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An Efficient and One Pot Synthesis of 2,4,5-Trisubstituted Imidazole Derivatives Catalyzed by Silver Nanoparticles

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Silver nanoparticles (AgNPs) have been used as an excellent and highly efficient catalyst for one pot synthesis of 2,4,5-trisubstituted imidazole derivatives in presence of ethanol as a solvent. This synthetic route involves multicomponent reaction of benzil, substituted aromatic aldehydes and ammonium acetate under reflux. The synthesized silver nanoparticles were characterized by UV-visible spectroscopy (UV-visible), X-ray diffraction (XRD) pattern, scanning electronic microscope (SEM) analysis. The process was simple and environmentally benign with high to excellent yield. The methods provides several advantages such as simple operation, clean reaction profile, short reaction time and high yield of product. The synthesized silver nanoparticles as catalyst was non-toxic, eco-friendly, low cost and green synthetic method.

Keywords: Benzil, Substituted benzaldehyde, Ammonium acetate, Silver nanoparticles.

INTRODUCTION

Imidazole and its derivatives have importance due to their widespread biological activity and their use in synthetic and pharmaceutical chemistry. This ring compounds is present in many important biological building blocks such as purine, histamine, nucleic acids and biotin [1]. Imidazole compounds operate as active parts in drug like losartan and eprosartan [2].

Imidazole and their derivatives were used for the synthesis of various types of medicinal compounds having a good therapeutic values such as antimicrobial [3,4], anti-HCV [5], antitumor [6], leishmanicidal [7], anticonvulsant [8], GABA up take inhibitory [9], cytotoxic [10,11], anticancer [12], antiproliferative [13,14], antitubercular [15], antifungal [16,17], anticandidal activity [18], antibacterial [19,20], anti-inflammatory [21,22], therapeutic activity [23] and antiviral [24,25] activities *etc*. Few substituted imidazoles act as plant growth regulators [26], p38α MAP kinase inhibitors [27], β-Raf kinase [28], glucagon receptors [29], antiamoebic activity [30], *etc*.

Japp & Radziszewski [31,32] proposed the first synthesis of imidazole core in 1882, synthesized from 1,2-dicarbonyl compounds, aldehydes and ammonia to obtained 2,4,5-triphenyl imidazoles. In recent years, numerous methods have been developed for the synthesis of 2,4,5-trisubstituted imidazole using various catalyst including sulfuric acid immobilized on silica gel [33], ceric ammonium nitrate [34], L-proline [35], $ZrCl_4$ [36], a metal-organic framework $Cu_2(BDC)_2(DABCO)$ [37], $KMnO_4/CuSO_4$ [38], PEG-400 [39], benzyltriphenyl phosphonium chloride (BTPPC) [40], 3-picolinic acid [41], HNO_3 in microwave irradiation [42], indium(III) triflate and magnesium sulfate heptahydrate [43], Fe_3O_4 and Cu_2O nanoparticles [44], fly ash supported Bi_2O_3-ZnO [45], *etc.* Although some methods are actually efficient and the synthetic protocols for imidazole derivatives. Therefore, the development of efficient, simple, environmentally safe, eco-friendly and high yield methods using new nanocatalyst for the preparation of these compounds.

In this work, an efficient method for one pot synthesis of 2,4,5-trisubstituted imidazole derivatives starting from benzil, various substituted benzaldehyde and ammonium acetate using silver nanoparticles (AgNPs) as a catalyst in presence of ethanol under reflux and provide a feasible alternative, since they are ecofriendly, less expensive and can be carried out in single step [46]. AgNPs can be prepared in low concentration of *Ocimum*

sanctum L. leaf extract without using any additional toxic chemicals [47].

EXPERIMENTAL

Benzil, substituted aromatic aldehydes and ammonium acetate were of analytical reagent (AR) grade purchased from commercial sources were used as without further purification. Silver nanoparticles (AgNPs) as catalyst were characterized by microscopic and spectroscopy techniques such as UV-visible spectroscopy, X-ray diffraction and scanning electron microscope (SEM). All the synthesized compounds were well known and identified by comparing with melting point, FT-IR, ^{1}H NMR, ^{13}C NMR and mass analysis (LC-MS).

The FT-IR spectroscopy were recorded on Shimadzu FT-IR 8400 using potassium Bromide pallets. The ^{1}H NMR and ^{13}C NMR spectroscopy were recorded in $CDCl_3$/DMSO-d_6 on BRUCKER-400 MHz and Mass analysis spectra were recorded on Shimadzu MODEL-8045 at ESI-APCI interface.

Preparation of plant extract: Fresh leaves of *Ocimum sanctum* L. were collected locally. This leaves were washed with distilled water and remove dust particles and then further dried. About 15 g of *Ocimum sanctum* L. leaves were ground into fine powder and transferred to a beaker containing 100 mL distilled water. The broth was boiled for 15 min. The plant extract were cooled to room temperature and filtered thought Whatman filer paper No. 1 to remove particulate matter. The filtrate obtained was then stored in refrigerator for further use.

Preparation of silver nanoparticles (AgNPs): Aqueous solution (0.01 M) of $AgNO_3$ was prepared in 250 mL conical flask and plant extract was added for reduction into Ag^+ ions. The mixture was then kept on hot plate for the period of 20 min at 60 ºC. The change in colour from yellow to dark brown indicated the formation of AgNPs [48].

Synthesis of 2,4,5-trisubstituted imidazole: The derivatives of 2,4,5-trisubstituted imidazole were synthesized by one pot method. The mixture of benzil (1 mmol), substituted aromatic aldehydes (1 mmol), ammonium acetate (3 mmol), 15 % mol of silver nanoparticles as a catalyst and ethanol as a solvent were fitted with 250 mL round bottom flask. Thereafter, the mixture was heated at 100 ºC under reflux. The product obtained were followed by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was diluted with ethanol (20 mL). The solid imidazole product was filtered, washed and recrystallized from ethanol (**Scheme-I**). The structural characterization and their authenticity of the product was established by their FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopies.

Spectral analysis

2,4,5-Triphenyl-1*H*-imidazole (1a): White solid, m.p.: 272-273 ºC, yield: 96%. FT-IR (KBr, ν_{max}, cm^{-1}): 3062.42, 1659.38, 1594.58, 1460.73, 1210.74, 1127.66, 765.48, 697.03, ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ ppm: 11.835 (s, 1H), 8.008-7.215 (m, 15H), ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ ppm: 194.63, 146.31, 134.95-125.55' Mass (LC-MS): Obs. (*m/z*) 296.40, calcd. (*m/z*) 297.0.

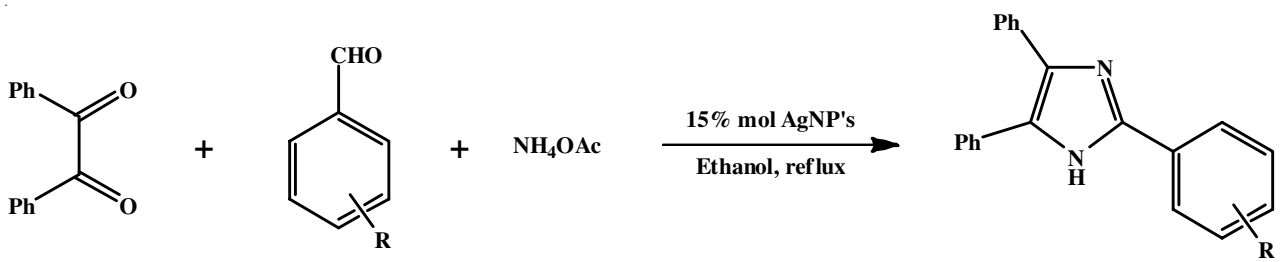
2-(4-Hydroxyphenyl)-4,5-diphenyl-1*H*-imidazole (1b): White solid, m.p.: 234-235 ºC, yield: 95%. FT-IR (KBr, ν_{max}, cm^{-1}): 2969.30, 2722.69, 1456.79, 1359.0, 1167.55, 973.34, 841.54, 808.68, ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ ppm: 9.366 (s, 1H), 7.846 (d, 2H), 7.470 (d, 2H), 7.452-6.753 (m, 10H); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ ppm: 158.0, 146.67, 128.38-126.98, 115.58; Mass (LC-MS): Obs. (*m/z*) 312.40, calcd. (*m/z*) 313.0.

2-(4-Chlorophenyl)-4,5-diphenyl-1*H*-imidazole (1c): White solid, m.p.: 258-260 ºC, yield: 96%. FT-IR (KBr, ν_{max}, cm^{-1}): 3522.84, 1695.80, 1591.12, 1486.05, 1328.11, 1186.37, 1089.69, 979.12, 823.67, 701.88, ^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6) δ ppm: 9.366 (s, 1H), 7.852 (d, 2H), 7.831 (d, 2H), 7.554-7.265 (m, 10H); ^{13}C NMR ($CDCl_3$/DMSO-d_6) δ ppm: 145.04, 133.47, 129.34-126.95; Mass (LC-MS): Obs. (*m/z*) 330.80, calcd. (*m/z*) 331.0.

RESULTS AND DISCUSSION

Initially, the reaction was carried by using different solvents and different % mol of silver nanoparticles as catalyst for the synthesis of 2,4,5-trisubstituted imidazoles to investigate the feasibility of the reaction. Benzil, substituted aromatic aldehydes and ammonium acetate in different solvents conditions in presence of silver nanoparticles as catalyst and the results are summarized in Table-1. It was observed that the yield of products are obtained in solvent free, DMSO, acetonitrile, dichloromethane, chloroform and ethanol even after 20 min. It was clearly observed that the reaction was carried out with ethanol as a solvent at 100 ºC provides 60% yield within 20 min. After finding suitable solvent, the reaction with different % mol of silver nanoparticles catalyst and observed that 15% mol of suitable to obtain a maximum yield of product is summarized in Table-2. No change was observed on further enhancing the % mol of catalyst.

With the optimized conditions, the reaction was performed with different substituted benzaldehyde to explore the scope and generally of the presence protocol and the results are summarized in Table-3.



Scheme-I: Synthetic route of 2,4,5-trisubstituted imidazole derivative catalyzed by silver nanoparticles

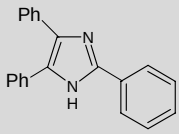
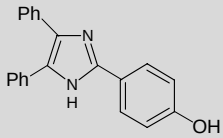
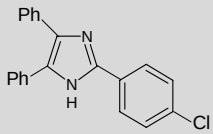
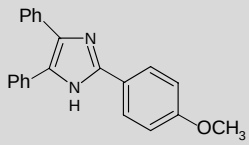
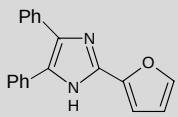
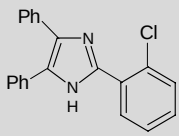
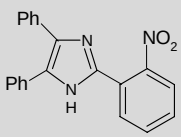
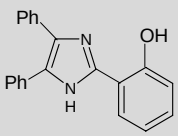
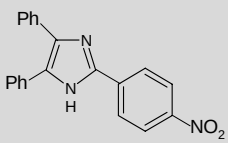
TABLE-1
SCREENING OF SOLVENTS FOR THE SYNTHESIS OF 2,4,5-TRISUBSTITUTED IMIDAZOLES

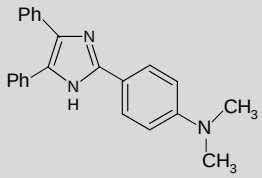
Solvents	Mole of catalyst (%)	Time (min)	Temp. (°C)	Yield (%)
Solvent free	5	60	100	20
DMSO	5	60	100	24
Acetonitrile	5	60	100	27
Dichloromethane	5	60	100	31
Chloroform	5	60	100	40
Ethanol	5	60	100	62

TABLE-2
EFFECT OF SILVER NANOPARTICLES CATALYST MOLE % ON SYNTHESIS OF 2,4,5-TRISUBSTITUTED IMIDAZOLES

Solvent	Amount of AgNP's (%)	Temp. (°C)	Time (min)	Yield of product (%)
Ethanol	5	100	60	62
Ethanol	10	100	40	78
Ethanol	15	100	20	96
Ethanol	20	100	20	96
Ethanol	30	100	20	96

TABLE-3
SILVER NANOPARTICLES CATALYZED BY THE SYNTHESIS OF 2,4,5-TRISUBSTITUTED IMIDAZOLE DERIVATIVES

Compd. No.	R-Ar-CHO	Product	Time (min)	Yield (%)	m.p. (°C)
1a	Ar-CHO		20	96	272-273
1b	4-OH-Ar-CHO		20	95	234-235
1c	4-Cl-Ar-CHO		20	96	258-260
1d	4-OCH_3-Ar-CHO		20	95	227-229
1e	Furfuraldehyde		20	94	200-202
1f	2-Cl-Ar-CHO		20	95	193-194
1g	2-NO_2-Ar-CHO		20	96	298-300
1h	2-OH-Ar-CHO		20	95	209-210
1i	4-NO_2-Ar-CHO		20	96	199-201

1j	4-Dimethylamino-Ar-CHO		20	96	257-258

UV-visible spectrum analysis of AgNPs: UV-visible absorbance spectrum recorded for silver nanoparticles exhibited maximum absorbance peak (ν_{max}) at 418.40 nm in *Ocimum sanctum* L. (Fig. 1) due to surface plasmon resonance of AgNPs. The flat curves of the graph indicated the formation of polydisperse large nanoparticles due to the slow reduction rate.

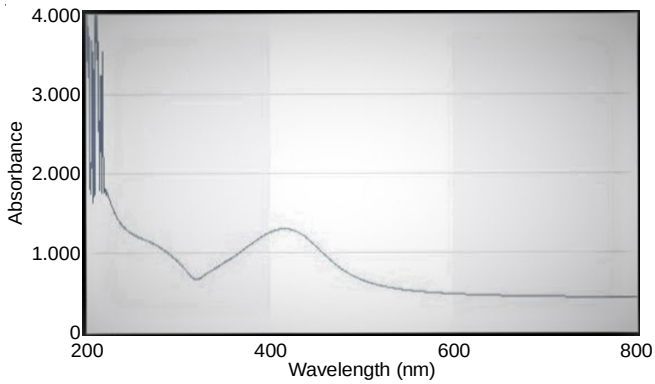


Fig. 1. UV analysis of synthesized silver nanoparticles

X-ray diffraction (XRD) pattern of AgNPs: The silver nanoparticles was further confirmed by X-ray diffraction pattern. The X-ray diffraction pattern of synthesized AgNPs using *Ocimum sanctum* L. leaf extract as shown in Fig. 2. The peak is observed at 2θ = 32.22º, 38.23º and 64.65º corresponds to (111), (200) and (220), respectively lattice planes. The XRD pattern of synthesized Ag NP's is crystalline and face centered cubic (FCC) structure.

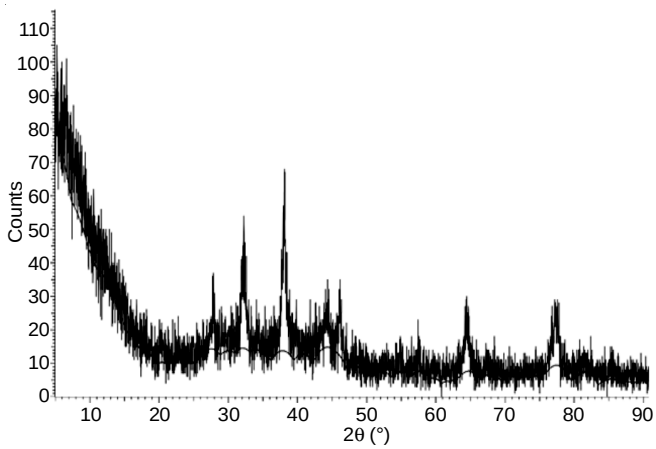


Fig. 2. XRD analysis of synthesized silver nanoparticles

SEM studies of AgNPs: The SEM image exhibited that the synthesized AgNPs from *Ocimum sanctum* L. extract were mostly spherical in shape (Fig. 3). The average size of synthesized AgNPs is about 28-47 nm.

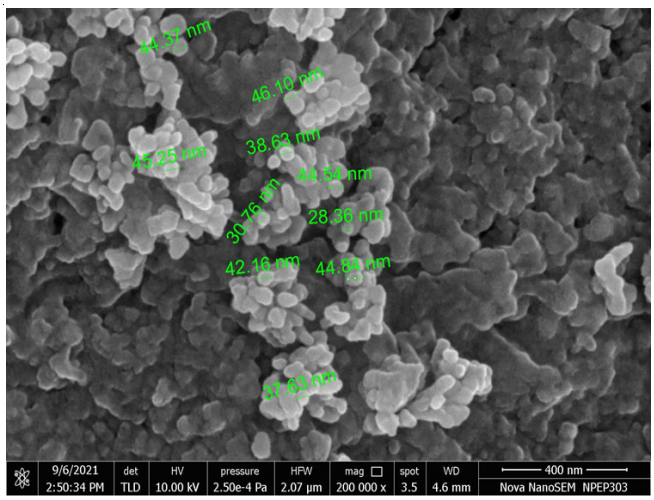


Fig. 3. SEM analysis of synthesized silver nanoparticles

Conclusion

An efficient, simple, one pot, a green synthetic method of 2,4,5-trisubstituted imidazole derivatives using silver nanoparticles as catalyst and ethanol as a solvent is develped. The simplicity of this method includes its simplicity of operation, clean reaction and excellent yield of the product. The silver nanoparticles catalyst is easy for the separation, non-toxic, eco-friendly and environmentally safe.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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