Received: 5 November 2019 | Revised: 20 January 2020 | Accepted: 25 January 2020

DOI: 10.1002/aoc.5599

FULL PAPER

Applied Organometallic Chemistry WILEY

$CoFe_2O_4@SiO_2$-PA-CC-guanidine nanoparticles: A novel, efficient, and recyclable catalyst for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives

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Funding information
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A new and efficient procedure for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives by $CoFe_2O_4@SiO_2$-PA-CC-guanidine magnetic nanoparticles (MNPs) was reported. 3,5-Disubstituted-2,6-dicyanoaniline derivatives were synthesized from malononitrile, aldehydes, and β-nitrostyrene derivatives in good yields. MNPs used for the synthesis of aniline derivatives were easy to recover and reuse. The $CoFe_2O_4@SiO_2$-PA-CC-guanidine MNPs were characterized by Fourier-transform infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction, thermogravimetric analysis, and vibration sample magnetometry techniques.

KEYWORDS

3,5-disubstituted-2,6-dicyanoaniline, aldehydes, magnetic nanoparticles, malononitrile, β-Nitrostyrene

1 | INTRODUCTION

Polysubstituted benzenes[1] are important groups in organic chemistry. These compounds have specific applications in the natural products chemistry, medicinal chemistry, and material chemistry.[2] However, their synthesis remains an important challenge. 2,6-Dicyanoaniline derivatives are an interesting class of substituted benzenes which consist of acceptor–donor–acceptor systems.[3] These systems contain one donor group (NH_2) and two acceptor groups (CN). Organic dyes consist of donor–acceptor systems and demonstrate various optical properties.[4] In addition, 2,6-dicyanoanilines are found in the structure of various polymers[5]; light-emitting diodes[6]; and biological compounds such as benzofurans,[7] fluorenes,[8] 9-oxofluorenes,[9] quinolines,[10] isoquinolines,[11] tetrahydroisoquinolines,[12] indoles,[13] indazoles,[14] imines,[15] 6H-benzo[c]chromenes,[16] steroids,[17] naphthalenes,[18] coumarins,[19] phenoxazines,[20] quinazolines,[15] and dibenzo[b,d]furans.[21] Substituted 2,6-dicyanoanilines, which contain 2,6-dicyanoanilines derivatives in their structures, have biological activities such as anticancer,[22] antimicrobial,[23] antileishmanial,[24] antihyperglycemic,[25] anti-amyotrophic lateral sclerosis,[26] and growth-promoting properties.[27] There are many examples of 2,6-dicyanoanilines that have substituted alkyl, aryl, or heteroaryl groups in the C3, C4, and C5 position.[5] 3,5-Disubstituted-2,6-dicyanoaniline derivatives constitute an important class of 2,6-dicyanoanilines. For the synthesis of these compounds, many procedures have been reported, one of which is one-pot multicomponent reaction (MCR)[28] using malononitrile and aldehydes or ketones in the presence base such as NaOH, K_2CO_3, 4-dimethylaminopyridine, ethanediamine, or piperidine.[29] One-pot MCRs are an efficient and green route for the synthesis of novel and useful organic compounds. One-pot MCRs are associated with limited waste generation, less reaction time, decreased cost, and without the need to separate the intermediate. These reactions have high atom economy and save energy.[30] Therefore, the one-pot MCR method is convenient for the synthesis of 2,6-dicyanoanilines and their different derivatives.

https://doi.org/10.1002/aoc.5599

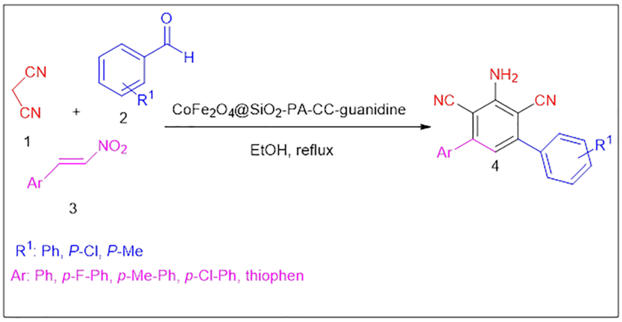
Nowadays, the use of nanoparticles[31,32] as the catalyst for the synthesis of organic compounds has increased. Nanoparticles are heterogeneous catalysts.[33] Because the activity of heterogeneous catalysts is lower than that of homogeneous catalysts,[34] nanoparticles not only have activity similar to the homogeneous catalysts but can also be easily separated from the reaction mixture. Nanoparticles such as Fe_3O_4 and $CoFe_2O_4$[35–38] have magnetic property and thus can be simply separated from the reaction mixture using an external magnet without need for complex methods such as filtration or centrifugation and can be recovered and reused.[39] Therefore, magnetic nanoparticles (MNPs) are an ideal option for organic synthesis.

Considering the importance of 2,6-dicyanoanilines and their derivatives, we herein report a one-pot MCR for the synthesis of 3,5-disubstituted 2,6-dicyanoaniline derivatives using $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs (Scheme 1).

2 | EXPERIMENTAL

2.1 | Chemicals and instrumentation

All chemical and solvents were purchased from Sigma-Aldrich, Merck, Ilam, Iran, and Fluka. Infrared (IR) spectra (KBr; in reciprocal centimeters [cm^{-1}]) were obtained using a spectrometer (Bruker, Germany), while ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra (in Hertz) were obtained using a Bruker DRX-250 AVANCE instrument in $CDCl_3$ operating at 250 MHz for ^1H NMR and 62.5 MHz for ^{13}C NMR, with δ in parts per million (ppm). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed using a JEOL JEM-2010 instrument, and X-ray diffraction (XRD) was recorded using a Holland Philips X. Thermogravimetric analysis (TGA) was carried out on a thermogravimetric analyzer (NETZSCH, Germany) and superparamagnetic properties of the catalyst were measured using vibration sample magnetometry (VSM; MDKFD).



SCHEME 1 Synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives

2.2 | Synthesis of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs

2.2.1 | Synthesis of $CoFe_2O_4$ MNPs

First, a mixture of $CoCl_2{\cdot}6H_2O$ (0.005 mol, 1.19 g) and $FeCl_3{\cdot}6H_2O$ (0.01 mol, 2.705 g) was dissolved in 50 mL water. Second, 3 g of NaOH was dissolved in 25 mL water and dropwise added to the mixture. The mixture was then refluxed for 1 h. Finally, the mixture was cooled down to room temperature, and the resulting black precipitate extracted with an external magnet and washed several times with H_2O and EtOH, respectively, and dried at room temperature.

2.2.2 | Synthesis of $CoFe_2O_4$@SiO_2 MNPs

For the synthesis of $CoFe_2O_4$@SiO_2 MNPs, $CoFe_2O_4$ (1 g) was sonicated in water (10 mL) for 30 min. Then, EtOH (25 mL), polyethylene glycol (2.68 g), H_2O (10 mL), ammonium solution (5 mL), and tetraethyl orthosilicate (TEOS; 1 mL) were added to the mixture and stirred at room temperature for 38 h. The product was then extracted by an external magnet and washed several times with EtOH and dried at room temperature.

2.2.3 | Synthesis of $CoFe_2O_4$@SiO_2-PA MNPs

$CoFe_2O_4$@SiO_2 MNPs (1.5 g) were sonicated in 50 mL EtOH for 30 min. Next, 2 mL of 3-aminopropyltrimethoxysilane was added to the mixture and refluxed for 12 h. After completion of the reaction, the mixture was cooled down to room temperature, and $CoFe_2O_4$@SiO_2-PA MNPs were extracted using an external magnet and washed three times with EtOH and dried at room temperature.

2.2.4 | Synthesis of $CoFe_2O_4$@SiO_2-PA-CC MNPs

Cyanuric chloride (CC; 1.85 g, 10 mmol) and Et_3N (1.4 mL, 10 mmol) were added to $CoFe_2O_4$@SiO_2-PA MNPs (2 g) in tetrahydrofuran (THF; 10 mL), and this reaction mixture was stirred at room temperature for 10 h. The product was then extracted using an external magnet and washed five times with hot THF and dried at room temperature.

2.2.5 | Synthesis of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs

For the synthesis of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs, guanidine chloride (0.764 g, 8 mmol) and Et_3N (1.1 mL, 8 mmol) were added to $CoFe_2O_4$@SiO_2-PA-CC (1 g) in dimethylformamide (12 mL) and stirred for 12 h at 60 °C. After completion of the reaction, the catalyst was separated from the product using an external magnet and washed five times with hot EtOH and dried at room temperature.

2.3 | General procedure for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives

A mixture of malononitrile (1 mmol), benzaldehyde derivatives (0.5 mmol), β-nitrostyrene derivatives (0.5 mmol), and $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs (0.06 g) in EtOH (3 mL) was refluxed for 1 h. After completion of the reaction, MNPs were separated using an external magnet and the product was extracted with CH_2Cl_2. For further purification of the products, column chromatography (*n*-hexane/ethyl acetate 9:1) was used.

5′-amino-4-chloro-4″-fluoro-[1,1′:3′,1″-terphenyl]-4′,6′- dicarbonitrile (4d): Light yellow solid; melting point (MP) = 220–222 °C; IR (KBr) (v_{max}/cm^{-1}): 1493–1653 (Ar), 2221 (CN), 3323–3459 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.17 (s, 2H, NH_2), 7.17–7.97 (m, 9H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 88.3, 110.1, 110.7, 115.0, 116.8, 117.2, 127.4, 129.0, 129.6, 130.1, 131.8, 133.5, 143.9, 158.4.

5′-amino-4-methyl-[1,1′:3′,1″-terphenyl]-4′,6′-dicarbonitrile (4e): Light yellow solid; MP = 159–161 °C; IR (KBr) (v_{max}/cm^{-1}): 1562–1648 (Ar), 2207 (CN), 3354–3420 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 5.28 (s, 2H, NH_2), 7.02–7.47 (m, 10H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 21.2, 88.5, 110.5, 111.0, 115.3, 126.1, 127.5, 127.7, 128.4, 129.2, 129.6, 129.8, 130.3, 130.4, 131.0, 135.5, 139.6, 143.9.

5′-amino-4-fluoro-[1,1′:3′,1″-terphenyl]-4′,6′-dicarbonitrile (4f): Light yellow solid; MP = 186–188 °C; IR (KBr) (v_{max}/cm^{-1}): 1511–1651 (Ar), 2209 (CN), 3350–3452 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.22 (s, 2H, NH_2), 7.12–7.47 (m, 10H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 88.4, 110.2, 110.8, 115.1, 116.8, 117.2, 127.6, 128.8, 129.7, 131.1, 143.7.

5′-amino-4-chloro-[1,1′:3′,1″-terphenyl]-4′,6′-dicarbonitrile (4g): Light yellow solid; MP = 212–214 °C; IR (KBr) (v_{max}/cm^{-1}): 1492–1653 (Ar), 2222 (CN), 3273–3320 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.22 (s, 2H, NH_2), 7.15–7.47 (m, 10H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 88.2, 110.2, 110.6, 114.9, 116.5, 124.7, 127.6, 129.0, 129.7, 129.8, 130.1, 131.1, 133.6, 137.6, 143.7.

5′-amino-4-methyl-[1,1′:3′,1″-terphenyl]-4′,6′-dicarbonitrile (4h): Light yellow solid; MP = 163–165 °C; IR (KBr) (v_{max}/cm^{-1}): 1515–1650 (Ar), 2207 (CN), 3352–3445 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 2.45 (s, 3H, CH_3), 5.12 (s, 2H, NH_2), 7.11–7.47 (m, 10H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 21.2, 88.5, 110.5, 110.9, 115.2, 127.5, 127.6, 128.4, 128.7, 129.7, 129.8, 130.3, 130.5, 131.0, 143.7.

3-amino-5-(thiophen-2-yl)-[1,1′-biphenyl]-2,4-dicarbonitrile (4i): Light yellow solid; MP = 156–158 °C; IR (KBr) (v_{max}/cm^{-1}): 1495–1648 (Ar), 2225 (CN), 3349–3435 (NH_2); ^1H NMR (250 MHz, $CDCl_3$): δ 5.13 (s, 2H, NH_2), 7.02–7.87 (m, 9H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 88.4, 110.3, 115.1, 127.7, 128.4, 129.7, 129.8, 131.0, 135.3, 136.9.

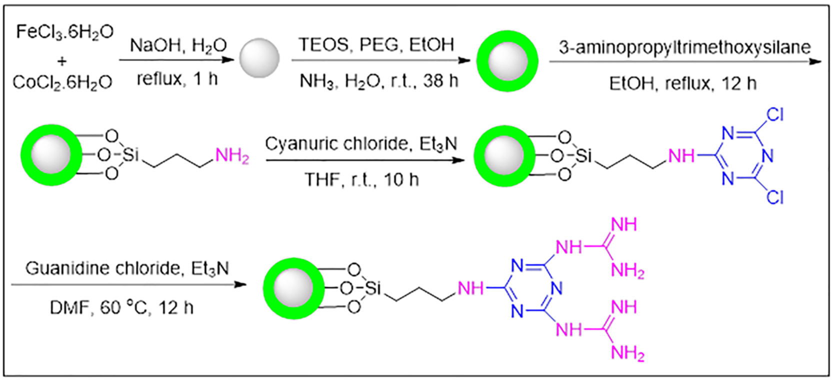
3 | RESULTS AND DISCUSSION

3.1 | Characterization of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs

Steps involved in the synthesis of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs are presented in Scheme 2.[31,40–42] Initially, $CoFe_2O_4$ MNPs were synthesized from $CoCl_2{\cdot}6H_2O$ and $FeCl_3{\cdot}6H_2O$. Then, $CoFe_2O_4$ MNPs were coated with SiO_2 using TEOS, and 3-aminopropyltrimethoxysilane was immobilized onto $CoFe_2O_4$@SiO_2 MNPs to synthesize $CoFe_2O_4$@SiO_2-PA MNPs. Then, CC was supported on the surface of $CoFe_2O_4$@SiO_2-PA MNPs for the synthesis of $CoFe_2O_4$@SiO_2-PA-CC MNPs. Eventually, guanidine stabilized on the surface of $CoFe_2O_4$@SiO_2-PA-CC to synthesize $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs. The $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs synthesized were characterized by Fourier-transform infrared (FT-IR), SEM, EDX, XRD, TGA, and VSM techniques.

3.1.1 | FT-IR analysis

The FT-IR spectra of $CoFe_2O_4$, $CoFe_2O_4$@SiO_2, $CoFe_2O_4$@SiO_2-PA, $CoFe_2O_4$@SiO_2-PA-CC, and $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs are presented in



SCHEME 2 Synthesis route for the CoFe2O4@SiO2-PA-CC-Guanidine MNPs

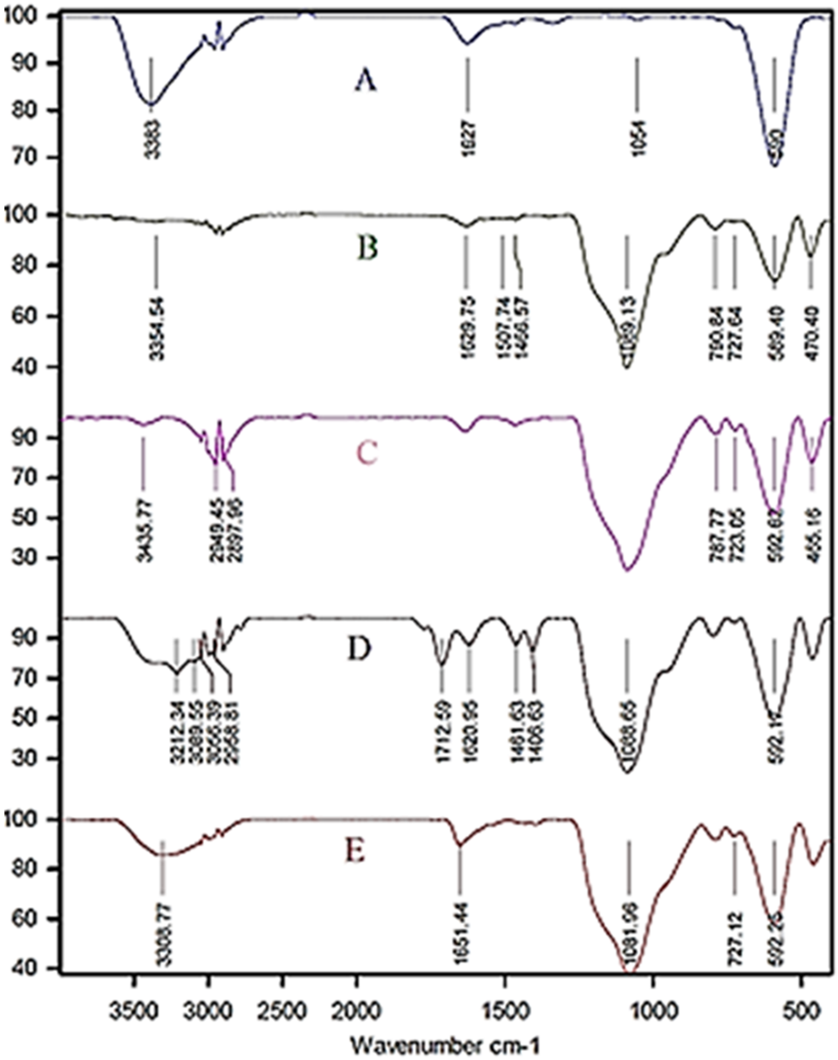


FIGURE 1 FT-IR spectrum of CoFe2O4 (A), CoFe2O4@SiO2 (B), CoFe2O4@SiO2-PA (C), CoFe2O4@SiO2-PA-CC (D) and CoFe2O4@SiO2-PA-CC-guanidine (E) MNPs

Figure 1A–E, respectively. The stretching vibrations at 3383 and 590 cm^{-1}, respectively, are related to the O–H and Co–O bands that confirmed the successful synthesis of $CoFe_2O_4$ MNPs (Figure 1A). The presence of SiO_2 at the surface of $CoFe_2O_4$ MNPs was confirmed by the stretching vibration at 1089 cm^{-1}, which represents a peak corresponding to the Si–O band (Figure 1B). Obvious peaks at 2897–2949 cm^{-1} were attributed to the stretching vibration of methylene groups (CH_2) and the broadening peak at 3435 cm^{-1} can be related to the NH_2 group, which indicates the presence of 3-aminopropyltrimethoxysilane on the surface of $CoFe_2O_4@SiO_2$ (Figure 1C). Two peaks appear at 1406 and 1712 cm^{-1} and these can be related to the C=N band in CC. These peaks correspond to the stretching vibrations indicating the presence of CC on the surface of

$CoFe_2O_4$ (Figure 1D). The presence of guanidine in the structure of $CoFe_2O_4$ MNPs was confirmed by the stretching vibration at 1651 cm^{-1} which corresponds to the C=N bands of guanidine that overlap with the C=N peak of the ring. Furthermore, the peak near 3300 cm^{-1} confirms the existence of guanidine (Figure 1E).

3.1.2 | SEM analysis

The morphology and size of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs were determined by SEM. An SEM image of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs shows that nanoparticles obtained were spherical with their particles sizes in the nano range (Figure 2).

3.1.3 | EDX analysis

EDX is one of the best approaches to determine elements present in nanoparticles and purity of nanoparticles. The EDX spectrum of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs is illustrated in Figure 3 which confirms the presence of Fe, Co, O, Si, and C in the catalyst and proves the successful synthesis of nanoparticles. It must be noted that the nitrogen peak is not observed because of the overlap between the peak of nitrogen and other elements.

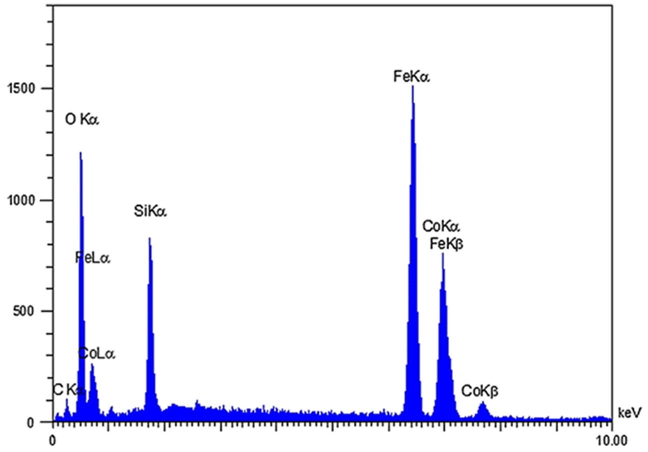


FIGURE 3 EDX spectra of CoFe2O4@SiO2-PA-CC-guanidine MNPs

3.1.4 | XRD analysis

The structure of the $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs was investigated by X-ray diffraction (XRD). XRD patterns for the $CoFe_2O_4$ (orange) and $CoFe_2O_4$@SiO_2-

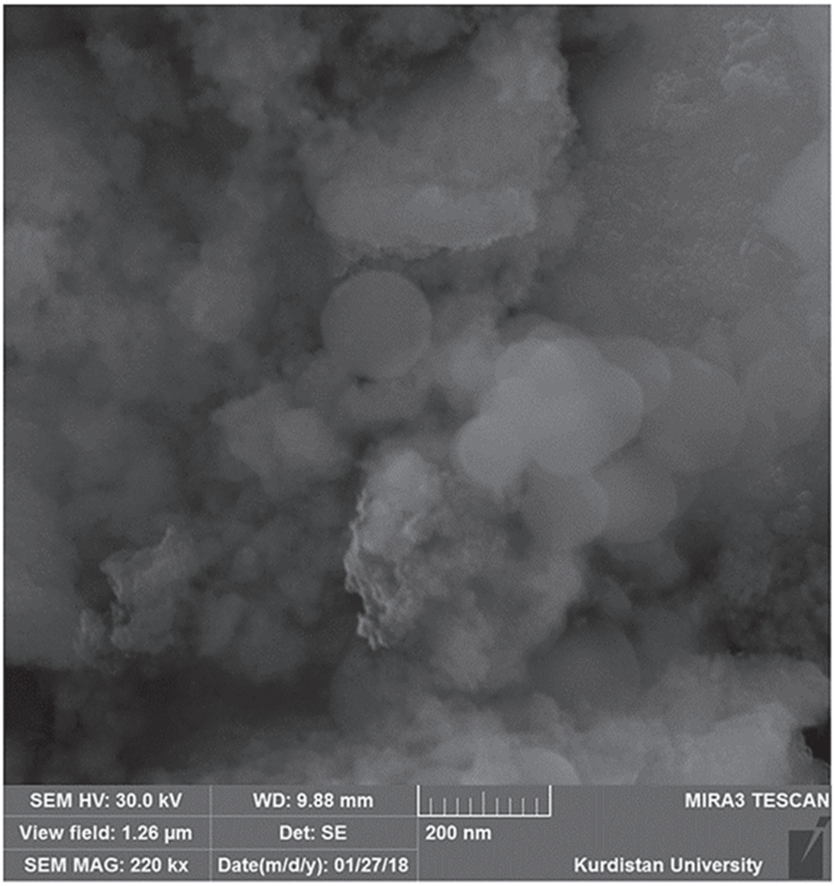


FIGURE 2 SEM image of CoFe2O4@SiO2-PA-CC-guanidine MNPs

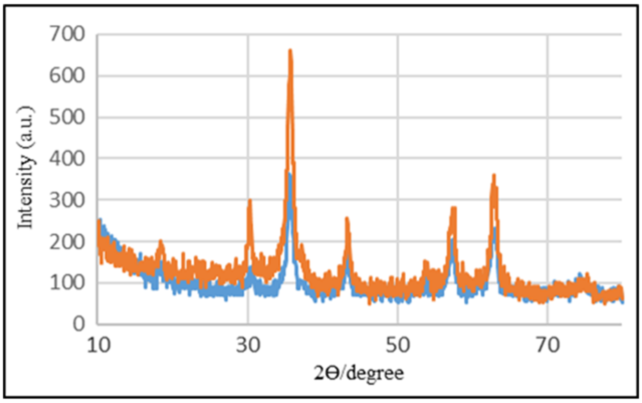


FIGURE 4 XRD patterns of CoFe2O4 (orange color) and CoFe2O4@SiO2-PA-CC-guanidine (blue color) MNPs

PA-CC-guanidine (blue) MNPs are shown in Figure 4. The patterns demonstrate six peaks at 2 = 30.21°, 35.76°, 43.36°, 54.06°, 57.61°, and 63.16°. These peaks confirm the structure of $CoFe_2O_4$@SiO_2-PA-CC-guanidine that agrees with the standard pattern. Besides, the XRD patterns confirm that the crystalline structure of $CoFe_2O_4$ did not change with the functionalization of the surface of the nanoparticles.

3.1.5 | TGA

The thermal stability of $CoFe_2O_4$@SiO_2-PA-CC-guanidine was investigated using TGA. The TGA curve of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs is shown in Figure 5, which illustrates that thermal decomposition occurred in two steps. The first weight loss was observed below 250 °C due to the removal of physically adsorbed solvent and OH groups from the surface of the catalyst and the second weight loss occurred between 250 and 800 °C, which is related to the decomposition of organic groups on the surface of the catalyst.

3.1.6 | VSM analysis

To investigate the magnetization of $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs, VSM was employed. Magnetization curves of $CoFe_2O_4$ (blue) and $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs (orange) are illustrated in Figure 6. The amounts of saturation magnetization for $CoFe_2O_4$ and $CoFe_2O_4$@SiO_2-PA-CC-guanidine are 40 and 28 emu/g, respectively. The decrease of saturation magnetization in the prepared nanocatalyst is due to the presence of silica shell around the $CoFe_2O_4$ MNPs.

3.2 | Catalytic studies

Following the synthesis and characterization, $CoFe_2O_4$@SiO_2-PA-CC-guanidine MNPs (nanocatalysts) were used for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives. For this purpose, the reaction between malononitrile, benzaldehyde, and β-nitrostyrene was chosen as the model reaction and various conditions including different catalyst amounts, solvents, and temperatures were examined. The results show that the best efficiency and the highest yield were obtained when the reaction was carried out in EtOH at reflux conditions (Table 1, Entry 2). To investigate the optimal amount of catalyst required, the model reaction was carried out with various amounts of catalyst. Eventually, 0.06 g amount of catalyst was found to be the best amount to carry out the reaction (Table 1, Entry 2). The obtained results are presented in Table 1.

After optimization of the reaction, new derivatives of 3,5-disubstituted-2,6-dicyanoaniline were synthesized

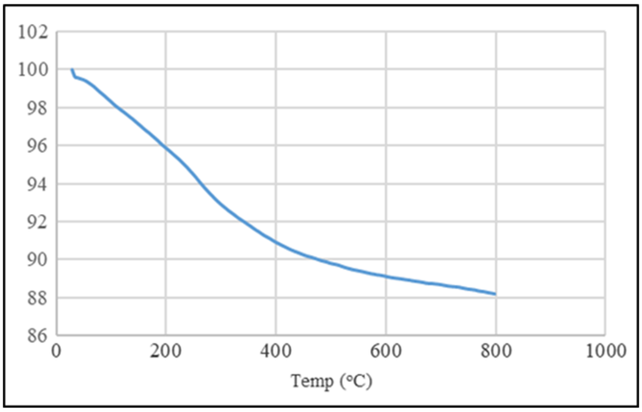


FIGURE 5 TGA curve of CoFe2O4@SiO2-PA-CC-guanidine MNPs

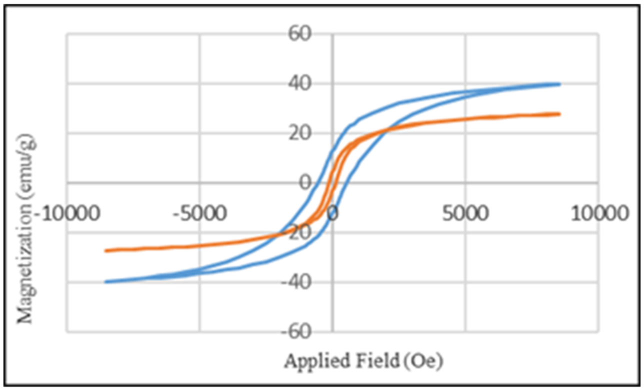
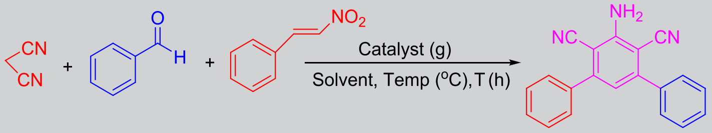


FIGURE 6 VSM curves of CoFe2O4 (blue curve) and CoFe2O4@SiO2-PA-CC-guanidine (orange curve) MNPs

TABLE 1 Optimizing the reaction conditions for the synthesis of 3,5-disubstituted-2,6-dicyanoanilines **4** using $CoFe_2O_4@SiO_2$-PA-CC-guanidine as the catalyst[a]



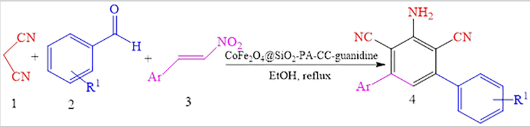
Entry	Solvent	Temp (°C)	Catalyst (g)	Time (h)	Yield (%)
1	EtOH	Reflux	0.05	1	75
2[b]	**EtOH**	**Reflux**	**0.06**	**1**	**91**
3	EtOH	Reflux	0.07	1	91
4	H_2O	80	0.06	1	75
5	H_2O	100	0.06	1	80
6	Dimethylformamide	100	0.06	1	60
7	Polyethylene glycol	100	0.06	1	50
8	Acetonitrile	Reflux	0.06	1	50
9	Solvent free	100	0.06	1	70

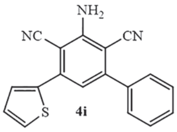
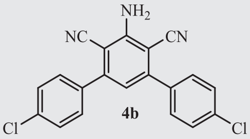
Note. Bold is the optimum condition for perform reaction.

[a] Reaction conditions: malononitrile (1 mmol), benzaldehyde (0.5 mmol), β-nitrostyrene (0.5 mmol), catalyst (0.06 g), reflux, 3 mL solvent, 1 h.

[b] Optimum conditions.

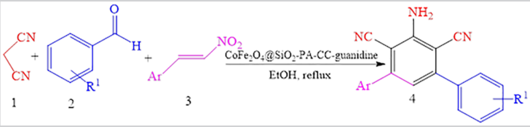
TABLE 2 Synthesis of 3,5-disubstituted-2,6-dicyanoanilines **4**

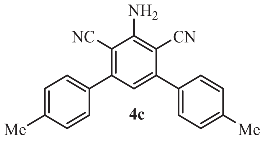
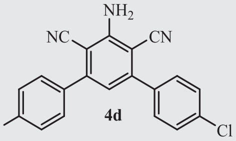
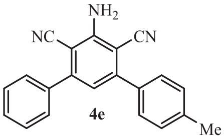
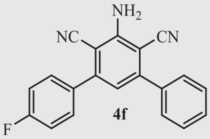
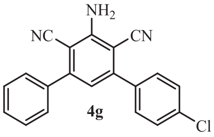
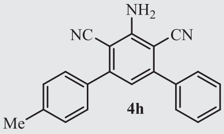


Entry	R[a]	Ar	Product	Yield (%)	MP (°C) (Reference)
1	H	Ph	 4i	90	215–214[43]
2	4-C1	4-C1-Ph	 4b	83	259–261[43]
3	4-Me	4-Me-Ph		87	226–228[43]

(Continues)

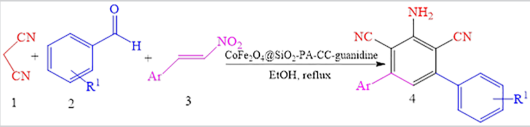
TABLE 2 (Continued)

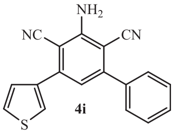


Entry	R^{a}	Ar	Product	Yield (%)	MP (°C) (Reference)
			 4c		
4	4-Cl	4-F-Ph	 4d	88	220–222
5	4-Me	Ph	 4e	85	159–161
6	H	4-F-Ph	 4f	83	186–188
7	4-Cl	Ph	 4g	79	212–214
8	H	4-Me-Ph	 4h	90	163–165
9	H	Thiphen		80	156–158

(Continues)

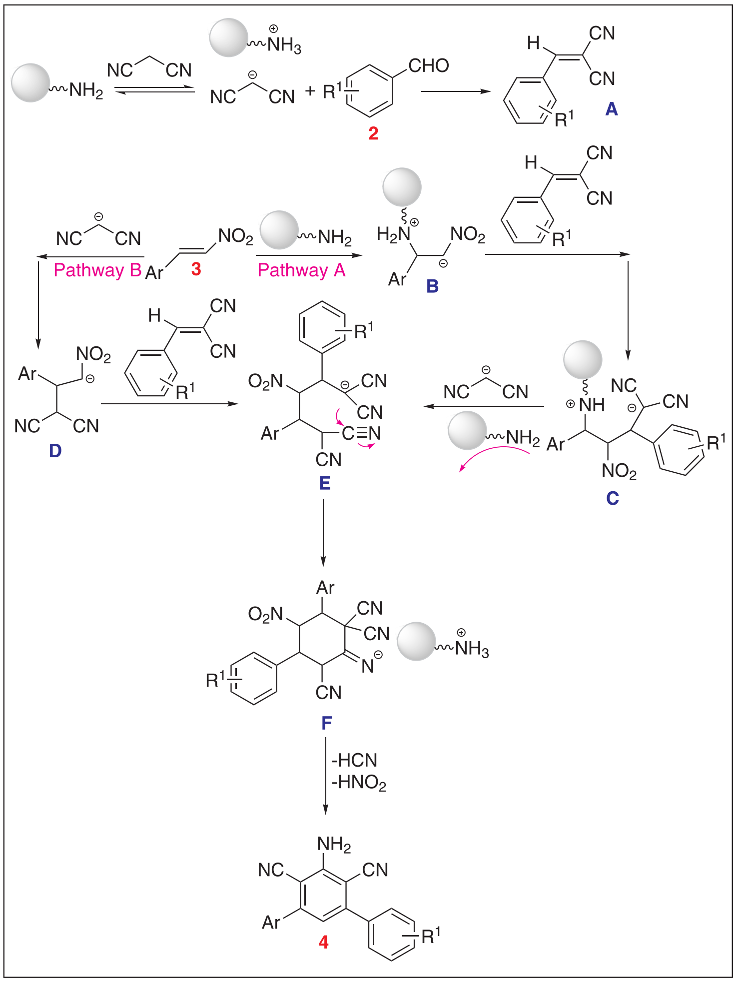
TABLE 2 (Continued)



Entry	R^a	Ar	Product	Yield (%)	MP (°C) (Reference)
					

[a] Substitution of benzaldehyde derivative.

CC, cyanuric chloride; MP, melting point.



SCHEME 3 Possible mechanism for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives

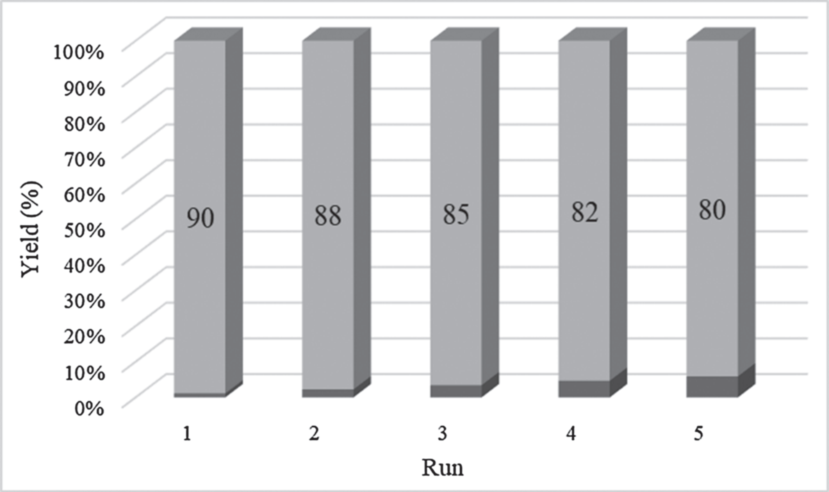


FIGURE 7 Reusability of CoFe2O4@SiO2-PA-CC-guanidine MNPs for the synthesis of compound 4a

and results are presented in Table 2.

3.3 | Proposed mechanism

The possible mechanism for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives reported in the literature is shown in Scheme 3.[43] Initially, in the presence of a basic nanocatalyst, malononitrile was reacted with aldehyde **2** and intermediate **A** is produced. This reaction can be accomplished using two pathways to generate product **4**: A and B. In pathway A, by reacting the basic nanocatalyst with nitroolefin, intermediate **C** is produced. In the following step, intermediate **C** was reacted with malononitrile in the presence of the basic nanocatalyst to generate intermediate **E**. Then, intermediate **E** undergoes an intramolecular cyclization to form intermediate **F**. Finally, by eliminating **HCN** and **HNO_2** from intermediate **F**, product **4** is produced. In pathway B, by reacting nitroolefin with malononitrile in the presence of the basic nanocatalyst, intermediate **D** is prepared. In the following, intermediate **D** was reacted with intermediate **A** to generate intermediate **E**. Then, intermediate **E** undergoes an intramolecular cyclization and intermediate **F** is formed. Finally, by eliminating of **HCN** and **HNO_2** from intermediate **F** product **4** is produced.

3.4 | Recovery and reusability of the catalyst

One of the most important advantages of the catalyst synthesized in this work is its magnetism. This property allows the recoverability of the catalyst and simplifies its separation. Because recovery and reusability are important aspects for the nanoparticles, we investigated these properties of the catalyst in the model reaction under optimized conditions. After completion of the reaction, the catalyst was separated from the reaction mixture using an external magnet, washed with EtOH, and then dried to be used for the next run. Overall, the catalyst was used for five continuous runs without significant loss of its catalytic activity. The results are illustrated in Figure 7. This catalyst was very active and stable to both air and moisture.

4 | CONCLUSIONS

In summary, we have successfully synthesized a new reusable catalyst by grafting guanidine onto $CoFe_2O_4$. The catalyst was used in the one-pot synthesis of 3,5-disubstituted 2,6-dicyanoanilines, which was performed using simple and readily available materials including aldehydes, malononitrile, and β-nitrostyrenes with EtOH as solvent. Employment of one-pot MCR, greenness, recyclability of the catalyst with no loss in its activity, short reaction times, easy separation of the catalyst by an external magnet, and easy workup procedure are important features of this protocol for the synthesis of 3,5-disubstituted 2,6-dicyanoaniline derivatives. Complete spectra consist of FT-IR, 1H, 13C NMR for new compounds are provided in the supporting information.

ACKNOWLEDGEMENTS

Authors thank of Ilam University, Ilam, Iran, for financial support of this research project.

CONFLICT OF INTEREST

The authors no conflict of interest.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Rostami H, Shiri L. $CoFe_2O_4@SiO_2$-PA-CC-guanidine nanoparticles: A novel, efficient, and recyclable catalyst for the synthesis of 3,5-disubstituted-2,6-dicyanoaniline derivatives. *Appl Organometal Chem*. 2020;e5599. https://doi.org/10.1002/aoc.5599