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CuI nanoparticles: A highly efficient catalyst for expedient and mild synthesis of dihydrochromeno[*b*]chromenone derivatives

Narges Barghmadi and Shahrzad Abdolmohammadi*

Department of Chemistry, Faculty of Science, East Tehran Branch, Islamic Azad University, PO Box 33955-163, Tehran, Iran.

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Abstract: A novel and practically useful protocol is described for the synthesis of dihydrochromeno[*b*]chromenone derivatives, by a coupling reaction of salicylaldehydes with 4-hydroxycoumarin catalyzed by copper (I) iodide nanoparticles (CuI NPs) as an efficient heterogeneous catalyst in green media-water.

Keywords: Aqueous media, CuI nanoparticles (CuI NPs), Dihydrochromeno[*b*]chromenone.

Introduction

In the last few years, the use of nanosized heterogeneous catalysts in organic synthesis has proved to be useful in several scientific and technological areas. The good catalytic performance of nanosized catalysts is closely related to the activation of adsorbed compounds and the reaction rate enhancement, easier work-up, reusability of the catalyst and the environmental friendly reaction conditions [1, 2]. Currently, application of CuI nanoparticles (CuI NPs) as a Leiws acid nanocatalyst in organic reactions aroused a strong interest not only for its low cost and easy availability but also for many important advantages such as non-toxicity, simplicity of operation, decreasing reactor and plant corrosion problems and environmentally safe disposal [3-5].

Chromenes constitute a major class of biologically active compounds [6, 7], and interest in their chemistry continues unabated because of their wide range of pharmacological activities like antifungal [8], antioxidant [9] and antimicrobial activity [10].

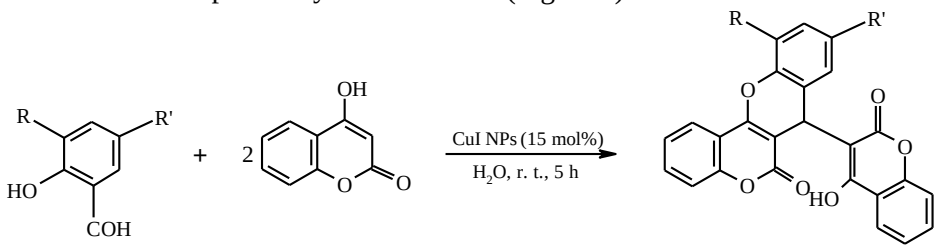
*Corresponding author. Tel: (+98) 21 3359 4950, Fax: (+98) 21 3359 4332, E-mail: s.abdolmohamadi@iauet.ac.ir

Literature reveals several approaches have been developed for the synthesis of the chromenes [11-17]. In order to avoid the disadvantages such as low yields, long reaction time and use of toxic organic solvents that a few of these methods have, we report herein a green aqueous media procedure for the synthesis of a number of dihydrochromeno[4,3-*b*]chromenone derivatives **3a-h** *via* a coupling reaction of salicylaldehydes with 4-hydroxycoumarin catalyzed by copper (I) iodide nanoparticles (CuI NPs) as catalyst, which is readily synthesized according to the literature protocol [18] (Scheme **1**).

In view of the above mentioned useful properties of chromenes, a few synthetic methods have been developed for the preparation of 7-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-ones [19, 20]. Although, these procedures offer several advantages, there is always a need for efficient new methods for the synthesis of these biologically important compounds. To the best of our knowledge, a CuI NPs catalyzed synthesis of dihydrochromeno[*b*]chromenones has not been reported in the literature until now.

Results and discussion

Firstly, we prepared CuI NPs catalyst through a simple precipitation route by using glucose as a green reducing agent, which has been reported by Salavati-Niasari and co-workers [18]. The SEM image of the catalyst shows that the size of the particles was approximately 30-40 nm, and the morphology of CuI nanoparticles was composed of triangular-like shape (Figure **1**).



1 **2** **3**

Scheme 1: Synthesis of dihydrochromeno[*b*]chromenones.

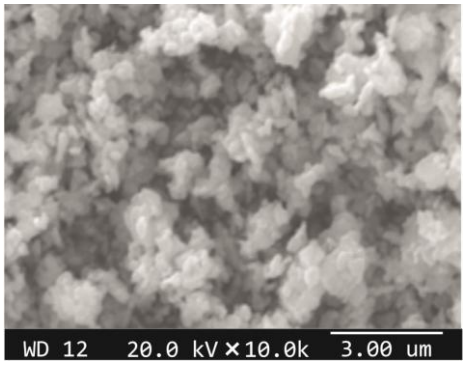


Figure 1: SEM image of the synthesized CuI NPs.

Optimization was the further run of our experiments, for this purpose, salicylaldehyde (**1a**) was chosen as a model for the reaction with 4-hydroxycoumarin (**2**) under various conditions (Table **1**).

In order to prove the catalytic efficiency of CuI NPs, a blank reaction was carried out in the absence of catalyst under refluxing H_2O. After 6 h stirring, only 56% of the product was obtained (Table **1**, entry 1). Surprisingly, 97% of the desired product was isolated after about 5 h, just by using 15 mol% of CuI NPs catalyst in H_2O at room temperature (Table **1**, entry 2).

It is worth noting that, with decreasing the amount of catalyst from 15% to 10%, the yield of product dropped even after 7 h, meanwhile on increasing the amount of the catalyst to 20 mol%, no significant improvement was observed (Table **1**, entries 2-4).

In evaluating the effect of the temperature, it was found that the increasing of the reaction temperature to 60 ˚C just decreased the reaction time to 3 h (Table **1**, entries 2 and 5).

We also explored the role of the reaction media, it was seen that H_2O is suitable reaction media compared with other solvents (Table **1**, entries 2 and 6-9).

Table 1: The synthesis of 7-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-6*H*,7*H*-chromeno[4,3-*b*]chromen-6-one (**3a**) under different conditions.

Entry	Solvent	Catalyst (mol%)	Temp. (˚C)	Time (h)	Yield (%)[a]
1	H_2O	No catalyst	reflux	6	56
2	H_2O	CuI NPs (15 %)	r.t.	5	97
3	H_2O	CuI NPs (10 %)	r.t.	7	74

4	H_2O	CuI NPs (20 %)	r.t.	5	96
5	H_2O	CuI NPs (15 %)	60	3	97
6	C_2H_5OH	CuI NPs (15 %)	r.t.	6	75
7	CH_3CN	CuI NPs (15 %)	r.t.	6	72
8	CH_2Cl_2	CuI NPs (15 %)	r.t.	5	69
9	DMF	CuI NPs (15 %)	r.t.	6	81

[a]Isolated yield.

To prove the generality of the protocol, salicylaldehydes with different substitutents were employed. The results are summarized in Table **2**.

A suggested mechanism for the formation of dihydrochromeno[*b*]chromenones **3** is presented in Scheme **2**. It is reasonable that CuI NPs catalyzes the formation of carbocation **4** from salicylaldehyde **1** which then undergoes a Knoevenagel condensation with 4-hydroxycoumarin **2**, to generate alkene **6**. Another mole of 4-hydroxycoumarin **2**, adds to alkene **6** to produce the Michael adduct **7**. Intramolecular cyclization of **7** gives product **3**, after dehydration.

Table 2: Synthesis of dihydrochromeno[*b*]chromenones **3(a-h)** using CuI NPs as catalyst.

Product	R	R'	Yield (%)[a,b]	MP (˚C)	
				Obs.	Lit.
3a	H	H	97	252-254	255-256 [19]
3b	H	Br	97	330-332	330-331 [19]
3c	Br	Br	95	207-209	208-210 [19]
3d	Br	Cl	96	203-205	204-206 [19]
3e	Cl	Cl	94	201-203	200-202 [19]
3f	OCH_3	H	97	294-296	292-293 [19]
3g	H	CH_3	96	326-327	328-329 [19]
3h	H	NO_2	98	296-298	299-301 [19]

[a]Yields refer to those of pure isolated products characterized by IR, ^{1}H NMR spectroscopy and elemental analysis.
[b]In all cases, reaction time was 5 h stirring at room temperature.

The structures of known compounds **3a-h** were established by their satisfactory elemental analyses, IR and ^{1}H NMR spectroscopy, which were found to be identical with those described in the literature. Selected spectroscopic data are reported.

After completion the model reaction, the catalyst was recovered from the reaction mixture by procedure as mentioned in experimental section and reuses up to three times without significant loss of catalytic potential (Figure **2**).

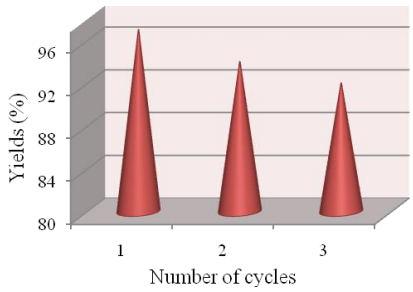
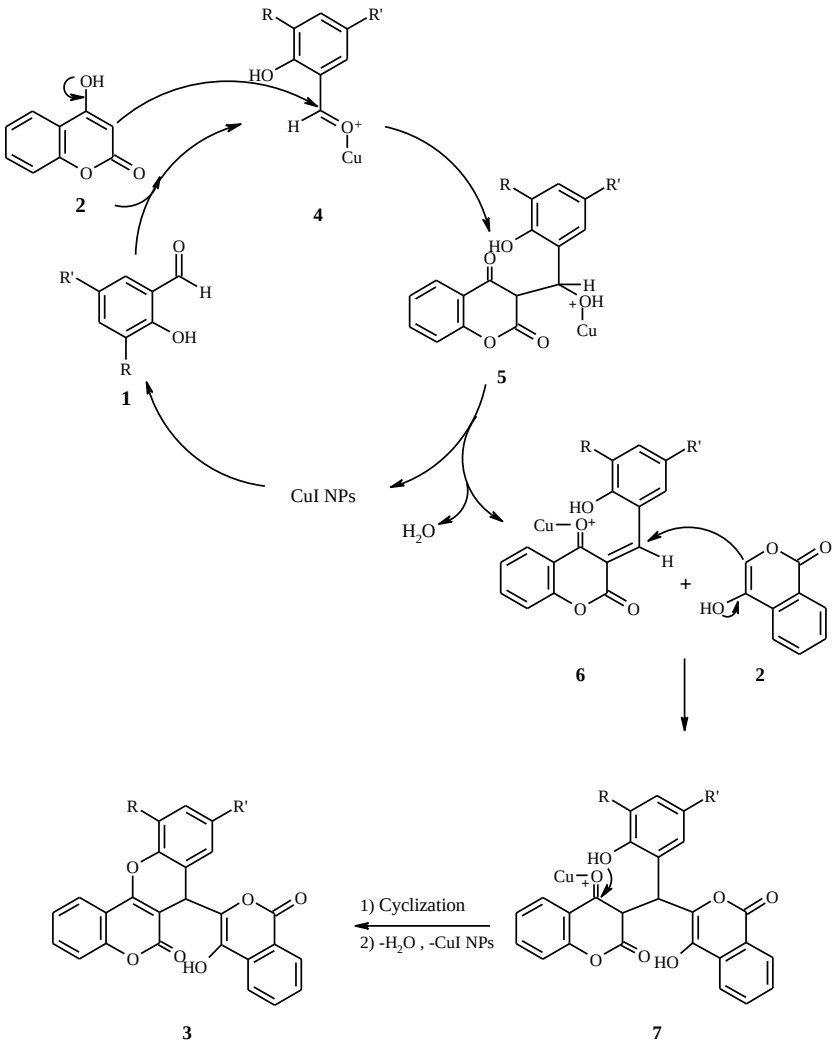


Figure 2: Reusing of CuI NPs for the synthesis of **3a**.



Scheme 2: Propsed mechanism for the synthesis of dihydrochromeno[*b*]chromenones catalyzed by CuI NPs.

Conclusion

We have developed a practically efficient and novel protocol for the synthesis of dihydrochromeno[*b*]chromenone derivatives using CuI NPs as the catalyst in green aqueous media. This new protocol is endowed with high yields of products, reusability of catalyst, mild reaction conditions and very simple operation.

Experimental

All chemicals used in this work were purchased from *Fluka* and used without further purification. Melting points were determined with *Electrothermal 9100* melting point apparatus and were uncorrected. IR spectra were obtained on an *ABB FT-IR* (FTLA 2000) spectrometer. ^{1}H NMR spectra were run on a *Bruker DRX-500 AVANCE* at 500 MHz using TMS as internal standard and DMSO-d_6 as solvent. Elemental analyses were carried out using a *Heraeus CHN*-O-rapid analyzer.

General Procedure for Preparation of Compounds 3a-h:

A mixture of salicylaldehyde **1** (1 mmol), 4-hydroxycoumarin (**2**, 2 mmol), and CuI NPs (29 mg, 15 mol%) in H_2O (5 mL) was stirred at room temperature for 5 h. The progress of the reaction was monitored with TLC. Upon completion of the reaction, the reaction mixture was filtered, the solid mass was then eluted with DMF (2 mL), and the mixture was centrifuged at 2000–3000 rpm, for 5 min to remove the nano CuI catalyst. The organic solution was then poured into cold water (10 mL), filtered and washed

with 50% aqueous ethanol to afford the pure product **3** in high yields.

Selected spectral data:

7-(4-Hydroxy-2-oxo-2H-chromen-3-yl)-6H,7H-chromeno[4,3-b]chromen-6-one (3a):

White solid, yield: 0.398 g (97%), m.p. 252-254 ˚C (lit: 255-256 [19]). IR (KBr) (ν_{max}/cm^{-1}): 3261, 1710, 1671, 1629, 1572, 1488, 1392, 745. ^{1}H-NMR: δ = 5.73 (s, CH), 7.13 (dt, J = 7.1, 2.0 Hz, CH), 7.20 (brd, J = 7.5 Hz, CH), 7.31 (m, 4 CH), 7.43 (d, J = 8.2 Hz, CH), 7.46 (t, J = 7.5 Hz, CH), 7.58 (dt, J = 7.8, 1.3 Hz, CH), 7.68 (dt, J = 7.8, 1.3 Hz, CH), 8.04 (brs, CH), 8.07 (dd, J = 7.9, 1.3 Hz, CH), 12.25 (brs, 1 H, OH) ppm. Anal. Clacd. for $C_{25}H_{14}O_6$ (410.38): C 73.16, H 3.44; Found: C 73.20, H 3.47.

9-Bromo-7-(4-hydroxy-2-oxo-2H-chromen-3-yl)-6H,7H-chromeno[4,3-b]chromen-6-one (3b):

White solid, yield: 0.475 g (97%), m.p. 330-332 ˚C (lit: 330-331 [19]). IR (KBr) (ν_{max}/cm^{-1}): 3270, 1707, 1670, 1629, 1568, 1477, 1391, 747. ^{1}H-NMR: δ = 5.70 (s, CH), 7.31 (m, 4 CH), 7.44 (m, 3 CH), 7.59 (t, J = 7.5 Hz, CH), 7.67 (t, J = 7.5 Hz, CH), 8.05 (m, 2 CH), 12.50 (brs, 1 H, OH) ppm. Anal. Clacd. for $C_{25}H_{13}BrO_6$ (489.28): C 61.37, H 2.68; found: C 61.29, H 2.74.

7-(4-Hydroxy-2-oxo-2H-chromen-3-yl)-11-methoxy-6H,7H-chromeno[4,3-b]chromen-6-one (3f):

White solid, yield: 0.427 g (97%), m.p. 294-296 ˚C (lit: 292-293 [19]). IR (KBr) (ν_{max}/cm^{-1}): 3074, 1720, 1661, 1639, 1570, 1481, 1399, 755. ^{1}H-NMR: δ = 3.92 (s, 3 H, OCH_3), 5.71 (s, CH), 6.74 (d, J = 7.4 Hz, CH), 6.99 (d, J = 7.9 Hz, CH), 7.06 (t, J = 7.9 Hz, CH), 7.29 (m, 2 CH), 7.43 (d, J = 8.3 Hz, CH), 7.48 (t, J = 7.6 Hz, CH), 7.58 (t, J = 7.6 Hz, CH), 7.67 (t, J = 7.4 Hz, CH), 7.99 (m, 2 CH), 12.30 (brs, 1 H, OH) ppm. Anal. Clacd. for $C_{26}H_{16}O_7$ (440.41): C 70.90, H 3.63; found: C 70.96, H 3.67.

7-(4-Hydroxy-2-oxo-2H-chromen-3-yl)-9-methyl-6H,7H-chromeno[4,3-b]chromen-6-one (3g):

White solid, yield: 0.407 g (96%), m.p. 326-327 ˚C (lit: 328-329 [19]). IR (KBr) (ν_{max}/cm^{-1}): 3257, 1712, 1666, 1631, 1573, 1453, 1394, 761. ^{1}H-NMR: δ = 2.20 (s, 3 H, CH_3), 5.69 (s, CH), 6.98 (brs, CH), 7.08 (d, J = 7.1 Hz, CH), 7.19 (t, J = 8.3 Hz, CH), 7.31 (m, 2 CH), 7.44 (m, 2 CH), 7.58 (t, J = 7.3 Hz, CH), 7.66 (t, J = 7.3 Hz, CH), 8.05 (m, 2 CH), 12.61 (brs, 1 H, OH) ppm. Anal. Clacd. for $C_{26}H_{16}O_6$ (424.41): C 73.56, H 3.77; found: C 73.50, H 3.73.

7-(4-Hydroxy-2-oxo-2H-chromen-3-yl)-9-nitro-6H,7H-chromeno[4,3-b]chromen-6-one (3h):

White solid, yield: 0.446 g (98%), m.p. 296-298 ˚C (lit: 299-301 [19]). IR (KBr) (ν_{max}/cm^{-1}): 3239, 1699, 1637, 1569, 1523, 1496, 1338, 750. ^{1}H-NMR: δ = 5.81 (s, CH), 7.31 (d, J = 8.2 Hz, CH), 7.38 (t, J = 7.3 Hz, CH), 7.50 (m, 2 CH), 7.61 (m, 2 CH), 7.72 (t, J = 7.3 Hz, CH), 8.13 (m, 4 CH), 12.30 (brs, 1 H, OH) ppm. Anal. Clacd. for $C_{25}H_{13}NO_8$ (455.38): C 65.93, H 2.88, N 3.07; found: C 65.86, H 2.93, N 3.11.

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