### **IRANIAN JOURNAL OF CATALYSIS**



# Novel and cost-effective biocatalyst consisting of nanofibrillated cellulose and TiCl<sub>3</sub> for the synthesis of 2,3'-dihydroquinazolin-4-(1H)-ones

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### ABSTRACT

A novel and cost-effective catalyst for synthesis of 2,3'-dihydroquinazolin-4-(1*H*)-ones was developed utilizing a combined nanocomposite obtained from bonding TiCl<sub>3</sub> to hydroxyl groups of nanofibrillated cellulose as a green and inexpensive support. The structure of the catalyst was investigated using the Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS) techniques and transmission electron microscopy (TEM). The prepared new nanopolymer-based composite has been investigated successfully to obtain some 2,3'-dihydroquinazolin-4-(1*H*)-ones via the reaction of 2-aminobenzamide and various kinds of aldehydes/ cyclic ketones in refluxing ethanol. Short reaction times, the low amount of catalyst, high yields of products, utilizing a wide-range of aldehydes/ ketones, easy work-up procedure, in addition to the accelerating effect of the newly synthesized biodegradable nano composite, are some highlighted features of the reported protocol.

Keywords: Nanofibrillated cellulose, Titanium chloride, Heterogeneous catalyst, 2,3'-Dihydroquinazolin-4-(1H)-ones.

### 1. Introduction

Research efforts are being directed to develop environmentally eco-friendly methods via utilizing natural materials. Cellulose is the most abundant natural biopolymer available on earth, it has attracted great attention in multidisciplinary areas due to its unique advantages, such as low cost, renewability, non-toxicity, biodegradability, and biocompatibility [1, 2]. Cellulose has been used as an efficient support to prevent nanoparticle agglomeration in heterogeneous catalytic systems because of free OH moieties with nucleophilic character on the surface. Within the family of cellulose derivatives, the nano cellulose is particularly appealing because of important cellulose properties combining with features of nano materials.

On the other hand,  $TiCl_3$  derivation has several advantages such as availability, mild temperature reaction, short reaction time and highly selective oxygen species [3].

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A number of researchers have reported the use of TiCl<sub>3</sub> based catalysts such as applications of TiCl<sub>3</sub> for the detection of nitro and *N*-oxide compounds [3], TiCl<sub>3</sub>-Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl for preparation of ethylene-1-hexene copolymer [4],  $\beta$ -carbonylenaminederived [O-NS]TiCl<sub>3</sub> complexes in ethylene homo- and copolymerization [5], TiCl<sub>3</sub>-Al-EtOH for pinacol coupling [6], TiCl<sub>3</sub>–NaBH<sub>3</sub>CN for oxime reduction [7] and so on. Also, in other approaches, TiCl<sub>3</sub> was used as a precursor for synthesis of TiO<sub>2</sub> [8,9]. Heterogeneous catalysts involving f supported catalytic systems have been applied due to the advantages related to simple handling and storage, easy work-up and reusability. In these catalysts, when the size of the support decreases to the nanometer scale, the surface area increases.

2,3'-Dihydroquinazolin-4-(1*H*)-ones are *N*-containing heterocycles which possess a wide range of biological and pharmaceutical activities such as anti-malarial [10], anti-fungal [11], and anti-coalescence [12] activities. The main route to obtain this class of organics is based on the cyclization reaction of 2-aminobenzamide and aldehydes/ ketones in the presence of various catalytic systems including nickel complex anchored onto MCM-41 (MCM-41-dtz-Ni) [13], dodecylbenzenesulfonic acid with the ultrasound irradiation assistance [14], TiO<sub>2</sub>

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nanoparticles [15], and cyanuric chloride [16], tannic acid-SO<sub>3</sub>H on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles [17], polyethylene glycol-bonded tetraethyl ammonium hydroxide ([PEG-TEA]OH) [18], Ni-biurea complex supported on functionalized MCM-41 [19], carbon-SO<sub>3</sub>H derived from glycerol (C-SO<sub>3</sub>H) [20], ZnFe<sub>2</sub>O<sub>4</sub> [21] and copper(I) complex of 1,3-DimethylBarbituric acid modified SBA-15 [22].

This study aims to develop a novel complex catalyst consisting of nanocellulose and  $TiCl_3$  as a biodegradable and cost-effective nano-biocatalyst for the synthesis of 2,3'-Dihydroquinazolin-4-(1*H*)-ones.

### 2. Experimental

All chemicals were purchased from Merck and Aldrich Chemical Companies and used without further purification. The commercial grade of nanofibrillated cellulose was purchased from the Nano Novin Polymer Company. The morphology of the samples was analyzed using a Tescan Mira2 field emission scanning electron microscope. The samples were coated with gold using a vacuum sputter-coater. The EDS analysis was done using a SAMx-analyzer. FT-IR spectra were recorded from KBr disk using an FT-IR Bruker Tensor 27 instrument. Mass spectroscopy has been obtained by the GC-Mass 5973 network, mass selective detector and GC 6690 Agilent device. Progress of the was monitored by the thin reaction layer chromatography (TLC) technique using commercially available silica gel sheets. Melting points were determined on an Electrothermal 9200 analyzer and are uncorrected. <sup>1</sup>HNMR spectra were recorded with a Bruker drx 300 MHz, and <sup>13</sup>CNMR spectra were recorded with a Bruker drx 75 MHz machine in DMSO $d_6$  solvent. TEM images have been taken with a Philips, model cm30.

### 2.1. Preparation of catalyst

In a round bottom flask, 5 mL of TiCl<sub>3</sub> was added dropwise to 5 g of nanofibrillated cellulose (NFC) suspension in 20 mL chloroform. After 1h of vigorously stirring at room temperature, the resulting precipitation was separated by filtration, washed and dried at room temperature. The powder is the newly synthesized obtained nanostructure.

2.2. General procedure for the synthesis of 2,3'-dihydroquinazolin-4-(1H)-ones (3a-o)

A mixture of 2-aminobenzamide (1, 1 mmol), aromatic aldehydes/ cyclic ketones (2a-o, 1 mmol), and the catalyst (0.04 g, 0.72 mol%) in ethanol (5 mL) was

stirred and refluxed for the appropriate reaction time monitored by TLC (*n*-hexan/ EtOAc eluent, 1:1). After completion of the reaction, the pure products 3a-o were gained through recrystallization by ethanol. Characterization data of the new compounds are presented below.

### Selected spectral data

### 2-(4-Hydroxy-3-methoxyphenyl)-2,3'-dihydroquinazolin-4-(1H)-one (**3f**):

m.p.: 189-191 °C. IR (KBr):  $\bar{\nu} = 3353$ , 3200, 2924, 1648, 1607, 1464, 1277, 1212 cm<sup>-1</sup>. <sup>1</sup>HNMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta = 3.76$  (s, 3H, -OCH<sub>3</sub>), 6.65 (t, 1H, J = 7.11 Hz, -ArH), 6.76-6.78 (m, 2H, -ArH), 6.94 (d, 1H, J = 8.37 Hz, -ArH), 7.16 (brs, 1H, OH), 7.24 (t, 1H, J = 7.48 Hz, -ArH), 7.63 (d, 1H, J = 7.51 Hz, -ArH), 8.16 (brs, 1H, NH), 9.21 (brs, 1H, NH) ppm. <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 75 MHz):  $\delta = 39.5$ , 66.9, 111.19, 114.51, 115.00, 115.06, 117.19, 119.70, 127.42, 131.92, 133.29, 146.98, 147.48, 148.25, 163.92 ppm. Gc-Mass: m/z= 270 ([M<sup>+</sup>]), 268 (M<sup>+</sup>-2H), 222 ([M<sup>+</sup>]-OMe, -OH), 145 ([M<sup>+</sup>]-methoxyphenol), 136 (ethoxybenzamidyl).

## 2-(2-Hydroxy-5-nitrophenyl)-2,3'-dihydroquinazolin-4-(1H)-one (**3k**):

m.p.= 190 °C (dec). IR (KBr):  $\bar{\nu}$  = 3379, 3349, 3073, 1641, 1488, 1447, 1339, 1293, 1156 cm<sup>-1</sup>. <sup>1</sup>HNMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$ = 6.04 (brs, 1H, -CH), 6.66 (t, 1H, *J* = 7.41 Hz, -ArH), 6.93 (brs, 1H, OH), 6.79 (d, 1H, *J* = 8.07 Hz, -ArH), 7.05 (d, 1H, *J* = 8.96 Hz, -ArH), 7.21-7.27 (m, 1H, -ArH), 7.64 (d, 1H, *J* = 6.75 Hz, -ArH), 8.16 (brs, 1H, NH), 9.21 (brs, 1H, NH) ppm. <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 75 MHz):  $\delta$ = 60.89, 114.67, 116.02, 117.51, 123.38, 125.83, 127.44, 128.35, 138.51, 139.26, 147.67, 161.38, 163.79 ppm. Gc-Mass: m/z= 285 ([M<sup>+</sup>]), 149 (M<sup>+</sup>-nitrophenyl), 105 (M<sup>+</sup>-nitrophenyl), -CONH), 77 (phenyl).

2-(4-Hydroxy-3-methoxyphenyl)-2,3'-dihydroquinazolin-4-(1H)-one (**3***l*):

m.p.= 89-91 °C. IR (KBr):  $\bar{\nu}$  = 3355, 2926, 1665, 1609, 1483, 1246, 1157 cm<sup>-1</sup>. <sup>1</sup>HNMR (DMSO-*d*<sub>6</sub>, 300 MHz):  $\delta$ = 3.81 (s, 3H, -OCH<sub>3</sub>), 6.02 (s, 1H, -CH), 6.67-6.82 (m, 1H, -ArH), 6.73-6.78 (m, 1H, -ArH), 7.13-7.16 (m, 2H, -ArH, OH), 7.53-7.59 (m, 1H, -ArH), 7.79-7.82 (m, 3H, -2ArH, NH), 7.87-7.88 (m, 1H, -ArH), 9.01 (brs, 1H, NH) ppm. <sup>13</sup>CNMR (DMSO-*d*<sub>6</sub>, 75 MHz):  $\delta$ = 39.5, 66.08, 111.65, 113.56, 114.48, 115.60, 116.97, 118.88, 127.77, 133.13, 135.02, 143.54, 148.72, 149.60, 163.88 ppm. Gc-Mass: m/z= 270 ([M<sup>+</sup>]), 268 (M<sup>+</sup>-2H), 222 ([M<sup>+</sup>]-OMe, -OH), 149 ([M<sup>+</sup>]-methoxyphenol), 136 (ethoxybenzamidyl).

### 3. Results and Discussion

### 3.1. Structural Characterization of the catalyst

Consistent structure of the catalyst was found by FTIR, FE-SEM and EDS analyses. The FTIR spectra of NFC and TiCl<sub>3</sub>/NFC are shown in Fig. 1. The broad band at approximately 3300-3400 cm<sup>-1</sup> is attributed to stretching vibrations of OH group. Other peaks around 1630, 1060 and 1160 cm<sup>-1</sup> display the H-O-H bending and stretching vibrations of the C–O bonds, respectively (Fig. 1a). In the FT-IR spectra of the TiCl<sub>3</sub>/NFC, a decrease in the intensity of the OH bond indicated that a fraction of the surface hydroxyl groups of the cellulose reacted with the TiCl<sub>3</sub>. The peak around 500 cm<sup>-1</sup> in the FT-IR spectrum of composite originates from the combination of Ti-O-Ti vibrations and Ti-O-C vibrations [23]. The little fluctuations around 800 cm<sup>-1</sup> could be corresponding to the stretching vibration of Ti-O-C bond (Fig. 1b) [2, 24, 25].

The morphology of the catalyst was investigated by FE-SEM (Fig. 2). SEM images of composite showed TiCl<sub>3</sub> species coated uniformly nanocellulose surface. The EDS results presented in Fig. 2c, also indicate the successful impregnation of TiCl<sub>3</sub> into the nanocellulose scaffolds. It clearly exhibits the presence of C, O, Cl and Ti elements. The percentages of Ti and Cl in TiCl<sub>3</sub> are 31.03% and 68.96%, respectively. Thus, the amounts of Ti and Cl in EDS data (Ti: 28.26%, Cl: 14.97%) indicate the absence of any unreacted TiCl<sub>3</sub> in catalyst.

The amount of  $TiCl_3$  was calculated through the following equation [26] using the Cl content of  $TiCl_3$  from EDS analysis:

$$\frac{mol}{g} = \frac{\left[Wt \times \frac{100}{X}\right] \times \left[100/(100 - wt \times \frac{100}{X}\right]}{Y}$$
(1)

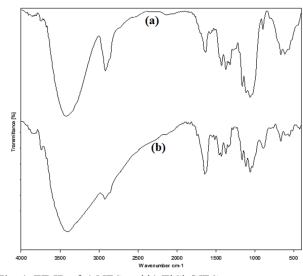


Fig. 1. FT-IR of a) NFC and b) TiCl<sub>3</sub>/NFC.

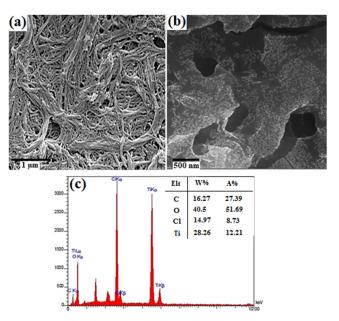


Fig. 2. SEM image of a) NFC b) TiCl<sub>3</sub>/NFC c) EDS analysis of TiCl<sub>3</sub>/NFC.

Where Wt is the weight percent of the element measured, X is the theoretical weight percent of the element in the molecule and Y is the theoretical  $M_w$  of the molecule. Based on this equation, the amount of TiCl<sub>3</sub> calculated from the Cl content is 0.18 mol g<sup>-1</sup> (180 mmol g<sup>-1</sup>).

TEM image of TiCl<sub>3</sub>/NFC was shown in Fig. 3. It showed that the nearly spherical dark areas with diameters of less than 80 nm can be related to  $TiCl_3$  nucleus.

### 3.2. Catalytic reaction

Second, in order to examine the catalytic activity of the prepared nanostructure, we decided to obtain some potent biologically potent active

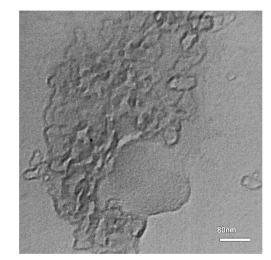


Fig. 3. TEM image of TiCl<sub>3</sub>/NFC.

2,3'-dihydroquinazolin-4-(1*H*)-ones via the reaction of 2-ethoxybenzamides and (hetero)aromatic aldehydes/ cyclic ketones.

То optimize the reaction conditions, the reaction of 2-ethoxybenzamide (1, 1 mmol) and 4-cholorbenzaldehyde (2e, 1 mmol), in the presence of nano-size TiCl<sub>3</sub>/NFC was picked as the model reaction. The effects of various factors such as temperature, solvent, and the catalyst amount have been checked. According to Table 1, entry 1, examining the model condensation in the absence of catalyst confirmed the accelerating effect of the TiCl<sub>3</sub>/NFC on the progress of the reaction. The best temperature was seen in reflux conditions (entries 3, 8, and 9). Investigation of solvents in entries 3, and 5-7, confirmed that the reaction was performed well in ethanol. The catalyst amount, as another item, has also been examined and 0.04 g of TiCl<sub>3</sub>/NFC provided us with the best result (entries 1-4). As could be seen in entry 4, increasing the amount up to 0.048 g did not affect the results.

Following the optimized conditions, the reaction of various 2-aminobenzamides (1) with (hetero) aromatic aldehydes (**2a-m**), and cyclic aliphatic ketones (**2n-o**) in 1:1molar ratio was proceeded in the presence of the catalytic of TiCl<sub>3</sub>/NFC (0.04 g) in refluxing ethanol. The resultants are summarized in Table 2. As could be deduced, the reaction of benzaldehyde (**2a**) with 1 and its electron-donating as well as electron-withdrawing groups progressed successfully within a short period of time (Table 2, entries 1-6). Terephthaldehyde (**2g**) has also performed the reaction successfully.

The regioselectivity of the method has also been affirmed in the preparation of 3g since no by-products relating to condensation on one of the aldehydic group of terephthaldehyde were not obtained and both of the functional groups underwent the reaction to get 2,2'-(1,4-phenylene)bis(2,3'-dihydroquinazolin-4-(1H)one) (3g). 2-Fufrfural (2m), as an heteroaroamtic candidate, aldehyde has also performed the condensation well and the corresponding 2-(furan-2-yl)-2,3'-dihydroquinazolin-4(1H)-one (**3m**) was obtained in 90% yield (entry 13). In order to examine the widerange efficacy of the procedure, the condensation of cyclic ketones instead of aromatic aldehydes has been checked in the same reaction conditions. The result (entries 14 & 15) reported that the adducts including 2-cyclohexyl-2,3'-dihydroquinazolin-4(1H)-one (3n)2-cyclopentyl-2,3'-dihydroquinazolin-4(1H)-one and (30) have been gained successfully.

We have expressed a plausible mechanism for the formation of 2,3'-dihydroquinazolin-4-(1*H*)-ones. It must be mentioned that the newly-prepared bio-catalyst has two acidic moieties which are Bronsted acidic sites relating to hydroxyl groups of NFC and also Lewis acid sites of TiCl<sub>3</sub>. These dual acidic groups on TiCl<sub>3</sub>/NFC activated carbonyl group of (1), = to be condensed with 2-aminobenzamide (1) to give intermediate (**B**). Secondly intermediate (**B**) lead to the desired product **3** through intramolecular cyclization followed by water removal and further proton-exchange of intermediate (**C**) (Scheme 1). The released catalyst can be used in another cycle.

Table I. Kationalization of the f	eaction conditions for the synthes
O NH <sub>2</sub> + CHO NH <sub>2</sub> + CHO	
1 2e	3e Scl

|--|

1	2e	<b>3e</b>		
Entry	Solve	ent <sup>a</sup> / Temp. (°C)/TiCl <sub>3</sub> /NFC amount (g)	Time (min)	Yield (%) <sup>b</sup>
1		C <sub>2</sub> H <sub>5</sub> OH/ reflux/ -	30	-
2		C <sub>2</sub> H <sub>5</sub> OH/ reflux/ 0.02	20	81
3		C <sub>2</sub> H <sub>5</sub> OH/ reflux/ 0.04	10	90
4		C <sub>2</sub> H <sub>5</sub> OH/ reflux/ 0.048	10	90
5		H <sub>2</sub> O/ reflux/ 0.04	15	71
6		CH <sub>3</sub> CN/ reflux/ 0.04	15	63
7		-/ 80/ 0.04	30	34
8		C <sub>2</sub> H <sub>5</sub> OH/ rt/ 0.04	30	15
9		C <sub>2</sub> H <sub>5</sub> OH/ 70/ 0.04	15	65

<sup>a</sup>5 mL of each solvent has been used.

<sup>b</sup>Isolated yield.

Entry	Aldehyde	e	Product		Time (min)	Yield (%) <sup>a</sup>	TOF (h <sup>-1</sup> )	m.p. (°C)	Ref.
1	CHO	2a	O NH H	3a	20	85	357.74	223-224	[27]
2	NMe <sub>2</sub>	2b	O NH NH H NHe <sub>2</sub>	3b	10	89	727.12	208-209	[28]
3	CHO NO <sub>2</sub>	2c	NH NH NH NO <sub>2</sub>	3c	5	87	1455.82	193-194	[29]
4	CHO OH	2d	O NH NH H OH	3d	20	88	370.37	278-280	[30]
5	CHO Cl	2e	O NH NH H Cl	3e	10	90	781.25	199-201	[31]
6	CHO OMe OH	2f	O NH NH OMe OH	3f	5	90	1506.02	189-191	[32]
7	CHO CHO	2g	O NH NH H NH H NH	3g	10	70	607.64	243-245	[33]
8	CHO NO <sub>2</sub>	2h	O NH NH H NO <sub>2</sub>	3h	5	90	1506.02	200-202	[28]
9	CHO NO <sub>2</sub>	2i	O NH NO <sub>2</sub> N H	3i	5	88	1472.56	190-191	[27]
10	CHO CH3	2j	O NH NH CH <sub>3</sub>	3j	20	89	374.58	223-224	[27]
11	CHO O <sub>2</sub> N OH	2k	O NH OH N H	3k	5	90	1506.02	190	New compour

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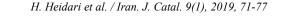
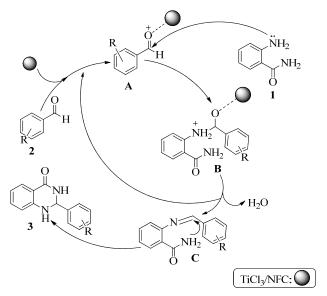


Table 2. (Continued). Ö CHO NH OH .OH 12 21 31 5 86 1439.08 89-91 [34] OMe OMe 13 2m 3m 10 90 781.25 164-165 [35] CHO 14 2n 3n 15 91 505.55 220-221 [27] ١H 5 15 20 30 93 1556.22 257-260 [36]

<sup>a</sup>Isolated yield.



Scheme 1. Possible mechanism for the synthesis of 2,3'-dihydroquinazolin-4-(1*H*)-ones.

In the next step, to show merit of the present work with the previous reported results in the literature, preparation of 3a has been compared in Table 3. As can be seen, the time of the reaction in our work is shorter in comparison to other previously reported methods.

### 4. Conclusions

In summary, we have shown the preparation and characterization of novel, eco-friendly and inexpensive  $TiCl_3/NFC$  composite with excellent catalytic activity in the synthesis of 2,3'-dihydroquinazolin-4-(1*H*)-ones.

Selecting a green and cost-effective biopolymer as the support and introducing a novel and effective nanocatalyst lead to short reaction times, high yields of products with the low amount of catalyst and easy workup procedure are the main advantages of this work.

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Entry	Catalyst (amount)	Conditions	Time (min)	Yield (%)	Ref.
1	TiCl <sub>3</sub> /NFC (0.72 mol%)	EtOH, reflux	20	85	This work
2	Ga(Otf) <sub>3</sub> (1 mol%)	EtOH, 70 °C	40	91	[30]
3	PPA-SiO <sub>2</sub> (1.25 mol%)	Solvent-free, 70 °C	90	91	[37]
4	Bu <sub>4</sub> NBr (40 mol%)	Solvent-free,100 °C	90	82	[38]
5	2-morpholinoethanesulfonic acid (10 mol%)	EtOH/H <sub>2</sub> O (1:1), 60 °C	150	93	[28]
6	Fe <sub>3</sub> O <sub>4</sub> -SA-PPCA (7 mol%)	EtOH, reflux	120	97	[31]

**Table 3.** Comparison of the reactivity of different catalytic systems in the preparation of 2-(phenyl)-2,3'-dihydroquinazolin-4-(1*H*)-one (**3a**).

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