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Article

[Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O: A Novel Reusable Heterogeneous Catalyst for Synthesis of Polyhydroquinoline and 2,3-Dihydroquinazoline-4(1*H*)-one Derivatives

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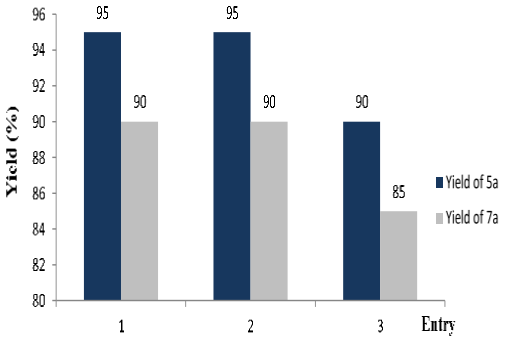
Abstract: Herein, the catalytic performance of [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex has been examined in synthesis of polyhydroquinoline and 2,3-dihydroquinazoline-4(1*H*)-one derivatives. The catalytic reactions have been carried out in solvent-free conditions. The obtained results have showed that the complex has high catalytic activity, so that the desired products were obtained in good to high yields. Moreover, the investigated catalyst was found to be reusable, which could be achieved after third run with a considerable catalytic activity.

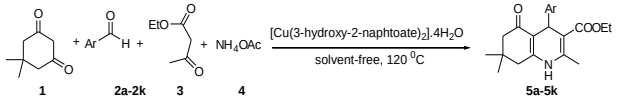


Keywords: Heterogeneous catalysis; Polyhydroquinolines; Quinazolines; Solvent free; Copper(II) complex.

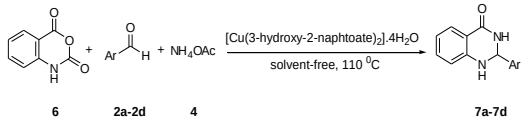
1. INTRODUCTION

In recent years, multicomponent reactions (MCRs) have been significant role in the synthesis of organic compounds.[1-7] Polyhydroquinolines and quinazolines are important category of organic compounds in terms of biological activity.[6, 8-14]. Different methods have been used to synthesis these compounds. One of the most applicable and useful methods is catalytic method. Various catalysts were utilized to synthesis polyhydroquinolines and quinazolines. For example, Fe_3O_4@MCM-41@Cu-P$_2$C,[15] SBA-15@Glycin-Ni,[16] Fe_3O_4@D-NH-$(CH_2)_4$-SO_3H[6] and [TBA]$_2$[w_6O_{19}][17] have been used in synthesis of polyhydroquinoline derivatives; ionic liquids,[18] β-cylodextrin-SO_3H[19] and Fe_3O_4 nanoparticles[20] have also been used for synthesis of 2,3-dihydroquinazoline-4(1H)-one derivatives.

Due to our interest in synthesis of heterocyclic compounds[17, 21-23] and as part of our researchs on the development of environmentally friendly methods for synthesis of organic compounds by using reusable catalysts,[4, 6, 17, 24-28] we decided to use metal complex ([Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O) as catalyst for preparation of polyhydroquinoline and 2,3-dihydro-quinazoline-4(1H)-one derivatives (Scheme 1). The reactions have been occurred in the solvent-free conditions, which is very valuable in green chemistry.



Reaction1: synthesis of polyhydroquinoline derivatives



Reaction2: synthesis of 2,3-dihydroquinozaline-4(H)-one derivatives

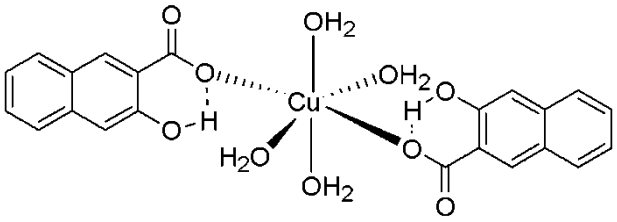
Scheme 1. [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyzed synthesis of polyhydroquinoline and 2,3-dihydroquinazoline-4(1H)-one derivatives

2. EXPERIMENTL

Synthesis of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex

3-hydroxy-2-naphtoicacid (2 mmol) and Cu(OAc)$_2$.4H$_2$O (1 mmol) were added to the distilled water (2 mL) and the solution

was stirred for 2 hours. Then, the formed precipitation was filtered, washed with distilled water and dried in 90 °C. (decomposed at T > 300 °C) (Scheme 2).[29]



Scheme 2. Structure of the investigated catalyst, the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex

Synthesis of polyhydroquinolines 5a-5k

A mixture of dimedone **1** (1 mmol), aryl aldehyde **2a-2k** (1 mmol), ethyl acetoacetate **3** (1 mmol), ammonium acetate **4** (1 mmol) and [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O (0.03 g) was heated in an oil bath at 120 °C for 10-20 min.

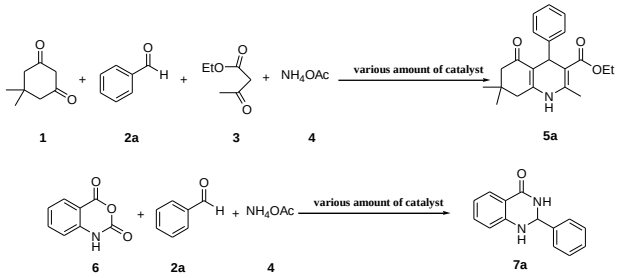
Synthesis of 2,3-dihydroquinazoline-4(1H)-one 7a-7d

A mixture of isatoicanhydryd **6** (1 mmol), aryl aldehyde **2a-2d** (1 mmol), ammonium acetate **4** (1 mmol) and [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O (0.06 g) was heated in an oil bath at 100 °C for 15-25 min.

All synthesis reactions were monitored by TLC. Upon completion of the transformation, the reactions mixture was cooled to room temperature and boiling ethanol was added. This resulted in the precipitation of the catalyst, which was collected by filtration. The products were collected from the filtrate after cooling to room temperature and recrystallized from ethanol to give compounds **5a-5k** and **7a-7d** in high yields. Melting points were recorded on a Stuart SMP3 melting point apparatus. The IR spectra were obtained using a Tensor 27 Bruker spectrophotometer as KBr disks. The ^{1}H NMR (400 and 500 MHz) spectra were recorded with Bruker 400 and 500 spectrometers.

3. RESULTS AND DISCUSSION

To optimize the reactions conditions, for both reactions, a selected model reaction was carried out in different sets of conditions (Scheme 3).



Scheme 3. Model reactions for optimization of reaction conditions

The obtained results are summarized in Table 1, which clearly reveal the essentiality as well as high catalytic activity of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex to yield compound **5a** and **7a** in high yield and short reaction time. Using the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O species as catalyst, we evaluated the reactions in various solvents and under solvent-free conditions. In refluxing H$_2$O, yeild of the reactions was low, even after 240 min of reaction (entry 15), whereas relatively good yields were obtained in refluxed reactions in CH$_2$Cl$_2$, CH$_3$CN or EtOH solvents (Table 1, entries 16-18). However, the best results for yield as well as reaction time were obtained under solvent-free condition (Table 1, entry 9 and 12). It was also found that the yield of compounds **5a** and **7a** were strongly affected by the catalyst amount and reaction temperature in solvent-free conditions. Without any catalyst, no product was observed when the reactions were carried out under solvent-free conditions even after prolonged reaction time (entry 1).

For the model reaction 1 (Scheme 1), the best results were obtained at 120 °C and 0.03 g of the complex as catalyst (Table 1, entry 9). Also, the highest yield of the model reaction 2 was related to 110 °C and 0.06 g of the catalyst conditions (Table 1, entry 12).

Table 1. Effect of amount of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyst, solvent and temparature on the investigated model reactions

Reaction 1						Reaction 2					
Entry	**Catalyst (g)**	**Solvent**	**T (°C)**	**Time (min)**	**Yield (%)[a]**	**Entry**	**Catalyst (g)**	**Solvent**	**T (°C)**	**Time (min)**	**Yield (%)[a]**
1	-	-	120	120	-	1	-	-	120	120	-
2	0.01	-	60	20	51	2	0.01	-	60	20	51
3	0.01	-	90	20	58	3	0.01	-	90	20	58
4	0.01	-	110	15	61	4	0.01	-	110	15	60
5	0.01	-	120	15	63	5	0.01	-	120	15	60
6	0.03	-	60	20	73	6	0.03	-	60	20	63
7	0.03	-	90	20	75	7	0.03	-	90	20	68
8	0.03	-	110	15	86	8	0.03	-	110	15	70
9	**0.03**	**-**	**120**	**10**	**95**	9	0.03	-	120	10	75
10	0.05	-	60	20	80	10	0.06	-	60	20	80
11	0.05	-	90	20	81	11	0.06	-	90	20	85
12	0.05	-	110	15	86	**12**	**0.06**	**-**	**110**	**15**	**90**
13	0.05	-	120	15	90	13	0.06	-	120	15	90
14	0.07	-	120	15	85	14	0.07	-	120	15	85
15	0.03	H$_2$O	Reflux	240	42	15	0.06	H$_2$O	Reflux	240	32
16	0.03	CH$_2$Cl$_2$	Reflux	240	63	16	0.06	CH$_2$Cl$_2$	Reflux	240	54
17	0.03	CH$_3$CN	Reflux	240	65	17	0.06	CH$_3$CN	Reflux	240	58
18	0.03	EtOH	Reflux	240	75	18	0.06	EtOH	Reflux	240	70

[a]Isolated yields.

Table 2. [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyzed synthesis of the **5a-5k** polyhydroquinolines and **7a-7d** dihydroquinazolines

Entry	Ar	Products[a]	Time (min)	Yields (%)[b]	m.p. (°C)	
					Found	Reported
1	C_6H_5	**5a**	10	95	214-216	209-210 [30]
2	4-BrC_6H_4	**5b**	10	90	259-260	254-255 [31]
3	2-ClC_6H_4	**5c**	15	85	206-208	206-208 [32]
4	4-ClC_6H_4	**5d**	10	95	246-248	244-246 [33]
5	3-HOC_6H_4	**5e**	20	86	225-227	218-220 [32]
6	4-HOC_6H_4	**5f**	20	91	239-241	237-238 [30]
7	4-MeOC_6H_4	**5g**	10	82	257-259	258-259 [31]
8	4-MeC_6H_4	**5h**	10	88	257-260	260-261[34]
9	3-O_2NC_6H_4	**5i**	20	83	181-183	178-180 [33]
10	4-O_2NC_6H_4	**5j**	15	83	245-247	244-246 [32]
11	2-furyl	**5k**	20	88	240-243	245-247 [33]
12	C_6H_5	**7a**	15	95	218-219	221-223 [35]
13	4-BrC_6H_4	**7b**	15	93	200-202	197-199 [35]
14	2-ClC_6H_4	**7c**	20	85	227-229	230-231 [35]
15	4-ClC_6H_4	**7d**	15	90	205-207	205-206 [35]

[a]All the products were characterized by exploring their IR spectral data and a comparision of their melting points with those of authentic samples. Structures of some products were also confirmed by ^{1}H NMR analysis. [b]Isolated yields.

To evaluate generality of this method, the 1 and 2 reactions were investigated with a variety of aromatic aldehydes under optimized reactions conditions. The obtained results are gathered in Table 2, which approve that the used protocol is useful for different aromatic aldehydes bearing both electron withdrawing and donating substituents in their aromatic rings.

The principle advantage of the use of heterogeneous solid catalysts in organic transformations is their reusability.[4, 6, 36-39] In this work, the used catalyst could be readily recovered from mixture of both reactions according to the procedure outlined in the experimental section. Before reuse in a similar reaction, the separated catalyst was washed with cold ethanol and subsequently dried at 90 °C under vacuum for 1 h. We found that the catalyst could be reused at least three times with only a slight reduction in activity (Figure 1). Furthermore, retention of the structure of the catalyst was confirmed by comparing the FT-IR spectra of the recovered catalysts (Figure 2b-2e) with that of the fresh catalyst (Figure 2a). As seen, these spectra are almost identical.

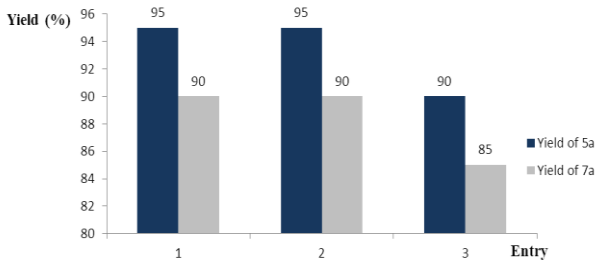


Figure 1. Performance of recovered [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O in synthesis of compounds **5a** and **7a**.

A mechanistic rationalization for the reaction 1 is provided in Scheme 3. On the basis of our previous reports,[17] it is reasonable to assume that [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O can play a dual role. Thus, we propose that the Cu^{2+} ion induces the polarization of the carbonyl groups, whereas the oxygen atoms in the 3-hydroxy-2-naphtoate anions ($C_{11}H_7O_3^-$), are slightly basic and can promote the necessary reactions. The [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyst can therefore activate the reactants as well as the intermediates in this reaction. As shown in Scheme 3, polyhydroquinolines may be formed either through path A or through path B. We propose that the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyst facilitates the formation of the intermediates **I** and **II,** which subsequently react together to give the final products **5a-5k**.

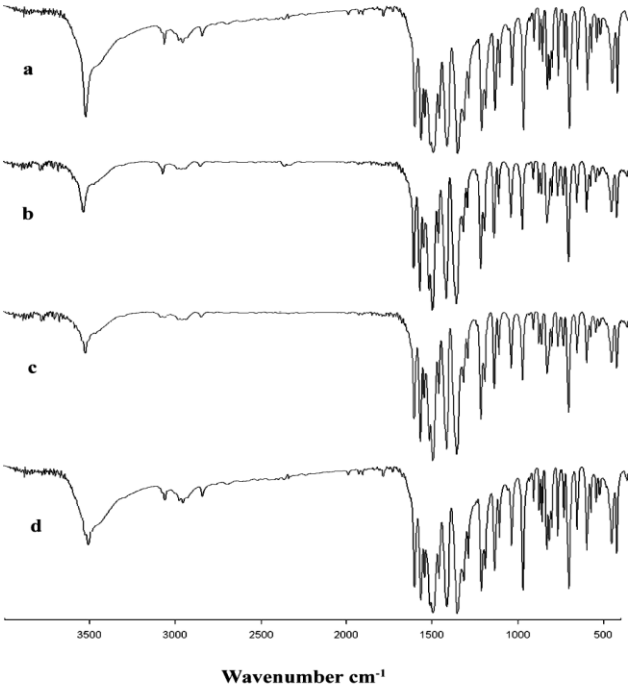
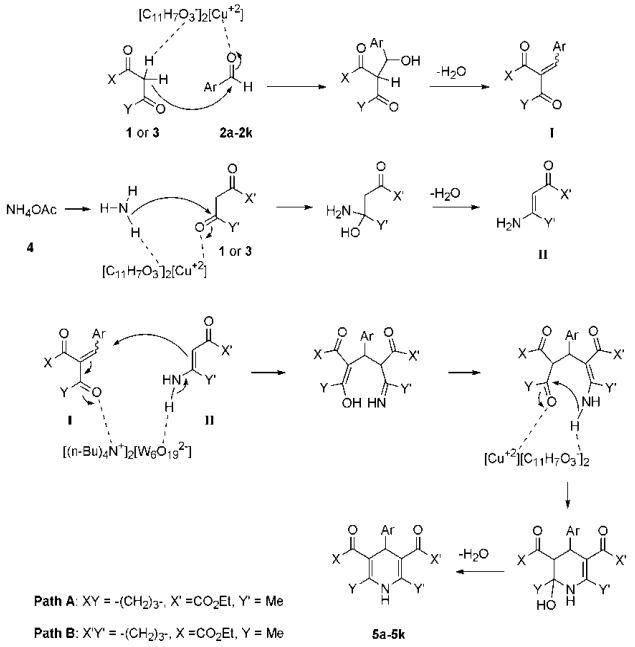
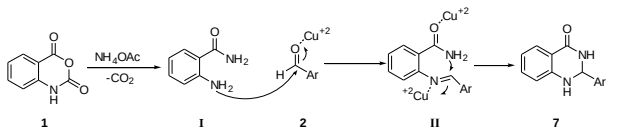


Figure 2. FT-IR spectra of (**a**) fresh catalyst (first run), and recovered catalysts (**b-d**) for the synthesis of compound **5a**.



Scheme 3. Plausible mechanism for formation of polyhydroquinolines in the presence of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O catalyst

Also, a plausible mechanism has been proposed for synthesis of 2,3-dihydroquinazoline-(1H)-4-one deravatives **7a-7d** in presence of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O as catalyst (Scheme 4). Firstly, the condensation of isatoic anhydride **1** with amonium acetate **3** produces CO_2 and anthranilamide (intermediate **I**). In comparison with the previous reaction (Scheme 3), the carbonyl groups is more polarized by the Cu^{2+} ion. Hence, the reaction 2 could be faster than the reaction 1. The intermediate **II** is produced by nucleophilic addition of **I** with aldehydes. The intermediate **II** could be converted to species **7** by an intramolecular cyclocondensation in peresence of the catalyst.



Scheme 4. Plausible mechanism for formation of 2,3-dihydroquinazoline-(1H)-4-ones in the presence of the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex as catalyst

4. CONCLUSIONS

In this work, we have reported a simple, convenient, and practical method for synthesis of the polyhydroquinolines and 2,3-dihydroquinazoline-(1H)-4-ones through multicomponent reactions using the [Cu(3-hydroxy-2-naphtoate)$_2$].4H$_2$O complex as catalyst. The best yields are related to the solvent-free conditions. The used method offers several noteworthy advantages including short reaction times, high yields of products, easy work-up, reusability and stability of the catalyst as well as absence of any hazardous organic solvents.

CONFLICTS OF INTEREST

The authors have declared that there is no conflict of interest.

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