

Magnetic nano copper ferrite catalyzed one pot synthesis of substituted quinoline derivatives under Ultrasonication

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Abstract: An efficient and facile method for the preparation of 2-amino-4-arylquinoline-3-carbonitrile derivatives were developed and described through nano copper ferrite (CuFe_2O_4) catalyzed one pot three-component cyclization of various aromatic aldehydes, malononitrile and aromatic amines under Ultrasonication. The cubic magnetic copper ferrite nano particles were synthesized by sol-gel citrate precursor method and characterized by FTIR, XRD, SEM and TEM techniques and the structures of the synthesized quinolines were assigned by IR, MASS, ^1H NMR. The catalyst was separated with a strong Neodymium magnet from the reaction mixture and reused for five consecutive reactions without noticeable loss of activity.

Keywords - Quinoline derivatives, one pot three component cyclization, nano copper ferrite, ultrasonication

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I. Introduction

Synthesis of organic transformations by using conventional methods is expensive and has long reaction periods. Sonicated reactions produce different reaction pathways other than conventional reactions and enhance the reactivity of the reactants by nearly a million-fold. Green chemistry is the driving force for organic chemists to provide environmentally benign routes for the synthesis of novel organic compounds, which leads to the privileged heterocyclics in short reaction time, mild conditions and higher yields over conventional methods [1-3]. In Ultrasonication, an acoustic pressure wave propagates through a reaction mixture; it facilitates the breakdown of micrometer sized bubbles in the solution [4].

Heterocyclic's, particularly nitrogen-containing heterocyclic compounds are the most important class of compounds in natural products and also have wide range of applications in medicinal chemistry and these are the key intermediates in large number of bioactive molecules and materials in chemistry [5-6]. Quinoline moieties possess various medicinal properties such as antiasthmatic, tyrosine Kinase inhibiting agents, antimalarial, antihypertensive, anti-inflammatory, anti bacterial agents [7].

Several methods have been reported for the synthesis of quinoline derivatives such as Friedlander annulations [8], Skraup synthesis [9], Gould-Jacobs reaction [10], Combes synthesis [11], Doebner-von Miller reactions [12], reductive cyclization of Baylis-Hillman adducts [13], metal-catalyzed cyclizations with anilines [14], Aza-Diels-Alder reactions with N-Arylaldamines [15], cascade reactions of alkynes [16], Friedlander synthesis is carried out in presence of an acid and a base catalysts [17-18], yttrium triflate [19], magnesium chloride [20], ceric ammonium nitrate [21], zirconium nitrate [22], phosphoric acid [23] and an ionic liquid $[\text{HBIm}][\text{BF}_4]$ [24].

Many of these procedures have significant drawbacks including long reaction times [29], recyclability of the catalyst [20, 21, 23 and 29] and difficulties in workup. The main disadvantage of these procedures involves that the catalysts are destroyed during the course of the reaction and cannot be recovered. Previously, nano copper ferrite catalyst was synthesized, characterized and applied for various organic transformations including one-pot synthesis of 2,4,5-trisubstituted imidazoles [25], nano copper ferrite catalyzed one-pot synthesis of tri and tetra substituted imidazoles under Ultrasonication [26], microwave assisted Nickel Cobalt ferrite catalyzed one-pot synthesis of β -acetamido ketones [27] and nano copper ferrite catalyzed improved procedure for one-pot synthesis of poly substituted pyridine derivatives [28], Magnetic nano cobalt ferrite catalyzed synthesis of 4H - Pyrano [3, 2-h] quinoline derivatives under Microwave irradiation [30]

As part of our ongoing pursuit of discovering new reaction pathways, we report a simple, cost-effective, green and expeditious method for synthesis of quinoline derivatives via a three component reaction of aromatic aldehyde, malononitrile, aromatic amine in ethanol catalyzed by nano copper ferrite under Ultrasonication. This present method has several advantages like short reaction time, better yields, low catalyst loading, magnetic recoverability, reusability and ecofriendly benign process.

II. Experiment

Solvents and chemicals are of AR grade and used without further purification. For the characterization of the calcined as-synthesized nano copper ferrite, the XRD spectra were recorded on PANalytical-Xpertpro diffractometer and the average crystallite size was determined from the corresponding XRD data. The microstructural morphology was studied with a Scanning Electron Microscope (SEM) model JEOL –JSM 6610 LV. FTIR spectra were recorded on BRUKER ALPHA FT-IR with Opus 6.1 version. Specific surface area (SBET) of samples was determined by BET surface area analyzer (Nova 2000 series, Quanta chrome Instruments, UK). ¹H NMR was recorded on the Bruker-Avance 300-MHz spectrometer in DMSO-d₆/CDCl₃, using TMS as internal standard. Chemical shifts are given in parts per million (ppm). The FT-IR spectroscopy of samples was carried out on a Perkin Elmer, precisely 100 FT-IR spectrometer in the 400–4000 cm⁻¹ region. NCMS mass spectra were recorded on a MASPEC low resolution mass spectrometer operating at 70 eV. Ultrasonication was performed in a Rivotek ultrasonic cleaner with Transducer PZT crystals (Morgan Matrac, UK make) bonded on the base of the tank with welbond technique (frequency of 40 kHz and an output power of 250 W) and the purity of products was checked out on thin layer chromatography (TLC) on aluminum-backed plates coated with Merck Kieselgel60 F254 silica gel, visualizing the spots under ultraviolet light.

2.1 General procedure for the synthesis of catalyst

Magnetic spinel nano copper ferrite catalyst with composition CuFe₂O₄ was chosen for this study. For the preparation of catalyst, aqueous solutions of stoichiometric amounts of copper nitrate along with ferric citrate were reacted with citric acid in 1:1 molar ratio. P^H of the solution was increased to 7 by addition of ammonia to complete the reaction and ethanediol was added. The solution was evaporated very slowly over a period of ten to twelve hours to dryness. Viscosity and color changed as the solution turned into puffy, porous and dry gel. As soon as the solvent removal is completed, dried precursor undergoes a self-ignition reaction to form a very fine powder known as as-synthesized powder. The as-synthesized powder thus obtained was calcined in a muffle furnace at 500 °C for 2 hours to remove the residual carbon.

2.2 General procedure for the one-pot synthesis of quinoline derivatives catalyzed by nano copper ferrite (4a-4i):

About 500 mg of the catalyst was taken and activated at 500 °C for 2 hours and cooled to room temperature before the experiment. In a beaker, equimolar quantities of aromatic aldehyde (10 mmol) and malononitrile (10 mmol) were mixed together along with the catalyst and 5ml of ethanol were added. Now the beaker was kept in ultrasonic bath, where the surface of reactants is slightly lower than the level of water. The reactants are irradiated at temperature 40 °C, to produce arylidenemalononitrile as a solid product. After formation of arylidenemalononitrile, 10 mmol of aromatic amine was added and irradiation is continued till the reaction is completed. The completion of the reaction was monitored by TLC (n-hexane: ethyl acetate 3:1), the formed product mixture was cooled to room temperature and ethyl alcohol added until the product was dissolved. The products were isolated by removing the catalyst magnetically from the reaction mixture. All the products were characterized by spectral analysis IR, ¹H NMR and Mass Spectral techniques.

2.2.1. 2-amino-6-chloro-4-(3-nitrophenyl) quinoline-3-carbonitrile (4a)

White solid, (IR, KBr, ν Cm⁻¹); 3446.61 (NH₂, str), 2225.80 (CN, str), 1596.00 (C=N, str); ¹H NMR (400MHz, CDCl₃, δ -ppm); 8.7 (s, 1H, Ar), 7.8-8.0 (m, 3H, Ar), 7.9 (s, 1H, Ar), 8.5-8.6 (d, 2H, Ar), 7.3 (s, 2H, NH₂); Molecular formula (C₁₆H₉ClN₄O₂): MASS (NCMS) (m/z):325, [M+1]:326.

2.2.2. 2-amino-6-chloro-4-(4-methoxyphenyl) quinoline-3-carbonitrile (4b)

White solid, (IR, KBr, ν Cm⁻¹); 3446.61 (NH₂, str), 2225.80 (CN, str), 1570.72 (C=N, str); ¹H NMR (400MHz, CDCl₃, δ -ppm); 7.8-8.0 (d, 1H, Ar), 7.7 (s, 1H, Ar), 7.3 (s, 2H, NH₂), 7.1-7.0 (d, 1H, Ar), 7.0 (d, 2H, Ar), 6.6 (d, 2H, Ar), 3.9-4.0 (s, 3H, OCH₃); Molecular formula (C₁₇H₁₂ClN₃O): MASS (NCMS) (m/z):309, [M+1]:310.

2.2.3. 2-amino-4-(4-bromophenyl)-6-chloroquinoline-3-carbonitrile (4c)

White solid, (IR, KBr, ν Cm⁻¹); 3571.87, 3453.10 (NH₂, str), 2226.00 (CN, str), 1578.91 (C=N, str); ¹H NMR (400MHz, CDCl₃, δ -ppm); 7.7 (s, 1H, Ar), 7.8 (d, 2H, Ar), 7.6 (d, 4H, Ar), 7.3 (s, 2H, NH₂); Molecular formula (C₁₆H₉BrClN₃): MASS (NCMS) (m/z):358, [M+1]:359.

2.2.4. 2-amino-4-(4-methoxyphenyl)-6-nitroquinoline-3-carbonitrile (4d)

White solid, (IR, KBr, ν Cm⁻¹); 3475.42, 3453.68 (NH₂, str), 2222.08 (CN, str), 1571.52 (C=N, str); ¹H NMR (400MHz, CDCl₃, δ -ppm); 8.1-8.0 (d, 2H, Ar), 7.9-8.0 (d, 2H, Ar), 7.5-7.6 (s, 1H, Ar), 7.3 (s, 2H, NH₂), 6.6-6.7 (d, 2H, Ar), 3.9-4.0 (s, 3H, OCH₃); Molecular formula (C₁₇H₁₂N₄O₃): MASS (NCMS) (m/z):320, [M+1]:321.

2.2.5. 2-amino-4-(4-chlorophenyl)-6-nitroquinoline-3-carbonitrile (4e)

White solid, (IR, KBr, ν Cm^{-1}); 3446.32, 3422.50 (NH_2 , str), 2226.13 (CN, str), 1584.37 (C=N, str); ^1H NMR (400MHz, CDCl_3 , δ -ppm); 8.1 (d, 2H, Ar), 7.8 (d, 2H, Ar), 6.6 (d, 2H, Ar), 7.3 (s, 2H, NH_2), 7.7 (s, 1H, Ar), 7.5 (d, 2H, Ar); Molecular formula ($\text{C}_{16}\text{H}_9\text{ClN}_4\text{O}_2$): MASS (NCMS) (m/z):324, [M+1]:325.

2.2.6. 3-amino-1-(4-chlorophenyl) benzo[f]quinoline-2-carbonitrile (4f)

White solid, (IR, KBr, ν Cm^{-1}); 3422.48 (NH_2 , str), 2226.27 (CN, str), 1583.97 (C=N, str); ^1H NMR (400MHz, CDCl_3 , δ -ppm); 8.2-8.3 (d, 2H, Ar), 8.0 (d, 2H, Ar), 7.9-7.8 (d, 2H, Ar), 7.7 (d, 2H, Ar), 7.5 (d, 2H, Ar), 7.2-7.3 (s, 2H, NH_2); Molecular formula ($\text{C}_{20}\text{H}_{12}\text{ClN}_3$): MASS (NCMS) (m/z):329, [M+1]:330.

2.2.7. 3-amino-1-(4-methoxyphenyl) benzo[f]quinoline-2-carbonitrile (4g)

White solid, (IR, KBr, ν Cm^{-1}); 3424.24 (NH_2 , str), 2221.75 (CN, str), 1571.86 (C=N, str); ^1H NMR (400MHz, CDCl_3 , δ -ppm); 7.8-8.0 (d, 2H, Ar), 7.6-7.7 (d, 2H, Ar), 7.4-7.5 (d, 2H, Ar), 7.0 (d, 2H, Ar), 6.7-6.8 (d, 2H, Ar), 7.3 (s, 2H, NH_2), 3.9-4.0 (s, 3H, OCH_3); Molecular formula ($\text{C}_{21}\text{H}_{15}\text{N}_3\text{O}$): MASS (NCMS) (m/z):325, [M+1]:326.

2.2.8. 2-amino-4-(4-chlorophenyl) quinoline-3-carbonitrile (4h)

White solid, (IR, KBr, ν Cm^{-1}); 3423.95, (NH_2 , str), 2226.88 (CN, str), 1584.28 (C=N, str); ^1H NMR (400MHz, CDCl_3 , δ -ppm); 7.8 (d, 2H, Ar), 7.5 (d, 2H, Ar), 7.1 (m, 1H, Ar), 7.1 (s, 2H, NH_2), 6.9-7.0 (s, 2H, Ar), 7.2 (m, 1H, Ar); Molecular formula ($\text{C}_{16}\text{H}_{10}\text{ClN}_3$): MASS (NCMS) (m/z):279, [M+1]:280.

2.2.9. 2-amino-4-(4-bromophenyl) quinoline-3-carbonitrile (4i)

White solid, (IR, KBr, ν Cm^{-1}); 3454.33, (NH_2 , str), 2224.18 (CN, str), 1577.97 (C=N, str); ^1H NMR (400MHz, CDCl_3 , δ -ppm); 8.0-7.9 (d, 2H, Ar), 7.7-7.8 (d, 2H, Ar), 7.6-7.7 (d, 2H, Ar), 7.3 (s, 2H, NH_2), 7.4-7.5 (d, 2H, Ar); Molecular formula ($\text{C}_{16}\text{H}_{10}\text{BrN}_3$): MASS (NCMS) (m/z):323, [M+1]:324.

III. Results and Discussion

3.1 Characterization of Nano copper ferrite by X-Ray Diffraction (XRD) Analysis

Figure 1 shows typical XRD pattern for nano copper ferrite sample which was sintered at 500 °C. The pattern shows all the characteristic peaks of a spinal structure and confirms the phase formation indicating the absence of other impurity phases. The XRD parameters of various peaks were compared with the standard data of the cubic copper ferrite (JCPDS # 77-10) and found to be in cubic phase. The particle size and other characteristics of the copper nano particles obtained from the XRD pattern using Scherer's formula was found to be 30 and reported in Table 1. The peaks can be indexed to (220), (311), (400), (422), (511) and (440) planes of a cubic unit cell.

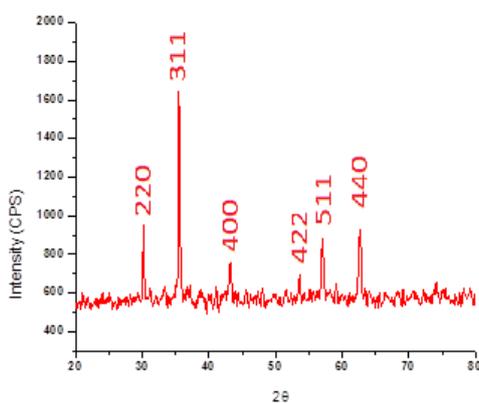


Fig 1- XRD Spectrum of nano copper ferrite powder

Table 1:- Particle size and other characteristics of the nano CuFe_2O_4 obtained from the XRD analysis

Lattice Parameter	Density (%)	FWHM	Porosity	Grain Size	Particle Size nm
8.374	93.4	0.284	8.2	1.42	30

3.2 Infrared Spectroscopy

In order to confirm the formation of the spinel phase and to understand the nature of the residual carbon in the samples, the FT-IR spectra of the as-synthesized powder and thermally treated powder were recorded and shown in Figure 2. The as-synthesized sample shows characteristic absorptions of ferrite phase with a strong absorption around 600 cm^{-1} . Waldron studied the vibrational spectra of ferrites and attributed the sharp absorption band around 580 cm^{-1} to the intrinsic vibrations of the tetrahedral groups and the other band of the octahedral groups. There are two weak and broad absorptions around 1040 , 1400 , 1600 , 3400 cm^{-1} corresponding to the presence of small amount of residual carbon in the samples. These absorptions in the present case are very weak which indicate that the residual carbon has mostly burnt away during the sintering process.

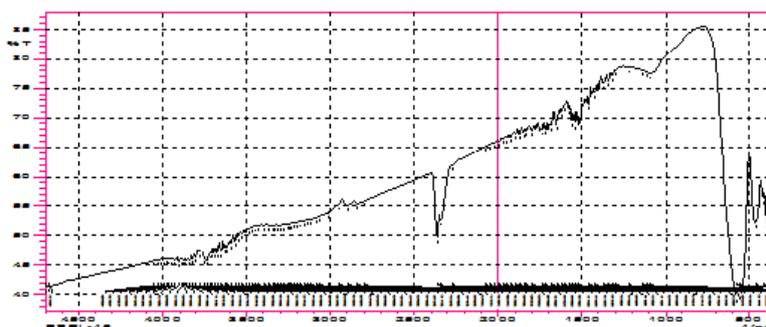


Fig 2- FTIR Spectrum of nano copper ferrite powder

3.3 Morphological and Elemental Analysis (SEM&EDX)

Figure 3 shows the typical SEM image of the nano copper ferrite sintered at $500\text{ }^{\circ}\text{C}$. The crystallite size calculated from XRD is in the range of below 30 nm which is in agreement with the SEM image. The structural composition and crystallinity of the copper ferrite nano particles was further examined by using SEM and TEM. The iron and copper ratio in the nano crystals as determined by EDX analysis was very much close to the atomic ratio in the formula CuFe_2O_4

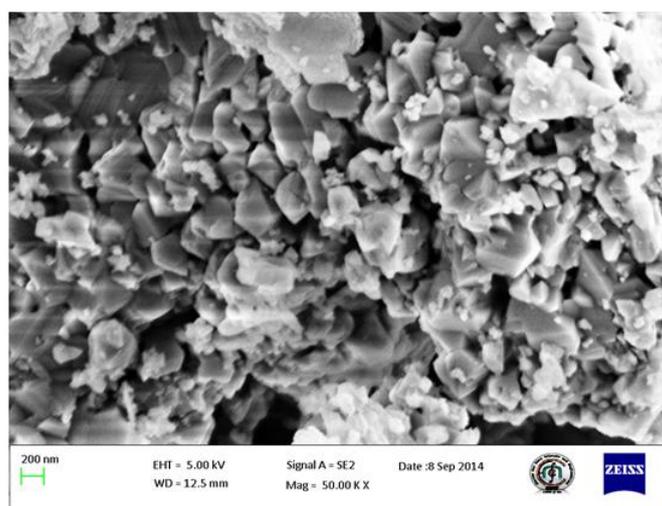


Figure 3: SEM image of CuFe_2O_4

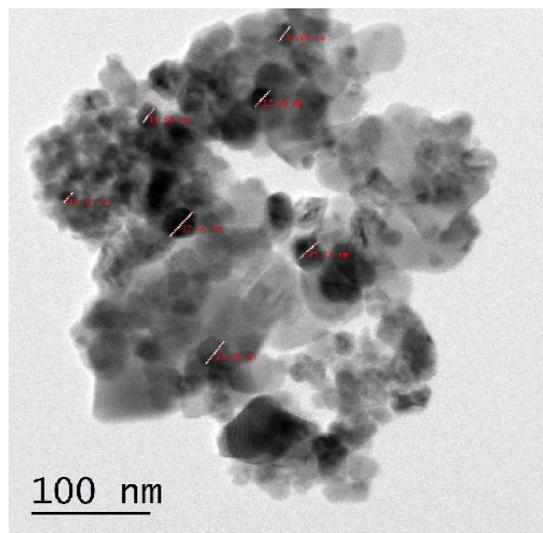


Fig 4- TEM image of CuFe₂O₄

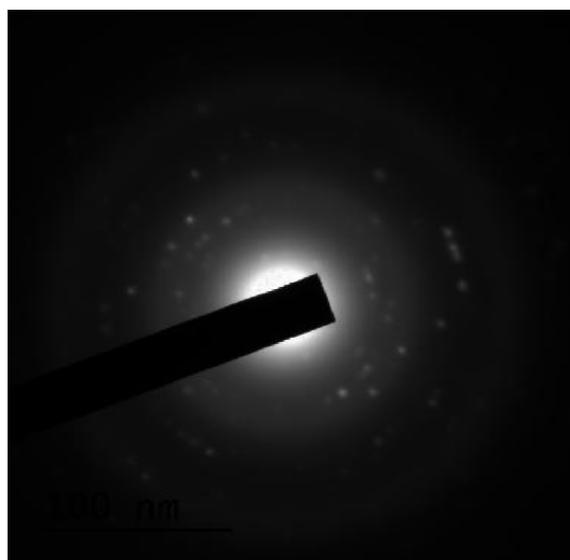


Fig 5: Selected area electron diffraction of nano CuFe₂O₄

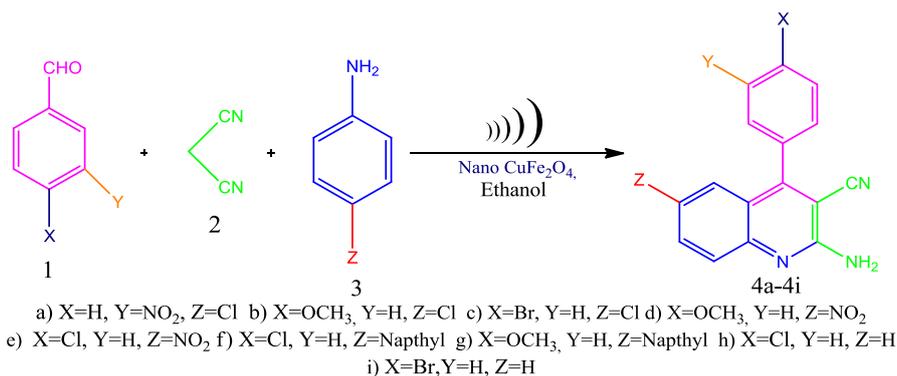
The Transmission Electron Microscope image as shown Figure 4. Bright Field TEM Image of CuFe₂O₄ and the Selected Area Electron Diffraction of CuFe₂O₄ are shown in Figure 5. The average size of the nano copper ferrite particles is close to 25 nm

3.4 BET surface area analysis

The BET surface area of the CuFe₂O₄ is found to be 135m²/g respectively.

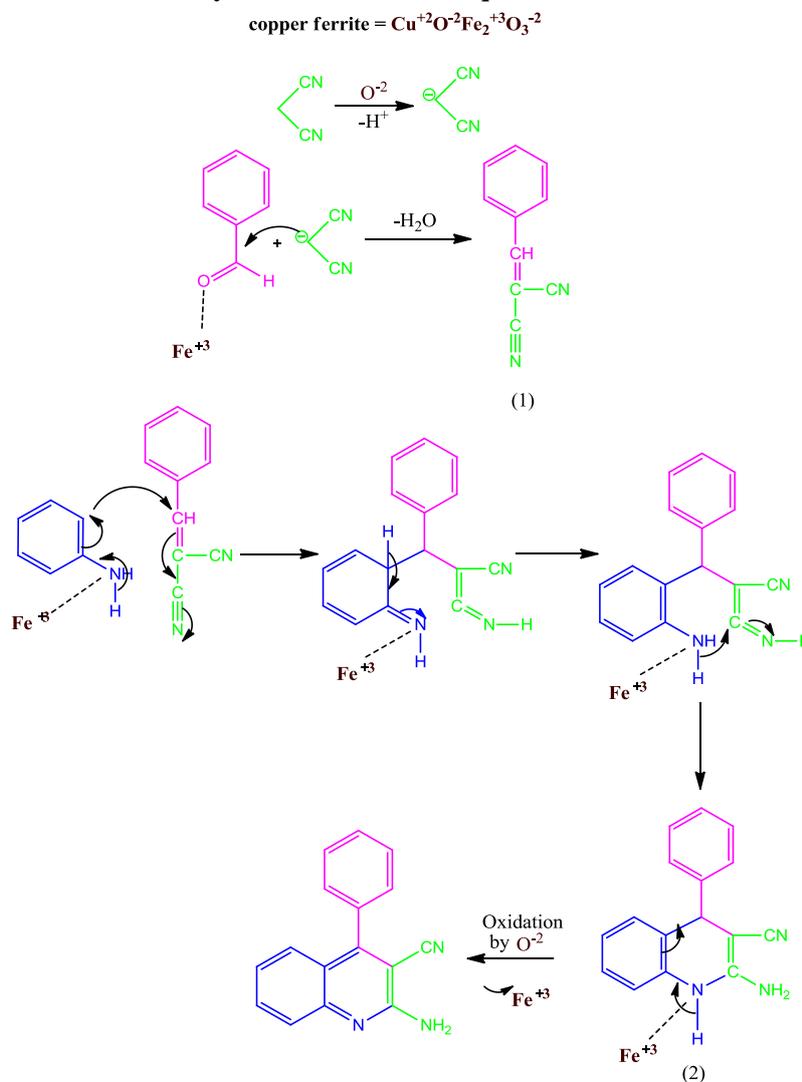
3.5 Catalytic Study

In this study, nano copper ferrite catalyzed one-pot three component intermolecular cyclization of aromatic aldehydes, malononitrile and aromatic amines is described as a simple model reaction and shown in Scheme 1. The results are reported in Table-4



Scheme1:- Nano copper ferrite catalyzed green synthesis of quinoline derivatives under Ultrasonication (4a-4i)

3.5.1. Plausible mechanism for the synthesis of substituted quinoline derivatives



Scheme 2:- Plausible mechanism for the synthesis of substituted quinoline derivatives

Initially malononitrile undergo deprotonation in presence of Lewis base (O^{2-}) of CuFe_2O_4 to form carbanion which further undergoes nucleophilic addition with aromatic aldehyde in presence of Lewis acid (Fe^{+3}) produce an intermediate product arylidene malononitrile (1). In the next step, the aromatic amine

undergoes Micheal addition with arylidenemalononitrile (1) leads to cyclization to form dihydro quinoline derivative (2). During the course of the reaction process, the Lewis bases (O^{2-}) in $CuFe_2O_4$ cause the oxidation process, leading to aromatization finally to form quinoline derivatives shown in Scheme 2.

From the literature, a similar synthesis of 2-amino-4-arylquinoline-3-carbonitrile reported by Ali Khalafi-Nezhad et al [29] used L-Proline as a catalyst, which has several disadvantages like high loading amount of organic catalyst, lesser yields and longer reaction time periods. Keeping in view of this, a new approach to develop the target derivatives of quinolines carried out via a one pot three-component cyclization between equimolar quantities of aromatic aldehyde, malononitrile and aromatic amine in ethanol catalyzed by nano copper ferrite under Ultrasonication is described.

3.5.2. Optimization of the reaction parameters

In this study, effect of loading catalyst, nature of the solvent and reaction time on the synthesis of quinoline derivatives were investigated and the results are tabulated in Table 2 and Table 3.

Table 2:- Comparative study of nano copper ferrite catalyst with L-Proline for the synthesis of the quinoline derivatives

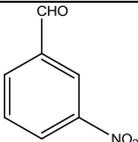
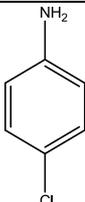
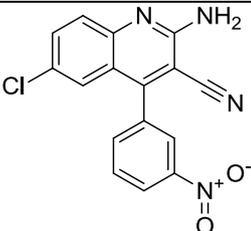
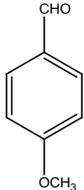
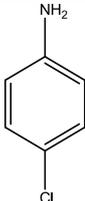
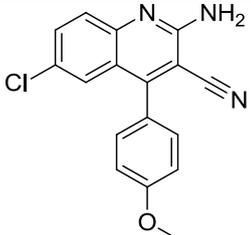
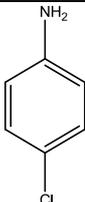
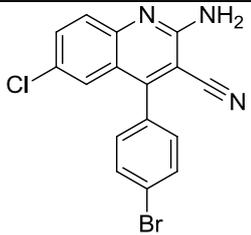
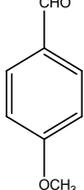
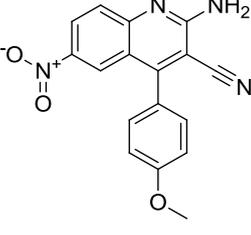
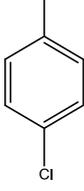
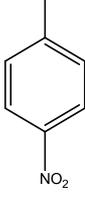
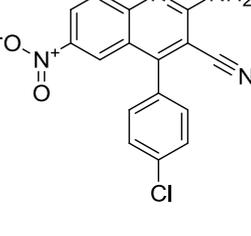
Catalyst	Solvent used	Method	Time (hours)	Yield (%)	Ref.
$CuFe_2O_4$	EtOH	Ultra-sonication	2	95	Present
L-Proline	H ₂ O	Reflux	12	89	29

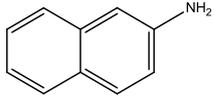
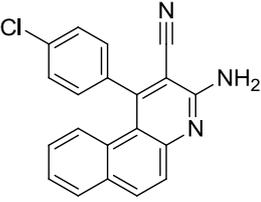
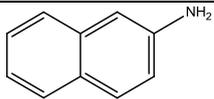
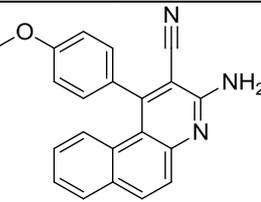
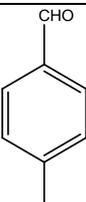
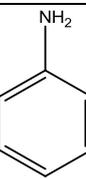
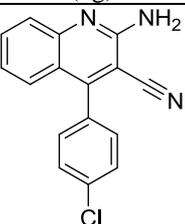
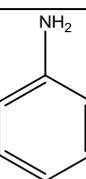
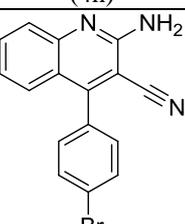
Table 3:- Effect of amount of nano copper ferrite catalyst loading and solvent on the synthesis of quinoline derivatives.

Entry	$CuFe_2O_4$ (mg)	Solvent	Time (min)	Yield (%)
1	No catalyst	Ethanol	150	Trace
2	500	Dimethylsulphoxide	150	20
3	500	Dimethylformamide	150	10
4	500	Toluene	150	30
5	500	Dioxane	150	45
6	500	Acetonitrile	145	53
7	500	Dichloromethane	130	40
8	500	Tetrahydrofuran	130	45
9	500	Ethyl acetate	120	60
10	500	Ethanol	120	95
11	600	Ethanol	120	96
12	300	Ethanol	140	85
13	200	Ethanol	140	70
14	200	Ethanol	160	70

From the catalyst evaluation, nano $CuFe_2O_4$ was superior to L-Proline [29] to produce the better yields of the target 2-amino-4aryl quinoline-3-carbonitrile (4a-4i) in shorter durations and also for the catalyst recovery and reuse. Moreover, non polar solvents like toluene and Tetrahydrofuran led to lower yields, when compared to polar solvents like ethyl acetate and ethanol. The best conversion was observed when the reaction was performed in ethanol (95%). From the experimental data, it was found that 500mg of $CuFe_2O_4$ catalyst was enough to afford (4a-4i) with 95% of isolated yield (Table 3-Entry 10). The product yield remain unaffected when, $CuFe_2O_4$ catalyst loading was increased to 600mg (Table 3-Entry 11). However, the yield was decreased when the $CuFe_2O_4$ catalyst loading was reduced to 500 to 200mg (Table 3-Entry 12 and 13). Moreover prolonging the reaction time did not increase the yield (Table 3-Entry 14).

Table 4:- Synthesis of quinoline derivatives catalyzed by nano copper ferrite

Aldehyde	Amine	Product	Time (min)	Yield (%)
		 (4a)	120	95
		 (4b)	110	93
		 (4c)	110	90
		 (4d)	120	95
		 (4e)	120	80

		 (4f)	120	90
		 (4g)	110	85
		 (4h)	120	93
		 (4i)	120	95

IV. Recycling of the catalyst

The recyclability is the most important factor of the nano CuFe_2O_4 catalyst. After, the completion of the reaction, catalyst was separated by using strong neodymium magnet. The catalyst was washed thrice with ethyl acetate, dried and fresh substrate dissolved in ethyl alcohol under similar conditions without further purification. Finally the catalyst could be used for five, six runs without perceptible decrease in the formation of quinoline derivatives.

V. Conclusion

In this study, we developed an efficient and simplistic method for the synthesis of quinoline derivatives using a nano copper ferrite as a Heterogeneous catalyst. This method has several features like increasing the yield of products, low temperature conditions, minimum reaction times, easy separation of catalyst by strong neodymium (N35) magnet, reusability and recyclability of the catalyst. Moreover, this methodology has various aspects such as to avoid toxic nature of the solvents and give an emphasis to green chemistry

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