Supporting Information

A silver-functionalized metal–organic framework with effective antibacterial activity

Ya-Meng Wu[a], Pei-Chen Zhao[a], Bin Jia[b], Zhe Li[b], Shuai Yuan[a] and Cheng-Hui Li[a,*]

[a]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210023, P. R. China.

[b]National Laboratory of Solid State Microstructures, College of Engineering and Applied Sciences, School of Physics, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

E-mail: chli@nju.edu.cn

Materials and instrumentation. All reagents and solvents were commercially available and used without further purification unless otherwise indicated. Powder X-ray diffraction (PXRD) patterns were collected with a scan speed of 0.1 s·step^{-1} (0.02°/step) on a Bruker Advance D8 (40 kV, 40 mA) diffractometer with Cu radiation (λ= 1.54056 Å) at room temperature. Calculated PXRD patterns were generated using Mercury 3.0. Magnetization measurements were performed using a Quantum Design SQUID VSM magnetometer on polycrystalline samples for all compounds. Precise elemental concentrations of Ag and Zn were determined by inductively coupled plasma–mass spectrometry (ICP–MS) on an Optima 5300DV plasma ion spectrum mass spectrometer, for which the samples were prepared by dissolving NPs in HNO_3 at controlled concentrations. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker DRX 400 NMR spectrometer in deuterated dimethyl sulfoxide or chloroform at 25 °C. Scanning electron microscopy (SEM) analysis was carried out on an FEI Quanta 250 field emission scanning electron microscope (SEM) at an accelerating voltage of 10 kV.

X-Ray Crystallographic Analysis

Single-crystal X-ray diffraction intensity data for **Zn-MOF** were collected on a Bruker D8 Venture diffractometer fitted with a PHOTON-100 CMOS detector, monochromatized microfocus Mo Kα radiation (λ= 0.71073 Å), and a nitrogen flow controlled by a KRYOFLEX II low temperature

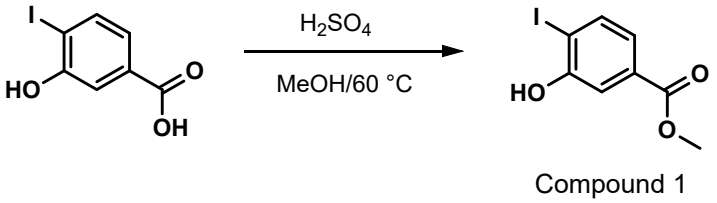
attachment operating at 193 K. Raw data collection and reduction were controlled using APEX3 software[1]. The structures were determined by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package[2]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of 2,2'-bis(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylic acid were placed at calculated ideal positions and isotropic displacement parameters were used. Those free solvent molecules of DMF or water were highly disordered and were unable to be located and refined. The solvent contents are not represented in the unit cell formula in the crystal data. CCDC 2128492 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis and characterization of ligands and crystals.

1. Synthesis of methyl 3-hydroxy-4-iodobenzoate (Compound 1).

To a solution of 3-hydroxy-4-iodobenzoic acid (10.00 g, 0.038 mol) in 140 mL methanol was added 3.5 mL concentrated sulfuric acid. The mixture was heated to 60 °C for 10 h and then allowed to cool to 0 °C with an ice-water bath. After adjusting the pH to 7 with saturated sodium bicarbonate solution, the solution was concentrated by rotary evaporation at 45 °C. The product was extracted 3 times with 60 mL of ethyl acetate, washed with saturated sodium chloride solution and dried with anhydrous sodium

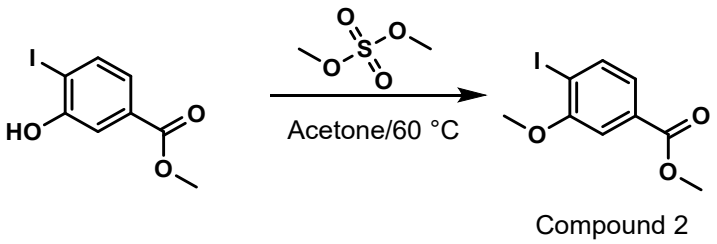
sulfate. ^{1}H NMR of methyl 3-hydroxy-4-iodobenzoate (**Compound 1**) (400 MHz, DMSO, δ, ppm): 10.76 (s, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.15 (dd, *J* = 8.1 Hz, 2 Hz, 1H), 3.83 (s, 3H) (Figure S1).



Scheme S1. Synthesis route of **Compound 1**.

2. Synthesis of methyl 4-iodo-3-methoxybenzoate (Compound 2).

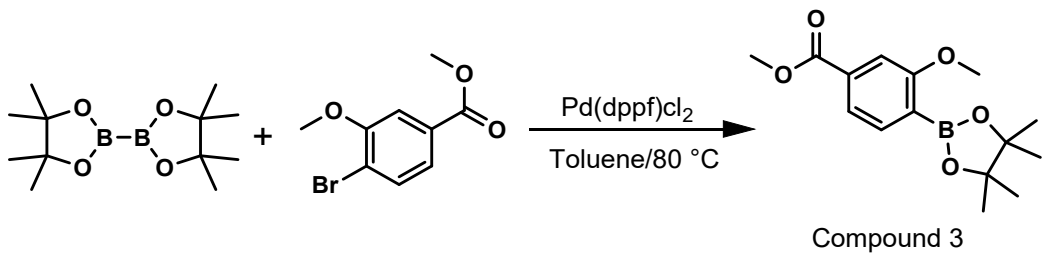
Compound 1 (9.67 g, 0.035 mol) and K_2CO_3 (5.87 g, 0.042 mol) were dissolved in 150 mL acetone, and then 4 mL dimethyl sulfate was added while stirring. The mixture was stirred for 4 h at 55 °C under an argon atmosphere, and then deionized water was added. After that, the solution was concentrated by rotary evaporation at 45 °C to remove acetone. The products were extracted 3 times with dichloromethane and then filtered after drying with anhydrous Mg_2SO_4. Finally, the solution was concentrated by rotary evaporation at 30 °C, and dark-red oily liquid was obtained. ^{1}H NMR of methyl 4-iodo-3-methoxybenzoate (**Compound 2**) (400 MHz, $CDCl_3$, δ, ppm): 7.73 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 1.8 Hz, 1H), 7.24 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 6H) (Figure S2).



Scheme S2. Synthesis route of **Compound 2**.

3. Synthesis of methyl 3-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (Compound 3).

To a solution of [1,1'-bis(diphenylphosphino)ferrocene], palladium(II) chloride (0.60 g, 0.82 mmol) and potassium acetate (8.00 g, 0.081 mol) in 30 mL toluene was added to methyl 4-bromo-3-methoxybenzoate (10.00 g, 0.041 mol), and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (11.45 g, 0.045 mol) in 120 mL toluene. The mixture was stirred for 12 h at 80 °C. Then, the extract was extracted with deionized water to obtain a black product, and the extract was extracted with ethyl acetate to obtain a brown–black oily substance, which was the target product. ^{1}H NMR of methyl 3-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (**Compound 3**) (400 MHz, $CDCl_3$, δ, ppm): 7.63 (d, J = 7.5 Hz, 1H), 7.53 (dd, J = 7.6 Hz, 1.3 Hz, 1H), 7.43 (d, J = 1.3 Hz, 1H), 3.83 (d, J = 12.8 Hz, 6H), 1.30 (s, 13H) (Figure S3).

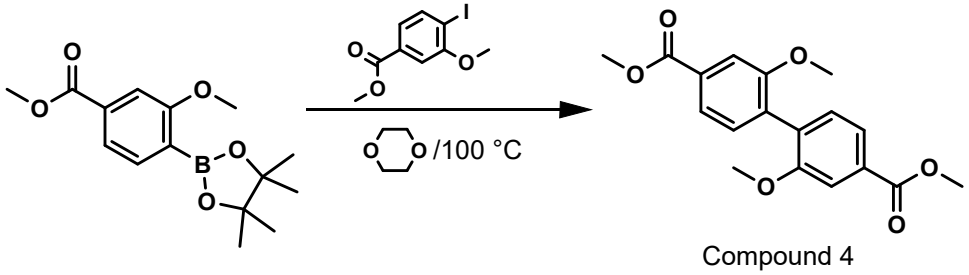


Scheme S3. Synthesis route of **Compound 3**.

4. Synthesis of dimethyl 2,2'-dimethoxy-[1,1'-biphenyl]-4,4'-

dicarboxylate (Compound 4).

Compound 3 (8.40 g, 0.029 mol) and Compound 2 (7.00 g, 0.024 mol) were mixed in 120 mL 1,4-Dioxane, followed by the addition of $Pd(PPh_3)_4$ (0.17 g, 0.145 mmol) and Cs_2CO_3 (15.62 g, 0.048 mol). The mixture was stirred for 48 h at 100 °C under an argon atmosphere, and the color changed from off-white to yellow–green. The solution was concentrated by rotary evaporation at 65 °C to remove 1,4-dioxane, followed by the addition of 50 mL deionized water, after which it was dissolved and filtered to remove Cs_2CO_3. The products were purified by column chromatography with ethyl acetate:petroleum ether = 1:15 as the eluent, and then the final product was obtained. ^{1}H NMR of dimethyl 2,2'-dimethoxy-[1,1'-biphenyl]-4,4'-dicarboxylate (**Compound 4**) (400 MHz, $CDCl_3$, δ, ppm): 7.63 (dd, J = 7.8 Hz, 1.5 Hz, 1H), 7.57 (d, J = 1.6 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H) (Figure S4).

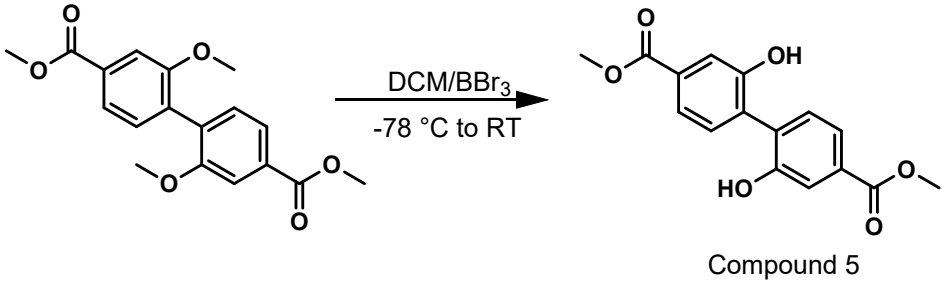


Scheme S4. Synthesis route of **Compound 4**.

5. Synthesis of dimethyl 2,2'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (Compound 5).

To a solution of Compound 4 (6.40 g, 0.019 mol) in 100 mL anhydrous CH_2Cl_2, the mixture was stirred for 10 minutes at -78 °C under argon

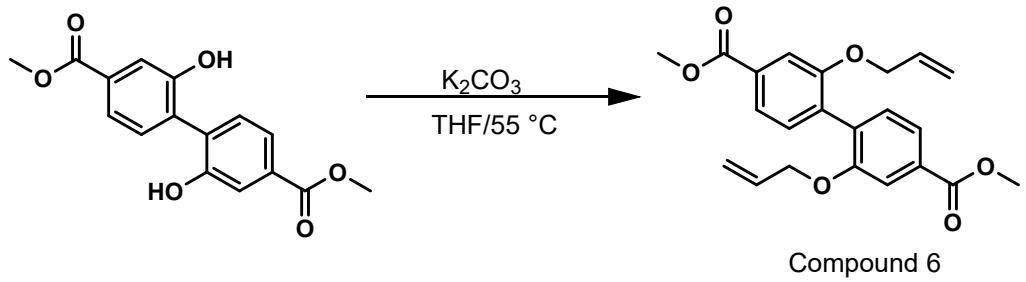
atmosphere, which was added slowly by BBr_3 (10.47 g, 0.042 mol) in 50 mL anhydrous CH_2Cl_2. The mixture was slowly raised to room temperature and reacted for 12 h. Then, 20 mL deionized water was added to quench the reaction. The solution was concentrated by rotary evaporation at 30 °C to remove CH_2Cl_2. The residue was filtered and washed with deionized water. The final product was subjected to vacuum evaporation to remove the solvent (compound 5 was directly used to synthesize 6 after synthesis).



Scheme S5. Synthesis route of **Compound 5**.

6. Synthesis of dimethyl 2,2'-bis(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylate (Compound 6).

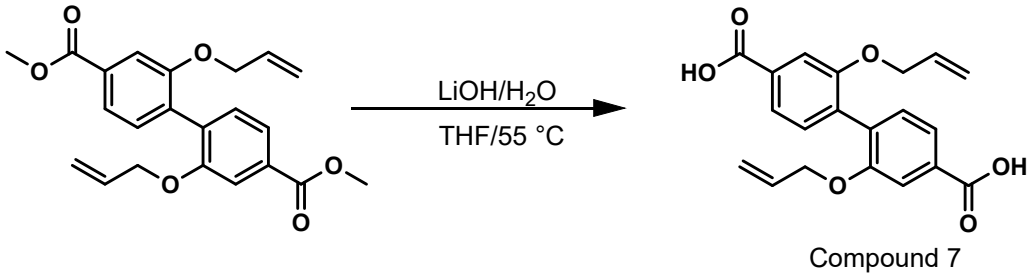
Compound 5 (4.81 g, 0.016 mol) and 3-bromoprop-1-ene (4.84 g, 0.4 mol) were mixed in 150 mL anhydrous DMF, to which K_2CO_3 (22.11 g, 0.16 mol) was added. The mixture was stirred for 24 h at 70 °C under argon atmosphere. When the reaction was complete, it was cooled to room temperature and purified by column chromatography with ethyl acetate: petroleum ether from 1:8 to 1:5 as the eluent (compound 6 was directly used to synthesize 7 after synthesis).



Scheme S6. Synthesis route of **Compound 6**.

7. Synthesis of 2,2'-bis(allyloxy)-[1,1'-biphenyl]-4,4'-dicarboxylic acid (Compound 7).

To a solution of Compound 6 (2.78 g, 0.007 mol) in 50 mL tetrahydrofuran, LiOH (4.17 g, 0.17 mol) was added to 30 mL deionized water. The mixture was stirred for 12 h at 75 °C under argon atmosphere. Then, the mixture was cooled to room temperature and concentrated by rotary evaporation at 45 °C to remove tetrahydrofuran. The pH was adjusted to 3-4 with HCl and filtered, and the final product was subjected to vacuum evaporation to remove the solvent. (**Compound 7**) (400 MHz, $CDCl_3$, δ, ppm): ^{1}H NMR (400 MHz, DMSO) δ 13.06 (s, 1H), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.56 (d, *J* = 1.5 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 5.99-5.85 (m, 1H), 5.23-5.12 (m, 2H), 4.59 (dt, *J* = 4.8, 1.8 Hz, 2H) (Figure S5).



Scheme S7. Synthesis route of **Compound 7**.

8. Solvothermal synthesis of Zn-MOF.

Briefly, compound 7 (10 mg, 0.028 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (33.6 mg,

0.113 mmol) were dissolved in 3 mL *N, N*-dimethylformamide (DMF). The mixture was heated from 40 ℃ to 90 ℃ at a rate of 5 ℃/h, kept at 90 ℃ for 72 h, and then decreased from 90 ℃ to 30 ℃ at a rate of 5 ℃/h. The crystalline products were filtered and washed with DMF three times.

9. Synthesis of Ag@Zn-MOF.

Zn-MOF (4 mg) was added to a 10 mL dichloromethane (DCM) solution of 10 mg $AgBF_4$, soaked for 12 h and kept away from light. Then, the processed MOFs were exchanged 2 times (once every half an hour) by hexane for BET.

10. Bacterial Cell Growth Assay.

Single colonies of *S. aureus* and *E. coli* strains were obtained from LB agar plates. These two bacterial strain cultures were grown overnight from a single colony in LB medium at 37 °C. After dilution with LB medium to adjust the initial density of the bacterial strains, *E. coli* and *S. aureus* had an initial density of 1×10^6 CFU/mL.

According to the following different experimental groups, the growth curves were determined. Zn-MOF, Ag@Zn-MOF (5 μg cm^{-3}), and Ag@Zn-MOF (25 μg cm^{-3}) were added to the bacterial suspension. (*E. coli* and *S. aureus*, 1×10^6 CFU/mL) to establish different experimental groups in a 96-well plate. MOFs were dissolved in diluted DMSO (HPLC grade) to ensure that the solution was clear and did not interfere with the test. *E. coli* and *S. aureus* suspensions treated with diluted DMSO (HPLC grade)

were used as controls.

All these groups used a SpectraMax iD3 microplate reader (Molecular Devices, USA) to measure cell growth at 37 °C and obtain an optical density reading (600 nm) within 24 h. The OD600 values were measured every 10 min, and the suspensions were shaken for 10 s before each measurement.

Results and Discussion

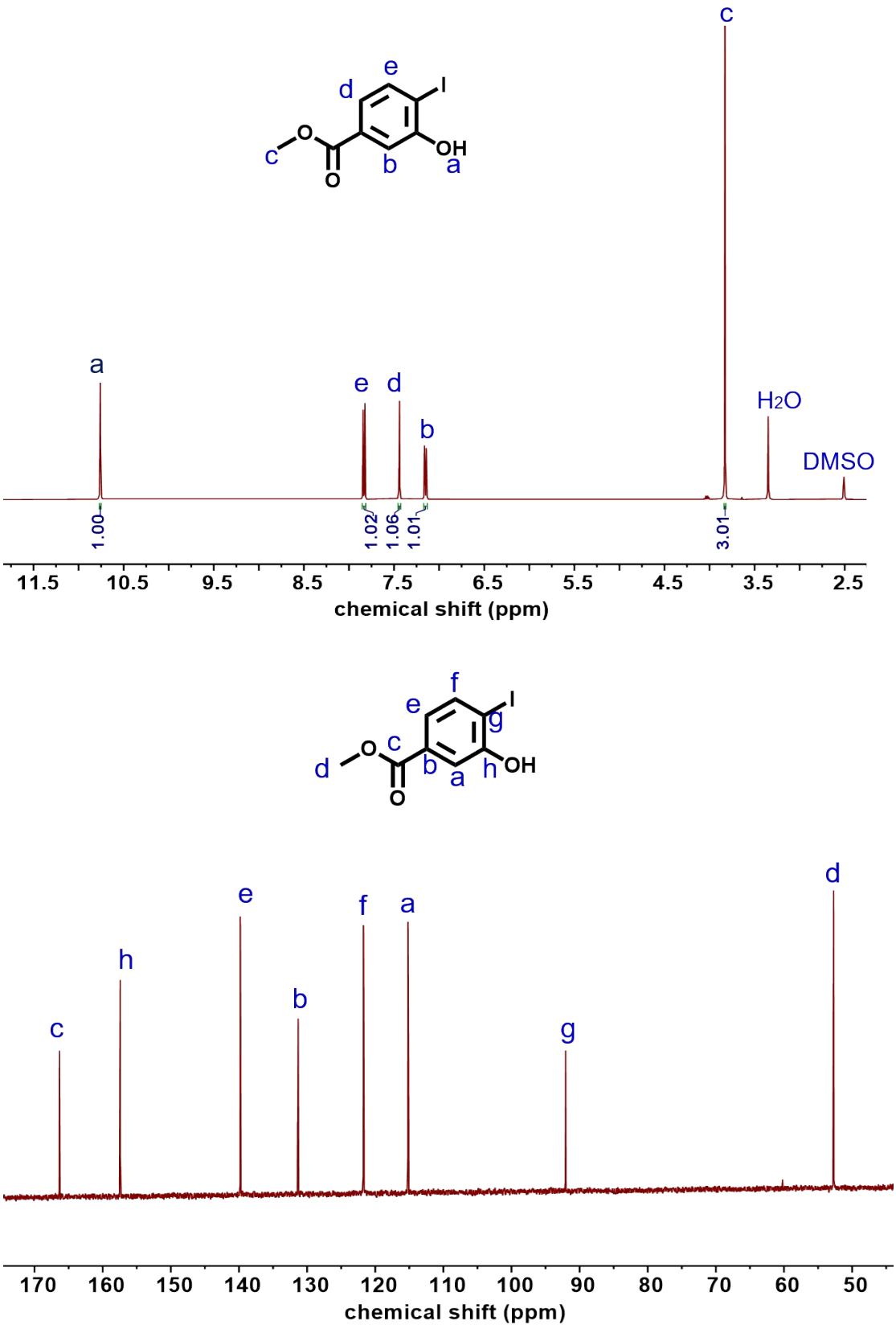


Fig. S1 ^{1}H NMR (top) and ^{13}C NMR (below) spectra for Compound 1.

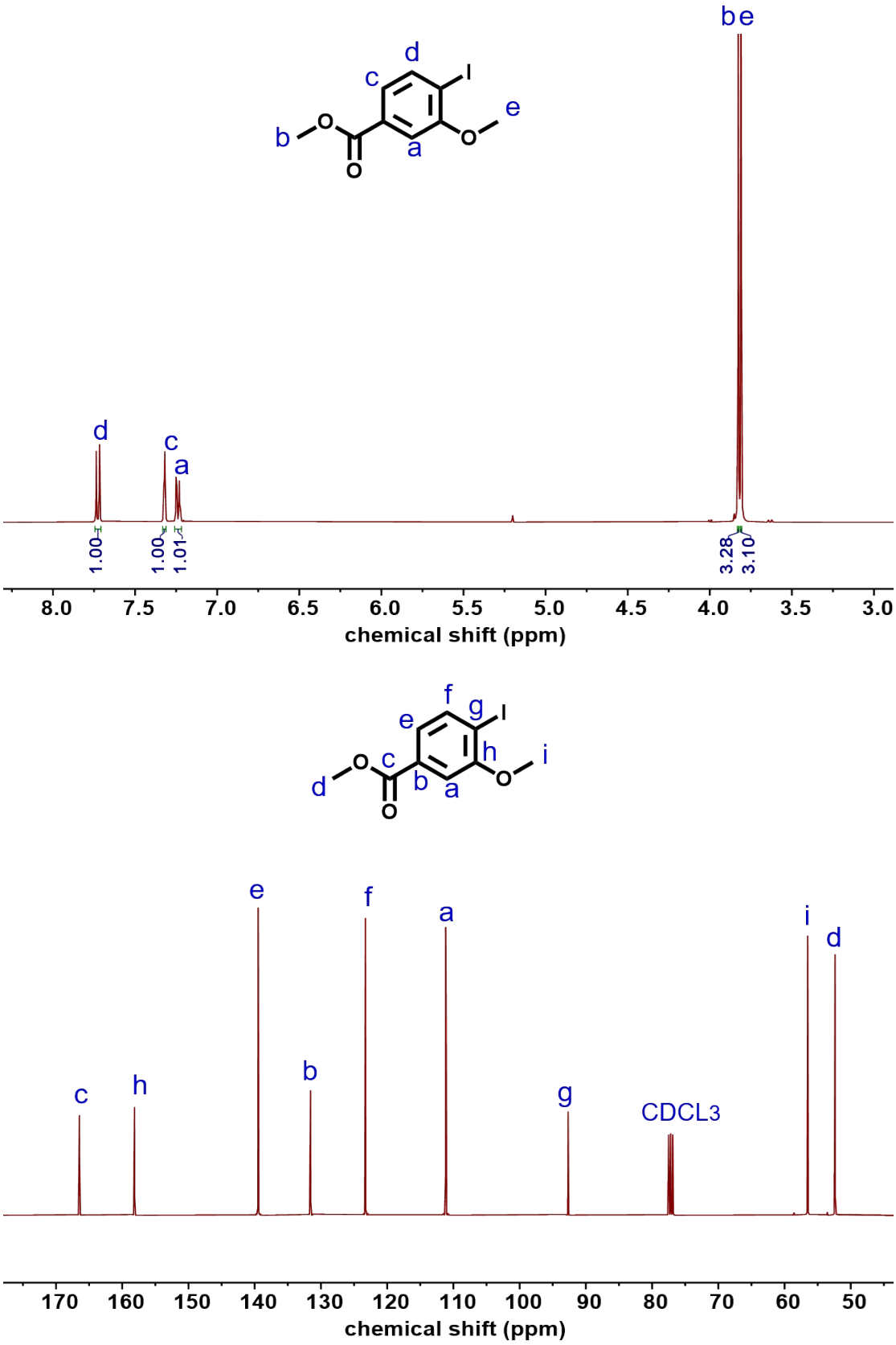


Fig. S2 ^{1}H NMR (top) and ^{13}C NMR (below) spectra for Compound 2.

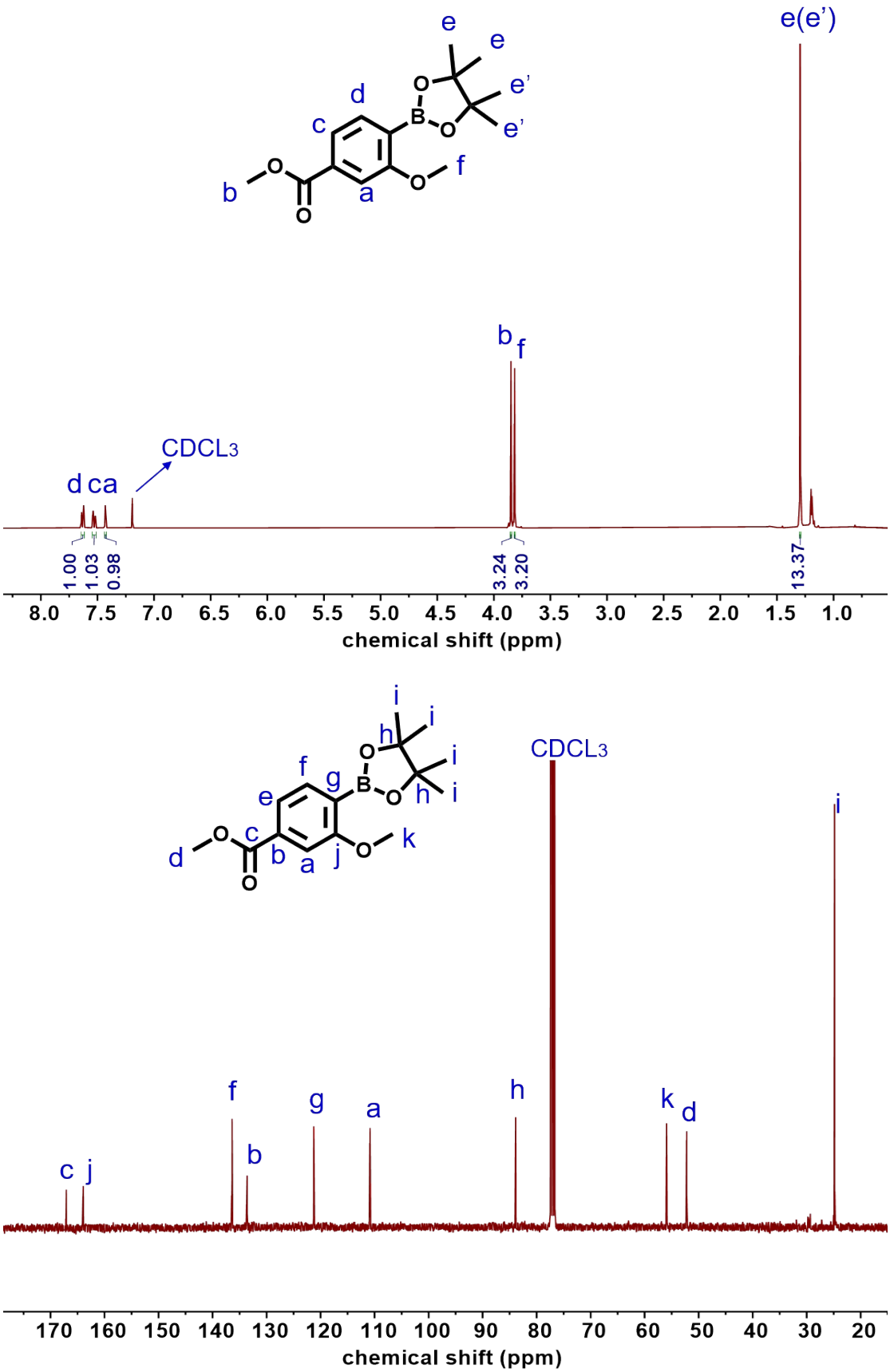


Fig. S3 ^{1}H NMR (top) and ^{13}C NMR (below) spectra for Compound 3.

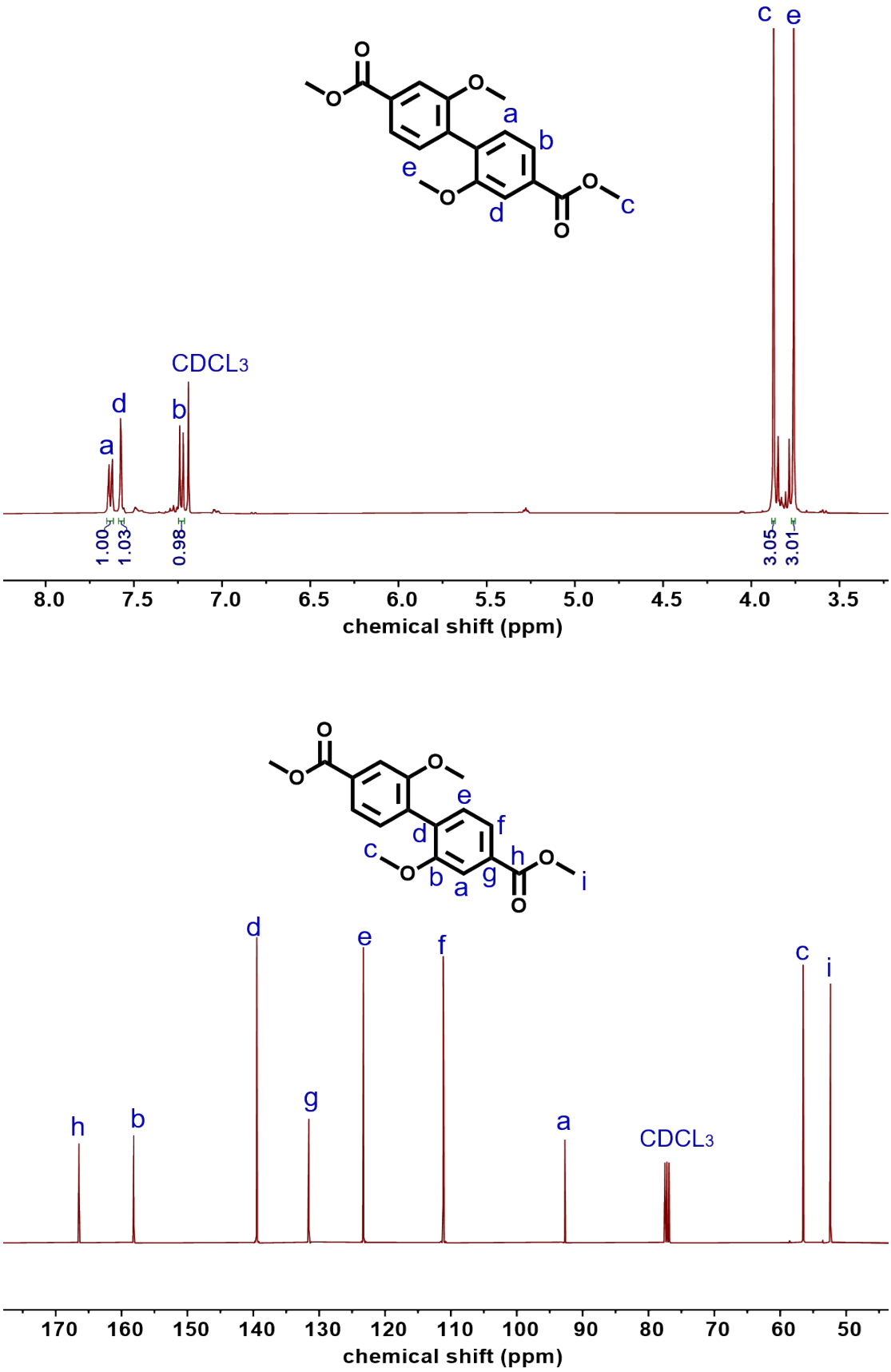


Fig. S4 ^{1}H NMR (top) and ^{13}C NMR (below) spectra for Compound 4.

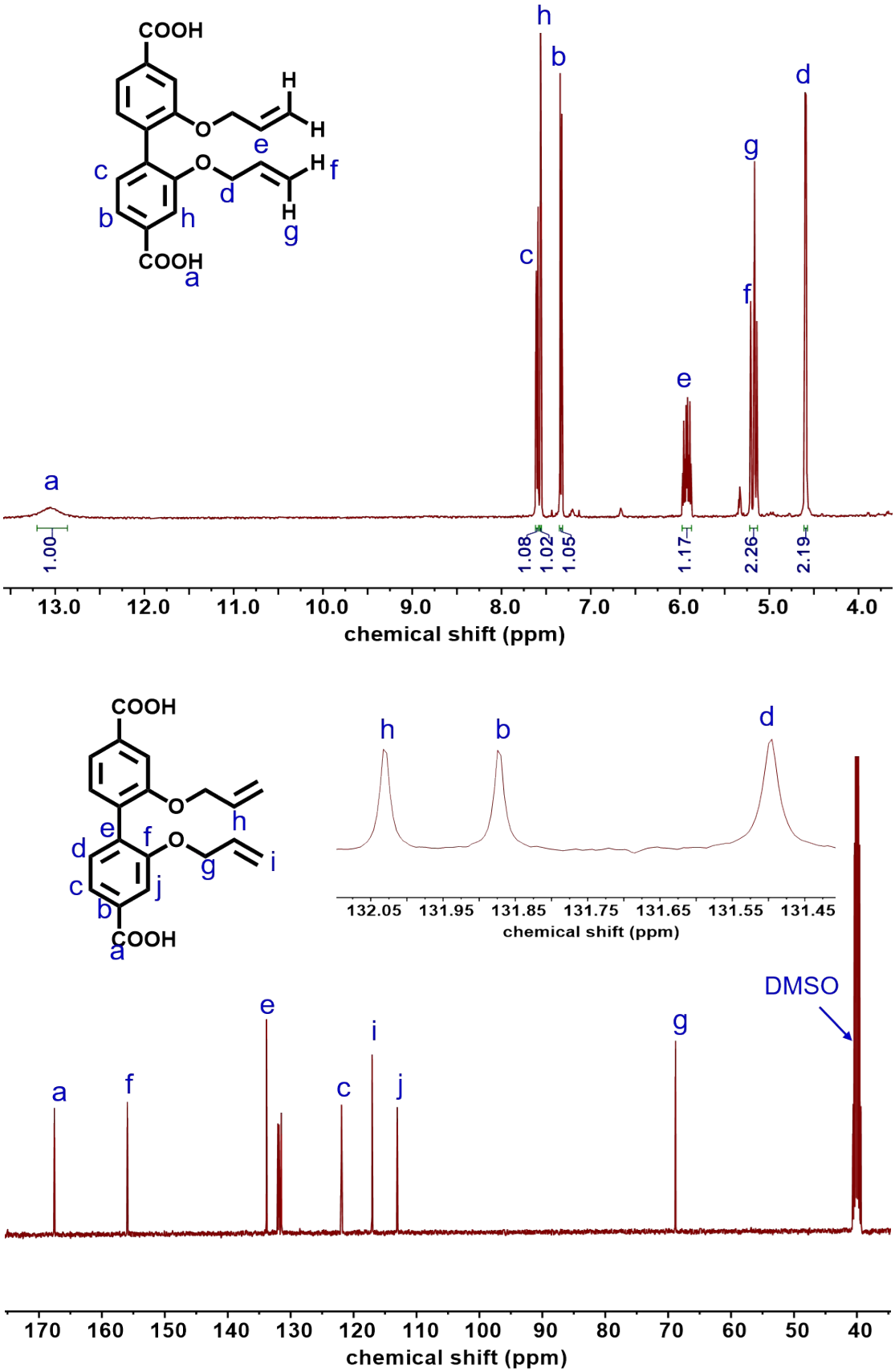


Fig. S5 ^{1}H NMR (top) and ^{13}C NMR (below) spectra for Compound 7.

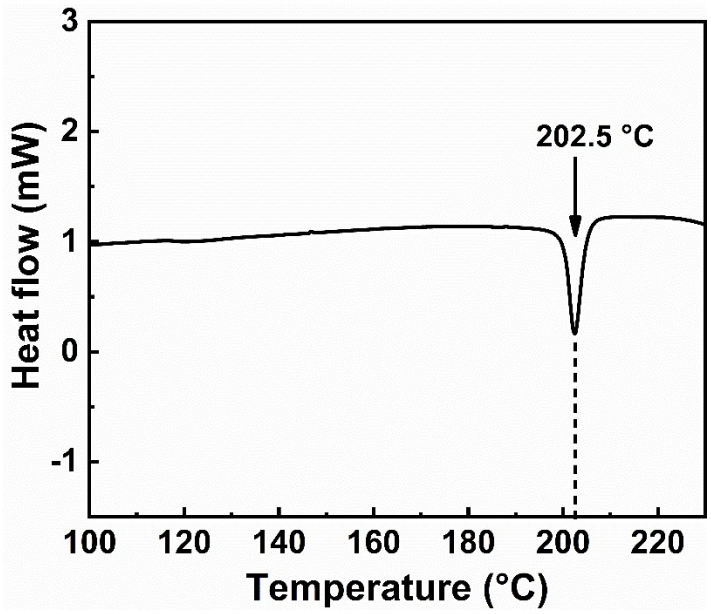


Fig. S6 DSC curve of Compound **7**.

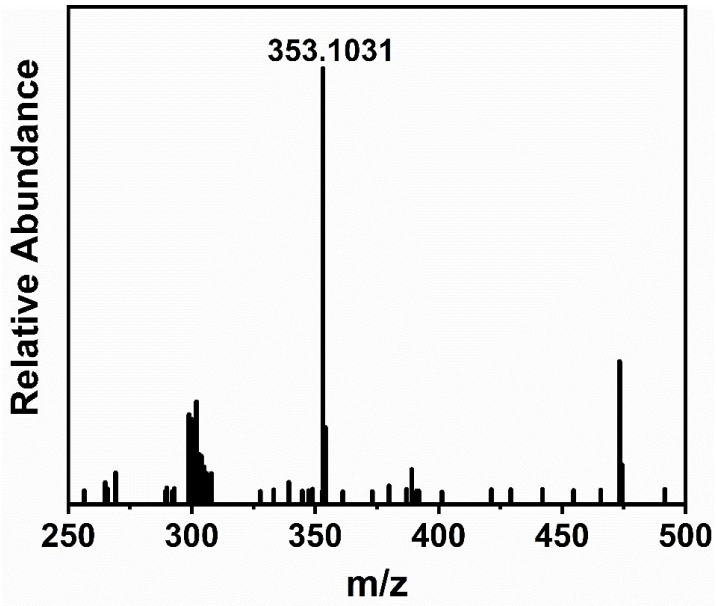


Fig. S7 Mass spectrometry of Compound **7**.

Table S1 Crystal data and structure refinement for Zn-MOF

Identification code	Zn-MOF
Empirical formula	$C_{60}H_{52}O_{21}Zn_4$
Formula weight	1370.58
Temperature/K	173
Crystal system	monoclinic
Space group	C2/m
a/Å	22.248(3)
b/Å	25.890(3)
c/Å	17.197(2)
α/°	90
β/°	97.589(4)
γ/°	90
Volume/Å^3	9819(2)
Z	4
Calculated density (g/cm^3)	0.927
μ/mm^{-1}	1.012
F(000)	2800
Crystal size/mm^3	0.10 × 0.11 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.0 to 27.6
Index ranges	-28 ≤ h ≤ 23, -33 ≤ k ≤ 33, -21 ≤ l ≤ 22
Reflections collected	42940
Independent reflections	11418 [R_{int} = 0.1013, R_{sigma} = 0.0949]
Data/restraints/parameters	11425/535/489
Goodness-of-fit on F^2	1.073
R_1, wR_2 [I>=2σ (I)] [a]	0.0953/ 0.2177
R_1, wR_2 [all data] [b]	0.1162/ 0.2260
Largest diff. peak/hole / e Å^{-3}	1.26/-1.14
CCDC number	2128492

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

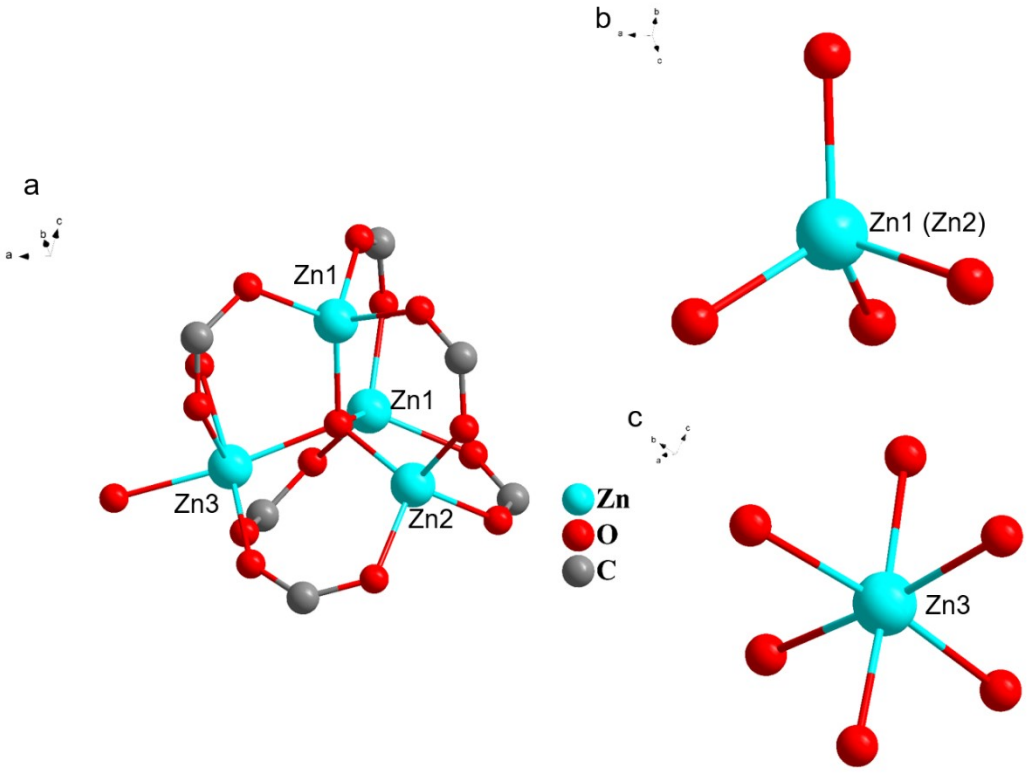


Fig. S8 (a) Second building unit (SBU) of $Zn_4O(H_2O)_2$ $(-CO_2)_6$. (b) The formation a ZnO_4 tetrahedron. (c) The formation of Zn3 six coordination.

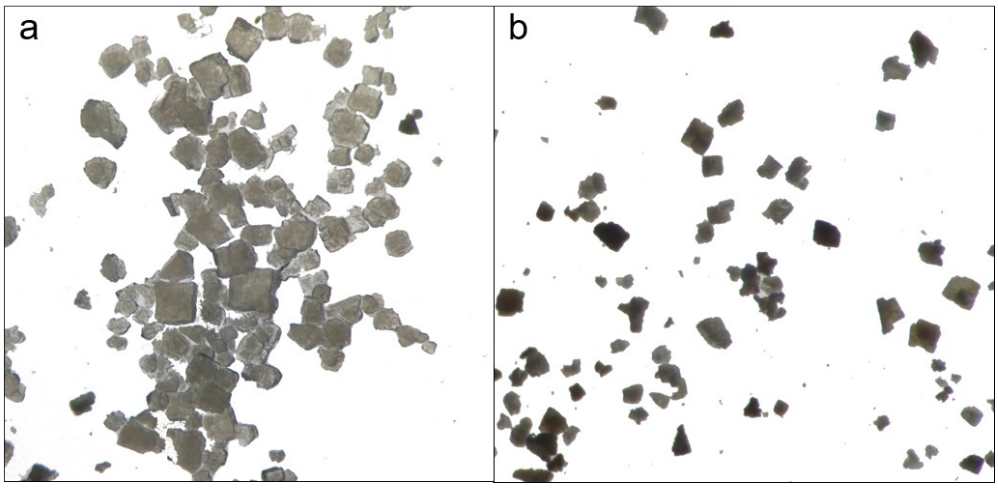


Fig. S9 Optical microscopy images of Zn-MOF (a) and Ag@Zn-MOF (b).

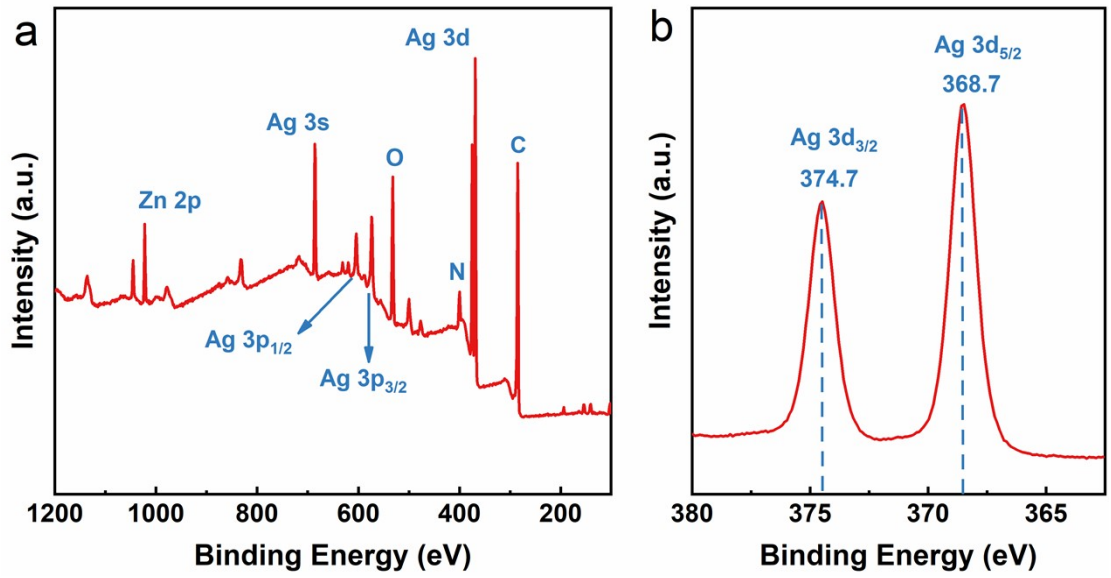


Fig. S10 (a) The survey spectrum of Ag@Zn-MOF. (b) XPS spectra of Ag@Zn-MOF.

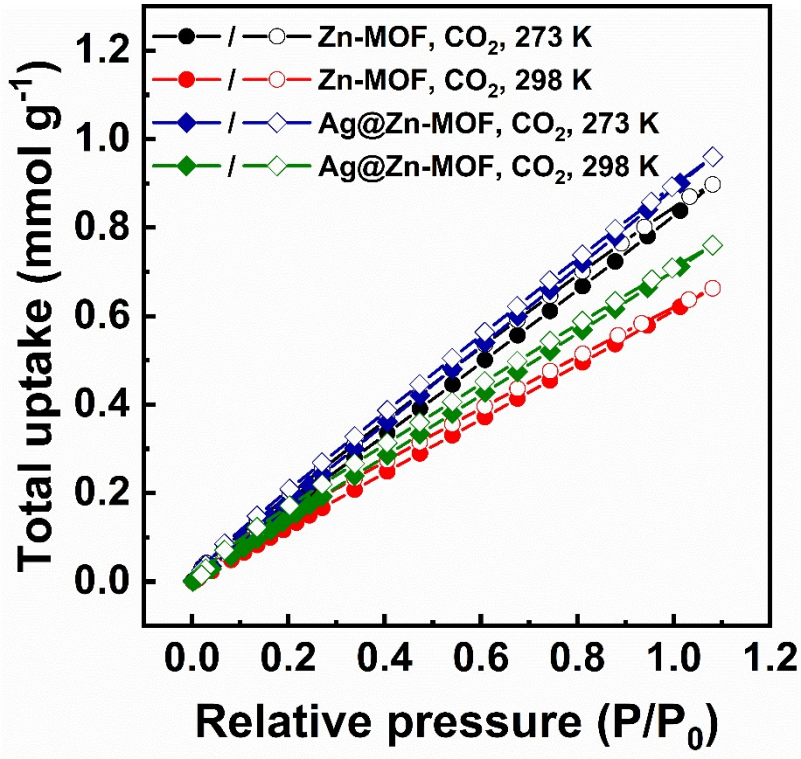


Fig. S11 CO_2 sorption isotherms of Zn-MOF and Ag@Zn-MOF at 273 K and 298 K. (filled, adsorption; open, desorption).

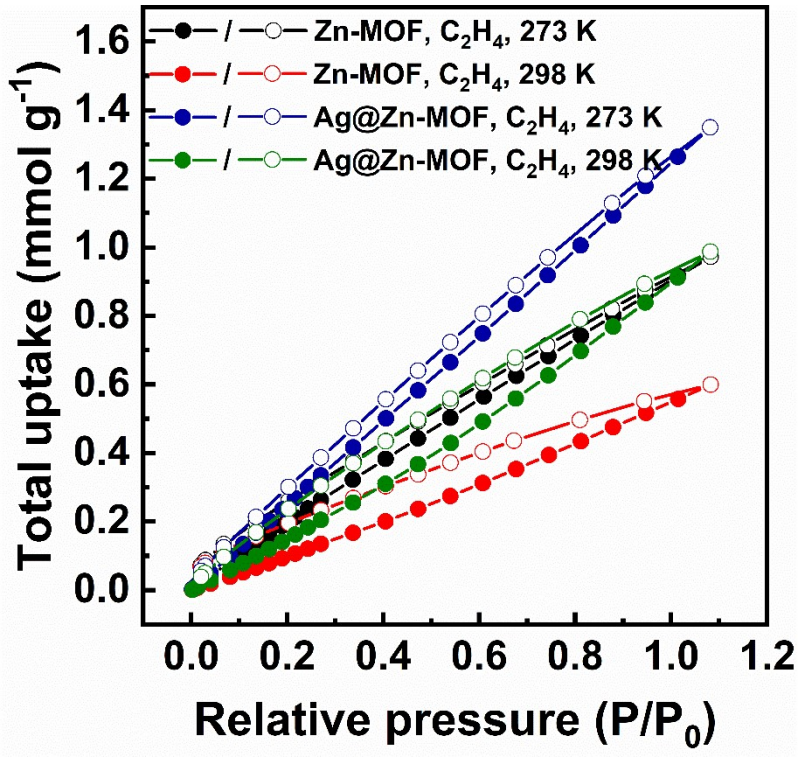


Fig. S12 C_2H_4 sorption isotherms of Zn-MOF and Ag@Zn-MOF at 273 K and 298 K. (filled, adsorption; open, desorption).

Reference

1. C. H. Gorbitz, *Acta Crystallogr. A*., 1999**, 55**, 441-441.
2. U. Isabel, E. M. S. Clare, M. L. David, M. S. George, *Acta Crystallogr. D Biol. Crystallogr.*, 2007, **63**, 1069-1074.