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ORIGINAL PAPER

Metal–organic frameworks of Cu_2(TPTC)-catalyzed cascade C–S coupling/C_{sp2}–H hydroxylation reaction

An-Qi Tian[1] · Shan Liu[1] · Zhi-Lin Ren[2] · Long Wang[1,3] · Dong-Sheng Li[1]

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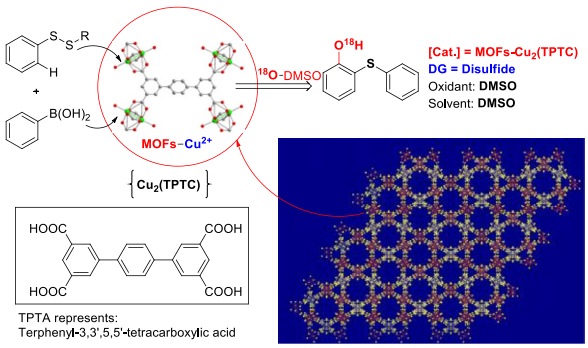
Abstract

This paper reports a novel disulfide-directed C_{sp2}–H hydroxylation cascade reaction strategy catalyzed by Cu_2(TPTC), a metal–organic framework material with binuclear Cu(II) paddlewheel nodes. In the strategy, Cu_2(TPTC) MOF can effectively catalyze the coupling reaction of disulfide and arylboronic acid, and realize the disulfide-directed C_{sp2}–H hydroxylation reaction. This reaction proceeded well under Cu_2(TPTC) MOF catalyst with good yields, which provides an efficient method to the synthesis of functional organic molecules, such as 2-(phenylthio)phenols derivatives.

Graphic abstract



Keywords Disulfide directed · C–H hydroxylation · Cascade reaction · Metal–organic frameworks

An-Qi Tian and Shan Liu have contributed equally to this work.

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✉ Long Wang
wanglongchem@ctgu.edu.cn

✉ Dong-Sheng Li
lidongsheng1@126.com

[1] Key Laboratory of Inorganic Nonmetallic Crystalline and Energy Conversion Materials, College of Materials and Chemical Engineering, China Three Gorges University, Yichang 443002, Hubei, China

[2] College of Chemical Engineering, Hubei University of Arts and Science, Xiangyang 441053, Hubei, China

[3] Material Analysis and Testing Center, China Three Gorges University, Yichang 443002, Hubei, China

Introduction

2-(Phenylthio)phenol derivatives play an important role in the field of medicinal chemistry due to their pharmacological potential, sensors and pigments [1–5]. In view of their pharmaceutical potential, the synthesis of 2-(phenylthio) phenol derivatives has attracted Chemists' much attention, and various efficient methods have been developed over the past decades [6, 7].

The development of C_{sp2}–H hydroxylation is a challenging process in organic synthesis. Transition-metal-catalyzed C–H activation, which the directing group plays an important role, has been recognized as one of the most efficient strategies for the hydroxylation of the arenes in the past few years [8–11]. Because of the strong coordination between

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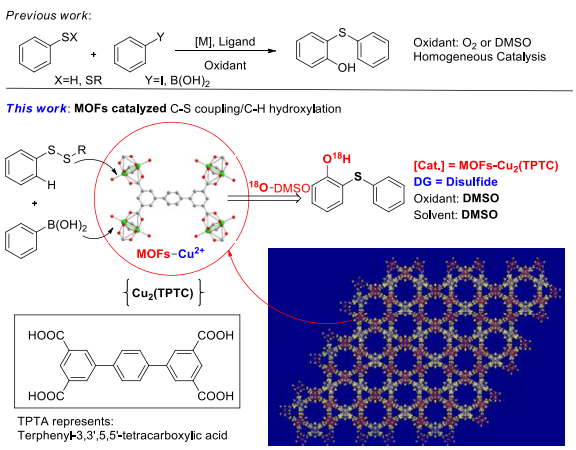
sulfur and metal cations, the application sulfur directing group, especially for disulfide as directing group, for transition-metal-catalyzed C–H activation is much more difficult, while the directing functional group containing N, O and P atoms has been widely reported [12–15]. For example, Yu et al. reported the N atom or carboxylic acid directed Pd-catalyzed ortho-hydroxylation of arenes [16, 17]. In addition, several other scientists also developed transition-metal-catalyzed C–H hydroxylation by changing the directing group or the oxidants or by applying other strategies [18–30]. However, the C–H hydroxylation with S atom as directing group remains a challenging issue. Wang et al. [31] described the synthesis of 2-(phenylthio)phenols via copper-catalyzed hydroxylation and S-arylation from thiophenols and aryl boronic acids. Meanwhile, Wang et al. [32] also described copper-catalyzed C–H hydroxylation from arylthiols and aryl iodides and some other works [33–43]. In 2010, Pan et al. reported the synthesis of 2-(phenylthio) phenols from thiophenols and aromatic halides for the first (Scheme 1) [44]. We also reported a disulfide-directed C–H hydrolytic reaction by a copper-catalyzed with oxygen as the oxidant [45] and lots of other works [46–58]. Several other scientists also put their efforts to C–H activation by sulfur directing group [59–62]. Among these limited successful examples for the C–H hydroxylation reaction, homogeneous metal complexes are usually used as catalysts.

Metal–organic frameworks (MOFs) are kinds of new porous functional materials. Through the coordination of different organic ligands with metal centers, MOFs are endowed with the functions in organic catalysis, optical, electrical and magnetic catalysis, adsorption and storage, gas selective separation, sensing, proton conduction, etc., and are widely used in catalysis, nonlinear optics, molecular magnetism, chemical sensors, material separation and many other fields [63–68]. Especially in catalysis field, the new material, relying on its unique properties, can significantly integrate the advantages of both homogeneous catalysis and heterogeneous catalysis, which can significantly improve some problems of homogeneous metal catalysis such as: uneconomic, unenvironmental, unhealth and unsafe issues, and has received increasing attention in recent years [69–72]. In this regard, Cu_2(TPTC) is one of the well-known mesoporous MOF, which is composed between Cu^{2+} ion and TPTC (terphenyl-3,3′,5,5′-tetracarboxylic acid) as linker [73]. Cu_2(TPTC) is of slurry wheel structure formed by a double-core copper cluster composed of two copper atoms and four TPTA ligands. Therefore, it has received extensive attention in the field of organic synthesis, such as oxidation, reduction, condensation and other fields [74–77]. However, to the best of our knowledge, there have been no reports on the application of Cu_2(TPTC) in C_{sp2}–H hydroxylation. Based on our previous studies [78–86], we developed a cascade C–S coupling/C_{sp2}–H hydroxylation reaction strategy catalyzed by Cu_2(TPTC) MOF, a metal–organic framework material with double-core copper cluster. A series of 2-(arylthio)phenols were synthesized using the tandem reaction.



Scheme 1 Cu_2(TPTC) MOF-catalyzed disulfide-directed C–S coupling/C–H hydroxylation

Experimental

Experimental details

All reagents, solvents were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 400 MHz spectrometers or a Bruker ACF-400 spectrometer with deuterated chloroform as solvent. Chemical shifts were reported relative to internal tetramethylsilane (d 0.00 ppm), $CDCl_3$ (d 7.26 ppm) for ^{1}H NMR and $CDCl_3$ (d 77.23 ppm) for ^{13}C NMR. The morphology of the crystals was determined by field-emission scanning electron microscope (SEM, JEOLJSM-6700F). XRD was recorded on a Rigaku Ultima IV (Rigaku, Japan), and thermogravimetric (TG) curves were operated on a NETZSCH449C thermal analyzer with a heating rate of 10 °C/min under oxygen atmosphere.

Typical procedure for the synthesis of 3

A mixture of disulfide **1a** (1 mmol) and boronic acid **2a** (2 mmol) in DMSO (5 mL) was stirred in a Schlenk tube at room temperature under protected by N_2 conditions. Whereafter, Cat (Cu_2(TPTC) MOF) (0.2 mmol) and base Cs_2CO_3 (2 mmol) were added into the Schlenk tube. The mixture was heated under 90 °C for 12 h. After the reaction was completed, the water (20 mL) and CH_2Cl_2 (3 × 15 mL) were used to extract the crude product. After the solvent has been removed under reduced pressure, the resulting

crude was purified by column chromatography with petroleum ether/ethyl acetate (25:1, v/v) as the eluent to give **3a** [45]. 5-chloro-2-(phenylthio)phenol (**3a**); light yellow oil, yield 86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.47 (d, J = 8.4 Hz, 1H, Ar–H), 7.25–7.19 (m, 2H, Ar–H), 7.19–7.14(m, 1H, Ar–H), 7.10–7.06 (m, 3H, Ar–H), 6.94 (dd, J = 8.4, 2.4 Hz, 1H, Ar–H), 6.56 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.8, 137.7, 137.5, 131.2, 129.3, 126.9, 126.4, 121.7, 116.0, 115.0.

5-chloro-2-(p-tolylthio)phenol (3b) [45] Light yellow oil, yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, J = 8.4 Hz, 1H, Ar–H), 7.11–6.87 (m, 6H, Ar–H), 6.56 (s, 1H, OH), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.6, 137.2, 136.7, 132.4, 131.5, 130.1, 127.6, 121.6, 116.0, 159.9, 20.9..

5-chloro-2-((4-methoxyphenyl)thio)phenol (3c) [45] Light yellow oil, yield 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.42 (d, J = 8.4 Hz, 1H, Ar–H), 7.19–7.09 (m, 2H, Ar–H), 7.03 (d, J = 2.0 Hz, 1H, Ar–H), 6.90 (dd, J = 8.0, 1.0 Hz, 1H, Ar–H), 6.87–6.75 (m, 2H, Ar–H), 6.60 (s, 1H, OH), 3.75 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 159.0, 157.2, 137.1, 136.7, 130.3, 125.4, 121.5, 117.4, 115.8, 115.1, 55.4.

5-chloro-2-((4-ethylphenyl)thio)phenol (3d) [45] Light yellow oil, yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, J = 8.4 Hz, 1H, Ar–H), 7.08 (d, J = 8.4 Hz, 3H, Ar–H), 7.08 (d, J = 8.4 Hz, 2H, Ar–H), 6.92 (dd, J = 8.4, 2.0 Hz, 1H, Ar–H), 6.60 (s, 1H, OH), 2.58 (q, J = 7.6 Hz, 2H, CH_2), 1.19 (t, J = 7.6 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.6, 143.0, 137.4, 137.3, 131.7, 128.9, 127.6, 121.6, 116.0, 115.9, 28.3, 15.4.

5-chloro-2-(m-tolylthio)phenol (3e) [45] Light yellow solid (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.4 Hz, 1H, Ar–H), 7.20–6.94 (m, 5H, Ar–H), 6.66 (d, J = 8.0 Hz, 1H, Ar–H), 6.45 (s, 1H, O–H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 137.6, 137.5, 135.7, 134.3, 130.5, 126.9, 126.2, 125.9, 121.8, 116.0, 114.7, 20.0.

2-((4-bromophenyl)thio)-5-chlorophenol (3f) [45] Light yellow oil, yield 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, J = 8.0 Hz, 1H, Ar–H), 7.37–7.33 (m, 2H, Ar–H), 7.09 (d, J = 2.4 Hz, 1H, Ar–H), 6.97–6.90 (m, 3H, Ar–H), 6.50 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.70, 138.08, 137.43, 134.50, 132.32, 128.43, 121.87, 120.30, 116.22, 114.54.

Methyl 4-((4-chloro-2-hydroxyphenyl)thio)benzoate (3g) [45] Light yellow oil, yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (d, J = 8.4 Hz, 2H, Ar–H), 7.45 (d, J = 8.0 Hz, 1H, Ar–H), 7.13 (d, J = 2.0 Hz, 1H, Ar–H), 7.06 (d, J = 8.4 Hz, 2H, Ar–H), 6.99 (dd, J = 8.0, 2.0 Hz, 1H, Ar–H), 6.47 (s, 1H, OH), 3.88 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4, 158.0, 141.8, 138.4, 137.7, 130.4, 127.9, 125.7, 122.0, 116.4, 113.4, 52.1.

2-(m-tolylthio)phenol (3h) [45] Light yellow oil, yield 82%; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.48 (d, J = 7.8, 1H, Ar–H), 7.39 (t, J = 7.8 Hz, 1H, Ar–H), 7.16 (d, J = 7.2 Hz, 1H, Ar–H), 7.10–6.95 (m, 4H, Ar–H), 6.65 (d, J = 7.8 Hz, 1H, Ar–H), 6.41 (s, 1H, OH), 2.45 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.8, 136.9, 135.4, 132.9, 132.1, 130.3, 126.8, 125.8, 125.7, 121.4, 115.5, 110.0, 20.1.

5-fluoro-2-((4-methoxyphenyl)thio)phenol (3i) [45] Light yellow oil, yield 77%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (dd, J = 8.4, 6.0 Hz, 1H, Ar–H), 7.12–7.06 (m, 2H, Ar–H), 6.84–6.60 (m, 5H, Ar–H, OH), 3.75 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 166.1, 163.6, 158.9, 158.3, 158.2, 137.5, 137.4, 129.7, 125.9, 125.9, 115.0, 113.9, 113.9, 108.7, 108.5, 103.2, 102.9, 55.3.

3-methyl-2-(phenylthio)phenol (3j) [45] Light yellow oil, yield 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31–7.10 (m, 4H, Ar–H), 7.03–6.98(m, 2H, Ar–H), 6.94 (d, J = 8.4 Hz, 1H, Ar–H), 6.88 (d, J = 7.6 Hz, 1H, Ar–H), 6.83 (s, 2H, OH), 2.38 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 157.7, 144.3, 135.1, 131.4, 129.2, 126.1, 125.8, 122.3, 115.6, 112.63, 21.1.

3-chloro-2-(phenylthio)phenol (3k) [45] Light yellow oil, yield 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.32–7.17 (m, 4H, Ar–H), 7.13–7.07 (m, 3H, Ar–H), 7.01 (dd, J = 8.4, 1.2 Hz, 1H, Ar–H), 6.93 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 158.8, 140.5, 134.0, 132.2, 129.3, 127.0, 126.5, 121.9, 116.3, 113.8.

4-methoxy-2-((4-methoxyphenyl)thio)phenol (3l) [45] Light yellow oil, yield 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, J = 8.8 Hz, 2H, Ar–H), 7.14 (t, J = 7.6 Hz, 1H, Ar–H), 6.90 (d, J = 8.4 Hz, 2H, Ar–H), 6.78–6.65 (m, 3H, Ar–H, OH), 3.82 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 156.0, 140.1, 135.6, 129.7, 123.9, 120.3, 115.0, 114.8, 113.4, 111.4, 55.4, 55.2.

Results and discussion

Structural characterization of the Cu_2(TPTC) MOF

Initially, the Cu_2(TPTC) MOF was synthesized from $Cu(NO_3)_2$, terphenyl-3,3′,5,5′-tetracarboxylic acid and HNO_3 according to the literature [73]. The Cu_2(TPTC) MOF

was characterized through X-ray power diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The SEM pattern of the as-synthesized Cu-MOF catalyst is shown in Fig. 1. According to the scanning electron microscopy analysis (Fig. 1), the morphology of the crystalline material is well-defined blue-green triangular diamond block crystal (0.07 × 0.24 × 0.26 mm). The XRD pattern of the as-synthesized Cu-MOF catalyst is shown in Fig. 2. The PXRD pattern of this material is substantially matched to the diffraction peaks simulated by its single-crystal structure, except for a slight increase in the diffraction peaks and the enhancement or attenuation of the diffraction peaks of some crystal faces. This can qualitatively indicate that Cu-MOF is a pure phase. The TGA pattern of the as-synthesized Cu-MOF catalyst is shown in Fig. 3. The thermogravimetric curve of the crystalline material Cu-MOF-2 is mainly represented by the three-step main weight loss: the first stage is the loss of lattice water and coordination water, which occurs in the temperature range of 25–105 °C. (Theoretical value: 8.9%, experimental value: 9.5%); the mass loss in the second stage is derived from the decomposition of solvent molecules such as free DMF in the channel, and the decomposition temperature range is: 195–420 °C (theoretical value: 27.5%), experimental value: 28.0%); the last weight loss interval is 425–695 °C, this phase corresponds to the decomposition of the ligand, the final thermal decomposition product may be CuO (theoretical value: 53.0%, experimental value: 51.5%).

Optimization of reaction conditions

We selected the simple disulfide **1a** and phenylboronic acid **2a** as model substrate to study the hydroxylation reaction of disulfides and aryl boronic acids. As shown in Table 1, the reaction was strongly catalyst dependent. When using copper salts such as $CuBr_2$, $CuCl_2$, CuCl, $Cu(NO_3)_2$ or Cu_2O as the catalyst in DMSO under protected by N_2

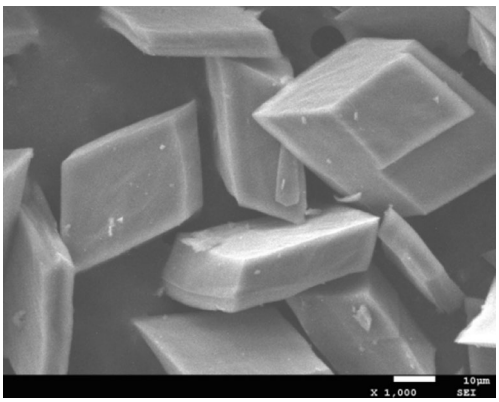


Fig. 1 SEM image of Cu_2(TPTC)

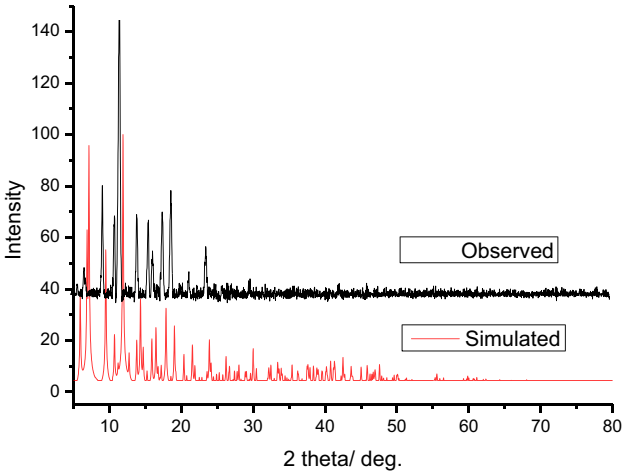


Fig. 2 XRD pattern of Cu_2(TPTC)

conditions at 90 °C, we only got the desired product **3a** at no more than 26% yield (entries 1–5, Table 1). To our great delight, the desired product **3a** was obtained at 86% yield when Cu_2(TPTC) MOF was used as the catalyst (entries 6, Table 1). Next, the solvent experiments were explored and the results showed that DMSO was the best solvent for this transformation (entries 6–10, Table 1). In addition, the screening of bases and reaction temperatures was also conducted; the results revealed that Cs_2CO_3 was the best base for this transformation and heating was beneficial to the reaction (entries 11–15, Table 1). Subsequently, the dosages of Cu_2(TPTC) MOF were examined; we found 10 mol% of Cu_2(TPTC) MOF gave the best yield (entry 6, Table 1), while 5 mol% and 20 mol% only provided 59% and 79% yield, respectively (entries 16–17, Table 1).

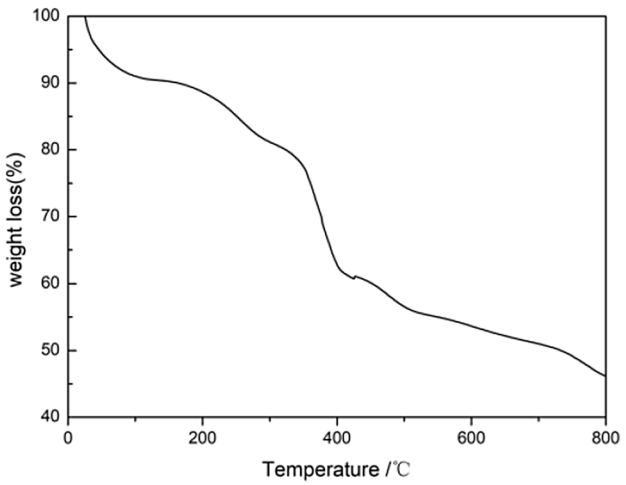
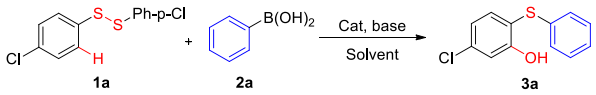


Fig. 3 TGA pattern of Cu_2(TPTC)

Table 1 Screening of reaction conditions



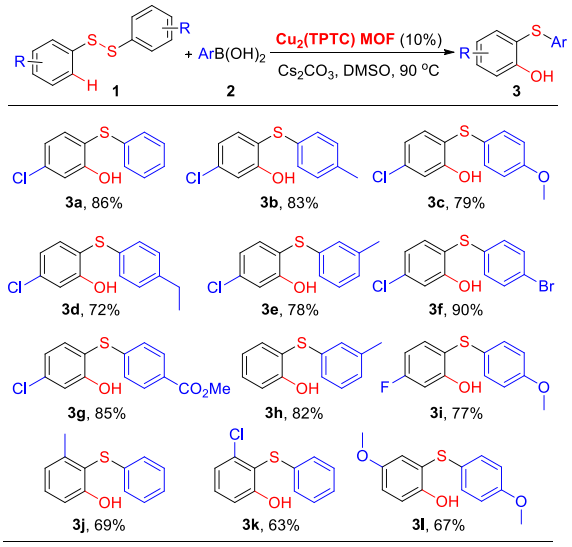
Entry	Catalyst	Base	Solvent	Yield (%)[a]
1	$CuBr_2$	Cs_2CO_3	DMSO	26
2	$CuCl_2$	Cs_2CO_3	DMSO	13
3	CuCl	Cs_2CO_3	DMSO	24
4	$Cu(NO_3)_2$	Cs_2CO_3	DMSO	17
5	Cu_2O	Cs_2CO_3	DMSO	15
6	Cu_2(TPTC) MOF	Cs_2CO_3	DMSO	86
7	Cu_2(TPTC) MOF	Cs_2CO_3	DMF	0
8	Cu_2(TPTC) MOF	Cs_2CO_3	Toluene	0
9	Cu_2(TPTC) MOF	Cs_2CO_3	THF	0
10	Cu_2(TPTC) MOF	Cs_2CO_3	DCM	0
11	Cu_2(TPTC) MOF	K_2CO_3	DMSO	46
12	Cu_2(TPTC) MOF	Na_2CO_3	DMSO	21
13	Cu_2(TPTC) MOF	*t*-BuOK	DMSO	0
14	Cu_2(TPTC) MOF	K_3PO_4	DMSO	19
15	Cu_2(TPTC) MOF	Cs_2CO_3	DMSO	45[b]
16	Cu_2(TPTC) MOF	Cs_2CO_3	DMSO	59[c]
17	Cu_2(TPTC) MOF	Cs_2CO_3	DMSO	79[d]

Conditions: **1a** (1 mmol), **2a** (2 mmol), cat (10 mol% to **1a**), base (2 mmol), solvent (5 mL), protected by N_2, 12 h, 90 °C. [a]Yields based on **1a.** [b]60 °C. [c]Yields based on cat (5 mol% to **1a**).[d]Yields based on cat (20 mol% to **1a**)

Synthesis of substrates

Having established the optimal conditions, we explored the scope of the disulfide-directed Cu_2(TPTC) MOF-catalyzed hydroxylation reaction and the results were summarized in Scheme 2. Generally, all the 2-(phenylthio)phenols could be obtained with good yields. As shown in Scheme 2, aryl boronic acid with electron-withdrawing substituents gave good yields, while disulfide with electron-donating substituents gave good yields. To our great joy, the desired product 2-(phenylthio)phenols **3** can be still obtained at moderate yields when R are ortho-substituents such as 2-Cl and 2-Me. Notably, ester which is included in aryl boronic acid is well tolerated in this reaction such as **3g**.

To better understand the reaction, we investigated the reaction mechanism. The control experiment of diphenyl sulfide as a substrate was carried on. The result showed that the product of 2-(phenylthio)phenol was not obtained (Scheme 3a). Meanwhile, the reaction cannot happen in DMF under nitrogen atmosphere (Scheme 3b). The labeling experiment was carried on to further understand the reaction mechanism. The using of the ^{18}O isotope-labeled DMSO

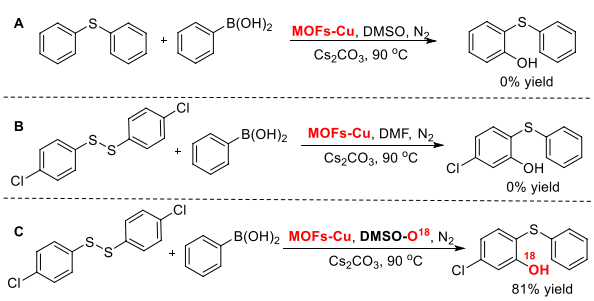


Scheme 2 The synthesis of 2-(phenylthio)phenols catalyzed by Cu_2(TPTC) MOF. Conditions: **1** (1 mmol), **2** (2 mmol), Cu_2(TPTC) (10 mol% to **1**), Cs_2CO_3 (2 mmol), DMSO (5 mL), protected by N_2, 12 h, 90 °C. Yields based on **1**

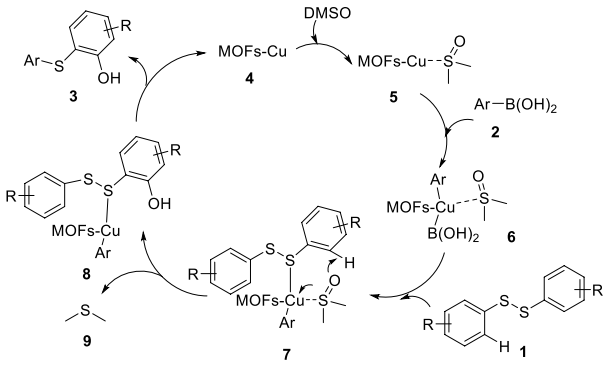
gave the product with ^{18}O on the phenol (Scheme 3c). Therefore, based on these experiments, we consider that the oxidant of the reaction is DMSO and the oxygen atom of product may be from DMSO, which was consistent with Wang' and Pan' work [31–44].

In order to understand of the C_{sp2}–H hydroxylation reaction, we proposed a possible reaction mechanism according to the references and our previous studies (Scheme 4). Firstly, the key intermediate **5** was formed under the presence of DMSO; then reacted with aryl boronic acid **2** to produce intermediate **6**; the disulfides **1** captured the intermediate **6** to generate **7**; and then hydroxylation of the C_{sp2}–H was occurred in the intermediate **7** to produce the key intermediate **8**. Finally, the product **3** was produced and the MOF-Cu catalyst **4** was released in situ.

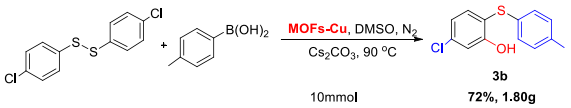
With this methodology in hand, a scale-up experiment was tested in order to assess the applicability of the reaction. We obtained **3b** in gram quantity with a good yield of 72% (Scheme 5).



Scheme 3 The investigations of the possible pathway



Scheme 4 The proposed possible mechanism



Scheme 5 Synthesis of the product **3b** on gram scale

Conclusion

In summary, this paper reports a novel disulfide-directed C_{sp2}–H hydroxylation cascade reaction strategy catalyzed by Cu_2(TPTC), a metal–organic framework material with binuclear Cu(II) paddlewheel nodes. In the strategy, Cu_2(TPTC) MOF can effectively catalyze the coupling reaction of disulfide and arylboronic acid, and realize the disulfide-directed C_{sp2}–H hydroxylation reaction. This reaction proceeded well under Cu_2(TPTC) MOF catalyst with good yields, which provides an efficient method to the synthesis of functional organic molecules, such as 2-(phenylthio)phenols derivatives. The preliminary mechanism investigation revealed that thioether could not realize this transformation and oxygen atom of product may be from DMSO.

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