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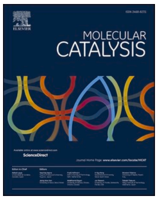

Heterocyclic reaction inducted by Brønsted–Lewis dual acidic Hf-MOF under microwave irradiation

Linh Ho Thuy Nguyen [a,b,c], Trang Thi Thu Nguyen [a,c], Minh-Huy Dinh Dang [a,c], Phuong Hoang Tran [b,c,*], Tan Le Hoang Doan [a,c,*]

[a] *Center for Innovative Materials and Architectures (INOMAR), VNU-HCM, Ho Chi Minh City, 721337, Viet Nam*
[b] *Faculty of Chemistry, University of Science, VNU-HCM, Ho Chi Minh City, 721337, Viet Nam*
[c] *Vietnam National University – Ho Chi Minh City (VNU-HCM), Ho Chi Minh City, 721337, Viet Nam*

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ABSTRACT

Use of green chemistry and alternative strategies has been explored to prepare diverse organic derivatives. The combination between heterogeneous catalyst, environmentally benign reaction and high-yielding methods is gaining momentum. Herein, a defective 6-connected Hf-MOF, named Hf-BTC, was efficiently synthesized and characterized for the heterogeneous catalysis under microwave irradiation. The MOF features including structural defect, porosity, acidity, and stability was analyzed by powder X-ray diffraction, N_2 sorption isotherms, acid-base titration, and thermal gravimetric analysis. In the catalytic studies, the Brønsted-Lewis dual acidic Hf-BTC was efficiently applied for the synthesis of the heterocyclic compounds via the microwave-assisted cycloaddition and condensation reactions. The reactions proceeded smoothly in the presence of the Hf-MOF with a broad scope of substrates provided the expected products in high to excellent yields (up to 99 %) for few minutes and the catalyst could be easily recycle over many consecutive reactions without loss of its reactivity and structure.

Introduction

Aromatic heterocyclic rings containing nitrogen, including benzoxazole, benzimidazole, benzothiazole, quinazolinone, and their derivatives are an important class of heterocyclic compounds due to biological and pharmaceutical activities [1]. These compounds are also valuable precursors for the synthesis of various commercial drugs [2–4]. Traditionally, these compounds could be prepared via the reactions of 2-aminophenol, *o*-phenylenediamine, 2-aminothiophenol and anthranilamide with arylating reagents, for examples aldehydes, ketone, or carboxylic acid derivatives in the presence of acidic catalysts [5–8]. Although the synthesis could be effective in the catalysis of Brønsted or Lewis acids, such as ionic liquids [9], zeolites [10], resin [11], and halogen salts [12], the several drawbacks including large amounts of the catalysts, difficulty in recycling the catalysts, toxic and corrosive reactants, and a large amount of wastes from organic solvents and additives need to be overcome [13]. Besides that, the development of new methods for the synthesis of nitrogen-containing heterocycles is still a focus of intense and containing the interest in the organic chemistry, as well as in pharmaceutical and agrochemical chemistry [14]. The convenient and economic way to synthesize these heterocyclic classes by using microwave irradiation would be beneficial for improved product yields and reduction of reaction time as compared to those observed for the synthesis under conventional heating [15–18].

Metal-organic frameworks (MOFs), constructed by metal-connecting nodes and polydentate bridging linker, have attracted much attention of the scientific community for the past decades [19]. With many outstanding features such as large pores, thermal and chemical stability, and ease of tailoring the original material structure as well as post-synthesis on MOF materials, MOFs can be used for many applications such as adsorption and gas separation [20,21] catalysis [22–31], sensors [32–35], nanocarriers [36,37], electrochemical [33,38], and environmental treatment [39–41]. The water-stable MOFs, for examples Zr- and Hf- based MOFs, with structural stability at high temperature and in water at a wide range of pH have been good candidates for catalyst [23,42,43]. Moreover, these MOFs consist of Zr_6-octahedra capped with by μ_3-O and μ_3–OH groups which can attribute as the Brønsted acid catalytic sites in their structure [14,44,45]. Among them,

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* Corresponding authors.
E-mail addresses: thphuong@hcmus.edu.vn (P.H. Tran), dlhtan@inomar.edu.vn (T.L.H. Doan).

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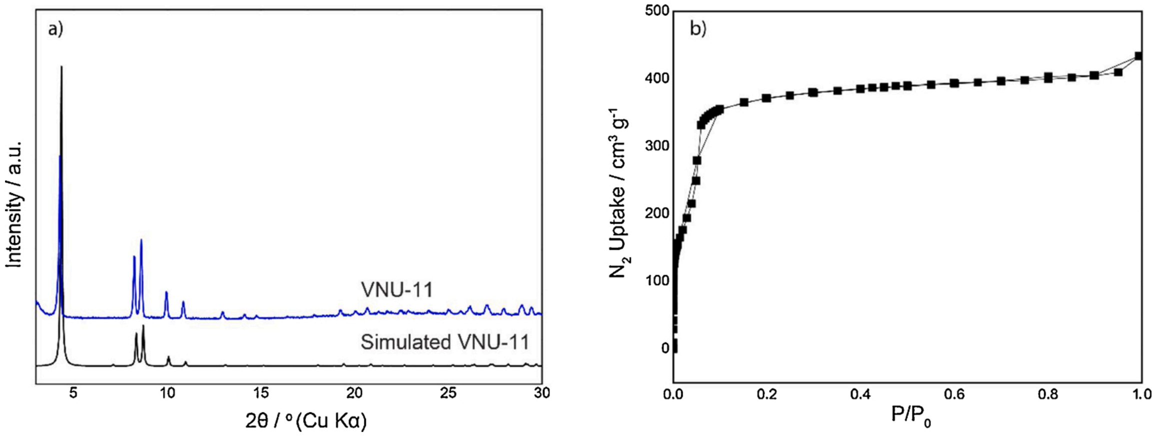


Fig. 1. a) PXRD patterns of Hf-BTC, simulated and activated. b) N_2 isotherms of Hf-BTC (The filled and opened symbols represent the adsorption and desorption processes respectively).

Hf-BTC is a defect MOF, constructed from $Hf_6(\mu_3\text{-}O)_4(\mu_3{-}OH)_4\text{-}(HCOO)_6$ clusters and tricarboxylate linkers (BTC^{3-}), which have OH groups and formic acid on Hf cluster to play an active sites for catalysis [17,46–49].

This work deals with the synthesis of 2-substituted benzoxazoles, benzimidazoles, benzothiazoles, quinazolinone derivatives through the reaction of *o*-amino aromatics coupled with different arylating reagent employing a Hf-MOF, named Hf-BYC, as an efficient Brønsted and Lewis dual acidic catalyst under microwave irradiation and solvent-free conditions. The MOF could be recycled and reused several times without significant decrease operation of catalyst.

Experimental

Materials

All materials and reagents were purchased from Merck and Acros Company and used without further purification. UiO-66 (Zr, Hf), Zr-BTC were prepared based on previously reported method [47,50].

General methods

Gas chromatography-mass spectrometry measurements were carried out on an Agilent GC System 7890 equipped with a mass selective detector (Agilent 5973 N) and a capillary DB-5MS column (30 m × 250 μm × 0.25 μm). Analytical thin-layer chromatography (TLC) was performed on F-254 silica gel coated aluminum plates from Merck. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance II 500 MHz NMR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded using a D8 Advance diffractometer equipped with a LYNXEYE detector (Bragg–Brentano geometry, Cu Kα radiation $\lambda = 1.54056$ Å). Fourier Transform infrared (FT-IR) spectra were recorded from KBr pellets using a Bruker Vertex 70 system. Thermal gravimetric analysis (TGA) was performed on a TA Q500 thermal analysis system with the sample held in a platinum pan in a continuous airflow. Microwave irradiation was performed on a CEM Discover BenchMate apparatus.

Synthesis and preparation of MOF

Synthesis of Zr-BTC and Hf-BTC were prepared according to methods reported in the literature [51]. An equimolar solution (8.5 mM) of $HfCl_4$ salt (or $ZrCl_4$ salt) and the tricarboxylic acid H_3BTC in 320 mL solvent mixture of DMF and formic acid (v/v = 1:1) in 500-mL capped bottle was heated in an oven at 120 °C for 3 days under static conditions. After cooling the bottle to room temperature, the precipitates were collected by centrifugation. The sample was washed with fresh DMF (3 × 20 mL) for 3 days and dispersed in deionized water (3 × 20 mL). Then, the white solid was immersed in 20 mL of anhydrous acetone for once times, replaced nine successive times in 3 days. Finally, the materials were dried under reduced pressure at room temperature for 24 h and activated at 150 °C for 24 h.

Evaluation of brønsted acidity

The Brønsted acidity of material is defined by potentiometric acid-base titrations protocol [52]. 50 mg of each MOFs were immersed in 60 mL of 0.01 M aqueous $NaNO_3$ in an Erlenmeyer flask with the stopper and allowed to equilibrate in 18 h. Then, 15 mL were withdrawn from each solution and added to each 25 mL titration flask. Using 0.1 M aqueous HCl to adjust the pH of the solution to 3 and then titrating with 0.1 M aqueous NaOH until the pH reach approximately 10. Titration curves were repeated for three times to get an average value.

Typical procedure for the cycloaddition reaction

A mixture of Hf-BTC (1 mol %), anthramide (0,5 mmol) and ketone (0.5 mmol) was heated under microwave irradiation in a CEM Discover apparatus monitored by TLC. After completion of the reaction, the catalyst was filtered from the reaction mixture and extract with ethanol (50 mL). The solvent was removed on a rotary evaporator and the crude product was purity by flash chromatography (90:10 acetone/petroleum ether to give a corresponding product. The purity and identity of the products were confirmed by GC–MS spectra, which were compared with the spectra in the NIST library, and by ^1H and ^{13}C NMR spectroscopy.

Typical procedure for the condensation reaction

A mixture of Hf-BTC (1 mol %), benzoyl chloride (0.140 g, 1 mmol) and an 2-aminophenol (0.119 g, 1 mmol) was heated under microwave irradiation at 120 °C for 15 min in a CEM Discover apparatus monitored by TLC. After completion of the reaction, the catalyst was filtered from the reaction mixture. The filtrate was diluted with ethyl acetate (50 mL), washed with H_2O (3 × 20 mL), aqueous $NaHCO_3$ (2 × 20 mL), and brine (20 mL), and dried over Na_2SO_4. The solvent was removed on a rotary evaporator. The crude product was purified by flash chromatography (90:10 acetone/petroleum ether to give a corresponding product. The purity and identity of the products were confirmed by GC–MS spectra, which were compared with the spectra in the NIST library, and by ^1H and ^{13}C NMR spectroscopy. They were obtained by the same microwave irradiation procedure as that for preparation of 2-aryl substituted benzimidazole and 2-aryl substituted benzothiazole using 1,2-

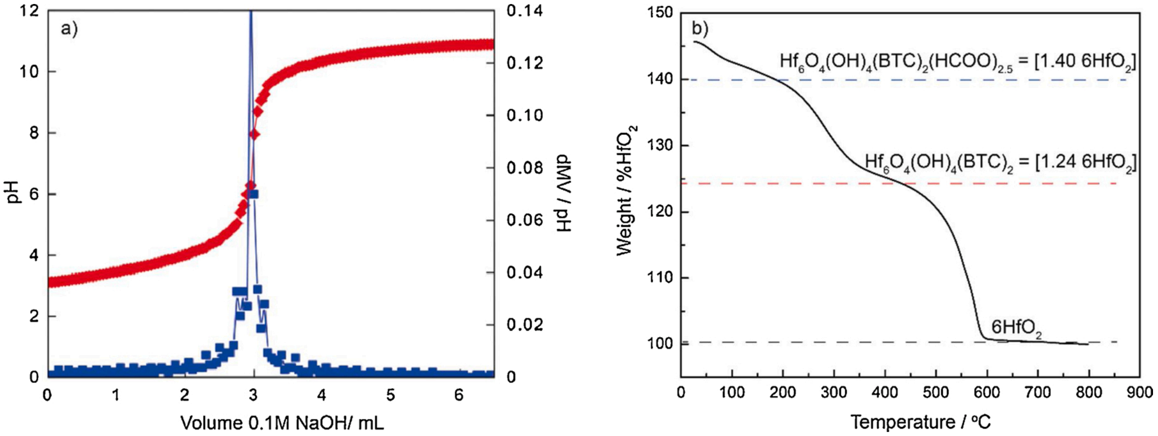


Fig. 2. Acid–base titration curve of Hf-BTC (blue) and first derivative (red). b) TGA curve of activated Hf-BTC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

phenylenediamine (0.108 g, 1 mmol) or 2-aminothiophenol (0.125 g, 1 mmol) instead of 2-aminophenol.

Result and discussion

Catalysts characterization

The Hf-BTC was synthesized from tricarboxylic acid (H_3BTC) and hafnium tetrachloride according to method reported in the literature with the high yield after a simple the purification step [51]. The phase purity of synthesized Hf-BTC was further confirmed by PXRD, TGA, and N_2 isothermal. Powder X-ray diffraction (PXRD) patterns between experimental and the simulated pattern has been recognized in Fig. 1a to show the match well with reported literature [51]. The characteristic peaks of Hf-BTC at 2θ values of 8.3, 8.7, 10.1, 11.0 and 13.1 corresponding to (311), (222), (400), (331), and (511) index planes respectively. N_2 isotherm of Hf-BTC at low relative pressures and 77 K exhibited type1with Brunauer–Emmett–Teller of 1540 m^2/g, a pore volume of 0.13 cm^3/g and an average pore diameter of about 14 Å. (Fig. 1b)

To quantify the defects in Hf-BTC, potentiometric acid-base titration method was performed for Hf-BTC and Zr-BTC as a verification material. Accordingly, the pKa value at 3.67 was recorded by acid-base titration of activated Zr-BTC at distinct equivalent point (5.8) (Fig. S3, Section S2, SI), corresponding with appear representative of MOF with Zr nodes with μ_3−OH proton in the previous report [52]. For Hf-BTC, the pKa value was 3.48 at equivalent calculated point (5.9) (Fig. 2a). Comparing with Zr-BTC, the more flexibility of proton of Hf-μ_3−OH than Zr-μ_3−OH is understood since the coordination between Hf and oxygen is stronger than Zr and oxygen, leading to p*K*a of Hf-BTC is lower than Zr-BTC and Brønsted acidic of Hf-BTC is higher than Zr-BTC. These results opened up the potential of Hf-BTC for catalytic activity in diverse organic reactions.

TGA measurements were carried out for the Hf-BTC sample under air flow and TGA curve was built per 100 % of the residual hafnium oxide (Fig. 2b). Fig. 2b shows two distinct weight loss steps, corresponding to the presence of defect sites ($HCOO^-$) and the decomposition of BTC^{3-} linkers. In the first step (200−300 °C), a weight percentage loss over $6HfO_2$, attributed to formate groups, was lower than the calculated form the crystal structure (1.40 and 1.45 wt % over $6HfO_2$ for the experimental and theoretical, respectively) [45,52]. In the second step above 450 °C, the weight loss over HfO_2, corresponded to the complete decomposition of the linkers, decreased lower than the expected value for the crystal structure (1.24 and 1.28, respectively). It is note that TGA supported for identification the mixing linker and defect sites in the structure.

Table 1
Study of the effect of various catalysts in the solvent-free synthesis of 2,2-diphenyl-2,3-dihydroquinazolinone-4(1*H*)-one.

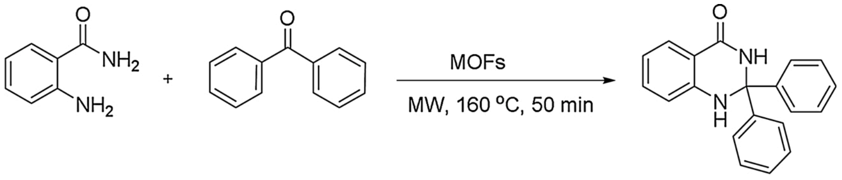
Entry	MOF catalyst	Types of active sites	Average pore size (Å)	GC yield (%)	TOF (h^{-1})
1	None	–		0	0
2	UiO-66 (Zr)	12-connected Zr_6	10.5 [54]	36	1.08
3	UiO-66 (Hf)	12-connected Hf_6	10.5	65	1.95
4	Zr-BTC	6-connected Zr_6	14	85	5.10
5	Hf-BTC	6-connected Hf_6	14	96	5.76

Reaction conditions: anthranilamide (0.5 mmol), benzophenone (0.5 mmol) and the catalyst (0.2 mmol %) were stirred under microwave irradiation without using solvent at 160 °C for 50 min. TOF (turnover frequency) was moles of product formed per mol of catalyst per hour.

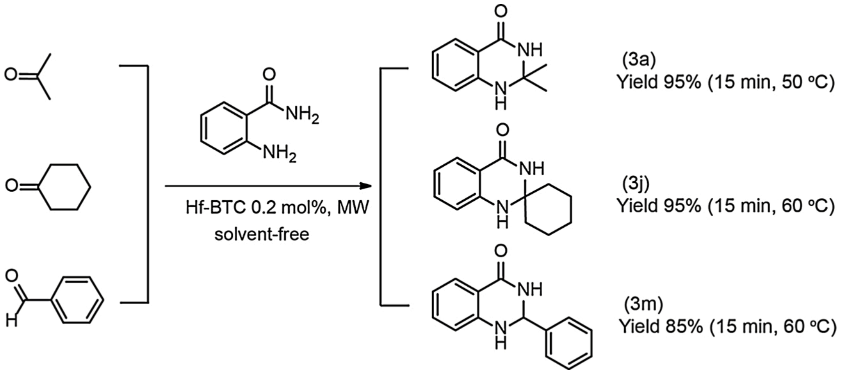
Catalytic performance

Synthesis of cycloaddition reaction

In our previous study, the synthesis 2,3-dihydroquinazolin-4(1*H*)-ones in the presence of UiO-66 catalyst under traditional heating required the reaction time prolonged to 8 h to get the desired product [53]. According to the structural characterization of Hf-BTC, our expectation is using Hf-BTC which higher Brønsted acidity in catalyst and microwave irradiation method for the preparation of this reaction to scale down the reaction time and enhance the yield of the products.

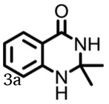
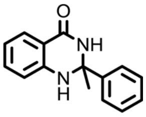
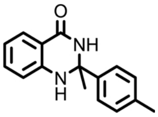
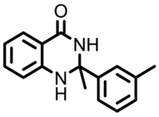
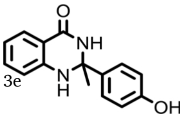
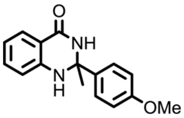
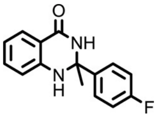
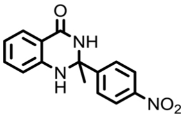
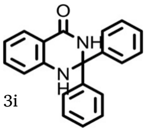
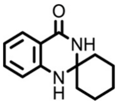
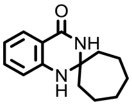
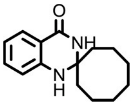


Scheme 1. The cyclization reaction between anthranilamide and benzophenone.



Scheme 2. Catalytic application of Hf-BTC for the preparation of quinazolinone derivatives.

Table 2
GC yields for reaction of the Hf-BTC catalyzed synthesis of various functionalization from the anthranilamide and ketone.

 3a 5 min, 50 °C Yield: 95 % MP (°C): 185−188	 3b 40 min, 60 °C Yield: 96 % MP (°C): 223−188	 3c 50 min, 80 °C Yield: 83 % MP (°C): 167−170	 3d 50 min, 100 °C Yield: 91 % MP (°C): 165−172
 3e 50 min, 50 °C Yield: 75 % MP (°C): 223−225	 3f 50 min, 100 °C Yield: 85 % MP (°C): 165−168	 3g 30 min, 100 °C Yield: 85 % MP (°C): 195−203	 3h 40 min, 80 °C Yield: 93 % MP (°C): 201−204
 3i 50 min, 160 °C Yield: 96 % MP (°C): 208−211	 3j 15 min, 60 °C Yield: 95 % MP (°C): 202−205	 3k 40 min, 80 °C Yield: 92 % MP (°C): 205−207	 3 L 40 min, 60 °C Yield: 70 % MP (°C): 202−205

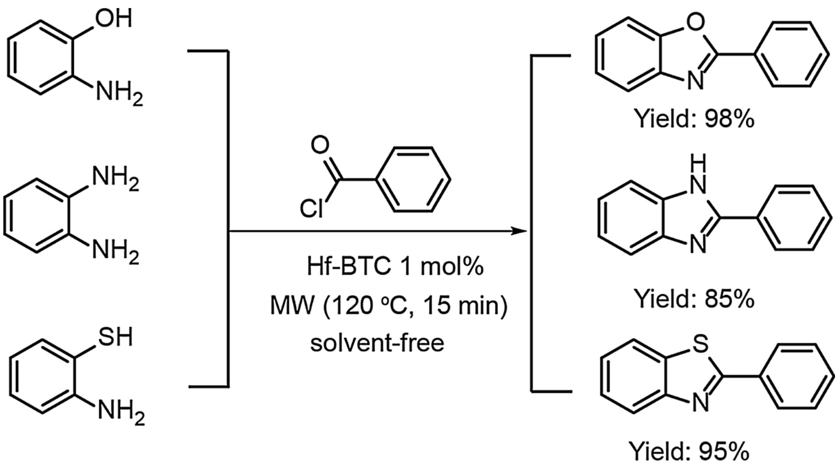
With the goal of evaluating the catalytic behavior of MOF based on the node connectivity, the model reaction between anthranilamide and benzophenone in the catalysis of Zr-, Hf-UiO-66 (12-connected), and Zr-/ Hf-BTC (6-connected) under microwave irradiation and solvent-free at 160 °C for 50 min (Scheme 1) was applied to evaluate the catalytic behavior. As shown in Table 1, a clear distinction was made among the various catalysts in this reaction. The failure in the formation of this product was observed in the absence of the catalyst (Table 1, entry 1). The desired product was achieved with the performance when using Hf-BTC as a heterogeneous catalyst (Table 1, entry 5) while much lower efficiency was observed in the reaction catalyzed by other MOFs (Table 1, entries 2–4). This mainly results from the acidic features of the Hf−OH/Hf−OH_2 facing the pores and the large pore of Hf-BTC which made its catalytically active sites accelerate the cycloaddition reaction [16,45].

Table 3
The comparison of the microwave irradiation method and solvent-free with previous literatures in the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one.

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	H_2SO_4	Few min	68–78	[55, 50]
2	2-morpholinoethanesulfonic acid (MES)	10 min, 60 °C	95	[56, 51]
3	Co-CNTs	59 min, 100 W	50	[57, 52]
4	Amberlyst-15	3 min, 130 °C, 360 W	78	[58, 53]
5	Catalyst free	3 min, 60 °C, 300 W	91	[55, 50]
6	Hf-BTC	15 min, 60 °C, 80 W	85	This work

We next proceeded to evaluate the scope and limitation of Hf-BTC in the cyclization reaction with a variety of ketones and aldehydes (Scheme 2). The investigation results indicated that the best result obtained in two cases ketone such as acetone and cyclohexanone could effort the 2,2-dimethyl-2,3-dihydroquinazolin-4(1*H*)-one and spiroquinazolin-4-(1*H*)-one with excellent yields of 95 %. The effect of the cumbersome structure of cyclohexanone required increasing temperature reaction to 60 °C for a quantitative transformation into expected the yield of spiroquinazolin-4-(1*H*)-one. Similarly, the benzaldehyde has a certain effect on the yields of the desired products. The resonance effect of benzene on carbonyl group lead this carbonyl less reactivity in cycloaddition reaction.

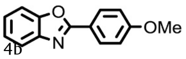
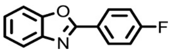
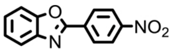
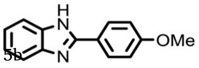
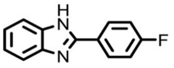
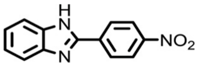
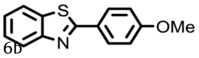
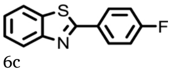
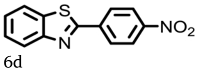
We expanded the reaction scope over many ketones in the formation of quinazolin-4(1*H*)-one. The summarized data in the Table 2 illustrated



Scheme 3. Catalytic application of Hf-BTC for the preparation of 2-phenylbenzoxazole, 2-phenylbenzimidazole and 2-phenylbenzithiazole.

Table 4

GC yields for reaction of the Hf-BTC catalyzed synthesis of various functionalization from the 2-aminophenol, 1,2-phenylenediamine, 2-aminothiophenol and aromatic carbonyl chloride.

 4b Yied: 85 % MP 103–104 (°C)	 4c Yied: 51 % MP 99–100 (°C)	 4d Yied: 30 % MP 156–157 (°C)
 5b Yield: 90 % MP 203–204 (°C)	 5c Yield: 55 % MP 253–254 (°C)	 5d Yield: 62 % MP 234–236 (°C)
 6b Yield: 98 % MP 123–124 (°C)	 6c Yield: 98 % MP 110–111 (°C)	 6d Yield: 95 % MP 206–207 (°C)

Reaction conditions: 2-aminophenol, 1,2-phenylenediamine, or 2-aminothiophenol (1 mmol), aromatic carbonyl chloride (1 mmol) and the catalyst (1 mmol %) were stirred under microwave irradiation without using solvent at 120 °C for 15 min.

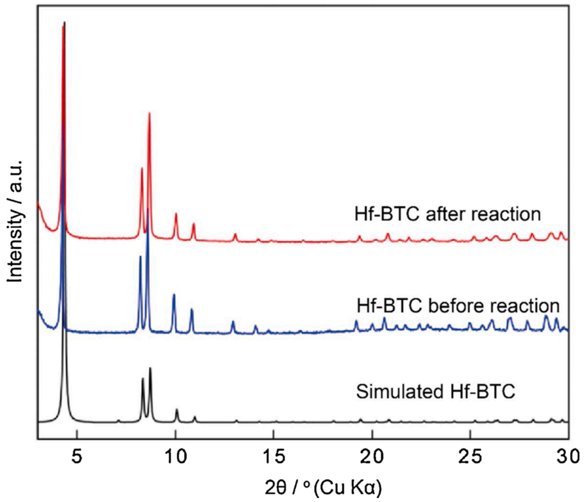


Fig. 3. PXRD patterns of Hf-BTC before (blue) and after (red) 5 consecutive condensation reactions in comparison to the simulated pattern (black). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

that all reactions performed under short time with high reaction yields. Comparing with the traditional heating method, microwave method exhibited as a powerful to enhance catalytic activity of Hf-BTC in the reaction with high yield and short reaction times. Interestingly, the reaction time under microwave irradiation for a few minutes could obtain 2,2-diphenyl-2,3-dihydroquinazolin-4(1*H*)-one whereas using the conventional heating required hours for obtained the same yield of this product.

It is essential to compare our work with previous literature using acidic catalysis. A comparative study of the microwave irradiation method with previous literatures was reported in Table 3, efficiency of Hf-BTC catalyzed condensation between anthranilamide and benzaldehyde afforded the 2,3-dihydroquinazolin-4(1*H*)-one product under of lower temperature and power MWI heating.

Synthesis of condensation reaction

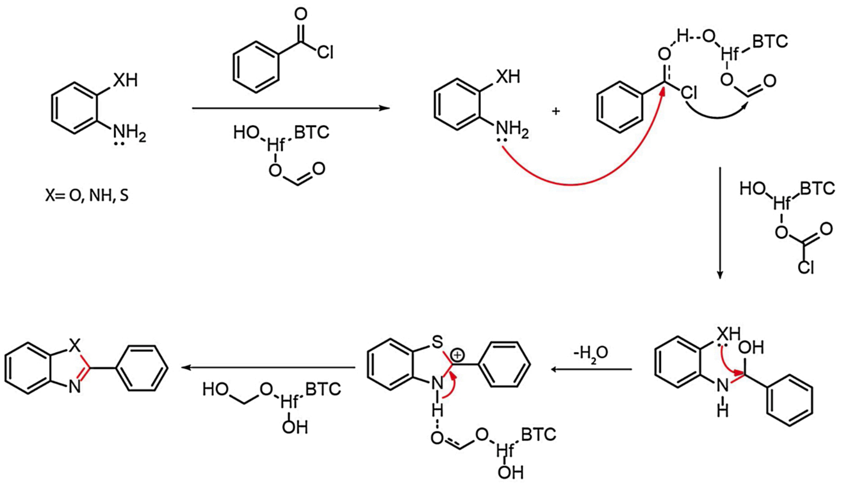
After investigating the catalytic efficiency of Hf-BTC in the cycloaddition reaction, the MOF was used as catalyst for solvent-free preparation of heterocyclic analogues including 2-arylbenzoxazole, 2-arylbenzimidazole, and 2-arylbenzothiazole derivaties through a condensation reaction under microwave irradiation. The effect of important parameters such as amount of catalyst, temperature and solvent free conditions was examined for the model reaction. Under the obtained optimized set of reaction time, the promising results under microwave irradiation and solvent free conditions, at 120 °C in the presence of 1 mol % of Hf-BTC (Scheme 3). The increasing yield of products in this model reaction were 98 %, 95 % and 85 % for 2-phenylbenzoxazole, 2-phenylbenzothiazole and 2-phenylbenzimidazole, respectively. While 2-aminothiophenol was able to undergo the arylation with the same ease as 2-aminophenol, *o*-phenylenediamine transformation maintained in the prolonging reaction time with up to 30 min.

We explored the reaction scope over many aromatic carbonyl chlorides in the formation of 2-arylbenzoxazoles and other analogues (Table 4). In general, a series of 2-substituted benzaldehyde smoothly reacted with 2-aminophenol, 1,2-phenylenediamine, and 2-aminothiophenol provide 2-arylbenzoxazole, 2-arylbenzimidazole and 2-arylbenzothiazole in excellent yields. As a common trend, the reactions between 2-aminothiophenol and aromatic carbonyl derivatives

Table 5

Reusability of Hf-BTC in the synthesis of 2-phenylbenzoxazole.

Run	1	2	3	4	5
Isolated yield (%)	98	97	97	95	95



Scheme 4. Proposed mechanism for the synthesis of 2-aryl benzoxazole, 2-aryl benzimidazole, 2-aryl benzothiazole using Hf-BTC as catalyst.

proceeded smoothly to give the corresponding products in excellent yields. Intuitively, the electronic properties of substituents of benzaldehydes exhibited a little effect on the reaction. Electron-donating group on benzoyl chloride, such as 4-methoxybenzoyl chloride, gave the expected products in excellent yield (85–98 %). Electron-withdrawing groups on benzoyl chloride, such as 4-nitrobenzoyl chloride, was all effectively reactive and provided the corresponding products in good yields. Benzoyl chloride bearing halogen substituents could also react smoothly to attain the expected products in high yields (51–98 %).

The recyclability of Hf-BTC was surveyed on the optimized condensation reaction of a 2-aminophenol and benzoyl chloride. Upon completion of the reaction, the recovered catalyst was easily separated by centrifuging and washing many times with ethyl acetate. The catalyst was collected by filtration, washed with acetone, reactivated under vacuum at 120 °C for 24 h before the reuse for consecutive cycles. PXRD patterns corresponding to the fresh and used Hf-BTC after 5 times were observed without a changed structure (Fig. 3). Furthermore, no loss of catalytic activity in the recycling test of this catalyst is the most prominence of microwave method (Table 5).

According to the literatures and our experiment results, we suggest a mechanism for the formation of 2-arylbenzoxazole, in Scheme 4. The μ3−OH and format groups act both as Brønsted acid and Lewis acid to protonate of the carbonyl oxygen from benzoyl chloride. The intermediate A was formed through the reaction of the amino group on the substrate with activated carbonyl. Then the termination, cyclization and dehydration take place to form the desired product.

Conclusions

A defective Hf-BTC has been successfully synthesized via solvothermal reaction and characterized to define the defective sites and the structural features. The catalytic ability of the MOF in the solvent-free cyclization and condensation reactions for synthesis of heterocyclic compounds was investigated under microwave irradiation. Notably, Hf-BTC exhibited the highly catalytic efficiency in the reactions due to its large pore size and acidic features. The material was proven as an effectively heterogeneous catalyst for the reactions with high yield and selectivity as well as ease of recycling without losing its performance and crystallinity.

CRediT authorship contribution statement

Linh Ho Thuy Nguyen: Investigation, Formal analysis, Writing - original draft. **Trang Thi Thu Nguyen:** Methodology, Formal analysis, Validation. **Minh-Huy Dinh Dang:** Methodology, Formal analysis, Validation. **Phuong Hoang Tran:** Validation, Resources, Supervision, Conceptualization, Methodology, Writing - review & editing, Visualization, Project administration. **Tan Le Hoang Doan:** Validation, Resources, Supervision, Conceptualization, Methodology, Writing - review & editing, Visualization, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111291.

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