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# Synthesis of quinolines in water using nano KF/Clinoptilolite: An effective heterogeneous nanocatalyst base

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**Abstract:** A proficient, green and environmentally benign one-pot four-component synthesis of functionalized quinolines was developed by condensation reactions of aniline, diethyl oxalate, activated acetylenic compounds, and thioles in the presence of KF/CP (NPs) as a heterogeneous base nanocatalyst, at room temperature in water**.**

**Keywords:** Thiol, Heterogeneous nanocatalyst, KF/Clinoptilolite nanoparticles, Aniline, Activated acetylenic compounds.

## Introduction

Heterocyclic compounds hold a prominent position in medicinal chemistry owing to their wide spectrum of biological activities such as antimalarial [1], antimicrobial [2], antitumor [3], anticancer [4], antidepressant [5], antiviral [6], antidiabetic [7], anti-inflammatory [8] and anti-HIV [9]. Moreover, they also contribute in the feld of material science [10], dyes and pigment science [11] as well as agrochemistry [12]. Therefore, there is considerable thrust for the development of efficient synthetic strategies for producing these compounds. MCRs open diverse avenues to create novel concatenations in one pot fashion leading to diverse biologically potent heterocyclic scaffolds [13, 14]. Having a cascade of reactions occurring in one pot is highly beneficial in the context of modern trends for organic synthesis, where sustainability is as relevant as efficiency and selectivity. Multicomponent reactions being atom economic, efficient and extremely convergent in nature offer a number of advantages over stepwise sequential approaches [15–17] and could be performed in the presence of nanocatalyst and produce heterocyclic compounds [18-20].

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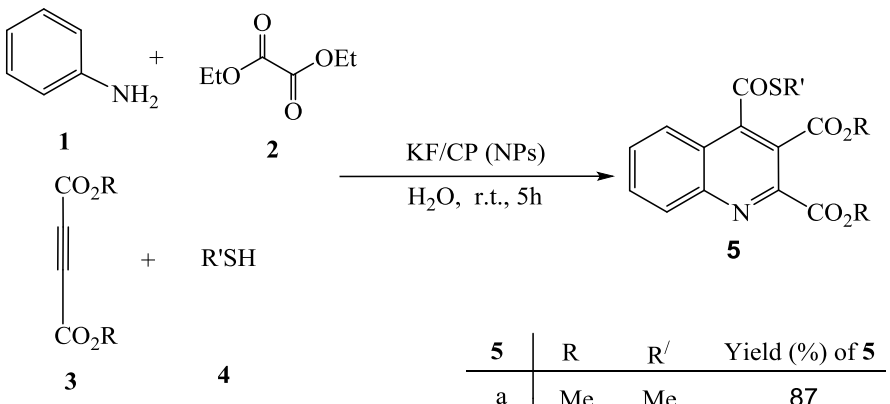
Heterocycles with nitrogen group are a main piece of natural and unnatural compounds with significant biological activity [21]. Quinolines are important groups of *N*-based heterocyclic compounds and are generally known to have a broad range of applications in medicinal, bioorganic, and industrial chemistry as well as in the field of synthetic organic chemistry [22]. Some key biological activities of quinoline derivatives include antimalarial, antibacterial, anti-asthmatic, antihypertensive, anti-staphylococcal, antiplatelet and anti-inflammatory [23-30]. Lately, there has been an enhanced interest for new applications of potassium fluoride impregnated on zeolites and clays, as a new natural and inexpensive solid base system [31-38]. Among them Clinoptilolite, a natural zeolite with a high internal surface area, is much more effective because of its high exchange capability for cations particularly for $K^+$, therefore, more free fluoride anions are capable of functioning as an effective base. On the other hand, the preparation of potassium fluoride impregnated Clinoptilolite (KF/CP) is very simple without the need for any pre-activation [39, 40]. Herein, we report an efficient and green synthesis of functionalized quinolines **5a-e** through the reaction of aniline **1**, diethyl oxalate **2**, activated acetylenic compounds **3** and thioles **4** in the presence of catalytic

amount of KF/CP (NPs) in water as the solvent at room temperature (Scheme **1**).




| 5 | R | R/ | Yield (%) of 5 |
|---|---|---|---|
| a | Me | Me | 87 |
| b | Me | Et | 90 |
| c | Et | Me | 90 |
| d | Me | $^{n}$Pr | 92 |
| e | Et | Et | 90 |

**Scheme 1:** Synthesis of functionalized quinolines **5**.

## Results and discussion

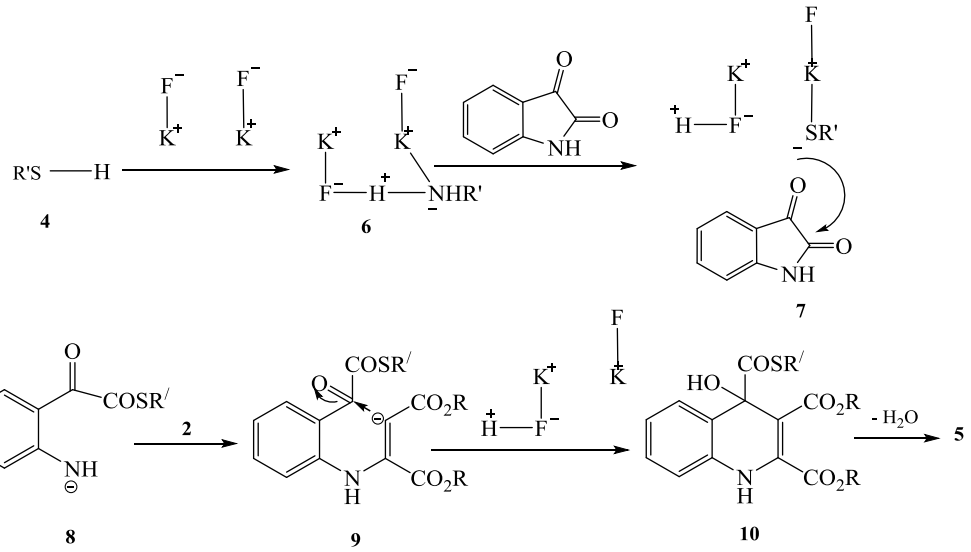
To achieve the optimum conditions the condensation reaction of aniline **1**, diethyl oxalate **2**, dimethyl acetylenedicarboxylate **3a** and methan thiol **4a** was performed by varying the catalyst, solvent and temperature for preparation of the product **4a**. $Et_3N$, pyridine, piperidine, $K_2CO_3$, KF/CP (NPs), and ZnO (NPs) were used as catalyst. According to the outcomes of optimization, 10% (w/w) KF/CP (NPs) as catalyst, water as solvent and room temperature were estimated to be the optimum reaction conditions.

Having established the optimal reaction conditions, the scope of the reaction was examined using aniline **1**, diethyl oxalate **2**, activated acetylenic compounds **3** and thiol **4** in the presence of catalytic amount of KF/CP (NPs) in water as the solvent at room temperature (Scheme **1**). The structures of compounds **5a-5e** were apparent from the $^{1}$H NMR, $^{13}$C NMR, IR and mass spectra which were in agreement with the proposed structures. The $^{1}$H NMR spectrum of **5a** showed three singlet for methoxy protons at $\delta$ = 3.89 and 3.98 ppm along with characteristic signals for the aromatic moiety. The resonances of carbonyl groups of ester in the $^{13}$C NMR spectra of **5a** found at $\delta$ = 165.5, 165.6 and 165.7 ppm. The mass spectrum of **5a** displayed the molecular ion peak at *m/z* = 303.

The reaction can be described as occurring by the mechanism proposed in Scheme **2**. It is conceivable that the reaction starts with the formation of hydrogen bonding between fluoride ion and proton of the thiol giving rise to the intermediate **6**, followed by nucleophilic substitution at position C-2 of the isatin **7**, leading to the opening of the heterocyclic ring enabling the formation of anion intermediate **8**. The nucleophilic attack of ring-opened intermediate **8** to **3** leads to the formation of anionic intermediate **8** which undergoes intramolecular exo-trig cyclization to generate functionalized quinolines **5** after elimination of $H_2O$**.**

## Conclusion

Regarding results of this study, an efficient, green and environmentally benign method has been developed for the synthesis of functionalized quinolines derivatives *via* a one pot four components condensation reaction between aniline, diethyl oxalate, activated acetylenic compounds and thioles in the presence of KF/CP (NPs) as a heterogeneous base nanocatalyst, at room temperature in water. The advantages of proposed method are the mild and clean reaction Conditions, low catalyst loading, use of natural catalyst and cost efficiency which make this approach an interesting alternative to the existing methods.



**Scheme 2:** Plausible mechanism for the generation of **5**.

## Experimental

### *Material and Methods:*

All chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification. Clinoptilolite was obtained from Afrandtooska Company in the region of Semnan. Elemental analyses for C, H, and N were performed using a Heraeus CHN–O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MAT 8430 spectrometer operating at an ionization potential of 70 eV. IR spectra were measured on a Shimadzu IR-460 spectrometer. The morphology of nanoparticles of KF/Clinoptilolite was characterized by scanning electron microscopy (SEM) using a Holland Philips XL30 microscope. Crystalline structure of KF/CP (NPs) was characterized by X-ray diffraction (XRD) analysis at room temperature using a Holland Philips Xpert X-ray powder diffractometer, with $CuK_{\alpha}$ radiation (λ=0.15406 nm), with 2θ ranging from 20 to 80° [37]. The average crystallite size was calculated using Scherrer's formula; D= 0.9λ/β cosθ [37], where D is the diameter of the nanoparticles, λ ($CuK_{\alpha}$) =1.5406 Å and $\beta$ is the full-width at half-maximum of the diffraction lines [38]. $^{1}H$, and $^{13}C$ NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1 and 125.8 MHz, respectively. $^{1}H$ and $^{13}C$ spectra were obtained for solutions in $CDCl_3$ using TMS as internal standard or 85% $H_3PO_4$ as external standard.

### *Preparation of Nano KF/Clinoptilolite:*

Nano sized natural Clinoptilolite zeolite was prepared by grinding in a planetary ball mill using a zirconia vial set in dry conditions with a time period of about 20 min. Then, the KF/CP (NPs) catalyst was prepared according to previously reported procedure [39-40].

### *General procedure for the preparation of 4a-4e:*

A mixture of 0.298 g (2 mmol) of isatin (**1**) and activated acetylenic compound **2** (2 mmol) in water (5 mL) was added to a stirred mixture of the amine **3** (2 mmol) and KF/CP (NPs) (10% w/w, 0.38 g) in water (5 mL) at room temperature. After completion of the reaction [8 h; TLC (EtOAc/hexane 2:1)], water (15 ml) was poured into the mixture of reaction. The solid phase was filtered, washed with diethyl ether. The solvent was evaporated, and the residue was purified by column chromatography [silica gel (230–240 mesh; Merck), hexane/EtOAc 4:1)].

### *Spectral data of products*

### *Trimethyl 2,3,4-quinoline tricarboxylate (4a):*

Orange oil, yield 90%. IR (KBr) ($\gamma_{max}$/cm$^{-1}$): 1697, 1614, 1569, 1532, 1488, 1189 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ = 3.89 (3H, s, MeO), 3.98 (6 H, s, MeO), 7.63 (1 H, t, $^3J$ = 7.2 Hz, CH), 7.77 (1 H, t, $^3J$ = 7.2 Hz, CH), 7.95 (1 H, d, $^3J$ = 8.4 Hz, CH), 8.16 (1 H, d, $^3J$ = 8.5 Hz, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 52.9 (MeO), 53.0 (MeO), 53.2 (MeO), 122.8 (C), 123.5 (C), 125.4 (CH), 129.8 (CH), 130.2 (CH), 131.9 (CH), 139.8 (C), 147.4 (C), 147.7 (C), 165.5 (C=O), 165.6 (C=O), 165.7 (C=O). MS (EI, 70 eV): m/z (%) = 303 (M+, 10), 273 (88), 258 (49), 244 (65), 187 (82), 129 (100). Anal.Calcd for $C_{15}H_{13}NO_6$ (303.26): C, 59.41; H, 4.32; N, 4.62. Found: C, 59.67; H, 4.24; N, 4.55.

***4-Ethyl 2,3-dimethyl 2,3,4-quinolinetricarboxylate (4b):***

Yellow Oil, yield 91%. IR (KBr) ($\gamma_{max}$/cm$^{-1}$): 1722, 1718, 1706, 1533, 1445, 1384 cm$^{-1}$. $^1$H NMR(500 MHz, $CDCl_3$): δ = 1.40 (3 H, t, $^3J$ = 7.3, Me), 3.98 (3H, s, MeO), 4.03 (3H, s, MeO), 4.51 (2H, q, $^3J$ = 7.3, $OCH_2$), 7.70 (1H, t, $^3J$ = 7.4 CH), 7.84 (1 H, t, $^3J$ = 7.4, CH), 8.05 (1 H, d, $^3J$ =7.5, CH), 8.24 (1 H, d, $^3J$=7.4, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): δ=13.9 (Me), 52.8 (MeO), 53.2 (MeO), 62.6 ($CH_2O$), 122.3 (C), 123.5 (C), 125.4 (CH), 129.7 (CH), 131.9 (CH), 133.0 (CH), 140.1 (C), 147.5 (C), 147.7(C), 165.1 (C=O), 165.3 (C=O), 165.7 (C=O). EI-MS: 317 (M$^+$, 15), 129 (100). Anal.Calcd for $C_{16}H_{15}NO_6$ (317.29): C, 60.57; H, 4.76; N, 4.41; found: C, 60.23; H, 5.12; N, 4.33%.

***2,3-Diethyl4-methyl 2,3,4-quinolinetricarboxylate (4c):***

Yellow Oil, yield 90%. IR (KBr) ($\gamma_{max}$/cm$^{-1}$): 1744, 1707, 1676, 1599, 1487 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.38 (3 H, t, $^3J$ = 7.2, Me), 1.43 (3 H, t, $^3J$ = 7.2, Me), 4.04 (3H, s, MeO), 4.41 (2 H, q, $^3J$ = 7.2, $CH_2O$), 4.50 (2 H, q, $^3J$ = 7.2, $CH_2O$), 7.70 (1 H, t, $^3J$ =7.6, CH), 7.85 (1H, t, $^3J$ =7.6, CH), 7.99 (1 H, d, $^3J$=7.8, CH), 8.25 (1 H, d, $^3J$=7.8, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): δ=13.8 (Me), 13.9 (Me), 53.0 (MeO), 62.3 ($CH_2O$), 62.4 ($CH_2O$), 122.5 (C), 123.7 (C), 125.4 (CH), 129.7 (CH), 130.3 (CH), 131.7 (CH), 140.2 (C), 147.5 (C), 149.7 (C), 165.1 (C=O), 165.3 (C=O), 165.9 (C=O). EI-MS: 331 (M$^+$, 23), 129 (100). Anal.Calcd for $C_{17}H_{17}NO_6$ (331.32): C, 61.63; H, 5.17; N, 4.23; found: C, 61.54; H, 5.08; N, 4.05%.

***2,3-Dimethyl 4-propyl2,3,4-quinoline tricarboxylate (4d):***

Yellow Oil, yield 92%. IR (KBr) ($\gamma_{max}$/cm$^{-1}$): 1740, 1583, 1490, 1407, 1366, 1294 cm$^{-1}$. $^1$H NMR(500 MHz, $CDCl_3$): δ = 0.90 (3 H, t, $^3J$ = 7.3, Me), 1.70 (2 H, m, $CH_2$), 3.86 (3 H, s, MeO), 3.95 (3 H, s, MeO), 4.32 (2 H, t, $^3J$ = 7.3, $CH_2O$), 7.59 (1 H, t, $^3J$ = 8.0, CH), 7.73 (1 H, t, $^3J$ = 8.2, CH), 7.94 (1 H, d, $^3J$ = 8.5, CH), 8.12 (1 H, d,$^3J$ = 8.5, CH). $^{13}$C NMR (125 MHz, $CDCl_3$): δ=10.2 (Me), 21.6 ($CH_2$), 52.9 (MeO), 53.1 (MeO), 68.2 ($CH_2O$), 122.7 (C), 123.6 (C), 125.4 (CH), 129.8 (CH), 130.3 (CH), 131.9 (CH), 140.3 (C), 147.4 (C), 147.8 (C), 165.2 (C=O), 165.6 (C=O), 165.7 (C=O). EI-MS: 331 (M+, 18), 129 (100). Anal.Calcd for $C_{17}H_{17}NO_6$ (331.32): C, 61.63; H, 5.17; N, 4.23; found: C, 61.33; H, 5.12; N, 4.12%.

***Triethyl 2,3,4-quinoline tricarboxylate (4e):***

Yellow Oil, yield 93%. IR (KBr) ($\gamma_{max}$/cm$^{-1}$): 1727, 1660, 1607, 1567, 1477, 1351 cm$^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ = 1.31 (3 H, t, $^3J$ = 7.2, Me), 1.34 (3 H, t, $^3J$ = 7.2, Me), 1.37 (3 H, t, $^3J$ = 7.2, Me), 4.35 (2 H, q, $^3J$ = 7.2, $CH_2O$), 4.42 (2 H, q, $^3J$ = 7.2, $CH_2O$), 4.46 (2 H, q, $^3$J = 7.2, $CH_2O$), 7.63 (1 H, t, $^3J$ = 7.8, CH), 7.78 (1 H, t, $^3J$ = 7.8, CH), 7.95 (1 H, d, $^3J$ = 8.4, CH), 8.15 (1 H, d, $^3J$ = 8.2, CH). $^{13}$C NMR(125 MHz, $CDCl_3$):δ= 13.8 (Me), 13.9 (Me), 14.0 (Me), 62.3 ($CH_2O$), 62.4 ($CH_2O$), 62.5 ($CH_2O$), 123.5 (C), 124.3 (C), 125.4 (CH), 129.7 (CH), 130.2 (CH), 131.9 (CH), 147.4 (C), 148.6 (C), 150.5 (C), 165.1 (C=O), 165.3 (C=O), 165.4 (C=O). EI-MS: 345 (M+, 25), 129 (100). Anal.Calcd for $C_{18}H_{19}NO_6$ (345.35): C, 62.60; H, 5.55; N, 4.06; found: C, 61.98; H, 5.45; N, 4.04%.

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