Molecular Catalysis 450 (2018) 104–111

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Mild direct amination of benzoxazoles using interpenetrating Cobalt(II)-based metal-organic framework as an efficient heterogeneous catalyst

Sheng-Chun Chen[a], Nan Li[a], Feng Tian[b], Nan-Nan Chai[a], Ming-Yang He[a,b,**], Qun Chen[a,*]

[a] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China
[b] School of Chemical Engineering, Nanjing University of Science & Technology, Nanjing 210094, China

ARTICLE INFO

Keywords:
Co(II) MOF
Heterogeneous catalysis
Direct amination
Benzoxazoles

ABSTRACT

Based on the acid-base mixed-ligand assembly strategy, a new acid- and base-stable cobalt(II) metal-organic framework $\{[Co(tcpa)(Fbtx)(H_2O)_2]\cdot 0.5H_2O\}_n$ (denoted as Co-MOF, Fbtx = 1,4-bis(1,2,4-triazole-1-ylmethyl)-2,3,5,6-tetrafluorobenzene, H_2tcpa = 3,4,5,6-tetrachloro-phthalic acid) was synthesized under hydrothermal conditions and characterized by various spectral and analytical techniques. Single-crystal X-ray diffraction analysis revealed that Co-MOF features a rare three-dimensional two-fold interpenetrating **cds**-type framework. The crystalline Co-MOF exhibited excellent activity toward the direct amination of 5-methylbenzoxazoles with TBHP as oxidant and acetic acid as an additive under mild reaction conditions, and various 2-aminobenzoxazoles were synthesized in moderate to good yields under optimized reaction conditions. Furthermore, the Co-MOF catalyst could be easily recovered and reused several times without loss of its crystallinity and activity.

1. Introduction

2-Aminobenzoxazole derivatives not only occur as substructures in a variety of biologically active natural products [1], but also are promising targets for the treatment of schizophrenia [2], insomnia [3], CNS disorders [4], and Alzheimer's disease [5]. Methods for the efficient synthesis of 2-aminobenzoxazoles have thus attracted much attention from synthetic organic chemists in recent years [6–10]. In this field, transition-metal-catalyzed direct oxidative cross-dehydrogenative coupling (CDC) amination of benzoxazoles with unactivated amines represents one of the most efficient routes [11]. To date, a range of homogeneous Cu- [12], Ni- [13], Mn- [14], Co- [15], and Hf-based [16] catalysts in combination with stoichiometric amount of oxidants have been developed for the direct oxidative CDC amination of benzoxazoles. Nevertheless, a major drawback of homogeneous catalytic systems is the difficult recovery of these metal catalysts. From both economical and sustainable point of view, it is especially important to develop heterogeneous catalysts for amination of benzoxazoles, because these protocols would offer several advantages over homogeneous ones, including the ease of handling, recyclability and reusability. For example, Panda and Ghosh with their co-workers reported recyclable γ-MnO_2 as heterogeneous catalyst for oxidative CDC amination of benzoxazoles with molecular oxygen as oxidant [17]. Very recently, Zhao and co-workers developed a heterogeneous catalytic system using manganese octahedral molecular sieve supported copper hydroxide as catalyst for the oxidative synthesis of benzoxazoles at room temperature [18].

Metal-organic frameworks (MOFs) are an emerging class of functional organic-inorganic hybrid materials, providing a highly tunable platform to develop new heterogeneous catalysts for important organic transformations [19–22]. In the past decade, the MOFs-catalyzed heterogeneous C—H activation transformations have been recently reported by several research groups [23–26]. Recently, Phan and co-workers reported that a series of Cu(II) [27], Ni(II) [28], and Hf(IV)-based [29] MOFs could efficiently catalyze the direct heterocycle C—H arylation reactions to synthesize 2-substituted benzoxazoles under heterogeneous conditions. Similarly, Wu and co-workers prepared an anionic zeolite-like Cu(I)-based MOF that also showed catalytic activity for the C—H activation of benzoxazoles [30]. While remarkable progress has been made in the field, many challenging issues still remain unsolved. With the rapid development of heterogeneous catalytic C—H activation, new efficient MOF-based catalysts with well-defined structure are still in high demand. Moreover, some of the MOF catalysts are extremely sensitive to air, moisture and organic solvents. Thus far, these shortcomings have limited the practicality of MOFs in some catalytic transformations.

On the basis of the Irving-Williams series [31], late 3d transition

* Corresponding author.
** Corresponding author at: Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou 213164, China.
E-mail addresses: hemingyangjpu@yahoo.com (M.-Y. He), chenqunjpu@yahoo.com (Q. Chen).

https://doi.org/10.1016/j.mcat.2018.03.011
Received 2 March 2018; Accepted 10 March 2018
2468-8231/ © 2018 Elsevier B.V. All rights reserved.

metal ions (soft Lewis acids, such as Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}), being coordinated with *N*-heterocyclic aromatic ligands (soft Lewis bases, such as pyridine-, imidazole-, or triazole-based ligands), can favor the formation of stable complexes. Recently, Garcia and co-workers have illustrated that acid-base mixed-ligand MOFs possess superior robust and catalytic activity over those with only single ligand [32]. Previously, we synthesized a new stable Cu-MOF based on mixed ligands of Fbtx and phthalic acid and found that this MOF could be used as a highly efficient heterogeneous catalyst for selective aerobic oxidation of alcohols to aldehydes [33]. To further demonstrate the utility of mixed-ligand strategy, herein we wish to report the synthesis and characterization of a new Co(II)-based MOF $\{[Co(tcpa)(Fbtx)(H_2O)_2]\ 0.5H_2O\}_n$, denoted as Co-MOF, constructed from mixed ligands of 1,4-bis(1,2,4-triazole-1-ylmethyl)-2,3,5,6-tetrafluorobenzene (Fbtx) and 3,4,5,6-tetrachlorophthalic acid (H_2tcpa). The crystalline Co-MOF with a rare two-fold interpenetrating **cds**-type framework indicated good chemical stability toward dilute acidic and basic aqueous solutions as well as various boiling solvent systems, and was shown to a highly active, readily recyclable and reusable catalyst for oxidative CDC amination of benzoxazoles through C−H bond activation under mild conditions. The Co-MOF also exhibited higher catalytic activity than that of Co-containing hydrotalcite CO_3^{2-}-Co_4Al-LDH and Co-doped zeolites including Co-Ets-10, Co-ZSM-5 and Co-Beta.

2. Experimental

2.1. Preparation of Co-MOF catalyst

In a typical preparation, a mixture of $Co(OAc)_2{\cdot}4H_2O$ (24.9 mg, 0.1 mmol), H_2tcpa (30.4 mg, 0.1 mmol), Fbtx (31.2 mg, 0.1 mmol) and water (6 mL) was stirred for 60 min at room temperature and then sealed in a 15-mL Teflon-lined stainless steel autoclave, which was heated to 140 °C for 2 days. After it was cooled down to room temperature at a rate of 5 °C h^{-1}, pink block-shaped crystals suitable for X-ray diffraction analysis were obtained in *ca.* 65% yield (46.5 mg, based on H_2tcpa). Anal. calcd for $C_{20}H_{10}Cl_4CoF_4N_6O_{6.5}$: C, 33.59; H, 1.39; N, 11.75%; found: 33.68; H, 1.38; N, 11.72%. IR (cm^{-1}, KBr pellet): 3433 br, 3124 m, 3118 m, 2976 m, 1587 s, 1536 m, 1491 s, 1414 m, 1382 s, 1336 m, 1285 s, 1208 w, 1124 s, 1034 s, 898 m, 854 w, 784 m, 661 s, 610 m.

2.2. Catalytic studies

Co-MOF-catalyzed CDC amination of benzoxazoles: in a typical procedure, 5-methylbenzoxazole (0.5 mmol, 1.0 equiv), morpholine (0.6 mmol, 1.2 equiv), Co-MOF (0.015 mmol, 3 mol%), acetic acid (1 mmol, 2 equiv), TBHP (70% in H_2O) (1 mmol, 2 equiv) and acetonitrile (2 mL) were taken in a 10-mL Schlenk flask. The reaction mixture was stirred for 12 h at room temperature under air atmosphere. The progress of the reaction was monitored via gas chromatography (Shimadzu GC-2010AF) equipped with fused silica capillary HP-5 column (30 m × 0.32 mm) and a flame ionization detector. The products were further confirmed by using GC–MS, ^{1}H NMR and ^{13}C NMR. The concentration of 5-methylbenzoxazole and 5-methyl-2-(4-morpholinyl)benzoxazole was calibrated by external standard method with standard samples. The reaction solution containing Co-MOF catalyst was easily separated by filtration, and the catalyst was washed with DMF and ethanol and dried under vacuum before reutilization.

2.3. Single crystal X-ray diffraction

The crystal data of Co-MOF were collected on a Bruker Apex II CCD diffractometer at 293 K with Mo Kα radiation (λ = 0.71073 Å). A semiempirical absorption correction was applied using SADABS [34], and the program SAINT was used for integration of the diffraction profiles [35]. The structure was solved by the direct methods using SHELXS program of SHELXTL packages and refined anisotropically for all non-hydrogen atoms by full-matrix least squares on F^2 with SHELXL [36]. C-bound hydrogen atoms were placed in geometrically calculated positions by using a riding model. O-bound hydrogen atoms were firstly localized by difference Fourier maps and then fixed geometrically with isotropic temperature factors. Further crystal data and structural refinement parameters are summarized in Table S1.

CCDC-1814834 (Co-MOF) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223–336033; or deposit@ccdc.cam.ac.uk).

2.4. Characterization of Co-MOF catalyst

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku D/max-2000 diffractometer at 40 kV and 100 mA for a Cu-target tube (λ = 1.5418 Å), and the calculated PXRD patterns were obtained from the single-crystal diffraction data using the PLATON software [37]. Thermogravimetric analysis (TGA) experiment was carried out in the temperature range of 25–800 °C on a Dupont thermal analyzer under N_2 atmosphere at a heating rate of 10 °C min^{-1}. BET surface area analysis was performed by nitrogen sorption isotherms in a Micromeritics ASAP2460 surface area analyzer at 77 K. Scanning electron microscopy (SEM) images were obtained on a field scanning emission Gemini Zeiss SUPRA55 at an accelerating voltage of 5 kev. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI 5000 Versa Probe II XPS system with a monochromatic Al Kα X-ray source (*hv* = 1486.7 eV) and a charger neutralizer. The Fourier transform (FT) IR spectra (KBr pellet) were taken on a Nicolet ESP 460 FT-IR spectrometer in the range of 4000–400 cm^{-1}. Elemental analyses were performed on a PE–2400II (Perkin-Elmer) analyzer. Gas chromatographic analyses were carried out using an Agilent 7890 B GC system equipped with fused silica capillary HP-5 column (30 m × 0.32 mm) and a flame ionization detector (FID).

3. Results and discussion

3.1. Synthesis and characterization of catalyst

During the acid-base mixed-ligand self-assembly process, the nature of organic ligands plays a crucial role in determining the final MOF structures and properties [38]. Recently, our group has utilized a series of halogen-substituted dicarboxylate acids and *N*-heterocyclic bridging ligands as the functional and structural units to develop families of halogen-modified metal-organic hybrid materials [39–45]. Meanwhile, a new stable copper(II) MOF based on the mixed ligands of Fbtx and phthalic acid has been reported by us [33]. Considering the unique coordination geometry of cobalt(II) ion and its potential catalytic properties, we hoped to build more robust cobalt(II) complexes based on mixed halogen-substituted ligands of acid- and base-type. Although many attempts have been devoted to the combination of Fbtx with several analogues dicarboxylate ligands, such as phthalic acid, 3,4,5,6-tetrafluoro-phthalic acid, 3,4,5,6-tetrabromo-phthalic acid, it was a pity that pink precipitates but not crystals which are unsuitable for X-ray single-crystal analyses were always obtained. Therefore, it should be pointed out that the choice of carboxylate ligands plays an important role in the self-assembly. In addition, when cobalt(II) sources including $Co(NO_3)_2$ and $CoCl_2$ were used, only amorphous powders were obtained under the similar reaction conditions. Moreover, the introduction of NaOH, KOH or Et_3N to adjust the pH value was also examined, where such bases were ineffective during the assembly processes.

As shown in Fig. 1a, photo of single crystals of Co-MOF shows high quantity. Single-crystal X-ray diffraction analysis reveals that Co-MOF crystallizes in the monoclinic system with the *C*2/*c* space group, and shows a three-dimensional two-fold interpenetrating framework with

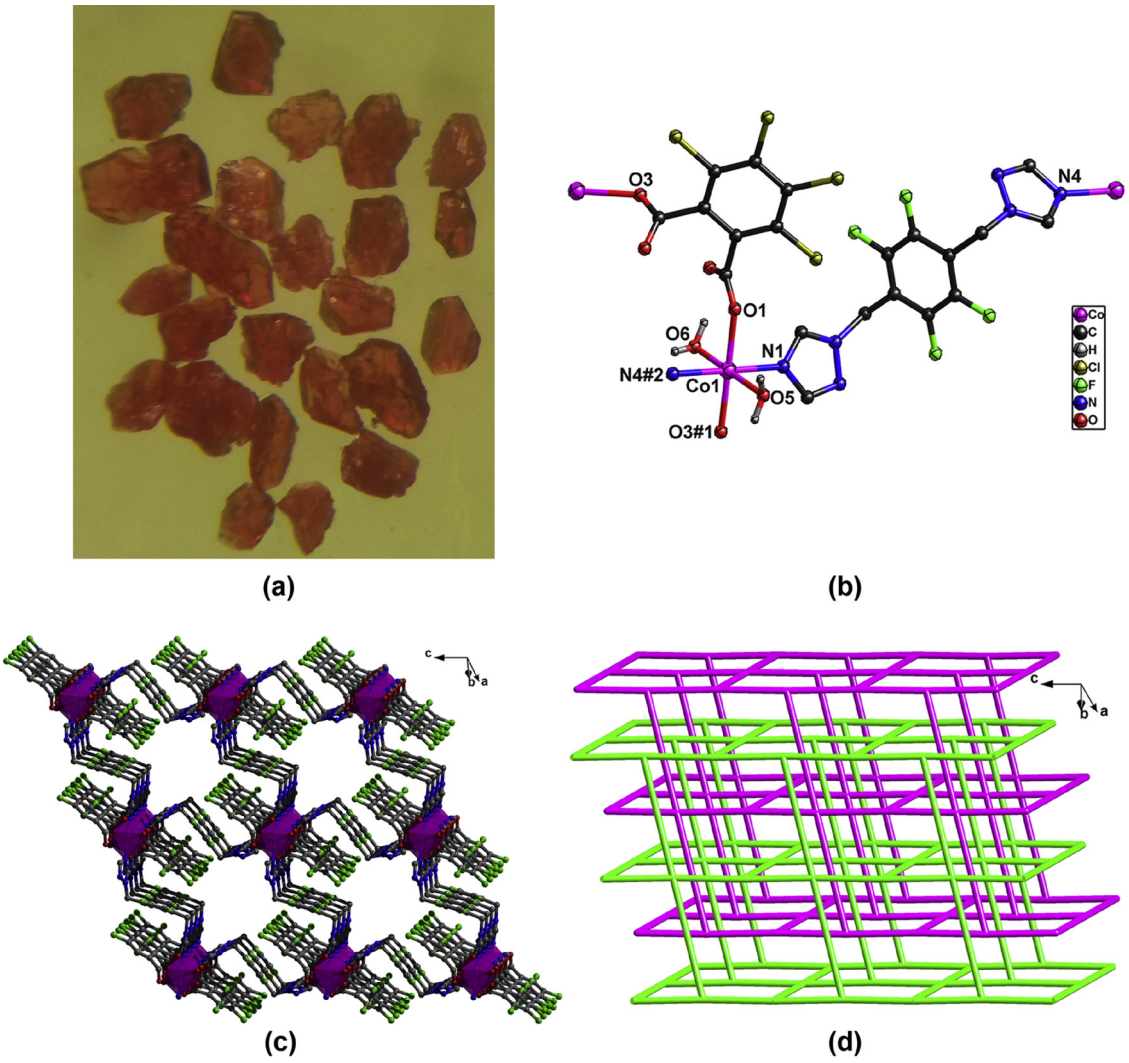


Fig. 1. Views of: (a) image showing block single crystals of Co-MOF; (b) the coordination environment of Co(II) center; (c) the 3D coordination framework, (d) the two-fold interpenetrated topological network.

6^5·8-**cds** topology. The asymmetry unit consists of one Co(II) ion, one Fbtx ligand, one tcpa anion, two coordination water molecules and a half guest water molecule. As shown in Fig. 1b, each Co(II) displays a distorted octahedral geometry (CoN_2O_4), coordinated by four oxygen atoms from two tcpa ligands and two coordinating water [Co–O = 2.098(3) −2.116(3) Å] and two nitrogen atoms from two Fbtx ligands [Co–N = 2.109(4) −2.114(4) Å]. The V-shaped tcpa ligand adopts the monodentate coordination mode for each carboxylate, linking adjacent Co(II) ions to form one-dimensional $[Co(tcpa)]_n$ chains, which is linked to four neighboring chains through the trans-Fbtx ligands, resulting in three-dimensional framework with large open channels (see Fig. 1c). The remarkable structural feature of Co-MOF is that the channel is large enough to allow the interpenetration of another identical framework to generate a 2-fold interpenetrating network, as illustrated in Fig. 1d. Topologically, if each Co(II) ion is considered as a 4-connected node and tcpa/Fbtx both are viewed as linkers, the whole framework of Co-MOF can be simplified as a rare 2-fold interpenetrating **cds** topological network [46].

Phase purity of the as-synthesized Co-MOF was confirmed by comparison of its PXRD peaks with that calculated from single-crystal X-ray diffraction analysis (Fig. S1). The TG curve (Fig. S2) showed that the first weight loss of 6.53% from 85 °C to 140 °C is in accordance with the release of both coordinated and lattice water molecules (calculated: 6.29%), and pyrolysis of the remaining framework is observed upon heating to ca. 215 °C. The thermal stability was further characterized by the measured temperature-dependent PXRD patterns, where Co-MOF could retain its structure and crystallinity in air up to 200 °C (Fig. S3). In order to estimate the chemical stability of Co-MOF, the as-synthesized samples were immersed in aqueous solutions with pH values in the range of 3–11 at room temperature for one day, or suspended in boiling water and several organic solvents for one day. The measured PXRD patterns (Fig. 2a and b) indicated that Co-MOF remained intact without loss of crystallinity. It should be pointed that, to the best of our knowledge, Co-MOF is one of the rare MOFs that can be much more resistant to the attack of dilute acidic and basic aqueous solutions, as well as various boiling solvent systems [47]. In addition, bulk elemental analysis of Co-MOF was consistent with the molecular formula of $\{[Co(tcpa)(Fbtx)(H_2O)_2]\ 0.5H_2O\}_n$. Finally, the FT-IR spectra of Co-MOF displayed the presence of both tcpa and Fbtx ligands (Fig. S4).

3.2. Catalytic activity

5-Methylbenzoxazole is a privileged structural motif often found in many important organic compounds [48]. The direct functionalization of 5-methylbenzoxazole to construct complex organic compounds would be a significantly valuable synthetic method for the rapid access to substituted benzoxazole derivatives [49]. We started our evaluation of reaction parameters with 5-methylbenzoxazole and morpholine as

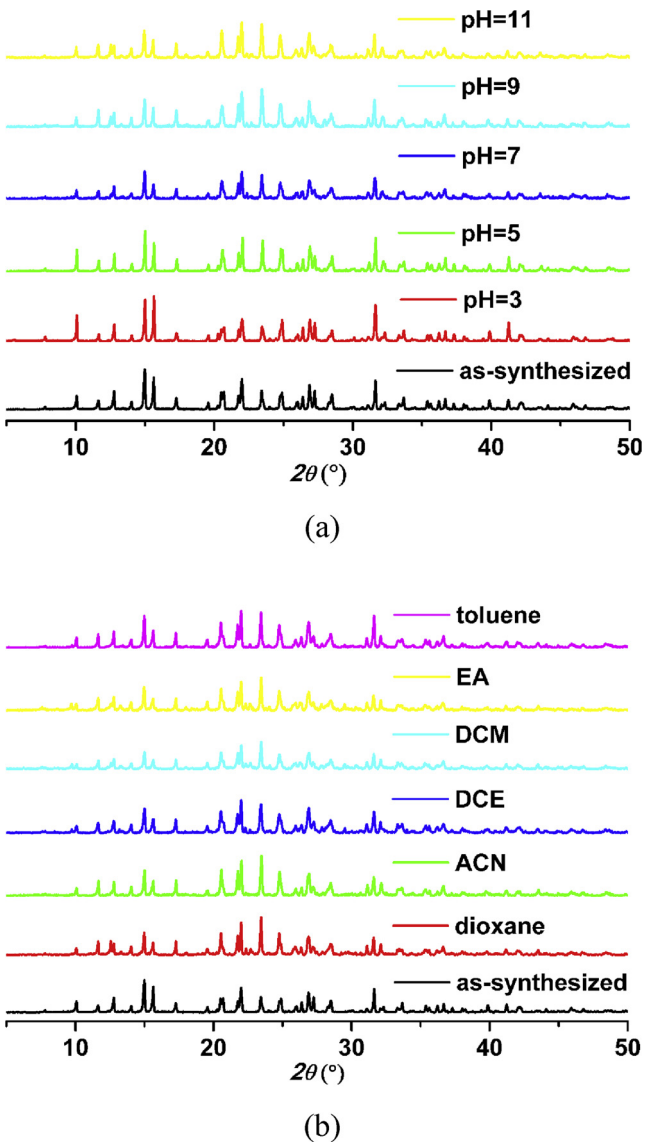


Fig. 2. PXRD patterns of Co-MOF for (a) different pH values and (b) various boiling solvent systems.

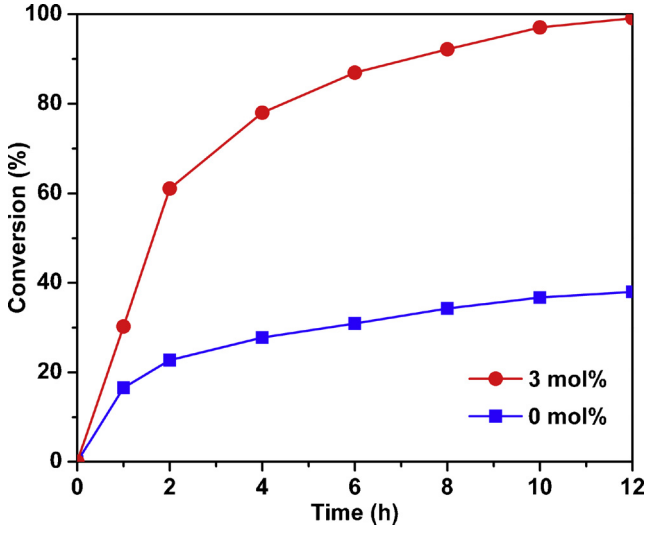


Fig. 3. Effect of the Co-MOF catalyst on reaction conversion.

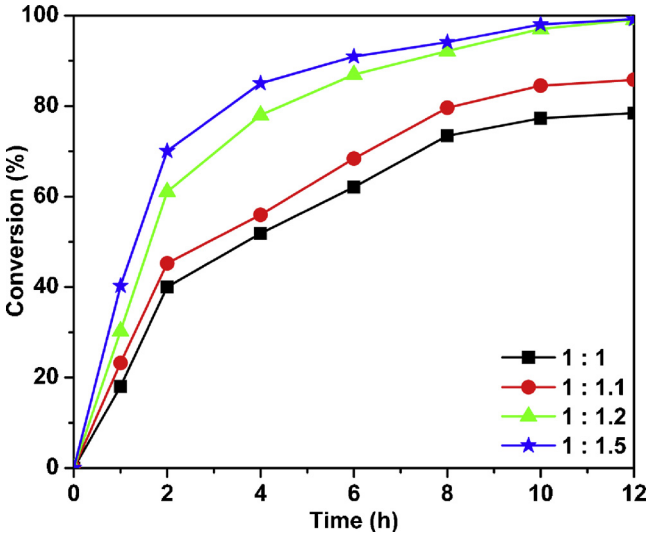


Fig. 4. Effect of reagent molar ratio on reaction conversion.

mode substrates to study the Co-MOF-catalyzed direct CDC amination at room temperature. As reported by Chang et al. [14] and Mori et al. [50], the direct oxidative amination of azoles would be strictly affected by the combined action of the nature of catalysts, solvent polarity, acid additives and oxidant species. Fig. 3 shows the dependence of conversion on the effect of Co-MOF catalyst and reaction time. It was found that the oxidative CDC amination reaction in the absence of Co-MOF catalyst gave a low conversion, while addition of 3 mol% Co-MOF catalyst into the system could significantly enhance the reaction conversions and > 99% 5-methylbenzoxazole conversion was observed after 12 h. Panda et al. reported the heterogeneous γ-MnO_2-catalyzed CDC amination of benzoxazole with 58 mol% catalyst loadings, where the reaction was accomplished in 92% conversion within 24 h at 50 °C [17]. Phan et al. previously employed 10 mol% [$Ni_2(BDC)_2(DABCO)$] as efficient heterogeneous catalyst for C—H activation of benzoxazole [51]. The outstanding catalytic performance of Co-MOF may be related the characteristic of the Co(II) coordination environment and mixed linkers [31].

We next studied the effect of the reagent molar ratio, since excess morpholine should be required. Fig. 4 shows the dependence of conversion on the effect of reagent molar ratio and reaction time. At 3 mol % catalyst loadings, nearly quantitative conversion was achieved after 12 h at room temperature when 1.5 equivalents of morpholine were used. The large decrease in reaction efficiency was also detected when lower amounts of morpholine were employed. Addition of a base such as NEt_3 or K_2CO_3 exhibited no conversion, indicating that it failed to undergo oxidative amination. Moreover, not even trace amounts of product were obtained in the absence of acid. As a consequence, the influence of acid additives (formic acid, acetic acid, benzoic acid and trifluoroacetic acid) was also examined. As shown in Fig. 5, formic acid, benzoic acid and trifluoroacetic acid are apparently unfavorable, where lower conversions were obtained. However, this reaction proceeded to nearly full conversion when acetic acid was employed. Further studies of the amount of acetic acid revealed that 2.0 equiv of acetic acid is favored (Fig. S5).

For organic transformations under heterogeneous conditions, the choice of solvent might induce a dramatic impact on the reaction rate, which is depended on the nature of the catalyst used. Hence, influence of different solvents, including CH_3CN, CH_2Cl_2, DMF, 1,4-dioxane, toluene, and hexane, were screened on the Co-MOF-catalyzed CDC amination of 5-methylbenzoxazole (Fig. 6). Indeed, the reaction efficiency was significantly affected by the system solvents used. The reactions proceeded with low efficiency in hexane, toluene and CH_2Cl_2, where < 45% conversions were detected. In contrast, conducting the

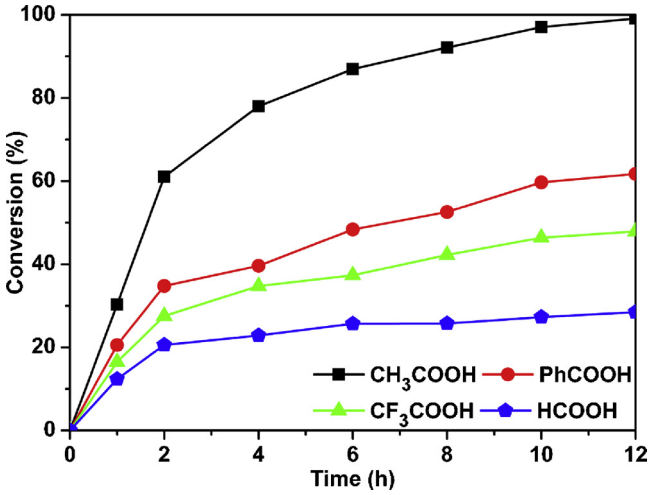


Fig. 5. Effect of different carboxylic acids on reaction conversion.

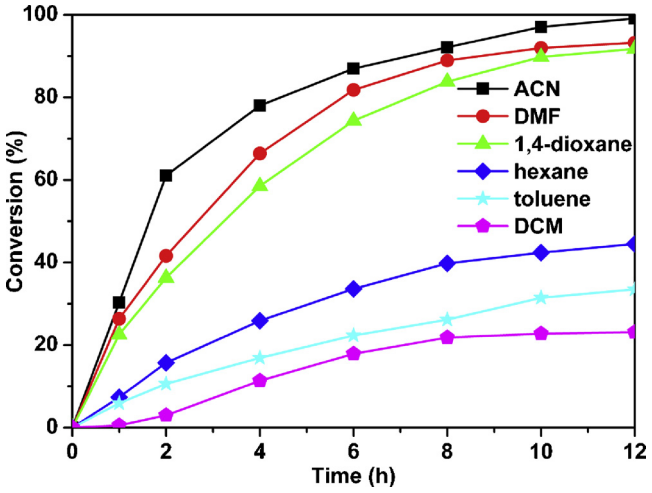


Fig. 6. Effect of different solvents on reaction conversion.

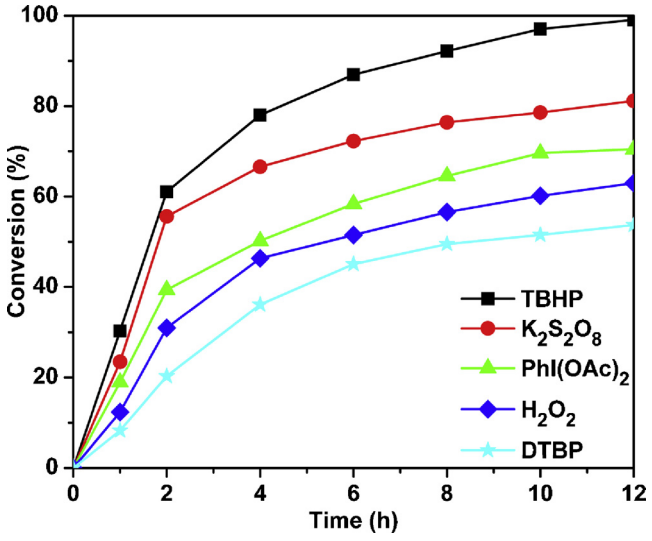


Fig. 7. Effect of different oxidants on reaction conversion.

reaction in polar solvents such as 1,4-dioxane, CH_3CN and DMF gave moderate to good conversions, and CH_3CN was found to be more effective to give a high conversion (> 99%). On the basis of the Co-catalyzed oxidative amination of azoles reported by Chang et al. [14], the

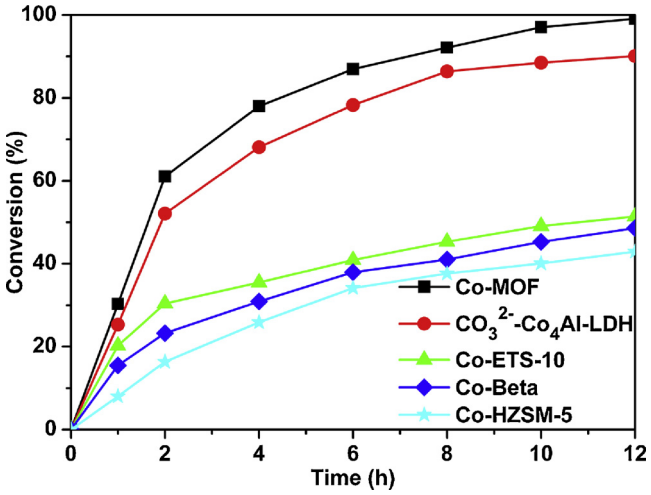


Fig. 8. Effect of Co-doped zeolites and Co-containing hydrotalcite on reaction conversion.

oxidant is crucial for this reaction. Therefore, we decided to attempt the oxidative coupling reaction with various oxidants at room temperature (Fig. 7). Experiments indicated that the efficiency of the oxidants such as H_2O_2, DTBP, $PhI(OAc)_2$ and $K_2S_2O_8$ proved less effective compared to TBHP. Moreover, the amination reaction would not take place without TBHP. Further investigation revealed that the reaction proceeded well with 2.0 equiv TBHP at room temperature in CH_3CN (Fig. S6).

In our previous work, Cu-doped zeolites and Co-containing layer double hydroxides (HLDs) have been developed for oxidative coupling and alcohol oxidation reactions, respectively [52,53]. As an ongoing effort, we also tested the catalytic activities of Co-doped zeolites (Co-Beta, Co-HZSM-5 and Co-ETS-10) and Co-containing hydrotalcite $CO_3^{2-}Co_4Al$-LDH in the oxidative CDC amination of 5-methylbenzoxazole. Compared with the Co-MOF catalyst, both Co-doped zeolites and Co-containing LDH exhibited lower catalytic performance under the similar reaction conditions, as shown in Fig. 8. Furthermore, the heterogeneous nature of the Co-MOF-catalyzed amination process was demonstrated by a leaching test (Fig. 9), where the reaction was stopped at partial conversion (~30%) and the Co-MOF was quickly removed by centrifugation at room temperature. After removal of the Co-MOF catalyst, the solution in the absence of solid was again stirred. After additional 11 h, no further product formation was detected. On the other hand, examination by Inductively Coupled Plasma (ICP)

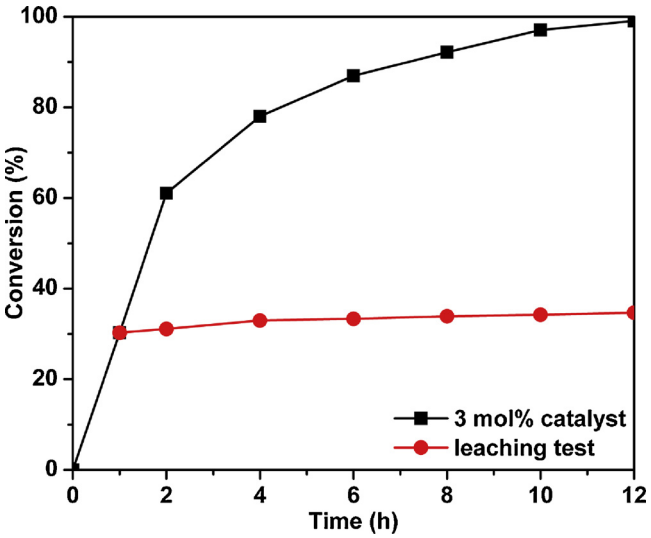
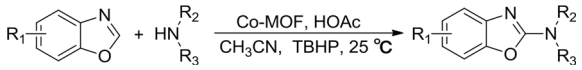
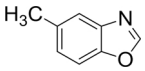
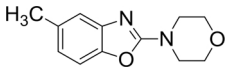
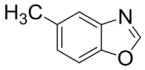
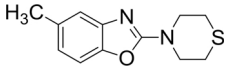
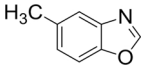
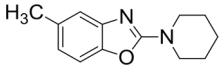
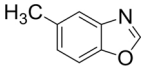
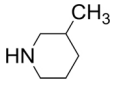
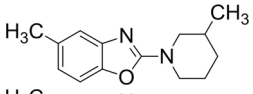
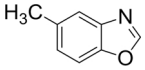
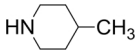
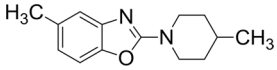
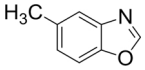
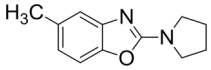
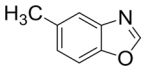
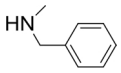
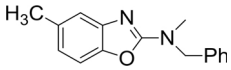
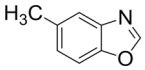
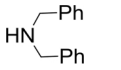
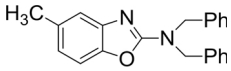
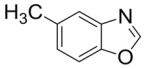
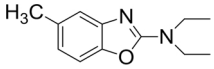
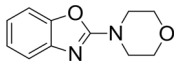
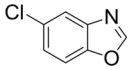
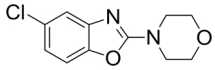
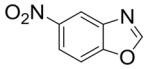
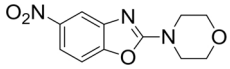


Fig. 9. Leaching test with Co-MOF removal during the amination process.

Table 1
Direct oxidative amination of benzoxazoles with secondary amines catalyzed by Co-MOF.



Entry	Benzoxazoles	Amines	Product	Isolated yield (%)
1				96
2				88
3				93
4				80
5				75
6				53
7				77
8				64
9				26
10				89
11				68
12				42

Reaction conditions: benzoxazoles (1 mmol), amines (1.2 mmol), Co-MOF (0.03 mmol, 3 mol%), HOAc (2 mmol), TBHP (2 mmol), CH_3CN (2 mL), 12 h, 25 °C.

analysis of the filtrate revealed negligible leaching amounts (< 1 ppm) of the cobalt. Hence, it can be concluded that the catalytic process should be truly heterogeneous.

Subsequently, the scope of the Co-MOF-catalyzed amination reaction was explored with diverse substituted benzoxazoles and different secondary amines under the optimized conditions (Table 1). Co-MOF was found to quite efficiently catalyze the six-membered cyclic amines to obtain the aminated products in excellent yields (entries 1–3), where methyl-substituted piperidines at C3 and C4 positions generated the corresponding aminated products with relatively low yield (entries 4 and 5). Moreover, under the same catalytic systems, the cross-dehydrogenative C—N bond formation of 5-methylbenzoxazole with five-membered pyrrole could be achieved in a good yield of 62% (entry 6). Non-cyclic amines such as *N*-methylbenzylamine, dibenzylamine and diethylamine could also be used as suitable amine sources in this transformation, affording reasonable yields (entries 7–9). Notably, although the amination reactions proceeded well with 5-methylbenzoxazole, benzoxazole, or 5-chlorobenzoxazole (entries 1, 10 and 11), a lower yield of 42% of the aminated product was obtained when benzoxazole bearing a nitro group at the C5 position of benzoxazole was used (entry 12).

3.3. Catalyst stability and recycling

In order to assess the catalyst stability and reusability, the oxidative CDC amination reactions were conducted as described above except for the use of the recovered Co-MOF catalyst. When the reaction was completed, the Co-MOF catalyst was collected by centrifugation and washed with ethanol. After drying at 60 °C overnight, the recovered Co-MOF can be reused for the next run under the same reaction conditions. PXRD, XPS, FI-IR and SEM analyses were performed on the recycled and fresh Co-MOF samples, and the results strongly exhibited good catalyst stability under the reaction conditions (Fig. 10). The recovered Co-MOF catalyst could almost maintain its high activity with no significant decrease even after six consecutive tests (Fig. 11).

3.4. Proposed mechanism

On the basis of the Co-catalyzed amination reported by Chang et al., a plausible mechanism for the Co-MOF-catalyzed amination of 5-methylbenzoxazole was proposed. As shown in Fig. 12, the starting 5-methylbenzoxazole substrate initially undergoes the protonation with the acid additive to generate the intermediate **A**. Subsequent nucleophilic addition of secondary amines is followed to afford the intermediate **B**. The oxidation of the intermediate **B** by alkoxy and alkylperoxy radicals then leads to the formation of the aminated product, where the generation of radicals in situ is promoted by the Co-MOF. (Fig. 12)

In addition, both single crystal photo (Fig. 1a) and SEM image (Fig. 10d) reveal that the crystalline Co-MOF particles have block morphology. BET surface area and pore size distribution have been measured (see Fig. S7). The results show that Co-MOF with the

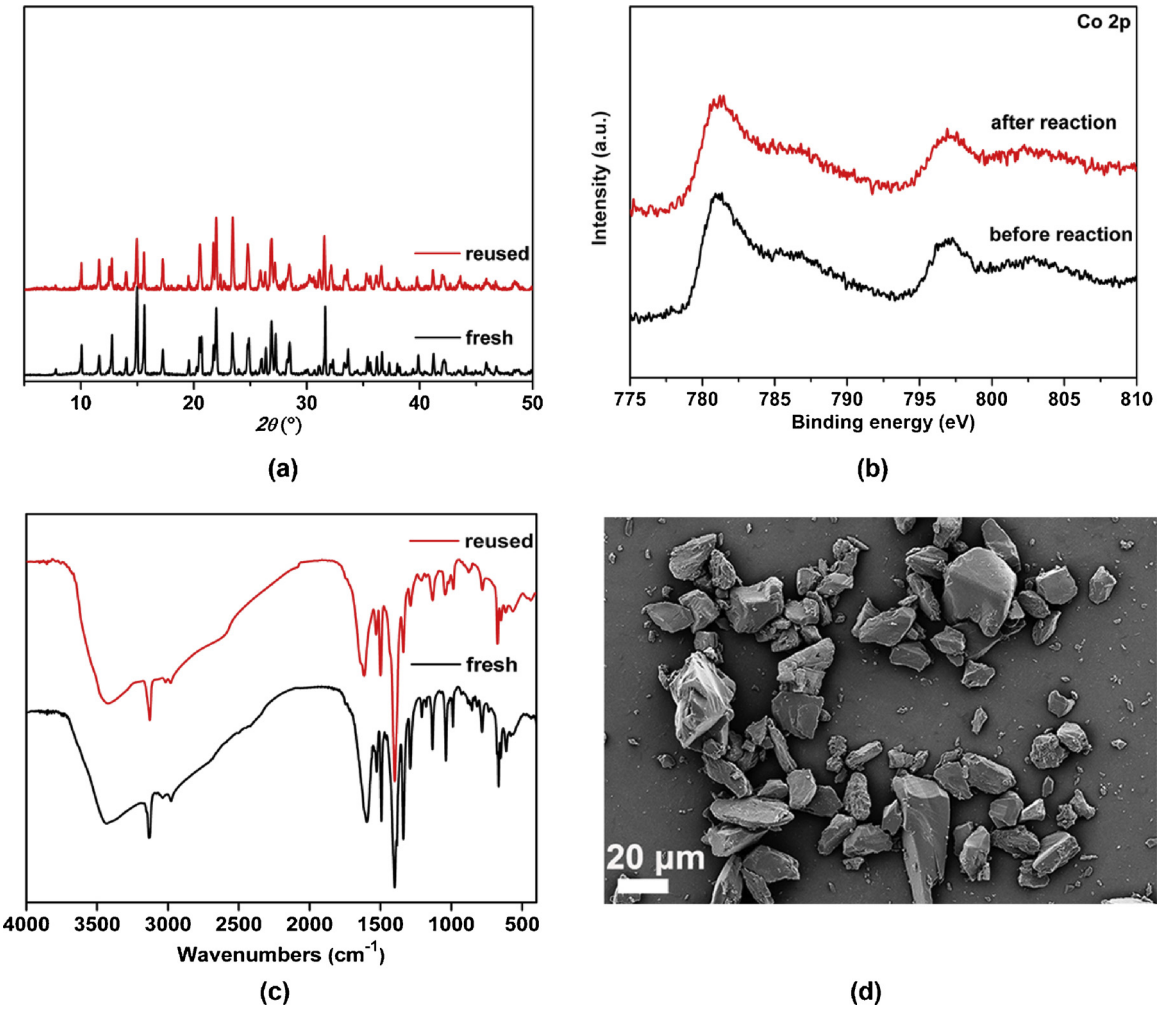


Fig. 10. PXRD (a), XPS (b), FT-IR (c) and SEM (d) studies of the fresh and reused Co-MOF.

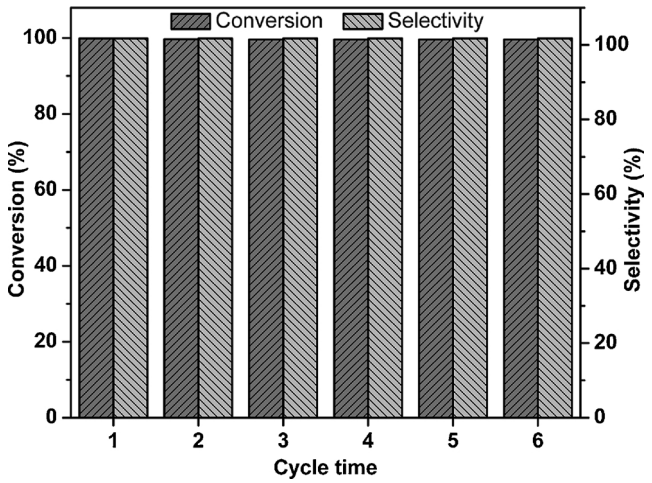


Fig. 11. Catalyst recycling studies.

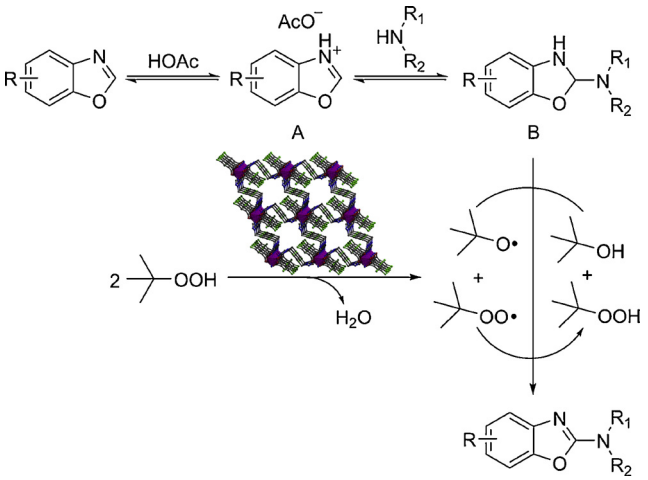


Fig. 12. Proposed reaction mechanism for the Co-MOF-catalyzed CDC amination of benzoxazoles.

interpenetrated structure has a very small surface area of 3.74 $m^2 g^{-1}$ and has no accessible pore distribution, which is consisted with the void space analysis as calculated by PLATON. Therefore, similar to reactions catalyzed by the interpenetrated MOFs [54,55], the Co-MOF-catalyzed amination reaction only occurs on exterior solid surfaces.

4. Conclusion

In summary, a new interpenetrated Co-based MOF catalyst was synthesized by the mixed-ligand synthetic strategy under hydrothermal conditions, and characterized by a variety of techniques including Single-crystal diffraction, PXRD, SEM, XPS, TGA, FI-IR, and nitrogen adsorption measurements. Crystal structure analysis revealed that Co-

MOF features a three-dimensional two-fold interpenetrating framework, which is a rare example of **cds**-type network. It should be noted that the as-synthesized Co-MOF exhibited good chemical stabilities. Moreover, this crystalline material was shown to be highly active, recyclable, and reusable heterogeneous catalyst in the direct amination of benzoxazoles under mild conditions, where good conversion, functional group tolerance and substrate scope were observed. The high activity was possibly attributed to the generation of radical species from the oxidants promoted by the Co-MOF. This work highlights the feasibility of using the mixed-ligand strategy to construct Co-based MOFs, aiming at the exploration of highly active heterogeneous catalyst for important organic transformations.

Acknowledgments

We gratefully acknowledge financial support by the National Natural Science Foundation of China (21676030), Jiangsu Province Prospective Industry-University-Research Cooperative Research Program of China (NO. BY2016029-08), and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mcat.2018.03.011.

References

[1] M.A.P. Martins, C.P. Frizzo, D.N. Moreira, L. Buriol, P. Machado, Chem. Rev. 109 (2009) 4140–4182.
[2] G. Zanatta, G. Nunes, E.M. Bezerra, R.F. da-Costa, A. Martins, E.W.S. Caetano, V.N. Freire, C. Gottfried, ACS Chem. Neurosci. 7 (2016) 1331–1347.
[3] C.D. Cox, M.J. Breslin, D.B. Whitman, J.D. Schreier, G.B. McGaughey, M.J. Bogusky, A.J. Roecker, S.P. Mercer, R.A. Bednar, W. Lemaire, J.G. Bruno, D.R. Reiss, C.M. Harrell, K.L. Murphy, S.L. Garson, S.M. Doran, T. Prueksaritanont, W.B. Anderson, C. Tang, S. Roller, T.D. Cabalu, D. Cui, G.D. Hartman, S.D. Young, K.S. Koblan, C.J. Winrow, J.J. Renger, P.J. Coleman, J. Med. Chem. 53 (2010) 5320–1117.
[4] S.C. Annedi, J. Ramnauth, S.P. Maddaford, P. Renton, S. Rakhit, G. Maldenova, P. Dove, S. Silverman, J.S. Andrews, M.D. Felice, F. Porreca, J. Med. Chem. 55 (2012) 943–955.
[5] K.G. Liu, J.R. Lo, T.A. Comery, G.M. Zhang, J.Y. Zhang, D.M. Kowal, D.L. Smith, L. Di, E.H. Kerns, L.E. Schechter, A.J. Robichaud, Bioorg. Med. Chem. Lett. 19 (2009) 1115–1117.
[6] E. Rattanangkool, M. Sukwattanasinitt, S. Wacharasindhu, J. Org. Chem. 82 (2017) 13256–13262.
[7] W.-J. Gao, W.-C. Li, C.-C. Zeng, H.-Y. Tian, L.-M. Hu, R.D. Little, J. Org. Chem. 79 (2014) 9613–9618.
[8] D. Yu, S. Lee, Y.N. Sum, Y. Zhang, Adv. Synth. Catal. 354 (2012) 1672–1678.
[9] T. Froehr, C.P. Sindlinger, U. Kloeckner, P. Finkbeiner, B.J. Nachtsheim, Org. Lett. 13 (2011) 3754–3757.
[10] M. Lamani, K.R. Prabhu, J. Org. Chem. 76 (2011) 7938–7944.
[11] A. Armstrong, J.C. Collins, Angew. Chem. Int. Ed. 49 (2010) 2282–2285.
[12] T. Kawano, K. Hirano, T. Satoh, M. Miura, J. Am. Chem. Soc. 132 (2010) 6900–6901.
[13] Y. Li, J. Liu, Y. Xie, R. Zhang, K. Jin, X. Wang, C. Duan, Org. Biomol. Chem. 10 (2012) 3715–3720.
[14] J.Y. Kim, S.H. Cho, J. Joseph, S. Chang, Angew. Chem. Int. Ed. 49 (2010) 9899–9903.
[15] S.H. Cho, J.Y. Kim, J. Kwak, S. Chang, Chem. Soc. Rev. 40 (2011) 5068–5083.
[16] J. Wang, J.-T. Hou, J. Wen, J. Zhang, X.-Q. Yu, Chem. Commun. 47 (2011) 3652–3654.
[17] P. Pal, A.K. Giri, H. Singh, S.C. Ghosh, A.B. Panda, Chem. – Asian J. 9 (2014) 2392–2396.
[18] X. Meng, Y. Wang, Y. Wang, B. Chen, Z. Jing, G. Chen, P. Zhao, J. Org. Chem. 82 (2017) 6922–6931.
[19] M. Yoon, R. Srirambalaji, K. Kim, Chem. Rev. 112 (2012) 1196–1231.
[20] J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang, C.-Y. Su, Chem. Soc. Rev. 43 (2014) 6011–6061.
[21] J. Gascon, A. Corma, F. Kapteijn, F.X. Llabrés i Xamena, ACS Catal. 4 (2014) 361–378.
[22] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem. Commun. 48 (2012) 11275–11288.
[23] X.-L. Lv, K. Wang, B. Wang, J. Su, X. Zou, Y. Xie, J.-R. Li, H.-C. Zhou, J. Am. Chem. Soc. 139 (2017) 211–217.
[24] K. Manna, T. Zhang, F.X. Greene, W. Lin, J. Am. Chem. Soc. 137 (2015) 2665–2673.
[25] N.T.S. Phan, P.H.L. Vu, T.T. Nguyen, J. Catal. 306 (2013) 38–46.
[26] T.-H. Park, A.J. Hickman, K. Koh, S. Martin, A.G. Wong-Foy, M.S. Sanford, A.J. Matzger, J. Am. Chem. Soc. 133 (2011) 20138–20141.
[27] H.T.N. Le, T.T. Nguyen, P.H.L. Vu, T. Truong, N.T.S. Phan, J. Mol. Catal. A: Chem. 391 (2014) 74–82.
[28] H.T.T. Nguyen, D.N.A. Doan, T. Truong, J. Mol. Catal. A: Chem. 426 (2017) 141–149.
[29] L.H.T. Nguyen, T.T. Nguyen, H.L. Nguyen, T.L.H. Doan, P.H. Tran, Catal. Sci. Technol. 7 (2017) 4346–4350.
[30] C. Huang, J. Wu, C. Song, R. Ding, Y. Qiao, H. Hou, J. Chang, Y. Fan, Chem. Commun. 51 (2015) 10353–10356.
[31] H. Irving, R.J.P. Williams, J. Chem. Soc. (1953) 3192–3210.
[32] A. Dhakshinamoorthy, A.M. Asiri, H. Garcia, Catal. Sci. Technol. 6 (2016) 5238–5261.
[33] S.-C. Chen, S.-N. Lu, F. Tian, N. Li, H.-Y. Qian, A.-J. Cui, M.-Y. He, Q. Chen, Catal. Commun. 95 (2017) 6–11.
[34] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germanny, 1997.
[35] A.X.S. Bruker, SAINT Software Reference Manual, (1998) (Madison, WI).
[36] G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germanny, 1997.
[37] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2002.
[38] M. Du, C.-P. Li, C.-S. Liu, S.-M. Fang, Coord. Chem. Rev. 257 (2013) 1282–1305.
[39] S.-C. Chen, A.-Q. Dai, K.-L. Huang, Z.-H. Zhang, A.-J. Cui, M.-Y. He, Q. Chen, Dalton Trans. 45 (2016) 3577–3589.
[40] S.-C. Chen, F. Tian, K.-L. Huang, C.-P. Li, J. Zhong, M.-Y. He, Z.-H. Zhang, H.-N. Wang, M. Du, Q. Chen, CrystEngComm 16 (2014) 7673–7680.
[41] S.-C. Chen, Z.-H. Zhang, K.-L. Huang, H.-K. Luo, M.-Y. He, M. Du, Q. Chen, CrystEngComm 15 (2013) 9613–9622.
[42] S.-C. Chen, Z.-H. Zhang, Q. Chen, L.-Q. Wang, J. Xu, M.-Y. He, M. Du, X.-P. Yang, R.A. Jones, Chem. Commun. 49 (2013) 1270–1272.
[43] S.-C. Chen, Z.-H. Zhang, Y.-S. Zhou, W.-Y. Zhou, Y.-Z. Li, M.-Y. He, Q. Chen, M. Du, Cryst. Growth Des. 11 (2011) 4190–4197.
[44] Z.-H. Zhang, S.-C. Chen, J.-L. Mi, M.-Y. He, Q. Chen, M. Du, Chem. Commun. 46 (2010) 8427–8429.
[45] S.-C. Chen, Z.-H. Zhang, K.-L. Huang, Q. Chen, M.-Y. He, A.-J. Cui, C. Li, Q. Liu, M. Du, Cryst. Growth Des. 8 (2008) 3437–3445.
[46] W.-Q. Kan, J. Yang, Y.-Y. Liu, J.-F. Ma, CrystEngComm 14 (2012) 6934–6945.
[47] D.-X. Xue, Y. Belmabkhout, O. Shekhah, H. Jiang, K. Adil, A.J. Cairns, M. Eddaoudi, J. Am. Chem. Soc. 1379 (2015) 5034–5040.
[48] R. Hili, A.K. Yudin, Nat. Chem. Biol. 2 (2006) 284–287.
[49] I.V. Seregin, V. Gevorgan, Chem. Soc. Rev. 36 (2007) 1173–1193.
[50] D. Monguchi, T. Fujiwara, H. Furukawa, A. Mori, Org. Lett. 11 (2009) 1607–1610.
[51] N.T.S. Phan, C.K. Nguyen, T.T. Nguyen, T. Truong, Catal. Sci. Technol. 4 (2014) 369–377.
[52] S. Chen, Z. Shao, Z. Fang, Q. Chen, T. Tang, W. Fu, L. Zhang, T. Tang, J. Catal. 338 (2016) 38–46.
[53] W.-Y. Zhou, P. Tian, F. Sun, M.-Y. He, Q. Chen, J. Catal. 335 (2016) 105–116.
[54] L. Ma, C.-D. Wu, M.M. Wanderley, W. Lin, Angew. Chem. Int. Ed. 49 (2010) 8244–8248.
[55] A. Burgun, R.S. Crees, M.L. Cole, C.J. Doonan, C.J. Sumby, Chem. Commun. 50 (2014) 11760–11763.