Catalysis Letters
https://doi.org/10.1007/s10562-019-02747-1

A New Pathway to 2-Arylbenzoxazoles and 2-Arylbenzothiazoles Via One-Pot Oxidative Cyclization Reactions Under Iron-Organic Framework Catalysis

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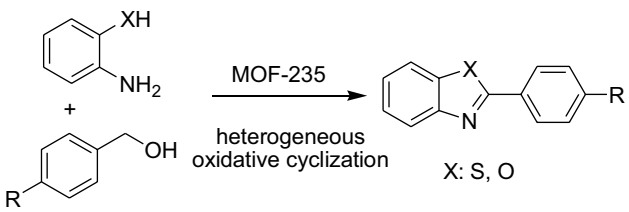
Received: 16 January 2019 / Accepted: 11 March 2019

Abstract
Iron-organic framework MOF-235 was synthesized, and consequently utilized as a productive heterogeneous catalyst for the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via one-pot oxidative cyclization reactions between 2-aminophenols or 2-aminothiophenols and alcohols. The transformation was considerably controlled by the oxidant and the nature of solvent, and the system of di-*tert*-butylperoxide with xylene led to best yield of major products. The MOF-235 catalyst presented higher catalytic efficiency for the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles than a number of MOF-based catalysts and established homogeneous catalysts. Recovering and reutilizing the framework catalyst for the cyclization transformation was possible while its catalytic activity was retained. To the best of our knowledge, this iron-catalyzed one-pot oxidative transformation to produce 2-arylbenzoxazoles and 2-arylbenzothiazoles under heterogeneous catalysis conditions was not previously reported in the literature.

Graphical Abstract



Keywords Iron-organic framework · Benzoxazoles · Benzothiazoles · Heterogeneous catalyst · One-pot

1 Introduction

Benzoxazoles and benzothiazoles are valuable scaffolds, widely occurring in a series of natural products, therapeutically useful compounds, and agrochemicals, as well as in numerous functional polymers [1]. Due to their valuable properties, a variety of synthetic protocols have been investigated for these heterocyclic skeletons [2]. Traditional approaches to achieve benzoxazole and benzothiazole structures included the condensation of 2-aminophenols or 2-aminothiophenols with either aldehydes or carboxylic acids, suffering advantages of severe reaction conditions [2–4]. Rubin and co-workers previously reported a direct *ortho*-C–H functionalization, followed by Beckman

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-019-02747-1) contains supplementary material, which is available to authorized users.

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Published online: 05 April 2019

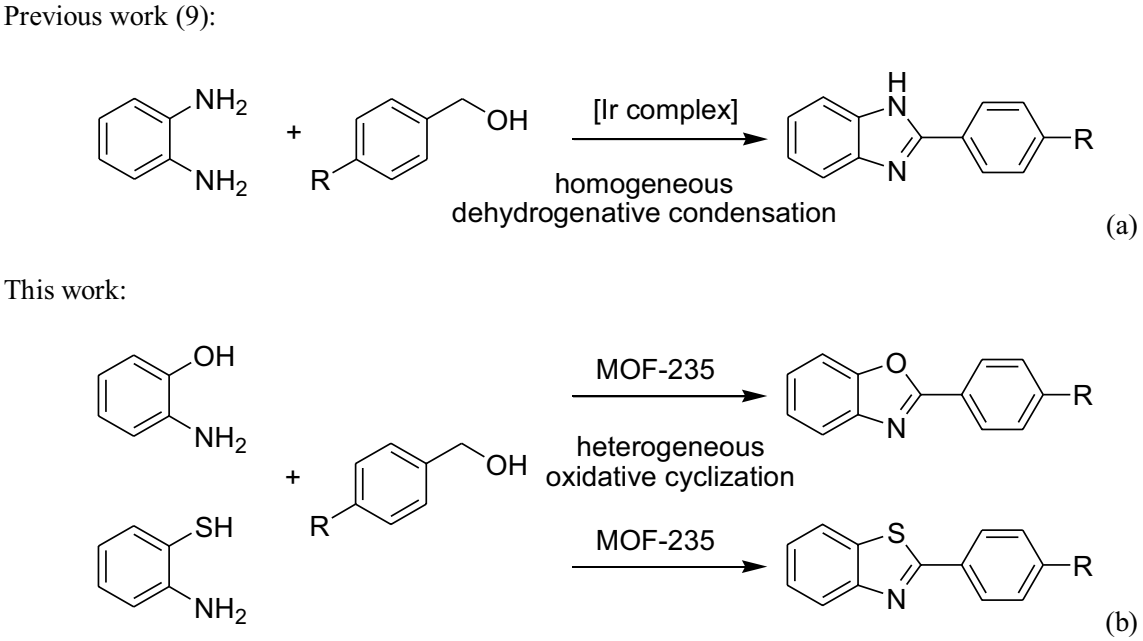
rearrangement and intramolecular cyclocondensation to generate benzoxazoles [5]. Bhanage and co-workers demonstrated a CuCl-catalyzed synthesis of benzoxazoles via a tandem cyclization of 2-halophenols with amidines [6]. Sun and co-workers prepared benzoxazoles and benzothiazoles by using one-pot $Pd(OAc)_2$-catalyzed cyclization reactions between aryl iodides and 2-hydroxyl/mercapto nitrobenzenes [7]. Narender and co-workers synthesized benzothiazoles from the I_2-mediated oxidative cyclization of 2-aminothiophenols with benzylamines [8]. Kempe and co-workers previously demonstrated an efficient approach to obtain benzimidazoles from aromatic diamines and alcohols by iridium complex-catalyzed acceptorless dehydrogenative alkylation (Scheme 1a) [9]. Owing to the significant aspects of these heterocyclic structures, the field needs to be expanded, and heterogeneous catalysts should be targeted.

The discovery of metal–organic frameworks (MOFs), a new family of synthetic crystalline porous materials, has gained appreciable attention during the last 20 years, since these structures present huge opportunities for transforming industrial applications [10–15]. MOFs possess nodes including metal cations or polyvalent metal clusters connected by organic linkers, leading to the generation of numerous frameworks with different architectures and appealing properties [16]. Both the metals and the functionality as well as the length of the organic linkers control the shape and the size of pores, offering massive feasibility to diversify framework structures [17–20]. A long series of MOFs were produced, and many of them have been explored for catalytic applications [21–29]. All metal nodes and functionalities on the organic linkers in the frameworks could serve as active sites, and therefore offering advantages for catalytic transformations [21, 30]. Certainly, a broad series of organic reactions have recently been performed under metal–organic framework catalysis conditions [31–39]. In this work, we wish to report the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via one-pot oxidative cyclization reactions between 2-aminophenols or 2-aminothiophenols and alcohols in the presence of iron-organic framework MOF-235 as a recyclable catalyst (Scheme 1b). To the best of our knowledge, this iron-catalyzed one-pot oxidative transformation to produce 2-arylbenzoxazoles and 2-arylbenzothiazoles under heterogeneous catalysis conditions was not previously reported in the literature.

2 Experimental

2.1 Catalyst Synthesis

The MOF-235 was prepared by utilizing a literature approach [40–42]. In a representative experiment, H_2BDC (H_2BDC = 1,4-benzenedicarboxylic acid; 0.332 g, 2.0 mmol) and $FeCl_3{\cdot}6H_2O$ (0.541 g, 2.0 mmol) were dissolved in a mixture of DMF (DMF = *N*,*N*′-dimethylformamide; 40 mL) and ethanol (40 mL). The mixture was vigorously stirred to obtain a clear solution, and then equally added to eight 20-mL vials. The vials were carefully capped and consequently heated at 85 °C in an oven for 48 h. Light orange crystals were produced on the wall of the vials during the



Scheme 1 The difference between our work and previous work [9]

experiment. After cooling the vial to ambient temperature, the crystals were separated by decantation, and washed thoroughly with DMF (3 × 10 mL). Solvent exchange was consequently conducted with ethanol (3 × 10 mL) at room temperature. The Fe-MOF product was subsequently dried under vacuum at 140 °C for 6 h, obtaining 0.306 g of MOF-235 in the form of brick red crystals (45% based on H_2BDC).

2.2 Catalytic Reactions

In a representative catalytic experiment, benzyl alcohol (0.135 g, 1 mmol), 2-aminophenol (0.204 mL, 2 mmol), and diphenyl ether (0.1 mL) as an internal standard were dissolved in xylene (4 mL). The solution was added into a round bottom flask. The Fe-MOF catalyst with pre-calculated quantity was then introduced to the reactor. The catalyst amount was worked out regarding the iron/ benzyl alcohol molar ratio. The reaction mixture was stirred under magnetic stirring for 5 min to dispense the catalyst in the liquid phase. Subsequently, di-*tert*-butyl peroxide (*t*BuO*O**t*Bu, 0.63 mL, 3 mmol) was added dropwise to the reactor. The mixture was magnetically stirred at 120 °C for 360 min. Samples were taken at different time periods, quenched with NaCl solution (5% w/w, 1 mL). The organic ingredients were afterwards extracted into ethyl acetate phase (3 mL), dried with Na_2SO_4, and analyzed by GC concerning the internal standard. The desired product, 2-phenylbenzo[*d*]oxazole, was isolated by silica gel column chromatography. ^{1}H NMR, ^{13}C NMR, and GC-MS experiments were performed to verify the product structure. To explore the recyclability, the iron-based framework was collected by centrifugation, washed thoroughly with methanol to remove product and excess reagents, heated under vacuum on a Shlenkline at 120 °C for 3 h, and reutilized for new catalytic experiment.

3 Results and Discussion

3.1 Catalyst Characterization

The MOF-235 was prepared from 1,4-benzenedicarboxylic acid and iron(III) chloride by following a literature approach [40, 41]. The material was subsequently characterized using conventional analysis methods such as XRD, SEM, TEM, TGA, FT-IR, AAS, and nitrogen physisorption measurements (Figs. S1–S7 in Supporting information). Sheykhi [41], Yaghi [42] and co-workers previously demonstrated that iron atoms in MOF-235 are in trivalent form. Additionally, it was reported that MOF-235 is constructed from octahedral iron trimers which are connected through linear terephthalic acid linkers, forming high symmetric acs topology [41, 42]. Possessing high content of trivalent iron in the framework, MOF-235 have been utilized as a heterogeneous catalyst for the synthesis of 1,5-benzodiazepines [43], the synthesis of α-acyloxy ethers [44], and the derivatization of indoles [45]. XRD analysis exhibited sharp peaks, indicating that the Fe-MOF was highly crystalline (Fig. S1). SEM observation displayed homogeneity with respect to octahedral crystals (Fig. S2). The TEM image verified that a porous framework was obtained (Fig. S3). Pore size distribution analysis confirmed that the Fe-MOF was microporous (Fig. S4). Langmuir surface areas of 770 m^2/g were recorded, based on nitrogen physisorption measurements (Fig. S5). TGA results indicated that the framework was thermally stable up to over 300 °C (Fig. S6). FT-IR data revealed the presence of carboxylate linkers in the material, being different from those of the 1,4-benzenedicarboxylic acid (Fig. S7).

3.2 Catalytic Studies

The iron-based framework was explored as a heterogeneous catalyst for the one-pot oxidative cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole as the major product (Scheme 1 b). Initially, the impact of temperature on the yield of the principal product was addressed. The reaction was conducted at 5 mol% catalyst in xylene for 360 min, with two equivalents of 2-aminophenol, using 3 equivalents of di-*tert*-butyl peroxide as the oxidant, at room temperature, 80 °C, 100 °C, 120 °C, and 140 °C, respectively (Fig. 1). The cyclization reaction did not proceed at room temperature, with no evidence of the expected product being noticed after 360 min. The transformation performed at 80 °C afforded 21% yield after 360 min. As anticipated, raising the temperature led to a remarkable improvement in the yield of 2-phenylbenzo[*d*]

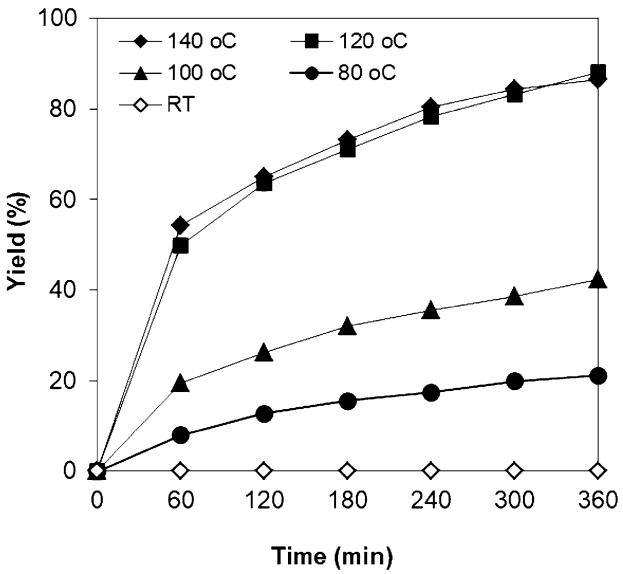


Fig. 1 Yields of 2-phenylbenzo[*d*]oxazole versus temperature

oxazole. Certainly, 42% yield was recorded after 360 min for the experiment executed at 100 °C. Boosting the temperature to 120 °C, the yield of the desired product was upgraded to 88% after 360 min. It was noted that extending the reaction temperature to 140 °C did not intensify the yield considerably, and therefore the catalytic reaction should be performed at 120 °C.

Comparable to other oxidative reactions, the requirement of an oxidant in the catalytic cycle should be inevitable for the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole. Consequently, the impact of diverse oxidants on the yield of the major product was investigated, having employed di-*tert*-butyl peroxide (DTBP), aqueous *tert*-butyl hydroperoxide [TBHP (water)], *tert*-butyl hydroperoxide in decade [TBHP (decade)], cumyl hydroperoxide (CHP), hydrogen peroxide, and potassium peroxodisulfate, respectively, for the transformation (Fig. 2). The reaction was conducted at 120 °C in xylene for 360 min, with 2 equivalents of 2-aminophenol, in the presence of 5 mol% catalyst, using three equivalents of the oxidant. Potassium peroxodisulfate was found to be inappropriate for this transformation, and no evidence of 2-phenylbenzo[*d*]oxazole was detected after 360 min. The reaction using hydrogen peroxide afforded only 15% yield after 360 min, while 24% yield was recorded for that using cumyl hydroperoxide. *Tert*-butyl hydroperoxide displayed better performance, in which using the oxidant in water led to 49% yield after 360 min, and using the one in decane resulted in 70% yield after 360 min. In this series of oxidants, di-*tert*-butyl peroxide emerged to be the best option for the reaction, affording 2-phenylbenzo[*d*]oxazole in 88% yield after 360 min. Additionally, the amount of di-*tert*-butyl peroxide also exhibited a notable impact on the oxidative cyclization reaction (Fig. 3). Best result was achieved when three equivalents of oxidant was utilized. Extending the amount of the oxidant did not improve the reaction yield, while dropping the quantity of the oxidant expressed a negative effect. It was noted that no 2-phenylbenzo[*d*]oxazole was detected in the absence of the oxidant, verifying the requisite of the oxidant for the formation of the benzoxazole.

In numerous organic transformations utilizing heterogeneous catalysts, the solvent might display a remarkable influence on the reaction rate, being subject to the characteristic of the catalyst. Kempe and co-workers previously pointed out that diglyme was the best solvent for the synthesis of benzimidazoles from aromatic diamines and alcohols by iridium complex-catalyzed acceptorless dehydrogenative alkylation [9]. It was accordingly resolute to survey the impact of various solvents on the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole (Fig. 4). The reaction was performed at 120 °C for 360 min, with two equivalents of 2-aminophenol, in the presence of 5 mol% catalyst, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in xylene, mesitylene, benzene, chlorobenzene, toluene, and diglyme, respectively. It should be noted that a pressurized vial reactor was required for solvents with low boiling point. While diglyme was the best solvent for the synthesis of benzimidazoles from aromatic diamines and alcohols [9], it was not appropriate for the formation of 2-phenylbenzo[*d*]oxazole with only 21% yield being noted after 360 min.

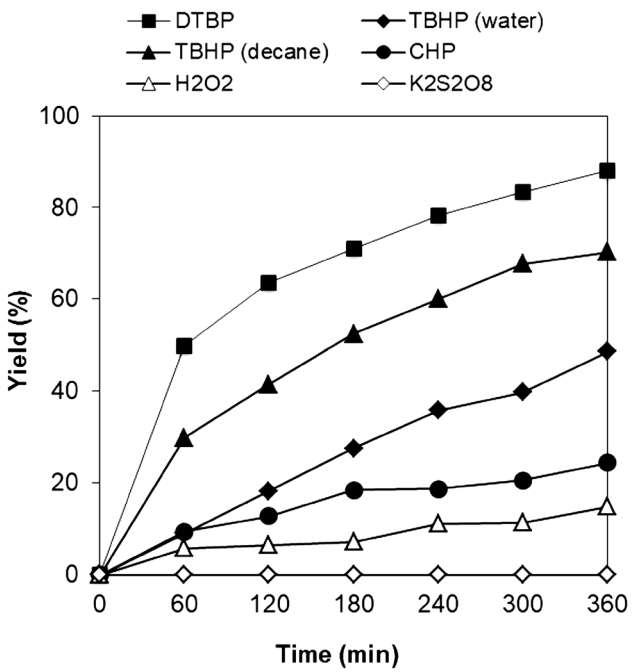


Fig. 2 Yields of 2-phenylbenzo[*d*]oxazole versus oxidant

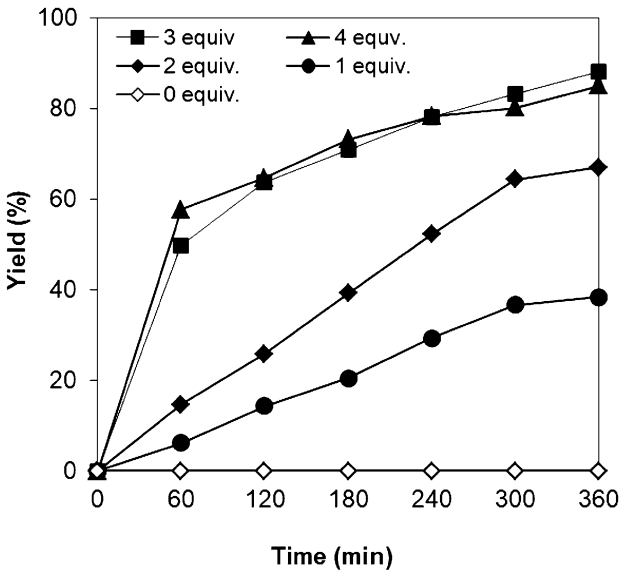


Fig. 3 Yields of 2-phenylbenzo[*d*]oxazole versusoxidant quantity

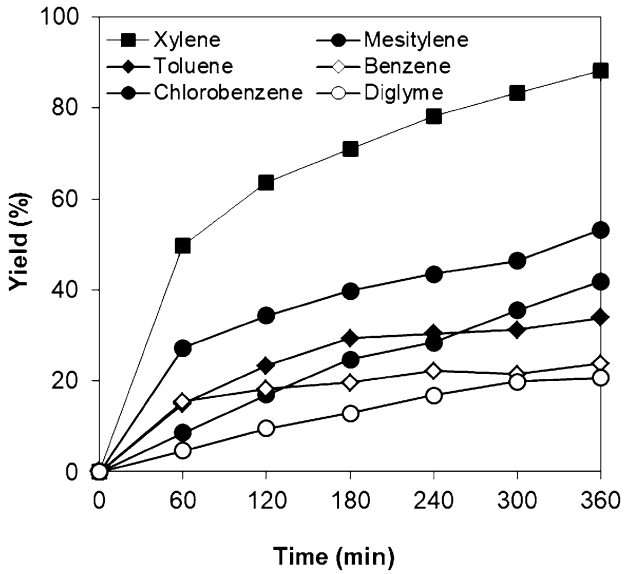


Fig. 4 Yields of 2-phenylbenzo[*d*]oxazole versus solvent

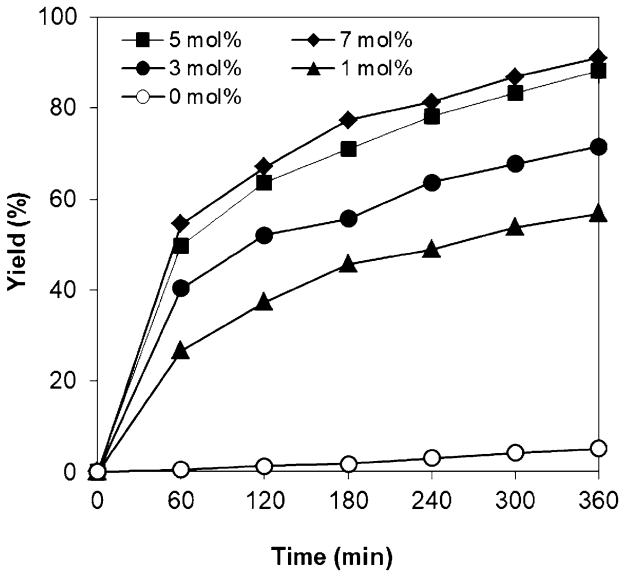


Fig. 5 Yields of 2-phenylbenzo[*d*]oxazole versus catalyst amount

Benzene, toluene, and mesitylene exhibited poor performance, producing the desired product in 24%, 34%, and 42% yields, respectively after 360 min. The cyclization reaction was accelerated when conducted in chlorobenzene, and 53% yield was recorded after 360 min. Among this solvent series, xylene emerged as the best solvent for the synthesis of 2-phenylbenzo[*d*]oxazole via the cyclization transformation, achieving 88% yield after 360 min.

One more factor that must be explored for the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole is the required catalyst amount (Fig. 5). The reaction was conducted in xylene at 120 °C for 360 min, with 2 equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 1 mol%, 3 mol%, 5 mol%, and 7 mol% catalyst, respectively. It was noted that 5% yield of 2-phenylbenzo[*d*]oxazole was recorded after 360 min, verifying that the catalyst was obligatory for the cyclization reaction. The yield of the expected product was substantially accelerated in the presence of the iron-organic framework catalyst. The transformation employing 1 mol% catalyst managed to reach 57% yield after 360 min. Extending the catalyst amount to 3 mol% led to the production of 2-phenylbenzo[*d*]oxazole in 72% yield after 360 min. As previously noted, the reaction continued to 88% yield after 360 min when 5 mol% catalyst was utilized. Expanding the catalyst range to 7 mol% slightly improved the reaction yield to 91% after 360 min. Furthermore, the influence of benzyl acohol:2-aminophenol molar ratio to the generation of 2-phenylbenzo[*d*]oxazole should be considered (Fig. 6). The reaction was implemented in xylene at 120 °C for 360 min, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst, with 1, 1.5, 2, and 2.5 equivalents of 2-aminophenol, respectively. The reaction using 1 equivalent of benzyl alcohol afforded only 43% yield after 360 min, while this value was upgraded to 63% for that employing 1.5 equivalents of benzyl alcohol. Nevertheless, utilizing more than two equivalents of benzyl alcohol did not lead to a remarkable improvement in the yield of 2-phenylbenzo[*d*]oxazole.

Since the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole

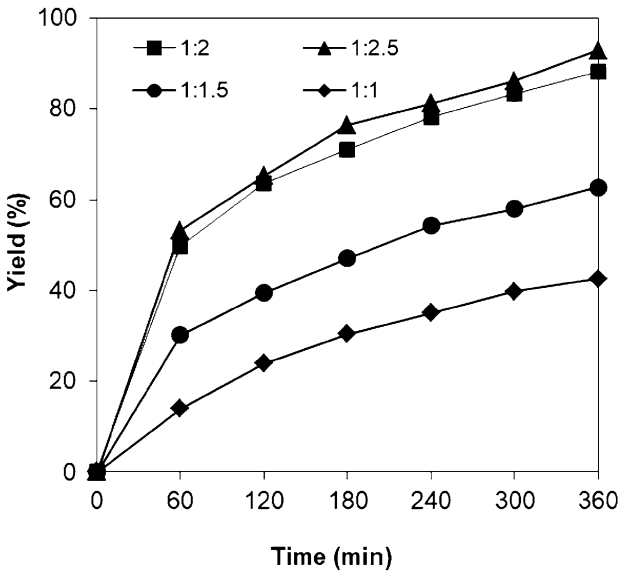


Fig. 6 Yields of 2-phenylbenzo[*d*]oxazole versus benzyl acohol:2-aminophenol molar ratio

employing the Fe-MOF catalyst was implemented in solution phase, the leaching analysis must be conducted. In a number of situations, despite the fact that a solid catalyst was applied, the reaction did not progress under real heterogeneous catalysis circumstances attributable to the leaching matter. In order to test if iron species migrated from the solid iron-organic framework donated noticeably to the generation of 2-phenylbenzo[*d*]oxazole though the cyclization reaction, a control experiment was executed (Fig. 7). The reaction was conducted in xylene at 120 °C for 360 min, with 2 equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. Succeeding to the first 60 min with 48% yield being noted, the solid iron-based framework catalyst was removed. The liquid phase was afterwards transferred to a fresh reactor, and heated at 120 °C for an additional 300 min. The yield of 2-phenylbenzo[*d*]oxazole during this period was assessed by GC analysis as previously described. It was noted that virtually no further product produced by leached iron species, if any, was probed during this experiment. These data would affirm that the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole was able to progress only with the solid iron-based framework, and the contribution of homogeneous catalysis to the production of 2-phenylbenzo[*d*]oxazole was inconsequential.

In order to comprehend the pathway of the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole, more control experiments were performed. In the first experiment series, pyridine was utilized as catalyst poison (Fig. 8). The reaction

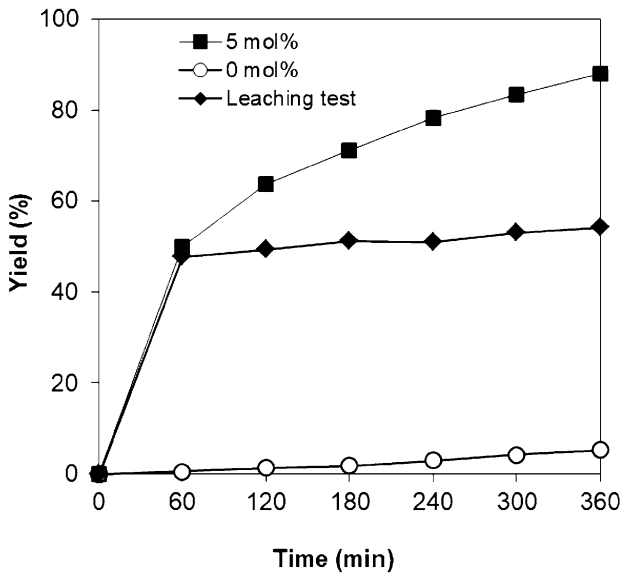


Fig. 7 2-Phenylbenzo[*d*]oxazole was only produced with the solid iron-based framework

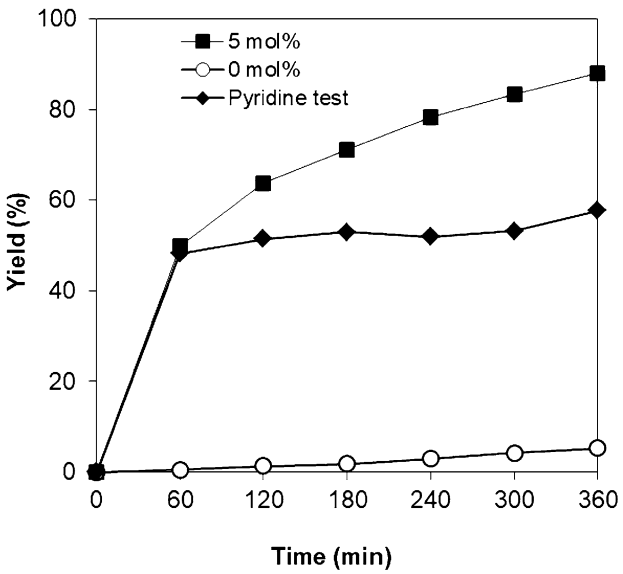


Fig. 8 Yields of 2-phenylbenzo[*d*]oxazole versus catalyst poison

was carried out in xylene at 120 °C for 360 min, with 2 equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. Succeeding to the first 60 min with 48% yield being detected, pyridine was added to the reactor. The reaction mixture was subsequently heated at 120 °C for an extra 300 min. Almost no additional 2-phenylbenzo[*d*]oxazole was detected when pyridine as the catalyst poison was present in the reaction mixture. This observation affirmed that the interaction between pyridine as a Lewis base and iron as an Lewis acid resulted in the deactivation of the Fe-MOF catalyst. In another experiment series, in order to substantiate the prerequisite of the oxidant for this cyclization reaction, curcumin, ((*1E,6E*)-1,7-*bis*(4-hydroxy-3-methoxyphenyl) -1,6-heptadiene-3,5-dione), and TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl) were utilized as the antioxidant (Fig. 9). Following the first 60 min with 48% yield being noted, curcumin was added to the reactor, and the reaction mixture was subsequently heated at 120 °C for an extra 300 min. It was confirmed that the cyclization reaction did not continue in the presence of curcumin. Similarly, the presence of TEMPO in the reaction mixture restrained the generation of 2-phenylbenzo[*d*]oxazole. These data verified that curcumin or TEMPO trapped the radicals generated in the catalytic cycle, accordingly discontinuing the cyclization.

Based on previous reports [46–49] and the above results, a plausible reaction pathway was proposed (Scheme 2). The reaction may proceed via following steps. Initially, *tert*-butoxide anion and *tert*-butoxy radical would be formed through the cleavage of DTBP with the assistance of Fe(II). Hydrogen abstraction of benzaldehyde by the *tert*-butoxy

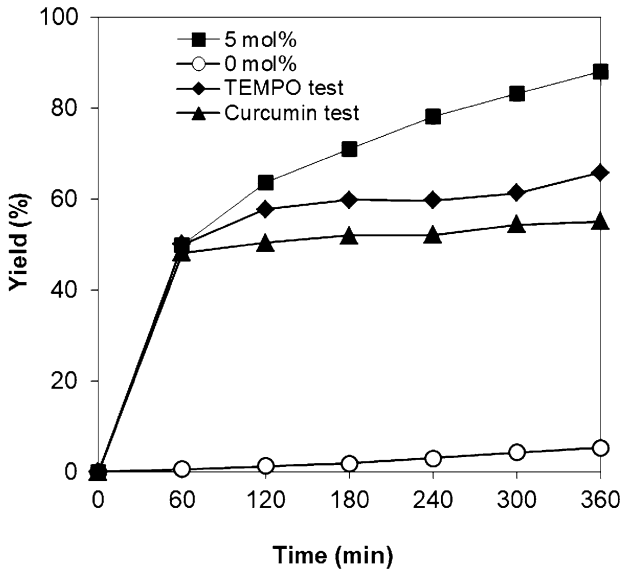
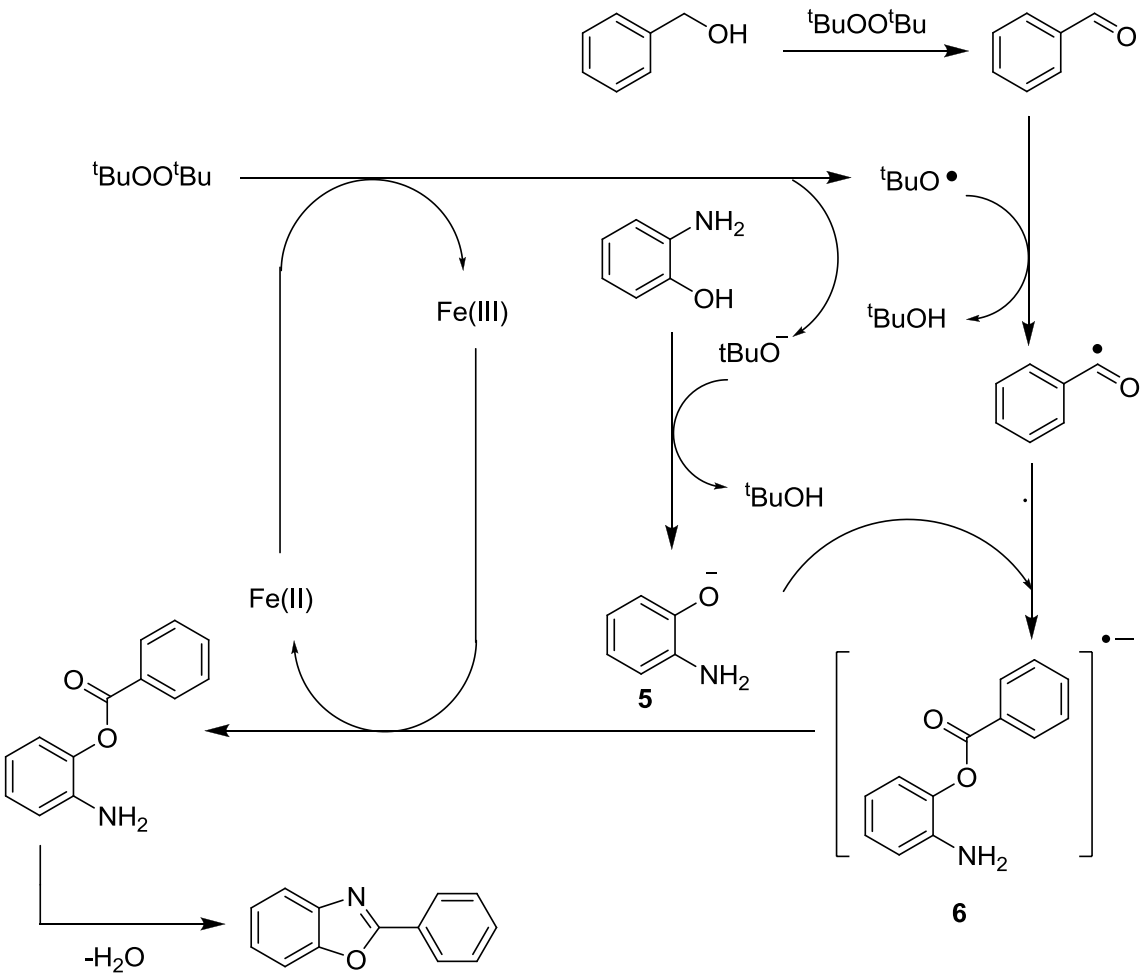


Fig. 9 Yields of 2-phenylbenzo[*d*]oxazole versus antioxidant

radical would form an acyl radical. At the same time, the reaction between 2-aminophenol and *tert*-butoxide anion would result in anion intermediate **5**. The key C–O bond formation step would occur through the radical addition between the acyl radical and intermediate **5** to provide the radical anion **6**. Subsequently, single electron transfer between **6** and Fe(III) would form 2-aminophenyl benzoate and regenerate Fe(II), which would continue the catalytic cycle. Indeed, GC-MS analysis indicated the presence of 2-aminophenyl benzoate in the reaction mixture (Fig. S26). At the final step, 2-aminophenyl benzoate would undergo the catalyst-free condensation process to generate 2-phenylbenzo[d]oxazole. Additionally, it should be noted that xylene was not oxidized under the present experimental conditions, with no oxidized products being detected by GC-MS.

To insist the remarkable points of this work, the catalytic activity of MOF-235 in the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole was correlated with that of



Scheme 2 Plausible reaction pathway

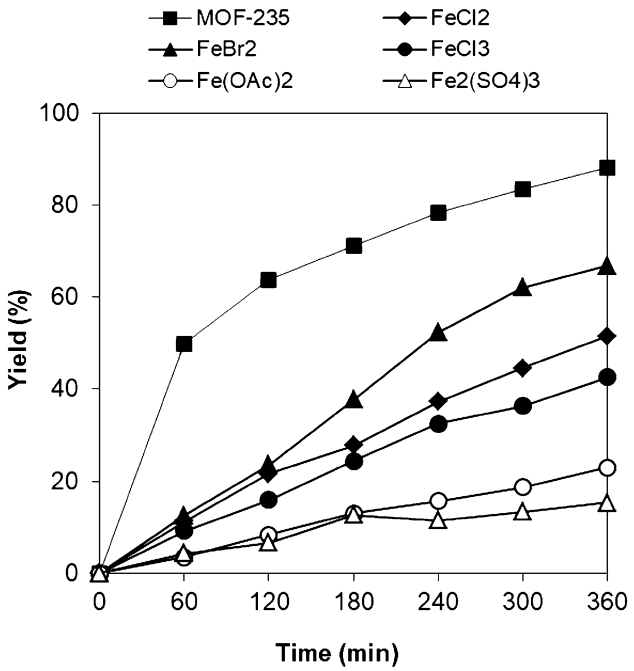


Fig. 10 Yields of 2-phenylbenzo[*d*]oxazole versus homogeneous iron catalysts

numerous iron homogeneous catalysts, including $FeCl_2$, $FeBr_2$, $Fe(OAc)_2$, $FeCl_3$, and $Fe_2(SO_4)_3$ (Fig. 10). The reaction was implemented in xylene at 120 °C for 360 min, with two equivalents of 2-aminophenol, using 3 equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. It was noted that the nature of anions in these iron salts displayed an extraordinary effect on the catalytic efficiency. The cyclization reaction progressed steadily in the presence of $Fe_2(SO_4)_3$ catalyst, providing only 15% yield of the expected product after 360 min. Similarly, $Fe(OAc)_2$ catalyst was noticed to be inappropriate for the synthesis of 2-phenylbenzo[*d*]oxazole, with 23% yield being recorded after 360 min. $FeCl_3$ offered higher catalytic activity than $Fe_2(SO_4)_3$ and $Fe(OAc)_2$, and the $FeCl_3$-catalyzed cyclization reaction afforded 43% yield of 2-phenylbenzo[*d*]oxazole after 360 min. The yield of the desired product was improved to 52% after 360 min when $FeCl_2$ was utilized as catalyst. $FeBr_3$ emerged to be more active than $FeCl_2$ for the production of 2-phenylbenzo[*d*]oxazole, and 67% yield was obtained after 360 min. As previously noted, the reaction employing MOF-235 catalyst progressed to 88% yield of 2-phenylbenzo[*d*]oxazole under similar conditions, thus exhibiting superior aspects than homogeneous iron-based catalysts.

To additionally highlight the benefit of MOF-235 for the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole, its performance was differentiated with that of other MOF-based catalysts, including $Fe_3O(BPDC)_3$, Fe-BTC, $Cu_2(BDC)_2(DABCO)$, $Cu_2(OBA)_2(BPY)$, $Cu_3(BTC)_2$, $Co_2(BDC)_2(DABCO)$, and $Ni_2(BDC)_2(DABCO)$ (Fig. 11). The reaction was conducted in xylene at 120 °C for 360 min, with two equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. $Ni_2(BDC)_2(DABCO)$ was noted to be unsuitable for the synthesis of 2-phenylbenzo[*d*]oxazole, reaching only 27% yield after 360 min. In the same way, $Co_2(BDC)_2(DABCO)$ displayed low efficiency in the cyclization reaction, providing the desired product in 35% yield after 360 min. Copper-based frameworks also presented low activity in the cyclization transformation. The reaction using $Cu_3(BTC)_2$ catalyst provided 39% yield of 2-phenylbenzo[*d*]oxazole after 360 min, while 42% yield was observed for the case of $Cu_2(OBA)_2(BPY)$. Similarly, in the presence of $Cu_2(BDC)_2(DABCO)$ as catalyst, the reaction progressed to 48% yield after 360 min. Fe-BTC emerged to have lower catalytic efficiency in the synthesis of 2-phenylbenzo[*d*]oxazole as other iron-organic frameworks, although the transformation reached 49% yield after 360 min under this condition. The yield of the major benzoxazole product was amended to 77% after 360 min when $Fe_3O(BPDC)_3$ was employed as catalyst. In this series of MOF-based catalysts, MOF-235 emerged as the most appropriate candidate, providing the principal product in 88% yield after 360 min. This could be attributed to the differences in the structure of these Fe-MOFs. The structure of MOF-235 is decorated

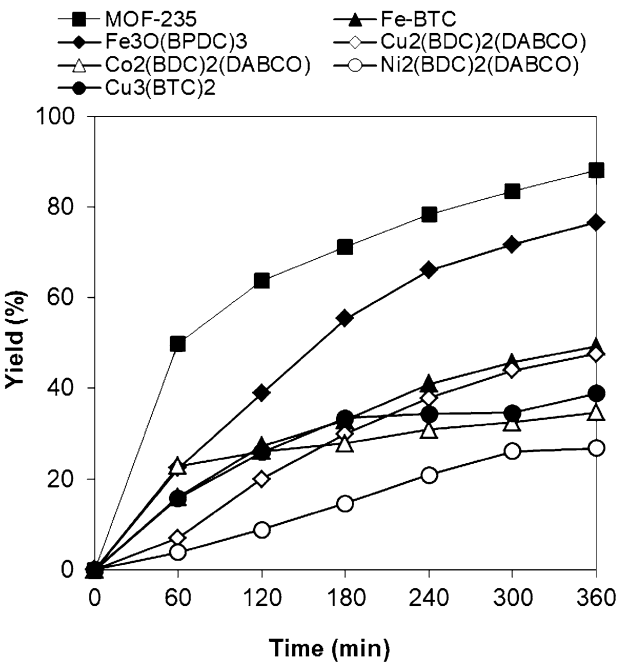


Fig. 11 Yields of 2-phenylbenzo[*d*]oxazole versus heterogeneous iron catalysts

and expanded form of the acs net with flexible links, in which each six-coordinate vertex is substituted by a trigonal prism and separated from each other by the two-coordinated organic links [40–42]. In comparison, both Fe-BTC [50] and $Fe_3O(BPDC)_3$ [51, 52] possess a rigid structure in the frameworks, thus making active sites less accessible to reactants.

As previously noted, the MOF-235 displayed higher efficiency than a number of homogeneous and heterogeneous catalysts in the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole. To additionally underline the extraordinary features of using this iron-organic framework, one important aspect that must be explored is the readiness of reusability after each catalytic run. For organic transformations conducted with heterogeneous catalysts, it would be demanded that the catalyst could be recovered and reutilized for numerous runs. The iron-organic framework was accordingly considered for reusability in the synthesis of 2-phenylbenzo[*d*]oxazole. The reaction was performed in xylene at 120 °C for 360 min, with 2 equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. Following the first run with 88% yield of 2-phenylbenzo[*d*]oxazole being recorded, the iron-based catalyst was collected, washed thoroughly with methanol to remove product and excess reagents, heated under vacuum on a Shlenkline at 120 °C for 3 h, and reutilized for new catalytic experiment. Experimental data revealed that it was possible to reutilize the catalyst for the cyclization reaction between 2-aminophenol and benzyl alcohol to produce 2-phenylbenzo[*d*]oxazole. In the 6th catalytic run, 85% yield of the major product was detected (Fig. 12). ICP-OES analysis results indicated that the amount of iron in the fresh and reused MOF-235 were 16.8% (wt/wt) and 16.5% (wt/wt), respectively. Moreover, the structure of the iron-based was retained under these reaction conditions, as demonstrated by XRD (Fig. 13) as well as FT-IR (Fig. 14) analysis results.

With all of these results in hand, we additionally investigated the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via the one-pot oxidative cyclization reaction employing the iron-based framework catalyst (Table 1). In the first experiment series, the reaction was implemented in xylene at 120 °C for 360 min, with 2 equivalents of 2-aminophenol, using three equivalents of di-*tert*-butyl peroxide as the oxidant, in the presence of 5 mol% catalyst. The product was isolated on silica gel column chromatography. Following this protocol, 2-phenylbenzo[*d*]oxazole was achieved in 84% isolated yield via the cyclization reaction between 2-aminophenol and benzyl alcohol (Entry 1). It was noticed that benzyl alcohol possessing substituent reacted readily with 2-aminophenol under these condition. Certainly, 72% of 2-(4-bromophenyl)benzo[*d*]oxazole (Entry 2) was obtained for the reaction of 4-bromobenzyl alcohol, while 85% yield

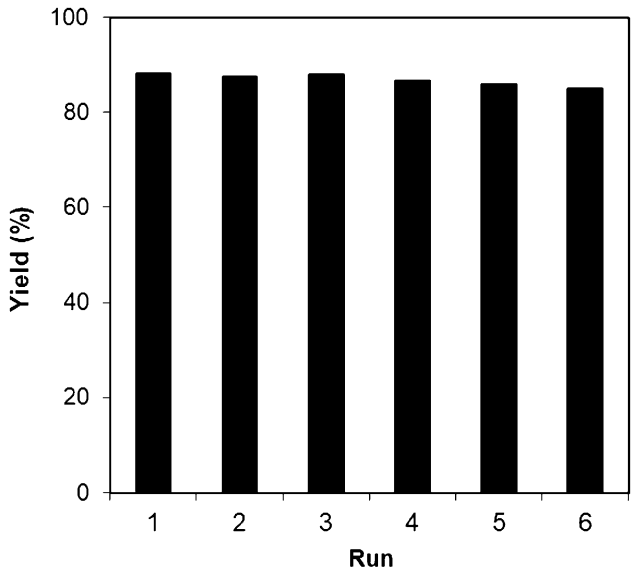


Fig. 12 Catalyst reutilizing investigation

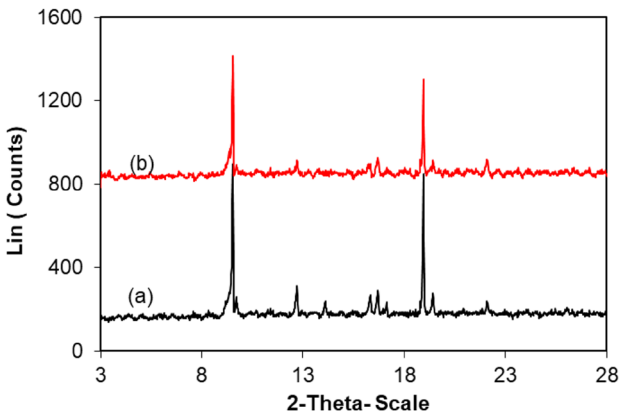


Fig. 13 XRD results of the new (a) and reutilized (b) catalyst

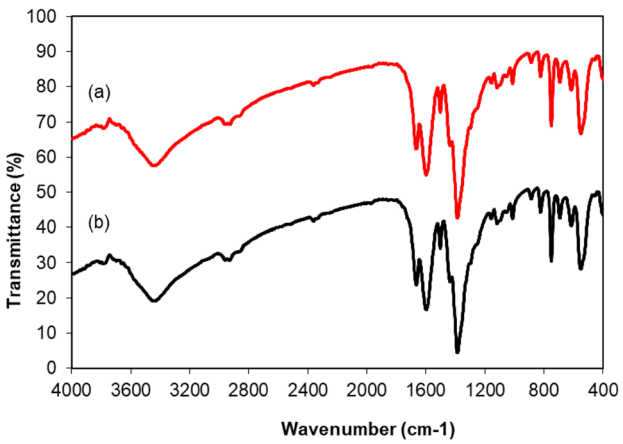
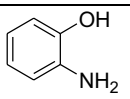
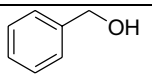
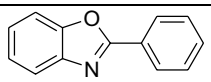
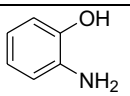
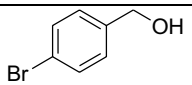
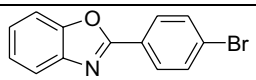
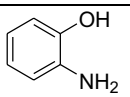
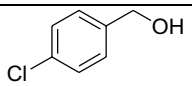
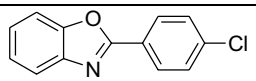
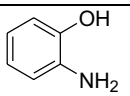
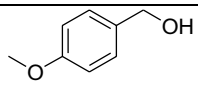
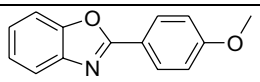
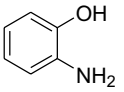
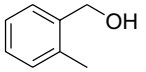
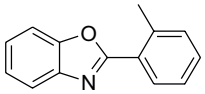
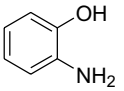
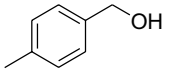
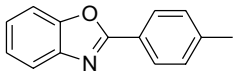
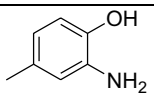
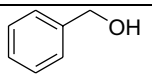
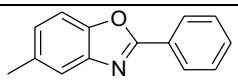
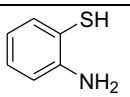
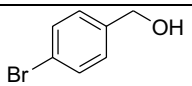
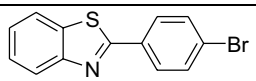
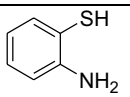
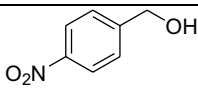
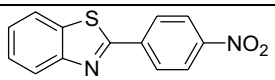


Fig. 14 FT-IR results of the new (a) and reutilized (b) catalyst

Table 1 The synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via the one-pot oxidative cyclization reaction

Entry	Reactant 1	Reactant 2	Product	Isolated yield (%)
1				84
2				72
3				85
4				86
5				85
6				87
7				82
8				69
9				80

of 2-(4-chlorophenyl)benzo[*d*]oxazole was recorded for the case of 4-chlorobenzyl alcohol (Entry 3). Benzyl alcohol with electron-donating substituent was reactive towards the cyclization reaction with 2-aminophenol, generating 2-(4-methoxyphenyl)benzo[*d*]oxazole in 86% yield (Entry 4). In the same way, 2-*o*-tolylbenzo[*d*]oxazole was produced in 85% yield for the case of 2-methyl benzyl alcohol (Entry 5), and 2-*p*-tolylbenzo[d]oxazole was achieved in 87% yield for the case of 4-methyl benzyl alcohol (Entry 6). 2-Amino-4-methylphenol was also reactive towards the transformation, generating 5-methyl-2-phenylbenzo[*d*]oxazole in 82% yield (Entry 7). Next, the transformation was expanded to the cyclization of 2-aminothiophenol. Employing the same approach, 69% yield of 2-(4-bromophenyl) benzo[*d*]thiazole (Entry 8) was achieved via the reaction between 2-aminothiophenol and 4-bromobenzyl alcohol. 4-Nitrobenzyl alcohol was reactive towards the cylization reaction, forming 2-(4-nitrophenyl)benzo[*d*]thiazole in 80% yield (Entry 9).

4 Conclusions

Iron-organic framework MOF-235 was synthesized, and consequently utilized as an effective heterogeneous catalyst for the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles via one-pot oxidative cyclization reactions between 2-aminophenols or 2-aminothiophenols and alcohols. The solvent character expressed a considerable impact on the cyclization reaction, and xylene was the most appropriate

solvent for this synthetic protocol. The transformation required the presence of an oxidant, and the system of di-*tert*-butylperoxide with xylene led to best yield of major products. The MOF-235 catalyst presented higher catalytic effectiveness for the synthesis of 2-arylbenzoxazoles and 2-arylbenzothiazoles than a number of MOF-based catalysts and established homogeneous catalysts. The cyclization reaction was able to progress only with the solid iron-based framework, and the contribution of homogeneous catalysis to the production of major products was inconsequential. It was feasible to recover and reutilize the framework catalyst for the cyclization transformation various times while its catalytic efficiency was retained. The benefits that 2-arylbenzoxazoles and 2-arylbenzothiazoles could be synthesized through one-pot oxidative cyclization reactions between 2-aminophenols or 2-aminothiophenols and alcohols utilizing a recyclable catalyst would provide advantages over classical homogeneous approaches, and therefore would be engaging to the chemical industry.

Acknowledgements The Viet Nam National University—Ho Chi Minh City (VNU-HCM) is acknowledged for financial support via project No. NV2019-20-02.

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