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#### FULL PAPER



# Synthesis of 1-aminoalkyl-2-naphthols derivatives using an engineered copper-based nanomagnetic catalyst (Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> @phenylacetylene@Cu)

Tahereh Akbarpour <sup>1</sup> 💿 🕴	Ardeshir Khazaei <sup>1</sup> 🗅	Jaber Yousefi Seyf <sup>2</sup> 💿	Ι
Negin Sarmasti <sup>1</sup> 💿			

<sup>1</sup>Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran

<sup>2</sup>Department of Chemical Engineering, Hamedan University of Technology, Hamedan, Iran

#### Correspondence

Ardeshir Khazaei, Professor, Faculty of Chemistry, Bu-Ali Sina University, Hamedan, Iran. Email: a\_khazaei@basu.ac.ir

#### Abstract

In the present study, a molecular level engineered-based method was used to synthesis a copper-based nanomagnetic catalyst (Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu). The as-synthesized catalyst was characterized using different techniques, including infrared (IR), X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX) and EDX elemental mapping, induced coupled plasma (ICP), thermal gravimetric analysis (TGA) and differential thermal analysis (DTA), and vibrating sample magnetometer (VSM). The Fe<sub>3</sub>O<sub>4</sub> nanoparticles surface were protected using carbon quantum dots (CQDs) instead of conventional SiO<sub>2</sub>. The activity of the as-synthesized catalyst was evaluated in the synthesis of 1-aminoalkyl-2-naphthols derivatives. The solvent-free condition with low reaction time and high reaction yield is the results of the prepared catalyst. How the reaction was triggered by the catalyst was determined by the IR. The as-synthesized catalyst provides an 87.5% reaction yield after five cycles. Fourier Transform Infrared (FTIR), EDX, TEM, TGA, and mapping analyses were taken to examine the stability of the recovered catalyst. All elements, especially Cu with 2.4 wt%, are present in the recovered catalyst. These findings provide strong evidence for the stability of the as-synthesized novel copper-based heterogeneous magnetic nanocatalyst. The effect of temperature and the amount of the catalyst (optimum reaction condition) were determined using a systematic approach, namely, the design of experiment (DOE).

#### K E Y W O R D S

1-aminoalkyl-2-naphthols, copper-based catalyst, design of experiment (DOE)

# **1** | INTRODUCTION

The multicomponent reactions (MCRs) have proven a valuable asset in organic and pharmaceutical chemistry. MCRs can be used in drug design and discovery because of the simplicity, efficiency, and high selectivity of the MCRs.<sup>[1]</sup> The synthesis of biologically complex molecules, besides the minimum workup procedure, by MCRs, is easy, fast, and efficient.<sup>[2]</sup> Nitrogen-containing biologically active compounds as a significant branch of organic synthesis are medically important.<sup>[3–5]</sup> Since 1900, aminoalkyl naphthols have been synthesized by the three-component condensation of secondary amines, aromatic aldehydes, and naphthols.<sup>[6]</sup> In 1900, Mario Betti synthesized aminoalkyl naphthols (so-called Betti bases) for the first time.<sup>[7]</sup> Interest in the chemistry of Betti base<sup>[8]</sup> has recently intensified because of their attractive catalytic<sup>[9]</sup> and biological<sup>[8]</sup> properties. The Betti reaction is useful in the synthesis of substituted aminonaphthols. Compounds such as  $1-(\alpha-\text{aminoalkyl})-2-\text{naphthols}$  are often found in naturally occurring biologically active products and potent drugs, such as nucleoside antibiotics and HIV proteinase inhibitors.<sup>[10-13]</sup> These compounds are also important precursors in the synthesis of compounds that are often used in biologically important natural products and drugs.<sup>[12]</sup> Several catalysts have been applied to synthesize of  $1-(\alpha$ aminoalkyl)-2-naphthols derivatives, including deep eutectic solvent (DES),<sup>[14]</sup> glycerol,<sup>[15]</sup> Triton X-100 in H<sub>2</sub>O,<sup>[16]</sup> Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs),<sup>[17]</sup> microwave irradiation,<sup>[18]</sup> nano TiO<sub>2</sub>-HClO<sub>4</sub>.<sup>[19]</sup> and ionic liquid.<sup>[20]</sup>

In recent years, nanomaterials have been used as a solid support material for the design of benign environmental heterogeneous catalysts.<sup>[21-23]</sup> A variety of methods have been developed to synthesize magnetite nanoparticles of various shapes, sizes, and compositions, but their successful applications are highly dependent on the stability conditions of these particles.<sup>[24,25]</sup> MNPs have a high affinity to agglomeration, and therefore, suitable protective materials have been investigated for their stabilization.<sup>[26-34]</sup> Surfactant/polymer, silica, and carboncoating or embedding them in a matrix/support are some of the critical approaches adopted to stabilize nanostructured particles.<sup>[35,36]</sup> It is noteworthy to note that the outer protective shells created as a result of the coating not only stabilize nanoparticles but also provide interaction sites with other synthetic atoms, nanoparticles, and organic groups suitable for their intended applications. Recently, the focus has been on the functionality of MNPs to expand their application, especially in the field of catalysis, as evidenced by the use of MNPs for the manufacture of magnetite-based catalysts.[37-39]

In light of these, this study intends to coat the surface of  $Fe_3O_4$  nanoparticles using carbon quantum dots

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(CQDs) instead of conventional SiO<sub>2</sub>.<sup>[40]</sup> The major objective of this study is to synthesize a novel copper-based heterogeneous magnetic nanocatalyst and its usage in the synthesis of 1-( $\alpha$ -aminoalkyl)-2-naphthols derivatives.

### **2** | EXPERIMENTAL SECTION

#### 2.1 | Material and methods

FeCl<sub>2</sub>.4H<sub>2</sub>O, FeCl<sub>3</sub>.6H<sub>2</sub>O, ammonia (28%wt), glucose, 3-(trimethoxysilyl)-propylamine (TMPA), toluene (anhydrous), cyanuric chloride, tetrahydrofuran (THF), NaN<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, acetone, phenylacetylene, NaOH, CH<sub>3</sub>CN, Cu (OAc)<sub>2</sub>, and MeOH all were purchased from Merck company.

The FTIR spectra (Perkin-Elmer 1600 spectrometer using KBr disks), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), energy-dispersive X-ray analysis (EDXA), thermal gravimetric analysis (TGA), and vibrating sample magnetometer (VSM) were used in the characterization of the as-synthesized catalyst.

Beta-naphthol, benzaldehyde derivatives, and secondary amines (morpholine and piperidine) were used in the synthesis of 1-aminoalkyl-2-naphthols derivatives. Products were characterized using melting point, FTIR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR techniques.

# 2.1.1 | Preparation of $Fe_3O_4$ nanoparticles<sup>[41]</sup>

Fe<sub>3</sub>O<sub>4</sub> nanoparticles were synthesized using the co-precipitation method. First, FeCl<sub>3</sub>.6H<sub>2</sub>O (15.2 gr, 56.34 mmol) and FeCl<sub>2</sub>.4H<sub>2</sub>O (5.6 gr, 28.17 mmol) were dissolved in deionized H<sub>2</sub>O at 80°C. After the dissolution of both salts, ammonia (25 ml, 28%wt) was added to the solution at once. The obtained black suspension was vigorously stirred at 80°C for 2 h under a nitrogen atmosphere. The synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles were separated using an external magnet. Nanoparticles were dried in an oven after washing several times with H<sub>2</sub>O and acetone.

# 2.1.2 | Preparation of CQD by $glucose^{[29,42]}$

Glucose (10 gr, 55.5 mmol) was added to the hot edible oil (250°C) and heated until completely blackened. H<sub>2</sub>O (50 ml) and diethyl ether (20 ml) were added to the solution after cooling. The extraction procedure was repeated three times so that all the synthesized CQDs enter the aqueous phase and the oil enters the organic phase.

## 2.1.3 | Preparation of nano-Fe<sub>3</sub>O<sub>4</sub>@CQD

Of the previous step synthesized Fe<sub>3</sub>O<sub>4</sub> nanoparticles, 1 gr was dispersed in deionized H<sub>2</sub>O (50 ml) using an ultrasonic bath for 30 min. Then, CQDs (0.05 gr) were added to the dispersion and were stirred for 24 h at room temperature. CQDs are dissolved in water in a molecularlike form so that a low amount of CODs can cover 1000 mg of nano-Fe<sub>3</sub>O<sub>4</sub> (in particle form). The obtained nano-Fe<sub>3</sub>O<sub>4</sub>@CQD nanoparticles were separated using an external magnet and were dried in an oven after washing with deionized H<sub>2</sub>O. The used CQDs (50 mg) is excess so that after the separation of nano-Fe<sub>3</sub>O<sub>4</sub>@CQD nanoparticles, the solution also contains CODs (brown solution).

# 2.1.4 | Surface modification of $Fe_3O_4@CQD@Si(OEt)(CH_2)_3NH_2^{[43]}$

Of the previous step synthesized nano-Fe<sub>3</sub>O<sub>4</sub>@CQD nanoparticles, 2 gr was dispersed in toluene using an ultrasonic bath for 25 min. The previous step was carried out multiple times and does not violate the mass conservation of law. TMPA (2 ml) was added to the dispersion and was refluxed under a nitrogen atmosphere for 24 h (at 110–120°C). The obtained Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> nanoparticles were separated using an external magnet and were dried in an oven after washing with toluene and H<sub>2</sub>O.

# 2.1.5 | Preparation of $Fe_3O_4$ @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC<sup>[44]</sup>

Cyanuric chloride (CC, 2.76 gr, 15 mmol) was dissolved in THF (30 ml) at a nitrogen atmosphere (at 0°C for 3 h). Of the Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> nanoparticles, 1 gr was added to the solution and dispersed using an ultrasonic bath for 30 min then was stirred at 0°C for 24 h. The obtained Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>@CC nanoparticles were separated using an external magnet and were dried in an oven after washing with EtOH and THF.

# 2.1.6 | Preparation of $Fe_3O_4$ @CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub><sup>[45]</sup>

Sodium azide (1.56, 24 mmol) together with  $K_2CO_3$  (1.66 gr, 12 mmol) as a base were dissolved in 20-ml deionized  $H_2O$  (mixture A). Of the Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>@CC nanoparticles, 1 gr was added to a

solution composed of H<sub>2</sub>O (40 ml) and acetone (20 ml) and was dispersed for 15 min using an ultrasonic bath (mixture A). Mixture A was added to mixture B and was stirred at room temperature for 6 h. The obtained Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> nanoparticles were separated using an external magnet and then were dried in an oven after washing with H<sub>2</sub>O and acetone. To confirm the nucleophilic substitution of Cl<sup>-</sup> by  $N_3^-$ , Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> was burned in a porcelain crucible and its ash was dissolved in acid. Then, AgNO<sub>3(aq)</sub> was added to the solution so that the failure to observe AgCl precipitation is a reason for the nucleophilic substitution of Cl<sup>-</sup> by  $N_3^-$ .

## 2.1.7 | Preparation of $Fe_3O_4@CQD@Si$ (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene<sup>[46]</sup>

Of the Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> nanoparticles, 1 gr was dispersed in CH<sub>3</sub>CN using an ultrasonic bath. Then phenylacetylene (2.5 ml) and NaOH (0.5%w/v) were added to the dispersion, and it was stirred at room temperature for 6 h. The obtained Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> @phenylacetylene nanoparticles were separated using an external magnet and then were dried in an oven after washing with CH<sub>3</sub>CN and H<sub>2</sub>O.

## 2.1.8 | $Fe_3O_4@CQD@Si(OEt)$ (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@cu<sup>[47]</sup>

First, a 5% (w/v) solution of Cu (OAc)<sub>2</sub> was prepared in MeOH (solution A). About 1 gr Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene nanoparticles was dispersed in MeOH (50 ml) using an ultrasonic bath for 15 min (dispersion B). Then the solution A was added to the dispersion B dropwise. After refluxing the dispersion for 24 h, the obtained Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu

nanoparticles were separated using an external magnet and were dried in an oven after washing several times with MeOH. This is the final experimental step in the preparation of a heterogeneous copper-based nanomagnetic catalyst. Scheme 1 illustrates the conceptual procedure synthesis of copper-based nanomagnetic catalyst, namely,  $Fe_3O_4@CQD@Si$  (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu.

To further study the structure of the formed catalyst, density functional theory (DFT) calculation was performed using  $DMol^3$  module of the material studio software. The CC@N<sub>3</sub>@phenylacetylene parts of the catalyst were studied in the DFT calculation to find the parts of



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Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si(OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu

SCHEME 1 The proposed procedure for the synthesis of copper-based nanomagnetic catalyst, namely, Fe<sub>3</sub>O<sub>4</sub>@COD@Si (OEt)(CH2)3NH@CC@N3@phenylacetylene@Cu

CC@N3@phenylacetylene with higher electron density. Figure 1 displays the electron density of CC@N3@phenylacetylene. As is shown, nitrogen atoms have higher electron density so that the proposed structure is entropically favorable and it is easier to coordinate copper with two rings.

#### General procedure for the synthesis 2.2 of 1-aminoalkyl-2-naphthols derivatives

 $\beta$ -naphthol (0.144 gr, 1 mmol), arvl aldehyde (1 mmol), and secondary amine including morpholine or piperidine (1 mmol) together with 0.05 gr of the as-synthesized catalyst were added to a test tube. Then the mixture was stirred at the obtained optimal condition, including 0.05-gr catalyst at 104°C. The reaction procedure was monitored using thin-layer chromatography (TLC). Hot EtOH (20 ml) was added to the reaction mixture after the completion of the reaction. The heterogeneous catalyst was separated from the reaction mixture using an external magnet, and the pure products were obtained through recrystallization in EtOH. Haghtalab and Yousefi Seyf<sup>[48]</sup> and Yousefi Seyf and Asgari<sup>[49]</sup> have extended the UNIQUAC-SAC model to fast screening



The proposed structure for the as-synthesized FIGURE 1 catalyst. Electron density was determined using density function theory (DFT)



**SCHEME 2** The synthesis of 1-aminoalkyl-2-naphthols derivatives in the presence of the as-synthesized copper-based nanomagnetic catalyst

130 solvents for the crystallization operation. The solvent of crystallization was obtained by this method. Scheme 2 presents the conceptual synthesis procedure of the 1-aminoalkyl-2-naphthols derivatives in the presence of the as-synthesized copper-based nanomagnetic catalyst.

#### 3 **RESULTS AND DISCUSSION**

#### Characterization of the catalyst 3.1

Various techniques including infrared (IR) spectroscopy, X-ray powder diffraction (XRD), FESEM, TEM, induced coupled plasma (ICP), EDXA, energy-dispersive X-ray spectroscopy (EDX) elemental mapping, TGA, and VSM were used to characterize the as-synthesized catalyst.

#### Infrared 3.1.1

IR technique was used to identify different functional groups in the as-synthesized nanoparticles qualitatively.

Figure 2 presents the (Fourier Transform Infrared) FTIR spectra of the Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@CQD, Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC, Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene, Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> and @phenylacetylene@Cu. The wave numbers of 584 and 3396  $\text{cm}^{-1}$  are attributed to the Fe-O bending and Fe-O stretching, respectively (red spectrum). The wave numbers of 1619 and 3296  $\text{cm}^{-1}$  are attributed to the carbonyl and hydroxyl groups in CQD, respectively (green spectrum). The wave numbers of 1034, 2922, and 3454  $\text{cm}^{-1}$ belong to the Si-O, C-H stretching and NH<sub>2</sub> stretching in the Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub> nanoparticles (blue spectrum). The band at 1654  $\text{cm}^{-1}$  is an indication of the presence of the C=N functional group in cyanuric chloride that proves the formation of Fe<sub>3</sub>O<sub>4</sub>@COD@Si (OEt)(CH<sub>2</sub>)<sub>2</sub>NH@CC nanoparticles (magenta spectrum). The wave numbers of 2036 and 2136  $\text{cm}^{-1}$  confirm the formation Fe<sub>3</sub>O<sub>4</sub>@COD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> nanoparticles with azide functional group (black spectrum). The reaction between the azide group and phenylacetylene gives rise to the formation of a pentagonal triazole ring so that the azide wave number disappears. The emergence of a band at 1560 and 1620  $\text{cm}^{-1}$ implies to the presence of C=N and N=N groups in the

triazole ring (brown spectrum). However, accentuations and small frequency shifts are observed in the cyan IR spectrum; Cu-N peaks at 592 and 693 cm<sup>-1</sup> confirm the dative bond formation between copper and nitrogen atoms.<sup>[33,47,50]</sup>

#### 3.1.2 | X-ray powder diffraction

The resultants nanoparticles were then characterized by XRD technique. The powder diffraction patterns are given in Figure 3. Observed sharp peaks prove the crystallize nature of the nanoparticles. The sharper the diffraction peaks, the bigger the nanoparticle size.

# 3.1.3 | Field emission scanning electron microscopy and transmission electron microscopy

(Scanning electron microscope) SEM analysis is one of the most widely used analyses of the surface of nanocatalysts. Using this method, the microstructure of materials can be examined by the electron beam in surface scanning. The most important feature of scanning electron microscopy is the three-dimensional display of



**FIGURE 2** Infrared (IR) spectra of  $Fe_3O_4$ ,  $Fe_3O_4$ @CQD,  $Fe_3O_4$ @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH<sub>2</sub>,  $Fe_3O_4$ @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC,  $Fe_3O_4$ @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>,  $Fe_3O_4$ @CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene, and  $Fe_3O_4$ @CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene, and  $Fe_3O_4$ @CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@ CC@N<sub>3</sub>@phenylacetylene, and  $Fe_3O_4$ @CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@ CC@N<sub>3</sub>@phenylacetylene, and  $Fe_3O_4$ @CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@ CC@N<sub>3</sub>@phenylacetylene, and  $Fe_3O_4$ @ CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@ CC@N<sub>3</sub>@phenylacetylene, and (CH<sub>2</sub>) (CH<sub>2</sub>) (CH<sub>2</sub>)<sub>3</sub>NH@ CC@N<sub>3</sub>@phenylacetylene, and



Fe<sub>2</sub>O<sub>2</sub>@CQD@

50

Angle 2 $\Theta$  (degree)

FIGURE 3 X-ray diffractograms of the as-synthesized nanoparticles

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I)(CH

60

70

80

**FIGURE 4** The field emission scanning electron microscopy (FESEM) image of the as-synthesized heterogeneous copper base magnetic nanocatalyst, namely,  $Fe_3O_4@CQD@Si(OEt)(CH_2)_3NH@CC@N_3@phenylacetylene@Cu$ 

images due to its great depth of field. This technique is used to determine the shape, size, and morphology of the nanoparticle surface. The FESEM images of the as-synthesized heterogeneous copper base magnetic nanocatalyst are shown in Figure 4. As is shown in this figure, the obtained nanocatalyst is spherical.

To further investigate the structure of the assynthesized copper-based magnetic nanocatalyst, the TEM technique was used. Figure 5. provides the detailed structure of the as-synthesized nanoparticles. The TEM image of the as-synthesized catalyst shows a layer anchoring around the core of the  $Fe_3O_4$  nanoparticle, confirming the core-shell structure of the as-synthesized nanoparticles. The gray background between the nanoparticles is attributed to the CQDs.

#### 3.1.4 | EDX and EDX elemental mapping

The EDX technique is used to determine the elemental analysis of a sample. The EDX analysis of the assynthesized copper-based magnetic nanocatalyst is shown in Figure 6. This figure confirms the presence of the Fe, O, C, Si, N, and Cu elements in the final asprepared catalyst. The mass percent of the Fe, O, C, Si, N, and Cu elements is 29.35, 24.62, 8.50, 0.90, 2.25, and

20

30

40



FIGURE 5 Transmission electron microscopy (TEM) micrographs of the as-synthesized heterogeneous copper base magnetic nanocatalyst, namely,  $Fe_3O_4@CQD@$  Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu



**FIGURE 6** The energy-dispersive X-ray spectroscopy (EDX) of the as-synthesized catalyst, namely,  $Fe_3O_4@CQD@$  Si (OEt)  $(CH_2)_3NH@CC@N_3@phenylacetylene@Cu$ 

34.37, respectively. Based on the ICP technique, besides, the mass percent of obtained copper is equal to 21.64%. These findings confirm the presence of copper in the assynthesized catalyst so that 5.4 mmol copper is loaded per gram of the catalyst (5.4 mmol Cu/g catalyst). To prove the presence of different elements in the assynthesized catalyst structure, the EDX elemental mapping was taken (Figure 7). As shown in this figure, carbon, copper, iron, nitrogen, oxygen, and silicon form the elemental composition of the catalyst.

# 3.1.5 | Thermal gravimetric analysis and differential thermal analysis

TGA and differential thermal analysis (DTA) were used to evaluate the thermal stability of the as-synthesized catalyst. TAG and DTA of the copper-based magnetic nanocatalyst are shown in Figure 8. Weight loss before



**FIGURE 7** Energy-dispersive X-ray spectroscopy (EDX) elemental mapping of the as-synthesized catalyst, namely,  $Fe_3O_4@CQD@Si(OEt)(CH_2)_3NH@CC@N_3@phenylacetylene@Cu$ 



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**FIGURE 8** Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) of the as-synthesized catalyst, namely, Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu

FIGURE 9 Magnetization curves of the  $Fe_3O_4$ , and the as-synthesized catalyst, namely  $Fe_3O_4$ @CQD@ Si (OEt)  $(CH_2)_3NH@CC@N_3@phenylacetylene@Cu catalyst$ 



 $\label{eq:FIGURE10} \begin{array}{l} \mbox{Size distribution of the as-synthesized catalyst,} \\ \mbox{namely Fe}_{3}O_{4}@CQD@Si~(OEt) \end{array}$ 

(CH2)3NH@CC@N3@phenylacetylene@Cu catalyst

**TABLE 1**Effect of various solvents on the reaction time andyield (in the presence of the as-synthesized catalyst)

			Yield <sup>[a]</sup> (%)
Entry	Solvent	Time (min)	60°C
1		5	90
2	EtOAc	13	75
3	CH3CN	17	69
4	H2O	15	84
5	n-Hexane	20	37
6	EtOH	13	88

<sup>a</sup>Isolated yield.

**TABLE 2**Levels of theindependent variables and thecorresponding reaction yields using theCCD method

 $100^{\circ}$ C is attributed to the H<sub>2</sub>O and solvents trapped in the as-synthesized catalyst structure (A). Drops in regions B to F are related to different layers loaded on the synthesized catalyst. As is shown in this figure, the as-prepared catalyst is stable at high temperatures, especially up to  $700^{\circ}$ C (this catalyst losses only 20%wt of its mass).

#### 3.1.6 | Vibrating sample magnetometer

This technique is used to identify the magnetic properties of a material. The magnetization curves of the Fe<sub>3</sub>O<sub>4</sub> and the final as-synthesized catalyst are shown in Figure 9. Loading different layers on the Fe<sub>3</sub>O<sub>4</sub> reduces the saturation magnetization (from 54 emu/g in Fe<sub>3</sub>O<sub>4</sub> to 25 emu/g in the as-synthesized catalyst). However, the magnetization (25 emu/g) is enough that Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu

nanoparticles could be easily recovered from reaction media using an external magnet.

#### 3.1.7 | Size distribution

Figure 10 shows the size distribution of the assynthesized particles. The mean size value of the particles with a 95% probability of random errors is equal to 21.55  $\pm$  5.38 nm. This result implies that the as-synthesized particles have a nanoscale diameter.

#### 3.1.8 | Heterogeneity test

For the proof of heterogeneity, two reactions were carried out in parallel in two test tubes using  $\beta$ -naphthol,

runs	X <sub>1</sub> (amount of catalyst)	X <sub>2</sub> (temperature)	Yield (%)
1	0.05	70	82
2	0.03	110	74
3	0.03	70	75
4	0.01	70	60
5	0.05	30	61
6	0.03	70	73
7	0.01	30	49
8	0.03	30	58
9	0.01	110	70
10	0.05	110	84
11	0.03	70	69

Abbreviation: CCD, central composite design.

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benzaldehyde, and morpholine as starting materials at 110°C and solvent-free condition (0.05 gr catalyst). After 2.5 min, one of them was stopped completely with a yield equal to 42%. At the same time, the catalyst was separated from the reaction medium in another test tube and the reaction was continued without catalyst for up to 30 min with a yield equal to 44%. No significant change in % conversion confirms the heterogeneity and role of the as-synthesized catalyst.

# 4 | EVALUATION OF THE CATALYTIC ACTIVITY OF NANO-Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub> NH@CC@N<sub>3</sub>@phenylacetylene @Cu catalyst

#### 4.1 | Effect of solvent on the reaction

The reaction between  $\beta$ -naphthol, benzaldehyde, and morpholine was selected as a prototype reaction to

TABLE 3 Analysis of variance for reaction yield

Parameter	p-val. prob. > $F$
Model (yield)	0.003
X <sub>1</sub>	0.002
X <sub>2</sub>	0.0005
R <sup>2</sup>	0.86
Predicted $R^2$	0.74
Lack of fit	0.32

investigate the effect of solvent on the reaction yield and time. The prototype reaction was carried out in ethyl acetate,  $CH_3CN$ ,  $H_2O$ , n-hexane, EtOH, and solvent-free condition. The results are given in Table 1. As is provided, solvents increase the reaction time to achieve a specified reaction yield. That is, the solvent-free condition has the minimum and maximum reaction time and yield, respectively. So the solvent-free condition was used to investigate the reaction further. The isolated yield, in this table, indicates the recrystallization yield in ethanol.

## 4.2 | Effect of catalysts and temperature on the reaction yield by the design of experiment

Briefly, central composite design (CCD) was used as a design of experiment (DOE) method.<sup>[51-53]</sup> CCD is a useful and practical subclass of response surface methodology (RSM) used to find a mathematical relationship between the dependent variable (here reaction yield) and independent variables (here temperature and the amount of catalyst). For the selected prototype reaction, temperature  $(X_1)$  and the amount of catalyst  $(X_2)$  are two independent variables that must change to find the maximum yield of the reaction. Due to the importance of the central experiment, it was carried out three times. The values of the independent variables along with the corresponding reaction vields are given in Table 2. It is important to note that all reactions in Table 2 were stopped after 5 min to investigate the effect of the catalyst and the temperature.



FIGURE 11 Two- and three-dimensional reaction yields in terms of the amount of the catalyst and temperature

TABLE 4	$Synthesized \ 1-aminoalkyl-2-naphthols \ derivatives \ at \ the \ optimum \ prototype \ reaction \ condition \ using \ nano-Fe_3O_4@CQD@Si$
$(OEt)(CH_2)_3N$	H@CC@N <sub>3</sub> @phenylacetylene@Cu catalyst

Product	1	2	3	4	5
m.p. (°C) Yield Time (min) <b>Product</b>	$ \begin{array}{c} 0 \\ N \\ HO \\ HO \\ \hline 0 \\ \hline \end{array} $ $ \begin{array}{c} 181-184 \\ 93 \\ 5 \\ 6 \\ \hline 0 \\ \hline \end{array} $	$ \begin{array}{c} 0 \\ 0 \\ HO \\ HO$	$ \begin{array}{c}                                     $	$\begin{array}{c} 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ $	0       Br         H0       U         174-178         81         5         10
	HO	HO		HO	но
m.p. (°C) Viold	176–179	126-128	181-183	183-188	198.4-202
Time (min)	94	5	8	91	5
Product	11	12	13	14	15
	HO	F N HO	F HO		
m.p. (°C)	160–164	160-167	160–161	196.8–197.2	197.4–198
Yield	81	78	75	69	75
Time (min)	12	6	8	5	6
Product	16	17 OMe HO	18	19	20 $Br$ $HO$ $HO$ $HO$
m.p. (°C)	188.2–191.2	156.7–164	159.5–161	193.1–194.3	180-183.5
Yield	58	70	84	72	73
Time (min)	5	8	7	10	10

(Continues)

 TABLE 4
 (Continued)

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Product	21	22	23	24	25
		HO HO	OH HO		HO
m.p. (°C)	159.5–164	159–161	165–171	205–211	198–202
Yield	58	88	71	63	77
Time (min)	12	8	10	14	12
Product	26	27	28	29	30
		HN N HO S	HN N HO	HN CI N HO	HN Cl HO
m.p. (°C)	188–196	197–204	188–189	167-168.5	153–158
Yield	72	84	72	69	76
Time (min)	6	5	8	9	5
Product	31	32 Br	33	34	35
	HN MeO N HO		HN HO		HN F
m.p. (°C)	180–182.6	150–152	181–184	131–134	116–120
Yield	82	73	93	89	85
Time (min)	6	9	5	3	7

Statistical methods are used to find a mathematical relation between independent and dependent variables. Statistical analysis showed that a linear model could best describe this relation. The linear model shows that there is no interaction between temperature and catalyst. The analysis of variance (ANOVA), also, is given in Table 3. The value of the correlation coefficient ( $R^2$ ) for the reaction yield is equal to 0.86 indicates a good agreement between the experimental results and the obtained linear model. The value of *p*-value (0.003),

also, indicates that the model is statistically significant and reliable (Table 3).

The following expression states the dependency of reaction yield to the temperature and the amount of catalyst.

$$Yield = 39.14 + 400 \times X_1 + 0.25 \times X_2$$

In general, expressions marked with + and - have an increasing and decreasing effect on the reaction yield,

respectively. The magnitude of the effect of X on reaction yield is indicated by the coefficient values. Figure 11 shows the two- and three-dimensional reaction yields in terms of the amount of the catalyst and temperature. This figure shows that as the amount of catalyst and temperature increases, the amount of reaction yield increases so that the 0.05-gr catalyst and 110°C are the optimum reaction condition.

## 4.3 | Synthesis of the 1-aminoalkyl-2-naphthols derivatives at optimum condition

Using the obtained optimal reaction condition for the prototype reaction, different derivatives of 1-aminoalkyl-2-naphthols were synthesized using  $\beta$ -naphthol, various aryl halides, and secondary amines (morpholine and piperidine) in the presence of the as-synthesized catalyst. These derivatives are given in Table 4 with their values of time, crystallization reaction yield after completion of corresponding reaction, and melting point. As Table 4 shows, these derivatives can be obtained with moderate to high yield (67%–95%) and short reaction times (3–15 min). The characterizations of the synthesized products are given in the supporting information DATA S1.

Table 5 provides the some recent research in the synthesis of 1-aminoalkyl-2-naphthols derivatives using glycerol,<sup>[15]</sup> acidic alumina in MW,<sup>[18]</sup> ionic liquid,<sup>[20]</sup> Fe<sub>3</sub>O<sub>4</sub> MNPs,<sup>[17]</sup> catalyst-free,<sup>[54]</sup> Triton X-100,<sup>[16]</sup> and DES (urea: choline chloride)<sup>[14]</sup> as catalysts. As given in Table 4 the as-synthesized copper-based heterogeneous magnetic nanocatalyst gives the maximum yield at low time, namely, 5 min than mentioned studied catalysts. In addition, the reaction between  $\beta$ -naphthol, benzaldehyde,





**SCHEME 3** The plausible proposed mechanism for the synthesis of 1-aminoalkyl-2-naphthols derivatives using the assynthesized catalyst, namely,  $Fe_3O_4@CQD@$  Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu



**FIGURE 12** The yield of the prototype reaction versus cycles using Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> @phenylacetylene@Cu as-synthesized catalyst

TABLE 5	Comparison of the as-synthesized copper-based nanocatalyst with the available research catalyst, including catalyst type,
condition, tin	ie, and yield

Entry	Catalyst	Condition	Time	Yield	Reference
1	DES (urea:choline chloride)	DES 1 ml, 60°C	1–3 h	95	[14]
2	Glycerol	2 ml cat, 90°C	10 min	71	[15]
3	Triton X-100	5 mol % cat $H_2O$ , r.t.	2.5 h	93	[16]
4	Fe <sub>3</sub> O <sub>4</sub> magnetic nanoparticles	0.1 g cat, U. S, 80°C	25 min	90	[17]
5	Acidic alumina in MW	2 g cat, solvent-free 80°C	5 min	73	[18]
6	Ionic liquid	1 eq cat, EtOH, 80°C	1 h	85	[20]
7	Catalyst-free	Dichloromethane, r.t.	2 h	90	[54]
8	This work (nanocatalyst)	0.05 g cat, S. F, 104°C	5 min	93	-

Abbreviations: r.t., room temperature, MW, microwave.



FIGURE 13 Energy-dispersive X-ray spectroscopy (EDX) of the recovered Fe<sub>3</sub>O<sub>4</sub>@CQD@ Si (OEt) (CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub>@phenylacetylene@Cu catalyst







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and morpholine as starting materials was carried out using Cu  $(OAc)_2.2H_2O$ , dry Cu  $(OAc)_2$ , and the assynthesized catalyst. Both Cu  $(OAc)_2.2H_2O$ , dry Cu (OAc) provide yield equal to 62%, while the assynthesized catalyst provides yield equal to 93%. All three reactions were stopped after 5 min. These findings confirm the effective catalytic activity of the as-synthesized catalyst compared to the Cu  $(OAc)_2.2H_2O$ , dry Cu  $(OAc)_2$ .

#### 5 | PROPOSED MECHANISM

The proposed mechanism for the prototype reaction Scheme 3. is given in To investigate the reaction mechanism, IR spectra were taken from the mixture of Fe<sub>3</sub>O<sub>4</sub>@CQD@Si (OEt)(CH<sub>2</sub>)<sub>3</sub>NH@CC@N<sub>3</sub> @phenylacetylene@Cu with benzaldehyde or  $\beta$ -naphthol or morpholine. The IR spectrum shows that the catalyst does not react with morpholine because there is no change in the wave number, but the catalyst interacts with benzaldehyde and beta naphthol so that the wave number in benzaldehyde shifts from 1686 to  $1662 \text{ cm}^{-1}$ and the wave number of the hydroxy group in beta naphthol shifts from 3209 to  $3218 \text{ cm}^{-1}$ . These evidences imply that the copper present on the catalyst surface interacts with the carbonyl group of the benzaldehyde and the hydroxy groups of the  $\beta$ -naphthol that triggers the reaction. Based on these evidences, the proposed mechanism is given in Scheme 3. As is seen in Scheme 3, in the first stage, the as-synthesized catalyst interacts with benzaldehyde and then morpholine attacks the benzaldehyde, creating an imine intermediate. In the next step, the activated  $\beta$ -naphthol by the as-synthesized

catalyst attacks the imine intermediate. Aromatization driving force entails the formation of 1-aminoalkyl-2-naphthols.

## 6 | RETRIEVAL OF THE CATALYST

After completion of the prototype reaction at the obtained optimum condition, the as-synthesized catalyst was separated using an external magnet and used in the next cycles. The reduction in reaction yield compared to the different cycles is shown in Figure 12, so that the catalyst provides 87.5% reaction yield after five cycles. Reactions were stopped at 5 min per cycle. IR, EDX, and mapping analyses were taken to examine the stability of the recovered catalyst. Figure 13 presents the EDX of the as-synthesized retrieved catalyst, so that all elements, especially Cu with 2.4 wt%, are present in the recovered catalyst. Elemental mapping was used to further investigate the stability of the retrieved catalysts so that the qualitative spatial distribution of constituent elements including Fe, O, C, Si, N, and Cu is given in Figure 14. As is shown in this figure, all elements, in particular Cu, are present in the retrieved catalyst. This finding provides strong evidence for the stability of the as-synthesized novel copper-based heterogeneous magnetic nanocatalyst.

In another study, the TEM technique was used to confirm and re-prove the structure of the recovered catalyst. First, the catalyst was used in the six cycles so that Figure 15 displays the TEM images of the recovered catalyst. Compared to the intact catalyst (Figure 5), the structure of the recovered catalyst did not change



FIGURE 15 Transmission electron microscopy (TEM) micrographs of the as-synthesized heterogeneous recovered catalyst after six cycles



**FIGURE 16** Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) analysis of the as-synthesized catalyst after six cycles of recovery

**FIGURE 17** The FTIR spectra of the assynthesized catalyst before and after six cycles of recovery

significantly. It should be noted that these two catalysts (intact and recovered) have been synthesized in different batches and differences can be due to this issue.

Also, the TGA analysis of the recovered catalyst after six cycles was used to demonstrate the possible changes before and after the performance tests (Figure 16). As is shown, the recovered catalyst has multiple step-changes in mass similar to the neat as-synthesized catalyst. These analytical findings confirm the stability of the provided catalyst.

To further investigate the as-synthesized catalyst's stability, the FTIR spectrum was taken from the recovered catalyst after six cycles. Figure 17 compares the FTIR of the as-synthesized catalyst before and after recovery. As is shown, the FTIR of the recovered catalyst does not change compared to the virgin catalyst considerably. This proves the stability of the as-synthesized catalyst even after the recovery.

#### 7. CONCLUSION

The proposed precise and engineered method, in summary, can be used to synthesize novel Lewis acid-based heterogeneous catalysts, including Cu, Co, etc. These types of catalysts can be used in various organic transformations that require a Lewis acid. Of the solvent-free condition, low reaction time, high reaction yield, mild reaction condition, and stability of catalyst all are the main features of the as-synthesized catalyst. Besides, the findings of this study show that the use of DOE in organic chemistry to find the optimal conditions is a necessity that organic chemists should use in their research.

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#### AUTHOR CONTRIBUTIONS

Tahereh Akbarpour: Conceptualization; data curation; formal analysis; methodology. Ardeshir Khazaei: Funding acquisition; resources; supervision. Jaber Yousefi Seyf: Project administration; software; supervision; validation; visualization. Negin Sarmasti: Investigation; methodology; project administration.

#### DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

#### ORCID

Tahereh Akbarpour D https://orcid.org/0000-0002-0609-1228

Ardeshir Khazaei D https://orcid.org/0000-0001-7990-2266

Jaber Yousefi Seyf https://orcid.org/0000-0001-5919-0206

Negin Sarmasti 🗈 https://orcid.org/0000-0002-0319-0909

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