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Jian WU [a, b, *], Xianli DU [a, b], Juan MA [a, b], Yuping Zhang [a, b], Qingcai SHI [a, b], Lijun LUO [a, b], Baoan SONG [a, b,*], Song YANG [a, b], and Deyu Hu [a, b]

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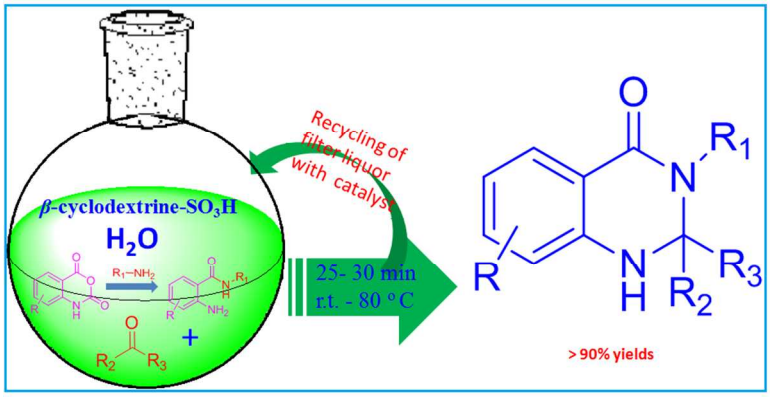

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ARTICLE TYPE

Preparation of 2, 3-Dihydroquinazolin-4(1*H*)-ones Derivatives in Aqueous Media with *β*-Cyclodextrine-SO_3H as Recyclable Catalyst

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A new *β*-Cyclodextrine-SO_3H-assisted, convenient and efficient strategy for the preparation of 2, 3-dihydroquinazolin-4(1*H*)-ones derivatives in aqueous media is described. The catalyst can be readily recovered and reused for next reaction for at least three runs without any significant impact on the yields of the products. The main advantages of this protocol include short reaction times, practical simplicity, high yields, and recyclable catalyst, and safety, cheapness of benign solvent.

Introduction

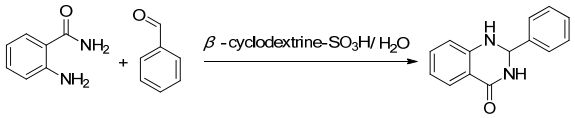
2, 3-Dihydroquinazolinone derivatives are an important class of fused heterocycles due to their broad range of potential biological pharmacological activities, [1-6] as well as the importance in preparation of drug molecules and natural products. [7-10] In recently years, a large numerous protocols for preparation of 2,3-dihydroquinazolin-4(1*H*)-ones have been developed in different ways by using gallium (III) triflate,[11] iodine,[12] silica sulfuric acid,[13] montmorillonite K-10,[14] [$Zn(PFO)_2$], [15] $KAl(SO_4)_2.12H_2O$, [16] MCM-41-SO_3H, [17] $Al(H_2PO4)_3$, [18] [bmim]BF_4, [19] sulfamic acid,[20] *β*-cyclodextrin,[21] cellulose-SO_3H,[22] ammonium chloride,[23] low-valent titanium reagents,[24] Cu-CNTs [25] and MNPs-PSA (*N*-propylsulfamic acid supported onto magnetic Fe_3O_4 nanoparticles) [26] as catalysts. These reported methodologies produce good results in many instances. However, some of synthetic strategies suffer with certain limitations such as expensive catalysts, low yields of products, long reaction times, high reaction temperature, tedious procedures for preparations of catalysts and tedious work-up conditions. Hence, the development of efficient, simple, easy work-up and environmentally benign protocol using recyclable catalyst and green solvent for the synthesis of quinazolinone derivatives is still desirable and in demand.

Aqueous media has received high priority as green media in organic synthesis due to its safety, cheapness, environmental friendless, and no toxicity. [27] An increasing number of publications [28] are indicative of the potential of aqueous media as 'designer solvents' for various chemical reactions, such as knoevenagel condensation reaction, [29] reformatsky reaction, [30] diels-alder reaction, [31] suzuki coupling, [32] michael addition, [33] claisen rearrangement, [34] stille coupling reaction, [35] *etc*. In the reported strategies for preparation of 2, 3-dihydroquinazolin-4(1*H*)-ones, several protocols were also carried out in aqueous media and showed good results [15, 16, 20, 21, 26].

In current works, we disclosed a novel methodology for synthesis of 2, 3-dihydroquinazolin-4(1*H*)-ones by ring closure of substituted 2-aminobenzamide with aldehydes (or ketone), and one-pot three-component condensation of substituted isatoic anhydride, a primary amine (or ammonium acetate) and a carbonyl derivatives in the presence of *β*-cyclodextrine-SO_3H in aqueous media, respectively. To the best of our knowledge, this is the first reported synthesis of this important class of fused heterocycles from the cheap and easily available starting materials by employing cheap, recyclable and easily available *β*-cyclodextrine-SO_3H as an efficient catalyst in a green media.

Results and discussion

Initially, the *β*-cyclodextrine-SO_3H was simply synthesized according to the method reported recently. [33] The $-SO_3H$ content measured obtained were in agreement with the proposed method, the value was 0.52 mequiv./g, and it matched that as reported in the literature. [36] Subsequently, to investigate the effects of solvent, reaction time, and the amount of catalyst on the yields, we carried out the reaction of 2-aminobenzamide with benzaldehyde as a model reaction (Scheme 1) in different solvents under different conditions. The results were summarized in Table 1.



Scheme 1 Synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one

After screening several solvents, it can be noted that the non-polar solvents such as benzene and toluene gave only moderate yields of the products (58% and 55%, respectively), the polar solvents (EtOH, MeCN, CH_2Cl_2 and MeOH) give much better yields than these of benzene and toluene, THF also gave good yield for the reaction(Table 1, entry 7). However, water can give an excellent yield (96%) for this reaction (Table 1, entry 9). Then, the reaction was conducted at room temperature for screening a suitable reaction time; the results showed that moderate yield (70%) could be given after reaction for 5 min (Table 1, entry 13), it was

observed that the yield (91%) was increased after reaction for 15 min (Table 1, entry 12), however, the yield was not enhanced obviously after 25 min. Based on these studies, the reaction temperature was further investigated, the results indicated the yields were not enhanced obviously by raising the temperature (Table 1, entries 14, 15). We next examined the effect of the amount of catalyst on this reaction, and the results (Table 1, entries 16-18) indicated that the amount of catalyst played an essential role in this reaction. As reported in reference,[21] the yield was low (Table 1, entry 18) in catalyst free condition may due to the poor solubility of benzaldehyde in water at elevated temperatures resulted in the formation of undesired products, but the 5% of catalyst can form a moderate yield (74%, Table 1, entry 17) for this reaction, when the increasing amount of catalyst can enhance the yield, the reaction proceeds smoothly to give higher yield (95%) by addition > 10% of amount of catalyst. Nevertheless, the yields were not enhanced obviously by further increasing the amount of catalyst (Table 1, entry 16). Moreover, *p*-TSA (Table 1, entry 19) and sulfamic acid (Table 1, entry 20) were employed as catalyst, but the yields were lower than these of *β*-Cyclodextrine-SO_3H. After the complication of the reaction, the product was precipitated and could be completely isolated by filtration from the aquatic phase. However, the catalyst *β*-cyclodextrine-SO_3H did remain still in filter liquor that could be used directly as a catalyst media for next reaction; and the yield was still around 90% after catalyst system was recycled for four runs (Table 1, entry 11).

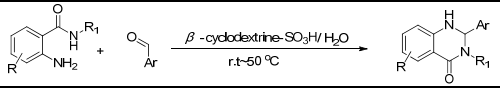
Table 1. Optimization for synthesis of 2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (model reaction) [a].

Entry	Solvent	Time (min)	Temp-erature	Amount of catalyst (mol%)	yield [b]
1	EtOH	60	r.t	10[c]	80
2	MeCN	60	r.t	10[c]	75
3	CH_2Cl_2	60	r.t	10[c]	76
5	Benzene	60	r.t	10[c]	58
6	Toluene	60	r.t	10[c]	55
7	THF	60	r.t	10[c]	70
8	MeOH	60	r.t	10[c]	78
9	H_2O	60	r.t	10[c]	96
10	H_2O	30	r.t	10[c]	95
11	H_2O	25	r.t	10[c]	95, 93, 90, 88[d]
12	H_2O	15	r.t	10[c]	91
13	H_2O	5	r.t	10[c]	70
14	H_2O	25	50	10[c]	96
15	H_2O	25	80	10[c]	96
16	H_2O	25	r.t.	15[c]	95
17	H_2O	25	r.t.	5[c]	74
18	H_2O	25	r.t.	0	56, 55 [21]
19	H_2O	25	r.t.	10[e]	80
20	H_2O	25	r.t.	10[f]	76

[a] All the reactions were carried out with 2-aminobenzamide (1 mmol), benzaldehyde (1 mmol), and water (10 mL); [b] isolated yields; [c] catalyst was *β*-cyclodextrine-SO_3H; [d] catalyst system was recycled for four runs; [e] catalyst was *p*-TSA; [f] catalyst system was sulfamic acid.

Encouraged by the initial success, we applied the optimal protocol to a variety of substituted 2-aminobenzamide and different aldehydes. Generally, the reactions were performed using 10% mol of *β*-cyclodextrine-SO_3H in H_2O under the room temperature for 25 min to give the desired products in good to excellent yields; the results were summarized in Table 2. It was observed that most of the reactions of substituted 2-aminobenzamide with aldehydes proceeded smoothly. However, the yields were slightly lower at the room temperature for part of the reaction (Table 2, entries 17-31) may due to the poor solubility of aldehydes in water, but when the reaction temperature was sited around 50 °C, the yields of the products can be enhanced (Table 2, entries 17-31) and the reactions proceeded smoothly. In addition, the substituent on the aromatic aldehydes showed slightly different effects on the yield, reactions of aromatic aldehydes with electron-donating groups afforded little better yields of products than those with the electron-withdrawing groups (Table 2, entries 17-31). Moreover, the reactions of heterocyclic aldehydes with furan (Table 2, entries 1, 3, 4, 7, 8, 9, 11, 13, and 15), pyridine (Table 2, entry 30), thiophene (Table 2, entry 31), and thiazole (Table 2, entry 32) also give excellent yields. Furthermore, the reusability of the catalyst also be checked randomly via several reactions using filter liquor with *β*-cyclodextrine-SO_3H in it as catalytic system for new runs (Table 2, entries 1, 6, 7, 15, 16), these results indicated that the aqueous media contained *β*-cyclodextrine-SO_3H could be reused for several times with slightly decreasing in the product yield.

Table 2. *β*-cyclodextrine-SO_3H catalyzed synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives.[a]

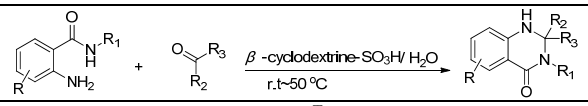


Entry	R[b]	R_1	Ar	Yield (%)	Mp (°C)
1	H	H		96, 94, 91,89[c]	166-168 (165-167) [14]
2	8-Me	Et		80, 95[d]	214-215
3	H	Et		92	119-120 (120-121) [37]
4	8-Me	Me		92	182-183
5	8-Me	Me		94	135-136
6	8-Me	Et		96, 93, 89,85[c]	152-153
7	8-Me	Et		96, 95, 91, 88[c]	106-107
8	8-Me-6-Cl	Me		96, 94[d]	155-156
9	8-Me-6-Cl	Et		95, 92[d]	168-170
10	8-Me-6-Cl	Et		97	228-230
11	8-Me-6-Cl	H		95	179-180
12	7-Cl	Me		92	211-213
13	7-Cl	Me		95	176-178
14	7-Cl	H		93.5	186-187
15	7-Cl	H		96, 94, 90, 88[c]	203-204
16	H	H		92, 91, 88, 88[c]	191-192 (189-193) [12b]
17	H	H		83, 90[d]	205-207 (204-206) [38]
18	H	H		82, 91[d]	182-183
19	8-Me	Me		85, 94[d]	122-124
20	8-Me	Et		86, 94[d]	111-112
21	H	H		87, 94[d]	147-149 (148-150) [39]
22	7-Cl	Me		81, 90.2[d]	270-271
23	7-Cl	Me		80,90.5[d]	207-209
24	7-Cl	Me		88, 97.1[d]	203-205
25	7-Cl	Me		86, 94.7[d]	189-190
26	7-Cl	Me		83, 91.3[d]	248-250
27	7-Cl	H		87, 94.5[d]	235-237
28	7-Cl	H		85, 95[d]	210-213
29	7-Cl	Me		85, 94[d]	171-172
30	H	H		80, 92[d]	191-193 (190-192) [24]
31	7-Cl	Me		82, 93.3[d]	193-195
32	7-Cl	Me		94	251-253

[a] All the reactions were conducted with substituted 2-aminobenzamide (1 mmol), aldehydes (1 mmol), *β*-cyclodextrine-SO_3H (0.1 mmol), and water (10 mL); [b]: The position of the R is referring to the structure of 2,3-dihydroquinazolin-4(1*H*)-one derivatives; [c]: Catalyst system was recycled for four runs; [d]: the second yields were carried out at 50 °C

The scope of reaction was further investigated by using several ketones instead of aldehydes. The results listed in Table 3 showed that the reactions also can be conducted smoothly, most of the reactions showed excellent yield. It is worthy noted that substituted 2, 3-dihydroquinazolin-4(1*H*)-one derivatives with a spiro could be prepared in excellent yields (Table 3, entries 5-15). The reusability of the catalyst was also investigated via the reaction of 2-aminobenzamide with cyclohexanone (Table 3, entry 5), we also found that the catalytic system can be reused for several times without significantly decreasing the yields of the products.

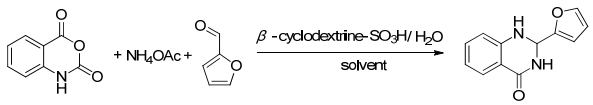
Table 3. *β*-cyclodextrine-SO_3H catalyzed synthesis of 2,3-dihydroquinazolin-4(1*H*)-one derivatives.[a]



Entry	R[b]	R_1		Temp-erature (°C)	Yield (%)	Mp (°C)
1	H	H		r.t.	92.3	182-183 (184-185) [12c]
2	8-Me	Me		r.t.	92	161-162
3	8-Me	Me		r.t.	94	205-207
4	7-Cl	Me		r.t.	92	161-163
5	H	H		50	94, 94, 91, 90[c]	220-221 (217-219) [24]
6	8-Me	Me		50	95.2	180-181
7	8-Me	Et		50	92	142-143
8	8-Me-6-Cl	Me		50	90	166-168
9	8-Me-6-Cl	H		50	96	201-202
10	8-Me-6-Cl	H		50	93	198-199
11	H	H		50	92	258-259 (257-260) [23]
12	7-Cl	Me		50	93	277-278
13	7-Cl	Me		50	94	213-215
14	7-Cl	H		50	92	223-224
15	7-Cl	H		50	95	209-210

[a]: All the reactions were conducted with substituted 2-aminobenzamide (1 mmol), ketones (1 mmol), *β*-cyclodextrine-SO_3H (0.1 mmol), and water (10 mL); [b]: The position of the R is referring to the structure of 2,3-dihydroquinazolin-4(1*H*)-one derivatives; [c] Catalyst system was recycled for four runs.

After we obtained an excellent yields by reaction of substituted 2-aminobenzamide with aldehydes (or ketone), since we noted that the substituted 2-aminobenzamide can be prepared from isatoic anhydride with amines. [40] And in recently years, several methods for preparation of 2,3-disubstituted quinazolin-4(3*H*)-ones via multi-component (isatoic anhydride, amines and aldehydes) reactions have been reported by using silica sulfuric acid, [13] zinc (II) perfluorooctanoate [$Zn(PFO)_2$], [15] $KAl(SO_4)_2{\cdot}12H_2O$,[16] ionic liquid, [19] and cellulose-SO_3H [22] as reusable catalyst. From this point of view, we sought to investigate multi-component reactions to prepare the 2,3-disubstituted quinazolin-4(3*H*)-ones by using *β*-cyclodextrine-SO_3H as catalyst may result in good catalytic effect. Hence, we firstly carried out the reaction of isatoic anhydride with NH_4OAc and furaldehyde as a model reaction in different conditions (Scheme 2). The results were summarized in Table 4.



Scheme 2 Synthesis of 2-(furan-2-yl)-2,3-dihydroquinazolin-4(1H)-one

Table 4. Optimization for *β*-cyclodextrine-SO_3H catalyzed synthesis of 2-(furan-2-yl)-2,3-dihydroquinazolin-4(1*H*)-one[a].

Entry	solvent	Time (min)	temperature	Amount of catalyst (mol%)	yield [b]
1	Benzene	30	r.t	10	40
2	Toluene	30	r.t	10	45
3	EtOH	30	r.t	10	69
4	MeCN	30	r.t	10	65
5	CH_2Cl_2	30	r.t	10	68
6	H_2O	30	r.t	10	72
7	H_2O	30	50	10	78
8	H_2O	30	80	10	85
9	H_2O	30	refluxing	10	86
10	H_2O	30	80	15	91, 90, 88[c]
11	H_2O	30	80	20	91
12	H_2O	40	80	15	92
13	H_2O	20	80	15	81
14	H_2O	30	70	15	87
15	H_2O	30	80	0	58

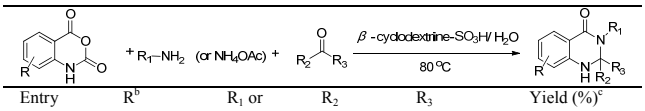
[a] All the reactions were carried out with isatoic anhydride (1 mmol), furaldehyde (1 mmol), NH_4OAc (1.2 mmol), and water (10 mL); [b] Isolated yields; [c] Catalyst system was recycled for three runs.

From the table, it was observed that the multi-component reaction was preceded poorly in benzene and toluene (the yields were less than 50%, Table 4, entries 1, 2). Nevertheless, the yields can be enhanced in solvents of ethanol (Table 4, entry 3), acetonitrile (Table 4, entry 4), dichloromethane (Table 4, entry 5) and H_2O (Table 4, entries 6-14). Especially, water is much more suitable for such a reaction (Table 4, entry 6). Then, the reaction was performed at different temperatures (Table 4, entries 7-10), and the results showed that good yield could be given at 80 °C (85%, Table 4, entry 8). Based on these studies, the reaction time and the amount of catalyst were further investigated; the results indicated the best amount of catalyst was 15%, and the time was 30 min (Table 4, entry 10), the yields were not obviously enhanced by increasing the amount of catalyst (Table 4, entry 11) and reaction time (Table 4, entry 12). And it can be seen from entry 15 (Table 4), the yield was decreased sharply (58%) when amount of catalyst was 0. Moreover, the yield was slightly affected by decreasing the reaction time (Table 4, entries 10, 12, 13). As same as the reaction of substituted 2-aminobenzamide with aldehydes, the product was conveniently isolated by filtration. And the filter liquor containing catalyst was used directly as a catalyst system media for the next reaction; the result showed in entry 10 suggested the catalyst system can be recycled for more than three times.

Encouraged by the initial success in production of 2-(furan-2-yl)-2, 3-dihydroquinazolin-4(1*H*)-one via the multi-component reaction strategy, to investigate the general scope and versatility of this strategy in the prareation of substituted 2,3-dihydroquinazolin-4(1*H*)-one, different substituted isatoic anhydrides, amines, aldehydes (or ketone) were examined in optimized condition, respectively. Excitingly, the corresponding substituted 2,3-dihydroquinazolin-4(1*H*)-one derivatives were successfully and smoothly obtained, and the results were listed in Table 5. From the table, it can be observed that most of the substituted 2, 3-dihydroquinazolin-4(1*H*)-one were obtained in good yields no matter if the isatoic anhydride were substituted or not, no matter if the amines were NH_4OAc (Table 5, entries 1, 4, 5, 15, 16, 18, 21, 24, and 25) or $MeNH_2$ (or $EtNH_2$), and no matter if the carbonyl compounds were aldehydes (entries 1-17) or ketone (Table 5, entries 18-25). These findings indicated

that the multi-component reactions precede smoothly using *β*-cyclodextrine-SO_3H as catalyst in aqueous media. In addition, several reaction (Table 5, entries 2, 8, and 21) were selected randomly to examine the recyclability of the catalyst system, the results indicated that the catalyst system can be recycled for several times.

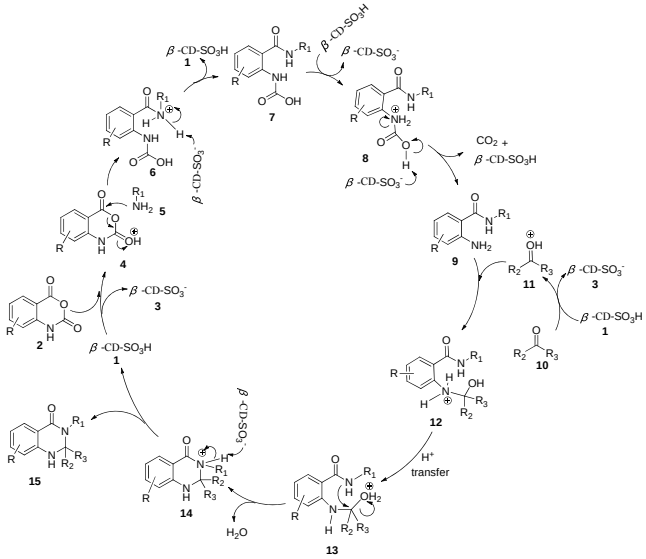
Table 5. *β*-cyclodextrine-SO_3H catalyzed synthesis of 2,3-dihydroquinazolin-4(1H)-one. [a]



Entry	R[b]	R_1 or NH_4OAc	R_2	R_3	Yield (%)[c]
1	H	NH_4OAc	H	$-C_6H_5$	90
2	8-Me	Et	H	$-C_6H_5$	88, 87, 84, 84[d]
3	7-Cl	Me	H	$-C_6H_5$	86
4	7-Cl	NH_4OAc	H	$-C_6H_5$	89
5	7-Cl	NH_4OAc	H	furan-2-yl	90
6	H	Et	H	furan-2-yl	89
7	8-Me	Me	H	furan-2-yl	84
8	8-Me	Et	H	furan-2-yl	85, 84, 83, 81[d]
9	8-Me-6-Cl	Me	H	furan-2-yl	86
10	8-Me-6-Cl	Et	H	furan-2-yl	87
11	7-Cl	Me	H	furan-2-yl	88
12	7-Cl	Me	H	2-Cl-6-F-C_6H_3	90
13	8-Me	Me	H	3-MeO-C_6H_4	85
14	7-Cl	Me	H	4-F_3O-C_6H_4	86
15	7-Cl	NH_4OAc	H	3-MeO-C_6H_4	89
16	7-Cl	NH_4OAc	H	4-F_3O-C_6H_4	89
17	7-Cl	Me	H	3-MeO-C_6H_4	85
18	H	NH_4OAc	Me	Et	88
19	8-Me	Me	Me	Et	87
20	7-Cl	Me	Me	Et	89
21	H	NH_4OAc	$-CH_2CH_2CH_2CH_2CH_2-$		86, 86, 83, 84[d]
22	8-Me	Me	$-CH_2CH_2CH_2CH_2CH_2-$		85
23	8-Me	Et	$-CH_2CH_2CH_2CH_2CH_2-$		85
24	H	NH_4OAc	$-CH_2CH_2CH_2CH_2-$		89
25	7-Cl	NH_4OAc	$-CH_2CH_2CH_2CH_2-$		88

[a] All the reactions were carried out with isatoic anhydride (1 mmol), furaldehyde (1 mmol), Amine (1.2 mmol), and water (10 mL); [b] The position of the R is referring to the structure of 2,3-dihydroquinazolin-4(1*H*)-one derivatives; [b] Isolated yields; [c] Catalyst system was recycled for three runs.

Some possible mechanisms for preparation of 2,3-dihydroquinazolin-4(1*H*)-ones from substituted-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (three component one-pot reaction) or substituted-2-aminobenzamide had been reported before[15, 18, 22]. According to experimental observation and also other mechanisms reported in the literatures[15], a plausible mechanism of the reaction is proposed as shown in **Scheme 3**. Firstly, the substituted-1*H*-benzo[*d*][1,3]oxazine-2,4-dione (**1**) was activated by *β*-cyclodextrine-SO_3H (**2**) to give an intermediate (**4**), then the carbonyl unit of the intermediate (**3**) was attacked by *N*-nucleophilic amine (**5**) to produce an intermediate (**6**), which in turn affords an intermediate (**7**). Then intermediate (**8**) was formed in the presence of *β*-cyclodextrine-SO_3H, and subsitituted-2-aminobenzamide (**9**) was formed through decarboxylation of **8**. Simultaneously, aldehydes (or ketones) (**10**) were activated by *β*-cyclodextrine-SO_3H to give intermediate (**11**). Subsequently, the reaction of intermediate (**11**) with **9** proceeds to resulting in formation of intermediate (**12**). Then proton transfer of **12** lead to intermediate (**13**). Finally, intermediate (**14**) was formed by a ring closure via dehydration, which in turn affords the target product (**15**).



Scheme 3. A possible mechanism for the formation of 2,3-dihydroquinazolin-4(1*H*)-one derivatives

Conclusions

In this work, we have described a successful strategy for the efficient and convenient proration of substituted 2,3-dihydroquinazolin-4(1*H*)-ones using *β*-cyclodextrine-SO_3H as catalyst in water by ring closure of substituted 2-aminobenzamide with aldehydes (or ketone) and the multi-component one-pot condensation of isatoic anhydride with amines and aldehydes (or ketone). It was suggested that *β*-cyclodextrine-SO_3H shows high catalytic activity. Moreover, the catalyst can be readily recovered and reused for at least three runs without any significant impact on the yield of the products, most important of all, the catalyst could be reused directly by using the filtrate as the next reaction without any treatment. The current strategy offers several advantages such as high yields and purity of products, low amount of catalyst, safe, cheap and environmentally benign solvent and an easy experimental workup procedure. Furthermore, we are trying our best to develop more reaction by using *β*-cyclodextrine-SO_3H as a catalyst in an environmental way, and the related work is underway in our laboratory.

Experimental section

General methods

Unless otherwise stated, all the reagents and reactants were purchased from commercial suppliers; melting points were uncorrected and determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China). The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL ECX 500 NMR spectrometer (JEOL Ltd., Japan) at room temperature operating at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR by using $CDCl_3$ or DMSO as solvents and TMS as an internal standard; infrared spectra were recorded in KBr on a IR Pristige-21 spectrometer (Shimadzu corporation, Japan); Mass spectra were measured on a Agilent 6890/5973 Inert (Agilent corporation, American). Elemental analysis was performed on an Elemental Vario-III CHN analyzer

(Elementar, German). The course of the reactions was monitored by TLC; analytical TLC was performed on silica gel GF 254.

Preparation of *β*-cyclodextrine-SO_3H: [36]

To a well stirred mixture of *β*-cyclodextrine (10.0 g, 4.5 mmol) in CH_2Cl_2 (50 mL), chlorosulfonic acid (2.00 g, 10 mmol) was added slowly at 0 °C during 3 h. The resulted mixture was stirred for another 2 h to remove HCl from reaction vessel. Then, the mixture was filtered and washed with methanol (50 mL) and dried at room temperature to obtain sulfonated *β*-cyclodextrine as white powder (10.56 g). The $-SO_3H$ content was measured by titration method and showed 0.52 mequiv./g.[36]

General procedure for the preparation of 2, 3-Dihydroquin- azolin-4(1*H*)-ones

The method of ring closure reaction: To a solution of *β*-cyclodextrine-SO_3H (0.1 mmol) in H_2O (10 mL), substituted 2-aminobenzamide (1 mmol) was added and stirred for 5 min at room temperature, then aldehyde/ keton (1 mmol) was added. The resulted solution was stirred under room temperature (or 50 °C) for 25 min. After completion of the reaction, the precipitated product was filtered, and recrystallized from EtOH. The catalyst *β*-cyclodextrine-SO_3H remain in filter liquor could be used directly as a catalyst media for next runs.

The method of one-pot three-component condensation: To a solution of *β*-cyclodextrine-SO_3H (0.15 mmol) in 10 mL H_2O, The amine (1.2 mmol) and substituted isatoic anhydride (1 mmol) were added, respectively. After 5 min later, aldehyde/ keton (1 mmol) was slowly added. The resulted solution was heated under 80 °C for 30 min. After completion of the reaction, the precipitated product was filtered, and recrystallized from EtOH. The catalyst *β*-cyclodextrine-SO_3H remain in filter liquor could be used directly as a catalyst media for next runs.

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Notes and references

[a] *Research and Development Center for Fine Chemicals, Guizhou University, Guiyang, People's Republic of China, 550025. Fax/Tel: +86-851-8292090; E-mails: wujian2691@126.com and basong@gzu.edu.cn . Homepage: http://fcc.gzu.edu.cn*

[b] *State Key Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Guiyang, People's Republic of China, 550025.; Fax/Tel: +86-851-8292090; E-mails: wujian2691@126.com and basong@gzu.edu.cn*

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