Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Electronic Supplementary Information

# Blue light-driven selective aerobic oxidation of amines by benzothiadiazole metal–organic framework photocatalysis

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# Contents

## 1.1 Materials and solvents

All reagents were obtained from commercial vendors and used in their original form. The ligand $H_2BTDB$ (97%) was purchased from Leyan. The ligand amino-TPDC (97%) was provided by Adamas. $ZrCl_4$ (99%) was obtained from Aladdin. Trifluoroacetic acid (TFA) (99.5%) was purchased from Acros. Benzoic acid (97%) was acquired from TCI. Anhydrous *N*,*N*-dimethylformamide (DMF, >99.9%) was obtained from INNOCHEM.

## 1.2 The synthesis of UiO-68-BT and UiO-68-$NH_2$

UiO-68-BT was synthesized according to a prior report.[1] The ligand $H_2BTDB$ (0.18 mmol, 67.74 mg) was dissolved in 6 mL anhydrous DMF. Meantime, $ZrCl_4$ (0.18 mmol, 42.00 mg) was dissolved in 6 mL anhydrous DMF, followed by adding TFA (2.70 mmol, 0.42 mL). Then the two above solutions were blended together and sealed in a Pyrex tube (35 mL). The mixture was sonicated for 10 min and heated at 150 °C for 24 h. After cooling to room temperature, the resulting yellow suspension was centrifuged and washed with DMF and acetonitrile ($CH_3CN$) three times, respectively. Finally, the product was dried at 120 °C under vacuum overnight before further use.

UiO-68-$NH_2$ was prepared according to a previous reference[2]. $ZrCl_4$ (0.25 mmol, 0.06 g) and benzoic acid (8.00 mmol, 0.97 g) were dissolved in 12 mL anhydrous DMF. Afterwards, the ligand amino-TPDC (0.30 mmol, 0.11 g) was added to the solution and sealed in a Pyrex tube (35 mL), followed by ultrasonication for 20 min. Then, the mixture was placed in an oven at 120 °C for 24 h. The resulting precipitate was collected by centrifugation and thoroughly washed with DMF (30 mL × 3) and anhydrous ethanol (30 mL × 3). Then the samples were dispersed in anhydrous ethanol and left overnight under constant stirring. Finally, brown crystals were dried at 120 °C under vacuum for 12 h.

### 1.3. General procedure for selective aerobic oxidation of amines

Generally, 5 mg of UiO-68-$NH_2$ or UiO-68-BT photocatalyst and 0.3 mmol of amine substrate were uniformly dispersed in 1 mL of $CH_3CN$ in a 10 mL Pyrex reaction vessel equipped with a pierced rubber stopper linked the system with the outer atmosphere. The reaction vessel was stirred at 1500 r $min^{-1}$ and triggered with 3 W × 4 blue light-emitting diodes (LEDs). Before and after irradiation, the suspension was taken out, and centrifuged at 10000 r $min^{-1}$ to remove the photocatalyst. To calculate the conversion rate and selectivity, the supernatant was quantitatively analyzed using a gas chromatograph (GC) with a frame ionization detector (FID).

### 1.4 Detection of $H_2O_2$

The presence of $H_2O_2$ was determined indirectly by the established iodimetry method. 1.0 mL of 0.40 mol $L^{-1}$ potassium iodide and 1.0 mL of 0.10 mol $L^{-1}$ potassium hydrogen phthalate solutions were mixed followed by the addition of 1.0 mL of the reaction supernatant by centrifugation. Then, the liquid sample was kept over 30 min to ensure that $H_2O_2$ completely reacted with $I^-$ under acidic conditions to form $I^{3-}$. Lastly, the mixture was measured by UV−vis spectroscopy.

### 1.5 Detection of $NH_3$

Benzylamine (0.30 mmol) and UiO-68-BT (5.0 mg) was mixed in acetonitrile (1.0 mL), which was stirred and irradiated by blue LEDs for 25 min at room temperature in air. Then, UiO-68-BT material was separated from the reaction mixture by centrifugation. After that, 2.0 mL distilled water was added into the above solution, which subsequently was extracted by 5.0 mL dichloromethane for three. The aqueous layer was subject to pH test, showing its basic solution (pH = 8–9, Fig. S14). However, the pH value of the reaction solution was 6–7 in the absence of UiO-68-BT, which also indicated that the $NH_3$ was released from the aerobic oxidation reaction.

### 2.1 Characterizations

Powder X-ray diffraction (PXRD) measurement was implemented a Rigaku/Miniflex 600 diffractometer with a filtered Cu Kα radiation, and the results were recorded from 2° to 30° at room temperature. The Fourier transform infrared (FTIR) spectra were carried out on a NICOLET 5700 FTIR Spectrometer with Continuum IR Microscope ranging from 400–4000 $cm^{-1}$. The thermogravimetric analysis (TGA) was recorded on a SDT Q600 thermogravimeter from 30 to 800 °C at a ramp of 10 °C $min^{-1}$ under an $N_2$ atmosphere. The $N_2$ isotherms and specific surface areas were determined at 77 K employing a Micromeritics ASAP 2460 automated system with the Brunauer–Emmet–Teller (BET) mode, the material was degassed in vacuum ($< 1 \times 10^{-5}$ bar) at 120 °C for 3 h. Scanning electron microscopy (SEM) was measured on a Zeiss Merlin Compact running at the acceleration voltage between 0.1 and 20 kV, and energy dispersive spectroscopy (EDS) was recorded on X-MaxN. High-resolution transmission electron microscopy (HRTEM) image was recorded on a JEM-200 operating at 200 kV. The UV–visible absorption spectra were detailed on a Shimadzu UV-3600 UV–vis spectrophotometer with a diffuse reflectance measurement accessory. Time-resolved PL (PL decay curves) was measured by monitoring the decay of the intensity at the PL peak wavelength using the time-correlated single-photon counting fluorescence lifetime system FluoTime 300 of PicoQuant Instruments. The electron paramagnetic resonance (EPR) spectra were collected on an EPR spectrometer (JES-FA300, JEOL, Japan). The targeted products imines were confirmed by the retention time comparison with that of standard samples through a gas chromatograph equipped with a flame ionization detector (Agilent 8890), using $N_2$ as the carrier gas and bromobenzene as the internal standard. The products were further verified by gas chromatography–mass spectrometry (GC–MS, Agilent 8890-5977B), using He as the carrier gas.

## 2.2 Conversion of amines and selectivity of the targeted imines

$$\text{Conv. (\%)} = [(C_0 - C_S)/C_0] \times 100$$

$$\text{Sel. (\%)} = [C_P/(C_0 - C_S)] \times 100$$

where $C_0$ is the initial concentration of amines, and $C_S$ and $C_p$ are the concentrations of amines and imines at a certain time during the photocatalytic reaction.

### 2.3 Electrochemical measurements

Electrochemical measurements were executed on a Metrohm Autolab PGSTAT302N in a three-electrode electrochemical cell equipped with an electrochemical station. The working electrodes were prepared as follow: 6 mg of catalyst was dispersed in 3.0 mL absolute ethanol and 50 μL Nafion mixture solution, which was ultrasonically dispersed for 30 min, and then 60 μL of mixture solution was dropped onto the ITO with $\pi \times (0.2)^2$ $cm^2$ illuminated area and dried at room temperature, and the samples were dried under infrared irradiation. With 0.1 M $Na_2SO_4$ aqueous solution or 0.1 M $NH_4PF_6$ acetonitrile solution supplied as the electrolyte, the Ag/AgCl electrode and platinum wire were the reference electrode and counter electrode, respectively. Meanwhile, blue LEDs placed at 2 cm away from the photoelectrochemical cell were employed as the light source.

### 2.4 DFT simulation details

The B3LYP (UB3LYP) hybridized functional and a mix basis set (LANL2MB basis set for Zr atoms and 6-31G(d) basis set for other atoms) were used to calculate the HOMO and LUMO orbitals with Gaussian16, Revision C.01.

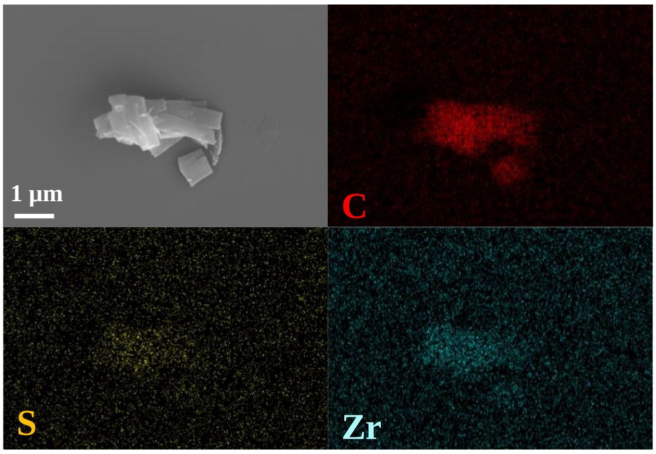


**Fig. S1.** EDX mappings of UiO-68-BT.

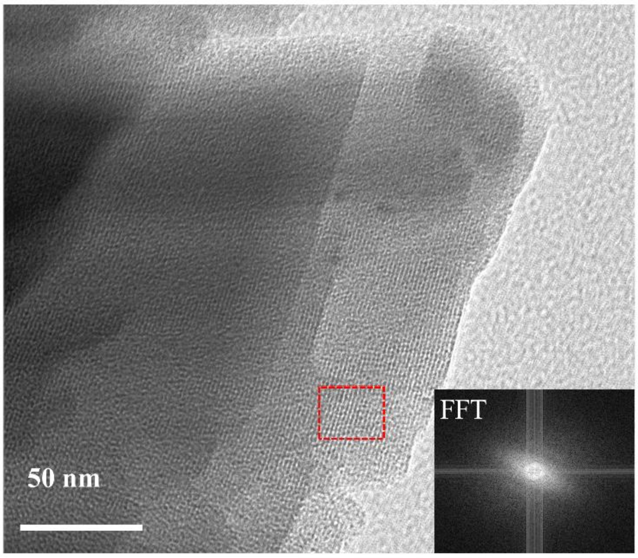


**Fig. S2.** HRTEM image of UiO-68-BT.

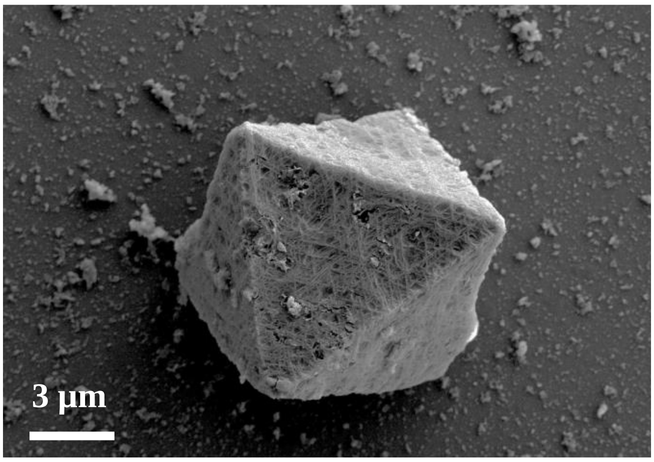


**Fig. S3.** FE-SEM image of UiO-68-$NH_2$.

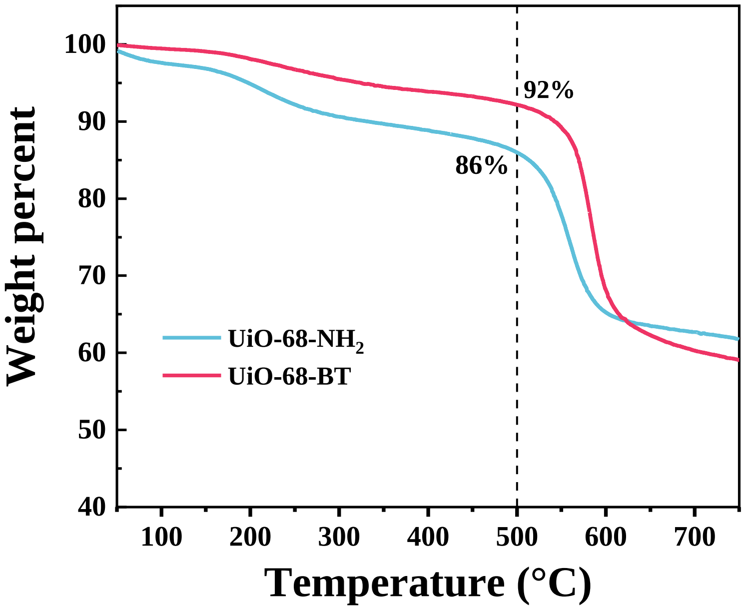


**Fig. S4.** The TGA trace of UiO-68-$NH_2$ and UiO-68-BT.

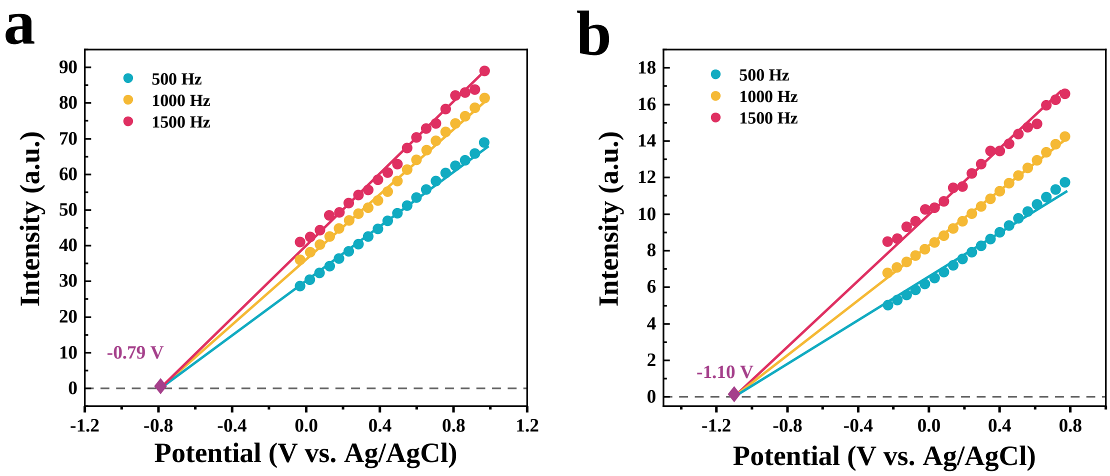


**Fig. S5.** Mott−Schottky plots of (a) UiO-68-$NH_2$ and (b) UiO-68-BT.

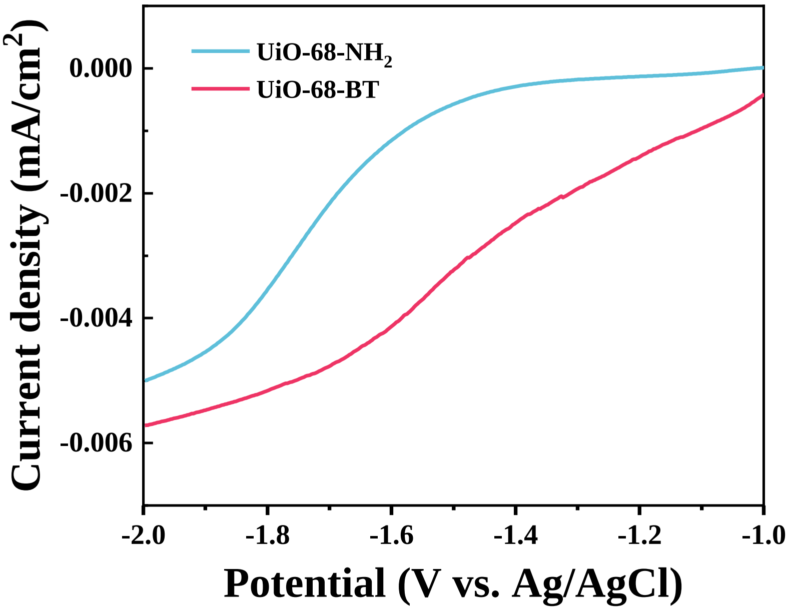


**Fig. S6.** LSV curves of UiO-68-$NH_2$ and UiO-68-BT.

**Table S1.** The effect of different solvents on the selective aerobic oxidation of benzylamine by UiO-68-BT[a].

| Entry | Solvents | Conv. (%) | Sel. (%) |
|---|---|---|---|
| 1 | $CH_3CN$ | 72 | 99 |
| 2 | $CH_3OH$ | 18 | 99 |
| 3 | $C_2H_5OH$ | 35 | 99 |

[a] Reaction conditions: UiO-68-BT (5 mg), benzylamine (0.3 mmol), solvent (1 mL), air (1 atm), 25 min, 460 nm blue LEDs (3 W × 4).

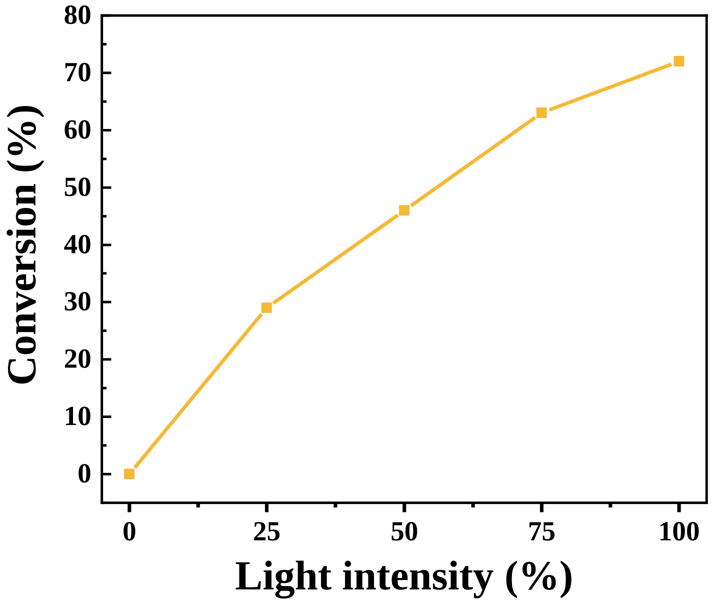


**Fig. S7.** The influence of light intensity for selective aerobic oxidation of benzylamine**.** Reaction conditions: UiO-68-BT (5 mg), benzylamine (0.3 mmol), solvent ($CH_3CN$, 1 mL), air (1 atm), 25 min, 460 nm blue LEDs (3 W × 4).

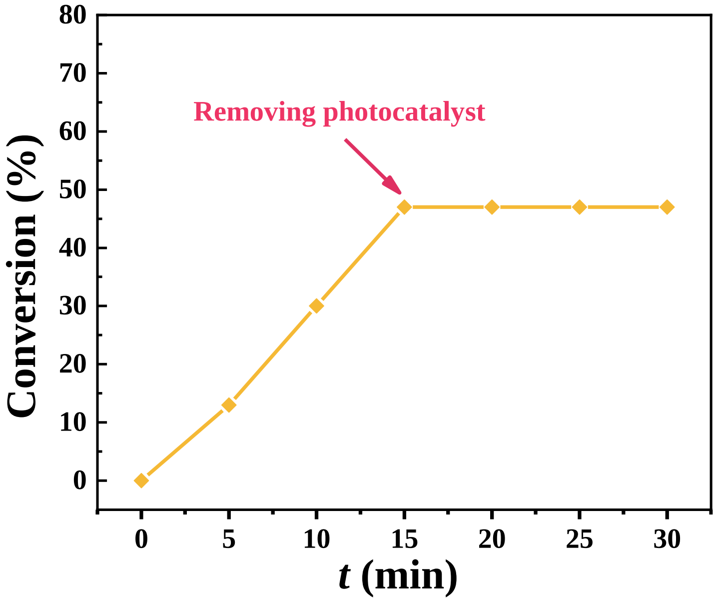


**Fig. S8.** The leaching test removing the UiO-68-BT photocatalyst after 15 min.

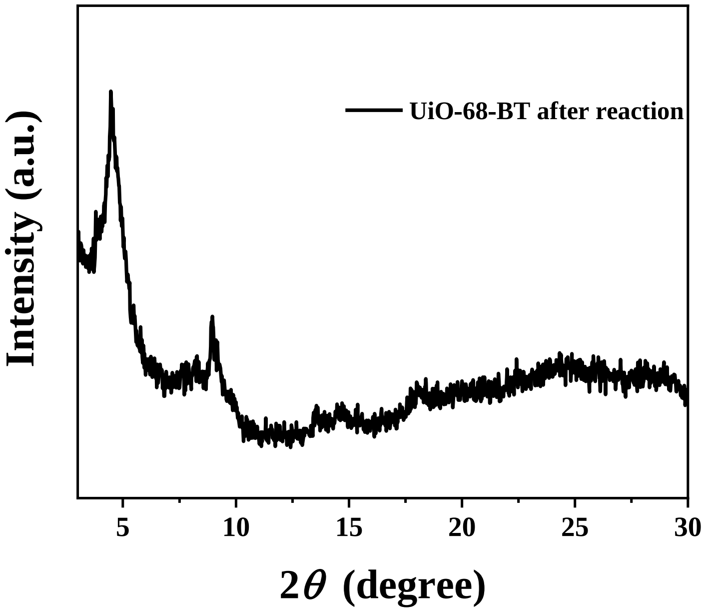


**Fig. S9.** The PXRD pattern of UiO-68-BT after the photocatalytic reaction.

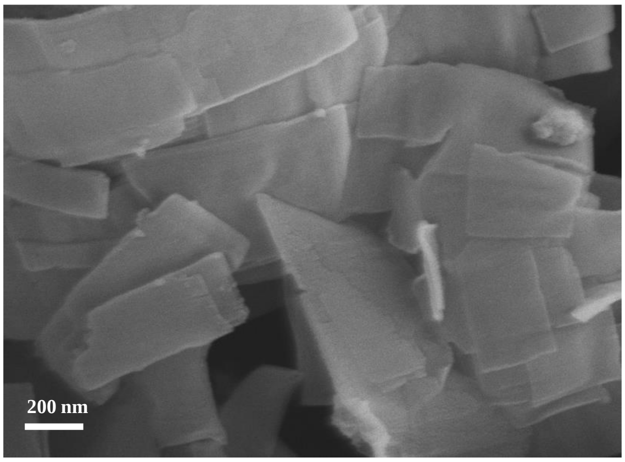


**Fig. S10.** The FE-SEM image of UiO-68-BT after the photocatalytic reaction.

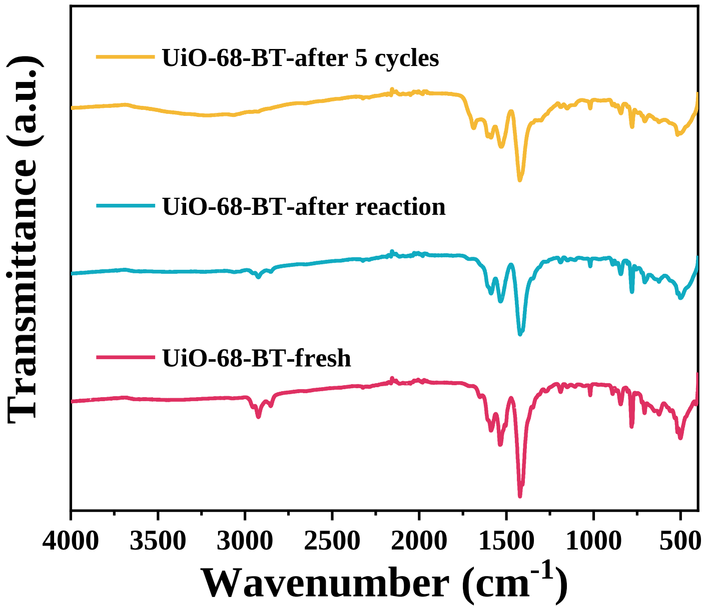


**Fig. S11.** The FTIR spectra of the fresh UiO-68-BT and UiO-68-BT after 5 cycles.

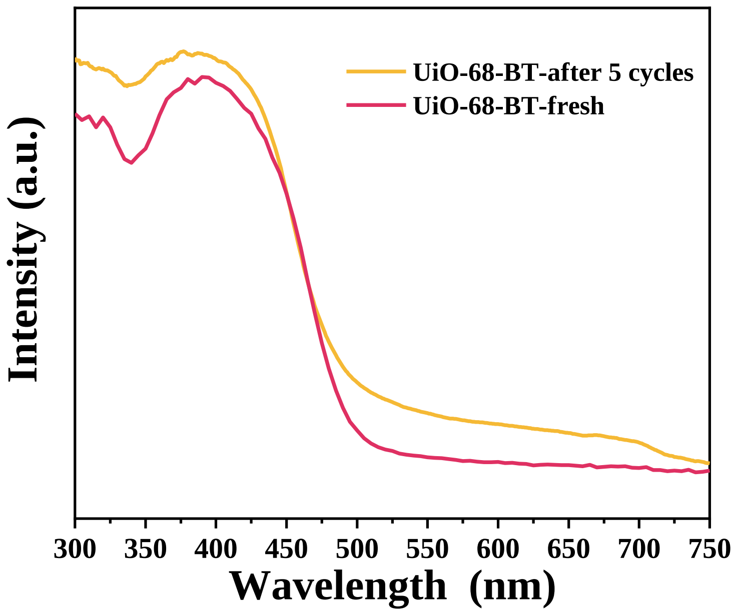


**Fig S12.** The UV–vis DRS spectra of UiO-68-BT and UiO-68-BT after 5 cycles.

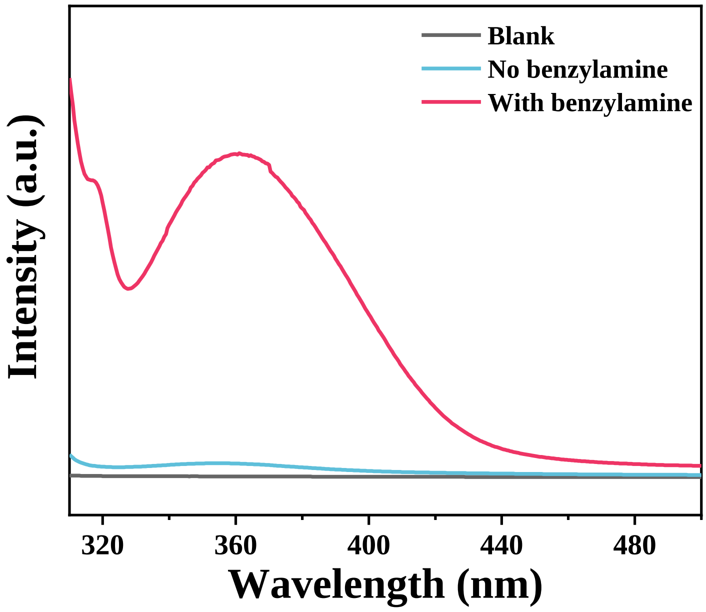


**Fig S13.** The UV–vis absorption spectra of the iodimetry solution.

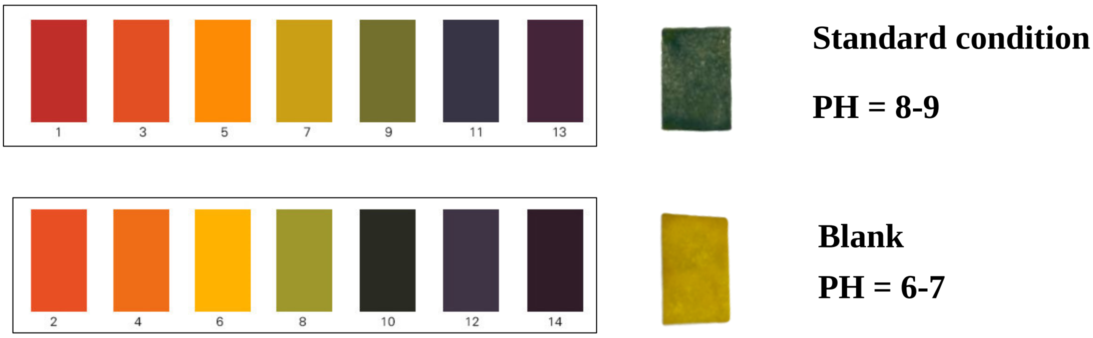
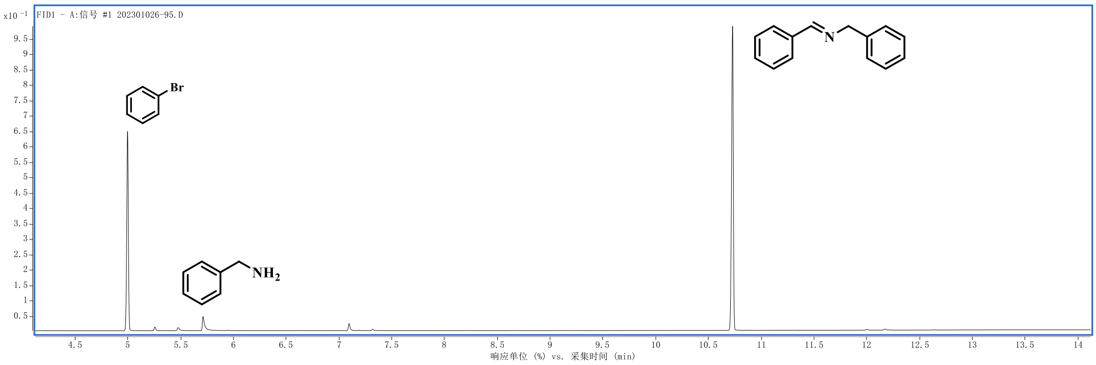


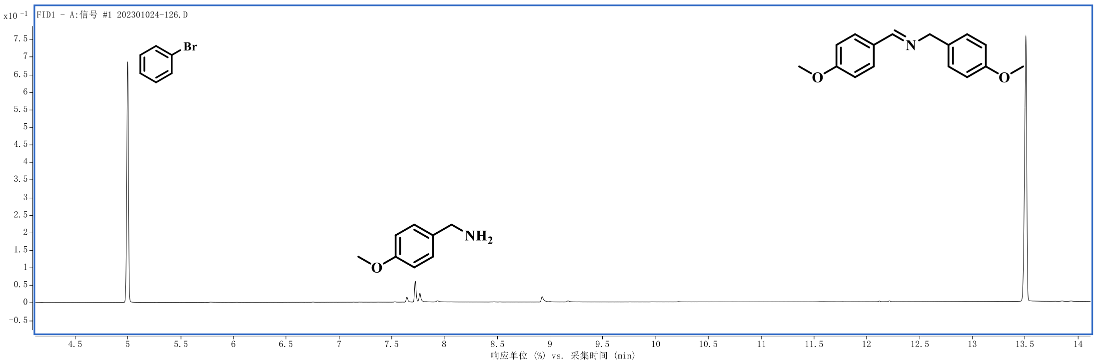
**Fig S14.** The pH test for the reaction solution after different conditions.

**Fig. S15.** GC–FID for results in Table 2.

## Table 2, Entry 1



## Table 2, Entry 2



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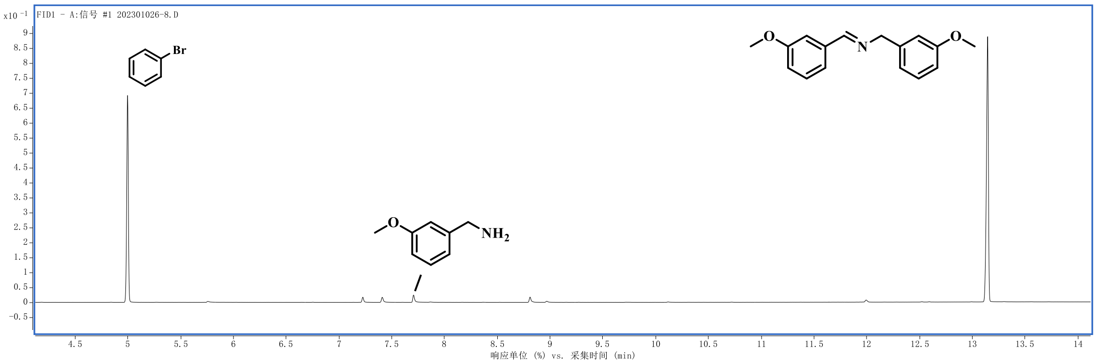

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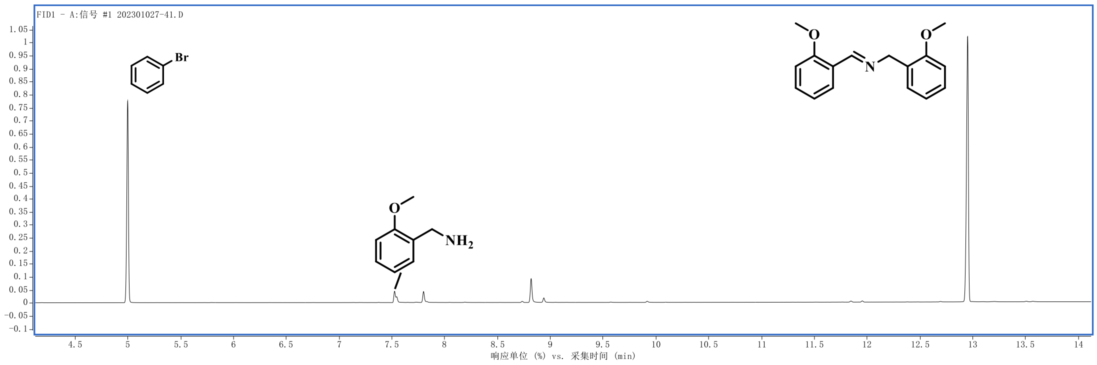

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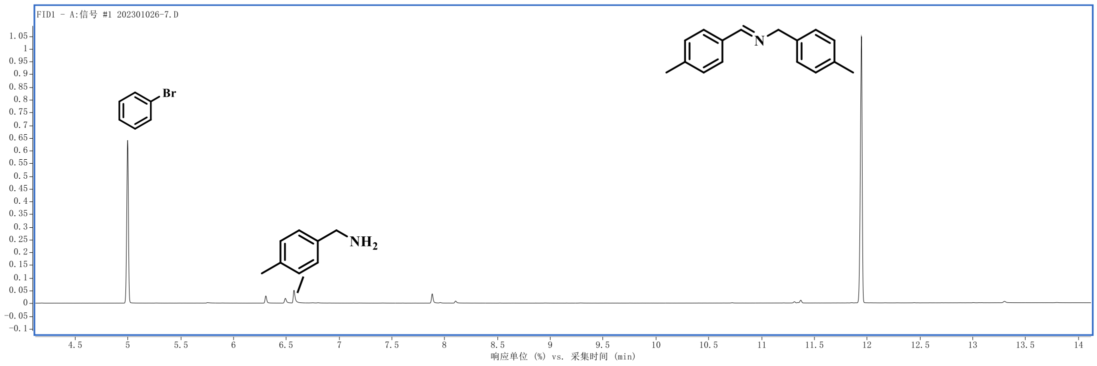

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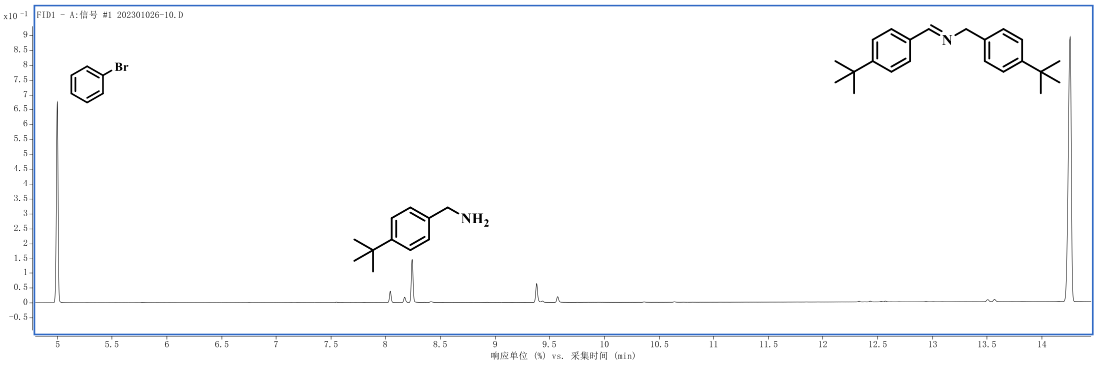

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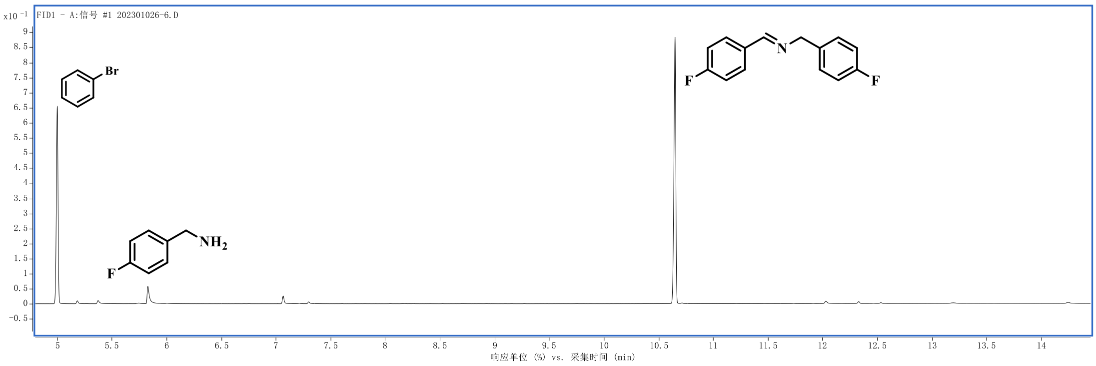

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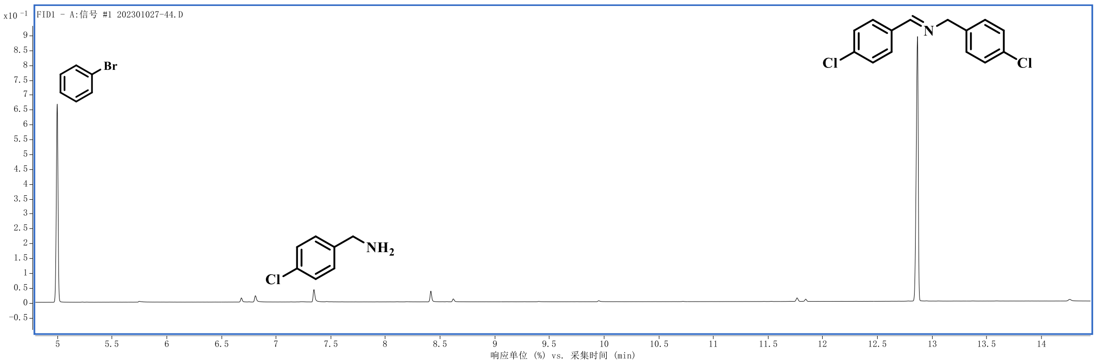

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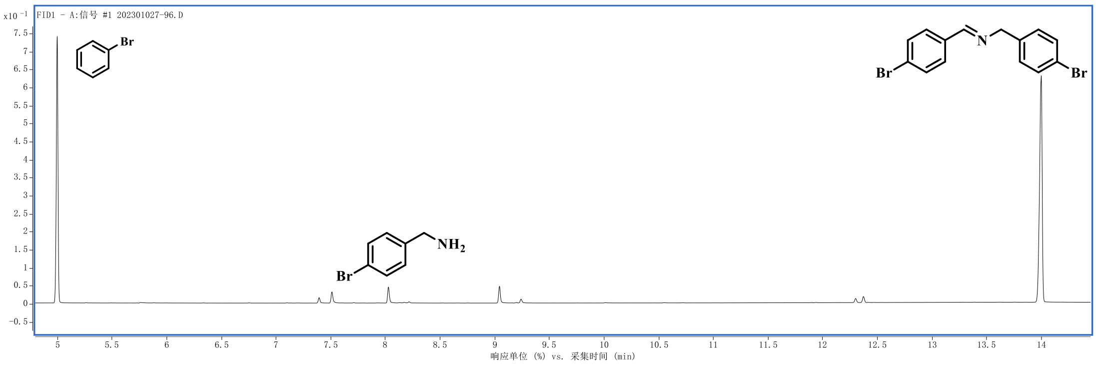

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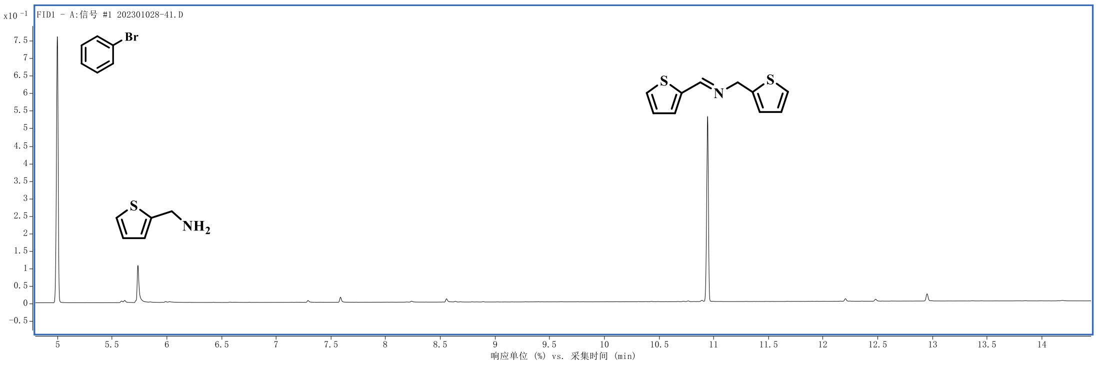

## 4. References

1. J. T. Jia, L. Gutiérrez-Arzaluz, O. Shekhah, N. Alsadun, J. Czaban-Józwiak, S. Zhou, O. M. Bakr, O. F. Mohammed and M. Eddaoudi, *J. Am. Chem. Soc.*, 2020, **142**, 8580–8584.
2. A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643–6651.