



A novel catalyst zinc(II) perfluorooctanoate [Zn(PFO)₂]-catalyzed three-component one-pot reaction: Synthesis of quinazolinone derivatives in aqueous micellar media

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ABSTRACT

A new type of Lewis acid-surfactant-combined catalyst (LASC), zinc(II) perfluorooctanoate [Zn(PFO)₂], was prepared and applied as a favorable surfactivity catalyst in three-component one-pot cyclocondensation reaction of isatoic anhydride with amines and aldehydes to afford the corresponding quinazolinone derivatives in good yields. Reactions occurred under aqueous micellar media in high atom economy. It was found that this catalyst could be easily quantitatively recovered after the reaction completed and could be reused for at least three cycles without any loss of activity. Furthermore, a mechanism to rationalize the reaction was proposed.

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1. Introduction

In recent years, the development of efficient and environmentally benign chemical processes or methodologies for widely used recyclable catalyst and unharmed solvent is one of the major challenges for chemists in organic synthesis [1]. Generally, water as a safe, cheap and green solvent could be considered as an alternative reaction media in organic procedures. However, one major disadvantage in the use of water as a solvent is that most organic compounds are insoluble in water and, as a result, most reactions are slowed. On the other hand, water often interferes with desired reactions, especially those using classical Lewis acid or organometallic reagents because they immediately react with water rather than the substrates resulting in their decomposition or deactivation. To circumvent these disadvantage, surfactants, which solubilize organic materials or form colloid dispersion with water, have been employed. Meanwhile, the use of surfactants instead of organic solvents gains importance from a view point of green chemistry [2]. Furthermore, much research has been devoted to development of novel procedures to separate homogeneous surfactant catalysts from the reaction mixture, in other words, simple separation of the catalysts could be realized through

monophasic catalysis coupled with biphasic separation. In an aqueous phase surfactant molecules aggregate, at ambient conditions, forming micelles with a hydrophobic core and a hydrophilic corona [3]. Micellar systems seemed to be well suitable for various separation and catalytic processes [4]. The use of micellar surfactants as catalysts is widespread and has been investigated in detail for different reactions in aqueous solutions [5], which provides a way for alternative synthesis routes in an aqueous medium [6]. Recently, Lewis acid-surfactant-combined catalyst (LASC) has received increasing attention as a novel type of water-tolerant green catalyst for organic synthesis, particularly, it would acts both as a catalyst to activate the substrate molecules and as a surfactant to form stable colloidal dispersion with water-insoluble substrates. Kobayashi and co-workers [7] have showed that Lewis acid-surfactant-combined catalysts were effective catalysts in water without using any organic co-solvents, as well as Brønsted acid-surfactant-combined catalysts (BASCs) [8]. Furthermore, a broad range of classical organic reactions have been studied in micellar media [7a,8,9], and micelle solution could also play an important role in the asymmetric catalytic reaction [10]. From the viewpoints of practicability and applicability, however, the surfactant-aided organic synthesis is still at the preliminary stage [7].

Fluorous biphasic catalysis (FBC), since the pioneering work of Horváth was reported, has provided an elegant solution to the separation of the catalysts from the products and their reuse [11].

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As a result, fluorous biphasic catalysis is now a well-established technique for catalyst/product separation and recycling that exploits the temperature-dependent miscibility of organic and fluorous solvents. Although FBC combines the advantage of homogeneous catalysis and heterogeneous catalysis, the large-scale use of perfluorocarbon solvents has some drawbacks: high cost and environmental persistence. In response to these limitations, Gladysz's group has developed fluorous metal catalysts containing varying numbers of "pony tails" of the formula $[(\text{CH}_2)_m(\text{CF}_2)_{n-1}]$ or $(\text{CH}_2)_m\text{R}_m$ for organic synthesis under homogeneous conditions without fluorous solvents [12].

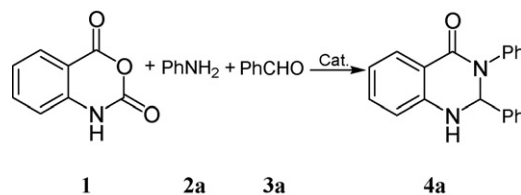
The type of micellar catalysis employed in this work is based on a soluble homogeneous catalyst [5], catalyst with high solubility and stability in water should be needed. And for environmental consciousness sake, exploring a new type of Lewis acid catalyst becomes more necessary [13]. The rare earth and transition metal catalysts with long perfluoro-chain have gained recognition as possible environmentally benign replacements of the conventional Lewis acid catalysts in various organic synthetic processes because of their excellent properties [14]. In continuation of our studies focused on rare earth and transition metal catalysts [15], we have developed transition metal perfluorooctanoates $[\text{M}(\text{PFO})_2]$, in particular, zinc perfluorooctanoate $[\text{Zn}(\text{PFO})_2]$ as a new, highly active, and reusable catalyst, which is easily prepared and stable enough to be stored. Additionally, this $\text{M}(\text{PFO})_2$ shows the favorable surfactivity and works as an excellent dispersant, thus, it is able to form micelles or vesicular structures in aqueous media.

Quinazolin-4(1H)-one has been reported that has an excellent characteristic of hypnosis, which would attract much interests in synthesizing the quinazolinone derivatives [16]. With physiological and pharmacological properties, it implies that the quinazolinone structure have various biological activities, such as anticancer [17], antidiabetic [18], anticonvulsant [19]. Many literatures had reported several methods for synthesis of quinazolinones, and common synthetic methods for aryl-substituted quinazolinone compounds included cyclization of *o*-acylaminobenzamides [20], amidation of 2-aminobenzonitrile followed by oxidative ring closure [21], solid-phase synthesis of 2-arylamino-substituted quinazolinones [22], reduction of the azide functionality [23], preparation from isatoic anhydrides and Schiff bases [24], and Pd-catalyzed heterocyclization of nitoarenes [25]. All these procedure have certain limitations such as tedious process, long reaction time, harsh reaction conditions, and low yields. Very recently, it was reported by Dandia et al. [26] that a rapid procedure for synthesis of quinazolinones under microwave irradiation. Dabiri and co-workers [27] explored that the reaction for the synthesis of quinolinones can be catalyzed by $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ to give good yields. Moreover, Hradil et al. [28] disclosed some new routes for preparation of quinolinones which showed good results.

Herein we describe a system composed of zinc(II) perfluorooctanoate, as a Lewis acid-surfactant-combined catalyst, for the synthesis of quinazolinone derivatives via three-component one-pot reaction in aqueous micellar media efficiently.

2. Results and discussion

At the outset, the relationship between the surface tension and the concentration of $\text{Zn}(\text{PFO})_2$ was measured by a surface-tensionmeter carried out in water at room temperature. It was suggested that the surface tension of water would be obviously decreased when the concentration of $\text{Zn}(\text{PFO})_2$ is increased, and the critical micelle concentrations (CMC) of $\text{Zn}(\text{PFO})_2$ in water was calculated to be about 0.005 mol L^{-1} , which was lower than the corresponding CMC value (0.027 mol L^{-1}) of potassium perfluor-



Scheme 1.

ooctanoate reported previously [29], and the minimum surface tension of $\text{Zn}(\text{PFO})_2$ micellar solutions was determined to be $19.76 \text{ dyn cm}^{-1}$. Then, the surfactivity of $\text{Zn}(\text{PFO})_2$ was enhanced because it contains two carbon-fluorine chains. Furthermore, we have examined the surfactivity of $\text{Zn}(\text{PFO})_2$ in some organic solvents, such as ethanol, and its surface tension was also decreased by increasing concentration of $\text{Zn}(\text{PFO})_2$, it is clear that $\text{Zn}(\text{PFO})_2$ could work as surfactant in organic solvents as well as in water. As compared to traditional surfactant containing hydrocarbons chain, $\text{Zn}(\text{PFO})_2$ is not only an excellent surfactant in water, but also in organic solvents.

To investigate the catalytic activity of different catalysts, we carried out the reaction of isatoic anhydride **1** (1 mmol) with aniline **2a** (1 mmol) and benzaldehyde **3a** (1 mmol) as a model reaction in the presence of catalysts in water (5 mL) under refluxing with vigorous stirring (Scheme 1). The results of this study were summarized in Table 1.

After screening several Lewis acids, it can be noted that the conventional Lewis acids such as SnCl_2 and ZnCl_2 were used as a catalyst in water and gave only poor yields of the products (26% and 24% yield, respectively). Ytterbium triflate $\text{Yb}(\text{OTf})_3$ is a strong Lewis acid because of the hard character of its metal cation and the strong withdrawing effect of trifluoromethanesulfonyl group. When using this rare earth metal salt as a catalyst in the model reaction, the corresponding product was obtained in unsatisfied yield (46% yield). Compared with $\text{Yb}(\text{OTf})_3$, the water-solubility of the reaction substrates are very poor, which resulted in formation of the two phases catalyst system. On the other hand, since $\text{Yb}(\text{OTf})_3$ does not work as a surfactant-type catalyst, it is unable to disperse reactants in aqueous media. Interestingly, we have found that $\text{Zn}(\text{PFO})_2$ could catalyze this reaction efficiently under similar reaction conditions. This experimental phenomenon mentioned here is shown as Fig. 1. While $\text{Zn}(\text{PFO})_2$ itself dissolved in water, a clear solution was given (Fig. 1(a)). When **1**, **2a** and **3a** were added, white emulsion was formed, and the reactants were diffused well in micellar media (Fig. 1(b)), then, the reaction proceeded smoothly to afford the desired adduct **4a** in high yield. At the end of the reaction (Fig. 1(c)), the product was precipitated and

Table 1

The reaction of isatoic anhydride, aniline and benzaldehyde in water: effect of catalysts^a

Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	Yield (%) ^b
1	None	–	24	–
2	SnCl_2	3	6	26
3	ZnCl_2	3	6	24
4	$\text{Yb}(\text{OTf})_3$	3	6	46
5	$\text{Zn}(\text{PFO})_2$	1	4	46
6	$\text{Zn}(\text{PFO})_2$	2.5	4	60 ^c
7	$\text{Zn}(\text{PFO})_2$	2.5	4	60, 58, 58 ^d
8	$\text{Zn}(\text{PFO})_2$	5	4	59

^a All reactions were performed in water (5 mL) under reflux.

^b Isolated yields.

^c CMC of $\text{Zn}(\text{PFO})_2$.

^d Catalyst system was recycled for three runs.

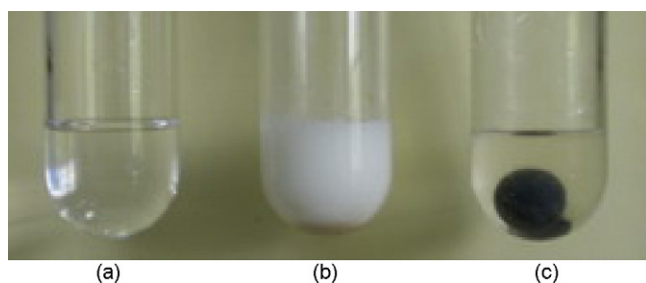


Fig. 1. Photographs of the $\text{Zn}(\text{PFO})_2$ -catalyzed reaction in water. (a) Mixture of $\text{Zn}(\text{PFO})_2$ in water; (b) emulsion solution when adding reagents **1**, **2a** and **3a** in the reactor; (c) the product was precipitated after finishing the reaction.

could be completely isolated by filtration from the emulsion phase. The catalyst $\text{Zn}(\text{PFO})_2$ did remain still in filter liquor that could be used directly as a catalyst micellar media for next reaction.

From the viewpoint of CMC [9 g], the effect of catalyst loading on the reaction efficiency was evaluated next, and the results were satisfactory. When the reaction proceeded in an emulsion solution of $\text{Zn}(\text{PFO})_2$ at its critical micelle concentrations, the reaction time was shorter and the yield of the reaction was enhanced (yield 59%, entry 6). Similar reaction in water, with the amount of catalyst being less than CMC, the results were in direct proportion with the catalyst concentration. However, when the catalyst concentration was more than CMC, the extra amount of catalyst could not increase the yield. Furthermore, the catalyst can be reused for several successive runs by recycled or recovered the micellar media directly (entry 7).

Although $\text{Zn}(\text{PFO})_2$ is efficient for the reaction in water, the satisfactory yield was not realized. We next examined the effect of different solvents in this reaction, and the results are listed in Table 2. It was found that $\text{Zn}(\text{PFO})_2$ catalyzed this reaction more efficiently not only in water but also in some solvents or water/organic biphasic media.

When the reaction was carried out in dichloromethane and EtOAc, moderate yield were observed (Table 2, entry 2 and 3). Whereas, the reaction in acetonitrile, toluene and ethanol gave better yields (Table 2, entries 4–6). It was found that the strong polar solvents such as acetonitrile and ethanol proved to be effective. However, due to the good solubility of the product in toluene at higher temperature, better yield of product is obtained in this non-polar solvent (Table 2, entry 5). These solvent effects indicated that organic solvent played an essential role in this

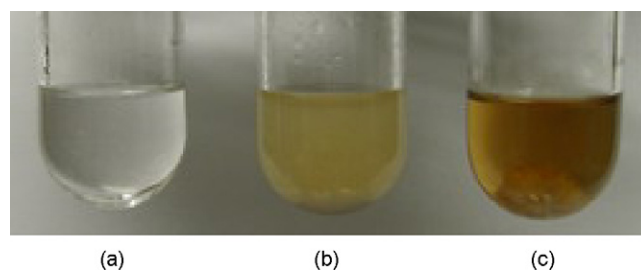


Fig. 2. Photographs of the $\text{Zn}(\text{PFO})_2$ -catalyzed reaction in a mixed solvent ($\text{H}_2\text{O}/\text{EtOH} = 1/3$). (a) Mixture of $\text{Zn}(\text{PFO})_2$ in $\text{H}_2\text{O}/\text{EtOH}$; (b) added reagents **1**, **2a** and **3a** in the reactor; (c) the product precipitation after the reaction completed.

reaction. Considering water and ethanol as green solvents, we tried to carry out the reaction in a mixture solvent system ($\text{H}_2\text{O}/\text{EtOH}$), the reaction also proceeded smoothly to give higher yield (60–82%) than that in pure H_2O .

The observed phenomenon under mixed solvent conditions was as followed: $\text{Zn}(\text{PFO})_2$ itself dissolved in $\text{H}_2\text{O}/\text{EtOH}$ (1/3 (v/v)) at room temperature to result in a clear solution (Fig. 2(a)). When the reagents **1**, **2a** and **3a** were added, slightly yellow shade emulsion was formed, and the reactants were dissolved well in aqueous ethanol (Fig. 2(b)). After completion of the reaction and cooling to room temperature, the desired product was precipitated, meanwhile, the catalyst was dissolved in the solution (Fig. 2(c)). The adduct could be completely isolated by filtration from the catalyst emulsion phase. On the other hand, the catalyst $\text{Zn}(\text{PFO})_2$ did remain in the filtrate that could be used directly as catalyst micellar media for the next reaction.

The reaction in $\text{H}_2\text{O}/\text{EtOH}$ (1/3 (v/v)), which has proven to be a good solvent for the reaction, resulted in high yield (Table 2, entry 8, 82%). Almost similar result was also observed in $\text{H}_2\text{O}/\text{EtOH}$ (1/5 (v/v)) (Table 2, entry 7, 81%). In the case of increase in the amount H_2O in the solvent mixture, slightly lower yields were observed (Table 2, entries 9–11). While the reaction was carried out in other mixed solvent systems, such as $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ and $\text{H}_2\text{O}/\text{toluene}$, the yields of product were moderate (64% and 55% yield, respectively) (Table 2, entries 12–13). It is noteworthy that the homogeneous catalyst system consisting of $\text{Zn}(\text{PFO})_2$ and mixed solvent of $\text{H}_2\text{O}/\text{EtOH}$ gave high yield. This is due to the following facts: (a) the reactants are soluble in aqueous ethanol; (b) the catalyst can be dissolved in the solvent mixture and shows an ability for effective micelle formation in this medium; (c) the product precipitation

Table 2
The reaction of isatoic anhydride, aniline and benzaldehyde^a: effect of solvents

Entry	Solvent	Time (h)	Yield (%) ^b
1	None	24	24
2	CH_2Cl_2	6	53
3	EtOAc	6	56
4	CH_3CN	6	74
5	Toluene	6	80
6	$\text{CH}_3\text{CH}_2\text{OH}$	6	82
7	$\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} = 1:5^c$	6	81
8	$\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} = 1:3$	6	82
9	$\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} = 1:1$	6	78
10	$\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} = 3:1$	6	69
11	$\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH} = 5:1$	6	60
12	$\text{H}_2\text{O}/\text{CH}_2\text{CN} = 1:3$	6	64
13	$\text{H}_2\text{O}/\text{toluene} = 1:3$	6	55
14	H_2O	4	60

^a All reactions were carried out in the presence of 2.5 mol% of $\text{Zn}(\text{PFO})_2$ with 5 mL solvents under reflux.

^b Isolated yields.

^c Volume ratio (v/v).

Table 3
Effect of catalysts in the reaction of isatoic anhydride, aniline and benzaldehyde^a

Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	Yield (%) ^b
1	$\text{CF}_3(\text{CF}_2)_6\text{COOH}$	5	10	19
2	$\text{Yb}(\text{OTf})_3$	3	6	80
3	ZnCl_2	3	6	55
4	SnCl_2	3	6	52
5	$\text{Yb}(\text{PFO})_3$	3	6	81
6	$\text{Sm}(\text{PFO})_3$	3	6	78
7	$\text{La}(\text{PFO})_3$	3	6	78
8	$\text{Fe}(\text{PFO})_3$	3	6	70
9	$\text{Co}(\text{PFO})_2$	3	6	71
10	$\text{Ni}(\text{PFO})_2$	3	6	66
11	$\text{Zn}(\text{PFO})_2$	2	6	75
12	$\text{Zn}(\text{PFO})_2$	2.5	6	82
13	$\text{Zn}(\text{PFO})_2$	3	6	82
14	$\text{Zn}(\text{PFO})_2$	5	6	81
15	$\text{Zn}(\text{PFO})_2^c$	3	6	82, 82, 81

^a All reactions were performed in $\text{H}_2\text{O}/\text{EtOH}$ (1/3 (v/v)) under refluxing.

^b Isolated yields.

^c Catalyst was reused for three runs.

after the reaction is complete. Therefore, we chose H₂O/EtOH (1/3 (v/v)) as the optimizing solvent system for the later experiments.

We then turned our attention to investigate the effect of different catalysts. Initially, the model reaction (Scheme 1) of isatoic anhydride (**1**), aniline (**2a**) and benzaldehyde (**3a**) was carried out in H₂O/EtOH (1/3 (v/v)) under reflux using different Lewis acids as catalysts. After screening several Lewis acids, it is of interest to note that different metal perfluorooctanoate salts catalysts are able to catalyze the reaction to high extent with 66–82% yield, especially Zn(PFO)₂ is very efficient for the reaction, and gave higher yield (Table 3, entry 12).

It was found that the perfluorooctanoic acid (CF₃(CF₂)₆COOH) showed poor effect to the yield of the product (Table 3, entry 1). This may partly explain that the metal perfluorooctanoate salts' catalytic activity is mainly owe to the metal positive ion. Although rare earth perfluorooctanoate salts and Yb(OTf)₃ for this reaction gave good yield (Table 3, entries 2, 5–7), compared with transition metal salts (Table 3, entries 8–11) such as Zn(PFO)₂, the yields of the product were almost the same. Therefore, we chose the transition metal salts for more economical reason. Among the transition metal salts (Table 3, entries 2–3 and 8–10), Zn(PFO)₂ gave an obviously higher yield, and Zn(PFO)₂ was select as the most promising catalyst. Further studies showed that the amount of Zn(PFO)₂ could effect the reaction significantly. Thus the reaction rate and yield were enhanced along with a increase in the amount of catalyst. In the presence of Zn(PFO)₂ (2.5 mol%) satisfactory yield was achieved, while the amount of catalyst did not brought obviously better yield (Table 3, entries 11–13). After the reaction completed, the catalyst could be recycled, and it could be subsequently reused for several times, as indicated in Table 3, entry 14. In this case almost no loss of activity was observed after three successive runs. The yields obtained were 82–81% (with yields of product **4a** being 82, 82, 81% in the first, second and third run, respectively).

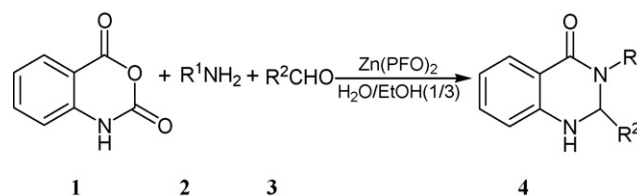
Due to the good results obtained, we applied the optimal protocol to a variety of amines and aldehydes, with isatoic anhydride. Generally, the reactions were performed using 2.5 mol% of Zn(PFO)₂ in H₂O/EtOH (1/3 (v/v)) under reflux for several hours, to give the desired products in good to excellent

Table 4Zn(PFO)₂-catalyzed synthesis of quinazolinone derivatives^a

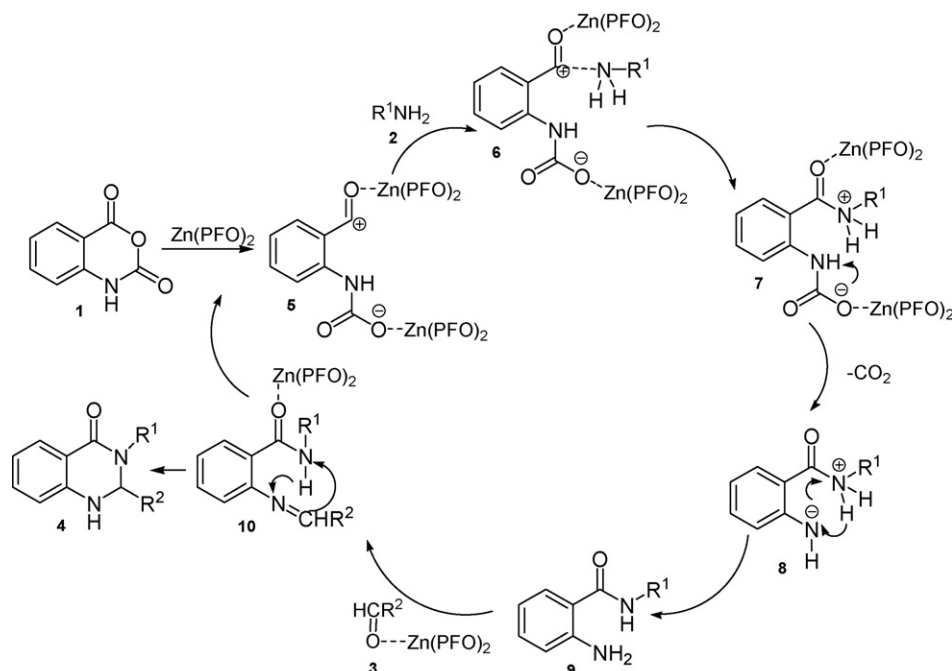
Entry	R ¹ /[(NH ₄) ⁺ X ⁻]	R ² (R ² CHO)	Time (h)	Product	Yield (%) ^b
1	C ₆ H ₅	C ₆ H ₅	6	4a	82
2	C ₆ H ₅	<i>p</i> -O ₂ NC ₆ H ₄	7	4b	80
3	C ₆ H ₅	<i>m</i> -O ₂ NC ₆ H ₄	7	4c	77
4	C ₆ H ₅	<i>p</i> -ClC ₆ H ₄	6	4d	80
5	C ₆ H ₅	<i>p</i> -BrC ₆ H ₄	6	4e	78
6	C ₆ H ₅	<i>p</i> -(CH ₃) ₂ NC ₆ H ₄	6	4f	86
7	C ₆ H ₅	<i>p</i> -CH ₃ OC ₆ H ₄	6	4g	85
8	<i>p</i> -ClC ₆ H ₄	C ₆ H ₅	6	4h	81
9	<i>p</i> -CH ₃ C ₆ H ₄	C ₆ H ₅	8	4i	78
10	<i>p</i> -NO ₂ C ₆ H ₄	C ₆ H ₅	6	4j	84
11	<i>p</i> -CH ₃ OC ₆ H ₄	C ₆ H ₅	6	4k	82
12	[(NH ₄) ⁺ Cl ⁻]	C ₆ H ₅	6	4l	79
13	[(NH ₄) ₂ ⁺ CO ₃ ²⁻]	C ₆ H ₅	6	4l	83
14	[(NH ₄) ⁺ AcO ⁻]	C ₆ H ₅	6	4l	78
15	C ₄ H ₉	C ₆ H ₅	6	4m	80

^a All reactions were carried out using 2.5 mol% of Zn(PFO)₂ in H₂O/EtOH (1/3 (v/v)) under reflux.

^b Isolated yields.

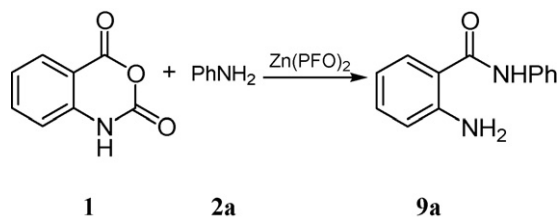
**Scheme 2.**

yields, and the results are summarized in Table 4. Most of the reactions of aromatic aldehydes with isatoic anhydride proceeded smoothly when aniline was employed in these reactions. However, the nature of substituents on the aromatic phenyl ring showed slightly different effects on the conversion. The reactions of aldehydes with electron-donating groups afforded better yields of products than those with the electron-withdrawing groups (Table 4, entries 1–7) (Scheme 2).

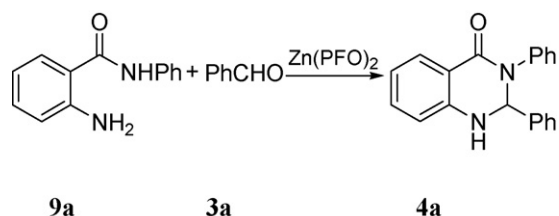
**Scheme 3.**

The scope of some amines was next examined. When benzaldehyde was used as an aldehyde component, it was found that both electron-rich and electron-deficient amines worked well, affording high yield of corresponding expected compounds with tiny difference (Table 4, entries 8–11). In addition, the aliphatic amine such as *n*-butyl amine can also serve as a substrate in this reaction, giving the products in 80% yield (Table 4, entry 15). Encouraged by the success above, the ammonium salts such as ammonium carbonate, ammonium chloride and ammonium acetate were employed as the source of ammonia, which was mixed with isatoic anhydride and benzaldehyde under reflux, and the desired products such as 2-aryl substituted 2,3-dihydroquinazolin-4(1H)-one **4l** were obtained in good yields (Table 4, entries 12–14).

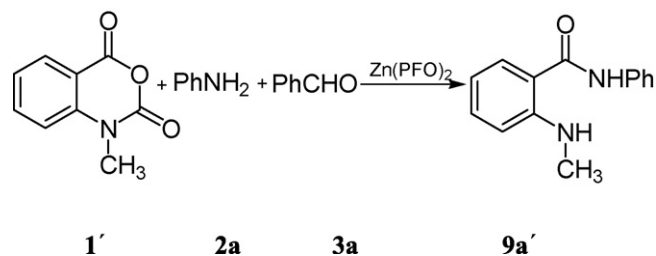
Some possible mechanisms of this three-component one-pot reaction had been reported before by Dabiri and co-workers [27] and Abdel-Jalil et al. [30]. By tracing the reaction by the TLC, we have found a new product on the TLC within a few minutes, which would be an important intermediate of the reaction. Fortunately, the intermediate (**9a**) 2-amino-*N*-substituted-amide was obtained from the reaction mixture. Based on our experimental results, a plausible mechanism of the three-component reaction is proposed in Scheme 3. In the presence of the catalyst such as $\text{Zn}(\text{PFO})_2$, first, the isatoic anhydride (**1**) is activated, to form an intermediate (**5**), then the *N*-nucleophilic amine (**2**) attacks on the carbonyl unit of an intermediate (**5**) to produce an intermediate (**7**), which in turn affords an intermediate (**8**) through decarboxylation reaction. The 2-amino-*N*-substituted-amide (**9**) is formed via proton transfer of an intermediate (**8**). Subsequently, the reaction of aldehyde activated by $\text{Zn}(\text{PFO})_2$ with (**9**) proceeds to resulting in formation of the imine intermediate (**10**), which follows by cyclization to yield the final product (**4**). To support this mechanism, several reactions were carried out under the optimized conditions. As the first try, treatment of isatoic anhydride with aniline yielded the corresponding 2-amino-*N*-phenylbenzamide (**9a**) (Scheme 4), which showed that the intermediate (**9**) was produced by the reaction of isatoic anhydride (**1**) with amine (**2**). Next, **9a** reacted with benzaldehyde (**3a**) to give the desired product, 2,3-diphenyl-2,3-dihydroquinazolin-4(1H)-one (**4a**) (Scheme 5). Furthermore, it is noted that when the reaction of *N*-methyl isatoic anhydride (**1'**) with aniline and benzaldehyde was conducted under the same conditions, it led only to formation of 2-methylamino-*N*-phenylbenzamide (**9a'**), however, the expected product was not detected (Scheme 6). Additionally, the reaction did not occur any more



Scheme 4.



Scheme 5.



Scheme 6.

without the catalyst. Clarification of the reaction mechanism of three-component one-pot reaction in detail is the next subject of our investigation.

3. Conclusions

In conclusion, we have successfully developed an efficient Lewis acid-surfactant-combined catalyst [$\text{Zn}(\text{PFO})_2$] for the synthesis of quinazolinone derivatives by the three-component one-pot condensation of isatoic anhydride with amines and aldehydes in high atom economy under aqueous micellar media conditions. It was suggested that $\text{Zn}(\text{PFO})_2$ shows the favorable surfactivity, particularly, and it would act both as a catalyst to activate the substrate molecules and as a surfactant to form stable colloidal dispersion with water-insoluble substrates. Moreover, the catalyst can be recovered conveniently and reused for at least three reaction cycles without any loss of activity. The catalyst system could be used directly as a micellar media for next reaction without any treatment. The present method offers several advantages including low loading of catalyst, high yields of products, a safe, cheap and environmentally benign solvent and an easy experimental workup procedure. In addition, the mechanism of this reaction has been proposed on the basis of the structure of the isolated intermediate such as 2-amino-*N*-phenylbenzamide (**9a**). Furthermore, this novel catalyst is expected to contribute the development of more benign reaction in water or aqueous micellar media, and the related work is underway in our laboratory.

4. Experimental

4.1. General experimental procedures

Melting points were determined on a Koflet hot plate. ^1H NMR and ^{13}C NMR spectra were recorded with Bruker WP-500SY (500 MHz) in CDCl_3 using TMS as internal standard. ^{19}F NMR spectra were recorded with Bruker DRX500 spectrometer at 470 MHz and chemical shifts are given in ppm relative to CCl_3F as internal standards. Mass spectra were determined on a Micromass GCT spectrometer. IR spectra were recorded on a Nicolet 5SXC FT-IR spectrometer by using the pressed KBr.

4.2. Catalyst preparation

The catalyst can be prepared from either rare earth or transition metal oxides as well as chlorides by stirring them with perfluorooctanoic acid, then the gained solid was collected, washed and dried in the air or vacuum for several hours. For example, to a stirring solution of perfluorooctanoic acid (2.5 g, 6 mmol) in H_2O (5 mL), ZnO_2 (0.29 g, 3 mmol) was added and the mixture was stirred for 12 h under reflux. The aqueous layer was decanted and washed with water to give gelatin-like solid. The solid was dried in vacuum at r.t. for 2 h to give white sheet solid.

Zn(PFO)₂ mp 79–81 °C; IR (KBr): $\nu = 3400\text{--}3500, 1650, 1450, 1200, 1150\text{ cm}^{-1}$; ICP-AES: Zn = 8.5%, Calcd. for Zn(PFO)₂: Zn = 7.69%; ¹⁹F NMR (500 MHz, DMSO): $\delta = -81.56$ (t, 6F, $J = 0.03$ Hz), -116.34 (t, 4F, $J = 0.02$ Hz), -121.37 (s, 4F), -123.74 (s, 4F), -124.51 (s, 8F), -126.73 (s, 4F); EDS (%): C, 27.69; O, 7.36; F, 54.72; Zn, 10.23.

4.3. General procedure for the synthesis of quinazolinone compounds

A stirred mixture of isatoic anhydride (1 mmol), amine (1.1 mmol), aldehyde (1 mmol) and Zn(PFO)₂ (0.027 g, 0.03 mmol) in H₂O/EtOH = 1:3 (5 mL) was refluxed for 6 h. When the reaction completed as indicated by TLC, the reaction mixture was cooled to room temperature. The resulting solid residue was filtered, washed with 3 × 5 mL water for three times and recrystallized from EtOH to give the pure product.

The filtrate containing the catalyst was evaporated under reduced pressure to give a solid, and the recovered catalyst could be reused without a loss of catalytic activity. Alternatively, the catalyst did remain in filtrate that could be used directly as catalyst micellar media for next reaction without any treatment.

4.3.1. 2,3-Diphenylquinazolin-4(1H)-one (4a)

mp 203–205 °C [27a] (recrystallized from hot ethanol). ¹H NMR (CDCl₃): δ (ppm) 8.13 (d, 1H, $J = 7.9$ Hz), 7.32–7.35 (m, 2H), 7.25–7.30 (m, 6H), 7.19–7.22 (m, 3H), 6.88–6.91 (m, 1H), 6.55 (d, 1H, $J = 8.0$ Hz), 6.20 (s, 1H), 4.75 (s, 1H).

4.3.2. 2-(4-Nitrophenyl)-3-phenylquinazolin-4(1H)-one (4b)

mp 194–196 °C [30]. ¹H NMR (CDCl₃): δ (ppm) 8.15 (d, 1H, $J = 7.9$ Hz), 7.88–7.91 (m, 2H), 7.34–7.36 (m, 2H), 7.24–7.31 (m, 6H), 6.89–6.91 (m, 1H), 6.58 (d, 1H, $J = 7.9$ Hz), 6.22 (s, 1H), 4.78 (s, 1H).

4.3.3. 2-(3-Nitrophenyl)-3-phenylquinazolin-4(1H)-one (4c)

mp 188–189 °C [30]. ¹H NMR (CDCl₃): δ (ppm) 8.13 (d, 1H, $J = 7.9$ Hz), 7.82–7.86 (m, 2H), 7.33–7.36 (m, 2H), 7.26–7.32 (m, 6H), 6.88–6.91 (m, 1H), 6.56 (d, 1H, $J = 7.9$ Hz), 6.20 (s, 1H), 4.76 (s, 1H).

4.3.4. 2-(4-Chlorophenyl)-3-phenylquinazolin-4(1H)-one (4d)

mp 217–219 °C [24]. ¹H NMR (CDCl₃): δ (ppm) 8.17 (d, 1H, $J = 7.9$ Hz), 7.48–7.56 (m, 2H), 7.29–7.35 (m, 5H), 7.15–7.20 (m, 3H), 6.90–6.94 (m, 1H), 6.67 (d, 1H, $J = 8.1$ Hz), 6.05 (s, 1H), 4.73 (s, 1H).

4.3.5. 2-(4-Bromophenyl)-3-phenylquinazolin-4(1H)-one (4e)

mp 222–225 °C [24]. ¹H NMR (CDCl₃): δ (ppm) 8.16 (d, 1H, $J = 7.9$ Hz), 7.46–7.53 (m, 2H), 7.31–7.36 (m, 5H), 7.17–7.21 (m, 3H), 6.87–6.93 (m, 1H), 6.74 (d, 1H, $J = 8.0$ Hz), 6.07 (s, 1H), 4.75 (s, 1H).

4.3.6. 2-(4-Dimethylaminophenyl)-3-phenylquinazolin-4(1H)-one (4f)

mp 184–185 °C. ¹H NMR (CDCl₃): δ (ppm) 8.12 (d, 1H, $J = 7.8$ Hz), 7.26–7.29 (m, 2H), 7.19–7.23 (m, 6H), 6.82–6.90 (m, 1H), 6.73 (d, 1H, $J = 8.0$ Hz), 6.58 (d, 2H, $J = 8.3$ Hz), 6.04 (s, 1H), 4.73 (s, 1H), 2.83 (s, 6H); MS: $m/z = 343$ (M⁺, 69.17), 344 (11.33), 251 (100); Anal. Calcd. for C₂₂H₂₁N₃O: C, 76.94; H, 6.16; N, 12.24%. Found: C, 76.90; H, 6.12; N, 12.30%.

4.3.7. 2-(4-Methoxyphenyl)-3-phenylquinazolin-4(1H)-one (4g)

mp 204–205 °C [30]. ¹H NMR (CDCl₃): δ (ppm) 8.19 (d, 1H, $J = 7.8$ Hz), 7.52–7.56 (m, 2H), 7.39–7.47 (m, 6H), 6.99–7.03 (m, 1H), 6.81 (d, 1H, $J = 8.1$ Hz), 6.65 (d, 2H, $J = 8.3$ Hz), 6.04 (s, 1H), 4.73 (s, 1H), 3.74 (s, 3H).

4.3.8. 2-Phenyl-3-(4-chlorophenyl)-quinazolin-4(1H)-one (4h)

mp 210–212 °C [24]. ¹H NMR (CDCl₃): δ (ppm) 8.12 (d, 1H, $J = 7.8$ Hz), 7.37–7.42 (m, 6H), 7.23–7.25 (m, 2H), 7.12–7.15 (m, 2H), 6.90–6.94 (m, 1H), 6.64 (d, 1H, $J = 7.9$ Hz), 6.08 (s, 1H), 4.76 (s, 1H).

4.3.9. 2-Phenyl-3-(4-methylphenyl)-quinazolin-4(1H)-one (4i)

mp 196–199 °C. ¹H NMR (CDCl₃): δ (ppm) 8.21 (d, 1H, $J = 7.8$ Hz), 7.48–7.50 (m, 2H), 7.42–7.45 (m, 1H), 7.35–7.40 (m, 7H), 7.01–7.03 (m, 1H), 6.75 (d, 1H, $J = 8.1$ Hz), 6.09 (s, 1H), 4.76 (s, 1H), 2.76 (s, 3H); Ms: $m/z = 314$ (M⁺, 100), 315 (21.45), 316 (1.69); Anal. Calcd. for C₂₁H₁₈N₂O: C, 80.23; H, 5.77; N, 8.91%. Found: C, 80.28; H, 5.71; N, 8.95%.

4.3.10. 2-Phenyl-3-(4-nitrophenyl)-quinazolin-4(1H)-one (4j)

mp 185–187 °C. ¹H NMR (CDCl₃): δ (ppm) 8.17 (d, 1H, $J = 7.9$ Hz), 7.79–7.86 (m, 4H), 7.26–7.33 (m, 6H), 6.91–6.94 (m, 1H), 6.58 (d, 1H, $J = 7.9$ Hz), 6.24 (s, 1H), 4.76 (s, 1H); Ms: $m/z = 345$ (M⁺, 100), 346 (14.69); Anal. Calcd. for C₂₀H₁₅N₃O₃: C, 69.56; H, 4.38; N, 12.17%. Found: C, 69.60; H, 4.32; N, 12.23%.

4.3.11. 2-Phenyl-3-(4-methoxyphenyl)-quinazolin-4(1H)-one (4k)

mp 209–211 °C [24]. ¹H NMR (CDCl₃): δ (ppm) 8.0 (d, 1H, $J = 7.80$ Hz), 7.36–7.39 (m, 2H), 7.3–7.35 (m, 2H), 7.24–7.30 (m, 2H), 7.05–7.08 (m, 2H), 6.83–6.85 (m, 1H), 6.78–6.81 (m, 2H), 6.62 (d, 1H, $J = 8.00$ Hz), 6.03 (s, 1H), 4.69 (s, 1H), 3.75 (s, 3H).

4.3.12. 2-Phenyl-2,3-dihydroquinazolin-4(1H)-one (4l)

mp 221–223 °C [27a]. ¹H NMR (CDCl₃): δ (ppm) 4.3 (s, 1H), 5.9 (s, 1H), 6.6 (d, 1H, $J = 8.0$ Hz), 6.9 (t, 1H, $J = 8.0$ Hz), 7.3 (m, 1H), 7.4–7.5 (m, 3H), 7.6 (m, 2H), 7.9 (d, 1H, $J = 7.8$ Hz).

4.3.13. 3-Butyl-2-phenyl-2,3-dihydroquinazolin-4(1H)-one (4m)

mp 120–122 °C [27a]. ¹H NMR (CDCl₃): δ (ppm) 0.9 (t, 3H, $J = 7.5$ Hz), 1.33 (m, 2H), 1.6 (m, 2H), 2.8 (m, 1H), 3.7 (m, 1H), 4.5 (s, 1H), 5.7 (s, 1H), 6.5 (d, 1H, $J = 7.9$ Hz), 6.8 (t, 1H, $J = 7.5$ Hz), 7.2 (m, 1H), 7.3–7.5 (m, 5H), 7.9 (d, 1H, $J = 7.5$ Hz).

4.3.14. 2-Amino-N-phenylbenzamide (9a)

mp 130–132 °C. ¹H NMR (CDCl₃): δ (ppm) 7.75 (s, 1H), 7.57 (d, 2H, $J = 7.6$ Hz), 7.45–7.50 (d, 1H, $J = 6.9$ Hz), 7.34–7.41 (m, 2H), 7.23–7.28 (m, 1H), 7.12–7.18 (m, 1H), 6.69–6.74 (m, 2H), 5.5 (s, 2H); ¹³C NMR (CDCl₃): $\delta = 118.1, 118.8, 119.2, 122.5, 126.7, 129.3, 131.8, 134.8, 139.5, 151.8, 169.2$; MS: $m/z = 212$ (M⁺, 100), 213 (13.35), 214 (1.00); IR (KBr): $\nu = 3418, 3290, 1643, 1511, 1438, 1260, 747\text{ cm}^{-1}$; HRMS: Anal. Calcd. for C₁₃H₁₂N₂O: 212.0993; Found: 212.0950.

4.3.15. 2-(Methylamino)-N-phenylbenzamide (9a')

mp 123–125 °C [31]. ¹H NMR (CDCl₃): δ (ppm) 2.8 (d, 3H, $J = 5.1$ Hz), 4.0 (s, 1H), 6.6 (d, 1H, $J = 7.5$ Hz), 6.7 (t, 1H, $J = 7.5$ Hz), 7.1 (m, 1H), 7.2–7.4 (m, 4H), 7.5 (t, 1H, $J = 7.6$ Hz), 7.6 (d, 1H, $J = 7.6$ Hz), 8.0 (s, 1H).

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