Amberlyst-15®: An Efficient, Cost-Effective and Recyclable Hetero Geneous Solid Acid Catalyst for the Synthesis of β-Enaminones and β-Enamino Esters

A. Venkat Narsaiah*, A.R. Reddy, B.V.S. Reddy and J.S. Yadav

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad-500 607, India

Abstract: The β-keto carbonyl compounds rapidly react with a variety of amines in the presence of Amberlyst-15® to produce β-enamino compounds in excellent yields. The reaction conditions are very mild and applicable to a wide range of substrates and the reactions are conveniently performed at ambient temperature. The catalyst is recovered by simple filtration and reused for further reactions.

Keywords: Ion-exchange resin, 1, 3-dicarbonyls, amines, enaminones, enaminoesters.

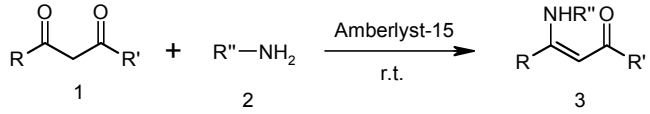
INTRODUCTION

The β-enaminone derivatives are very useful synthons for the synthesis of various biologically active heterocyclic compounds such as 1,4-dihydropyridines, pyrroles, oxazoles, pyridinones, quinolines, dibenzodiazepines, tetrahydrobenzoxazines, tetronic acids, azasteroids, (*1H*)-pyridin-2-one, pyrazolo-[1,5-a]-pyrimidine and isoxazole deriva tives which are well-known as anti-inflammatory, antitumor, antibacterial, and anti-convulsant agents [1,2]. They are versatile intermediates for the synthesis of several amino acids, amino alcohols, peptides and alkaloids [3]. Due to the wide range of utility in pharma ceutical industry, the enamination of β-dicarbonyl compounds with various amines has become an important transformation and consequently several methods have been developed for the synthesis of these compounds. Among them, the most simple and straightforward conventional method is the azeotropic removal of water by refluxing an amine and 1,3-diketone in aromatic solvents [4]. Subsequently, a variety of activators such as $InBr_3$ [5], $Zn(ClO_4)_2$ [6], I_2 [7], *p*-TSA [8], H_2SO_4 [9], $NaAuCl_4$ [10], $CeCl_3{\cdot}7H_2O$ [11], Al_2O_3, SiO_2 [12], $Sc(OTf)_3$ [13], montmorillonite-K10-microwave [14], ultra sound [15], TMS OTf [16], $BF_3.OEt_2$ [17], $HClO_4$-SiO_2 [18], ionic liquid [19], ammonium carbamate [20] and solid supported reagents under solvent-free conditions have been used to accomplish this reaction. However, many of these methods suffer from drawbacks, such as drastic reaction conditions, tedious work up procedures and unsatis factory yields, which limit their use. Therefore, the development of a simple, environ mentally benign and improved method for this transformation is in demand. A macro reticular sulfonic acid based polystyrene cation exchange resin, Amberlyst-15® is an inexpensive and commercially available solid acid catalyst, which is very familiar for various organic transformations. In recent years heterogeneous catalysts are gaining much importance due to their interesting reactivity as well as selectivity [21].

*Address correspondence to this author at the Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad-500 607, India; Fax: +91-40-27160512; E-mail: vnakkirala2001@yahoo.com

RESULTS AND DISCUSSION

As part of our ongoing program in developing various new synthetic methodologies [22] herein, we wish to present our findings on the preparation of β-enamino compounds from various amines and 1,3-dicarbonyl compounds using Amberlyst-15® as a heterogeneous solid acid catalyst as shown in the Scheme **1**.



Scheme 1.

In a typical experiment, ethylacetoacetate and benzyl amine were reacted in the presence of the catalyst Amberlyst-15® to afford the corresponding product, 3-benzylamino-but-2-enoic acid ethyl ester in 94% yield (**3a**). The reaction was completed within 2 h at room temperature in DCM. After completion of the reaction, the catalyst was separated by simple filtration and washed twice with DCM. Thus recovered catalyst was reused for further reactions successfully. The reusability of the catalyst was tested by conducting a series of reactions with the same reactants in which the first reaction yield was 94%, the second reaction yield was 92% and the third reaction yield was 92% respectively. Encouraged by the result obtained with the above reactions, we have applied this protocol to various amines such as 1-phenylethyl amine (**2b**), *n*-butyl amine (**2c**), 2-phenylethyl amine (**2d**), aniline (**2e**) and substituted anilines (**2f**) successfully. In a similar manner, we have used three different dicarbonyl compounds such as ethylacetoacetate, pentane-2,4-dione and benzylacetoacetate and reacted with the above mentioned amines successfully. In all the reactions, the catalyst Amberlist-15 was used 100 mg for 2 mmol of amine. In all the cases, the reactions were very clean and the products were obtained in very good yields. In general, all the reactions were completed within 3 hours of reaction time at room temperature in DCM. This method works well for both aromatic and aliphatic amines and the results were mentioned in the Table **1**.

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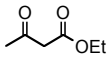
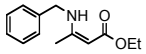
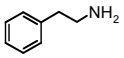
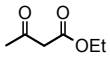
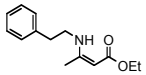
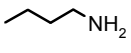
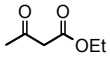
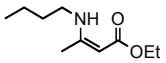
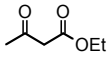
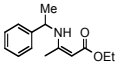
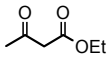
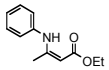
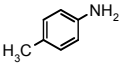
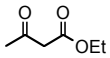
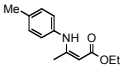
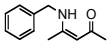
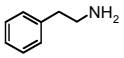
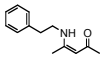
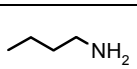
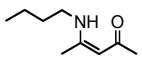
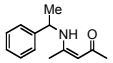
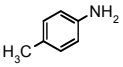
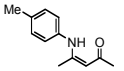
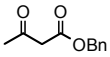
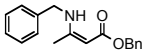
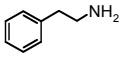
Table 1. Amberlyst-15® Catalyzed Synthesis of β-Enaminones and β-Enamino Esters

S. No.	Amine	1,3-Dicarbonyl Compound	Product (3a-3r)	Reaction Time (h)	Yield (%)
a				2.0	94
b				2.5	92
c				3.0	90
d				2.5	91
e				3.0	87
f				2.5	90
g				2.0	93
h				2.5	91
i				3.0	89
j				2.5	89
k				3.0	86
l				2.5	88
m				2.0	92
n				2.5	90
o				3.0	88
p				2.5	87
q				3.0	85
r				2.5	86

CONCLUSION

In summary, we have described an efficient and convenient method for the preparation of β-enamino compounds from 1,3-diketones and various amines using Amberlyst-15® as recyclable solid acid catalyst. This method offers significant advantages such as high reaction rates, excellent yields and the recyclability of the catalyst, which makes it quite simple, convenient and environmentally friendly process for the preparation of β-enaminones and β-enamino esters.

EXPERIMENTAL SECTION

General methods: IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectro photometer. ^{1}HNMR spectra were recorded on Bruker-300 MHz, spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectro meter operating at 70 eV.

General experimental procedure: To a mixture of β-ketoester (2.2 mmol) and benzyl amine (2 mmol) in DCM (10 ml) was added the Amberlyst-15® (100 mg). The resulting reaction mixture was stirred at room temperature for a specified time (see Table **1**) and the progress of the reaction was monitored by Thin Layer chromato graphy (TLC). After completion of the reaction as indicated by TLC, the reaction mixture was filtered and the catalyst was washed with DCM (2x10 mL). The combined filtrates were adsorbed on silica gel (60-120 mesh) and eluted with ethyl acetate-hexane mixture to obtain the pure products. All the products were confirmed by their ^{1}HNMR, IR and mass spectroscopy data.

Spectral Data for Selected Compounds

3-Benzylamino-but-2-enoic acid ethyl ester (3a): Colorless oil. IR (neat): ν 3294, 3041, 2971, 2839, 1628, 1605, 1561, 1456, 1375, 1281, 1231, 1169, 1057, 1012, 978, 846, 785, 741 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, 3H, *J* = 7.0 Hz), 1.90 (s, 3H), 4.09 (q, 2H, *J* = 7.0 Hz), 4.42 (d, 2H, *J* = 5.0 Hz), 4.50 (s, 1H), 7.20-7.40 (m, 5H), 8.98 (brs, 1H, NH). EIMS: *m/z* (%): 219 (m$^+$ 25), 178 (18), 134 (100), 106 (31), 77 (56), 52 (15).

3-Butylamino-but-2-enoic acid ethyl ester (3c): Light yellow oil. IR (neat): ν 3145, 3018, 2961, 1641, 1608, 1583, 1406, 1367, 1273, 1210, 1185, 1061, 1006, 961, 843, 755, 732 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, 3H, *J* = 6.8 Hz), 1.27 (t, 3H, *J* = 6.8 Hz), 1.90 (s, 3H), 4.09 (q, 2H, *J* = 7.0 Hz), 4.42 (d, 2H, *J* = 5.0 Hz), 4.50 (s, 1H), 7.20-7.40 (m, 5H), 8.98 (brs, 1H, NH). EIMS: *m/z* (%): 185 (m$^+$ 100), 153 (10), 140 (10), 96 (46), 71 (10), 67 (20), 55 (50), 43 (45).

3-Phenylamino-but-2-enoic acid ethyl ester (3e): Light red oil. IR (neat): ν 3261, 2980, 2853, 1695, 1653, 1619, 1596, 1497, 1441, 1385, 1359, 1271, 1231, 1164, 1093, 1059, 1023, 975, 788, 752, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.30 (t, 3H, *J* = 7.0 Hz), 1.99 (s, 3H), 4.15 (q, 2H, *J* = 7.0 Hz), 4.62 (s, 1H), 7.05-7.34 (m, 5H), 10.40 (brs, 1H, NH). EIMS: *m/z* (%): 205 (m$^+$ 10), 162 (15), 146 (10), 132 (20), 120 (18), 92 (10), 78 (100), 66 (18), 52 (25), 44 (10).

3-(4-Methylphenylamino)-but-2-enoic acid ethyl ester (3f): IR (neat): ν 3258, 3189, 2980, 2928, 1895, 1653, 1612, 1519, 1489, 1440, 1385, 1358, 1270, 1232, 1163, 1096, 1060, 1020, 975, 704 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28 (t, 3H, *J* = 7.0 Hz), 1.99 (s, 3H), 2.39 (s, 3H), 4.10 (q, 2H, *J* = 7.0 Hz), 4.60 (s, 1H), 6.98 (d, 2H, *J* = 7.0 Hz), 7.10 (d, 2H, *J* = 7.0 Hz), 10.40 (brs, 1H, NH). EIMS: *m/z* (%): 219 (m$^+$ 10), 178 (50), 176 (100), 161 (44), 147 (62), 134 (58), 109 (15), 93 (90), 91 (10), 79 (36), 67 (54), 58 (20), 44 (25).

4-Benzylamino-pent-3-en-2-one (3g): Yellowish syrup. IR (neat): ν 3423, 3142, 3029, 2961, 2852, 1606, 1579, 1507, 1458, 1351, 1294, 1210, 1167, 1030, 913, 841, 734 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.89 (s, 3H), 2.03 (s, 3H), 4.45 (d, 2H, *J* = 4.0 Hz), 5.01 (s, 1H), 7.20-7.38 (m, 5H), 11.18 (brs, 1H, NH). EIMS: *m/z* (%): 189 (m$^+$ 58), 174 (25), 146 (15), 106 (10), 91 (100), 77 (10), 65 (30), 51 (10), 43 (65).

4-Butylamino-pent-3-en-2-one (3i): Orange oil. IR (neat): ν 3453, 3172, 2963, 2938, 2839, 1618, 1608, 1569, 1472, 1351, 1289, 1204, 1137, 1027, 1006, 963, 851, 743 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.98 (t, 3H, *J* = 6.5 Hz), 1.40-1.48 (m, 2H), 1.53-1.62 (m, 2H), 1.90 (s, 3H), 1.96 (s, 3H), 3.24 (q, 2H, *J* = 6.5 Hz), 4.95 (s, 1H), 10.82 (brs, 1H, NH). EIMS: *m/z* (%): 156 (m$^+$ 55), 155 (25), 142 (100), 127 (10), 113 (15), 85 (18), 70 (10), 57 (10), 55 (12), 43 (20).

4-Phenylamino-pent-3-en-2-one (3j): Solid. Mp. 48-49 ^{0}C, IR (neat): ν 3453, 3137, 3028, 2974, 2846, 1622, 1576, 1510, 1461, 1329, 1274, 1205, 1187, 1031, 921, 856, 749 cm^{-1}.; ^{1}HNMR ($CDCl_3$): δ 0.95 (t, 3H, *J* = 6.8 Hz), 1.27 (t, 3H, *J* = 6.8 Hz), 1.90 (s, 3H), 4.09 (q, 2H, *J* = 7.0 Hz), 4.42 (d, 2H, *J* = 5.0 Hz), 4.50 (s, 1H), 7.20-7.40 (m, 5H), 8.98 (brs, 1H, NH).; EIMS: *m/z* (%): 175 (M$^+$ 15).

3-Benzylamino-but-2-enoic acid benzyl ester (3m): IR (neat): ν 3276, 3068, 2979, 2847, 1634, 1608, 1589, 1506, 1432, 1381, 1249, 1211, 1171, 1053, 1010, 968, 859, 743 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.90 (s, 3H), 4.42 (d, 1H, *J* = 5.0 Hz), 5.08 (s, 2H), 5.16 (s, 2H), 7.20-7.40 (m, 10H), 8.98 (brs, 1H, NH). EIMS: *m/z* (%): 281 (M$^+$ 10), 193 (10), 177 (40), 175 (100), 167 (35), 150 (80), 81 (75), 79 (45), 67 (30), 52 (15), 43 (100).

3-Butylamino-but-2-enoic acid benzyl ester (3o): IR (neat): ν 3239, 3057, 2938, 2846, 1619, 1581, 1510, 1432, 1324, 1267, 1253, 1134, 1083, 1011, 965, 873, 749 cm^{-1}.; ^{1}HN MR ($CDCl_3$): δ 0.98 (t, 3H, *J* = 7.0 Hz), 1.38-1.48 (m, 2H), 1.52-1.62 (m, 2H), 1.92 (s, 3H), 3.20 (q, 2H, *J* = 7.0 Hz), 3.42 (s, 1H), 5.05 (s, 2H), 7.25-7.35 (m, 5H), 8.55 (brs, 1H, NH). EIMS: *m/z* (%): 248 (M$^+$ 10), 209 (10), 193 (10), 156 (15), 142 (10), 108 (25), 99 (10), 92 (100), 78 (10), 67 (10), 52 (10), 43 (10).

3-Phenylamino-but-2-enoic acid benzyl ester (3q): IR (neat): ν 3256, 3071, 2954, 2832, 1629, 1602, 1573, 1504, 1429, 1362, 1251, 1249, 1163, 1057, 1005, 978, 863, 739 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3H), 3.42 (s, 1H), 5.15 (s, 2H), 5.18 (s, 2H), 7.10 (q, 2H, *J* = 6.5 Hz), 7.30-7.40 (m, 8H), 10.38 (brs, 1H, NH). EIMS: *m/z* (%): 267 (M$^+$ 50), 222 (18), 208 (10), 177 (20), 160 (100), 150 (15), 131 (95), 118 (98), 106 (10), 92 (96), 78 (10), 67 (10), 52 (10), 43 (10).

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REFERENCES

[1] (a) Michael, J.P.; Koning, C.B.; Hosken, G.D.; Stanbury. Reformatsky reactions with *N*-arylpyrrolidine-2-thiones: synthesis of tricyclic analogues of quinolone anti-bacterial agents. *Tetrahedron*., **2001**, *57*(47), 9635-9648. (b) Dannhardt, G.; Bauer, U.; Nowe, J. Non-steroidal anti-inflammatory agents. Part 23. Synthesis & Pharmacological activity of enaminones which inhibit both bovine cyclooxygenase & 5-lipoxygenase. *J. Prakt. Chem*., **1998**, *340*(3), 256-263.

[2] (a) Wang, Y.F.; Izawa, T.; Kobayashi, S.; Ohno, M. Stereocontrolled synthesis of (+)-negamycin from an acyclic homoallylamines by 1,3-asymmetric induction. *J. Am. Chem. Soc*., **1982**, *104*(23), 6465-6466. (b) Natalie, D.E.; Donna, S.C.; Khurana, M.; Noha, N. S.; James, P.S.; Sylvia, J.H.; Abraham, N.; Robert, S.T.; Jacqueline, A.M. Synthesis & anticonvulsant activity of enaminones: Part 7. Synthesis & anticonvulsant evaluation of ethyl-4-[(substitutedphenyl)-amino]-6-methyl-2-oxocyclohex-3-ene-1-carb oxylates & their corresponding 5-methylcyclohex-2-enone. *Eur. J. Med. Chem*., **2003**, *38*(1), 49-64.

[3] (a) Potin, D.; Dumas, F.; d'Angelo, J. New chiral auxiliaries: their use in the asym metric hydrogenation of β-acetamidocrotonates. *J. Am. Chem. Soc*., **1990**, *112*(9), 3483-3486. (b) Bartoli, G.; Cimarelli, C.; Marcantoni, E.; Palmieri, G.; Petrini, M. Chemo & diastereoselective reduction of β-enamino esters: a convenient synthesis of both *cis* & *trans*, gamma amino alcohols & β-amino esters. *J. Org. Chem*. **1994**, *59*(18), 5328-5335. (c) Palmieri, G.; Cimmerelli, C. Stereoselective reduction of enantiopure β-enamino esters by hydride: A convenient synthesis of both enantiopure β-amino esters. *J. Org. Chem*., **1996**, *61*(16), 5557-5563. (d) Ferraz, H.M.C.; Pereira, F.L.C.; Leite, F.S.; Nuns, M.R.S.; Payretarrua, M.E. Synthesis of *N*-substituted pyrrole & tetrahydroindole derivatives from alkenyl β-dicarbonyl compounds. *Tetrahedron*, **1999**, *55*(36), 10915-10924. (e) David, O.; Blot, J.; Bellec, C.; Bellassoued, M.C.F.; Haviari, G.; Celerier, J.P.; Lhommet, G.; Gramain, J.C.; Garadette, D. Enamino ester reduction: a short enantio selective route to pyrrolizidine & indolizidine alkaloids. Synthesis of (+)-Laburnine, (+)-Tashiromine & (+)-Isoretronecanol. *J. Org. Chem*., **1999**, 64(9), 3122-3131.

[4] (a) Baraldi, P.G.; Simoni, D.; Manfredini, S. An improved preparation of enamino nes from 1,3-diketones & ammonium acetate or amine acetates. *Synthesis*, **1983**, *11*, 902-903. (b) Corey, E.J.; Garner, R.H.; Hayes, A.W. Spectral studies on cyclic enamino ketones. *J. Org. Chem*., **1972**, *37*(26), 4436-4439.

[5] Zhang, Z.H.; Yin, L.; Wand, Y.M. A general & efficient method for the preparation of β-enamino ketones & esters catalyzed by $InBr_3$. *Adv. Synth. Catal*., **2006**, *348*, 184-190.

[6] Bartoli, G.; Bosco, M.; Locatelli, M.; Marcantoni, E.; Melchiorre, 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**, *2*, 239-242.

[7] Hauser, C.R.; Reynolds, G.A. Reactions of β-keto esters with aromatic amines. Synthesis of 2-&4-hydroxyquinoline derivatives. *J. Am. Chem. Soc*., **1948**, *70*(7), 2402 -2404.

[8] Hickmott, P.W.; Sheppard, G. Enamine chemistry. Part XIV. Reaction of α,β-unsaturated acid chlorides with tertiary enamino ketones & esters. *Perkin Trans* 1, **1972**, 1038-1040.

[9] Martin, D.F.; Janusonis, G.A.; Martin, B.B. Stabilities of bivalent metal complexes of some β-ketoimines. *J. Am. Chem. Soc*., **1961**, *83*(1), 73-75.

[10] Arcadi, A.; Bianchi, G.; Di Giuseppe, S.; Marinelli, F. Gold catalysis in the reactions of 1,3-dicarbonyls with nucleophiles. *Green Chem*., **2003**, *5*, 64-67.

[11] (a) Khodaei, M.M.; Khosropour, A.R.; Kookhazadeh, M. Enamination of β-di carbonyl compounds catalyzed by $CeCl_3 \cdot 7H_2O$ at ambient conditions: ionic liquid & solvent-free media. *Synlett*, **2004**, *11*,1980-1984. (b) Khodaei, M.M.; Khosropour, A.R.; Kookhazadeh, M. β-enaminones (III), (V) & (VII) are synthesized in aqueous medium. High yields, high regioselectivity, mild reaction conditions & ecological safety are the main advantages. *Russian J. Org. Chem*., **2005**, *41*, 1445-1448.

[12] Bouliet. T.T. A simple, convenient & mild synthesis of imines on alumina surface without solvent. *Synthesis*, **1985**, 679-680.

[13] Yadav, J.S.; Kumar, V.N.; Rao, R.S.; Priyadarshini, A.D.; Rao, P.P.; Reddy, B.V. S.; Nagaiah, K. $Sc(OTf)_3$ Catalyzed highly rapid & efficient synthesis of β-enamino compounds under solvent-free conditions. *J. Mol. Catal A Chem*., **2006**, *256*, 234-237.

[14] (a) Rechsteimer, B.; Boullet, F.T.; Hamelin, J. Synthesis in dry media coupled with microwave irradiation: application to the preparation of enaminoketones. *Tetrahedron Lett*., **1993**, *34*(32), 5071-5074. (b) Silva, F.C.; De Souza, M.C.B.V.; Ferreira, V.F.; Sabino, S.J.; Antunes, O.A.C. Natural clays as efficient catalysts for obtaining chiral β-enamino esters. *Catal. Commun*., **2004**, *5*(3), 151-155.

[15] (a) Valduga, C.J.; Squizani, A.; Braibante, H.S.; Braibante, M.E.F. The use of K-10/Ultrasound in the selective synthesis of unsymmetrical *β*-enamino ketones. *Synthesis*. **1998**, *7*, 1019-1022. (b) Silva, F.C.; DeSouza, M.C.B.V.; Ferreira, V.F.; Sabino, S.J.; Antunes, O.A.C. Efficient synthetic method for β-enamino esters using ultrasound. *Synthesis*, **2004**, *10*, 1557-1559.

[16] Martin, C.P.C.; Henderson, D.G.; Soeder, R.W. Synthesis of enaminones using TMS (OTf) as an activator. *Synth. Commun*., **1997**, *27*(24), 4275-4283.

[17] Stefane, B.; Polanc, S. A new regio & chemoselective approach to β-keto amides & β-enamino carboxamides *via* 1,3,2-dioxaborinanes. *Synlett*, **2004**, *4*, 698-702.

[18] Das, B.; Lu, K.V.; Majhi, A.; Reddy, M.R.; Reddy, K. N.; Rao, Y. K.; Kumar, K. R.; Sridhar, B. Highly efficient, mild & chemo & stereoselective synthesis of enaminones & enamino esters using $HClO_4$-SiO_2 under solvent-free conditions. *J. Mol. Catal A*, **2006**, *246*, 276-281.

[19] Gholap, A.R.; Chakor, N.S.; Daniel, T.; Lahoti, R.J.; Srinivasan, K.V. A remar- kably rapid regioselective synthesis of β-enaminones using SiO_2Cl in a heterogeneous as well as an ionic liquid in a homogeneous medium at room temperature. *J. Mol. Catal A*, **2006**, *245*, 37-46.

[20] Litvic, M.; Filipan, M.; Pogorelic, I.; Cepanec, I. $NH_4O_2CNH_2$: Mild, selective & efficient ammonia source for preparation of β-amino-α,β-unsaturated esters at room temperature. *Green Chem*., **2005**, *7*(11), 771-774.

[21] (a) Coppola, G.M. Amberlyst-15, a superior acid catalyst for the cleavage of acetals. *Synthesis*, **1984**, 1021-1022. (b) Ramesh, C.; Banerjee, J.; Pal, R.; Das, B. $NaHSO_4.SiO_2$ & Amberlyst-15: two efficient heterogeneous catalysts for facile synthesis of bis & tris-(1*H*-indol-3-yl)-methanes from indoles & carbonyl compounds. *Adv. Synth. Catal*., **2003**, *345*(5), 557-559. (c) Yadav, J.S.; Reddy, B.V.S.; Sekhar, K.C.; Sekar, D.G. Amber lyst-15-catalyzed novel synthesis of tetrahydropyranols. *Synthesis*, **2001**, *6*, 885-888.

[22] (a) Narsaiah, A.V.; Kumar, J.K.; Narsimha, P. A simple & efficient method for the three-component synthesis of homoallylic amines catalyzed by $In(OTf)_3$. *Synthesis*., **2010**, *10*, 1609-1612. (b) Narsaiah, A.V.; Reddy, A.R.; Rao, Y.G.; Kumar, E.V.; Praka sham, R.S.; Reddy, B.V.S.; Yadav, J.S. Mg-$CdCl_2$, A bimetallic catalyst system for the allylation of aldehydes with allyl bromide: an efficient protocol for the synthesis of homo allylic alcohols. *Synthesis*, **2008**, *21*, 3461-3464. (c) Narsaiah, A.V.; Reddy, B.V.S.; Premlatha, K.; Reddy, S.S.; Yadav, J.S. Bismuth (III) catalyzed hydrolysis of epoxides & aziridines: an efficient synthesis of *vic*-diols & β-amino alcohols. *Catal. Lett*., **2009**, *131*, 480-484. (d) Narsaiah, A.V.; Reddy, A.R.; Reddy, B.V.S.; Yadav, J.S. $Sm(OTf)_3$ As mild & efficient catalyst for aza-Diels-Alder reaction: a facile synthesis of *cis*-fused pyrano & furano quinolines. *Synth. Commun*., **2010**, *40*(12), 1750-1757. (e) Narsaiah, A.V.; Nagaiah, B. Glycerine-$CeCl_3.7H_2O$: an efficient recyclable reaction medium for the synthesis of Hantzsch pyridines. *Asian J. Chem*., **2010**, *22*(10), 8099-8106.

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