Chemoselective Synthesis of 1,1-diacetate Using Ni2+@ Hydroxyapatite-core@shell γ-Fe2O3 Nanoparticles as an Efficient and Reusable Lewis Acid Catalyst under Solvent Free Conditions

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Abstract

A simple and efficient method for the chemoselective 1,1-diacetate protection of aromatic aldehydes with acetic anhydride by using Ni^{2+} supported on hydroxyapatite-core-shell magnetic γ-Fe_2O_3 nanoparticles (γ-Fe_2O_3@HAp-Ni^{2+}) under solvent free conditions. This method has several advantages, including high yield, short reaction time, simple work-up and recyclable property of the catalyst. The catalyst can be readily isolated by using an external magnet and no obvious loss of activity was observed when the catalyst was reused in five consecutive runs.

Keywords: γ-Fe_2O_3 nanoparticles, 1,1-diacetate; Chemoselective; Solvent free.

Introduction

In the past decade, the application of magnetic nanoparticles (MNPs) as catalysts has attractive and interesting materials because of their high surface area, unique magnetic properties and high catalytic activity, moreover, they have a wide range of novel applications in physical and chemical fields; such as magnetic fluids [1] catalysis [2,3] biology and medical applications [4] magnetic resonance imaging (MRI) [5, 6] data storage,[7] and environmental remediation [8,9]. Moreover, they can be used in various organic reactions such as knoevenagel reaction [10,11], nucleophilic substitution reactions of benzyl halides [12], epoxidation of alkenes [13], synthesis of α-amino nitriles [14], hydrogenation of alkynes [15], esterifications [16], CO_2 cycloaddition reactions [17], Suzuki coupling reactions [18] and three-component condensations [19].

Acylal formation plays a pivotal role in selective protection of carbonyl groups is an extremely important step in modern organic reactions. Among different carbonyl protecting groups 1, 1-diacetates (acylals) are very important because of their stability in neutral and basic media as well as to aqueous acids [20]. 1,1-Diacetates are main synthetic precursors for the preparation of α,β-unsaturated diacetates are important starting materials for Diels–Alder reactions [21] and useful intermediates in various transformations such as nucleophilic substitution reactions [22-26] and some their protecting role, acylals is also important precursors for the synthesis of dienes, chiral allyclic esters and as cross linking reagents for the cellulose in cotton [27-28]. It is usual in organic chemistry to produce 1, 1-diacetates by using aldehydes and acetic

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anhydride under acidic medium. A variety of catalysts including sulfamic acid [29], triflic acid [30], NBS [31], CAN [32], H_2SO_4-SiO_2 [33], $H_6P_2W_{18}O_{62}.24H_2O$ [34], $Bi(NO_3)_3.5H_2O$ [35], PVA-$FeCl_3$ [36], Fe^{+3} on montmorillonite [37], zirconium sulfophenyl phosphonate [38] and zeolites [39].

Although in many cases have convenient protocols with good to high yields most of these methods suffer from some disadvantages such as reaction under oxidizing conditions, prolonged reaction time, high reaction temperature, tedious work-up procedure, the use of expensive catalysts or harmful solvents, strong conditions and tedious work-up procedure. Therefore, it seems that there is still a need for development of novel methods that proceed under green and eco-friendly conditions.

We herein wish to report a fast and efficient procedure for the synthesis of acylals from various aldehydes with acetic anhydride using γ-Fe_2O_3@HAp-Ni^{2+}as a heterogeneous catalyst under solvent-free conditions.

Materials and Methods

Products were characterized by comparison of their spectroscopic data (^{1}H NMR, ^{13}C NMR and IR) and physical properties with those reported in the literature.

The reaction progress was checked by TLC on silica gel polygram SIL G UV 254 plates. Chemicals were purchased from Fluka, Merck, and Aldrich.
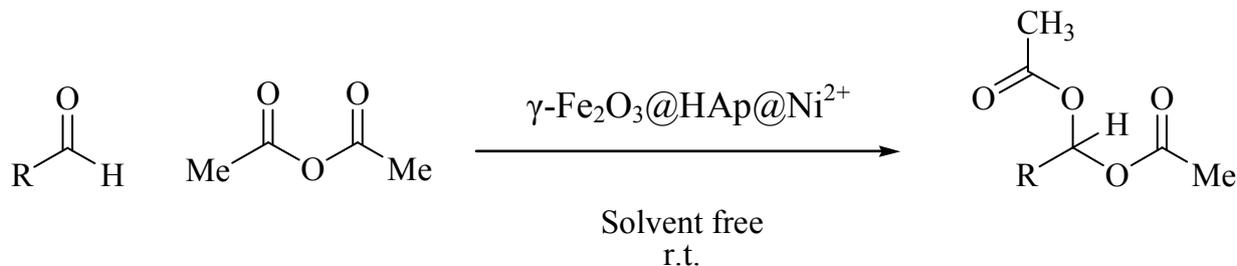
Preparation of γ-Fe$_2$O$_3$@HAp-Ni^{2+}

In this study, γ-Fe_2O_3@HAp-Ni^{2+} was prepared in two steps [40]. The Iron oxide magnetic particles (IOMP) were synthesized by co-precipitation method in the basic condition. IOMP/HAP was prepared by the impregnation method according to known procedures with some modifications. Then hydroxyapatite-encapsulated γ-Fe_2O_3 (0.6 g) was introduced into 100 ml of distilled water containing 6.4 mmol of $NiCl_2.6H_2O$. The mixture was stirred (500 rpm) for 48 h, filtered, and washed several times with ethanol. The recovered solid was dried at 50 °C overnight. The mean size and the surface morphology of the γ-Fe_2O_3@HAp-Ni^{2+} were characterized by TEM, SEM, VSM, XRD and FTIR techniques.

General procedure for formation of acylals

To a mixture of various aldehydes (1 mmol) in acetic anhydride (2 mmol), γ-Fe_2O_3@HAp-Ni^{2+} (20 mg) was added and then they were taken in a round bottom flask and stirred under solvent free condition at room temperature. The time required for each reaction is indicated in Table 3. The reaction was followed by
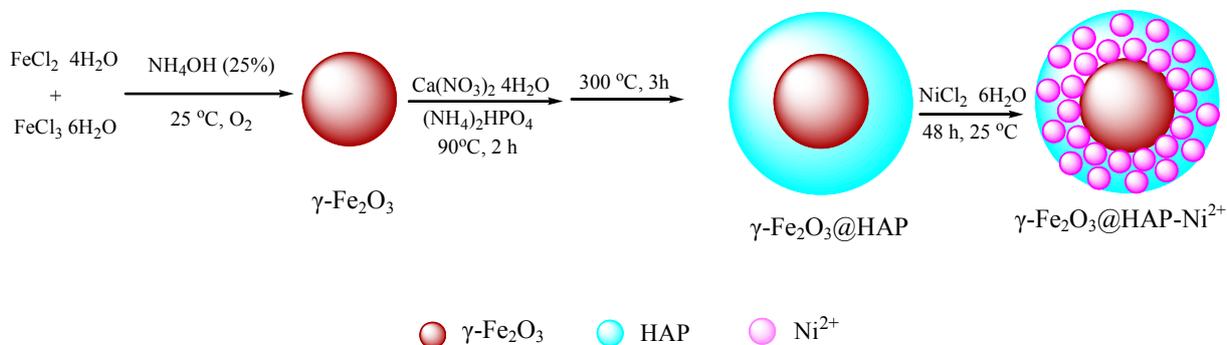
Scheme 1. Synthesis of Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe_2O_3

Solvent free
r.t.

Scheme 2. Preparation of 1,1-diacetates from aromatic aldehydes
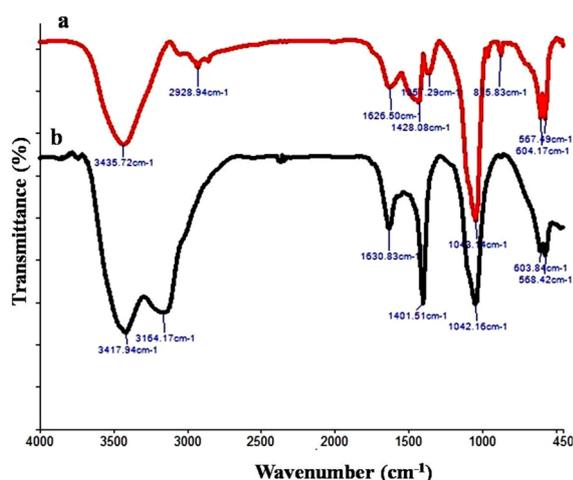
Figure 1. FT-IR spectra of (a) γ-Fe$_2$O$_3$@HAp, (b) γ-Fe$_2$O$_3$@HAp-Ni^{2+}.
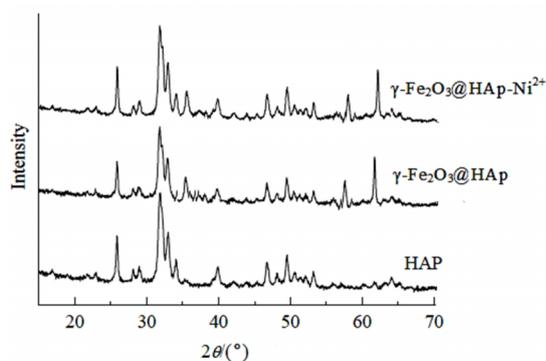
Figure 2. XRD pattern of HAP, γ-Fe$_2$O$_3$@HAp and γ-Fe$_2$O$_3$@HAp-Ni^{2+}

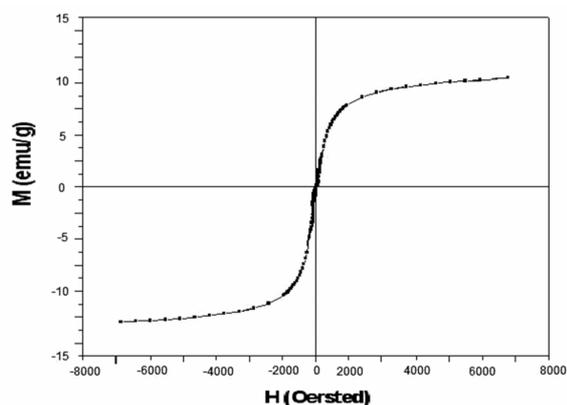**Figure 3**. Magnetization curves of γ-Fe$_2$O$_3$@HAp-Ni^{2+}

TLC (n-hexane:EtOAc, 5:1). After completion of the reaction, CH$_2$Cl$_2$ (30 mL) was added to the mixture and filtered and then again the solid material (γ-Fe$_2$O$_3$@HAp-Ni^{2+}) was washed with CH$_2$Cl$_2$ (2×5 mL) and collected for reusing. Evaporation of the solvent

followed by column chromatography on silica gel afforded the pure corresponding 1,1-diacetates. The structures of products were determined on the basis of their spectral data.The residual catalyst in the reaction vessel was washed and dried and then subjected to the next run directly.

Results and Discussion

An infrared spectrum was obtained in the 400-4000 cm^{-1} range, by a Perkin-Elmer FTIR spectrometer.The samples and KBr were fully dried before the FT-IR analyses exclude the influence of water. Fig. 1 presents the FTIR spectra of γ-Fe$_2$O$_3$@HAp, (b) γ-Fe$_2$O$_3$@HAp-Ni^{2+}. The characterization of Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ NPs was further carried out by FT-IR. The band at 3417 cm^{-1} was assigned to the stretching and bending modes of the OH groups in the hydroxyapatite structure. The bands at 1042 cm^{-1} were attributed to the asymmetric and symmetric stretching vibration of the phosphate group
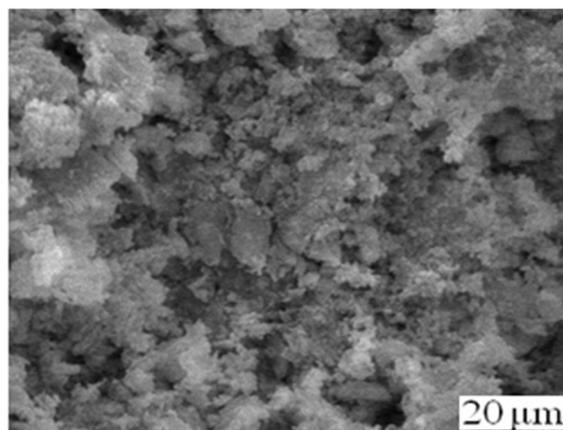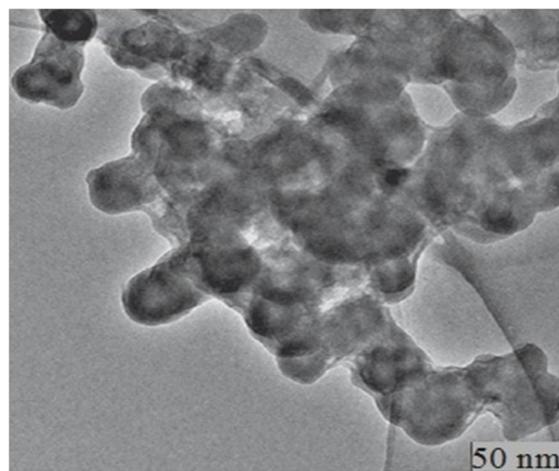

Figure 4. SEM images of γ-Fe$_2$O$_3$@HAp-Ni^{2+}

Figure 5. TEM images of γ-Fe$_2$O$_3$@HAp-Ni^{2+}

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Table 1. Optimization of the catalyst loading in solvent-free condition

Entry	Catalyst (%)	Time (min)	Yield (%)
1	-	24 h	5
2	0.01	10	99
3	0.03	25	91
4	0.05	35	89
5	0.07	40	90
6	0.1	55	86

Table 2. The solvent effect for synthesis of 1,1-diacetate

Entry	Solvent (10 ml)	Time (min)	Yield (%)
1	H_2O	80	76
2	EtOH	55	70
3	H_2O:EtOH	60	73
4	Acetonitrile	50	85
5	Ethyl acetate	90	66
6	*n*-Hexane	45	86
7	Dichloromethane	70	81
8	Solvent-Free	10	99

(PO_4^{-3}) and the bending modes of Fe–O was observed at 604, 558 cm^{-1}. In addition, the band at 875 cm^{-1} indicated that HPO_4^{-2} may also be present in the hydroxyapatite as an impurity.

The X-ray diffraction patterns of γ-Fe$_2$O$_3$@HAp and γ-Fe$_2$O$_3$@HAp-Ni^{2+}, is shown in Fig. 2.

Fig. 3. Shows the magnetization curves for Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ NPs. The magnetization curve gives a saturation magnetization value of 11.13 emu/g.

Scanning electronic microscopy (SEM), the morphology of the surface of Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ NPs was investigated using a scanning electronic microscope of XL30 type (Netherland).

The structural and morphological characterization of Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ NPs were performed by measuring SEM using a Philips XL30 scanning electron microscope (Fig. 4).

TEM micrographs provide more accurate information on the particle size, morphology and loading of Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ NPs. These nanoparticles which consist of relatively small, nearly spherical particles, with an average size of 50 nm, are much smaller than the sizes obtained from the XRD measurements (Fig.5).

Herein we wish to report a simple, efficient, and chemoselective method for the protection of aromatic compounds with acetic anhydride by using γ-Fe$_2$O$_3$@HAp-Ni^{2+} under solvent free conditions In the first, the catalytic effect of γ-Fe$_2$O$_3$@HAp-Ni^{2+} on the condensation reaction of benzaldehyde and acetic anhydride compound under solvent-free conditions described. The reaction in the without of catalyst in 5%
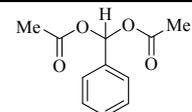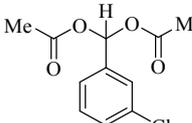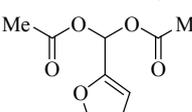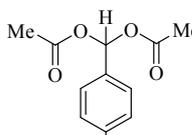
yield within 24 hours (Table 1, Entry 1), but in the presence of γ-Fe$_2$O$_3$@HAp-Ni^{2+} catalyst, reaction time was increased and the mixture of various 1,1-diacetates were produced. With used about 0.1 mol% of γ-Fe$_2$O$_3$@HAp-Ni^{2+} the reaction took longer time and low yield (Table 1, Entry 6). To improve the yield, the same rea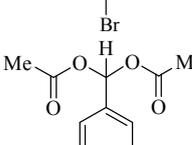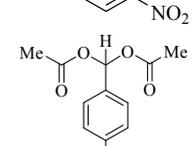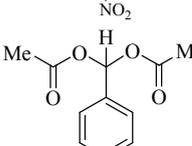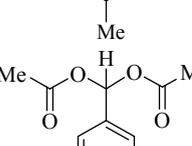ction was carried out in the presence of a catalytic amount of 0.01 mol% surprisingly, a significant improvement was observed and the excellent yield was dramatically increased to 99% (Table 1, Entry 2).

The use of this solvent-free conditions approach is better, because when the reaction is carried out in solvent including ethanol, water, mixture water-ethanol, and acetonitrile and it's at room temperature not improve the yields and it took longer reaction time 70–100 min (Table 1, Entries 1-7). Thus we have optimized the reaction condition at room temperature for 10 min and in the presence of a catalytic amount of 0.01 mol%, under solvent free condition (Table 2).

The results listed in Table 3 show that aldehydes aromatic and aliphatic reacts smoothly with acetic anhydride compound to afford the corresponding 1,1-diacetates that all these products are good to excellent of yield and reaction time. All the reactions were completed within 5-25 min with high yields (89–99 %). When the reaction was carried out using aromatic aldehydes we obtained good to excellent yields and reaction time better (Table 3, Entries 1, 5, 11, and 15). The powerful electron-releasing substituent Ome slightly decreased the yield and increased the reaction time (Table 3, Entry 14).

As it can be seen in Table 4, γ-Fe$_2$O$_3$@HAp-Ni^{2+} as a catalyst was afforded good results in comparison to the other catalysts.

Table 3. Conversion of aldehydes to acylals using γ-Fe$_2$O$_3$@HAp-Ni^{2+} under solvent-free condition at room temperature

Entry	Product	Time (min)	Yield(%)[a]	m.p. °C (Found)
1		10	99	42-44
2		7	95	60-62
3		8	96	49–51
4		20	95	63-65
5		8	97	95-96
6		20	92	91-93
7		15	94	129–131
8		10	95	81-82
9		8	96	128–130
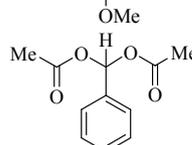
[a] isolated yield.

Catalyst reusability is of major importance for large scale operations and an industrial point of view. The recovery and reusability of the catalyst were studied using benzaldehyde, acetic anhydride as model reaction. Since the catalyst can be separated from the reaction mixture using an external magnetic field, it was recovered with a simple magnet after the dilution of the reaction mixture with ethanol. The catalyst was consecutively reused five times without any noticeable loss of its catalytic activity (Table 4).

Table 3. Conversion of aldehydes to acylals using γ-Fe$_2$O$_3$@HAp-Ni^{2+} under solvent-free condition at room temperature
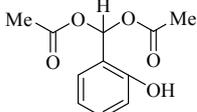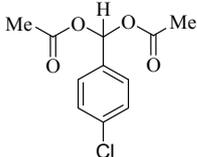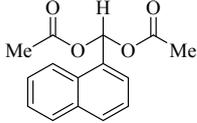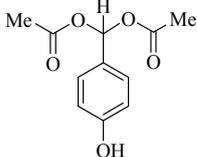
10		10	90	103-104
11		5	99	79-81
12		10	93	98-100
13		15	90	91-92
14		2	89	Oil
15		15	97	90-91
16		25	89	Oil
17		15	84	181-182
18		10	75	Oil
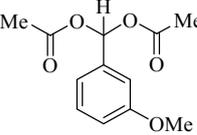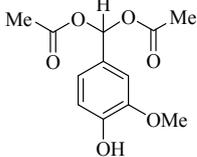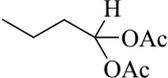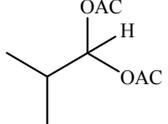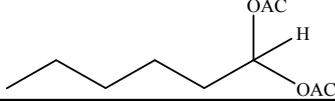
^{a} isolated yield.

Table 4. Comparison of catalytic ability of catalysts.

Entry	Catalyst/solvent/temperature	Reaction time (min)	Yield %	Ref.
1	SBSA/S.f^a/r.t.^{b}	4	98	41
2	CoPy$_2$Cl$_2$/ S.f/r.t.	3	98	42
3	SPDTSA/S.f/r.t.	4	94	43
4	RHA-SO$_3$H/ S.f/r.t.	0.5	93	44
5	SBA-15-Ph-PrSO$_3$H/H$_2$O/reflux	60	100	45
6	γ-Fe$_2$O$_3$@HAp-Ni^{2+}/S.f/r.t.	10	99	This work

^{a} Solvent free condition, ^{b} Room temperature.

Table 5. The catalytic activity of γ-Fe$_2$O$_3$@HAp-Ni^{2+} in 5 cycles

Run	1	2	3	4	5
Yield (%)	99	97	97	93	90

Conclusion

In this research, Ni^{2+} supported on hydroxyapatite-core-shell magnetic γ-Fe$_2$O$_3$ nanoparticles is a chemoselective and highly efficient catalyst for the formation of acylals from aldehydes. The advantages of the present procedure are its simplicity of operation, very short reaction times in comparison to the other procedures, and the high yields of products. In this way, the catalyst can be easily recovered by simple magnetic decantation and reused several times with no loss of activity.

References

1. Chikazumi S., Taketomi S., Ukita M., Mizukami M., Miyajima H., Setogawa M., Kurihara Y., Physics of magnetic fluids. *J. Magn. Magn. Mater* **65**:245-251 (1987).
2. Nemati F., Saeedirad R., Nano-Fe$_3$O$_4$ encapsulated-silica particles bearing sulfonic acid groups as a magnetically separable catalyst for green and efficient synthesis of functionalized pyrimido[4,5-b]131erminal131131 and indeno fused pyrido[2,3-d]pyrimidines in water. *Chin. Chem. Lett* **24**:370–372 (2013).
3. Maleki A., Fe$_3$O$_4$/SiO$_2$ nanoparticles: an efficient and magnetically recoverable nanocatalyst for the one-pot multicomponent synthesis of diazepines, *Tetrahedron* **68**:7827–7833 (2012).
4. Gupta A. K., Gupta M., Synthesis and surface engineering of iron oxide nanoparticles for biomedical applications. *Biomaterials* **26**: 3995-4021 (2005).
5. Mornet S., Vasseur S., Grasset F., Verveka P., Goglio G., Demourgues A., Portier J., Pollert E., Duguet E., Magnetic nanoparticle design for medical applications. *Prog. Solid State Chem* **34**:237-247 (2006).
6. Li Z., Wei L., Gao M. Y., Lei H., One-pot reaction to synthesize biocompatible magnetite nanoparticles. *Adv. Mater* **17**:1001-1005 (2005).
7. Hyeon T., Chemical synthesis of magnetic nanoparticles. *Chem. Commun* **8**: 927-934 (2003).
8. Elliott D. W., Zhang W.X., Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environ. Sci. Technol* **35**:4922-4926 (2001).
9. Takafuji M., Ide S., Ihara H., Xu Z., Preparation of poly(1-vinylimidazole)-grafted magnetic nanoparticles and their application for removal of metal ions. *Chem. Mater* **16**: 1977-1983 (2004).
10. Karaoğlu E., Baykal A., Senel M., Sözeri H., Toprak M. S., Synthesis and characterization of Piperidine-4-carboxylic acid functionalized Fe$_3$O$_4$ nanoparticles as a magnetic catalyst for Knoevenagel reaction. *Mater. Res. Bull* **47**:2480-2486 (2012).
11. Zhang Y., Xia C., Magnetic hydroxyapatite-encapsulated γ-Fe$_2$O$_3$ nanoparticles functionalized with basic ionic liquids for aqueous Knoevenagel condensation. *Appl. Catal. A: General* **366**:141-147 (2009).
12. Kiasat A. R., Nazari S., Magnetic nanoparticles grafted with β-cyclodextrin–polyurethane polymer as a novel nanomagnetic polymer brush catalyst for nucleophilic substitution reactions of benzyl halides in water. *J. Mol. Catal. A: Chem* **365**:80-86 (2012).
13. Kooti M., Afshari M., Phosphotungstic acid supported on magnetic nanoparticles as an efficient reusable catalyst for epoxidation of alkenes. *Mater. Res. Bull* **47**:3473 (2012).
14. Kassaee M. Z., Masrouri H., Movahedi F., Sulfamic acid-functionalized magnetic Fe$_3$O$_4$ nanoparticles as an efficient and reusable catalyst for one-pot synthesis of α-amino nitriles in water. *Appl. Catal. A: General* **395**:28-33 (2011).
15. Abu-Reziq R., Wang D., Post M., Alper H., Platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles: selective hydrogenation catalysts. *Adv. Synth. Catal* **349**:2145-2150 (2007).
16. Jiang Y. Y., Guo C., Xia H. S., Mahmood I., Liu C. Z., Liu H. Z., Magnetic nanoparticles supported ionic liquids for lipase immobilization: Enzyme activity in catalyzing esterification. *J. Mol. Catal. B: Enzym* **58**:103-109 (2009).
17. Zheng X. X., Luo S. Z., Zhang L., Cheng J. P., Magnetic nanoparticle supported ionic liquid catalysts for CO$_2$ cycloaddition reactions. *Green Chem* **11**:455-458 (2009).
18. Taber A., Kirn J. B., Jung J. Y., Ahn W. S., Jin M. J., Highly Active and Magnetically Recoverable Pd-NHC Catalyst Immobilized on Fe$_3$O$_4$ Nanoparticle-Ionic Liquid Matrix for Suzuki Reaction in Water. *Synlett* **15**:2477–2482 (2009).
19. Zhang Q., Su H., Luo J., Wei Y. Y., A magnetic nanoparticle supported dual acidic ionic liquid: a "quasi-homogeneous" catalyst for the one-pot synthesis of benzoxanthenes. *Green Chem*. **14**:201-208 (2012).
20. 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 131erminal diacetates. *J. Org. Chem* **48**:1765-1767 (1983)
21. Snider B. B., Amin S. G., An international journal for rapid communication of synthetic organic chemistry. *Synth. Commun* **8**:117-125 (1978).
22. Heerden F. R. V., Huyser J. J., Bradley W. D., Holzapfel C. W., Palladium-catalysed substitution reactions of 131erminal allylic diacetates. *Tetrahedron Lett* **39**: 5281-5284 (1998).
23. Sandberg M., Sydnes L. K., The chemistry of acylals. Part II. Formation of nitriles by treatment of acylals with trimethylsilyl azide in the presence of a Lewis acid. *Tetrahedron Lett* **39**:6361-6364 (1998).
24. Sandberg M., Sydnes L. K., The chemistry of acylals. 3. Cyanohydrin esters from acylals with cyanide reagents. Org. Lett **2**:687-689 (2000).
25. Sydness L. K., Sandberg M., The chemistry of acylals. Part I. The reactivity of acylals towards Grignard and organolithium reagents. *Tetrahedron* **53**:12679-12690 (1997).

26. Yadav J. S., Reddy B. V. S., Srihari P., Scandium triflate catalyzed allylation of acetals and gem-aiacetates: a facile synthesis of homoallyl ethers and acetates. *Synlett* **5**:673-675 (2001).

27. Frick J. G., Harper R. J., Acetals as crosslinking reagents for cotton. *J. Appl. Polym. Sci* **29**:1433-1447 (1984).

28. Shelke K., Sapkal S., Kategaonkar A., Shingate B., Shingare M. S., An efficient and green procedure for the preparation of acylals from aldehydes catalyzed by alum [Kal(SO$_4$)$_2$.12H$_2$O].   *South Afr. J. Chem* **62**:109-112 (2009).

29. Jin T. S., Sun G., Li Y. W., Li T. S., An efficient and convenient procedure for the preparation of 1,1-diacetates from aldehydes catalyzed by H$_2$NSO$_3$H. *Green Chem* **3**:255-256 (2002).

30. Firouzabadi H., Iranpoor N., Amani K., Heteropoly acids as heterogeneous catalysts for thioacetalization and transthioacetalization reactions. *Synthesis* **1**:59-60 (2002).

31. Karimi B., Seradj H., Ebrahimian G. R., Mild and efficient conversion of aldehydes to 1,1-diacetates catalyzed with N-bromosuccinimide (NBS). *Synlett* **5**:623-624 (2000).

32. Roy S.C., Banerjee B., A mild and efficient method for the chemoselective synthesis of acylals from aldehydes and their deprotections 132erminal132 by ceric ammonium nitrate. *Synlett* **10**:1677-1688 (2002).

33. Pourmousavi S. A., Zinati Z., H$_2$SO$_4$-silica as an efficient and chemoselective catalyst for the synthesis of acylal from aldehydes under solvent-free conditions. *Turk J Chem* **33**:385-392 (2009).

34. Romanelli G. P., Thomas H. J., Baronettic G. T., Autino J. C., Solvent-free catalytic preparation of 1,1-diacetates from aldehydes using a Wells–Dawson acid (H$_6$P$_2$W$_{18}$O$_{62}$·24H$_2$O). *Tetrahedron Lett* **44**:1301-1303 (2003).

35. 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* **60**:3675-3679 (2004).

36. 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* **30**:3913-3917

37. Li T.S., Zhang Z. H., Gao Y. J., A rapid preparation of acylals of aldehydes 132erminal132 by Fe^{3+} -montmorillonite, *Synth. Commun* **28**:4665-4671 (1998).

38. 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* **43**:2709-2711 (2002).

39. Kumar P., Hedge V. R., Kumar T. P., An efficient synthesis of diacetates from aldehydes using beta zeolite. *Tetrahedron Lett* **36**:601-602 (1995).

40. Sajjadifar S., Abbasi Z., Rezaee Nezhad E., Rahimi Moghadam M., Karimian S., Miri S., Ni^{2+} supported on hydroxyapatite-core-shell γ-Fe$_2$O$_3$ nanoparticles: a novel, highly efficient and reusable lewis acid catalyst for the regioselective azidolysis of epoxides in water. *J Iran Chem Soc* **11**:335-340 (2014).

41. Sajjadifar S., Rezayati S., Synthesis of 1,1-diacetates 132erminal132 by silica-supported boron sulfonic acid under solvent-free conditions and ambient temperature. *Chemical Papers* **68** (4):531–539 (2014).

42. Rezayati S., Erfani Z., Rezayati S., Hajinasiri R., Rekavandi M., Dipyridine cobalt chloride as an efficient and chemoselective catalyst for the synthesis of 1,1-diacetates under solvent-free conditions. *Iran. Chem. Commun* **2**:77-86 (2014).

43. Nouri Sefat M., Deris A., Niknam, K. Preparation of silica-bonded propyl-diethylene-triamine-N-sulfamic acid as a recyclable catalyst for chemoselective synthesis of 1,1-diacetates. *Chin. J. Chem* **29**:2361–2367 (2011).

44. Shirini F., Mamaghani M., Seddighi M., Sulfonated rice husk ash (RHA-SO$_3$H): A highly powerful and efficient solid acid catalyst for the chemoselective preparation and deprotection of 1,1-diacetates. *Catal. Commun* **36**:31–37 (2013).

45. Zareyee D., Moosavi S. M., Alaminezhad A., Chemoselective synthesis of 132erminal diacetates (acylals) usingeco-friendly reusable propylsulfonic acid based nanosilica(SBA-15-Ph-PrSO$_3$H) under solvent-free conditions. *J. Mol. Catal. A: Chem* 378:227– 231(2013).