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PC-ZnO Nanocomposites as Efficient and Reusable Catalyst for the Synthesis of α,β-Unsaturated Compounds and Aldimines

Anshu Dandia[a]*, Vijay Parewa[a], Shyam L. Gupta[a], Amit Sharma[a] and Narendra K. Agarwal[b]

[a]*Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur-302004, India;* [b]*Department of Physics, Malaviya National Institute of Technology, Jaipur. India*

Abstract: Polycarbonate (PC)-ZnO NPs composites have been successfully fabricated by solution casting technique in which ZnO NPs (45nm) were prepared *via* wet chemical method and used as dopant with different concentrations. These nanocomposites were characterized by XRD, SEM, optical micrographs, UV/VIS and FT-IR spectrum. ZnO NPs were uniformly distributed within the PC and create a new recyclable (10 times) catalytic system for the synthesis of α,β-unsaturated compounds and aldimines. Catalytic activity of the nanocomposites increased with ZnO NPs (5%) in PC matrix while at higher loading (9%) slight agglomeration of nanoparticles occurred, which hindered the catalytic effect of nanocomposite.

Keywords: Aldimines, ethyl lactate, heterogeneous catalyst, polycarbonate (PC)-ZnO NPs composites, α,β-unsaturated compounds.

1. INTRODUCTION

The α,β-unsaturated compounds have been widely used as intermediates in the synthesis of fine chemicals, natural products, functional polymers, compounds with biological significance, calcium antagonists, coumarin derivatives, cosmetics, perfumes and pharmaceuticals [1, 2]. Knoevenagel condensation, is a widely used reaction for the synthesis of α,β unsaturated carbonyl compounds [3] in the presence of an organic base such as pyridine, piperidine or ethylenediamine [4, 5]. Recently, attempts have been made to modify the reaction, avoiding organic bases to prevent unwanted by-products due to polymerization and self condensations. The use of different types of heterogeneous catalysts such as Xonotlite/tert-butoxide, cation-exchanged zeolites, SiO_2, calcite, fluorite, various metal oxides**,** and Lewis acids have been reported [6-9]. Similarly, utility of aldimines lies in their potent biological activity [10] and their usefulness as a starting material for the synthesis of various heterocyclic compounds [11]. Furthermore, they are used as versatile components in the formation of optically active α-alkyl aldehydes [12], in the preparation of secondary amines by hydrogenation [13], in nucleophilic addition with organometallic reagents [14] and in cycloaddition reactions [15]. Traditional syntheses of aldimines often involve the use of toxic solvents such as methylene chloride [16] or refluxing in petroleum-based solvents such as toluene as azeotroping agents [17]. In the last decade, increasing interest has been devoted to optimize the reaction conditions in order to reach very high yields and highly pure products. For this purpose, many catalysts have been investigated ($ZnCl_2$ [17], P_2O_5/SiO_2 [18], molecular sieves [19], $MgSO_4$-$Mg(ClO_4)_2$ [20]).

But harsh reaction conditions, non-recoverable catalysts, high-power microwaves, prolong reaction time, high reaction temperature and use of toxic metals have limited their utility. In recent years, many efforts have been made to prepare heterogeneous catalysts based on solid materials [21-28]. Although these catalysts have some advantages but the use of solvents were limited with prolonged reaction time. However, many potential applications of such immobilized catalysts are strongly hampered by leaching and the amount of leaching depends strongly on the choice of support and linker material used for the preparation of the immobilized catalyst [29, 30]. The ''leached catalyst'' literally poisons the solution of substrates and products, which is the main obstacle for using such catalytic systems and products in pharmaceutical industries. Further, leaching yields a lowering of the activity of the supported catalyst after every reaction cycle which limits its application in liquid media as fully recyclable catalyst. The development of catalysts that combine both low leaching and high recyclability is an ongoing challenge. Thorough analysis of the literature data indicated that none of the described procedures can be used to generate large sets of compounds for high-throughput biological screening because of low conversion, leaching of the catalysts and complicated purification protocols.

A characteristic high percentage of surface atoms and the associated quantum effects make nanoparticles (NPs) efficient and selective catalysts for several types of catalytic reactions [31]. However, for most practical catalytic applications, NPs must be immobilized on solid supports to prevent their aggregation and to facilitate the catalyst recovery [32]. In this sense, encapsulation of NPs in polymers seems advantageous because, in addition to stabilizing and protecting effects towards NPs, polymers offer unique possibilities for enhancing the access of reactants to the catalytic sites. Polycarbonate (PC) is one of the polymers which can be used as a matrix for NPs, which possess several distinct properties including transparency, dimensional stability, flame resistance, high heat distortion temperature, high impact strength, insolubility in a large majority of commonly used solvents and moisture insensitivity [33, 34].

In continuation of our efforts on the synthesis of nanomaterials, and their catalytic applications in heterocyclic synthesis [35-39], we herein report the synthesis, characterization of PC-ZnO nanocomposites and their catalytic application for efficient, leach free, stereoselective synthesis of α-β unsaturated compounds *via* Knoevenagel condensation in ethyl lactate (EL) under ultrasonic irradiation for the first time. (Scheme **1**).

*Address correspondence to this author at the Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur-302004, India; Tel: +91-9414073436; E-mail: dranshudandia@yahoo.co.in

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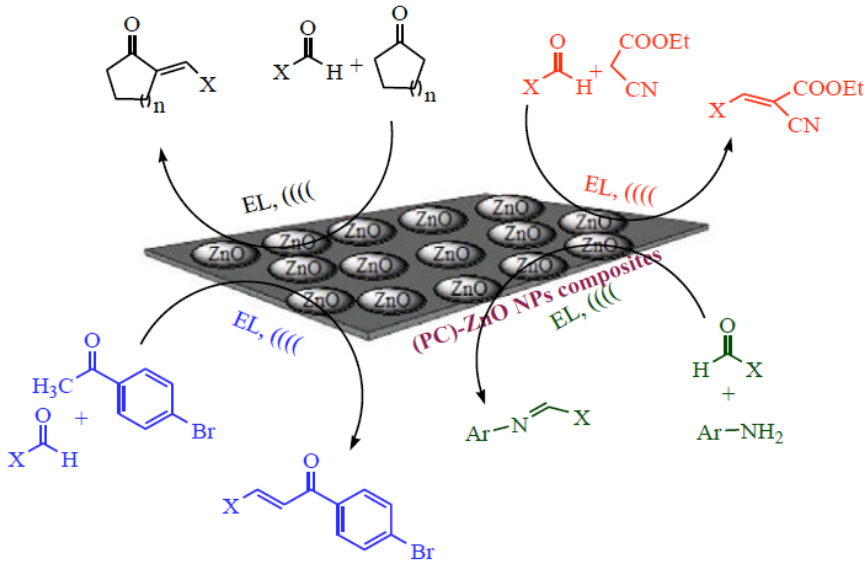


Scheme 1. Synthesis of α,β-unsaturated compounds.

2. EXPERIMENTAL

2.1. General

Zinc acetate dihydrate (99% purity), thioglycerol (99% purity), sodium hydroxide pellets (99% purity) and polycarbonate granules were used as the introductory material and supplied by Sigma-Aldrich chemicals. All the chemicals used were of research grade and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 and $CDCl_3$ using TMS as an internal standard on a Bruker spectrophotometer at 300 and 75 MHz respectively. UV-Visible spectral analysis was done using a double beam UV-Vis spectrophotometer (Shimadzu). XRD measurements were performed by an X' Pert Pro X-ray diffractometer (PAN alytical BV, The Netherlands) operated at a voltage of 45kV with Cu k(α) radiation of 1.54059 Å wavelength. SEM analysis was done using scanning electron microscope (Carl ZEISS EVOR -18) operated at 20kV. The FT-IR spectra of the samples were carried out on Shimadzu FT IR-8400S and Nicolet Megna IR 550 single beam FTIR spectrophotometer. Melting points were recorded on a Toshniwal apparatus and are uncorrected.

2.2. Catalyst Preparation

2.2.1. Synthesis of ZnO Nanoparticles

The ZnO nanoparticles were synthesized by the wet chemical method as follows. Firstly, zinc acetate dihydrate (99% purity) was dissolved in double-distilled water (0.1 M) and then obtained molar solution was stirred for 20 min at room temperature to achieve complete dissolution. NaOH was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first NaOH solution was added drop by drop to the zinc acetate solution and then an appropriate amount of thioglycerol as a capping agent was added to the reaction medium. As a result of this, the pale white aqueous solution was formed. After 3 hrs, the pale white precipitate was washed thoroughly with distilled water followed by ethanol to remove the impurities. Then a pale white powder of ZnO nanoparticles was obtained after drying at 60°C in vacuum oven over night.

2.2.2. Synthesis of PC-ZnO NPs Composites

ZnO doped polycarbonate membranes of different doping concentrations (2%, 5% and 9%) were prepared by solution casting method. Polycarbonate granules were weighed and dissolved in dichloromethane (CH_2Cl_2). The solution was stirred at room temperature for around 2-3 hours till a clear solution is formed. Then ZnO nanoparticles were dispersed in the solvent dichloromethane using ultra-sonicator followed by addition to the polycarbonate solution with stirring for 30 minutes (time for ultra-sonication increased in accordance with the increase in % concentration of ZnO doping). The solution was then poured into flat-bottomed Petri-dishes floating on mercury to ensure a uniform structure of the membranes. The solvent was allowed to evaporate slowly over a period of 10-12 hours. The films so obtained were peeled off using forceps.

2.3. Catalyst Activity Measurement and General Procedure for the Synthesis of α,β-unsaturated Compounds and Aldimines

A mixture of the aldehyde (1 mmol), ethylcynoacetate (1 mmol; 0.113 g)/ 4-bromoacetophenone (1 mmol; 0.199 g)/ cyclopentanone (1 mmol; 0.084 g)/ cyclohexanone (1 mmol; 0.098 g)/ toluidine (1 mmol; 0.107 g), and PC-ZnO nanocomposite (5 mg) in 5 ml ethyl lactate was introduced in a 20 mL heavy walled pear-shaped two necked flask with non-standard tapered outer joint. The flask was attached to a 12 mm tip diameter probe and the reaction mixture was sonicated at ambient temperature for the specified period at 50% power of the processor and in a 4 s pulse. After completion of the reaction, the catalyst was filtered out. After removing the solvent in a rotary evaporator the crude product was purified by recrystallization from ethanol. The recovered catalyst was washed with water and reused 10 times without any loss of catalytic activity.

2.4. Spectral Data for Synthesized Compounds

(E)-Ethyl-3-phenyl-2-cyanoacrylate (3a: 0.181 g) [40]

White solid, mp 48-50°C; IR (KBr) ν_{max}/cm^{-1}: 2248, 1660, 1596; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (s, 1H, =C-H), 7.61 (d, *J*=8.4Hz, 2H, Ar-H), 7.42 (d, J=8.4Hz, 2H, Ar-H), 7.28 (t, *J*=8.1Hz, 1H, Ar-H), 4.29 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.31 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.4 (>C=O), 153.6 (>C=C-CN), 132.2 (Ar-C_1), 131.8 (Ar-C_3,C_5), 129.7 (Ar-C_4), 128.5 (Ar-C_2,C_6), 114.1 (-CN), 102.5 (>C=C-CN), 62.2 (-OCH_2), 13.3 (-CH_3). MS (EI, m/z): 202 $[M+H]^+$.

(E)-Ethyl-3-(4-methylphenyl)-2-cyanoacrylate (3b: 0.217 g) [41]

White solid, mp 92-94°C; IR (KBr) ν_{max}/cm^{-1}: 2250, 1658, 1592; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.38 (s, 1H, =C-H), 7.74 (d, *J*=8.4Hz, 2H, Ar-H), 7.69 (d, *J*=8.4Hz, 2H, Ar-H), 4.30 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.91 (s, 3H, Ar-CH_3), 1.32 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.2 (>C=O), 153.1 (>C=C-CN), 131.7 (Ar-C_4), 131.1 (Ar-C_1), 130.6 (Ar-C_3,C_5), 128.3 (Ar-C_2,C_6), 113.7 (-CN), 102.3 (>C=C-CN), 61.9 (-OCH_2), 20.5 (-CH_3), 13.1 (-CH_3). MS (EI, m/z): 216 $[M+H]^+$.

(E)-Ethyl-3-(4-methoxyphenyl)-2-cyanoacrylate (3c: 0.229 g) [40]

White solid, mp 80-82°C; IR (KBr) ν_{max}/cm^{-1}: 2252, 1664, 1600 ; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.37 (s, 1H, =C-H), 7.32 (d, *J*=8.1Hz, 2H, Ar-H), 6.97 (d, *J*=8.1Hz, 2H, Ar-H), 4.31 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 3.77 (s, 3H, -OCH_3), 1.33 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7 (>C=O), 155.9 (Ar-C_4), 153.6 (>C=C-CN), 129.5 (Ar-C_1), 128.1 (Ar-C_2,C_6), 126.6 (Ar-C_3,C_5), 113.8 (-CN), 102.9 (>C=C-CN), 62.1 (-OCH_2), 55.3 (-OCH_3), 12.9 (-CH_3). MS (EI, m/z): 232 $[M+H]^+$.

(E)-Ethyl-3-(4-chlorophenyl)-2-cyanoacrylate (3d: 0.244 g) [42]

White solid, mp 88-90 °C; IR (KBr) ν_{max}/cm^{-1}: 2250, 1654, 1595; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.41 (s, 1H, =C-H), 8.02 (d, *J*=8.4Hz, 2H, Ar-H), 7.80 (d, *J*=8.4Hz, 2H, Ar-H), 4.33 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.34 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.5 (>C=O), 153.4 (>C=C-CN), 132.9 (Ar-C_4), 132.5 (Ar-C_1), 131.2 (Ar-C_3,C_5), 128.6 (Ar-C_2,C_6), 114.3 (-CN), 103.7 (>C=C-CN), 62.7 (-OCH_2), 13.7 (-CH_3). MS (EI, m/z): 236 $[M+H]^+$.

(E)-Ethyl-3-(4-bromophenyl)-2-cyanoacrylate (3e: 0.280 g) [43]

White solid, mp 97-99 °C; IR (KBr) ν_{max}/cm^{-1}: 2242, 1652, 1602; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.39 (s, 1H, =C-H), 7.98 (d, *J*=8.4Hz, 2H, Ar-H), 7.81 (d, *J*=8.4Hz, 2H, Ar-H), 4.32 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.31 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.6 (>C=O), 153.8 (>C=C-CN), 132.5 (Ar-C_1), 132.4 (Ar-C_3,C_5), 130.5 (Ar-C_2,C_6), 127.2 (Ar-C_4), 115.4 (-CN), 103.2 (>C=C-CN), 62.4 (-OCH_2), 13.9 (-CH_3). MS (EI, m/z): 281 $[M+H]^+$.

(E)-Ethyl-3-(4-fluorophenyl)-2-cyanoacrylate (3f: 0.227 g) [40]

White solid, mp 93-95°C; IR (KBr) ν_{max}/cm^{-1}: 2238, 1668, 1588; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.40 (s, 1H, =C-H), 8.05 (d, *J*=8.4Hz, 2H, Ar-H), 7.83 (d, *J*=8.4Hz, 2H, Ar-H), 4.32 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.33 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7 (>C=O), 153.7 (>C=C-CN), 133.1 (Ar-C_4), 132.9 (Ar-C_1), 130.5 (Ar-C_2,C_6), 128.8 (Ar-C_3,C_5), 115.7 (-CN), 104.2 (>C=C-CN), 62.8 (-OCH_2), 13.9 (-CH_3). MS (EI, m/z): 220 $[M+H]^+$.

(E)-Ethyl-2-cyano-3-(4-nitrophenyl)acrylate (3g: 0.248 g) [40]

Yellow solid, mp 165-167°C; IR (KBr) ν_{max}/cm^{-1}: 2242, 1666, 1604; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (s, 1H, =C-H), 8.41 (d, *J*=8.4Hz, 2H, Ar-H), 8.25 (d, *J*=8.4Hz, 2H, Ar-H), 4.35 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.32 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.6 (>C=O), 153.1 (>C=C-CN), 149.7 (Ar-C_4), 137.7 (Ar-C_1), 132.1 (Ar-C_2,C_6), 124.6 (Ar-C_3,C_5), 115.4 (-CN), 107.1 (>C=C-CN), 63.2 (-OCH_2), 14.4 (-CH_3). MS (EI, m/z): 247 $[M+H]^+$.

(E)-Ethyl-2-cyano-3-(4-hydroxyphenyl)acrylate (3h: 0.221 g) [40]

Yellow solid, mp 172-174°C; IR (KBr) ν_{max}/cm^{-1}: 2236, 1654, 1608; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.96 (s, 1H, -OH), 8.42 (s, 1H, =C-H), 7.26 (d, *J*=8.7Hz, 2H, Ar-H), 6.88 (d, *J*=8.7Hz, 2H, Ar-H), 4.30 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.31 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.9 (>C=O), 155.3 (Ar-C_4), 153.8 (>C=C-CN), 147.4 (Ar-C_1), 126.3 (Ar-C_2,C_6), 118.1 (Ar-C_3,C_5), 115.7 (-CN), 103.5 (>C=C-CN), 62.4 (-OCH_2), 13.2 (-CH_3). MS (EI, m/z): 218 $[M+H]^+$.

(E)-Ethyl-2-cyano-3-(4-dimethylaminophenyl)acrylate (3i: 0.241 g) [40]

Orange solid, mp 117-119 °C; IR (KBr) ν_{max}/cm^{-1}: 2248, 1660, 1592; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.37 (s, 1H, =C-H), 7.96 (d, *J*=8.7 Hz, 2H, Ar-H), 6.81 (d, *J*= 8.7 Hz, 2H, Ar-H), 4.32 (q, 2H, *J*=6.9 Hz, -O-CH_2-), 3.05 (s, 6H, -N-CH_3), 1.32 (t, 3H, *J*= 6.9 Hz, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.0 (>C=O), 155.7 (>C=C-CN), 149.8 (Ar-C_4), 135.6 (Ar-C_2,C_6), 119.2 (Ar-C_1), 116.3 (Ar-C_3,C_5), 113.5 (-CN), 102.9 (>C=C-CN), 62.7 (-OCH_2), 43.5 (-NCH_3), 13.6 (-CH_3). MS (EI, m/z): 245 $[M+H]^+$.

(E)-Ethyl-2-cyano-3-(thiophen-2-yl)acrylate (3m: 0.216 g) [44]

Yellow solid, mp 106-108 °C; IR (KBr) ν_{max}/cm^{-1}: 2254, 1662, 1588; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62 (s, 1H, =C-H), 8.22 (d, *J*=5.1Hz, 1H, Ar-H), 8.07 (d, *J*=3.3Hz, 1H, Ar-H), 7.36 (t, *J*=4.4 Hz, 1H, Ar-H), 4.30 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.31 (t, *J*=6.9 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.5 (>C=O), 148.0 (>C=C-CN), 140.7 (Ar-C_2), 137.6 (Ar-C_5), 136.0 (Ar-C_4), 129.2 (Ar-C_3), 116.3 (-CN), 98.2 (>C=C-CN), 62.5 (-OCH_2), 14.4 (-CH_3). MS (EI, m/z): 208 $[M+H]^+$.

(E)-Ethyl-2-cyano-3-(1H-indol-3-yl)acrylate (3n: 0.248 g) [44]

Yellow solid, mp 162-164 °C; IR (KBr) ν_{max}/cm^{-1}: 2242, 1668, 1594; ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.63 (brs, 1H, N-H), 8.59-7.25 (m, 5H, Ar-H), 4.29 (q, *J*=6.9 Hz, 2H, -O-CH_2-), 1.32 (t, *J*=3.4 Hz, 3H, -CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 163.2 (>C=O), 146.5 (>C=C-CN), 136.2 (Ar-C_9), 132.5 (Ar-C_2), 126.9 (Ar-C_4), 123.6 (Ar-C_7), 122.1 (Ar-C_6), 118.4 (Ar-C_5), 118.06 (-CN), 112.9 (Ar-C_3), 109.9 (Ar-C_8), 92.3 (>C=C-CN), 61.4 (-OCH_2), 14.1 (-CH_3). MS (EI, m/z): 241 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-phenylprop-2-en-1-one (5a: 0.264 g) [45]

Yellow solid, mp 160-162 °C; IR (KBr) ν_{max}/cm^{-1}: 1660, 1596, 1534, 724; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.36-7.85 (m, 9H, Ar-H), 7.71 (d, *J* =15.9 Hz, 1H, =C-H), 7.52 (d, *J*= 15.9 Hz, 1H, =C-H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.2 (>C=O), 147.8 (>C=C-CO), 137.4 (Ar-C_1), 136.2 (Ar-C'$_1$), 133.8 (Ar-C_2,C_6), 130.2 (Ar-C'$_2$,C'$_6$), 129.5 (Ar-C_3,C_5), 128.1(Ar-C_4, C'$_3$,C'$_5$), 123.1 (Ar-C'$_4$), 121.4 (>C=C-CO). MS (EI, m/z): 288 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(p-tolyl)prop-2-en-1-one (5b: 0.300 g) [46]

Yellow solid, mp 162-164°C; IR (KBr) ν_{max}/cm^{-1}: 1662, 1590, 1530, 722; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.21-7.84 (m, 8H, Ar-H), 7.73 (d, *J* =15.9 Hz, 1H, =CH-CO-), 7.54 (d, *J* = 15.9 Hz, 1H, =CH-Ar), 2.11 (s, 3H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.2 (>C=O), 147.8 (>C=C-CO), 137.4 (Ar-C_1), 136.2 (Ar-C'$_1$), 133.8 (Ar-C_3,C_5), 130.6 (Ar-C_2,C_6), 129.5 (Ar-C'$_2$,C'$_6$), 128.1 (Ar-C_4, C'$_3$,C'$_5$), 127.4 (Ar-C'$_4$), 122.6 (>C=C-CO), 21.8 (-CH_3). MS (EI, m/z): 302 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (5c: 0.312 g) [47]

Yellow solid, mp 144-146 °C; IR (KBr) ν_{max}/cm^{-1}: 1658, 1598, 1538, 720; ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 6.90-7.89 (m,

8H, Ar-H), 7.72 (d, *J* =15.9Hz, 1H, =CH-CO-), 7.52 (d, *J* = 15.9 Hz, 1H, =CH-Ar), 3.79 (s, 3H, -OCH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.4 (>C=O), 160.2 (Ar-C'$_4$), 147.3 (>C=C-CO), 137.6 (Ar-C$_1$), 133.4 (Ar-C'$_1$), 132.7 (Ar-C$_3$,C$_5$), 131.2 (Ar-C$_2$,C$_6$), 129.8 (Ar-C'$_2$,C'$_6$), 128.1 (Ar-C$_4$), 120.9 (>C=C-CO), 118.2 (Ar-C'$_3$,C'$_5$), 56.4 (-OCH$_3$). MS (EI,m/z): 318 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(4-chlorophenyl)prop-2-en-1-one (5d: 0.323 g) [48]

Yellow solid, mp 174-176°C; IR (KBr) ν_{max}/cm^{-1}: 1664, 1602, 1536, 724; ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.38-7.82 (m, 8H, Ar-H), 7.71 (d, *J* =16.2 Hz, 1H, =CH-CO-), 7.56 (d, *J* = 16.2 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.1 (>C=O), 147.5 (>C=C-CO), 138.1 (Ar-C$_1$), 136.9 (Ar-C'$_4$), 134.8 (Ar-C'$_1$), 132.5 (Ar-C$_3$,C$_5$), 131.8 (Ar-C$_2$,C$_6$), 130.2 (Ar-C'$_2$,C'$_6$), 129.7 (Ar-C'$_3$,C'$_5$), 126.2 (Ar-C$_4$), 122.2 (>C=C-CO). MS (EI,m/z): 322 $[M+H]^+$.

(E)-1,3-Bis(4-bromophenyl)prop-2-en-1-one (5e: 0.369 g) [48]

Yellow solid, mp 192-194 °C; IR (KBr) ν_{max}/cm^{-1}: 1656, 1600, 1542, 718; ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.42-7.81 (m, 8H, Ar-H), 7.74 (d, *J* =16.2 Hz, 1H, =CH-CO-), 7.53 (d, *J* = 16.2 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.2 (>C=O), 147.4 (>C=C-CO), 138.4 (Ar-C$_1$), 136.2 (Ar-C'$_1$), 135.7 (Ar-C$_3$,C$_5$), 134.3 (Ar-C$_2$,C$_6$), 133.8 (Ar-C'$_2$,C'$_6$), 132.5 (Ar-C'$_3$,C'$_5$), 129.4 (Ar-C$_4$), 128.6 (Ar-C'$_4$), 121.9 (>C=C-CO). MS (EI,m/z): 367 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (5f: 0.304 g) [49]

Yellow solid, mp 178-180 °C; IR (KBr) ν_{max}/cm^{-1}: 1664, 1604, 1532, 722; ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 7.26-7.87 (m, 8H, Ar-H), 7.74 (d, *J* =15.9 Hz, 1H, =CH-CO-), 7.56 (d, *J* = 15.9 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.8 (>C=O), 153.1 (Ar-C'$_4$), 147.5 (>C=C-CO), 138.3 (Ar-C$_1$), 134.1 (Ar-C'$_1$), 133.9 (Ar-C$_3$,C$_5$), 132.5 (Ar-C$_2$,C$_6$), 130.7 (Ar-C'$_2$,C'$_6$), 129.8 (Ar-C$_4$), 117.6 (Ar-C'$_3$,C'$_5$), 122.1 (>C=C-CO). MS (EI,m/z): 306 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(4-nitrophenyl)prop-2-en-1-one (5g: 0.329 g) [50]

Yellow solid, mp 169-171°C; IR (KBr) ν_{max}/cm^{-1}: 1660, 1592, 1534, 726; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.75-8.32 (m, 8H, Ar-H), 7.71 (d, *J* =16.2 Hz, 1H, =CH-CO-), 7.55 (d, *J* = 16.2 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.9 (>C=O), 150.6 (Ar-C'$_4$), 147.3 (>C=C-CO), 144.5 (Ar-C'$_1$), 138.2 (Ar-C$_1$), 134.8 (Ar-C$_3$,C$_5$), 132.6 (Ar-C$_2$,C$_6$), 131.9 (Ar-C'$_2$,C'$_6$), 130.5 (Ar-C$_4$), 126.3 (Ar-C'$_3$,C'$_5$), 122.3 (>C=C-CO). MS (EI, m/z): 333 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one (5h: 0.292 g) [51]

Yellow solid, mp 184-186 °C; IR (KBr) ν_{max}/cm^{-1}: 3656, 1658, 1602, 1540, 718; ^{1}H NMR (300 MHz, CDCl$_3$), δ (ppm): 8.98 (s, 1H, -OH), 6.71-7.80 (m, 8H, Ar-H), 7.72 (d, *J* =15.9 Hz, 1H, =CH-CO-), 7.52 (d, *J* = 15.9 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.2 (>C=O), 159.1 (Ar-C'$_4$), 146.9 (>C=C-CO), 138.7 (Ar-C$_1$), 133.9 (Ar-C$_3$,C$_5$), 132.8 (Ar-C$_2$,C$_6$), 131.2 (Ar-C'$_2$,C'$_6$), 130.3 (Ar-C'$_1$), 128.5 (Ar-C$_4$), 121.6 (>C=C-CO), 117.4 (Ar-C'$_3$,C'$_5$). MS (EI, m/z): 304 $[M+H]^+$.

(E)-1-(4-Bromophenyl)-3-(1H-indol-3-yl)prop-2-en-1-one (5j: 0.320 g) [52]

Yellow solid, mp 168-170 °C; IR (KBr) ν_{max}/cm^{-1}: 1660, 1596, 1538, 720; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 10.15 (s, 1H, N-H), 7.70-8.42 (m, 9H, Ar-H), 7.68 (d, *J* =15.9 Hz, 1H, =CH-CO-), 7.53 (d, *J* = 15.9 Hz, 1H, =CH-Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 188.5 (>C=O), 148.5 (>C=C-CO), 140.5 (Ar-C'$_9$), 136.5 (Ar-C$_1$), 132.3 (Ar-C$_3$,C$_5$), 131.1 (Ar-C$_2$,C$_6$), 130.6 (Ar-C'$_2$), 130.4 (Ar-C'$_4$), 128.2 (Ar-C$_4$), 127.8 (Ar-C'$_7$), 127.6 (Ar-C'$_6$), 126.0 (Ar-C'$_5$), 124.7 (Ar-C'$_3$), 124.3 (Ar-C'$_8$), 123.7 (>C=C-CO). MS (EI, m/z): 327 $[M+H]^+$.

2-(4-Fluorobenzylidene)cyclopentanone (6a: 0.193 g) [53]

White solid, mp 82-84°C; IR (KBr) ν_{max}/cm^{-1}: 2956, 2894, 1710, 1624, 1585, 1490, 1414, 1176, 1102, 1089, 1012, 908, 812; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.33 (s, 1H, =C-H), 6.74-7.26 (m, 4H, Ar-H), 2.94 (td, *J* = 7.6, 2.9 Hz, 2H, -CH$_2$-CO-), 2.40 (t, *J* = 7.6 Hz, 2H, -CH$_2$-CH=), 2.07 (m, 2H, -CH$_2$-). ^{13}C NMR (75 MHz, DMSO-d_6): δ 207.9 (>C=O), 136.7 (Ar-C$_4$), 135.4 (>C=C-CO), 134.1 (>C=C-CO), 131.8 (Ar-C$_1$), 129.3 (Ar-C$_2$,C$_6$), 128.2 (Ar-C$_3$,C$_5$), 37.5 (CH$_2$-CO), 29.3 (CH$_2$-CH$_2$-CH$_2$), 20.3 (CH$_2$-C=). MS (ESI) m/z: 191 $[M+H]^+$.

2-(4-Chlorobenzylidene)cyclopentanone (6b: 0.214 g) [54]

Yellow solid, mp 76-78 °C; IR (KBr) ν_{max}/cm^{-1}: 2960, 2892, 1712, 1622, 1581, 1493, 1415, 1173, 1101, 1090, 1012, 906, 812; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.36 (s, 1H, =C-H), 6.77-7.36 (m, 4H, Ar-H), 2.93 (td, *J* = 7.6, 2.9 Hz, 2H, -CH$_2$-CO-), 2.42 (t, *J* = 7.6 Hz, 2H, -CH$_2$-CH=), 2.08 (m, 2H, -CH$_2$-). ^{13}C NMR (75 MHz, DMSO-d_6): δ 208.1 (>C=O), 136.5 (Ar-C$_4$), 135.2 (>C=C-CO), 134.3 (>C=C-CO), 130.2 (Ar-C$_1$), 129.5 (Ar-C$_3$,C$_5$), 128.7 (Ar-C$_2$,C$_6$), 37.4 (CH$_2$-CO), 29.4 (CH$_2$-CH$_2$-CH$_2$), 20.5 (CH$_2$-C=). MS (ESI) m/z: 207 $[M+H]^+$.

2-(4- Fluorobenzylidene)cyclohexanone (6c: 0.206 g) [55]

Yellow solid, mp 94-96°C; IR (KBr) ν_{max}/cm^{-1}: 2952, 2891, 1716, 1584, 1492, 1406, 1172, 1108, 1089, 1012, 907, 818; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.35 (s, 1H, =C-H), 6.72-7.32 (m, 4H, Ar-H), 2.87 (m, 2H, -CH$_2$-CO-), 2.49 (t, *J* = 6.5 Hz, 2H, -CH$_2$-CH=), 1.77-1.92 (m, 4H, 2xCH$_2$); ^{13}C NMR (75 MHz, DMSO-d_6): δ 200.4 (>C=O), 141.0 (Ar-C$_4$), 132.8 (>C=C-CO), 128.7 (>C=C-CO), 126.9 (Ar-C$_1$), 123.2 (Ar-C$_2$,C$_6$), 117.9 (Ar-C$_3$,C$_5$), 39.8 (CH$_2$-CO), 28.3 (CH$_2$-CH$_2$-CH$_2$), 23.2 (CH$_2$-C=), 22.9 (CH$_2$-CH$_2$-CH$_2$-CO). MS (ESI) m/z: 205 $[M+H]^+$.

2-(4- Nitrobenzylidene)cyclohexanone (6d: 0.234 g) [56]

Yellow solid, mp 122-124°C; IR (KBr) ν_{max}/cm^{-1}: 2948, 2890, 1714, 1582, 1490, 1408, 1176, 1112, 1092, 1006, 908, 814; ^{1}H NMR (300 MHz, DMSO-d_6), δ (ppm): 7.47-8.16 (m, 4H, Ar-H), 7.42 (s, 1H, =C-H), 2.80 (m, 2H, -CH$_2$-CO-), 2.56 (t, *J* = 6.7 Hz, 2H, -CH$_2$-CH=), 1.78-1.95 (m, 4H, 2xCH$_2$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 201.6 (>C=O), 142.7 (Ar-C$_4$), 139.6 (>C=C-CO), 133.4 (>C=C-CO), 132.1 (Ar-C$_1$), 130.7 (Ar-C$_2$,C$_6$), 118.9 (Ar-C$_3$,C$_5$), 40.6 (CH$_2$-CO), 29.7 (CH$_2$-CH$_2$-CH$_2$), 23.5 (CH$_2$-C=), 23.4 (CH$_2$-CH$_2$-CH$_2$-CO). MS (ESI) m/z: 232 $[M+H]^+$.

(E)-N-(4-Chlorobenzylidene)-4-methylaniline (7a: 0.233 g) [57]

Mp126-128 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.60 (s, 1H, =C-H), 7.20-7.86(m, 8H, Ar-H), 2.10 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.5 (>C=N-), 148.4 (Ar-C$_1$), 135.7 (Ar-C'$_4$), 135.3 (Ar-C$_4$), 131.8 (Ar-C'$_2$), 130.3 (Ar-C'$_6$), 129.7 (Ar-C'$_1$), 124.8 (Ar-C'$_3$), 124.3 (Ar-C'$_5$), 122.6 (Ar-C$_3$), 121.0 (Ar-C$_5$), 119.1 (Ar-C$_2$), 111.8 (Ar-C$_6$), 20.6 (-CH$_3$). MS (m/z): 230 $[M+H]^+$.

(E)-4-Methyl-N-(4-nitrobenzylidene) aniline (7b: 0.248 g) [58]

Mp 122-124°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.76 (s, 1H, =C-H), 8.30 (d, J=8.4Hz, 2H, Ar-H), 8.23 (d, J=8.4Hz, 2H, Ar-H),

7.24 (s, 4H, Ar-H), 2.07 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.5 (>C=N-), 148.6 (Ar-C'$_4$), 147.8 (Ar-C$_1$), 141.6 (Ar-C'$_1$), 136.5 (Ar-C$_4$), 129.7 (Ar-C'$_2$,C'$_6$), 129.4 (Ar-C$_3$,C$_5$), 123.9 (Ar-C'$_3$,C'$_5$), 121.3 (Ar-C$_2$,C$_6$), 20.6 (-CH$_3$). MS (m/z): 241 [M+H]$^+$.

(E)-N-(4-Bromobenzylidene)-4-methylaniline (7c: 0.272 g) [59]

Mp 128-130°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.53 (s, 1H, =C-H), 7.60 (d, J=8.4Hz, 2H, Ar-H), 7.44 (d, J=8.4Hz, 2H, Ar-H), 7.11 (s, 4H, Ar-H), 2.09 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.2 (>C=N-), 147.3 (Ar-C$_1$), 135.1 (Ar-C$_4$), 132.1 (Ar-C'$_1$), 131.4 (Ar-C'$_3$), 130.9 (Ar-C'$_5$), 123.4 (Ar-C$_3$), 123.3 (Ar-C$_5$), 122.4 (Ar-C'$_2$), 120.7 (Ar-C'$_6$), 119.3 (Ar-C'$_4$) , 112.3 (Ar-C$_2$,C$_6$), 20.3 (-CH$_3$). MS (m/z): 274 [M+H]$^+$.

(E)-N-(4-Fluorobenzylidene)-4-methylaniline (7d: 0.213 g) [59]

Mp 110-112 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62 (s, 1H, =C-H), 7.24-8.03 (m, 8H, Ar-H), 2.08 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.2 (>C=N-), 160.8 (Ar-C'$_4$), 147.8 (Ar-C$_1$), 136.1 (Ar-C'$_1$), 134.6 (Ar-C$_4$), 132.2 (Ar-C'$_3$), 130.8 (Ar-C'$_5$), 128.6 (Ar-C$_3$,C$_5$), 125.4 (Ar-C'$_2$), 123.9 (Ar-C'$_6$), 122.2 (Ar-C$_2$), 120.7 (Ar-C$_6$), 20.8 (-CH$_3$). MS (m/z): 214 [M+H]$^+$.

(E)-4-Methyl-N-(3,4,5-trimethoxybenzylidene)aniline (7e: 0.291 g) [59]

Mp 170-172 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.59 (s, 1H, =C-H), 7.24-7.69 (m, 8H, Ar-H), 3.76 (s, 3H, -OCH$_3$), 3.70 (s, 6H, 2xOCH$_3$), 2.08 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 158.1 (>C=N-), 153.6 (Ar-C'$_3$, C'$_5$), 145.7 (Ar-C$_1$), 137.7 (Ar-C'$_4$), 135.1 (Ar-C$_4$), 131.2 (Ar-C'$_1$), 127.6 (Ar-C$_3$), 126.1 (Ar-C$_5$), 122.6 (Ar-C$_2$), 121.7 (Ar-C$_6$), 120.9 (Ar-C'$_2$), 118.2 (Ar-C'$_6$), 58.7 (-OCH$_3$), 55.4 (2xOCH$_3$), 20.6 (-CH$_3$). MS (m/z): 286 [M+H]$^+$.

(E)-N-(4-Methoxybenzylidene)-4-methylaniline (7f: 0.231 g) [60]

Mp 64-66 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.60 (s, 1H, =C-H), 7.12-7.72 (m, 8H, Ar-H), 3.77 (s, 3H, -OCH$_3$), 2.09 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.7 (Ar-C'$_4$), 157.8 (>C=N-), 146.2 (Ar-C$_1$), 135.8 (Ar-C$_4$), 132.8 (Ar-C'$_1$), 130.1 (Ar-C$_3$), 126.9 (Ar-C$_5$), 124.2 (Ar-C'$_2$), 123.9 (Ar-C'$_6$), 120.2 (Ar-C$_2$), 119.1 (Ar-C$_6$), 118.7 (Ar-C'$_3$), 114.5 (Ar- C'$_5$), 56.8 (-OCH$_3$), 20.1 (-CH$_3$). MS (m/z): 226 [M+H]$^+$.

(E)-N-(2-Chlorobenzylidene)-4-methylaniline (7g: 0.233 g) [61]

Mp 48-50 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.68 (s, 1H, =C-H), 7.22-7.83 (m, 8H, Ar-H), 2.10 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.1 (>C=N-), 147.2 (Ar-C$_1$), 136.7 (Ar-C'$_2$), 134.1 (Ar-C$_4$), 130.4 (Ar-C'$_1$), 129.8 (Ar-C$_3$), 129.1 (Ar-C$_5$), 124.2 (Ar-C'$_4$), 123.8 (Ar-C'$_3$), 121.5 (Ar-C'$_6$), 121.1 (Ar-C'$_5$), 119.8 (Ar-C$_2$), 113.2 (Ar-C$_6$), 20.2 (-CH$_3$). MS (m/z): 230 [M+H]$^+$.

(E)-4-Methyl-N-(2-nitrobenzylidene)aniline (7h: 0.240 g) [62]

Mp 72-74°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.79 (s, 1H, =C-H), 7.22-8.17 (m, 8H, Ar-H), 2.09 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.3 (>C=N-), 148.7 (Ar-C'$_2$), 146.3 (Ar-C$_1$), 138.9 (Ar-C'$_5$), 136.1 (Ar-C$_4$), 131.5 (Ar-C'$_4$,C'$_6$), 130.2 (Ar-C'$_1$), 124.1 (Ar-C'$_3$), 122.4 (Ar-C$_3$,C$_5$), 121.8 (Ar-C$_2$,C$_6$), 20.9 (-CH$_3$). MS (m/z): 241 [M+H]$^+$.

(E)-4-[(p-Tolylimino)methyl]phenol (7i: 0.218 g) [63]

Mp 216-218 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.63 (s, 1H, =C-H), 6.93-7.68 (m, 8H, Ar-H), 4.92 (s, 1H, -OH), 2.12 (s, 3H, -CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6): δ 161.1 (Ar-C'$_4$), 158.3 (>C=N-), 147.6 (Ar-C$_1$), 135.1 (Ar-C$_4$), 133.7 (Ar-C'$_2$, C'$_6$), 130.5 (Ar-C'$_1$), 127.1 (Ar-C$_3$,C$_5$), 122.1 (Ar-C$_2$), 121.9 (Ar-C$_6$), 119.4 (Ar-C'$_3$), 118.2 (Ar-C'$_5$), 20.4 (-CH$_3$). MS (m/z): 212 [M+H]$^+$.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of Catalyst

ZnO NPs were synthesized *via* wet chemical method [64, 65], and were thoroughly characterized by XRD and SEM (Figs. **1** and **2**). These characterizations substantiate the approximate spherical shape with the average diameter of about 45 nm.

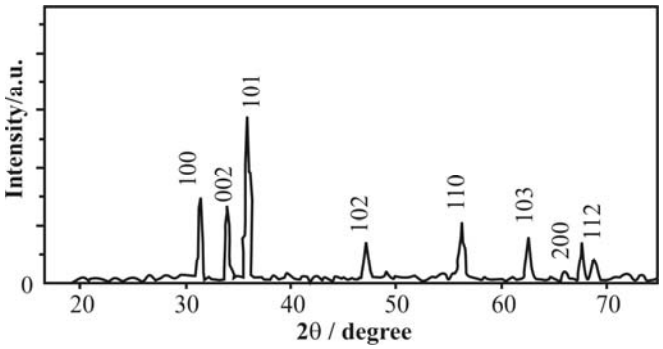


Fig. (1). XRD pattern of ZnO NPs.

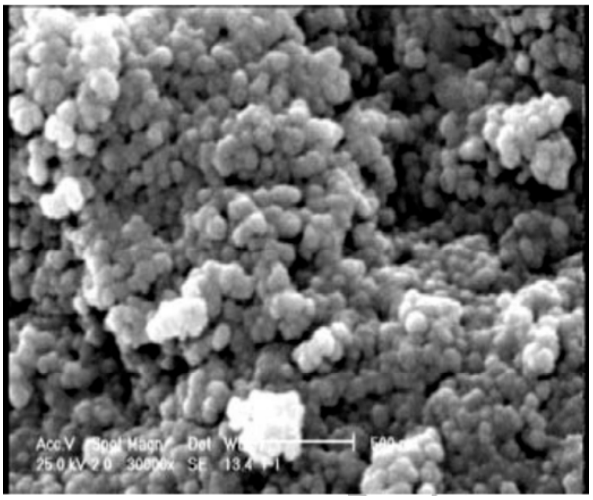


Fig. (2). SEM image of ZnO NPs.

Polycarbonate (PC)-ZnO NPs composites were fabricated by solution casting technique [66] with different concentrations (2 %, 5 % and 9 %) of ZnO NPs as dopent. The results of inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis support the doping of ZnO NPs (supporting information).

These nanocomposites were characterized by XRD, SEM, UV-VIS and FT-IR spectra. For both the membranes (with ZnO 5% and 9%), the XRD patterns (Fig. **3**) indicated that the films have a polycrystalline hexagonal wurtzite crystal structure (a=3.2392, c=5.1986 Å) and a strong diffraction peak of ZnO (0 0 2) [67-69], indicates that the membranes were successfully casted.

Fig. **4** represents the SEM picture of PC-ZnO NPs composites, which indicated that ZnO NPs at loading up to 5% in PC matrix oriented well while ZnO NPs at higher loading (9%) in PC matrix agglomerates, which is consistent with the results obtained through the optical micrographs of these NPs composites (Fig. **5**). Additionally for the (PC)-ZnO NPs composites, the grain size distribution is quite homogeneous.

The transmittance of PC-ZnO NPs composites is lower than that of the polycarbonate membrane, which is clearly revealed by the UV-VIS spectra of PC-ZnO NPs composites and polycarbonate membranes (Fig. **6**). FTIR spectra of treated and untreated samples

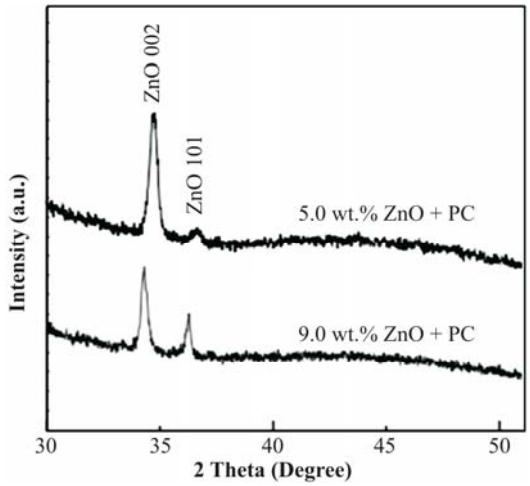


Fig. (3). XRD spectra of PC-ZnO NPs composites (5 % and 9 %).

showed that there is no change in the basic structure of the membrane material only the surface characteristics showed modifications. A band at 500 cm^{-1} is attributed to the ZnO stretching band (Fig. **7**).

3.2. Catalytic Activity for Knoevenagel Condensation

In the effort to evaluate the catalytic activity of the PC-ZnO NPs composites, the Knoevenagel condensation of 4-chloro benzaldehyde with ethyl cyanoacetate was used as a model reaction in ethyl lactate under ultrasonic irradiation. In the preliminary stage of investigation we focused on systematic evaluation of different catalysts (Table **1**). With ZnO NPs the reaction proceeded smoothly to afford the corresponding product in good yield. Optimization studies revealed that after 3rd recycle of ZnO NPs there was a sharp drop in the yield. This drop can be attributed to the coagulation of ZnO NPs which decreases the effective surface area of the catalyst. To facilitate the catalyst recovery and prevent their aggregation in reaction mixture ZnO NPs were immobilized on polycarbonate support. Further, the study of catalytic ability of PC-ZnO NPs

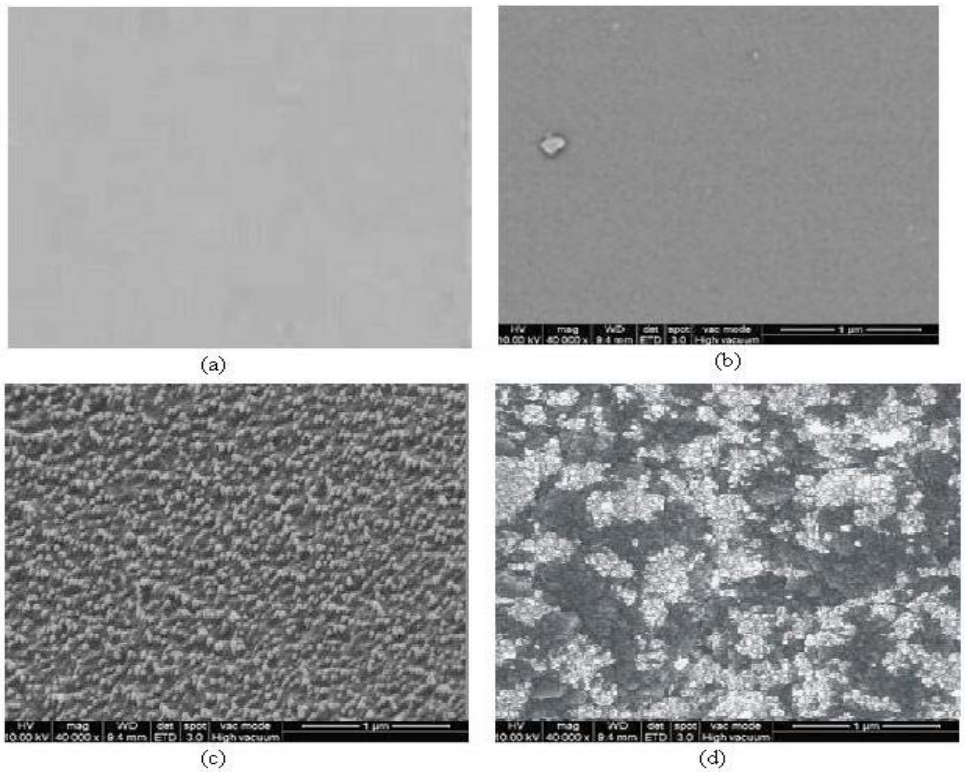
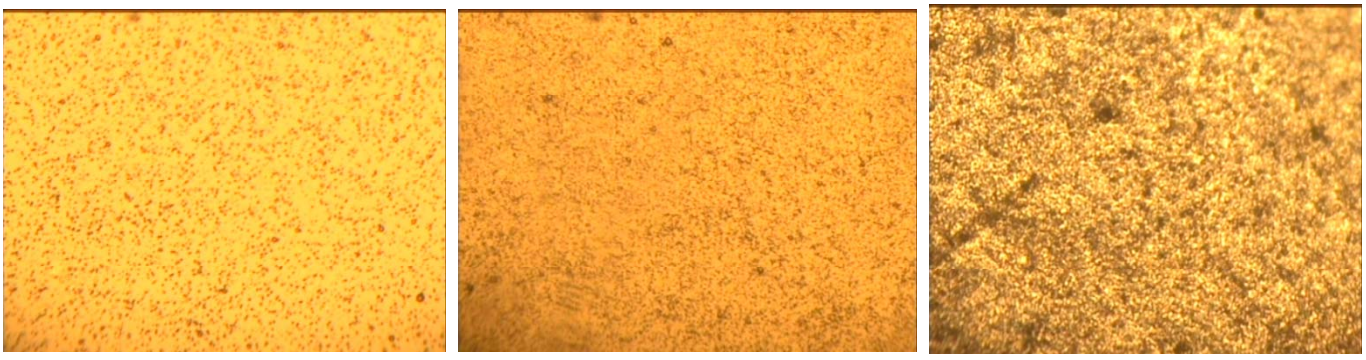


Fig. (4). SEM images of (**a**) pristine membranes and PC-ZnO NPs composites with various concentration of dopant (**b**) 2% (**c**) 5% (**d**) 9%.



(a) **(b)** **(c)**

Fig. (5). Optical micrographs of PC-ZnO NPs composites with various concentration of dopant (**a**) 2% (**b**) 5% (**c**) 9%.

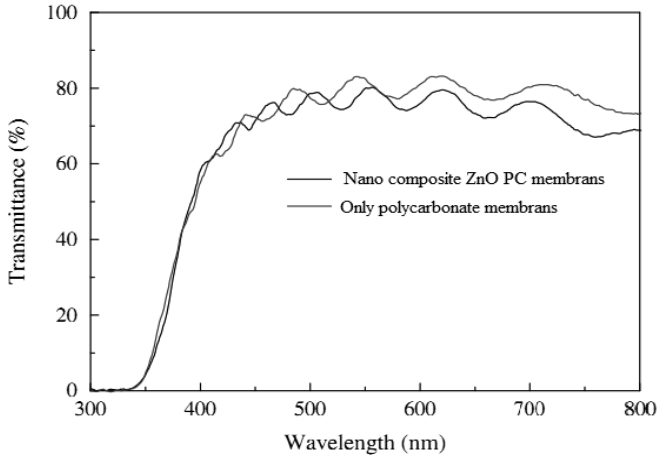


Fig. (6). UV-VIS spectra of PC-ZnO NPs composites and polycarbonate membranes.

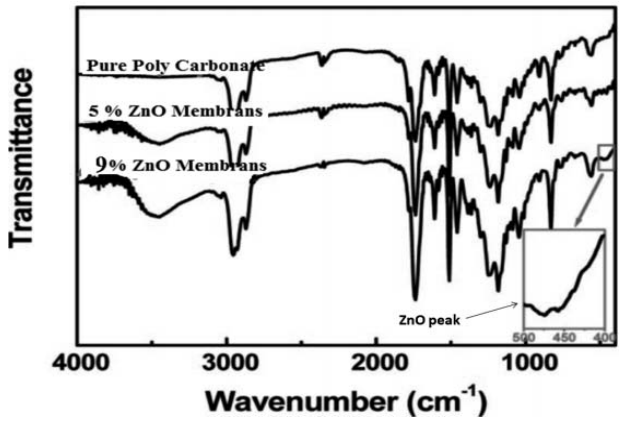


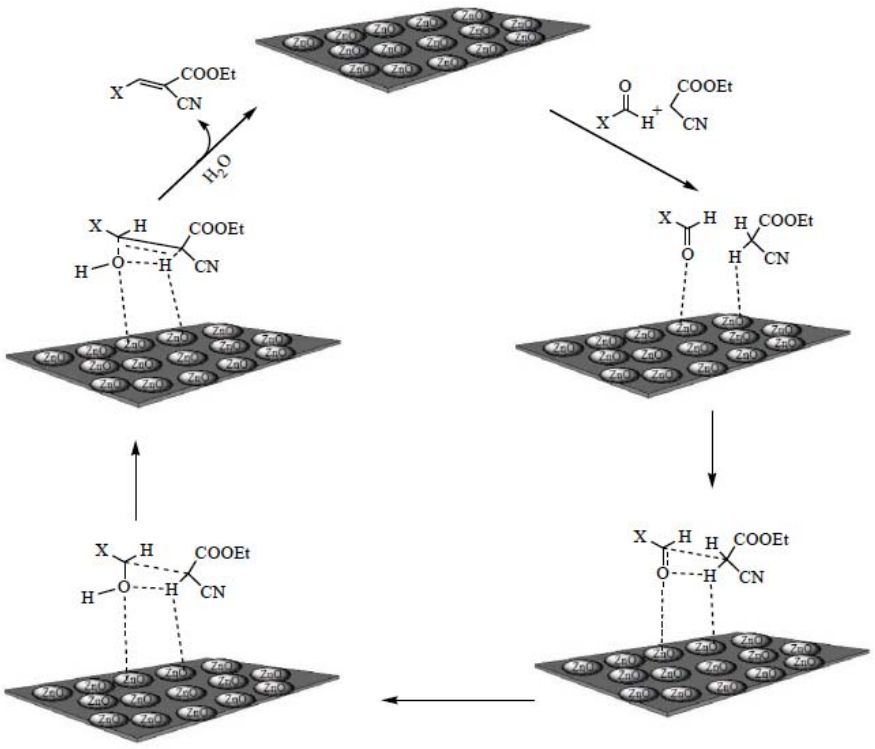
Fig. (7). FTIR spectra of PC-ZnO NPs composites.

Table 1. Comparison of catalytic activity of catalyst.

Entry	Condition	Time (min)	Yield(%)*
1	Blank	30	39
2.	$ZnSO_4$ (10 mol%), US	20	59
3.	$ZnCl_2$ (10 mol%), US	20	62
4.	Zn dust (10 mol%), US	20	67
5.	Powder ZnO (10 mol%), US	20	69
6.	ZnO NPs (10 mol%), US	14	77
7.	PC membrane	30	39
8.	PC-ZnO NPs composites (2%), US	4	84
9.	PC-ZnO NPs composites (5%), US	4	96
10.	PC-ZnO NPs composites (9%), US	4	88

*Isolated yield
Reaction conditions: 4-Chlorobenzaldehyde (1 mmol; 0.141 g), ethylcynoacetate (1 mmol; 0.113 g), in 5 ml ethyl lactate.

composites showed that loading of ZnO NPs in PC matrix increased the product yield to 96% and reducing the reaction time (4 min) with decrease the catalyst loading (a decrease in metal content) (Table **1**). The yield increases smoothly with ZnO NPs loading up to 5% in PC matrix while ZnO NPs at higher loading (9%) in PC matrix agglomerates, which hindered the catalytic effect of nano-composite. The amount of ZnO NPs incorporated in the thin films was determined by ICP-AES analysis. A comparison experiment was carried out by using polycarbonate (pristine membrane) under the same experimental conditions only 39% yield was observed which was comparable to that of blank reaction this indicated that the polycarbonate itself did not promote the reaction.



Scheme 2. Possible mechanism of Knoevenagel condensation catalyzed by PC-ZnO NPs composites.

Table 2. Reaction of ethylcyanoacetate with various aromatic aldehydes.

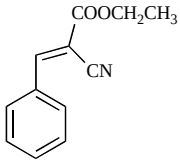
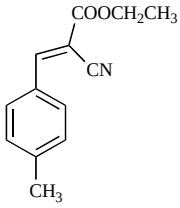
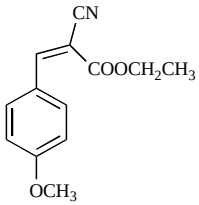
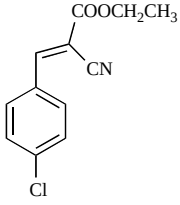
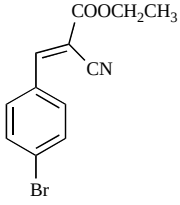
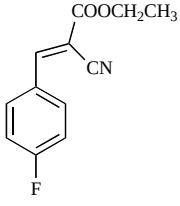
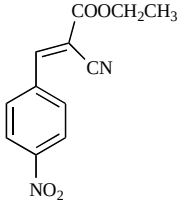
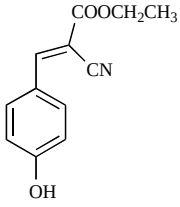
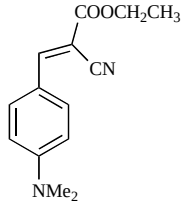
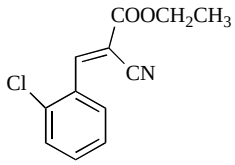
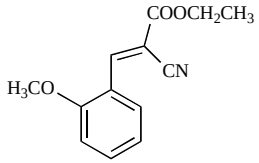
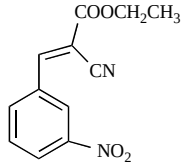
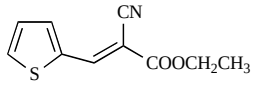
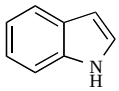
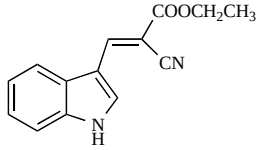
S. No.	X	Product	Time (min)	Yield*	Mp (°C)
3a	C_6H_5		5	90	48-50
3b	4-$CH_3C_6H_4$		6	93	92-94
3c	4-$OCH_3C_6H_4$		5	92	80-82
3d	4-ClC_6H_4		4	96	88-90
3e	4-BrC_6H_4		4	94	97-99
3f	4-FC_6H_4		4	96	93-95
3g	4-$NO_2C_6H_4$		5	94	165-167
3h	4-OHC_6H_4		5	94	172-174

Table 2. Contd……

S. No.	X	Product	Time (min)	Yield*	Mp (°C)
3i	4-$NMe_2C_6H_4$		6	92	117-119
3j	2-ClC_6H_4		4	94	45-47
3k	2-$OCH_3C_6H_4$		5	95	73-75
3l	3-$NO_2C_6H_4$		4	90	130-132
3m			5	96	106-108
3n			5	96	162-164

*Isolated Yield

Reaction conditions: Aromatic aldehyde (1 mmol), ethylcynoacetate (1 mmol; 0.113 g) and PC-ZnO NPs composites (5%), in 5 ml ethyl lactate under ultrasonic irradiation.

In the present case, the acidic and basic sites present in PC-ZnO NPs composites simultaneously interacts with carbonyl oxygen of the aldehyde group and active methylene of ethylcynoacetate, respectively, as given in (Scheme **2**). Due to these interactions, a weak bond is formed between the α-carbon of ethylcynoacetate and electron deficient carbonyl carbon as well as between carbonyl oxygen and α-hydrogen of ethylcynoacetate to afford the corresponding aldol product. Further, the aldol formed will again form a cyclic intermediate on the catalyst surface to undergo an elimination process which will lead to Knoevenagel adducts.

Under ultrasonic irradiation, the acoustic cavitation effects form microjects of liquid bombard on the surface of catalyst. This effect causes the exposition of unreacted surfaces of catalyst and increasing the interphase surface able to react which enhance the catalyst efficiency. In mandate to generalize the above catalytic protocol, reaction of ethylcyanoacetate with various aromatic aldehydes was studied (Table **2**). It was found that aldehyde with electron-withdrawing group was observed to be more reactive than that of electron-donating group. In order to evaluate the catalyst leaching, the product and filtrate was analyzed by ICP-AES (supporting information). These results show that, no leaching of nanoparticles has taken place.

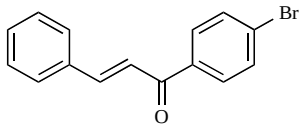
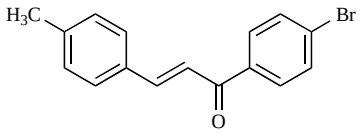
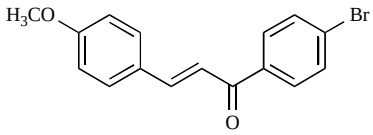
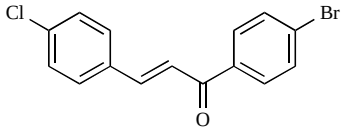
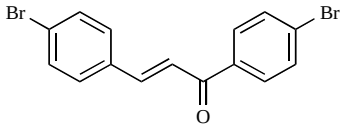
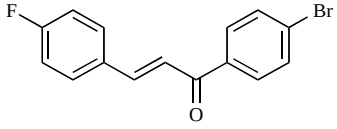
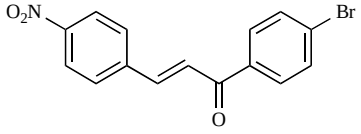
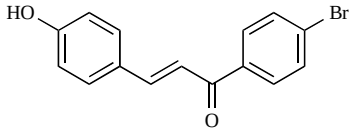
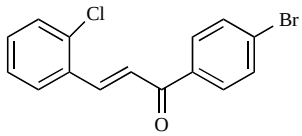
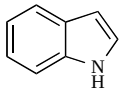
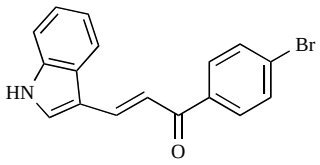
To further explore the scope and limitation of this methodology, 4-bromoacetophenone was condensed with a number of substituted aromatic aldehydes (Table **3**). Substitutions with both electron-withdrawing and electron-donating groups on the aromatic ring were well-tolerated and good to excellent yields were obtained. The ^{1}H NMR showed that these chalcones were geometrically pure with the ethylene moiety in the enone linkage having trans-conformation ($J_{H\alpha\text{-}H\beta}$ = 15-16 Hz).

Further, the reaction of aromatic aldehydes with cyclic ketones like cyclopentanone and cyclohexanone furnished the mono substituted α,β-unsatureted compounds exclusively instead of the bis-chalcone (Table **4**).

After the establishment of the best conditions for the synthesis of α,β-unsatureted compounds, we decided to extend the synthetic scope of this protocol for the synthesis of various aryl aldimines. The results are summarized in Table **5**.

Both electron-withdrawing and electron-donating substituents on the aldehyde aryl ring were well tolerated. Ortho and para-nitrobenzaldehydes produced the desired products (Table **5**) in similarly high yields indicating that the position of the electron-withdrawing substituent had no significant effect on the yield. A

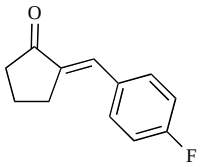
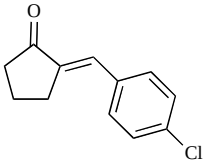
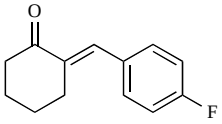
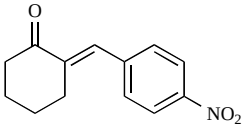
Table 3. Reaction of 4-bromoacetophenone with various aromatic aldehydes.

S. No.	X	Product	Time (min)	Yield*	Mp (°C)
5a	C_6H_5		8	92	160-162
5b	4-$CH_3C_6H_4$		7	94	162-164
5c	4-$OCH_3C_6H_4$		7	93	144-146
5d	4-ClC_6H_4		5	95	174-176
5e	4-BrC_6H_4		5	96	192-194
5f	4-FC_6H_4		5	94	178-180
5g	4-$NO_2C_6H_4$		6	94	169-171
5h	4-OHC_6H_4		8	91	184-186
5i	2-ClC_6H_4		5	92	112-114
5j			7	93	168-170

*Isolated yield

Reaction conditions: Aromatic aldehyde (1 mmol), 4-bromoacetophenone (1 mmol; 0.199 g) and PC-ZnO NPs composites (5%), in 5 ml ethyl lactate under ultrasonic irradiation.

Table 4. Reaction of cyclic ketones with various aromatic aldehydes.

S.No.	X	Cyclic ketone	Product	Time (min)	Yield*	Mp(°C)
6a	4-FC_6H_4	Cyclopentanone		5	93	82-84
6b	4-ClC_6H_4	Cyclopentanone		4	95	76-78
6c	4-FC_6H_4	Cyclohexanone		6	93	94-96
6d	4-$NO_2C_6H_4$	Cyclohexanone		4	94	122-124

*Isolated Yield

Reaction conditions: Aromatic aldehyde (1 mmol), cyclopentanone (1 mmol; 0.084 g)/ cyclohexanone (1 mmol; 0.098 g) and PC-ZnO NPs composites (5%), in 5 ml ethyl lactate under ultrasonic irradiation.

Table 5. Reaction of toluidine with various aromatic aldehydes.

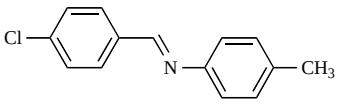
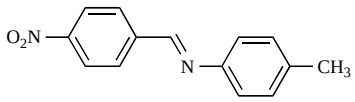
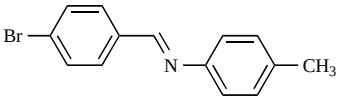
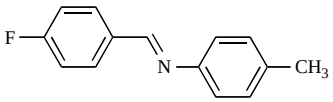
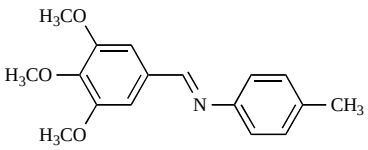
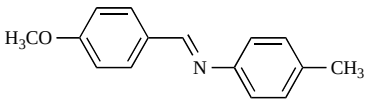
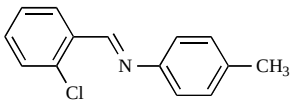
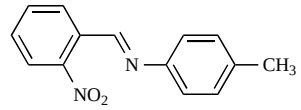
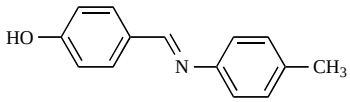
S.No.	R	Product	Time (min.)	Yield (%)*	Mp (^oC)
7a	4-Cl		5	94	126-128
7b	4-$N0_2$		4	96	122-124
7c	4-Br		6	93	128-130
7d	4-F		8	92	110-112
7e	3,4,5-OCH_3		5	96	170-172
7f	4-OCH_3		6	95	64-66
7g	2-Cl		6	94	48-50

Table 5. Contd……

S.No.	R	Product	Time (min.)	Yield (%)*	Mp (°C)
7h	2-NO_2		5	93	72-74
7i	4-OH		4	95	216-218

*Isolated Yield

Reaction conditions: Aromatic aldehyde (1 mmol), toluidine (1 mmol; 0.107 g) and PC-ZnO NPs composites (5%), in 5 ml ethyl lactate under ultrasonic irradiation.

similar trend was observed with electron-donating substituents. Introduction of -OH, and -OMe on the benzaldehyde aryl ring produced the corresponding aryl aldimines with excellent yields.

3.3. Recyclability

The polycarbonate (PC)-ZnO NPs composite was recovered by simple filtration, washed with water and reused 10 times without any loss of catalytic activity due to effective immobilization on polycarbonate matrix.

4. CONCLUSION

In summary, PC-ZnO NPs composites were successfully synthesized by solution casting method with different concentrations of ZnO NPs as dopent. FTIR, XRD, SEM, optical micrographs and UV-VIS spectra showed the effective structural modifications and confirmed the doping of ZnO NPs in PC matrix. These nanocomposites created a new robust recyclable catalytic system for the synthesis of α,β-unsaturated compounds and aldimines. Incorporation of ZnO NPs into PC matrix improved the catalyst recovery and prevents their aggregation in reaction mixture. The significant advantages of this methodology are mild reaction conditions, high yields, short reaction times, simple workup procedures, and low cost. Most importantly, removal and recovery of the polymer catalyst by simple filtration at the end of the reaction remarkably facilitates the work-up procedure.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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