Preparation, characterization and use of poly(4-vinylpyridinium) hydrogen sulfate salt as an eco-benign, efficient and reusable solid acid catalyst for the chemoselective 1,1-diacetate protection and deprotection of aldehydes

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ABSTRACT

Poly(4-vinylpyridinium) hydrogen sulfate solid acid was found to be efficient catalyst for preparation of 1,1-diacetate at room temperature and neat condition. Deprotection of the resulting 1,1-diacetates was achieved using the same catalyst in methanol solvent. This new method consistently has the advantage of excellent yields and short reaction times. Further, the catalyst can be reused and recovered for several times but they will be less active.

1. Introduction

Solid acids have many advantages over liquid acids in organic catalysis. They do less harm to environment and have no corrosion or disposal of effluent problems. They are reusable and easy to be separated from liquid products. As economically and ecologically benign catalysts, their research and application have attracted much attention in chemistry and industry. There are more than 100 industrial processes using over 103 solid acids as catalysts at the end of last century [1]. The replacement of traditional homogeneous catalysts with solid acids is becoming an inevitable trend.

Solid acid can be mainly divided into eight categories: oxides (Al_2O_3, SiO_2, etc.), sulfides (CdS, ZnS, etc.), metal salts ($AlPO_4$, $CuSO_4$, etc.), zeolites (HZSM-5, HY, H-β, etc.), heteropolyacids ($H_3PW_{12}O_{40}$, etc.), natural clays (kaolin, montmorillonite K10 and KSF, etc.), supported solid acids (BF_3/Al_2O_3, SO_4^{2-}/ZrO_2, etc.) and cationic ion-exchange resins (Amberlyst-15, Nafion NR 50, etc.).

Each of these solid acid catalysts offers unique properties that can influence the catalytic activity. However, these solid acid catalysts have also some disadvantages. Supported catalysts are in trouble with 'leaching' that leads to loss of activity [2]. Although zeolites catalysts have higher activity, reactions always give a variety of undesired by-product due to the higher temperature.

Ion exchange resins are limited in application because they are thermally unstable above 120 °C in the acid form [3]. Attractive alternatives to materials containing sulfonic acid groups are those containing hydrogen sulfate groups.

In several industrially important processes a large amount of sulfuric acid is required because the water by-products lows their action down by diluting the acid. At the end of these processes, a large amount of "spent acid" is obtained which, in batch reactions, is usually neutralized and disposed of, while, in continuous processes, it has to be recycled by complex techniques. Moreover, sulfuric acid is corrosive and dangerous to transport and handle [4,5]. The above mentioned disadvantages for the application of concentrated sulfuric acid have led to a substantial effort to develop viable alternatives, inter idea using some different types of new solid acids replacing sulfuric acid [6,7].

The 1,1-diacetates have been introduced as a suitable protection group for aldehyde because of their remarkable stability to neutral and basic conditions [8]. In addition, they can be converted into other useful functional groups by reaction with appropriate nucleophiles [9] and used as carbonyl surrogates for asymmetric synthesis [10]. 1,1-Diacetates, on the other hand, are ambident substrates containing two types of reactive carbon centres, the carbon atom of the protected aldehyde function and the carbonyl group in the ester moieties [11]. The relative acid stability of 1,1-diacetates is another interesting feature of such 1,1-diacetates in the field of *protection–deprotection* chemistry [12]. Usually, diacetates are prepared from the reaction of aldehydes

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Table 1
Acid strength of the P(4-VPH)HSO$_4$.

Catalysts	Indicator and $H0$		
	Anthraquinone	p-Nitrotoluene	4-Chloronitrobenzene
	−8.2	−11.35	−12.70
P(4-VPH)HSO$_4$	+	+/−	−

(+) Color changed clearly; (−) color unchanged; (+/−) color changed unclearly.

and acetic anhydride under the catalysis of a variety of protic acids such as sulfuric, phosphoric, methanesulfonic, perchloric acids[13–15], solid acidic materials like Nafion-H [16], and Lewis acids such as iodine [17], trimethylchlorosilane and sodium iodide [18], zinc chloride [19], FeCl$_3$ [12,20], FeSO$_4$ [21], phosphorus trichloride [22], indium trichloride [23], InBr$_3$ [24], Zr(HSO$_4$)$_4$ [25], VSO$_4$ [26], cyanuric chloride [27], Sc(OTf)$_3$ [28], Cu(OTf)$_2$ [29], Bi(OTf)$_3$ [30], LiOTf [31] and In(OTf)$_3$ [32]. The use of montmorillonite clay [33], expansive graphite [34], zeolites [35], N-bromosuccinimide [36], ceric ammonium nitrate [37], NH$_2$SO$_3$H [38], WCl$_6$ [39], AlPW$_{12}$O$_{40}$ [40], H$_6$P$_2$W$_{18}$O$_{62}$·24H$_2$O [41], zirconium sulfophenyl phosphonate [42], ZrCl$_4$ [43], LiBF$_4$ [44], LiBr [45], Zn(BF$_4$)$_2$ [46], Cu(BF$_4$)$_2$·xH2O [47] and Bi(NO$_3$)$_3$·5H$_2$O [48], LiClO$_4$ [49] and (ZrO$_2$/SO$_4^{2−}$) [50] as catalysts have also been reported. A few of the above mentioned catalysts are claimed to give protection as well as deprotection. Deprotection of 1,1-diacetates to their parent aldehydes is also of practical importance and several methods have been reported in the literature for this purpose [51].

2. Experimental

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparison of their melting points and spectral data with those reported in the literature. Progress of the reactions was monitored by TLC using silica gel SIL G/UV 254 plates. The reaction conversions were measured by GC on a Shimadzu model GC-16A instrument using a 25 m CBPI-S25 (0.32 mm ID, 0.5 µm coating) capillary column. The ^{1}H NMR (250 or 300 MHz) and ^{13}C NMR (62.5 or 75 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Microanalyses were performed on a Perkin-Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes. TG and SEM analyses were performed on Perkin-Elmer TG97 thermal analysis instrument (heating rate of 10 °C/min) and on a Quanta 200 microscope (the samples were coated with gold powder on 682 Gatan Inc.), respectively. All measurements were conducted under nitrogen.

2.1. Catalyst synthesis and characterization

H$_2$SO$_4$ (0.3 ml, 5.3 mmol, as a 96% standard solution) was added to the suspension of powdered poly(4-vinyl pyridine) (1.0 g) [poly(4-vinylpyridine)] cross-linked with 2% DVB ∼ 60 mesh, MW: 60,000; Fluka Chemika in 10 ml dry methanol. The mixture was stirred at room temperature for 8 h then methanol was removed under reduced pressure to form P(4-VPH)HSO$_4$ catalyst. The excessive sulfuric acid were washed by deionized water until the sulfate anions were absent in the liquid (checked by reaction with BaCl$_2$). The solid powder was dried under vacuum at 65 °C for 48 h to afford P(4-VPH)HSO$_4$ (0.5 mmol g^{-1}) as a pale yellow powder. The catalyst is washed with solvent and dried then reused for subsequent reactions.

2.2. General procedure for the preparation of 1,1-diacetates

A mixture of aldehyde (1 mmol), acetic anhydride (1.1–3.3 mmol) and P(4-VPH)HSO$_4$ (10 mg) was stirred at room temperature for the time mentioned in Table 1. After completion of the reaction (monitored by TLC), ethyl acetate (3 × 5 ml) was added to the reaction mixture and the catalyst was recovered by filtration and washed with ethyl acetate (5 ml) and acetone (5 ml). The organic layer was successively washed with a saturated solution of NaHCO$_3$ (10 ml), brine (2 × 10 ml) and water (2 × 10 ml). The organic phase was dried over anhydrous MgSO$_4$, filtered and the solvent was evaporated to give the pure desired compound. The solid crude product thus obtained was purified by recrystallization from cyclohexane, or by column chromatography on a silica gel column.

2.3. General procedure for the deprotection of 1,1-diacetates

A mixture of 1,1-diacetate (1 mmol), P(4-VPH)HSO$_4$ (10 mg) in methanol (2 ml) was stirred vigorously at room temperature for specified time in Table 1. After completion of the reaction (monitored by TLC), the reaction mixture was diluted by Et$_2$O (20 ml) and filtered to separate the catalyst. The filtrate was washed successively with 10% aq. NaHCO$_3$ (3 × 10 ml) to remove excess of Ac$_2$O and dried over MgSO$_4$. The solvent was evaporated under reduced pressure. The resultant product was passed through short column of silica gel (n-hexane-EtOAc, 9:1) to afford pure aldehyde.

2.4. Spectral data of some new products

2.4.1. **2b**
White solid, m.p. 81–83 °C (Lit. [65] m.p. 85–86 °C); IR (KBr): ν = 3100, 3050, 1760, 1740, 1587, 1454, 1430, 1370, 1350, 1232, 1198, 1095, 1060, 1010, 970, 938, 908, 786, 744 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.15 (s, 6 H, 2 × COCH$_3$), 7.57–7.61 (m, 1 H, ArH), 7.67–7.74 (m, 2 H, ArH) 8.05 (dd, J = 0.8, J = 7.6 Hz, 1 H, ArH), 8.20 [s, 1 H, CH(OAc)$_2$] ppm. C$_{11}$H$_{11}$NO$_6$ (253.21): calcd. C 52.18, H 4.38, N 5.53; found C 51.93, H 4.30, N 5.38.

2.4.2. **6b**
White solid: m.p. 80 °C (Lit. [65] m.p. 80 °C); IR (KBr): ν = 3090, 2990, 2920 1760, 1738, 1592, 1490, 1376, 1242, 1200, 1084, 1060, 1010, 993, 970, 938, 910, 840, 820, 608, 540 cm^{-1}.; ^{1}H NMR (CDCl$_3$): δ 7.64 (s, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.38 (d, J = 7.2 Hz, 2H), 2.11 (s, 6H). ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 20.5, 89.0, 128.1, 128.7, 133.9, 135.6, 168.6; Anal calcd for C$_{11}$H$_{11}$O$_4$Cl (242.709): C, 54.50; H, 4.60. Found: C, 54.43; H, 4.56.

2.4.3. **8b**
White solid, m.p. 86–88 °C (Lit. [65] m.p. 84 °C); IR (KBr): υ = 3100, 2992, 2930, 1743, 1590, 1482, 1370, 1230, 1210, 1060, 1010, 968, 940, 820, 717 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$): δ 2.10 (s, 6H, 2 × COCH$_3$), 7.39 (d, 2H, J = 8.4 Hz, ArH), 7.53 (d, 2H, J = 8.8 Hz, ArH), 7.61 (s, 1H, CH(OAc)$_2$) ppm. Anal. Calcd. for C$_{11}$H$_{11}$BrO$_4$ (287.10): C, 46.02; H, 3.86%. Found: C, 46.21; H, 3.80%.

2.4.4. **9b**
White solid, m.p. 65–67 °C; IR (KBr): ν 3650, 3500, 3010, 2910, 1760, 1610, 1590, 1490, 1430, 1370, 1245, 1200, 1160, 1060, 1010, 970, 940, 917, 790, 760, 700, 670, 600 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ 2.13 (s, 6H, 2 × COCH$_3$), 3.38 (s, 3H, CH$_3$), 7.02 (d, 1H, J = 7.9 Hz, ArH), 7.50 (d, 1H, J = 7.9 Hz, ArH), 7.60–7.66 (m, 2H, J = 8.3, J = 7.7 Hz, ArH), 8.04 (s, 1H, CH(OAc)$_2$) ppm. ^{13}C NMR (75 MHz, DMSO) δ 167.55, 147.74, 135.42, 133.82, 127.94, 125.12, 123.53, 87.83, 21.93, 21.00.

2.4.5. **11b**
White solid, m.p. 67–69 °C (Lit. [32] m.p. 73–74 °C); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (s, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.00 (t, J = 7.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 3.83

(s, 3H), 2.11 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.31, 156.71, 130.65, 128.68, 123.54, 120.19, 110.69, 85.38, 55.36, 20.60. Anal. Calcd for C$_{12}$H$_{14}$O$_5$: C, 60.50; H, 5.92. Found: C, 60.54; H, 5.96%.

2.4.6. 14b

White solid, m.p. 72–74 °C; IR (neat): ν 3035, 2985, 1760, 1610, 1595, 1530, 1465, 1370, 1310, 1245, 1210, 1170, 1100, 995, 970, 840, 760 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.10 (s, 6H, 2 × COCH$_3$), 3.06 (s, 3H, CH$_3$), 3.89 (s, 3H, CH$_3$), 6.81 (d, 1H, J = 4.9 Hz, ArH), 6.88 (dd, 1H, J = 4.9, J = 1.1 Hz, ArH), 6.98 (d, 1H, J = 1.1 Hz, ArH), 7.97 (s, 1H, CH(OAc)$_2$). ^{13}C NMR (75 MHz, DMSO) δ 167.55, 149.823, 148.37, 147.74, 123.53, 113.43, 113.32, 87.84, 55.66, 54.55, 23.30.

2.4.7. 15b

White Solid, m.p. 93–95 °C (Lit. [66] m.p. 105 °C); IR (KBr) υ = 3490, 3090, 3050, 3000, 2920, 1750, 1740, 1610, 1582, 1490, 1450, 1370, 1245, 1210, 1105, 1060, 1008, 980, 938, 880, 840, 850, 800, 760 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$, TMS) δ (ppm): 2.10 (s, 6H), 2.34 (s, 3H), 7.12 (d, J = 7.8 Hz, 1H), 7.28–7.32 (m, 1H), 7.41–7.45 (m, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.89 (s, 1H). IR (KBr): 1742, 1745 cm^{-1} (CO). C$_{13}$H$_{14}$O$_6$ (266.25): calcd. C 58.64, H 5.30; found C 58.58, H 5.28%.

2.4.8. 25b

White solid, m.p. 96–98 °C; IR (KBr): υ = 3002, 2920, 1752, 1430, 1362, 1340, 1240, 1200, 1158, 1106, 1060, 1000, 942, 910, 808, 710, 680, 650, 600, 530, 510 cm^{-1}. ^{1}H NMR (300 MHz, DMSO): δ 2.10 (s, 12H, 4 × COCH$_3$), 7.52 (d, 1H, J = 7.8 Hz, ArH), 8.00 (d, 1H, J = 7.9 Hz, ArH), 8.17 (s, 1H, CH(OAc)$_2$). 8.43 (dd, 2H, J = 7.6, J = 8.2 Hz, ArH). ^{13}C NMR (75 MHz, DMSO) δ 167.00, 141.19, 129.62, 128.82, 126.32, 102.33, 22.55.

2.4.9. 26b

White solid, m.p. 164–166 °C; IR (KBr): υ = 3020, 2910, 1758, 1430, 1378, 1338, 1200, 1118, 1060, 1008, 960, 940, 910, 852, 818, 604, 580, 540 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.37 (s, 6H, 2 × COCH$_3$), 7.29 (d, 1H, J = 5.7 Hz, ArH), 7.41 (d, 1H, J = 5.1 Hz, ArH), 8.26 (s, 1H, CH(OAc)$_2$). ^{13}C NMR (75 MHz, DMSO) δ 167.00, 141.19, 129.82, 104.33, 21.55. GC/MS (EI), m/e 278 (M$^+$−59), 235, 135 [96%].

3. Results and discussion

3.1. Studies to confirm the structure of the poly(4-vinyl pyridinium) hydrogen sulfate solid acid

Fig. 1 presents the FTIR spectra of starting P(4-VP) and polymer protonated by H$_2$SO$_4$. In the spectrum of starting P(4-VP) the absorption bands at 1598.88, 1554.52, 1496.66, and 1413.72 cm^{-1} corresponding to ν C=C and ν C=N stretching in pyridine ring appear [52,53]. On the other hand, the presence of an extra hydrogen atom on the pyridine nitrogen in the P(4-VP)-salt increases the number of vibrational modes and brings completely different FTIR spectrum [54,55]. As shown in Fig. 1 the spectrum of P(4-VP)-salt formed under protonation of pyridine units by H$_2$SO$_4$ is very different from that of P(4-VP)-base. The strong band at 1635.52 cm^{-1} arising from the protonated pyridine ion in the P(4-VP)-salt appears and the CH-aromatic bands at 2923.88 and 3028.03 cm^{-1} become weak. In pyridine, the electrons of carbon atoms and that of nitrogen atoms are delocalized to form aromatic rings. The observed effect may be therefore ascribed to "some changes in aromatic ring" as a consequence of pyridinium cation formation by the protonation reaction. As shown in Fig. 1 the intensity of band at 1554.52 cm^{-1} decreases whereas only band of pyridine ion at

1635.52 cm^{-1} appears. Thus, treatment of P(4-VP) with solution of sulfuric acid (96%) results in protonation of pyridine units of polymer. Furthermore, the appearance of band originating from the pyridinium ion indicates that sulfuric acid acted as the protonating agent. Thus, the incorporation of HSO$_4^-$ species in the form of counterions may be expected.

The broad band at 2937–3500 cm^{-1}, can be typically seen in the spectra of catalyst due to OH stretching. Medium broad vibrations observed in the IR spectrum in the range 1740–2786 cm^{-1} are assigned to overtones/combinations of hydrogen bonded OH bending modes which arise from proton tunneling and Fermi resonance interactions [56–60]. The SO$_2$ asymmetric vibration is found to be at 1325.01 cm^{-1} as a medium band in the IR spectrum and the symmetric SO$_2$ stretching vibration appears around 1172.64 cm^{-1} in IR [61,62]. By comparison with SOH bending frequencies in sulfuric acid and other sulfonic acids, the band at 1070.42 cm^{-1} is assigned to SOH bend [63].

X-ray diffraction studies are performed for initial P(4-VP) polymer and P(4-VPH)HSO$_4$ catalyst and the obtained diffractograms are displayed in Fig. 2. In the diffractogram of initial P(4-VP) two broad reflexes centred at 2Θ around 20.5° and 41.5° appear. After protonation of polymer by H$_2$SO$_4$ also one broad peak is present, however the position (2Θ around 23°) and the intensity different from the peak in initial P(4-VP). The intensity of P(4-VP) peak is higher than P(4-VPH)HSO$_4$. The broadening of peaks implies the decrease in crystalline size of P(4-VP). Deprotonation of this P(4-VPH)HSO$_4$ solid acid by washing with water and NaOH solution until the sulfate anions were absent in liquid (checked by reaction with BaCl$_2$), followed by drying in air gives the diffractogram almost identical to the one of initial P(4-VP). Incorporation of H$_2$SO$_4$ also leads to some changes in the diffractogram of P(4-VP) polymer. The relative intensity of the broad peak of the polymer (at 2Θ around 20.5°) is changed to some extent as well as the broad peak at 2Θ around 41 is disappeared. This peak appears after the thoroughly washing of P(4-VPH)HSO$_4$ catalyst thus indicating that its disappearance may be related to the presence of H$_2$SO$_4$ groups. Modification stage results also in some changes in the relative intensity of broad reflections originating from the polymer. Thus, incorporation of bulky anions like HSO$_4^-$ leads to a partial "disordering" of polymer packing that disappears after washing of the H$_2$SO$_4$ groups.

In the diffractogram of P(4-VPH)HSO$_4$ catalyst within the range of Pt-crystallites (2Θ 40° and 2Θ 46°) no distinct peaks appear, only very small and broad reflexion observed as slight increase of base line can be seen. This can indicate the particles of size in nanoscale, i.e. below the XRD detection limit.

As seen in SEM images, the aggregation of particles is retarded by loaded H$_2$SO$_4$ groups (Fig. 3). Both size reductions and retardation of aggregation result in increase in surface area of the catalyst. This increases the catalytic activity of the catalyst in the reaction. The SEM micrographs of polymer and catalyst showed that with chemical modification the primary structure of poly(4-vinylpyridine) changed.

The acid strength of the P(4-VPH)HSO$_4$ was characterized by the Hammett indicator method [64]. The P(4-VPH)HSO$_4$ was pretreated by being evacuated at 398K for 2 h, then cooled to room temperature and allowed to contact the vapor of the Hammett indicator. The acid strength was determined by observing the color change of the indicator adsorbed on the surface of the P(4-VPH)HSO$_4$. The anthraquinone ($H0$ = −8.2), p-nitrotoluene ($H0$ = −11.35) and 4-chloronitrobenzene ($H0$ = −12.70) were used as indicators and benzene was used as the solvent.

Acid contents of the P(4-VPH)HSO$_4$ were determined by acid–base titration. To a suspension of the P(4-VPH)HSO$_4$ in H$_2$O–EtOH (1:1) was added a standard NaOH solution. After the mixture was stirred for 2 h, a 0.01% solution of phenolph-
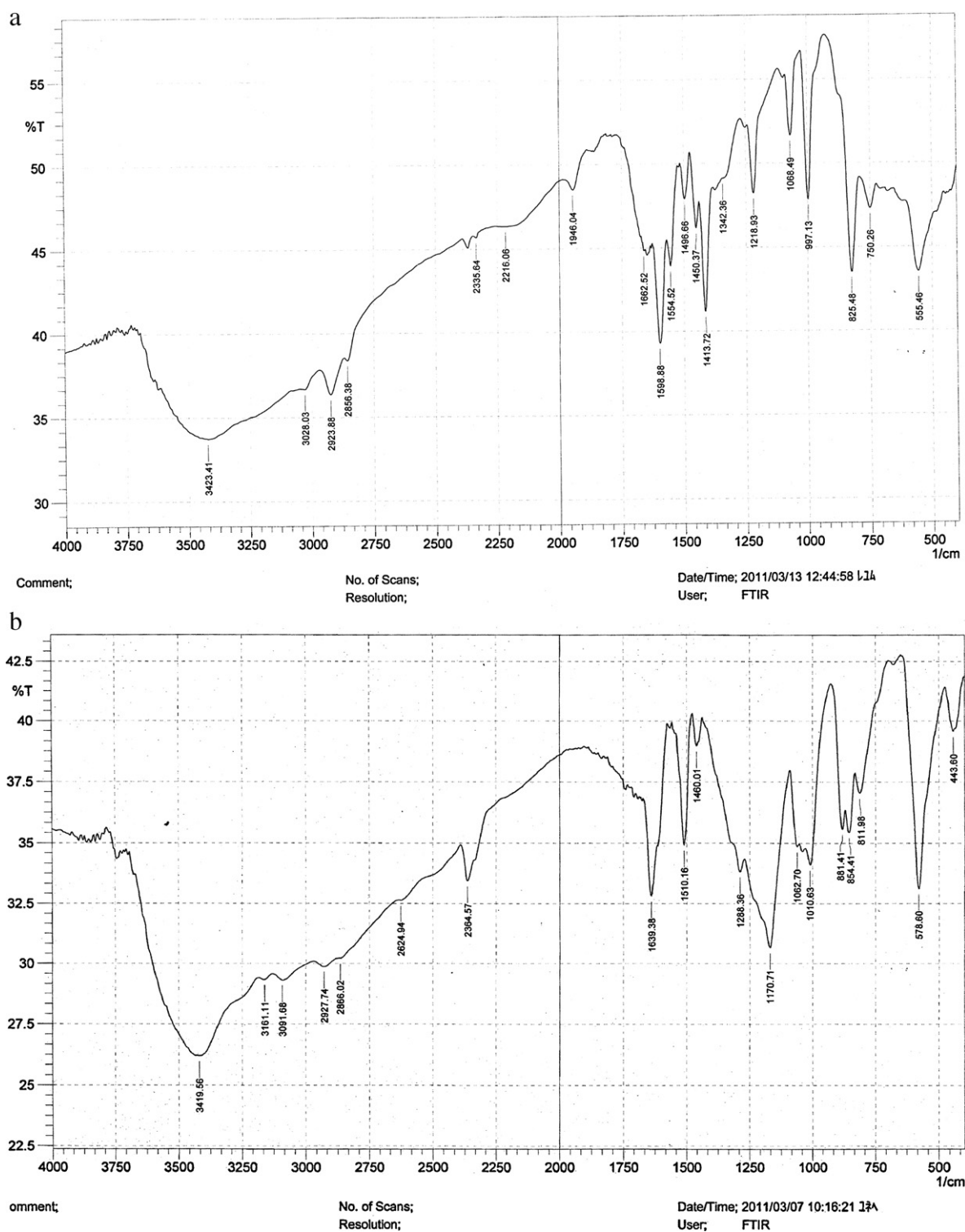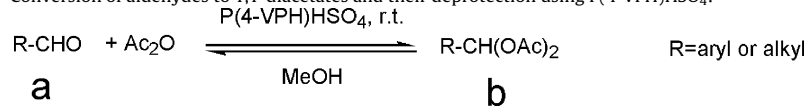
Fig. 1. FTIR spectra of P(4-VP) polymer and P(4-VPH)HSO$_4$. FTIR patterns of (a) P(4-VP) and (b) P(4-VPH)HSO$_4$.

thalein in EtOH was added to the suspension as an indicator. The solution was titrated with a standard HCl solution. The acid loading of the HClO$_4$/P(4-VP) was determined by several parallel experiments.

The acid loading of P(4-VPH)HSO$_4$ was found to be 3.10 and 3.21 mmol g^{-1} by several parallel experiments, respectively. The acid strength of P(4-VPH)HSO$_4$ determined with the Hammett indicators is listed in Table 1, which shows that P(4-VPH)HSO$_4$ shows high acid strength.

3.2. The chemoselective 1,1-diacetate protection and deprotection of aldehydes

We observed that no considerable amount of the corresponding 1,1-diacetate was formed upon the reaction of benzaldehyde with Ac$_2$O in the absence of P(4-VPH)HSO$_4$ (after 24 h ca: 22%). Several structurally varied aromatic and aliphatic aldehydes (a) were treated with 1.2 equivalent amount of acetic anhydride in the presence of 10 mg P(4-VPH)HSO$_4$ at room temperature

Table 2

Conversion of aldehydes to 1,1-diacetates and their deprotection using P(4-VPH)HSO$_4$.
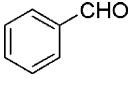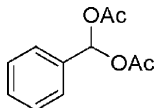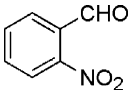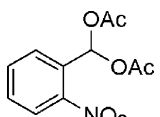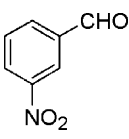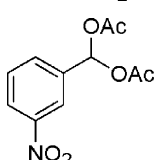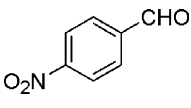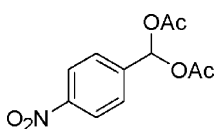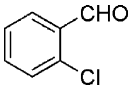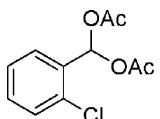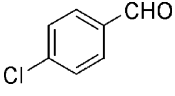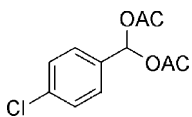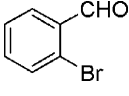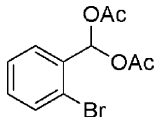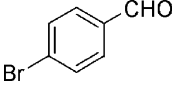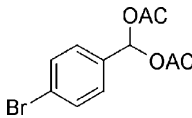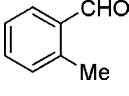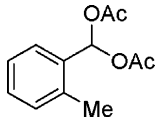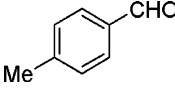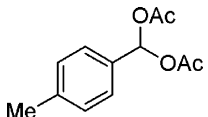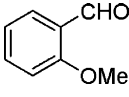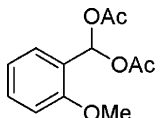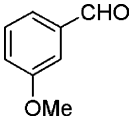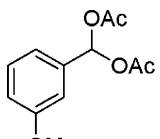
R-CHO + Ac$_2$O $\overset{\text{P(4-VPH)HSO}_4, \text{ r.t.}}{\underset{\text{MeOH}}{\rightleftharpoons}}$ R-CH(OAc)$_2$ R=aryl or alkyl

a   b

Entry	Substrate	product	Protection		Deprotection	
			Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
1	benzaldehyde	benzylidene diacetate	12	98	25	88
2	2-nitrobenzaldehyde	2-nitro product	13	95	28	90
3	3-nitrobenzaldehyde	3-nitro product	40	93	74	87
4	4-nitrobenzaldehyde	4-nitro product	4	98	7	94
5	2-chlorobenzaldehyde	2-chloro product	5	87	12	85
6	4-chlorobenzaldehyde	4-chloro product	10 (12, 12, 20)	88 (82, 76, 76)	18	82
7	2-bromobenzaldehyde	2-bromo product	42	86	75	83
8	4-bromobenzaldehyde	4-bromo product	45	92	88	90
9	2-methylbenzaldehyde	2-methyl product	4	88	10	85
10	4-methylbenzaldehyde	4-methyl product	2	94	5	92
11	2-methoxybenzaldehyde	2-methoxy product	82	86	111	76
12	3-methoxybenzaldehyde	3-methoxy product	49	91	88	92

Table 2 (*Continued*)
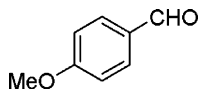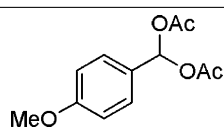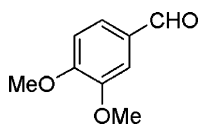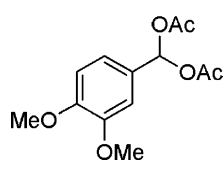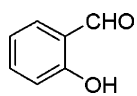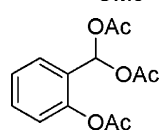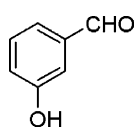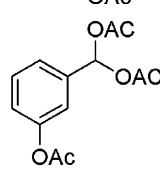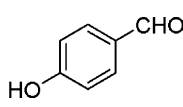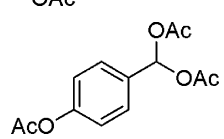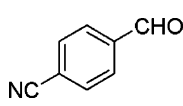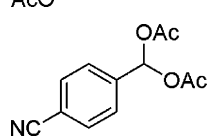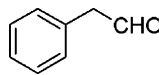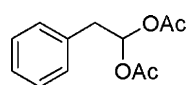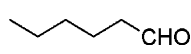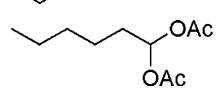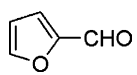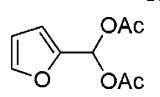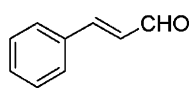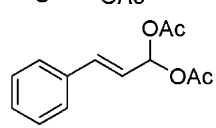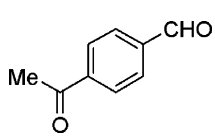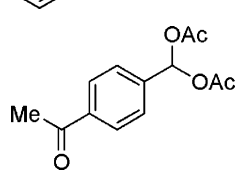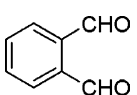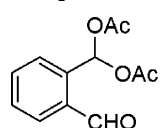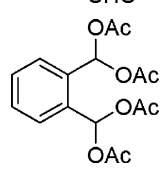
Entry	Substrate	product	Protection		Deprotection	
			Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
13			64	88	110	87
14			42	86	65	84
15			20	88[b]	38	78
16			32	75[b]	58	82
17			24	88[b]	50	86
18			55	72	112	76
19			31	85	60	84
20			64	96	130	92
21			42	94	80	88
22			5	93	12	92
23			47	92	75	90
24			12	85[c,d]	30	86
				12[c,d]		

Table 2 (*Continued*)

Entry	Substrate	product	Protection		Deprotection	
			Time (min)	Yield[a] (%)	Time (min)	Yield[a] (%)
25			5	87[c]	12	82
26			4	96[c]	10	91
27			6 h	–	–	–
28			6 h	–	–	–

[a] Yields refer to pure isolated products, characterized by m.p., IR, ^{1}H NMR.
[b] Acetic anhydride used (2.2 equiv).
[c] Acetic anhydride used (3.3 equiv).
[d] GC yields.
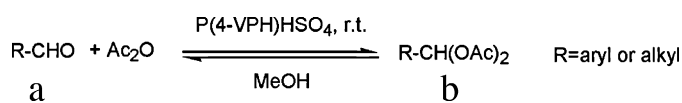
Scheme 1.
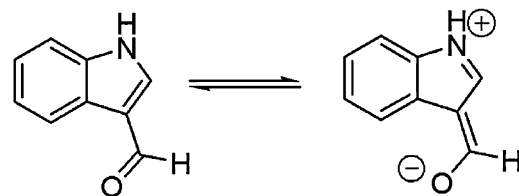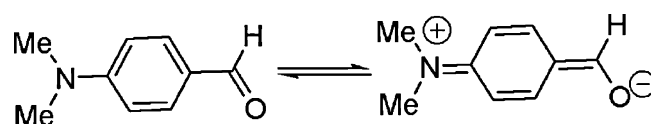
Scheme 3.

and neat condition, the corresponding 1,1-diacetates (b) were obtained in excellent yields (Scheme 1, Table 2). The results are shown in Table 2. Evidently, the present method is quite general and found to be effective for aromatic, heterocyclic, open-chain conjugated and aliphatic aldehydes (Table 2). The reaction conditions are mild enough not to induce any damage to moieties like methoxyl group (Table 2, entries 11–14) which often undergo cleavage in the presence of strong acids or certain Lewis acids. The aldehydes bearing electron withdrawing substituents such as
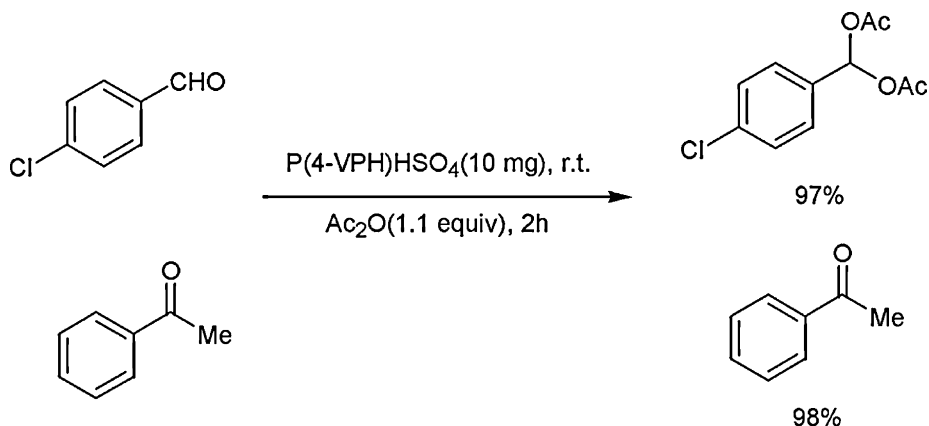
Scheme 2.
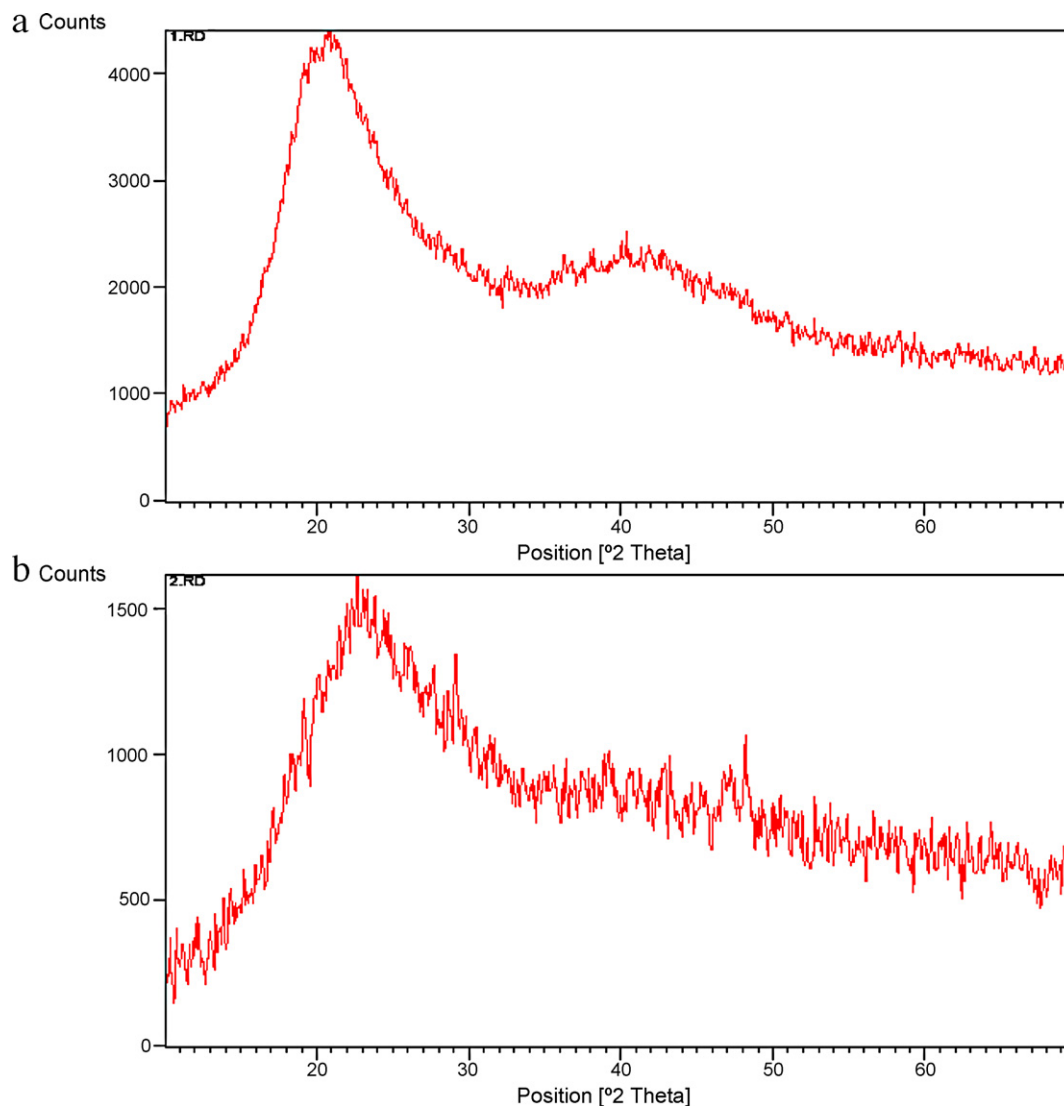
Fig. 2. XRD of poly(4-vinyl pyridine) and P(4-VPH)HSO$_4$. XRD patterns of (a) P(4-VP) and (b) P(4-VPH)HSO$_4$.

nitrobenzaldehyde (Table 2, entries 2–4) also gave good results under presented conditions. Mention must be made here that phenol groups were also protected as acetates in hydroxyl containing aromatic aldehydes (Table 2, entries 15–17) under these conditions. In addition, the hindered aldehydes (Table 2, entries 2, 5, 7, 9, 11, 15, 24) gave good yields of product. Acid sensitive substrates like furfural (Table 2, entry 21) was also diacetylated by this procedure, gave the corresponding 1,1-diacetates in good

yield without the formation of large amount of side products, which are normally observed under strongly acidic conditions. No isomerization for conjugated aldehydes was observed in the presence of P(4-VPH)HSO$_4$. Moreover, the protocol could also equally work with aliphatic aldehydes (Table 2, entries 19, 20). In our experiments, α,β-unsaturated cinnamaldehyde (Table 2, entry 22), was diacetylated smoothly without the isomerization of double bond.
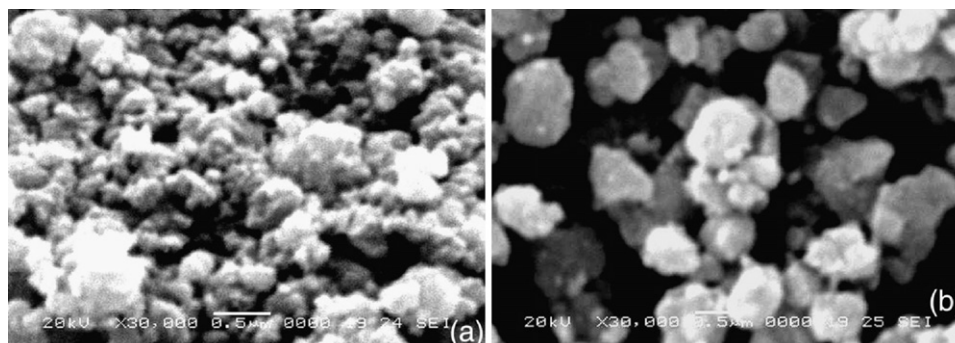
Fig. 3. SEM images of (a) initial P(4-VP) and (b) P(4-VPH)HSO$_4$.

Scheme 4.

It is also worth noting that ketone groups did not give any 1,1-diacetates under the same reaction conditions in ketone containing aromatic aldehydes (Table 1, entry 23) In a competitive experiment as shown in Scheme 2, equimolecular mixture of 4-chlorobenzaldehyde and acetophenone was allowed to react with acetic anhydride at room temperature in the presence of P(4-VPH)HSO$_4$, gave only 1,1-diacetates of benzaldehyde (GC-MS yield: 97%) while the ketone functionality remained unaffected. Hence, this method represents a chemoselective protection of aldehydes in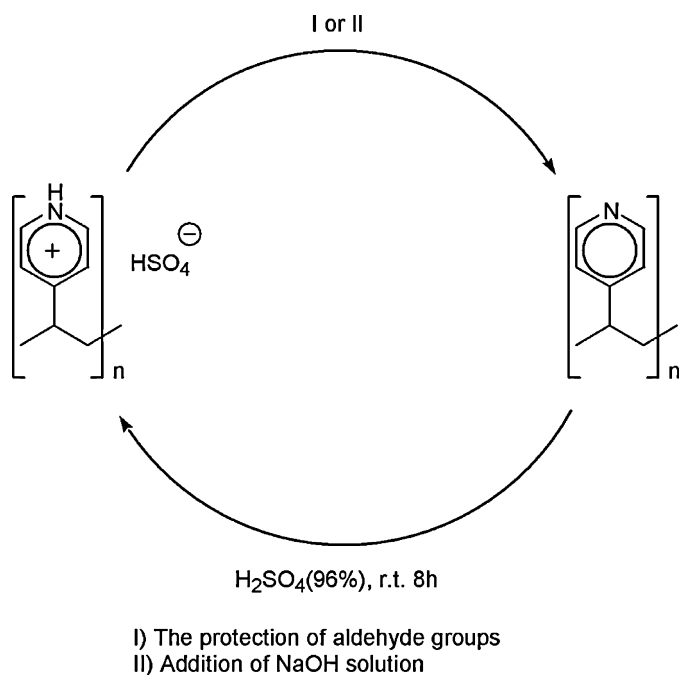 the presence of ketones. However, unfortunately both aliphatic and aromatic aldehydes showed similar reactivity and, in our system, no chemoselectivity was observed.

Attempted acetylation of benzenedicarbaldehydes (Table 1, entry 24–26), however, gave the diacetylated product in good moderate yield (85%) for phthaldialdehyde and a minor amount (12%) of tetracylated product was detected (GC-MS) accompanied with unchanged starting material. For iso-phthaldialdehyde and tere-phthaldialdehyde we obtained tetracylated products in good yields 87% and 96%, respectively.

In accordance with the fact reported in a previous literature, 4-dimethylamino benzaldehyde [33d] and indole-3-carbaldehyde (Table 1, entries 27 and 28) failed to give the corresponding 1,1-diacetate and the starting materials were quantitatively recovered under the same conditions. The explanation for this result may be due to the strong electron-donating dimethylamino and NH groups which will reduce the reactivity. A degree of tautomerisation may occur with formation of a quinonoid structure as shown in Scheme 3 and thus decrease the reactivity of the aldehyde group [38].

3.3. Recovering and reusing the catalyst (Scheme 4)

To raise the catalysts worth, recoverability and reusability of them were studied. For this purpose, the protection of 4-chlorobenzaldehyde with Ac$_2$O using P(4-VPH)HSO$_4$ was carried out several times, and the reaction mixtures were combined (Table 2, entry 6). Afterward, EtOAc was added to the combined reaction mixtures, stirred for 5 min, and filtered {product is soluble in EtOAc; however, the catalyst is not soluble in EtOAc}. In the aqueous media, a quantity of catalyst hydrolyzed to P(4-VP) and

H$_2$SO$_4$ (checked by reaction with BaCl$_2$). To complete hydrolysis of catalyst, and consequently formation of P(4-VP), a solution of NaOH (10%) was added to the filtrate, and stirred for 5 min. The solution was extracted with EtOAc, washed with H$_2$O and dried. Evaporation of the solvent gave P(4-VP). The recovered P(4-VP) was reacted with sulfuric acid to give P(4-VPH)HSO$_4$. The catalytic activity of the reproduced P(4-VPH)HSO$_4$ was as same as the first one. The recovery and reuse cycle of this catalysts are summarized in Scheme 4.

4. Conclusions

In summary, the use of P(4-VPH)HSO4 as catalyst for this transformation avoids the problem in the recovery of Lewis acid catalysts. This procedure has several advantages: (1) The preparation of P(4-VPH)HSO4 was very simple from easily available reagents; (2) P(4-VPH)HSO4 could be directly reused after simple extraction; (3) P(4-VPH)HSO4 shows efficient catalytic activity. These significant features are expected to contribute to the development of a green strategy for the 1,1-diacylation of aldehydes.

Acknowledgment

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