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# Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones from anthranilamide and ketones over Hβ zeolite in aqueous media*

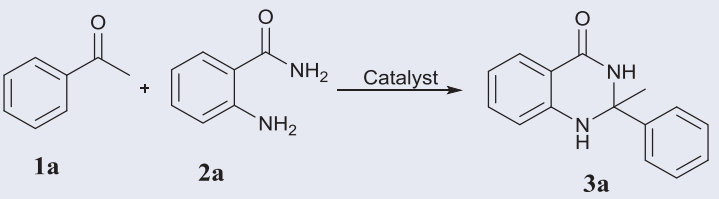
Krishna Sai Gajula[a,b], Naresh Mameda[a,b], Srujana Kodumuri[a], Durgaiah Chevella[a], Rammurthy Banothu[a,b], Vasu Amrutham[a,b], Boris Ivanovich Kutepov[c], and Narender Nama[a,b]

[a]C&FC Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana, India; [b]Academy of Scientific and Innovative Research, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana, India[c]IPC RAS, Oktyabrya, Russian Federation Ufa

**ABSTRACT**

The synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones by cyclocondensation of anthranilamide with ketones in aqueous media using H$\beta$ zeolite is reported. The scope of the reaction was explored by various ketones such as aromatic, aliphatic and cyclic ketones. Based on the preliminary mechanistic results, a tentative mechanism for the formation of 2,3-dihydroquinazolin-4(1*H*)-ones using zeolite catalyst (H$\beta$) is predicted. The reusability study, large-scale experiment and water as solvent showed significant benefits of this catalytic protocol in comparing to earlier methods.

**GRAPHICAL ABSTRACT**

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**KEYWORDS**
Aqueous media; cyclocondensation; 2,3-dihydroquinazolin-4(1H)-ones; ketones; zeolites

## Introduction

The synthesis of nitrogen-containing heterocycles has gained much attention for its chemical, biological, and technical significance.[1–5] Among the various well-known heterocyclic compounds, 2,3-dihydroquinazolin-4(1*H*)-ones are an important class of heterocycles, which show a broad spectrum of biological and pharmaceutical activities

CONTACT Nama Narender nama.iict@gov.in, narendern33@yahoo.co.in C&FC Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, Telangana 500007, India.
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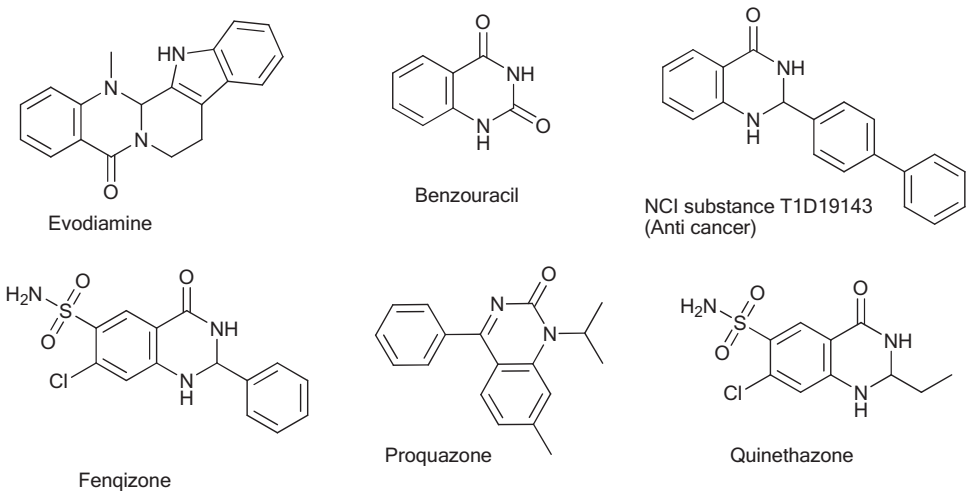
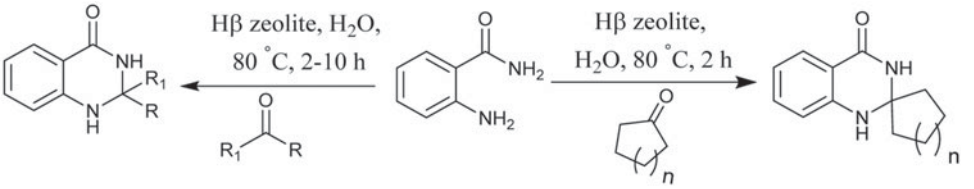



**Figure 1.** Illustrative examples of drugs possessing quinazolinone skeleton.

(Fig. 1).[6–14] Moreover, 2,3-dihydroquinazolinones are key synthetic intermediates for the preparation of biologically active 4(3*H*)-quinazolinones by oxidation, which exhibit many central nervous system effects, cardiovascular and anti-inflammatory activity and act as psychotropic, hypnotic, cardiotonic, and antihistamine agents.[15] Owing to their diverse pharmacological activities and synthetic utility, development of a modest and clean process for the production of 2, 3-dihydroquinazolin-4(1*H*)-ones is still in demand. Numerous strategies for their synthesis have been reported using several catalysts such as $Ga(OTf)_3$,[16] thiamine hydrochloride ($VB_1$),[17] ionic liquid,[18] $KAI(SO_4)_2{\cdot}12H_2O$,[19] ethylenediamine diacetate,[20] $\beta$-Cyclodextrin ($\beta$-CD),[21] nano-$In_2O_3$,[22] CuO nanoparticles,[23] microwave (MW) irradiation,[24] $ZrCl_4$,[25] amberlyst-15,[26] propylphosphonic anhydride,[27] 2-morpholinoethanesulfonic acid,[28] magnetic nanoparticles,[29] $\beta$-Cyclodextrin-$SO_3H$,[30] lactic acid,[31] and dodecylbenzenesulfonic acid.[32] Despite formidable advances, most of the methods suffer from one or more shortcomings, such as using hazardous organic solvents, moisture sensitive catalysts, strongly acidic conditions, high reaction temperatures, and tedious work-up procedures. Moreover, most of the methods limited to aldehydes, ketones have been less investigated. Owing to their diverse pharmacological activities and synthetic utility, the development of a general, green and environmentally benign synthetic protocol for the synthesis of 2,3-dihydroquinazolinones from ketones is highly desirable.

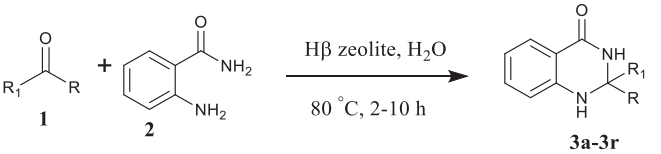
Lately, the development of novel methods that decrease pollution in the chemical industry has established an important consideration because of increasing environmental concerns. In this context, heterogeneous catalysis has seemed like an appropriate tool to reduce the waste production, lower contamination of the products, and recycling of the catalysts.[33–36] Also, pursuing organic reactions in aqueous media under mild conditions is of great importance in modern synthetic chemistry and paves the way to design green, safe, and economically viable processes.

Zeolite materials have a wide range of applications in petroleum and fine chemical industries,[37–40] this is mostly because zeolites have uniform channel size, unique molecular shape selectivity, firm acidity, and thermal/hydrothermal stability. The




**Scheme 1.** The synthesis of 2,3-dihydroquinazolinones from anthranilamide and ketones.

**Table 1.** Optimization for the synthesis of 2-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one from acetophenone and anthranilamide[a]




1 2 3a-3r

R = Aryl / Alkyl R1 = Alkyl

| Entry | Catalyst | Yield 3a (%)[b] |
|---|---|---|
| 1 | H$\beta$ | 75 |
| 2 | NaY | 20 |
| 3 | HZSM-5 (150) | 34 |
| 4 | H-Mordenite | 35 |
| 5 | HY | 41 |
| 6 | Montmorillonite K10 | 23 |
| 7 | HMCM-41 | 29 |
| 8 | Silica | 1 |
| 9 | Silica-alumina | 3 |
| 10 | Absence of catalyst | 00 |
| 11 | H$\beta$ | 77[c] |
| 12 | H$\beta$ | 98[d] |

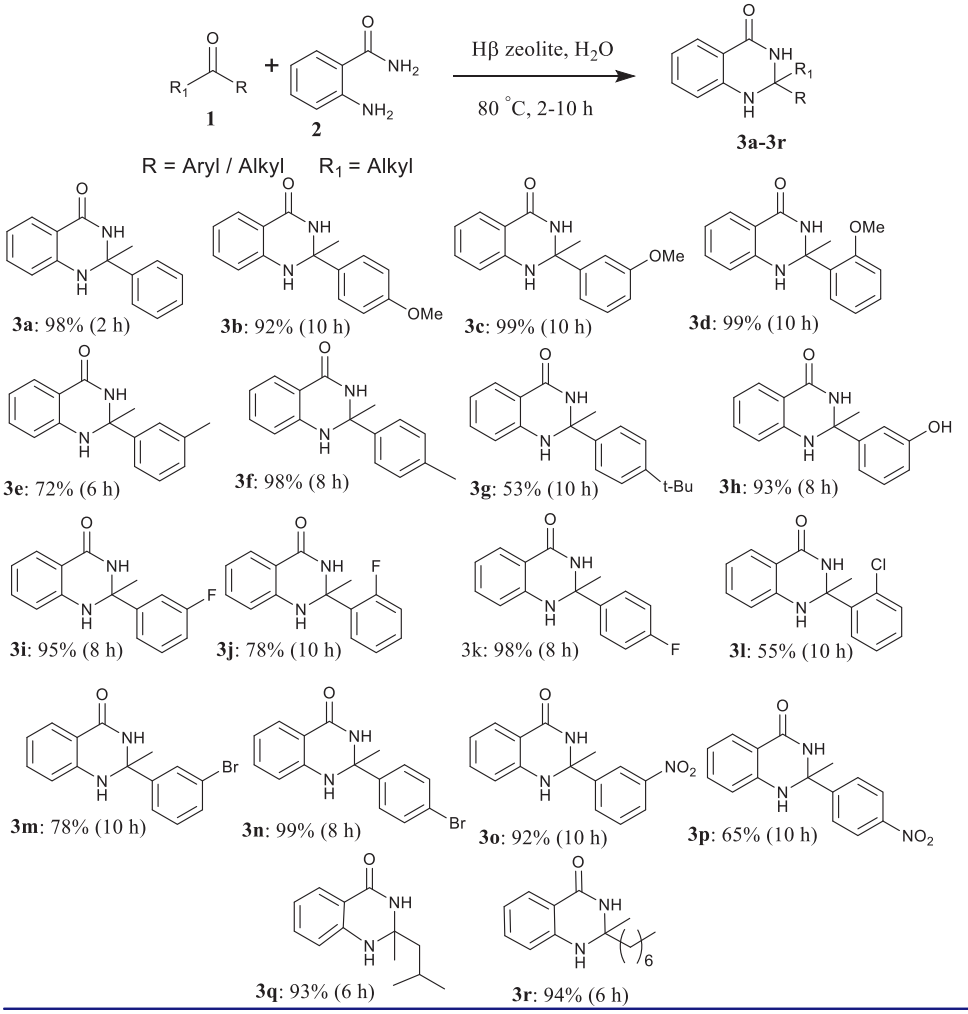
[a]Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), $H_2O$ (1 mL), catalyst (50 mg), 80 °C, 2 h, sealed tube; [b]Isolated yields; [c]100 °C, H$\beta$ (50 mg). [d]H$\beta$ (100 mg).

accessible substantial micropore volume, large-pore channel system and the presence of active sites in different concentrations make the BEA-type of zeolite (zeolite beta) as an alternative and promising candidate for an extensive array of diverse chemical reactions.[41–45] As part of our ongoing research interest to develop eco-friendly synthetic protocols using zeolites and modified zeolites,[46–53] herein we report a simple, green and environmentally benign approach for the synthesis of 2,3-dihydroquinazolinones from anthranilamide and ketones over H$\beta$ zeolite in aqueous media (Scheme 1).

## Results and discussion

The reaction between acetophenone (**1a**) (1 mmol) and anthranilamide (**2a**) (1 mmol) was chosen as a model system to govern the optimal conditions for the synthesis of 2-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (**3a**). The reaction was carried out over zeolites, MCM-41, montmorillonite K10, $SiO_2$ and $SiO_2$-$Al_2O_3$ to find out the best catalyst for this transformation (Table 1, entries 1–9). Among the catalysts examined, H$\beta$ zeolite exhibited the higher catalytic activity and gave the corresponding product (**3a**) in 75% yield that attributed strong acidic sites and unique three-dimensional large

**Table 2.** The scope of the condensation reaction of anthranilamide with various ketones over H$\beta$ zeolite[a].

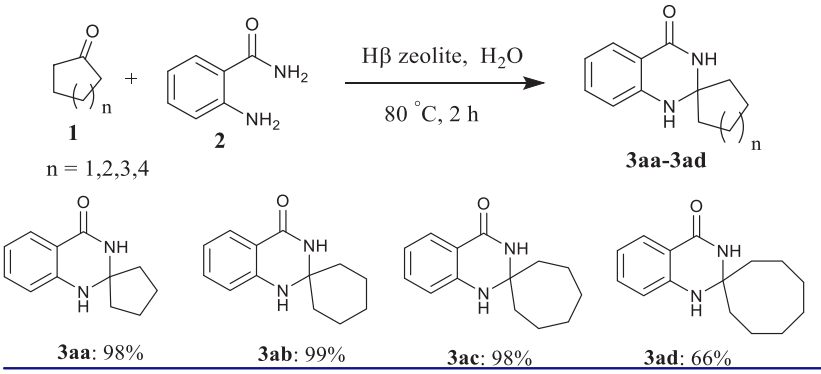



[a]Reaction conditions: **1** (1 mmol), **2** (1 mmol), $H_2O$ (1 mL), H$\beta$ zeolite (100 mg), 80 °C, Isolated yields.

size porous structure of H$\beta$ zeolite catalyst (Table 1, entry 1). The reaction did not proceed in the absence of a catalyst, thus supporting the role of catalyst in the reaction (Table 1, entry 10). Increase in reaction temperature could not help to improve the yield of **3a** (Table 1, entry 11), whereas increasing the amount of H$\beta$ zeolite catalyst (50–100 mg) leads to a higher yield of **3a** (Table 1, entry 12). From Table 1, 100 mg of H$\beta$ was ideal to get the maximum yield of the desired product in $H_2O$ (1 mL) at 80 °C (Table 1, entry 12).

We then motivated our attention on evaluating the scope of the H$\beta$ zeolite-catalyzed strategy by testing the reaction of anthranilamide with various ketones such as aralkyl, acyclic, and cyclic ketones under optimized reaction conditions (Tables 2 and 3). As showed in Tables 2 and 3, all the ketones reacted well with anthranilamide (**2a**) to afford moderate to excellent yields of the corresponding 2,3-dihydro-4(1*H*)-

**Table 3.** The scope of the condensation reaction of cyclic ketones with anthranilamide over H$\beta$ zeolite[a].



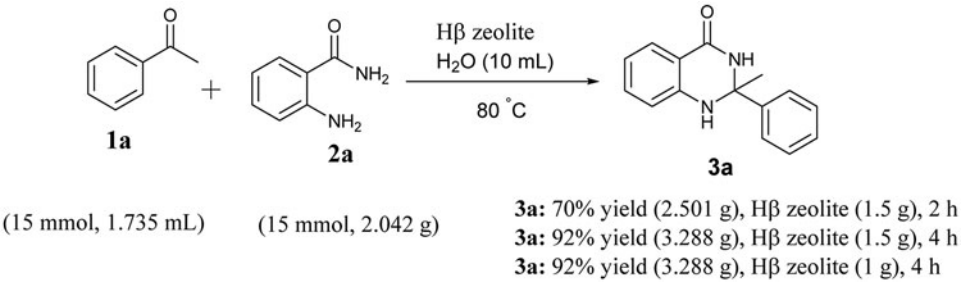

[a]Reaction conditions: 1 (1 mmol), 2 (1 mmol), $H_2O$ (1 mL), H$\beta$ zeolite (100 mg), 80 °C, 2 h, Isolated yields.

quinazolinone products. To find out the effect of substitution on the aromatic ring of acetophenone on the reaction path with this catalytic system, considered the condensation reaction with different substitutions. Activating groups present on the aromatic ring of acetophenone were efficiently transformed into the respective 2,3-dihydro-4(1*H*)-quinazolinone derivatives in 53–99% yields (Table 2, **3b**–**3h**). However, the bulky alkyl group-substituted acetophenone exhibited lower activity and presented the corresponding product in 53% yield (Table 2, **3g**). A highly deactivating group bearing acetophenones and halo-substituted acetophenones also participated well in this reaction to provide the desired products in 55–99% yields (Table 2, **3i**-**3p**). It is noteworthy that acetophenone having the same substituent at different positions on the phenyl ring had an influence on the reaction yield (Table 2, **3e**, **3f, 3i**, **3j, 3k, 3m**, 3n, 3o, **and 3p**). Next, performing the reaction with acyclic ketones and furnished the respective products in 93% and 94% yields, respectively (Table 2, **3q** and **3r**).

Finally, we investigated the effectiveness of this present catalytic system with cyclic ketones such as cyclopentanone, cyclohexanone, cycloheptanone, and cyclooctanone (Table 3). The outcome indicates that cyclic ketones efficiently underwent the reaction with anthranilamide and the corresponding 2,3-dihydro-4(1*H*)-quinazolinones products were obtained in excellent yields (Table 3, **3aa-3ad)**.

To illustrate the practical usefulness of this catalytic protocol, we have performed the reaction at gram scale process under the optimized conditions and the corresponding 2,3-dihydro-4(1*H*)-quinazolinone product **3a** was isolated in 70% yield (Scheme 2). It shows that there was a deviation in the yield of the respective product when compared to the small-scale reaction. However, a higher yield (92%) of **3a** was obtained with 1 g (or 1.5 g) of catalyst in 4 h.

To prove the potential recycling ability of H$\beta$ by performing the cyclocondensation reaction with acetophenone (**1a**) and anthranilamide (**2a**) under similar reaction conditions. After the reaction, the catalyst (H$\beta$) was easily separated from the reaction mixture by filtration, and the recovered catalyst was calcined at 450 °C to use in the next cycle. A similar protocol was maintained for other cycles, and no noticeable loss of catalytic activity was detected even after five cycles (Fig. S1, See in ESI). The XRD analysis suggests that catalyst was crystalline before and after the reaction (Fig. S2, See in ESI).




**Scheme 2.** Large-scale experiment for the synthesis of 2-methyl-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one from anthranilamide and acetophenone.

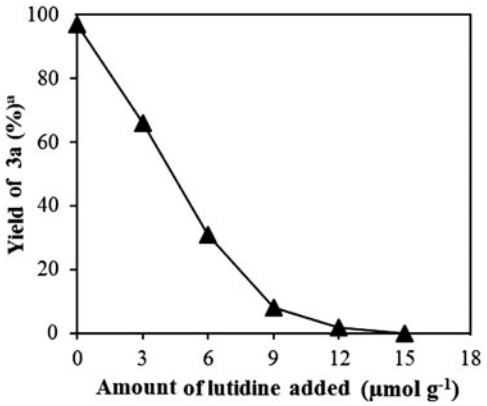
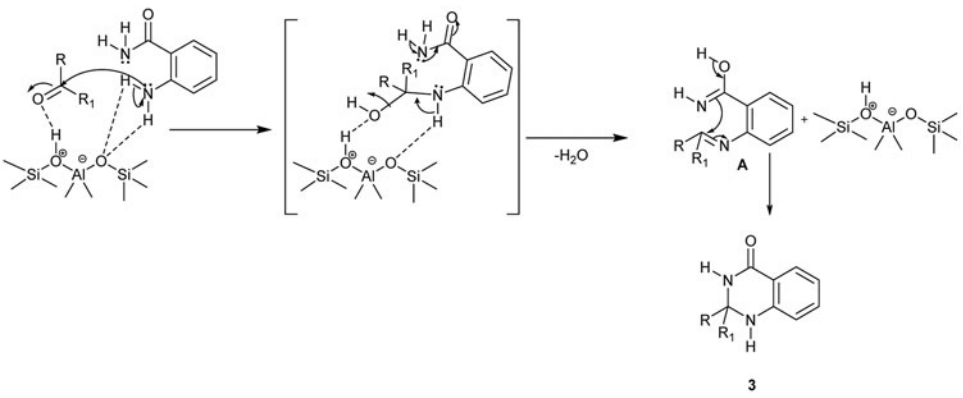



**Figure 2.** The dependence of the reaction yield of **3a** on the amount of 2,6-lutidine added to the H$\beta$-catalyzed cyclocondensation reaction between **1a** and **2a**. Reaction conditions: **1a** (1 mmol), **2a** (1 mmol), $H_2O$ (1 mL), H$\beta$ (100 mg), 80 °C, 2 h, 2,6-Lutidine (X μmol $g^{-1}$), sealed tube. [a]Isolated yields.

There was no leaching of aluminum or silicon from zeolite (H$\beta$) was observed by elemental analysis.

It is a well-known fact that apart from Bronsted acidity, there could be Lewis acidity exists in H$\beta$ zeolite. It is known that 2,6-lutidine selectively interacts with Br⊘nsted acid sites instead of Lewis acid sites due to the steric hindrance caused by its methyl groups.[54] The model reaction was performed under optimized condition by the addition of various amounts of 2,6-lutidine to elucidate the nature of the active sites for the cyclocondensation reaction. As can be seen in Figure 2, the yield of **3a** was gradually reduced by 2,6-lutidine and no yield of **3a** was observed over the 12 $\mu molg^{-1}$ addition of 2,6-lutidine to the reaction mixture. This observation revealed that the condensation reaction is mainly promoted by the Br⊘nsted acid sites of the H$\beta$ catalyst.

Based on the above observation study, a tentative reaction mechanism for the formation of 2,3-dihydroquinazolin-4(1*H*)-ones from anthranilamide and ketones over H$\beta$ is outlined in Scheme 3. It is hypothesized that the reaction is initiated by adsorption of ketone on the acid sites of H$\beta$ zeolite (Bronsted acid sites activates the carbonyl group of the ketone, and weak conjugate base [framework oxygen] activates the amine group of the anthranilamide), which subsequently reacts with anthranilamide (**2a**) to provide the intermediate (**A**) after loss of a water molecule. Then, an intramolecular




**Scheme 3.** The plausible reaction mechanism for the formation of 2,3-dihydroquinazolin-4(1*H*)-ones over H$\beta$ zeolite.

nucleophilic attack of intermediate (**A**), followed by 1,5-hydrogen shift yields the 2,3-dihydroquinazolin-4(1*H*)-ones (**3**).

## Experimental section

### General information

All chemicals were obtained and used as received from Sigma–Aldrich. The H$\beta$ zeolite (Si/Al = 12.5) was acquired from Alfa Aesar, England. $^1$HNMR spectra were recorded at 300, 400, or 500 MHz and 13CNMR spectra at 100 or 125 MHz in $CDCl_3$. The chemical shifts ($\delta$) are described in ppm units relative to TMS as an internal standard for $^1$HNMR and $CDCl_3$ for 13CNMR spectra. Coupling constants ($J$) are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), br s (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). The mass spectrometric analysis was performed by using high-resolution Q-TOF Mass Spectrometer. The GC analysis was carried out using GC Shimadzu (GC-2014) gas chromatograph equipped with FID detector and capillary column (EB-5, length 30 m, inner diameter 0.25 mm, film 0.25 mm). TLC inspections were carried out on Silica gel 60 $F_{254}$ plates. Column chromatography was performed on silica gel (100–200 mesh) using n-hexane-EtOAc as eluent. The XRD patterns of the zeolites were obtained on a Regaku miniflex X-ray Diffractometer using Ni-filtered CuK$\alpha$ radiation at $2\theta = 2$–$80^\circ$ with a scanning rate of $2^\circ$ min$^{-1}$ and the beam voltage and currents of 30 kV and 15 mA, respectively. ESI-HRMS were performed on Exactive orbitrap (Thermo scientific), mass accuracy $<1$ ppm.

### General procedure

H$\beta$ zeolite (100 mg) was added to the well-stirred solution of anthranilamide (1 mmol), ketone (1 mmol), and water (1 mL) in a 15 mL sealed tube and the reaction mixture was allowed to stir at 80 °C. After the disappearance of the anthranilamide (monitored by TLC) or after an appropriate time, the reaction mixture was cooled to room

temperature and diluted with ethyl acetate ($3 \times 10$ mL). Simple filtration separated the catalyst (H$\beta$ zeolite), and the removal of solvent in vacuo yielded crude. The crude was purified by column chromatography using silica gel (100–200 mesh) to afford pure products and these identified based on $^1$H, 13C NMR, and mass spectral data.

## Conclusions

In summary, a green and straightforward method for the synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones involving the condensation of anthranilamide with ketones over H$\beta$ zeolite in aqueous media was successfully developed. Broad substrate scope, water as a solvent, use of non-hazardous and reusable catalysts, higher yields of the desired products, and simple workup procedures are prominent advantages of this catalytic strategy. These findings highlight the potential of this protocol as an inexpensive and environmentally benign method.

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