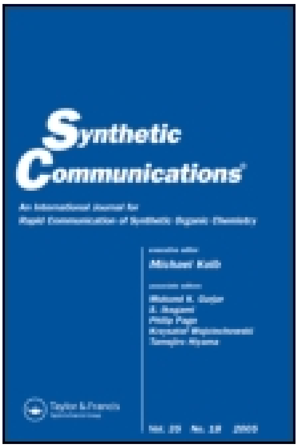


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Conjugate Polymer-Supported Acid Catalysts: An Efficient and Reusable Catalyst for the Synthesis of Geminal Diacetates (Acylals) Under Solvent-Free Conditions

Mohammad Reza Nabid [a], Seyed Jamal Tabatabaei Rezaei [a] & Mahvash Abedi [a]

[a] Department of Chemistry, Shahid Beheshti University, Tehran, Iran

To cite this article: Mohammad Reza Nabid, Seyed Jamal Tabatabaei Rezaei & Mahvash Abedi (2010) Conjugate Polymer-Supported Acid Catalysts: An Efficient and Reusable Catalyst for the Synthesis of Geminal Diacetates (Acylals) Under Solvent-Free Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:2, 191-199, DOI: 10.1080/00397910903531946

To link to this article: http://dx.doi.org/10.1080/00397910903531946

Synthetic Communications®, 41: 191–199, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910903531946

CONJUGATE POLYMER-SUPPORTED ACID CATALYSTS: AN EFFICIENT AND REUSABLE CATALYST FOR THE SYNTHESIS OF GEMINAL DIACETATES (ACYLALS) UNDER SOLVENT-FREE CONDITIONS

Mohammad Reza Nabid, Seyed Jamal Tabatabaei Rezaei, and Mahvash Abedi
Department of Chemistry, Shahid Beheshti University, Tehran, Iran

A comparative study on the catalytic activity of conducting polyaniline (PANI), polypyrrole (PPY), and poly-(3,4-ethylenedioxythiophene) (PEDOT) salts as solid acid catalysts for the synthesis of 1,1-diacetates (acylals) under solvent-free conditions has been presented. Use of the polypyrrole and poly-(3,4-ethylenedioxythiophene) salts as solid acid catalysts is reported for the first time. Preparation, recovery, and reusability of the catalysts were found to be good.

Keywords: 1,1-Diacetates; ecofriendly catalyst; polymer-supported catalyst; reusable catalyst

INTRODUCTION

To achieve the "triple bottom line," we need to develop new, more environmentally friendly chemical products and processes.[1] Catalysis, which has played such a vital role in the success of industry in the 20th century, will also play a very important role in the greener industry of the century. Catalysis cannot only help to green chemical processes (e.g., by replacing reagents or by enabling more efficient processes) but also by demonstrating their value (to reduce the environmental impact of processes and reduce the costs of the processes) will catalyze the greening of chemistry. Accordingly, there is a global effort to replace conventional catalysts with ecofriendly catalysts.

1,1-Diacetates (acylals) are synthetically useful as protecting groups for aldehydes because of their stability and easy conversion into parent aldehydes.[2,3] They are also important building blocks for the synthesis of dienes for Diels–Alder cycloaddition reaction.[4] In fact, protection of aldehydes is one of the most important reactions in organic synthesis.[5] Hence, there are numerous methods for the synthesis of acylals. Some of the catalysts that have been developed for this purpose include sulfuric acid,[6] triflic acid,[7] PCl_3,[8] I_2,[9] $FeCl_3$,[10] N-bromosuccinmide

Received October 8, 2009.

Address correspondence to Mohammad Reza Nabid, Department of Chemistry, Shahid Beheshti University, P. O. Box 1983963113, Tehran, Iran. E-mail: m-nabid@sbu.ac.ir

(NBS),[11] zeolites,[12] montmorillonite clay,[13] expansive graphite,[14] aluminum dodecatungstophosphate,[15] zeolite HSZ-360,[16] $Cu(OTf)_2$,[17] $Sc(OTf)_3$,[18] $Bi(OTf)_3$,[19] $Bi(NO_3)_3 \cdot 5H_2O$,[20] Zn $(BF_4)_2$,[21] silica sulfuric acid,[22] $HClO_4 \cdot SiO_2$,[23] $SbCl_3$,[24] $NbCl_5$,[25] and $ZrCl_4$.[26] Although there is progress for the protection and deprotection of aldehydes, developing economical and environmentally friendly procedures remains a challenge. Therefore, we are interested in recyclable, green, and metal-free catalysts for the production of acylals.

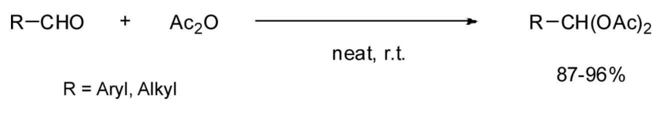
Conducting polymers are a new class of "synthetic metals" that combine the chemical and mechanical attributes of polymers with the electronic properties of metals and semiconductors. Among them, polyaniline is one of the most interesting materials because of its moderately high conductivity upon doping with acids, well-behaved electrochemistry, easy preparation, possible processability, and good environmental stability.[27] Among several reusable and heterogeneous catalysts designed and used in organic reactions, polyaniline salts (PANI salts) are attractive candidates to explore for supported catalysis.[28–30] The advantages of using conducting polymer-supported acid catalysts include straightforward synthetic route, easy preparation in large quantities, easy handling, good stability, easy recovery, recyclability and ecofriendliness.

RESULTS AND DISCUSSION

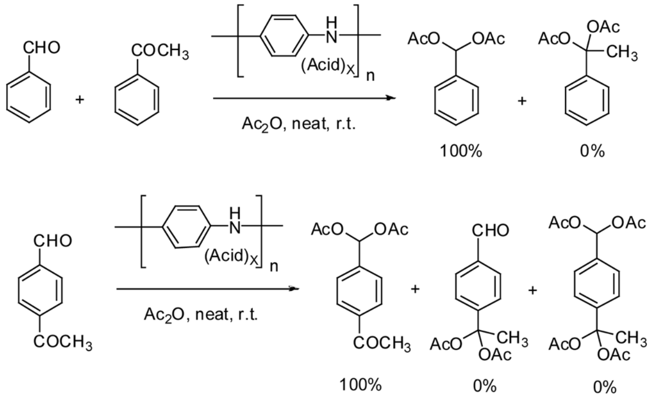
In continuation of our studies on the application of catalysts for development of useful new synthetic methodologies,[31–33] herein a simple, efficient, and high-yielding method for the protection of various aldehydes with acetic anhydride under solvent-free conditions in the presence of polyaniline, polypyrrole, and poly-(3,4-ethylenedioxythiophene) salts as catalyst is described (Schemes 1 and 2).

To find the standard experimental procedure, polyaniline salts were used as a model catalyst. We took benzaldehyde as model substrate and treated it with Ac_2O (under-solvent free conditions) in the presence of different PANI salts, including PANI hydrochloride, PANI sulfate, and PANI nitrate (Table 1). As a result, we found that PANI salts can effectively catalyze the reactions. Also, the results in Table 1 show that among these catalysts, PANI sulfate was the best catalyst of choice in terms of yield.

Next, we optimized the amount of PANI sulfate in the reaction of benzaldehyde and acetic anhydride. In the absence of the catalyst, product was obtained in poor yield (about 10%) after 4 h, whereas good results were obtained in the presence of PANI sulfate salt after 15 min. We found that 10 wt% (with respect to aldehyde) of PANI sulfate salt could effectively catalyze the reaction for the synthesis of the desired product. With inclusion of 5 wt% of PANI sulfate salt, the reaction took



Scheme 1. Synthesis of 1,1-diacetates in the presence of polyaniline-sulfate salt.



Scheme 2. Selectivity in 1,1-diacetates formation during inter- and intramolecular competition studies (based on GC and TLC analysis).

longer time. Using more than 10 wt% PANI sulfate salt had no effect on the yield and time of the reaction (Table 1).

Also, we investigated the catalytic activity of the polypyrrole and poly-(3,4-ethylenedioxythiophene) salts as solid acid catalysts under the optimized condition for the synthesis of diacetates. The results show that poly-(3,4-ethylenedioxythiophene)-sulfate and polypyrrole-sulfate have low activity in reactions compared to PANI sulfate salt. Using more than 10 wt% from these catalysts increased the yield of the reaction (Table 1). However, PANI sulfate is generally the best catalyst in terms of yield and time for various derivatives.

Table 1. Preparation of 1,1-diacetoxy-1-(phenyl)methane under various different reaction conditions[a]

Entry	Catalyst (wt%)	H^+ (mmol)	Yield[b] (%)
1	PANI–HCl(10)	0.041	84
2	PANI–HNO_3(10)	0.026	86
3	PANI–H_2SO_4(10)	0.024	92, 89, 90[c]
4	PANI–H_2SO_4(20)	0.048	93
5	PANI–H_2SO_4(5)	0.012	80
6	PPY-H_2SO_4(10)	0.018	52, 52, 49[c]
7	PPY-H_2SO_4(20)	0.036	65
8	PPY-H_2SO_4(30)	0.054	66
9	PEDOT-H_2SO_4(10)	0.009	50, 47, 49[c]
10	PEDOT-H_2SO_4(20)	0.018	63
11	PEDOT-H_2SO_4(30)	0.027	65
12	None	—	10[d]

[a] Reaction conditions: acetic anhydride (0.2 mL, 2 mmol), benzaldehyde (1 mmol), catalyst (1–5.4 mol%), 20 min, at rt.

[b] Isolated total yield.

[c] The yields of three subsequent runs using the same recovered catalyst.

[d] 30 °C for 5 h.

To evaluate the efficiency of this methodology, various aromatic, heteroaromatic, and aliphatic aldehydes were subjected to 1,1-diacetate formation under the catalytic influence of PANI sulfate (Table 2). Excellent results were obtained in 10–45 min. In general, the products obtained after usual workup were clean (spectral analyses) and did not require any further purification. The reaction was compatible with other functionality such as nitro, cyano, and ether. In the case of hydroxybenzaldehyde, the corresponding triacetates were formed (Table 2, entry 11). No diacetate formation was observed for acetophenone (at rt for 24 h or at 80 °C for 10 h). In the case of aromatic aldehydes, it was possible to monitor the reaction visually; a clear solution was obtained after mixing the aldehyde, Ac_2O, and the catalyst, and the formation of a solid precipitate (after stirring the reaction mixture for a few minutes) indicated the completion of the reaction. For aliphatic aldehydes, an exothermic reaction took place after addition of Ac_2O to the magnetically stirred mixture of the aldehyde and the catalyst, indicating the completion of the reaction.

The difference in the reactivity of aldehydes and ketones for 1,1-diacetate formation encouraged us to test the efficiency of PANI sulfate for selective 1,1-diacetate formation during inter- and intramolecular competitions between an aldehyde and a ketone. Thus, a mixture of benzaldehyde (1 mmol) and acetophenone (1 mmol) was treated with Ac_2O (1.5 mmol) for 15 min at room temperature in the presence of PANI sulfate (2.4 mol%) under solvent-free conditions (Scheme 2). Benzaldehyde 1,1-diacetate was obtained in quantitative yields, and no significant formation of the 1,1-diacetate of acetophenone was observed (NMR, GC). The treatment of 4-acetylbenzaldehyde (1 mmol) with Ac_2O (1.5 mmol) for 10 min under similar conditions resulted in exclusive formation of the 1,1-diacetate of the aldehyde group (Scheme 2).

Table 2. Preparation of acylals in the presence of polyaniline-sulfate salt under solvent-free conditions at rt

Entry	Substrate	Time (min)	Yield[a] (%)
1	Benzaldehyde	15	92
2	3-Nitrobenzaldehyde	10	96
3	4-Nitrobenzaldehyde	10	96
4	3-Chlorobenzaldehyde	15	93
5	4-Chlorobenzaldehyde	15	94
6	3-Bromobenzaldehyde	12	92
7	4-Bromobenzaldehyde	12	93
8	4-Cyanobenzaldehyde	15	90
9	4-Methylbenzaldehyde	15	94
10	4-Methoxybenzaldehyde	20	91
11	2-Hydroxybenzaldehyde	40	89
12	Cinnamaldehyde	10	94
13	Isobutyraldehyde	12	92
14	Hexanal	15	90
15	Furfural	15	87
16	Vanillin	45	87

[a] Isolated yields.

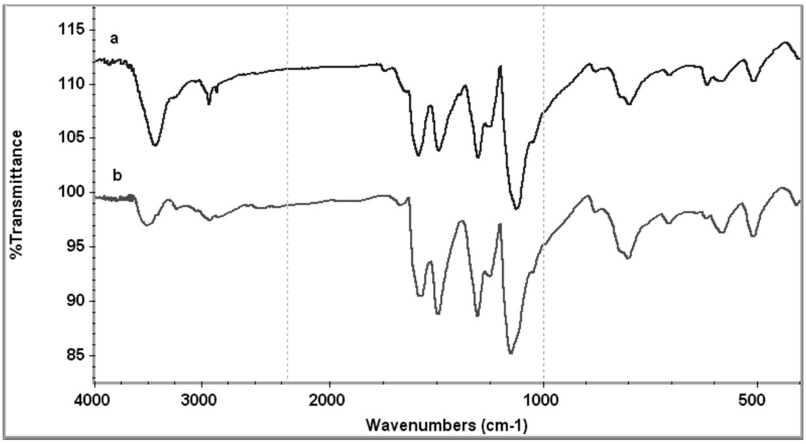


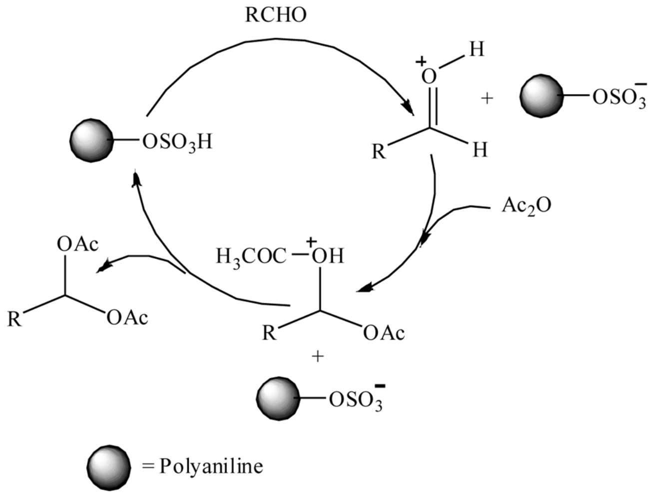
Figure 1. FTIR spectrum of polyaniline sulfate salt in KBr medium (a) as synthesized and (b) after three uses.

One of the advantages of solid acid catalysts is their ability to perform as a recyclable reaction media. The feasibility of recyclable properties of the PANI sulfate and other polymer-supported acid catalysts was also examined through a series of sequential reactions of benzaldehyde and Ac_2O as model substrates. In a typical reaction, the catalysts were simply filtered from the reaction and reused for three cycles (Table 1, entries 3, 6, and 9). The reaction proceeded smoothly with a good yield, and this result indicates that the catalysts do not lose activity and can be reused. After the third trial, the catalyst was recovered and characterized by infrared (IR), the amount of acid present in the polymer, and density measurements. A similar IR pattern was observed for the PANI salt as prepared and the sample after reaction (Fig. 1). Similarly, the value of the amount of acid group, density, and conductivity for the polymer salt samples (before and after reaction) are almost the same (see Table 3).

The suggested mechanism for PANI sulfate salt–catalyzed acetylation of aldehydes is shown in Scheme 3.

Table 3. Physical and electrical properties of polymer salts

	Before reaction			After the fourth trial		
Polymer salt	Conductivity (S/cm)	Dopant per monomeric unit	Density (g/cm^3)	Conductivity (S/cm)	Dopant per monomeric unit	Density (g/cm^3)
PANI–HCl	0.5×10^{-4}	0.45	1.22	0.46×10^{-4}	0.43	1.22
PANI–H_2SO_4	2.0×10^{-2}	0.30	1.22	1.95×10^{-2}	0.28	1.23
PANI–HNO_3	1.3×10^{-2}	0.33	1.21	1.28×10^{-2}	0.31	1.22
PPY-H_2SO_4	1.2×10^{-2}	0.14	1.42	1.11×10^{-2}	0.11	1.45
PEDOT-H_2SO_4	0.8×10^{-2}	0.13	1.47	0.72×10^{-2}	0.10	1.48



Scheme 3. A mechanistic proposal.

CONCLUSION

In conclusion, PANI sulfate is a new and highly efficient polymer-supported proton source catalyst for 1,1-diacetate formation from aldehydes. The advantages include recyclability of the catalyst with no loss in its activity, simple experimental procedure, use of very small quantities of catalyst, nontoxicity, noncorrosivity, short reaction times, inexpensive solid acid catalyst, operation at room temperature, excellent yields, and good selectivity. With the increasing tight legislation on the release of waste and use of toxic substances as a measure to control environmental pollution,[34] the use of solvent-free reaction conditions employed in the present method makes it environmentally friendly and suitable for large-scale synthesis.

EXPERIMENTAL

A polymer sample in the form of a cylindrical pellet (10 mm in diameter, 1–1.5 mm thick) was obtained by subjecting the sample to a pressure of 400 MPa. Resistance measurement of the pellet was carried out using a Keithley 213 Quad voltage source. Pellet density was measured from mass per unit volume of the pressed pellet. The amount of acid group present in the polymer chain was calculated based on the weight of redoped polymer salt and the weight of the used polymerbase. Melting points were measured on an Electrothermal 9200 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz, respectively. IR spectra were recorded on a Shimadzu IR-470 spectrometer.

General Procedure for the Preparation of Catalysts

In a 2-L round-bottomed flask, 100 ml of water were taken, and 20 ml (1.0 N) of acid solution were added slowly with stirring. To this mixture, 10 mmol of monomer was added, and the solution was kept under constant stirring at room temperature. To this solution, 25 ml aqueous solution containing ammonium persulfate (2.28 g) were added for 15–20 min. The reaction was allowed to continue for 4 h at room temperature (except for 3,4-ethylenedioxythiophene; 10 h). The precipitated polymer salt was recovered from the polymerization vessel by filtration and then washed with distilled water until the washing liquid was colorless. To remove oligomers and other organic by-products, the precipitate was washed with methanol until the methanol solution was colorless. Finally, the resulting polymer salt was washed twice with acetone and subsequently dried at 100 °C until it achieved a constant mass. The physical and electrical properties of polymer salts are shown in Table 3.

General Procedure for the Preparation of Acylals

Polymer-supported catalyst (10 wt% with respect to aldehyde) was added to a stirred solution of the respective aldehyde (1 mmol) in freshly distilled Ac_2O (0.2 mL, 2 mmol), and the mixture was stirred at room temperature for the time specified in Table 2. The reaction was followed by thin-layer chromatography (TLC; n-hexane–EtOAc, 9:1). After completion of the reaction, the mixture was diluted with Et_2O and filtered. The organic layer was washed with aqueous 10% $NaHCO_3$ and saturated $NaHSO_3$ solution and dried (Na_2SO_4). The solvent was evaporated under reduced pressure to give the corresponding pure 1,1-diacetate (Scheme 1 and Table 2). The spectral data of some selected 1,1-diacetates are listed.

All the products were characterized by spectral methods as well as by comparison of their spectral data with those reported earlier.[8–25]

Selected Spectral Data of the Products

1,1-Diacetoxy-1-(4-chlorophenyl)methane (Entry 5, Table 2). Mp 80–82 °C; IR (KBr): 3060, 3020, 1760, 1605, 1482, 1210, 1011, 780, 620 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.55 (s, 1 H), 7.3–7.2 (s, 4 H), 2.1 (s, 6 H).

1,1-Diacetoxy-1-(2-acetoxyphenyl)methane (Entry 11, Table 2). Mp 100–101 °C; IR (KBr): 3050, 2985, 1760, 1750, 1610, 1530, 1492, 1380, 1250, 1205, 1160, 1070, 990, 950, 810, 750 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.75 (s, 1 H), 7.25–7.15 (m, 2 H), 7.1–7.0 (m, 2 H), 2.18 (s, 3 H), 1.94 (s, 6 H).

ACKNOWLEDGMENT

We gratefully acknowledge the financial support from the Research Council of Shahid Beheshti University.

REFERENCES

1. Sheldon, R. A. Catalysis and pollution prevention. *Chem. Ind.* **1997**, *1*, 12–15.
2. Perez, E. R.; Marrero, A. L.; Perez, R.; Autie, M. A. An efficient microwave-assisted method to obtain 5-nitrofurfural without solvents on mineral solid supports. *Tetrahedron Lett.* **1995**, *36*, 1779–1782.

3. Kochhar, K. S.; Bal, B. S.; Deshpande, R. P.; Rajadhyaksha, S. N.; Pinnick, H. W. Protecting groups in organic synthesis, part 8: Conversion of aldehydes into geminal diacetates. *J. Org. Chem.* **1983**, *48*, 1765–1767.
4. Sinder, B. B.; Amin, S. G. An improved synthesis of 1α, 3β-dihydroxycholesta-5,7-diene. *Synth. Commun.* **1978**, *8*, 117–125.
5. Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, 1999.
6. Gregory, M. J. Evidence for a cyclic $A_{A1}1$ mechanism in the hydrolysis of benzylidene diacetates. *J. Chem. Soc. B* **1970**, 1201–1206.
7. Freeman, F.; Karcherski, E. M. Preparation and spectral properties of benzylidene diacetates. *J. Eng. Data* **1977**, *22*, 355–357.
8. Michie, J. K.; Miller, J. A. Phosphorus trichloride as catalyst in the preparation of 1,1-diacetates from aldehydes. *Synthesis*. **1981**, 824–824.
9. Deka, N.; Kalita, D. J.; Borah, R.; Sarma, J. C. Iodine as acetylation catalyst in the preparation of 1,1-diacetates from aldehydes. *J. Org. Chem.* **1997**, *62*, 1563–1564.
10. Li, Y. Q. A rapid and convenient synthesis of 1,1-diacetates from aldehydes and acetic anhydride catalyzed by PVC-$FeCl_3$ catalyst. *Synth. Commun*. **2000**, *30*, 3913–3917.
11. Karimi, B.; Seradj, H.; Ebrahimian, G. R. Mild and efficient conversion of aldehydes to 1,1-diacetates catalyzed with *N*-bromosuccinimide (NBS). *Synlett*. **2000**, 623–624.
12. Pereira, C.; Gigante, B.; Marcelo Curto, M. J.; Carreyra, H.; Perot, G.; Guisnat, M. Diacetates from aldehydes in the presence of zeolites. *Synthesis* **1995**, 1077–1078.
13. Joshi, M. V.; Narasimbam, C. S. Facile conversion of aldehydes to 1,1-diacetates catalyzed by H-ZSM-5 and tungstosilicic acid. *J. Catal.* **1993**, *141*, 308–310.
14. Jin, T. S.; Ma, Y. R.; Zhang, Z. H.; Li, T. S. An efficient and facile procedure for the deprotection of 1,1-diacetates catalysed by expansive graphite. *Synth. Commun.* **1997**, *27*, 3379–3383.
15. Ballini, R.; Bordoni, B.; Bosica, G.; Maggi, R.; Sartori, G. Solvent-free synthesis and deprotection of 1,1-diacetates over a commercially available zeolite Y as a reusable catalyst. *Tetrahedron Lett.* **1998**, *39*, 7587–7590.
16. Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O.; Nocchetti, M. Preparation and deprotection of 1,1-diacetates (acylals) using zirconium sulfophenyl phosphonate as catalyst. *Tetrahedron Lett.* **2002**, *43*, 2709–2711.
17. Chandra, K. L.; Saravanan, P.; Singh, V. K. An efficient method for diacetylation of aldehydes. *Synlett* **2000**, 359–360.
18. Aggarwal, V. K.; Fonquerna, S.; Vennall, G. P. $Sc(OTf)_3$, an efficient catalyst for formation and deprotection of geminal diacetates (acylals): Chemoselective protection of aldehydes in presence of ketones. *Synlett*. **1998**, 849–850.
19. Carrigan, M. D.; Eash, K. J.; Oswald, M. C.; Mohan, R. S. An efficient method for the chemoselective synthesis of acylals from aromatic aldehydes using bismuth triflate. *Tetrahedron Lett.* **2001**, *42*, 8133–8135.
20. Aggen, D. H.; Arnold, J. N.; Hayes, P. D.; Smoter, N. J.; Mohan, R. S. Bismuth compounds in organic synthesis: Bismuth nitrate–catalyzed chemoselective synthesis of acylals from aromatic aldehydes. *Tetrahedron*. **2004**, *60*, 3675–3679.
21. Ranu, B. C.; Dutta, J.; Das, A. Zinc tetrafluoroborate–catalyzed efficient conversion of aldehydes to geminal diacetates and cyanoacetates. *Chem. Lett.* **2003**, *32*, 366–367.
22. Hajipour, A. R.; Zarei, A.; Khazdooz, L.; Mirjalili, B.; Sheikhan, N.; Zahmatkesh, S.; Ruohoa, A. E. Silica sulfuric acid as an efficient heterogeneous catalyst for the synthesis of 1,1-diacetates under solvent-fsree conditions. *Synthesis* **2005**, 3644–3648.
23. Kumar, R.; Tiwari, P.; Maulik, P. R.; Misra, A. K. $HClO_4$-SiO_2-catalyzed chemoselective synthesis of acylals from aldehydes under solvent-free conditions. *J. Mol. Catal. A: Chem.* **2006**, *247*, 27–30.

24. Bhattacharya, A. K.; Mujahid, M.; Natu, A. A. An efficient method for the synthesis of acylals from aldehydes under solvent-free conditions catalyzed by antimony trichloride. *Synth. Commun.* **2008**, *38*, 128–134.
25. Gao, S. T.; Zhao, Y.; Li, C.; Ma, J. J.; Wang, C. $NbCl_5$ as an efficient catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions. *Synth. Commun.* **2009**, *39*, 2221–2229.
26. Smitha, G.; Sanjeeva Reddy, C. A facile and efficient $ZrCl_4$-catalyzed conversion of aldehydes to geminal-diacetates and dipivalates and their cleavage. *Tetrahedron* **2003**, *59*, 9571–9576.
27. Trivedi, D. C. *Handbook of Organic Conductive Molecules and Polymers*; H. S. Nalwa (Ed.); John Wiley & Sons: Chichester, 1997; vol. 2, chap. 12, pp. 505–507.
28. Palaniappan, S.; John, A.; Amarnath, C. A.; Rao, V. J. Mannich-type reaction in solvent-free condition using reusable polyaniline catalyst. *J. Mol. Catal. A: Chem.* **2004**, *218*, 47–53.
29. Amarnath, C. A.; Palaniappan, S.; Saravanan, C. Preparation of benzyl acetate using polyaniline saltsas catalysts, part II. *Polym. Adv. Technol.* **2004**, *15*, 118–121.
30. Gangadasu, B.; Palaniappan, S.; Amarnath, C. A.; Rao, V. J. Polyaniline salts and complexes: Efficient and reusable catalyst for the one-pot synthesis of 5-(methoxycarbonyl)-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one. *J. App. Polym. Sci.* **2006**, *102*, 1741–1745.
31. Nabid, M. R.; Sedghi, R.; Jamaat, P. R.; Safari, N.; Entezami, A. A. Catalytic oxidative polymerization of aniline by using transition-metal tetrasulfonated phthalocyanine. *App. Catal. A: Gen.* **2007**, *328*, 52–57.
32. Nabid, M. R.; Entezami, A. A. Enzymatic synthesis and characterization of a water-soluble, conducting poly(o-toluidine). *Eur. Polym. J.* **2003**, *39*, 1169–1175.
33. Nabid, M. R.; Tabatabaei Rezaei, S. J. Polyaniline-supported acid as an efficient and reusable catalyst for a one-pot synthesis of β-acetamido ketones via a four-component condensation reaction. *J. App. Catal. A: Gen.* **2009**, *366*, 108–113.
34. Garrett, R. L. In *Designing Safer Chemicals*; R. L. Garrett, S. C. De Vito (Eds.); Washington, DC, 1996; Chapter 1.