounds. As a result, such catalysts may be used repeatedly, which is profitable from the economic viewpoint and is environmentally benign. Thus, the use of poly(*N*-vinylimidazole) is promising from the viewpoint of ''green chemistry''.[68] The recovered catalyst was dried at 50 °C under a vacuum for 8 h. The recovered catalyst, after drying, was reused for four more consecutive acetylation reactions of benzyl alcohol (1.0 mmol) affording 98, 97, 97 and 96% yields in 2, 3, 3 and 5 min, respectively (Scheme 3).

One of the difficulties of most of the heterogeneous basic catalysts arises from rapid poisoning by CO_2 and H_2O contained in the environment and the reactants. To be active catalysts, they need pretreatment at a specific temperature to remove adsorbed CO_2 and H_2O. To obtain full capabilities of PVIm, the reaction system should be kept free of impurities.

Notably, we have noticed that the conversion of benzyl alcohol to the respective acetate product can be carried out even on a larger scale (10 mmol) in 82% yield for 10 min without any difficulty using 20 mg of PVIm. Therefore, it indicates that a large-scale reaction was possible using the same amount of catalyst. It is important to point out that the present method was much cleaner and did not involve any chromatographic separation for a large-scale reaction. The facts that heterogeneous catalysts have good mechanical stability, can be easily handled as they are invariably low toxic, non-corrosive free flowing powder and are easily separated from the reaction mixture through filtration and reused, make them suitable for industrial applications.

3.3. The spectral data of some representative and new products

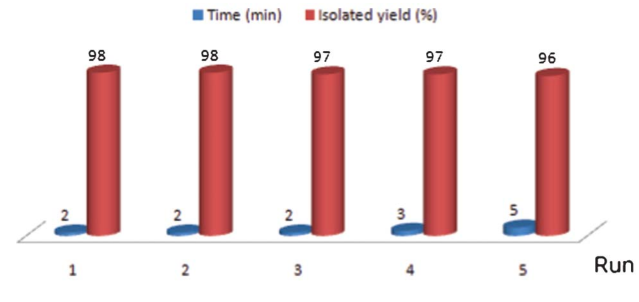
a) Table 2, entry 14: IR (neat) ν = 1738, 1697 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.23 (s, 3H), 6.84 (s, 1H), 7.32–7.53 (m, 8H), 7.95 (d, *J* = 8.8 Hz, 2H); ^{13}C ($CDCl_3$, 100 MHz) δ = 20.1, 77.2, 128.2, 128.3, 128.6, 128.8, 133.1, 133.1, 134.1, 169.9, 193.3 ppm.

b) Table 2, entry 16: IR (neat) ν = 1726 cm^{-1}; [α]25 = −38° (neat); ^1H NMR ($CDCl_3$, 400 MHz): δ = 0.82 (s, 3H), 0.88 (s, 3H), 0.92 (s, 3H), 1.26 (m, 4H), 1.72 (m, 2H), 2.08 (s, 3H), 2.36 (m, 1H), 4.89 (d, *J* = 9.8 Hz, 1H); ^{13}C ($CDCl_3$, 100 MHz) δ = 13.4, 18.7, 19.6, 21.2, 27.0, 28.0, 36.7, 44.8, 47.7, 48.6, 79.8, 171.3 ppm.

c) Table 2, entry 19: mp 70–72 °C; IR (KBr) ν = 1756 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.38 (s, 3H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.46 (m, 2H), 7.55 (s, 1H), 7.79 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 21.2, 118.5, 121.1, 125.7, 126.5, 127.6, 127.7, 129.4, 131.4, 133.7,148.3, 169.6 ppm.

d) Table 2, entry 23: IR (neat) ν = 1768 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.31 (s, 6H), 2.31 (s, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 8.8 and 7.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.2, 20.7, 120.7, 125.9, 134.7, 143.6, 167.0, 167.9 ppm; GCMS: m/z = 252 [M^+].

e) Table 2, entry 28: IR (neat) ν: 3295, 1635 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.48–7.87 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 22.8, 118.5, 122.3, 122.8, 125.2, 126.1, 127.3, 127.8, 128.4, 128.5, 133.1, 169.9 ppm.



Scheme 3 Recovery and reuse of the catalyst on the acetylation of benzyl alcohol with Ac_2O at room temperature under solvent-free conditions.

f) Table 2, entry 32: IR (neat) ν = 3320, 1730, 1682 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.16 (s, 3H), 2.36 (s, 3H), 7.14–7.17 (m, 2H), 7.22–7.25 (m, 1H), 7.39 (br s, 1H), 8.11 (d, *J* = 7.6 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.6, 22.7, 117.8, 120.7, 123.9, 125.9, 130.7, 140.5, 167.0, 167.9 ppm.

h) Table 2, entry 35: IR (neat) ν = 1765, 1679 cm^{-1}; ^1H NMR (400 MHz , CDCl3): δ = 2.33 (s, 3H), 2.45 (s, 3H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H) 7.53 (d, *J* = 7.6 Hz, 1H) ppm; ^{13}C-NMR (100 MHz, CDCl3): δ = 20.7, 26.2, 120.7, 125.9, 130.2, 134.7, 143.5, 167.0, 171.9 ppm.

i) Table 2, entry 36: IR (neat) ν = 1696 cm^{-1}; ^1H NMR (400 MHz, CDCl3): δ = 2.36 (s, 3H), 4.29 (s, 2H), 6.01 (d, *J* = 2.8 Hz, 1H), 6.23 (dd, *J* = 2.8 and 0.8 Hz, 1H), 7.22 (d, *J* = 0.8, 1H) ppm; ^{13}C-NMR (100 MHz, CDCl3): δ = 22.4, 29.7, 107.2, 110.7, 141.7, 152.7, 194.3 ppm.

4. Conclusions

PVIm is a new and highly efficient catalyst for acetylation of alcohols, phenols, thiols and amines. The low cost, ease of handling and, with the increasing environmental concern,[69] the solvent-free conditions employed in the present method make it ''environmentally friendly'' and therefore useful for industrial applications. The methodology of chemical efficiency, simplified experimental procedures and the minimization of the amount of organic solvent used which is to facilitate the separation of the product from the heterogeneous catalyst.

References

1 S. Bertelsen and K. A. Jørgensen, *Chem. Soc. Rev.*, 2009, **38**, 2178–2189.
2 D. W. C. McMillan, *Nature*, 2008, **45**, 304–308.
3 A. Dondoni and A. Massi, *Angew. Chem., Int. Ed.*, 2008, **47**, 4638–4660.
4 P. Melchiorre, M. Merigo, A. Carlone and G. Bartoli, *Angew. Chem., Int. Ed.*, 2008, **47**, 6138–6171.
5 C. F. Barbas, *Angew. Chem., Int. Ed.*, 2008, **47**, 42–47.
6 (*a*) ed., P. I. Dalko, *Enantioselective Organocatalysis*, Wiley-VCH, Weinheim, 2007; (*b*) A. J. Fatiadi, *Synthesis*, 1987, 85–127; (*c*) F. M. Menger and C. Lee, *J. Org. Chem.*, 1979, **44**, 3446–3448; (*d*) K. Smith, *Solid Supports and Catalysis in Organic Synthesis*, Ellis Horwood and PTR Prentice Hall, New York (1992); (*e*) P. Laszlo, *Comprehensive Organic Synthesis*, **Vol. 7**, ed.: Trost, B. M., New York, Pergamon, 1991, p 839; (*f*) ed., P.I. Dalko, *Enantioselective Organocatalysis,*Wiley-VCH, Weinheim, 2007.
7 I. V. Berezin and K. Martinek, *Osnovy fizicheskoi khimii fermentativnogo kataliza [Foundations of the Physical Chemistry of Enzymatic Catalysis]*, Vysshaya shkola, Moscow, 1977, 280pp, (in Russian).
8 M. L. Bender, R. J. Bergeron and M. Komiyama, *The Bioorganic Chemistry of Enzymatic Catalysis*, New York, Wiley, 1984. Translated under the title Bioorganicheskaya khimiya fermentativnogo kataliza, Moscow, Mir, 1987, p. 352.

9 (*a*) J. F. Kirsch and W. P. Jencks of Enzymatic, *Catalysis, Moscow: Vysshaya Shkola*, 1977, 280; (*b*) J. F. Kirsch and W. P. Jencks, *J. Am. Chem. Soc.*, 1964, **86**, 833–837.

10 D. H. Gold and H. P. Gregor, *J. Phys. Chem.*, 1960, **64**, 1461–1463.

11 I. M. Okhapkin, L. M. Bronstein, E. E. Makhaeva, V. G. Matveeva, E. M. Sulman, M. G. Sulman and A. R. Khokhlov, *Macromolecules*, 2004, **37**, 7879–7883.

12 V. L. Lozinsky, I. A. Simenel, V. K. Kulakova, E. A. Kurskaya, T. A. Babushkina, T. P. Klimova, T. V. Burova, A. S. Dubovik, V. Y. Grinberg, I. Y. Galaev, B. Mattiasson and A. R. Khokhlov, *Macromolecules*, 2003, **36**, 7308–7323.

13 I. P. Beletskaya, E. A. Tarasenko, A. R. Khokhlov and V. S. Tyurin, *Russ. J. Org. Chem.*, 2007, **43**, 1733–1736.

14 I. P. Beletskaya, E. A. Tarasenko, A. R. Khokhlov and V. S. Tyurin, *Russ. J. Org. Chem.*, 2010, **46**, 461–467.

15 N. L. Mazyar, V. V. Annenkov, V. A. Kruglova, S. M. Ananiev, E. N. Danilovtseva, A. V. Rokhin and S. V. Zinchenko, *Russ. Chem. Bull.*, 2000, **49**, 2013–2017.

16 N. L. Mazyar, V. V. Annenkov, V. A. Kruglova, D. C. D. Toriachinova and E. N. Danilovtseva, *Vysokomol. Soedin. A.*, 1999, **41**, 357–362.

17 V. V. Annenkov, E. A. Filina, E. N. Danilovtseva, S. V. Zinchenko and A. I. Michaleva, *J. Sol-Gel Sci. Technol.*, 2003, **27**, 163–166.

18 K. J. Liu and H. P. Gregor, *J. Phys. Chem.*, 1965, **69**, 1252–1259.

19 C. Tanford and M. L. Wagner, *J. Am. Chem. Soc.*, 1953, **75**, 434–435.

20 M. J. Molina, M. R. Gomez-Anton, B. L. Rivas, H. A. Maturana and I. F. Pierola, *J. Appl. Polym. Sci.*, 2001, **79**, 1467–1475.

21 (*a*) M. Takafuji, S. Ide, H. Ihara and Z. Xu, *Chem. Mater.*, 2004, **16**, 1977–1983; (*b*) R. C. Sutton, L. Thai, J. M. Hewitt, C. L. Voycheck and J. S. Tan, *Macromolecules*, 1988, **21**, 2432–2439.

22 T. Angelini, F. Fringuelli, D. Lanari, F. Pizzo and L. Vaccaro, *Tetrahedron Lett.*, 2010, **51**, 1566–1569.

23 F. Fringuelli, D. Lanari, F. Pizzo and L. Vaccaro, *Curr. Org. Synth.*, 2009, **6**, 203–208.

24 (*a*) J. Otera, *Esterification: Methods, Reactions and Applications*, 1st ed., Wiley–VCH, 2003; (*b*) T. W. Greene and P. G. M. Wutz, *Protective Groups in Organic Synthesis*, 3rd edn., Wiley, New York, 1999.

25 X. L. Sun, T. Kai, H. Takayanagi and K. Furuhata, *Synlett*, 1999, **9**, 1399–1341.

26 J. S. Yadav, A. V. Narsaiah, A. K. Basak, P. R. Goud, D. Sreenu and K. Nagaiah, *J. Mol. Catal. A: Chem.*, 2006, **255**, 78–80.

27 (*a*) E. F. V. Scriven, *Chem. Soc. Rev.*, 1983, **12**, 129–161; (*b*) G. Höfle, V. Steglich and H. Vorbrüggen, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 569–583; (*c*) A. Sakakura, K. Kawajiri, T. Ohkubo, Y. Kosugi and K. Ishihara, *J. Am. Chem. Soc.*, 2007, **129**, 14775–14779.

28 T. Sano, K. Ohashi and T. Oriyama, *Synthesis*, 1999, 1141–1144.

29 (*a*) E. Vedejs, N. S. Bennett, L. M. Conn, S. T. Diver, M. Gingras, S. Lin, P. A. Oliver and M. J. Peterson, *J. Org. Chem.*, 1993, **58**, 7286–7288; (*b*) E. Vedjes and T. S. Diver, *J. Am. Chem. Soc.*, 1993, **115**, 3358–3359.

30 (*a*) R. Borah, N. Deka and J. Sarma, *J. Chem. Res. (S)*, 1997, 110–111; (*b*) P. Phukan, *Tetrahedron Lett.*, 2004, **45**, 4785–4787.

31 A. C. Cope and E. C. Herrich, *Organic Synthesis Collective*, **vol. IV**, Wiley, New York, 1963, p. 304.

32 (*a*) S. S. Rana, J. J. Barlow and K. L. Matta, *Tetrahedron Lett.*, 1981, **22**, 5007–5010; (*b*) G. W. Breton, M. J. Kurtz and S. L. Kurtz, *Tetrahedron Lett.*, 1997, **38**, 3825–3828.

33 (*a*) A. X. Li, T. S. Li and T. H. Ding, *Chem. Commun.*, 1997, 1389–1390; (*b*) H. Hagiwara, K. Morohashi, T. Suzuki, M. Ando, I. Yamamoto and M. Kato, *Synth. Commun.*, 1998, **28**, 2001–2006.

34 R. Ballini, G. Bosica, S. Carloni, L. Ciaralli, R. Maggi and G. Sartori, *Tetrahedron Lett.*, 1998, **39**, 6049–6052.

35 M. Curini, F. Epifano, M. C. Marcotullio, O. Rosati and M. Rossi, *Synth.Commun.*, 2000, **30**, 1319–1329.

36 S. T. Kadam and S. S. Kim, *Synthesis*, 2008, 267–268.

37 A. T. Khan, L. H. Choudry and S. Ghosh, *Eur. J. Org. Chem.*, 2005, 2782–2787.

38 K. Ishihara, M. Kubota, H. Kurihara and H. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4560–4567.

39 (*a*) P. A. Procopiou, S. P. D. Baugh, S. S. Flack and G. G. A. Inglis, *Chem. Commun.*, 1996, 2625–2626; (*b*) P. A. Procopiou, S. P. D. Baugh, S. S. Flack and G. G. A. Inglis, *J. Org. Chem.*, 1998, **63**, 2342–2347.

40 (*a*) P. Saravanan and V. K. Singh, *Tetrahedron Lett.*, 1999, **40**, 2611–2614; (*b*) K. L. Chandra, P. Saravan, R. K. Singh and V. K. Singh, *Tetrahedron*, 2002, **58**, 1369–1374.

41 (*a*) A. K. Chakraborti, R. Gulhane and Shivani, *Synthesis*, 2004, 111–115; (*b*) A. K. Chakraborti and Shivani, *J. Org. Chem.*, 2006, **71**, 5785–5788.

42 K. K. Chauhan, C. G. Frost, I. Love and D. Waite, *Synlett*, 1999, 1743–1744.

43 R. Dalpozzo, A. D. Nino, L. Maiuolo, A. Procopiou, M. Nardi, G. Bartoli and R. Romeo, *Tetrahedron Lett.*, 2003, **44**, 5621–5624.

44 R. Das and D. Chakraborty, *Synthesis*, 2011, 1621–1625.

45 S. V. Pansare, M. G. Malusare and A. N. Rai, *Synth. Commun.*, 2000, **30**, 2587–2592.

46 I. Mohammadpoor-Baltork, H. Aliyan and A. R. Khosropour, *Tetrahedron*, 2001, **57**, 5851–5854.

47 (*a*) A. K. Chakraborti, L. Sharma, R. Gulhane and Shivani, *Tetrahedron*, 2003, **59**, 7661–7668; (*b*) A. K. Chakraborti and R. Gulhane, *Chem. Commun.*, 2003, 1896–1897; (*c*) A. K. Chakraborti and R. Gulhane, *Tetrahedron Lett.*, 2003, **44**, 3521–3525; (*d*) A. K. Chakraborti, R. Gulhane and Shivani, *Synlett*, 2003, **12**, 1805–1808.

48 A. Parmar, J. Kaur, R. Goyal, B. Kumar and H. Kumar, *Synth. Commun.*, 1998, **28**, 2821–2826.

49 R. H. Baker and F. G. Bordwell, *Organic Synthesis Collective*, **vol. III**, Wiley, New York, 1995, p. 141.

50 J. Iqbal and R. R. Srivastava, *J. Org. Chem.*, 1992, **57**, 2001–2007.

51 S. K. De, *Tetrahedron Lett.*, 2004, **45**, 2919–2922.

52 A. K. Chakraborti and R. Gulhane, *Tetrahedron Lett.*, 2003, **44**, 6749–6753.

53 A. K. Chakraborti and R. Gulhane, *Synlett*, 2004, 627–630.

54 S. Chandrasekhar, T. Ramachander and M. Takhi, *Tetrahedron Lett.*, 1998, **39**, 3263–3266.

55 M. L. Kantam, K. Aziz and P. R. Likhar, *Catal. Commun.*, 2006, **7**, 484–487.

56 V. Mirkhani, S. Tangestaninejad, M. Moghadam, B. Yadollahi and L. Alipanah, *Monatsh. Chem.*, 2004, **135**, 1257–1263.

57 J. A. Melero, R. van Grieken and G. Morales, *Chem. Rev.*, 2006, **106**, 3790–3812.

58 (*a*) A. Akelah and D. C. Sherindton, *Chem. Rev.*, 1981, **81**, 557–587; (*b*) D. C. Sherington and P. Hodge, *Synthesis and Separation Using Functional Polymers*, Wiley, Chichester (1988); (*c*) K. Takemoto, Y. Inaki and R. M. Ottenbrite, *Functional Monomers and Polymers*, Dekker, New York, 1987; (*d*) S. V. Ley, I. R. Baxendale, R. N. Bream, P. S. Jackson, A. G. Leach, D. A. Longbottom, M. Nesi, J. S. Scott, R. I. Storer and S. J. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 2000, **1**, 3815–4195.

59 F. Shirini and N. G. Khaligh, *J. Iran. Chem. Soc.*, 2012, **9**, 495–502.

60 (*a*) N. G. Khaligh, *J. Mol. Catal. A: Chem.*, 2011, **349**, 63–70; (*b*) N. G. Khaligh and F. Shirini, *J. Mol. Catal. A: Chem.*, 2011, **348**, 20–29; (*c*) F. Shirini and N. G. Khaligh, *Phosphorus, Sulfur Silicon Relat. Elem.*, 2011, **186**, 2156–2165.

61 (*a*) N. G. Khaligh, *Tetrahedron Lett.*, 2012, **53**, 1637–1640; (*b*) N. G. Khaligh, *Ultrason. Sonochem.*, 2012, **19**, 736–739; (*c*) N. G. Khaligh, *RSC Adv.*, 2012, **2**, 3321–3327; (*d*) F. Shirini and N. G. Khaligh, *Monatsh. Chem.*, 2012, **143**, 631–635.

62 A. Chapiro and Z. Mankowski, *Eur. Polym. J.*, 1988, **24**, 1019–1028.

63 B. Cabot, A. Deratani and A. Foissy, *Colloids Surf. A Physicochem. Eng. Aspects*, 1998, 139287–297.

64 (*a*) S. Xu, I. Held, B. Kempf, H. Mayr, W. Steglich and H. Zipse, *Chem. Eur. J.*, 2005, **11**, 4751–4757; (*b*) C. B. Fischer, S. Xu and H. Zipse, *Chem. Eur. J.*, 2006, **12**, 5779–5784.

65 (*a*) T. L. Gilchrist, in *Heterocyclic Chemistry*, 3rd edn., Longman, Singapore, 1997, Chapter 8; (*b*) M. R. Grimmett, in *Advances in Heterocyclic Chemistry*, ed.,A. R. Katritzky and A. J. Boulton, Academic Press, New York, **27**, 1980.

66 (*a*) K. A. Connors and N. K. Pandit, *Anal. Chem.*, 1978, **50**, 1542–1545; (*b*) N. K. Pandit and K. A. Connors, *J. Pharm. Sci.*, 1982, **71**, 485–491.

67 J. L. Lippert, J. A. Robertson, J. R. Havens and J. S. Tan, *Macromolecules*, 1985, **18**, 63–67.

68 R. A. Sheldon, I. W. C. E. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, Weinheim, Wiley, 2007.

69 R. L. Garrett, in *Designing Safer Chemicals*, ed. R. L. Garrett and S. C. De Vito, American Chemical Society Symposium Series 640, Washington DC, 1996, ch. 1.