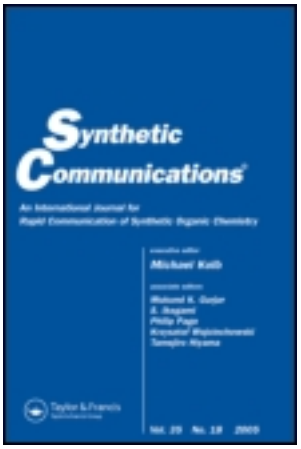


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

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

Phosphomolybdic Acid (PMA) Catalyzed Highly Efficient and Rapid Synthesis of β-Enaminones

K. Nagaiah [a], K. V. Purnima [a], D. Sreenu [a], S. Jhansi [a], R. Srinivasa Rao [a] & J. S. Yadav [a]

[a] Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad, India

Accepted author version posted online: 20 Jul 2011.Published online: 17 Oct 2011.

To cite this article: K. Nagaiah , K. V. Purnima , D. Sreenu , S. Jhansi , R. Srinivasa Rao & J. S. Yadav (2012) Phosphomolybdic Acid (PMA) Catalyzed Highly Efficient and Rapid Synthesis of β-Enaminones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:4, 461-468, DOI: 10.1080/00397911.2010.524339

To link to this article: http://dx.doi.org/10.1080/00397911.2010.524339

Synthetic Communications®, 42: 461–468, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.524339

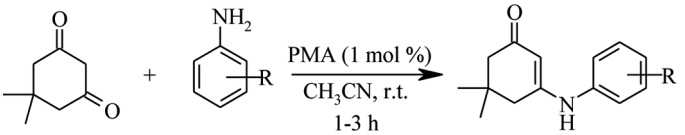
Taylor & Francis
Taylor & Francis Group

PHOSPHOMOLYBDIC ACID (PMA) CATALYZED HIGHLY EFFICIENT AND RAPID SYNTHESIS OF β-ENAMINONES

K. Nagaiah, K. V. Purnima, D. Sreenu, S. Jhansi, R. Srinivasa Rao, and J. S. Yadav

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad, India

GRAPHICAL ABSTRACT



Abstract β-*Enamino derivatives have been synthesized by the condensation of amines and* β-*dicarbonyl compounds in the presence of 1 mol% of phosphomolybdic acid (PMA) at room temperature in good to excellent yields.*

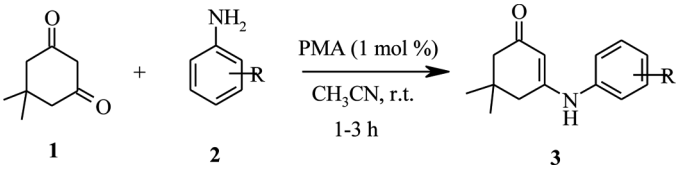
Keywords Amines; di carbonyl compounds; β-enaminones; phosphomolybdic acid

INTRODUCTION

β-Enamino compounds are important functionalized building blocks for the synthesis of a variety of valuable biologically active heterocyclic compounds,[1] which are important intermediates in the synthesis of pharmaceuticals,[2] amino acids,[3a–e] peptides,[3f] and alkaloids.[3g,h] Because of the importance of these compounds as intermediates in organic synthesis, a number of synthetic methods have been developed for their synthesis, including the reaction of amines and 1,3-dicarbonyl compounds supported on silica with microwave irradiation,[4] silica-supported perchloric acid,[5] $NaAuCl_4 \cdot 2H_2O$,[6] $Zn(ClO_4)_2 \cdot 6H_2O$,[7] $CeCl_3 \cdot 7H_2O$,[8] bismuth(III) triflouroacetate,[9] scandium(III) triflate,[10] erbium(III) triflate[11] or zirconium tetra chloride,[12] cyclization of amino acids,[13] yetterbium(III) triflate,[14a] and ionic liquids.[15] Recently, tungstophosphoric acid (PW) supported on different metal oxides (TiO_2, g-Al_2O_3, K-10, and KSF) and activated carbon were used in the synthesis of enaminones.[16] In addition, these compounds have been prepared by direct condensation of β-dicarbonyl compounds and primary amines under solvent-free

Received May 21, 2010.

Address correspondence to K. Nagaiah, Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad-500007, India. E-mail: nagaiah@iict.res.in



Scheme 1. Synthesis of β-enamine from β-carbonyl compound with amine.

conditions.[14b] However, these methods may suffer from one or more disadvantages such as the use of expensive or less readily available reagents, vigorous reaction conditions, longer reaction times, unsatisfactory yields, or the use of toxic solvents that limit these methods to small-scale synthesis. Because of the importance of these compounds in organic synthesis, the development of facile and "green" synthetic methods to the β-enaminones under mild reaction conditions is still worthwhile.

Heteropoly acids (HPAs) are environmentally, commercially, and economically feasible solid acids because of their catalytic reactivies, ease of handling, cleaner reactions in comparison to conventional catalysts, nontoxicity, and experimental simplicity and hence regarded as green catalysts. Among the HPAs, phosphomolybdic acid (PMA) is an inexpensive, commercially available catalyst. It is a new type of acid that is different from the traditional Lewis acids such as $AlCl_3$, $BF_3 \cdot OEt_2$, metal halides, and metal triflates. Therefore, in recent years, PMA has been exploited as a promising and selective reagent for a variety of functional group transformations, especially as a HPA in dehydration of alcohols,[17] tetrahedropyranylation,[18] Friedel–Crafts reactions,[19] aza-Diels–Alder reactions,[20] aziridinization of olefines,[21] ring opening of aziridines,[22] and synthesis of homoallylic amines.[23] However, there is no report of the application of PMA as catalyst for the direct one-pot condensation of β-dicarbonyl compounds with amines to produce β-enaminones.

As part of our program[20] in developing new selective, environmental friendly, commercial, and economical methodologies for the synthesis of fine chemicals, we were interested to find another enamination reaction. Herein we describe an efficient method for the condensation of β-dicarbonyls with amines (aliphatic and aromatic) in acetonitrile to afford enaminones in good to excellent yields using PMA as

Table 1. Optimization of the catalytic and solvent conditions for the reaction of dimidone **1** with aniline **2a**[a]

No.	Catalyst (mol%)	Solvent	Time (h)	Yield[b] (%)
1	1	Tolune	1.5	85
2	1	DCM	3.0	68
3	1	THF	3.0	76
4	0.5	CH_3CN	1.0	87
5	1	〃	〃	92
6	2	〃	〃	88
7	5	〃	〃	87

[a]Reaction conditions: dimidone (1 mmol), aniline (1 mmol), and solvent (5 ml).
[b]Isolated and unoptimized yields.

catalyst. Accordingly, β-dicarbonyl compound **1** with amine **2** in the presence of 1 mol% of PMA in acetonitrile to get the corresponding β-enamino compound **3** in 92% yield (Scheme 1) is described.

Initially we made a systematic study of this reaction for catalytic evolution of PMA for the reaction of β-dicarbonyl compound **1** (dimedone) and aniline **2a** with various solvents with different catalyst loads (Table 1). The best result was obtained with 1 mol% of the catalyst in acetonitrile as the solvent in terms of reaction time and yields.

RESULTS AND DISCUSSIONS

To investigate the scope of the PMA-catalyzed synthesis of β-enaminones, the reaction between dimedone and various amines was examined, and the results are summarized in Table 2. To show the efficacy of this method, several aromatic amines containing electron-withdrawing groups (such as chloro, fluoro, trifluoromethyl, nitro groups) and electron-donating groups (such as alkyl, aryl, methoxy) were treated with dimedone to afford the corresponding enaminones in good to excellent yields. This clearly demonstrates that the electronic nature of substituents of the aromatic ring did not show any obvious effects in terms of yields under these reaction conditions. Interestingly, aliphatic primary amines reacted more efficiently than aromatic amines with β-dicarbonyl compounds to afford the corresponding enaminones in excellent yields. Also this method offers several advantages such as better yields, shorter reaction times, cleaner reaction profiles, and simple experimental and workup procedures. The additional advantage of this method is the survival of various functional groups such as halo, alkyl, alkoxy, and nitro, thus allowing a wide range of substitution patterns in the substrates. All reactions were clean and efficient, and the products were obtained in good to excellent yields. The products were purified by column chromatography on silica gel and determined by ^{1}H NMR, mass, and infrared (IR) spectroscopic data.

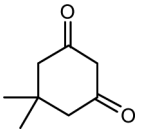
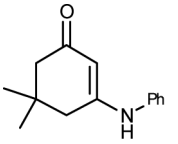
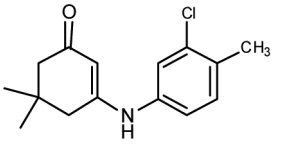
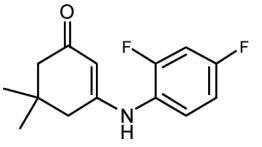
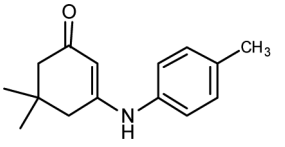
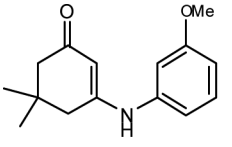
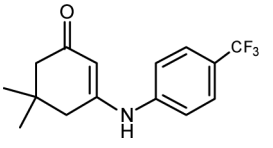
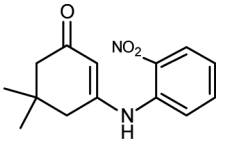
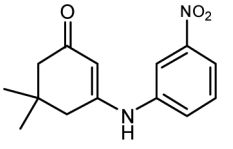
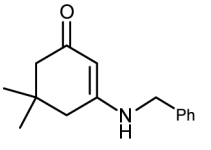
In conclusion, this procedure offers a highly efficient new procedure for the PMA-catalyzed synthesis of β-enaminones in good to excellent yields by the reaction of dimedone with aliphatic and aromatic amines. This method offers several advantages such as good yields, short reaction times, clean reaction profiles, and simple experimental and workup procedures.

EXPERIMENTAL

General Procedure

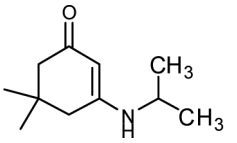
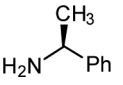
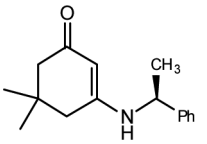
A mixture of dimedone (1 mmol), amines (1 mmol), and phosphomolybdic acid (1 mol%) in CH_3CN (5 ml) was stirred at room temperature for an appropriate time. After completion of the reaction as indicated by thin-layer chromatography (TLC), the reaction mixture was extracted with EtOAc (3×5 ml), and the organic layer was washed with water and brine and dried over Na_2SO_4. The reaction mixture was concentrated in vacuum, and the residue was purified by column chromatography to afford the corresponding pure β-enamino compounds.

Table 2. PMA-catalyzed synthesis of enamino compounds

Entry	Dicarbonyl compound **1**	Amine ($R\text{-}NH_2$) **2**	Product[a] **3**		Time (h)	Yield (%)[b]
a		R=Ph–		**3a**	1.5	92
b	〃	3-CI-4-CH_3-C_6H_3–		**3b**	2.0	90
c	〃	2,4-Difluoro-C_6H^3-		**3c**	3.0	87
d	〃	4-CH_3-C_6H_4–		**3d**	1.5	89
e	〃	3-CH_3O-C_6H_4–		**3e**	1.0	92
f	〃	4-CF_3-C_6H_4–		**3f**	3.0	87
g	〃	2-NO_2-C_6H_4–		**3g**	2.5	85
h	〃	3-NO_2-C_6H_4–		**3h**	2.0	83
i	〃	Ph-CH_2–		**3i**	1.0	97

(*Continued*)

Table 2. Continued

Entry	Dicarbonyl compound **1**	Amine (R-NH_2) **2**	Product[a] **3**		Time (h)	Yield (%)[b]
j	〃	CH_3-$CH(CH_3)$–		**3j**	1.0	97
k	〃			**3k**	1.0	95

[a]All products were characterized by ^{1}H NMR, IR, and mass spectroscopy.
[b]Isolated and unoptimized yields.

Spectral Data for Selected Compounds

5,5-Dimethyl-3-phenylamino-cyclohex-2-enone (3a). Yellow solid; mp: 115–117 °C; IR (KBr): ν_{max} 3236, 3060, 2953, 2888, 1629, 1599, 1571, 1492, 1446, 1241, 1150, 763, 706, 605, 519 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.10 (s, 2H), 2.35 (s, 2H), 5.50 (s, 1H), 7.00–7.20 (m, 3H), 7.25–7.40 (m, 2H), 8.30–8.40 (brs, 1H, NH); EIMS: m/z (%): 215 (M^+), 159, 144, 130, 118, 93, 92, 77, 65, 39.

3-(3-Chloro-4-methyl-phenylamino)-5,5-dimethyl-cyclohex-2-enone (3b). Yellow solid; mp: 210–212 °C; IR (KBr): ν_{max} 3219, 2957, 2927, 1726, 1571, 1516, 1462, 1274, 1149, 786, 727 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.10 (s, 2H), 2.22 (s, 3H), 2.40 (s, 2H), 4.80 (s, 1H), 7.00–7.20 (m, 2H,), 7.30 (d, $J = 7.8$ Hz, 1H,), 8.50 (brs, 1H, NH); EIMS: m/z (%): 263 (M^+), 221, 167, 149, 95, 69, 57.

3-(2,4-Difluoro-phenylamino)-5,5-dimethyl-cyclohex-2-enone (3c). Yellow solid; mp: 192–194 °C; IR (KBr): ν_{max} 3240, 3051, 2959, 2891, 1607, 1578, 1505, 1424, 1244, 1142, 961, 861, 815, 723, 656 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.10 (s, 2H), 2.38 (s, 2H), 5.00 (s, 1H), 6.90 (m, 2H), 7.25 (m, 1H), 8.20 (brs, 1H, NH); EIMS: m/z(%): 251 (M^+), 195, 155, 141, 121, 113, 93, 66, 39.

5,5-Dimethyl-3-*p*-tolylamino-cyclohex-2-enone (3d). Yellow solid; mp: 202–204 °C; IR (KBr): ν_{max} 3243, 3183, 3057, 2954, 1609,1576, 1516, 1409, 1275, 1239, 1145, 810, 715 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.10 (s, 2H), 2.34 (s, 5H), 5.35 (s, 1H), 7.00–7.10 (m, 4H), 8.20 (brs, 1H, NH); EIMS: m/z (%): 229 (M^+), 199, 172, 143, 130, 106, 91, 77, 55, 38.

3-(3-Methoxy-phenylamino)-5,5-dimethyl-cyclohex-2-enone (3e). Yellow solid; mp: 188–190 °C; IR (KBr): ν_{max} 3257, 3034, 2957, 1580, 1539, 1490, 1430, 1368, 1248, 1151, 1044, 778, 700 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 6H), 2.10 (s, 2H), 2.32 (s, 2H), 3.75 (s, 3H), 5.50 (s, 1H), 6.55–6.75 (m, 3H), 7.15 (t, $J = 8.2$ Hz, 1H), 8.30 (brs, 1H, NH); EIMS: m/z (%): 245 (M^+), 230, 95, 69, 55.

5,5-Dimethyl-3-(4-trifluoromethyl-phenylamino)-cyclohex-2-enone (3f). Brown solid; mp: 201–203 °C; IR (KBr): ν_{max} 3244, 3183, 3105, 3047, 2959, 1614, 1581, 1525, 1413, 1327, 1109, 855, 811, 697 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.12 (s, 2H), 2.38 (s, 2H), 5.60 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 8.75 (brs, 1H, NH); EIMS: m/z (%): 283 (M^+), 240, 227, 198, 141, 68, 57.

5,5-Dimethyl-3-(2-nitro-phenylamino)-cyclohex-2-enone (3g). Yellow solid; mp: 163–165 °C; IR (KBr): ν_{max} 3236, 3179, 3022, 2955, 1611, 1577, 1521, 1353, 1240, 1144, 860, 781, 655 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.15 (s, 2H), 2.42 (s, 2H), 5.60 (s, 1H), 7.20 (m, 1H), 7.60 (d, $J = 7.2$ Hz, 2H), 8.10 (d, $J = 8.2$ Hz, 1H), 8.70 (brs, 1H, NH); EIMS: m/z (%): 260 (M^+), 234, 206, 177, 162, 133, 95, 84, 56.

5,5-Dimethyl-3-(3-nitro-phenylamino)-cyclohex-2-enone (3h). Yellow solid; mp: 172–174 °C; IR (KBr): ν_{max}: 3442, 3259, 3195, 3118, 3064, 2958, 1614, 1578, 1535, 1352, 1263, 1241, 1146, 795, 677 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.10 (s, 6H), 2.18 (s, 2H), 2.40 (s, 2H), 5.60 (s, 1H), 7.30–7.40 (m, 2H), 7.90 (m, 1H), 8.00 (m, 1H), 8.80 (brs, 1H, NH); EIMS: m/z (%): 260 (M^+), 231, 203, 195, 141, 97, 83, 55.

3-Benzylamino-5,5-dimethyl-cyclohex-2-enone (3i). Yellow solid; mp: 126–128 °C; IR (KBr): ν_{max}: 3224, 3030, 2954, 2866, 1594, 1498, 1362, 1277, 1230, 1148, 999, 873, 772, 728, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 6H), 2.00 (s, 2H), 2.25 (s, 2H), 4.25 (m, 2H), 4.85 (s, 1H), 7.10–7.15 (brs, 1H, NH), 7.20–7.40 (m, 5H); EIMS: m/z (%): 229 (M^+), 169, 155, 141, 128, 115, 91, 69, 57, 41.

3-Isopropylamino-5,5-dimethyl-cyclohex-2-enone (3j). White solid; mp: 136–138 °C; IR (KBr): ν_{max} 3266, 3073, 2954, 2924, 2862, 1543, 1430, 1378, 1248, 1177, 1153, 797, 695 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 6H), 1.19 (s, 3H), 1.21 (s, 3H), 2.05 (s, 2H), 2.15 (s, 2H), 3.55–3.56 (m, 1H), 4.95 (s, 1H), 6.35–6.45 (brs, 1H, NH); EIMS: m/z (%): 181 (M^+), 180, 165, 152, 138, 125, 110, 96, 82, 77, 55, 41.

5,5-Dimethyl-3-(1-phenyl-ethylamino)-cyclohex-2-enone (3k). Yellow solid; mp: 106–108 °C; IR (KBr): ν_{max} 3270, 3055, 2958, 2924, 2862, 1600, 1536, 1447, 1376, 1249, 1150, 1124, 760, 698 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$): δ 1.05 (s, 6H), 1.44 (d, $J = 7.17$ Hz, 3H), 2.00 (s, 2H), 2.25 (s, 2H), 4.35–4.45 (m, 1H), 4.71 (s, 1H), 6.95–7.10 (brs, 1H, NH), 7.15–7.35 (m, 5H); EIMS: m/z (%): 243 (M^+), 157, 105, 83, 77, 41.

ACKNOWLEDGMENTS

K. V. P., D. S., and R. S. R. thank CSR and S. J. thanks UCG for awarding the fellowships.

REFERENCES

1. (a) Boyd, G. V. In *The Chemistry of Amidines and Imidates*, vol. 2; S. Patai, Z. Rappoport, (Eds.); John Wiley & Sons: Chichester, New York, 1991, 339; (b) Spivey, A. C.; Srikaran, R.;

Diaper, C. M.; Turner, D. J. Traceless solid-phase synthesis of 2-substituted pyrimidines using an "off-the-shelf" chlorogermane-functionalised resin. Org. *Biomol. Chem.* **2003**, 1638; (c) Hassneen, H. M.; Abdallah, T. A. New routes to pyridino[2,3-d]pyrimidin-4-one and pyridino-[2,3-d]triazolino[4,5-a]pyrimidin-5-one derivatives. *Molecules* **2003**, 333.

2. (a) Sweeney, T. R.; Strube, R. E. In *Burger's Medicinal Chemistry, Part II*, 4th ed.; M. E. Wolff (Ed.); Wiley: New York, 1979; p. 333; (b) Foster, J. E. : Nicholson, J. M.; Butcher, R.; Stables, J. P.; Edafiogho, I. O.; Goodwin, A. M.; Henson, M. C.; Smith, C. A.; Scott, K. R. Synthesis, characterization and anticonvulsant activity of enaminones, part 6: Synthesis of substituted vinylic benzamides as potential anticonvulsants. *Bioorg. Med. Chem.* **1999**, 2415.
3. (a) Palmieri, G.; Cimarelli, C. Stereoselective reduction of Enantiopure β-Enamino esters by hydride: A convenient synthesis of both Enantiopure β-amino esters. *J. Org. Chem.* **1996**, 5557; (b) Bartoli, G.; Cimarelli, C.; Marcantoni, E.; Palmieri, G.; Petrini, M. Chemo- and diastereoselective reduction of β-Enamino esters: A convenient synthesis of both cis- and trans-γ-Amino alcohols and β-amino esters. *J. Org. Chem.* **1994**, 5328; (c) Lubell, W. D.; Kitamura, M.; Noyori, R. Enantioselective synthesis of p-Amino acids based on BINAP-Ruthenium(II) catalyzed hydrogenation. *Tetrahedron: Asymmetry* **1999**, 10915; (d) Potin, D.; Dumas, F.; D'Angelo, J. New chiral auxiliaries: Their use in the asymmetric hydrogenation of beta-acetamidocrotonates. *J. Am. Chem. Soc.* **1990**, 3483; (e) Cimarelli, C.; Palmiri, G.; Volpini, E. An improved synthesis Of β–aminoacids. *Synth. Com.* **2001**, 2943; (f) Beholz, L. G.; Benovsky, R.; Ward, D. L.; Barta, N. S.; Stille, J. R. Formation of dihydropyridone- and pyridone-based peptide analogs through Aza-Annulation of β-Enamino ester and amide substrates with α-Amido acrylate derivatives. *J. Org. Chem.* **1997**, 1033; (g) David, O.; Blot, J.; Bellec, C.; Fargeau-bellassoue, M. C.; Haviari, G.; Celerier, J. P.; Lhommet, G.; Gramain, J. C.; Gardette, D. Enamino ester reduction: A short Enantioselective route to pyrrolizidine and indolizidine alkaloids. Synthesis of (+)-laburnine, (+)-tashiromine, and (−)-isoretronecanol. *J. Org. Chem.* **1999**, 3122; (h) Ferraz, H. M. C.; Pereira, F. L. C.; Leite, F. S.; Nunes, M. R. S.; Payret-Arrúa, M. E. Synthesis of N-substituted pyrrole and tetrahydroindole derivatives from alkenyl β-dicarbonyl compounds. *Tetrahedron* **1999**, 10915.
4. Rechsteiner, B.; Texier-Bollet, F.; Hamelin, J. Synthesis in dry media coupled with microwave irradiation : Application to the preparation of enaminoketones. *Tetrahedron Lett.* **1993**, 5071.
5. Das, B.; Venkateswarlu, K.; Majhi, A.; Reddy, M. R.; Reddy, K. N.; Rao, Y. K.; Ravikumar, K.; Sridhar, B. Highly efficient, mild, and chemo- and stereoselective synthesis of enaminones and enamino esters using silica-supported perchloric acid under solvent-free conditions. *J. Mol. Catal. A: Chem.* **2006**, *246*, 276.
6. Arcadi, A.; Bianchi, G.; Giuseppe, S. D.; Marinelli, F. Gold catalysis in the reactions of 1,3-dicarbonyls with nucleophiles. *Green Chem.* **2003**, *5*, 64.
7. Bartoli, G.; Bosco, M.; Locatelli, M.; Marcantoni, E.; Malchiorre, P.; Sambri, L. $Zn(ClO_4)_2 \cdot 6H_2O$ as a powerful catalyst for the conversion of β-Ketoesters into β-enamino esters. *Synlett* **2004**, 239.
8. Khodaei, M. M.; Khosropour, A. R.; Kookhazadeh, M. Enamination of β-dicarbonyl compounds catalyzed by $CeCl_3 \cdot 7H_2O$ at ambient conditions: Ionic liquid and solvent-free media. *Synlett* **2004**, 1980.
9. Khosropour, A. R.; Khodaei, M. M.; Kookhazadeh, M. A mild, efficient, and environmentally friendly method for the regio- and chemoselective synthesis of enaminones using $Bi(TFA)_3$ as a reusable catalyst in aqueous media. *Tetrahedron Lett.* **2004**, 1725.
10. Yadav, J. S.; Naveen Kumar, V.; Srinivasa Rao, R.; Diana Priyadarshini, A.; Purushothama Rao, P.; Reddy, B. V. S.; Nagaiah, K. $Sc(OTf)_3$-catalyzed highly rapid and efficient synthesis of β-enamino compounds under solvent-free conditions. *J. Mol. Catal. A. Chem.* **2006**, *256*, 234.

11. Dalpozzo, R.; De Nino, A.; Nardi, M.; Russo, B.; Procopio, A. Erbium(III) triflate: A valuable catalyst for the synthesis of aldimines, ketimines, and enaminones. *Synthesis* **2006**, 1127.
12. Lin, J.; Zhang, L. F. $ZrCl_4$-catalyzed efficient synthesis of enaminones and Enamino esters under solvent-free conditions. *Monatsh. Chem.* **2007**, 77, and references cited therein.
13. Turunen, B. J.; George, G. I. Amino acid–derived enaminones: A study in ring formation providing valuable asymmetric synthons. *J. Am. Chem. Soc.* **2006**, 8702.
14. (a) Epifano, F.; Genovese, S.; Curini, M. Ytterbium triflate–catalyzed synthesis of β-enaminones. *Tetrahedron Lett.* **2007**, 2717; (b) Vohra, R. K.; Renaud, J. L.; Bruneau, C. Tertiary 3-Aminopropenones and 3-Aminopropenoates: Their preparation, with and without Lewis acids, from secondary amines and 1,3-Diketo compounds. *Synthesis.* **2007**, 731.
15. Karthikeyan, G.; Perumal, P. T. Ionic liquid–promoted simple and efficient synthesis of _enamino esters and _enaminones from 1,3-dicarbonyl compounds: One-pot, three-component reaction for the synthesis of substituted pyridines. *Can. J. Chem.* **2005**, *83*, 1746.
16. Rafiee, E.; Mahdavi, H.; Eavani, S.; Joshaghani, M.; Shiri, F. Catalytic activity of tungstophosphoric acid supported on carriers of diverse acidity in the synthesis of enaminones. *Appl. Catal. A: Gen.* **2009**, *352*, 202.
17. Vázquez, P.; Pizzio, L.; Cáceres, C.; Blanco, M.; Thomas, H.; Alesso, E.; Finkielsztein, L.; Lantaño, B.; Moltrasio, G.; Aguirre, J. Silica-supported heteropolyacids as catalysts in alcohol dehydration reactions. *J. Mol. Catal. A: Chem.* **2000**, *161*, 223.
18. Romanelli, G.; Vázquez, P.; Pizzio, L.; Quaranta, N.; Autino, J.; Blanco, M. Cáceres. C. Phenol tetrahydropyranylation catalyzed by silica-alumina supported heteropolyacids with Keggin structure. *Appl. Catal. A: Gen.* **2004**, 163.
19. Pizzio, L. R.; Vázquez, P. G.; Cáceres, C. V.; Blanco, M. N.; Alesso, E. N.; Torviso, M. R.; Lantaño, B.; Moltrasio, G. Y.; Aguirre, J. M. C-Alkylation reactions catalyzed by silica-supported Keggin heteropolyacids. *Appl. Catal. A: Gen.* **2005**, *287*, 1.
20. Nagaiah, K.; Sreenu, D.; Srinivasa Rao, R.; Vashishta, G.; Yadav, J. S. Phosphomolybdic acid–catalyzed efficient one-pot three-component aza-Diels–Alder reactions under solvent-free conditions: A facile synthesis of trans-fused pyrano- and furanotetrahydroquinolines *Tetrahedron Lett.* **2006**, 4409.
21. Kishore Kumar, G. D.; Baskaran, S. Heteropoly acid as a novel nitrene transfer agent: A facile and practical aziridination of olefins with chloramine-T. *Chem. Commun.* **2004**, 1026.
22. Kishore Kumar, G. D.; Baskaran, S. Opening of N-tosyl aziridines with nucleophiles catalyzed by phosphomolybdic acid supported on silica gel. *Synlett.* **2004**, 1719.
23. Smitha, G.; Bruhaspathy, M.; Williamson, J. S. Phosphomolybdic acid-catalyzed efficient three-component reaction: A facile synthesis of protected homoallylic amines. *Synlett.* **2005**, 839.