Received: 23 November 2016 | Revised: 20 February 2017 | Accepted: 4 March 2017

DOI: 10.1002/aoc.3814

FULL PAPER

WILEY Applied Organometallic Chemistry

Facile one-pot synthesis of a series of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives catalyzed by cellulose-based magnetic nanocomposite

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A sulfonated magnetic cellulose-based nanocomposite was applied as an efficient, inexpensive and green catalyst for the one-pot three-component synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones starting from 1,3-indanedione, aromatic aldehydes and 1-naphthylamine under solvent-free conditions in high yields (79–98%) within short reaction times (2–5 min). The nanobiostructure catalyst can be easily separated from the reaction mixture by using an external magnet and reused several times.

KEYWORDS
green synthesis; solvent-free, indeno[1,2-*b*]quinoline-8-one, magnetic nanoparticles, multicomponent reaction, nanobiostructure catalyst

1 | INTRODUCTION

Multicomponent coupling reactions are very important synthetic tools for building of various complex molecular structures. These reactions are mainly defined as one-pot condensation reactions in which at least three starting materials are combined to give a product. Atom economy, operational simplicity, reduction in the number of workup procedures, easy construction of products in a one-pot process from simple molecules, being convergent and high bond-forming index are some advantages of these reactions.[1–4] Due to wide range of biological and pharmaceutical activities as well as synthetic, chemical and industrial applications, quinolines have attracted researcher's attentions. Some of their medicinal properties include anti-cancer,[5] anti-malarial,[6] anti-inflammatory,[7] anti-asthmatic, anti-pain,[8] anti-bacterial,[9] anti-virus,[10] anti-fungus,[11] cardiovascular[12] and anti-hypersensitive activities.[13] Indenoquinolines are one of the most important groups of quinoline derivatives that have a wide range of medicinal activities such as anticancer,[14] anti-inflammatory, anti-tumour[15] and inhibitor of steroid reductase, etc. Therefore, much effort have been focused on the synthesis of indenoquinoline skeletons from new, simple and direct methods.[16–23] Most of the literature reports require refluxing systems, organic solvents, expensive catalysts, multiple steps and tedious work-up procedures.[17] Also, using homogeneous catalysts such as tribromomelamine (TBM) create many problems such as difficult separation and impurities contaminations. Thus, due to importance of indeno[2,1-*b*]quinolineones in bioorganic and pharmaceutical chemistry, design and development of simple high-yielding and environmental-friendly methods by using new catalysts is of prime importance.

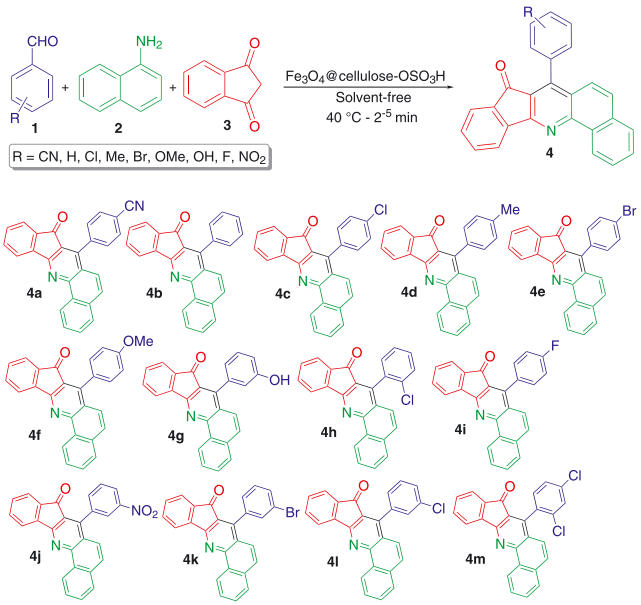
Nowadays, nanotechnology can help researchers to reinforce properties of nano-sized compounds by developing nanocomposites materials. Nanocomposites against conventional composites have higher thermal capacity and recyclablity.[24] Through suitable size and distribution of magnetic nanoparticles in polymeric materials, nanocomposites can be achieved with special magnetic properties and applications.[25] Biodegradability, eco-friendly and relatively low price of cellulose are some major reasons for its usage in the composite nanostructures.[24] Therefore, magnetic nanocomposites based on cellulose can be regarded as a green and efficient recoverable and biodegradable nanocatalyst.[26–31]

Recently, sulfonic acid-functionalized cellulose-coated Fe_3O_4 nanoparticles (Fe_3O_4@cellulose-SO_3H, MCSA) has been introduced in our laboratory.[4] Herein, in continuation of our previous works on catalysis,[32–37] MCSA as a non-toxic and environmentally-friendly heterogeneous nanocatalyst was used in the synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives via a one-pot multi-component reaction of 1,3-indanedione, aromatic aldehydes and 1-naphthylamine under solvent-free conditions at 40 °C (Scheme 1). To the best of our knowledge, this is the first report on the application of the present composite nanostructures in the synthesis of indenoquinoline derivatives. Furthermore, this work includes several advantages such as green reaction media, easy work-up procedures, high surface area, activity and recyclability of the nanocatalyst. MCSA could be separated easily from the reaction mixture by using an external magnet and can be reused several times.

2 | EXPERIMENTAL

2.1 | General

All the solvents, chemicals were taken from Merck, Sigma and Aldrich. Melting points of the products were measured using Electrothermal 9100 apparatus. UV lamp with a wavelength of 254 nm was used in thin layer chromatography (TLC) reaction. TLC performed by a silica gel and aluminum plate with thickness of 0.2 mm. Fourier transform infrared spectroscopy (FT-IR) spectra were taken by Shimadzu spectrometer by KBr discs. ^1H and ^{13}C NMR spectra were taken by Bruker DRX-500 and 300 Avance spectrometers. The magnetic property was measured at room temperature on a vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Co., Iran. Scanning electron micrograph (SEM) images and energy-dispersive X-ray spectroscopy (EDX) spectra sequentially were obtained with Seron AIS 2100 and Numerix DXP-X10P, respectively.



SCHEME 1 MCSA-catalyzed synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones **4a–m**

2.2 | Preparation of MCSA nanocatalyst

The nanocomposite was prepared according to our previous report,[4] as follows: first, NaOH, urea and water were combined at a ratio of 7:12:81 and decrease temperature of solution to −12 °C. Then, 2.0 g of cellulose was added to the solution. Next, an aqueous solution of 0.3 g of $FeCl_2.4H_2O$ and 0.8 g of $FeCl_3.6H_2O$ in 100 mL of water was added dropwise to the solution to form Fe_3O_4@cellulose microcrystals. After that, 5.0 g of the microcrystals were added to 20 mL of chloroform and stirred vigorously. Then, chlorosulfonic acid (1.0 g) was added dropwise at 0 °C during 2 h. When addition was completed, the mixture was stirred for 2 h and brown powder washed with methanol and dried at room temperature to yield the MCSA nanocatalyst.

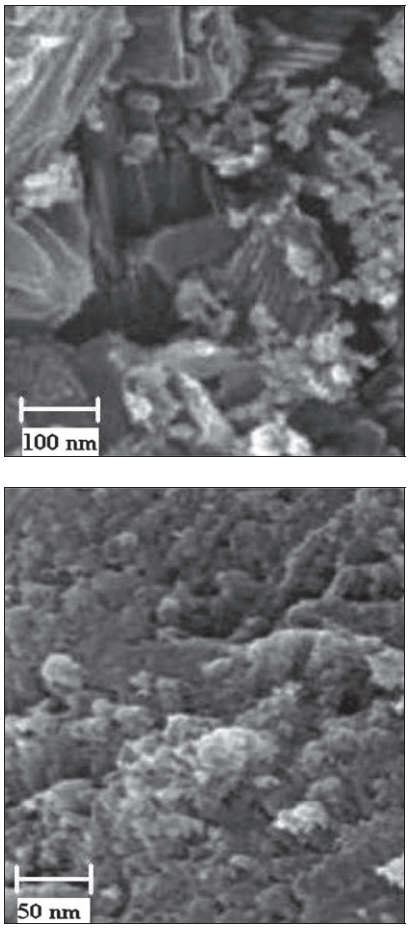


FIGURE 1 SEM images of MCSA

2.3 | General procedure for the synthesis of 7-aryl-8H-benzo[h]indeno[1,2-b]quinoline-8-one derivatives 4a–m

A mixture of an aromatic aldehyde **1** (1 mmol), 1,3-indanedione **2** (1 mmol), 1-naphthylamine **3** (1 mmol) and MCSA (0.03 g) was heated under solvent-free conditions in an oil bath at 40 °C for an appropriate time. After completion of the reaction (monitored by TLC), the reaction mixture was dissolved in ethyl acetate and the catalyst easily separated by an external magnet. Then, the pure products obtained by recrystallization from EtOH.

2.4 | Spectral data of 7-(4-cyano phenyl)-8H–benzo[h]indeno[1,2-b]quinoline-8-one 4a

Yellow solid: mp 240 °C. FT-IR (KBr) (υ_{max}, cm^{-1}): 3043, 2227, 1716, 1687, 1606, 3415. ^1H NMR (500 MHz, $CDCl_3$) (δ, ppm): 6.99–8.45 (13H, Ar-H), 9.47 (d, J = 7.8 Hz, 1H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) (δ, ppm): 113.3, 119.0, 122.0, 123.6, 124.4, 124.7, 126.2, 128.0, 128.2, 128.8, 130.0, 130.9, 131.9, 132.0, 132.4, 132.6, 134.1, 134.9, 135.9, 144.1, 145.2, 149.9, 162.1, 191.0.

3 | RESULTS AND DISCUSSION

3.1 | Characterization of the prepared MCSA nanocatalyst

The nanocomposite was prepared and characterized according to our previous report.[4] The structure, morphology and elemental analysis of MCSA nanocatalyst were confirmed by FT-IR spectra, SEM images (Figure 1) and EDX pattern analysis (carbon, oxygen, sulfur and iron elements were seen), respectively.

TABLE 1 Optimizing of the model reaction conditions under solvent-free conditions at 40 °C

Entry	Catalyst	Catalyst amount (mg)	Time (min)	Yield[a] (%)
1	-	-	90	10
2	Fe_3O_4@cellulose-OSO_3H	10	90	87
3	Fe_3O_4@cellulose-OSO_3H	20	90	91
4	Fe_3O_4@cellulose-OSO_3H	30	90	98
5	Fe_3O_4@cellulose-OSO_3H	40	90	95
6	Nano- Fe_3O_4	30	90	68
7	Cellulose	30	90	53
8	Fe_3O_4@cellulose	30	90	77
9	Fe_3O_4@cellulose-OSO_3H	30	5	98

[a]Isolated yields.

3.2 | Catalytic application of MCSA in the synthesis of desired 7-aryl-8H-benzo[h]indeno[1,2-b]quinoline-8-one derivatives

To optimize the reaction conditions, a pilot reaction for the synthesis of 7-(4-methyl phenyl)-8*H*–benzo[*h*]indeno[1,2-*b*]quinoline-8-one (**4d**) was carried out. The effects of the amount of the nanocatalyst, solvents and the reaction temperature were studied on the pilot reaction (Tables 1 and 2). First, we studied the effect of different amounts of MCSA nanocomposites. 0.03 g of MCSA represented the highest yields (98%) under solvent-free conditions at 40 °C after 5 min (Table 1, entry 9). As can be seen in Table 1, we have also investigated various components of the catalyst as the

TABLE 2 Optimizing of the solvent and temperature in the presence of 0.03 g of MCSA

Entry	Solvent	Temperature (°C)	Yield[a] (%)
1	Solvent-free	40	98
2	Ethanol	40	29
3	Water	40	96
4	Solvent-free	25	73
5	Solvent-free	70	98
6	Solvent-free	80	95

[a]Isolated yields after 90 min.

TABLE 3 Synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones **4a–m** by using MCSA

Entry	R	Product	Yield[a] (%)	Mp (°C)	
				Found	Reported
1	4-Cn	**4a**	98	240–241	-
2	H	**4b**	96	200–203	202–204[17]
3	4-cl	**4c**	98	245–246	259–261[16]
4	4-me	**4d**	98[b]	240-242	256-260[16]
5	4-Br	**4e**	96	225–226	218–220[17]
6	4-MeO	**4f**	90	230–233	233–235[17]
7	3-oh	**4g**	79	320–322	328–329[16]
8	2-cl	**4h**	91	284–285	289–291[16]
9	4-F	**4i**	97	240–242	231–235[16]
10	3-NO_2	**4j**	95	230–233	222–224[17]
11	3-Br	**4k**	96	240–241	236–238[17]
12	3-cl	**4l**	96	228–230	230–233[17]
13	2,4-*di*-cl	**4m**	91	212–215	220–222[17]

[a]Isolated yields after 5 min.

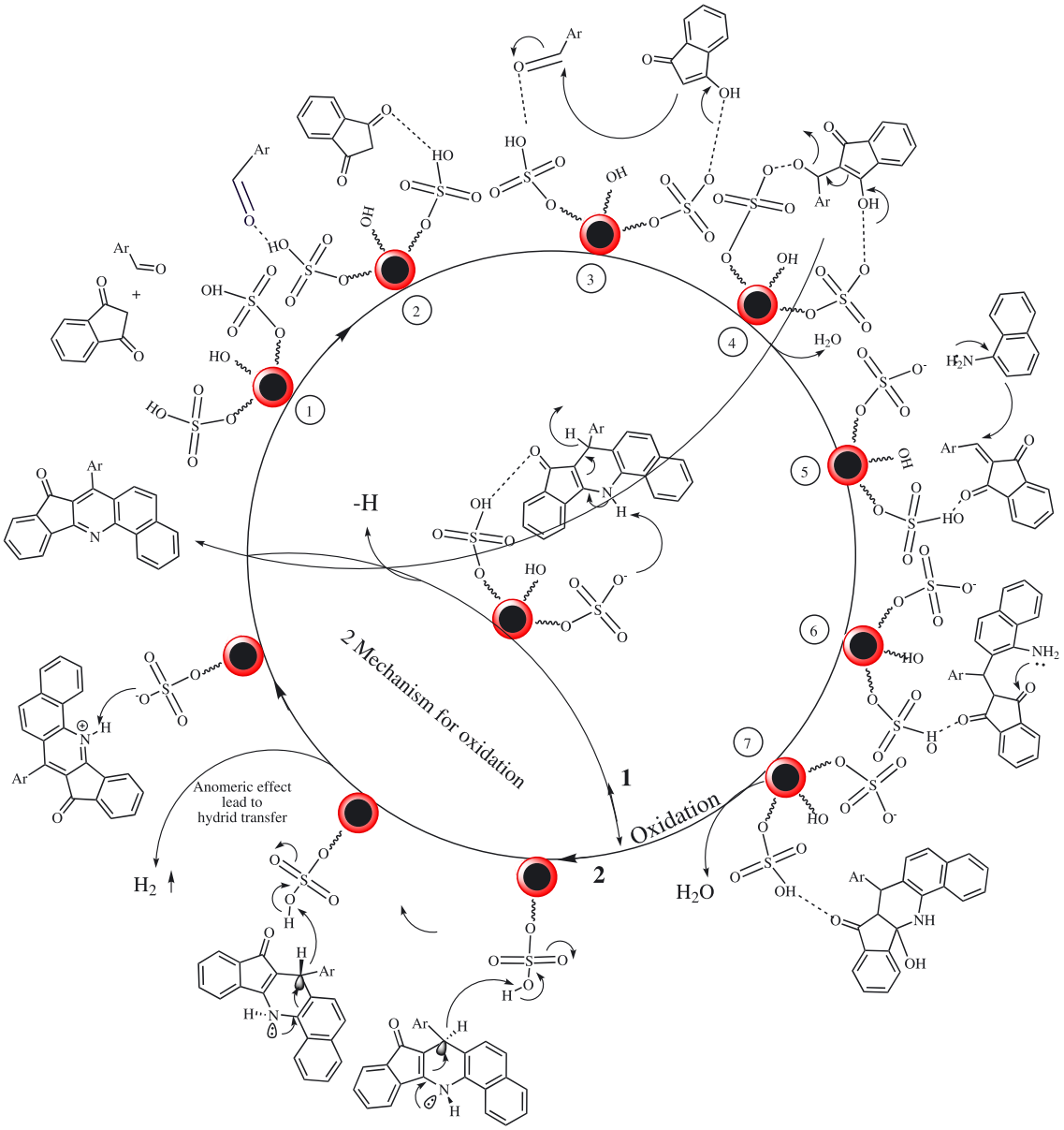
[b]Yields of the five subsequent runs by using the same recovered catalyst were 95, 93, 89, 87, and 82%, respectively.

catalyst in the pilot reaction. Then, different solvents and varies temperature were investigated. It was found that solvent-free conditions and heating at 40 °C were yielded the best results (Table 2, entry 1). After optimizing the reaction conditions, to investigate scope and limitation of the present approach, various 7-aryl-8*H*-benzo[*h*] indeno[1,2-*b*]quinoline-8-one derivatives were synthesized by using MCSA nanocomposite and the products were obtained in high yields within short reaction times (less than 5 min) (Table 3).

The suggested possible mechanism for the formation of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives (**4a**–**m**) is shown in Scheme 2. In the first step, a Knoevenagel condensation reaction was occurred between an activated aldehyde carbonyl group and 1,3-indanedione in the presence of MCSA nanocatalyst. Then, an intermediate was formed from 1-naphthylamine and 1,4-dihydroquinoline during ring formation by removing an H_2O molecule. In the final step, MCSA-promoted the oxidation of 1,4-dihydroindenoquinolines to the target product indenoquinolines[38–43] (Scheme 2).

3.3 | Recyclability study on MCSA nanocatalyst

One of the advantages of heterogeneous catalysts is their easy separation from the reaction mixture and ability for reusing in



SCHEME 2 The proposed mechanism for the synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-ones

the system. In addition, the separation of the magnetic catalysts from the reaction mixture is much easier than other heterogeneous catalysts. In this regard, recyclability and reuse of MCSA were evaluated in models reaction. MCSA was recycled and used in model reaction at least for five times without any significant decrease in efficiency (Table 3, entry 4).

4 | CONCLUSION

In summary, due to diverse chemical, biological and pharmaceutical importance of quinoline and indenoquinoline derivatives, herein, one-pot three-component synthesis of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives were described by using a green magnetic nanobiostructure catalyst. This method offers several advantages such as high yields, avoiding use of organic solvents, short reaction times, green recyclable organometallic nanostructure catalyst and mild reaction media and easy work-up procedure.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the partial support from the Research Council of the Iran University of Science and Technology.

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How to cite this article: Maleki A, Nooraie Yeganeh N. Facile one-pot synthesis of a series of 7-aryl-8*H*-benzo[*h*]indeno[1,2-*b*]quinoline-8-one derivatives catalyzed by cellulose-based magnetic nanocomposite. *Appl Organometal Chem*. 2017;e3814. https://doi.org/10.1002/aoc.3814