**Cavity Induced Enantioselectivity Reversal in A Chiral Metal-Organic Framework Brønsted Acid Catalyst**

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1. General Experimental

All of the solvents were purchased from Fisher and used without further purification. All of the coupling reactions were carried out under argon with the use of standard inert atmosphere and Schlenk techniques. Thermogravimetric analysis (TGA) was performed using a Shimadzu TGA-50 equipped with a platinum pan and heated at a rate of 5 °C per minute, under air. Single crystal X-ray diffraction and powder X-ray diffraction (PXRD) patterns were collected on a Bruker SMART APEX II diffractometer using Cu radiation. The PXRD patterns were processed with the APEX 2 package using phase ID plugin. Circular Dichroism (CD) spectra were recorded on an Applied Photophysics Pistar-180 Circular Dichroism/Fluorescence spectrometer.
2. Procedures for ligand synthesis

2.1 Synthesis of (R)-6,6'-dibromo-3,3'-diiodo-1,1'-binaphthyl-2,2'-diol (I)

3,3'-diiodo-2,2'-dimethoxy-1,1'-binaphthyl and 3,3'-diiodo-1,1'-binaphthyl-2,2'-diol, were synthesized according to the literature procedure.\(^1,2\)

To a CH\(_2\)Cl\(_2\) (500 mL) solution of 3,3'-diiodo-1,1'-binaphthyl-2,2'-diol (I) (4.60 g, 8.9 mmol) in an ice bath, Br\(_2\) (8.6 g, 54 mmol) was added slowly via a syringe. The reaction mixture was allowed to warm to room temperature, and then stirred at room temperature for three days. The resultant solution was washed with 100 mL 25% Na\(_2\)SO\(_3\) (aq.), 200 mL \(\times\) 2 water, and 100 mL \(\times\) 2 brine. The organic layer was dried over MgSO\(_4\) and the solvent was removed with a rotary evaporator. A pale white solid (5.77 g, 97%) was obtained. Purity of the product was verified by \(^1\)H NMR and the resulting product was used for subsequent reactions without further purification. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 8.41 (s, 2H), 7.95 (s, 2H), 7.37 (d, \(J = 9\) Hz, 2H), 6.90 (d, \(J = 9\) Hz, 2H), 5.46 (s, 2H).

2.2 Synthesis of (R)-6,6'-dibromo-2,2'-diethoxy-3,3'-diiodo-1,1'-binaphthyl (II)

To an acetone (100 mL) solution of (R)-6,6'-dibromo-3,3'-diiodo-1,1'-binaphthyl-2,2'-diol (I) (2.40 g, 2.87 mmol), bromoethane (2.9 g, 23 mmol) and KOH (1.3 g, 23 mmol) were added. The mixture was heated to reflux for 2 h. After being cooled to room temperature, the solvent was removed with a rotary evaporator, and the resulting solid was dissolved in 200
mL ethyl acetate. The organic layer was washed with H$_2$O and brine several times, collected and dried over MgSO$_4$. After removal of organic solvents with a rotary evaporator, a pale yellow solid (2.59 g, 96%) was obtained. $^1$HNMR (400 MHz, CDCl$_3$) δ: 8.54 (s, 2H), 7.96 (d, J = 2 Hz, 2H), 7.35 (dd, J = 2 Hz, 9 Hz, 2H), 6.93 (d, J = 9 Hz, 2H), 3.79 (m, 2H), 3.40 (m, 2H), 0.95 (m, 6H).

2.3 Synthesis of (R)-2,2'-diethoxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-methylbenzoate) (III).

To a mixture of (R)-3,3'-diiodo-6,6'-dibromo-2,2'-diethoxy-1,1'-binaphthylene (II) (1.20 g, 1.60 mmol) and 4-(methoxycarbonyl)phenylboronic acid (1.70 g, 9.4 mmol) in a 75 mL pressure vessel with a magnetic stirrer was added 35 mL ethylene glycol dimethyl ether (DME). After being degassed with argon for 15 min, CsF (2.9 g, 19 mmol) and Pd(PPh$_3$)$_4$ (300 mg, 0.26 mmol) was added to the solution. The resulting mixture was further degassed for 10 min, and then the pressure vessel was sealed, and the reaction mixture was heated to 100 °C in an oil bath for 3 days. After being cooled to room temperature, the mixture was extracted with CH$_2$Cl$_2$ and washed with H$_2$O several times. The organic layer was then dried with MgSO$_4$, and the solvent was removed with a rotary evaporator. The resulting crude product was purified by column chromatography using silica gel and 5~8% ethyl acetate in CH$_2$Cl$_2$ (v/v) as the eluent. III was obtained as light yellow solid after removal of the solvents (0.82 g, 62% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.07-8.17 (m, 6H); 8.13 (d, J = 8.4 Hz, 4H); 8.08 (s, 2H); 7.87 (d, J = 8.4 Hz, 4H); 7.77 (d, J = 8.4 Hz, 4H); 7.57 (dd, J = 1.6 Hz, 8.8 Hz, 2H); 7.30 (d, J = 8.8 Hz, 2H); 3.97 (s, 6H); 3.93 (s, 6H); 3.52 (m, 2H); 3.45 (m, 2H); 0.67 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.6; 166.5; 153.7; 144.8; 143.3; 136.2; 134.9.
2.4 Synthesis of (R)-2,2'-dihydroxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-benzoic acid) (IV)

To a solution of (R)-2,2'-diethoxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-methylbenzoate) (III) (0.50 g, 0.57 mmol) in 100 mL of degassed CH$_2$Cl$_2$ at 0 °C (with an ice/H$_2$O bath), 1.10 mL (11.4 mmol) of BBr$_3$ was added dropwise. The solution was then allowed to warm to room temperature and stirred for 1 day. The resulting mixture was then poured slowly into an ice/H$_2$O solution and gradually warmed to room temperature. The product was extracted with ethyl acetate and washed with H$_2$O. The organic layer was collected, dried, and the solvent was removed with a rotary evaporator to yield (IV) as a yellow powder (0.40 g, 91.5 %). $^1$H NMR (400 MHz, DMSO-$d_6$): δ 13.03(br, 4H); 8.41(s, 2H); 8.17(s, 2H); 8.03 to 8.09 (m, 8H); 7.87 to 7.89 (m, 8H); 7.69 (d, J=8.8 Hz, 2H); 7.08(d, J=8.8 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): δ 172.0; 167.4; 167.2; 152.0; 144.4; 143.3; 133.8; 133.6; 132.1; 131.6; 131.5; 131.1; 130.1; 129.8; 129.4; 129.3; 129.1; 128.9; 128.7; 126.7; 125.6; 125.0; 115.0. MS (ESI): 898.92 [calcd. for [C$_{48}$H$_{30}$O$_{10}$Cs]$^+$ ( [M+Cs]$^+$ ; 898.66)]; 1030.79 [calcd. for [C$_{48}$H$_{29}$O$_{10}$Cs$_2$]$^+$ ([M-H+Cs+Cs]$^+$); 1030.99].

2.5 Synthesis of (R)-2,2'-dihydroxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-methylbenzoate) (V).
To a solution of \((R)\)-2,2'-dihydroxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-benzoic acid) (IV) (0.215 g, 0.28 mmol) in MeOH (50 mL), was added several drops of conc. H\(_2\)SO\(_4\). After refluxing overnight, the solvent was removed with a rotary evaporator and the residue was extracted with ethyl acetate and washed with H\(_2\)O. The organic layer was then dried over MgSO\(_4\), and the solvent was removed by a rotary evaporator to yield the desired product as a yellow powder (0.23 g, 99% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.11 to 8.02 (m, 12H); 7.81 (d, d, J=8.4 Hz, 4H); 7.67 (d, J=8.4 Hz, 4H); 7.57 (d, J=8.8 Hz, 2H); 7.29 (d, J=8.8 Hz, 2H); 5.94 (s, 2H); 3.87 (s, 6H); 3.84 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 207; 166.8; 150.8; 144.9; 142.0; 135.9; 132.8; 132.2; 130.4; 130.1; 129.7; 129.6; 129.5; 129.2; 128.7; 127.0; 126.9; 124.9; 112.3; 52.1.

2.6 Synthesis of \((R)\)-3,3',6,6'-tetrakis(4-methylbenzoate)-1,1'-binaphthyl phosphate (L\(_1\)Me\(_4\)).

To a solution of \((R)\)-2,2'-dihydroxy-1,1'-binaphthyl-3,3',6,6'-tetrakis(4-methylbenzoate) (V)
(0.166 g, 0.20 mmol) in pyridine (0.5 mL) was added phosphorus oxychloride (0.07 mL, 0.8 mmol) at room temperature. After stirring at room temperature for 3 h, the reaction mixture was quenched by addition of H₂O (0.5 mL) and stirred for 20 min at room temperature. After evaporation of pyridine under vacuum, 5 M HCl (2 mL) was added to the residue. The mixture was stirred at room temperature for 1 h, the resulting solids were collected by filtration, washed with H₂O to give crude product. The resulting crude product was purified by column chromatography using silica gel and ethyl acetate/ methanol in (9:1, v/v) as the eluent. Pure desired product was obtained as light yellow solid after removal of the solvents (0.15 g, 85% yield). ¹H NMR (600 MHz, DMSO): δ 8.42 (s, 2H); 8.16 (s, 2H); 8.01 (d, J=78 Hz, 4H); 7.96 (s, 8H); 7.88 (d, J=7.8 Hz, 4H); 7.66 (d, J=8.4 Hz, 2H); 7.13 (d, J=9.0 Hz, 2H); 3.85 (s, 6H); 3.84 (s, 6H). ³¹P NMR (443 MHz, DMSO): δ 2.75. ¹³C NMR (150 MHz, DMSO): δ 166.3; 166.1; 147.1; 147.0; 143.8; 142.6; 142.5; 135.0; 133.5; 131.5; 130.4; 129.9; 128.8; 128.4; 128.3; 127.0; 126.9; 126.7; 125.6; 122.5; 52.2; 52.2.

2.7 Synthesis of (R)-3,3',6,6'-tetrakis(4-benzoic acid)-1,1'-binaphthyl phosphate (L₁H₄).

A solution of (R)-3,3’,6,6’-tetrakis(4-methylbenzoate)-1,1’-binaphthyl phosphate (0.22 g, 0.25 mmol) in methanol (20 mL), THF (10 mL) and 1M aqueous LiOH (2.5 mL) was heated at 50 °C for 24 h. The solution was cooled to r.t. and acidified to pH~1 with 3M HCl and extracted with ethyl acetate. The organic phase was dried over MgSO₄ and the solvent was evaporated under reduced pressure to give a white solid of L₁H₄ (Yield: 0.19 g, 92%). ¹H NMR (400 MHz, DMSO-d₆): δ 13.03 (br, 4H); 8.51 (s, 2H); 8.26 (s, 2H); 8.16 (d, J=7.2 Hz, 4H); 8.04 to 8.02 (m, 8H); 7.92 to 7.90 (m, 4H); 7.73 (d, J=8.8 Hz, 2H); 7.24 (d, J=8.8 Hz, 2H). ³¹P NMR
(162 MHz, DMSO-d$_6$): δ 3.34. $^{13}$C NMR (100 MHz, DMSO-d$_6$): δ 172.0; 170.4; 167.5; 167.3; 149.6; 147.9; 147.8; 142.2; 136.2; 135.2; 134.1; 131.7; 131.2; 130.4; 130.1; 130.0; 129.9; 129.6; 129.0; 128.5; 128.3; 126.8; 126.6; 125.4; 123.9; 122.6. MS (ESI): 961.58 [calcd. for [C$_{48}$H$_{29}$O$_{12}$PCs]$:^+ ([M-H+Cs]$): 961.62].

2.8 Synthesis of (R)-4,4',6,6'-tetrakis(4-benzoic acid)-1,1'-binaphthyl phosphate (L$_2$H$_4$).

![Reaction Scheme]

To a solution of (R)-2,2'-dihydroxy-1,1'-binaphthyl-4,4',6,6'-tetrakis(4-benzoic acid) (0.1 g, 0.13 mmol) in pyridine (0.5 mL) was added phosphorus oxychloride (0.36 mL, 3.9 mmol) at room temperature. After stirring at 50 °C for 3 h, the reaction mixture was quenched by addition of H$_2$O (0.5 mL) and stirred for 20 min at room temperature. After evaporation of pyridine under vacuum, 5 M HCl (2 mL) was added to the residue. The mixture was refluxed for 1 h. After cooling to 0 °C, the resulting solid material was collected by filtration, washed with H$_2$O to give the crude product. The resulting crude product was purified by column chromatography using silica gel and ethyl acetate / methanol (4:1, v/v) as the eluent. Pure desired product was obtained as light yellow solid after removal of the solvents (43 mg, 40 % yield). $^1$H NMR (400 MHz, DMSO-d$_6$): δ 13.03(br, 4H); 7.91 (s, 2H); 7.86 (d, J=6.8 Hz, 4H); 7.69 (d, J=6.8 Hz, 4H); 7.85 to 7.80 (m, 6H); 7.43 (d, J=6.8 Hz, 4H); 7.30 (d, J=8.4 Hz, 2H); 7.22 (s, 2H). $^{31}$P NMR (162 MHz, DMSO-d$_6$): δ 3.90. $^{13}$C NMR (150 MHz, DMSO-d$_6$): δ 172.1; 167.3; 167.2; 149.9; 149.9; 149.6; 143.9; 143.4; 141.4136.2; 135.8; 132.3; 130.6;
2.9 Synthesis of (R)-2,2'-dihydroxy-1,1'-binaphthyl-4,4',6,6'-tetrakis(4-methylbenzoate) (VI).

To a solution of (R)-2,2'-dihydroxy-1,1'-binaphthyl-4,4',6,6'-tetrakis(4-benzoic acid) (0.30 g, 0.39 mmol) in MeOH (50 mL), was added several drops of conc. H$_2$SO$_4$. After refluxing for overnight, the solvent was removed on a rotary evaporator and the residue was extracted with ethyl acetate and washed with H$_2$O. The organic layer was then dried with MgSO$_4$, and the solvent was removed by a rotary evaporator to yield the desired product as a yellow powder (0.31 g, 97% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 8.19 (d, J=8.0 Hz, 4H); 8.03 (s, 2H); 7.94 (d, J=8.4 Hz, 4H); 7.65 (d, J=7.6 Hz, 4H); 7.58 (d, J=8.8 Hz, 2H); 7.50 (d, J=8.0 Hz, 4H); 7.42 (d, J=8.4 Hz, 2H); 7.39 (s, 2H); 6.15 (s, 2H); 3.94 (s, 6H); 3.85 (s, 6H).

2.10 Synthesis of (R)-4,4',6,6'-tetrakis(4-methylbenzoate)-1,1'-binaphthyl phosphate (L$_2$Me$_4$).
To a solution of (R)-2,2′-dihydroxy-1,1′-binaphthyl-4,4′,6,6′-tetrakis(4-methylbenzoate) (VI) (0.166 g, 0.20 mmol) in pyridine (0.5 mL) was added phosphorus oxychloride (0.07 mL, 0.8 mmol) at room temperature. After stirring at room temperature for 3 h, the reaction mixture was quenched by addition of H₂O (0.5 mL) and stirred for 20 min at room temperature. After evaporation of pyridine under vacuum, 5 M HCl (2 mL) was added to the residue. The mixture was stirred at room temperature for 1 h, the resulting solids were collected by filtration, washed with H₂O to give crude product. The resulting crude product was purified by column chromatography using silica gel and ethyl acetate/ Methanol in (9:1, v/v) as the eluent. Pure desired product was obtained as light yellow solid after removal of the solvents (0.37 g, 85% yield). ^1H NMR (400 MHz, acetone-d₆): δ 8.18 (s, 2H); 8.10 (d, J=4.8 Hz, 2H); 7.98 (d, J=7.2 Hz, 6H); 7.75 (d, J=5.6 Hz, 4H); 7.67(d, J=7.2 Hz, 6H); 7.55 (d, J=5.6 Hz, 2H); 7.42 (s, 2H); 3.91 (s, 6H); 3.85 (s, 6H). ^31P NMR (162 MHz, acetone-d₆): δ 1.86. ^13C NMR (150 MHz, acetone-d₆): δ 166.8; 159.0; 158.8; 149.3; 145.3; 144.6; 142.8; 137.3; 133.2; 130.9; 130.7; 130.3; 130.0; 129.9; 129.5; 128.8; 127.8; 126.5; 125.1; 123.9; 122.3; 117.0; 115.2; 52.3; 52.2.

2.11 Synthesis (R)-2,2′-diethoxy-1,1′-binaphthyl-3,3′,6,6′-tetrakis(4-benzoic acid) (L₂H₄)
To a solution of (R)-2,2’-diethoxy-1,1’-binaphthyl-3,3’,6,6’-tetrakis(4-methylbenzoate) III (0.15 g, 0.17 mmol) in 10 mL MeOH and 10 mL THF was added 10 mL NaOH (6M, aq.). The mixture was heated to 80°C overnight. After similar workup procedure as L1H4, solid product of light yellow color was obtained (0.12 g, 86%). ¹H NMR (DMSO-d₆, 400 MHz): 12.96 (s, 4H), 8.51 (s, 2H), 8.30~7.78 overlapped (16H), 7.23 (s, 2H), 3.50 (m, 2H), 3.28 (m, 2H), 0.60 (m, 6H). ¹³C NMR (DMSO-d₆): δ 181.6; 167.0; 167.0; 162.2; 153.3; 143.6; 142.6; 135.5; 134.4; 132.8; 131.0; 130.3; 129.9; 129.8; 129.7; 129.2; 129.0; 126.7; 126.4; 125.9; 125.7; 125.2; 68.6; 14.7. MS (ESI): 845.20; calcd. for [C₅₂H₃₈O₁₀Na]⁺: 845.24.

3.1 [R – L₁Cu₂(H₂O)₂]•21DMF•12H₂O (CMOF-1)
A mixture of L₁H₄ (4 mg, 4.8 μmol) and Cu(NO₃)₂•2.5H₂O (2.4mg, 9.6 μmol ) was dissolved in a solvent mixture of DMF/H₂O (0.6 mL/0.2 mL) in a screw-capped vial. After addition of 8 μL HCl (3 M, aq.), the vial was capped and place in an oven at 80 °C for 2 days. Green crystals (6.0 mg, 45.6%) were obtained after filtration. Solvent content in the MOF channels was determined by ¹H NMR/TGA to be 55.6% DMF and 7.8% H₂O (calc. from the proposed formula: DMF, 55.8%; H₂O, 7.8%).

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Figure S3.1 $^1$H NMR (methanol-d$_4$) spectroscopic determination of solvent content in CMOF-1 (11 mg). 10 µL mesitylene (Mes) was added as an internal standard.

Figure S3.2 Thermogravimetric analysis (TGA) curve for CMOF-1. The sample was heated to 600 ºC at a heating rate of 5 ºC/min.
3.2 [\text{R – L}_2\text{Cu}_2(\text{H}_2\text{O})_2]\cdot27\text{DMF}\cdot17\text{H}_2\text{O} (\text{CMOF-2})

A mixture of \text{L}_2\text{H}_4 (4 mg, 4.8 \mu\text{mol}) and \text{Cu(NO}_3\text{)}_2\cdot2.5\text{H}_2\text{O} (2.4 mg, 9.6 \mu\text{mol}) was dissolved in a solvent mixture of DMF/H\text{}_2\text{O} (0.6 mL/0.2 mL) in a screw-capped vial. After addition of 8 \mu\text{L} H\text{Cl} (3 M, aq.), the vial was capped and placed in an oven at 80 \degree C for 2 days. Green crystals (1.5 mg, 11.4\%) were obtained after filtration. Solvent content in the MOF channels was determined by \textsuperscript{1}H NMR/TGA to be 60.3\% DMF and 9.2\% H\text{}_2\text{O} (calc. from the proposed formula: DMF, 60.2\%; H\text{}_2\text{O}, 9.3 \%).

\textbf{Figure S3.3} \textsuperscript{1}H NMR (methanol-d\textsubscript{4}) spectroscopic determination of solvent content in CMOF-2 (20.9 mg), 10 \mu\text{L} mesitylene (Mes) was added as an internal standard.
**Figure S3.4** TGA curve for CMOF-2. The sample was heated to 600 °C at a heating rate of 5 °C/min.

### 3.3 [R – L₄Cu₂(H₂O)₂]•21DEF•6H₂O (CMOF-3)

A mixture of L₃H₄ (6 mg, 0.0073 mmol) and Cu(NO₃)₂ • 2.5 H₂O (12 mg, 0.048 mmol) were dissolved in a solvent mixture of DEF/H₂O (2.1 mL/0.3 mL) in a screw-capped vial. After addition of 12 μL HCl (3 M, aq.), the vial was capped and placed in an oven at 80 °C for 3 days. Green-blue color crystals (12 mg, 52%) were obtained after filtration. Solvent content calc. from the proposed formula: DEF, 66.8%; H₂O, 3.4%; determined by ¹H NMR/TGA: DEF, 66.4%; H₂O, 3.6%.
Figure S3.5. $^1$HNMR (methanol-$d_4$) spectroscopic determination of solvent content in CMOF-3 (36 mg). 20 μL mesitylene (Mes) was added as an internal standard.

Figure S3.6. Thermogravimetric analysis (TGA) curve for CMOF-3. The sample was heated to 600 ºC at a heating rate of 5 ºC/min.

4. Quantitative determination of solvent molecules in the MOF channels

Fresh crystals were harvested by quick filtration and briefly dried on a filter paper under air for two minutes. The sample was then loaded into the sample tray for TGA or a
screw-capped vial for $^1$H NMR. To the vial, 1 mL CD$_3$OD was added. Then 10 µL mesitylene (Mes) was added as an internal standard. The crystals were then soaked overnight to ensure thorough solvent exchange from within the pores. The supernatant was then pipetted into an NMR tube and a $^1$H NMR spectrum is taken on a 400 MHz Bruker NMR spectrometer. As DMF is miscible with CD$_3$OD, the exact amount of these solvents was calculated against the internal standard from integration. Following determination of the total amount of solvent by TGA, the amount of water molecules can thus be calculated. The $^1$H NMR spectra and TGA results are shown in Figures S3.1-S3.6.

5. Single Crystal X-ray Structure Determination

All crystallographic measurements were made on a Bruker SMART Apex II CCD-based X-ray diffractometer system operated at 1600 watts (for Cu-target X-ray tube). The crystals were mounted inside a capillary (0.7 mm ID) with small amount of mother liquid to prevent solvent loss from the crystal frameworks. The frames were integrated with the Bruker SAINT® build in APEX II software package using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS. Structures were solved by direct methods and refined to convergence by least squares method on $F^2$ using the SHELXTL software suite. SQUEEZE subroutine of the PLATON software suite was applied to remove the scattering from the highly disordered guest molecules. The resulting new HKL4 files were used to further refine the structures. Due to the relatively weak diffraction and low resolution, which is not uncommon for this kind of framework with very large solvent accessible void space, restraints (SIMU and DELU) on displacement parameters, and DFIX for some bond lengths were applied, and all the phenyl rings were constrained to ideal six-membered rings.

For CMOF-1 and 3 the ligands in the structure exhibit orientation disorders. The two orientations of the ligand are present in equal probability and are related by a 2-fold rotational symmetry. Therefore the occupancy for each atom of the ligand was set to 0.5, and only isotropic refinements of displacement parameters were performed for those atoms.
Table 5.1. Crystal data and structure refinement for CMOF-1, 2 and 3.

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6. Powder X-ray diffraction

All the Powder X-ray diffraction (PXRD) patterns are taken when samples are sealed in capillary tubes with solvent to avoid sample desolvation. PXRD patterns were collected on a Bruker SMART APEX II diffractometer using Cu radiation and processed with the APEX 2 package using PILOT plug-in. The broad diffraction peak around 15-20° was due to diffraction of the glass capillary tube.

![Powder X-ray diffraction patterns of CMOF-3](image)

**Figure S6.1.** Powder X-ray diffraction patterns of CMOF-3. Simulated patterns from single crystal structure of CMOF-3 (red), as synthesized sample (blue), and evacuated sample (green).

7. X-ray Structure Figures
Figure S7.1. Space-filling model for CMOF-1 along the <100> or <010> directions. (figures produced using Materials Studio®)
**Figure S7.3.** Space-filling model for CMOF-1 along the <001> direction.

**Figure S7.4.** Space-filling model for CMOF-2 along the <001> direction.
Figure S7.5. Space-filling model for CMOF-2 along the <100> direction.

Figure S7.6. Space-filling model for CMOF-2 along the <110> direction.
Figure S7.7. Space-filling models showing packing diagrams of CMOF-3. The figures on the left shows the packing diagrams of CMOF-3 as viewed along the <001> direction. The figures on the right shows the packing diagrams of CMOF-3 viewed along <100> direction.

Figure S7.8. Schematic drawing shows the pts topology adopted by CMOF-3. The blue tetrahedra represent the BINOL tetracarboxylate ligand; the red square represent Cu₃(carboxylate)₄ SBU.

8. Procedures for N₂ adsorption measurements

After decanting the mother liquid, freshly prepared crystals of CMOFs-1, -2, or -3 were washed with methanol, then CH₂Cl₂ for several times. The resulting crystals were washed with benzene several times and then soaked in benzene overnight before loading into a BET sample cell. About 1 mL of benzene was left in the sample cell, and the sample cell was then frozen at 0°C. After three freeze-thaw cycles, the sample cell was placed in an ice/H₂O bath and evacuated under a dynamic vacuum for 24 h. The ice/H₂O bath was removed and the
sample was kept under vacuum at room temperature for another 12 h, and then heated under vacuum at 60 °C for 10 h. The resulting freeze-dried CMOF sample was used to perform gas uptake measurements.

Distortions of the frameworks were expected during the BET measurement, a phenomenon commonly observed for MOFs with large open channels. These framework distortions can reasonably account for the low value of N₂ uptake and irregular ads/des curves.

**Figure S8.1.** N₂ adsorption isotherms (77K) of CMOF-1.

**Figure S8.2.** N₂ adsorption isotherms (77K) of CMOF-2.
Figure S8.3. Nitrogen adsorption isotherm for CMOF-3.

Figure S8.4. BET plot of CMOF-3 (black squares, selected range of P/Po from 0.02 to 0.10); and its linear fit (red line).

9. General procedure for dye uptake measurements

Fresh crystals of CMOF-1 (2.1 mg, 0.51 μmol) were briefly dried on a filter paper, and then soaked in a methanol solution of Brilliant Blue R-250 (24 mM, 2 mL) overnight. The resulting blue crystals were washed with water thoroughly until the washings become colorless. The washed samples were digested with Na₂EDTA (0.05 M, 2 mL) and NaOH (6 M, 0.1 mL), the resultant clear solution with light blue color was diluted to 25 mL and adjusted to
a pH of 1.2. Absorption spectra were taken on a Shimadzu UV-2401PC UV-Vis spectrophotometer. The concentration of BBR-250 was determined by comparing the UV-Vis absorption with a standard curve.

The solubility of Brilliant Blue R-250 is 20g/L (30 °C) in water, and > 250 g/L in MeOH. Water was used to wash the BBR-250 on the external surfaces of the crystals.

![Absorption spectra](image)

**Figure S9.1.** UV-vis measurements of released BBR-250 from CMOF-1 and 2 (normalized).


10.1 General Procedure for Heterogeneous Catalytic Asymmetric Friedel-Crafts Reactions.

Fresh CMOF sample (10.2 μmol) was washed with MeOH three times, and then washed with anhydrous CH₂Cl₂ three times and soaked in CH₂Cl₂ overnight. The sample was washed with 1 mL× 3 of dry toluene, and then 1 mL dry toluene was added and the suspension was transferred to a dry Schlenk tube. N-sulfonyl imines 2 (0.1 mmol) was then added to the solution under argon. The solution was stirred for 30 minutes at room temperature before the addition of indole (0.5 mmol). The reaction mixture was allowed to stir for 2 days. The reaction was quenched with 10% NaHCO₃ (1 mL). The mixture was extracted with ethyl acetate (10 mL), followed by washing with H₂O (5 mL) and brine (5 mL), separated, and dried over anhydrous MgSO₄. The solvents were removed under reduced pressure and the
residue was purified by flash chromatography (ethyl acetate/hexane = 1/2) to afford the product.

10.2 General Procedure for Homogeneous Catalytic Asymmetric Friedel-Crafts Reactions.

To a dry Schlenk tube, N-sulfonyl imines 2 (0.1 mmol) and corresponding phosphoric acid \(L_1\text{Me}_4 / L_2\text{Me}_4\) (0.01 mmol) were dissolved in 1 mL of toluene under argon. The solution was stirred for 15 minutes at room temperature and then indole (0.5 mmol) was added. After the reaction was complete (monitored by TLC), 10% NaHCO\(_3\) (1 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (10 mL). The organic layer was washed with H\(_2\)O (5 mL) and brine (5 mL), separated, and dried over anhydrous MgSO\(_4\). The solvents were removed under reduced pressure and the residue was purified by flash chromatography (ethyl acetate/hexane = 1/2) to afford the product.

10.3 Characterization of products in asymmetric Friedel-Crafts reactions

10.3.1 N-((1H-indol-3-yl)(phenyl)methyl)benzenesulfonamide (3b)

![N-((1H-indol-3-yl)(phenyl)methyl)benzenesulfonamide](image)

\(R_f = 0.30\) (ethyl acetate/hexane= 1/2, v/v); colorless solid. Chiral HPLC: Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 mL / min, t (R-enantiomer) = 15.83 min, t (S-enantiomer) = 23.67 min; or Daicel Chiralcel OD-H, Hexanes / IPA = 80 / 20, 0.6 mL / min, t (R-enantiomer) = 30.53 min, t (S-enantiomer) = 49.49 min; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)

5.16 (d, \(J = 6.8\) Hz, 1H), 5.89 (d, \(J = 7.2\) Hz, 1H), 6.64 (d, \(J = 2.4\) Hz, 1H), 7.00 (t, \(J = 7.6\) Hz, 1H), 7.13-7.31 (m, 10H), 7.43 (t, \(J = 7.2\) Hz, 1H), 7.66 (d, \(J = 7.6\) Hz, 2H), 8.00 (br, 1H).

10.3.2 N-((1H-indol-3-yl)(phenyl)methyl)-4-methylbenzenesulfonamide (4b)
Rf = 0.30 (ethyl acetate/hexane = 1/2, v/v); colorless solid. Chiral HPLC: Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min, t (R-enantiomer) = 16.16 min, t (S-enantiomer) = 25.32 min. 'H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 5.31 (d, J = 6.8 Hz, 1H), 5.82 (d, J = 6.4 Hz, 1H), 5.97 (t, J = 7.8 Hz, 1H), 6.06 (d, J = 7.8 Hz, 2H), 7.11-7.27 (m, 8H), 7.53 (d, J = 8.0 Hz, 2H), 8.09 (br, 1H).

10.3.3 N-((4-bromophenyl)(1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide (5b)

Rf = 0.30 (ethyl acetate/hexane = 1/2, v/v); colorless solid. Chiral HPLC: Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min, t (R-enantiomer) = 16.08 min, t (S-enantiomer) = 23.96 min; or Daicel Chiralcel OD-H, Hexanes / IPA = 80 / 20, 0.6 ml / min, t (R-enantiomer) = 34.74 min, t (S-enantiomer) = 56.90 min. 'H NMR (400 MHz, CDCl₃) δ 2.39 (s, 3H), 5.00 (d, J = 6.4 Hz, 1H), 5.79 (d, J = 6.0 Hz, 1H), 6.63 (s, 1H), 7.00 (t, J = 7.6 Hz, 1H), 7.13-7.19 (m, 6H), 7.29-7.31 (m, 3H), 7.55 (d, J = 8.0 Hz, 2H), 8.00 (br, 1H).

10.3.4 N-((4-chlorophenyl)(1H-indol-3-yl)methyl)-4-methylbenzenesulfonamide (6b)

Rf = 0.30 (ethyl acetate/ hexane = 1/2, v/v); colorless solid. Chiral HPLC: Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min, t (R-enantiomer) = 17.33 min, t (S-enantiomer)
= 25.89 min; or Daicel Chiralcel OD-H, Hexanes / IPA = 80 / 20, 0.6 ml / min, t
(R-enantiomer) = 34.64 min, t (S-enantiomer) = 56.19 min. 1H NMR (400 MHz, CDCl3) δ 2.38 (s, 3H), 4.93 (d, J = 6.4 Hz, 1H), 5.78 (d, J = 6.4 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 7.00 (t, J = 6.8 Hz, 1H), 7.11-7.18 (m, 8H), 7.31 (d, J = 6.8 Hz, 1H), 7.55 (d, J = 8.4 Hz, 2H), 7.97 (br, 1H).

**10.4 Product HPLC traces for the Friedel-Crafts products listed in Table 2 of the paper.**

![HPLC trace](image1)

**Figure S10.1.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidenebenzenesulfonamide for entry 1 in Table 2, using CMOF-1 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 mL / min, t (major) = 15.83 min, t (minor) = 23.67 min].

![HPLC trace](image2)
**Figure S10.2.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidenebenzenesulfonamide for entry 2 in Table 2, using CMOF-1 as the catalyst (reuse). From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 mL / min, t (major) = 16.18 min, t (minor) = 24.24 min].

**Figure S10.3.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidene-4-methylbenzenesulfonamide for entry 3 in Table 2, using CMOF-1 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 mL / min, t (major) = 16.16 min, t (minor) = 25.32 min].

**Figure S10.4.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide for entry 4 in Table 2, using CMOF-1 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 mL / min, t (major) = 18.43 min, t (minor) = 28.34 min].
**Figure S10.5.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide for entry 5 in Table 2, using CMOF-1 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min, t (major) = 17.30 min, t (minor) = 26.15 min].

**Figure S10.6.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidenebenzenesulfonamide for entry 6 in Table 2, using L4Me4 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 80 / 20, 0.6 ml / min. t (minor) = 30.53 min, t (major) = 49.49 min].
**Figure S10.7.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidene-4-methylbenzenesulfonamide for entry 7 in Table 2, using L1Me4 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (minor) = 15.78 min, t (major) = 24.32 min].

**Figure S10.8.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide for entry 8 in Table 2, using L1Me4 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 80 / 20, 0.6 ml / min. t (minor) = 35.36 min, t (major) = 57.80 min].
**Figure S10.9.** HPLC trace of the Friedel-Crafts product between indole and \((E)-N-(4\text{-chlorobenzylidene})-4\text{-methylbenzenesulfonamide}\) for entry 9 in Table 2, using \(\text{LiMe}_4\) as the catalyst. From left to right: first peak, \((R)\)-enantiomer; second peak, \((S)\)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. \(t\) (minor) = 17.33 min, \(t\) (major) = 25.89 min].

**Figure S10.10.** HPLC trace of the Friedel-Crafts product between indole and \((E)-N\text{-benzylidenebenzenesulfonamide}\) for entry 10 in Table 2, using CMOF-2 as the catalyst. From left to right: first peak, \((R)\)-enantiomer; second peak, \((S)\)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. \(t\) (major) = 16.08 min, \(t\) (minor) = 23.96 min].
**Figure S10.11.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidenebenzenesulfonamide for entry 11 in Table 2, using CMOF-2 as the catalyst (reuse). From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 16.11 min, t (minor) = 24.09 min].

**Figure S10.12.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidene-4-methylbenzenesulfonamide for entry 12 in Table 2, using CMOF-2 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 15.91 min, t (minor) = 24.57 min].
**Figure S10.13.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide for entry 13 in Table 2, using CMOF-2 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 18.24 min, t (minor) = 27.84 min].

**Figure S10.14.** HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide for entry 14 in Table 2, using CMOF-2 as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 17.54 min, t (minor) = 26.51 min].
Figure S10.15. HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidenebenzenesulfonamide for entry 15 in Table 2, using $\text{L}_2\text{Me}_4$ as the catalyst. From left to right: first peak, ($R$)-enantiomer; second peak, ($S$)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. $t$ (major) = 16.53 min, $t$ (minor) = 24.68 min].

Figure S10.16. HPLC trace of the Friedel-Crafts product between indole and (E)-N-benzylidene-4-methylbenzenesulfonamide for entry 16 in Table 2, using $\text{L}_2\text{Me}_4$ as the catalyst. From left to right: first peak, ($R$)-enantiomer; second peak, ($S$)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. $t$ (major) = 16.05 min, $t$ (minor) = 24.90 min].
Figure S10.17. HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-bromobenzylidene)-4-methylbenzenesulfonamide for entry 17 in Table 2, using L2Me₄ as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 18.61 min, t (minor) = 28.48 min].

Figure S10.18. HPLC trace of the Friedel-Crafts product between indole and (E)-N-(4-chlorobenzylidene)-4-methylbenzenesulfonamide for entry 18 in Table 2, using L2Me₄ as the catalyst. From left to right: first peak, (R)-enantiomer; second peak, (S)-enantiomer. [Daicel Chiralcel OD-H, Hexanes / IPA = 70 / 30, 0.6 ml / min. t (major) = 17.31 min, t (minor) = 26.09 min].

10.5 Characterization of the byproduct for the CMOF catalyzed Friedel-Crafts reaction
Byproduct as a result of the decomposition of the immine reactant or the amine product followed by Friedel-Crafts addition of indole was observed in the CMOF catalyzed reactions. 3

The byproducts were indentified in 1H-NMR of the crude reaction mixture for all the reactions catalyzed by CMOF 1 and 2. The the aryl(bisindolyl)methane byproduct generated in the reactions between indole and 5a catalyzed by 1 was isolated by column.

3,3'-(4-bromophenyl)methylene)bis(1H-indole)

1H NMR (400 MHz, CDCl3) δ 5.83 (s, 1H), 6.61 (s, 2H), 7.004 (t, J = 9.6 Hz, 2H), 7.15-7.24 (m, 4H), 7.33-7.39 (m, 6H), 7.89 (br, 2H).

11. Details of QM/MM calculations

QM/MM calculations on the reaction between indole and imine 4a were performed using Gaussian 03 software suite. (R)-3,3'-diphenyl-1,1'-binaphthyl phosphate catalyst was selected as the catalyst model for homogeneous catalysis. Density functional theory at the level of B3LYP/6-311G(d) was employed for optimization of the transition states for the four possible intermediates in the homogeneous case (see manuscript, homo-TS-1 to 4, Scheme 1). Solvation was also considered in the calculation using conductor-like polarizable continuum model (CPCM). To simulate the cavity environment in CMOF-1, one repeating unit of CMOF-1 is taken into account (see the paper, Scheme 1) and treated with the semiempirical
approach PM6. Density functional theory at the same level as the homogeneous system was applied to the catalytic center and reactants. Solvation was considered using CPCM.

Figure S13.1 Optimized transition states of \((R)-3,3'\text{-diphenyl-1,1'\text{-binaphthyl phosphoric acid}}\) catalyzed Friedel-Crafts reaction between indole and imine 4a. (a) homo-TS-1, leading to S-product. (b) homo-TS-2, leading to S-product. (c) homo-TS-3, leading to R-product. (d) homo-TS-4, leading to R-product.
Figure S13.2 Space-filling model of the transition states of CMOF-1 catalyzed Friedel-Crafts reaction between indole and imine 4a. (a) and (c) CMOF-TS-3, leading to the S-product. (b) and (d) CMOF-TS-3, leading to R-product. The CMOF-1 framework is illustrated in cyan color; the PO$_3$ center is represented in purple; the indole molecule is in yellow; the imine 4a molecule is in green.

Reference:
5. Materials Studio v 5.0. Accelrys Software Inc., San Diego, CA 92121, USA.
