

# Amberlyst-15<sup>®</sup>: An Efficient, Cost-Effective and Recyclable Heterogeneous Solid Acid Catalyst for the Synthesis of $\beta$ -Enaminones and $\beta$ -Enamino Esters

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**Abstract:** The  $\beta$ -keto carbonyl compounds rapidly react with a variety of amines in the presence of Amberlyst-15<sup>®</sup> to produce  $\beta$ -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.

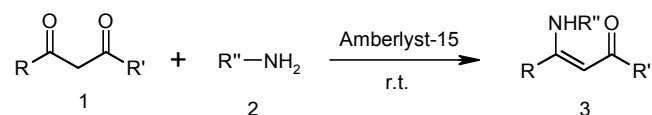
**Keywords:** Ion-exchange resin, 1, 3-dicarbonyls, amines, enaminones, enaminoesters.

## INTRODUCTION

The  $\beta$ -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, tetrone acids, azasteroids, (*1H*)-pyridin-2-one, pyrazolo-[1,5-*a*]-pyrimidine and isoxazole derivatives 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 pharmaceutical industry, the enamination of  $\beta$ -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  $\text{InBr}_3$  [5],  $\text{Zn}(\text{ClO}_4)_2$  [6],  $\text{I}_2$  [7], *p*-TSA [8],  $\text{H}_2\text{SO}_4$  [9],  $\text{NaAuCl}_4$  [10],  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  [11],  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  [12],  $\text{Sc}(\text{OTf})_3$  [13], montmorillonite-K10-microwave [14], ultra sound [15], TMS OTf [16],  $\text{BF}_3 \cdot \text{OEt}_2$  [17],  $\text{HClO}_4 \cdot \text{SiO}_2$  [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 unsatisfactory yields, which limit their use. Therefore, the development of a simple, environmentally benign and improved method for this transformation is in demand. A macro reticular sulfonic acid based polystyrene cation exchange resin, Amberlyst-15<sup>®</sup> 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].

## 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  $\beta$ -enamino compounds from various amines and 1,3-dicarbonyl compounds using Amberlyst-15<sup>®</sup> as a heterogeneous solid acid catalyst as shown in the Scheme 1.

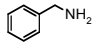
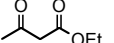
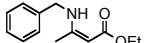
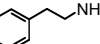
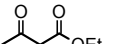
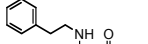
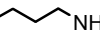
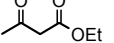
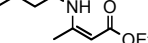
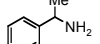
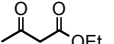
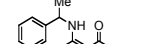
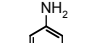

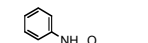
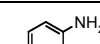
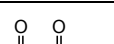
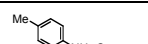
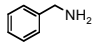
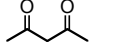
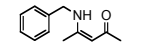
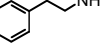
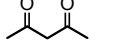
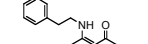
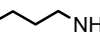
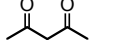
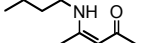
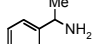
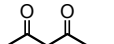
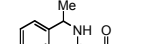
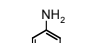
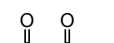
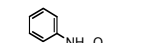
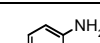
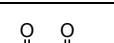
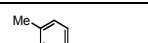
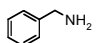
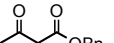
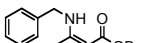
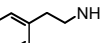
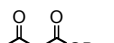
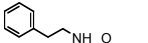
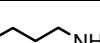

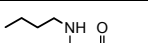
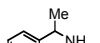

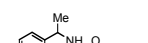
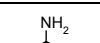
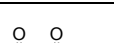
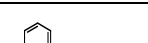
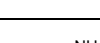
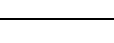
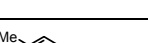


**Scheme 1.**

In a typical experiment, ethylacetoacetate and benzyl amine were reacted in the presence of the catalyst Amberlyst-15<sup>®</sup> 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 Amberlyst-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  $\beta$ -Enaminones and  $\beta$ -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  $\beta$ -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  $\beta$ -enaminones and  $\beta$ -enamino esters.

## EXPERIMENTAL SECTION

**General methods:** IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectro photometer. <sup>1</sup>H NMR spectra were recorded on Bruker-300 MHz, spectrometer in CDCl<sub>3</sub> 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  $\beta$ -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 chromatography (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 <sup>1</sup>H NMR, IR and mass spectroscopy data.

### Spectral Data for Selected Compounds

**3-Benzylamino-but-2-enoic acid ethyl ester (3a):** Colorless oil. IR (neat):  $\nu$  3294, 3041, 2971, 2839, 1628, 1605, 1561, 1456, 1375, 1281, 1231, 1169, 1057, 1012, 978, 846, 785, 741 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3145, 3018, 2961, 1641, 1608, 1583, 1406, 1367, 1273, 1210, 1185, 1061, 1006, 961, 843, 755, 732 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3261, 2980, 2853, 1695, 1653, 1619, 1596, 1497, 1441, 1385, 1359, 1271, 1231, 1164, 1093, 1059, 1023, 975, 788, 752, 697 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3258, 3189, 2980, 2928, 1895, 1653, 1612, 1519, 1489, 1440, 1385, 1358, 1270, 1232, 1163, 1096, 1060, 1020, 975, 704 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3423, 3142, 3029, 2961, 2852, 1606, 1579, 1507, 1458, 1351, 1294, 1210, 1167, 1030, 913, 841, 734 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3453, 3172, 2963, 2938, 2839, 1618, 1608, 1569, 1472, 1351, 1289, 1204, 1137, 1027, 1006, 963, 851, 743 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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 °C. IR (neat):  $\nu$  3453, 3137, 3028, 2974, 2846, 1622, 1576, 1510, 1461, 1329, 1274, 1205, 1187, 1031, 921, 856, 749 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 15).

**3-Benzylamino-but-2-enoic acid benzyl ester (3m):** IR (neat):  $\nu$  3276, 3068, 2979, 2847, 1634, 1608, 1589, 1506, 1432, 1381, 1249, 1211, 1171, 1053, 1010, 968, 859, 743 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3239, 3057, 2938, 2846, 1619, 1581, 1510, 1432, 1324, 1267, 1253, 1134, 1083, 1011, 965, 873, 749 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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):  $\nu$  3256, 3071, 2954, 2832, 1629, 1602, 1573, 1504, 1429, 1362, 1251, 1249, 1163, 1057, 1005, 978, 863, 739 cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  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<sup>+</sup> 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).

## ACKNOWLEDGEMENT

ARR thankful to UGC-New-Delhi for providing fellowship

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