Electronic Supplementary Information for

Asymmetric Catalytic Reactions by NbO-Type Chiral Metal-Organic Frameworks

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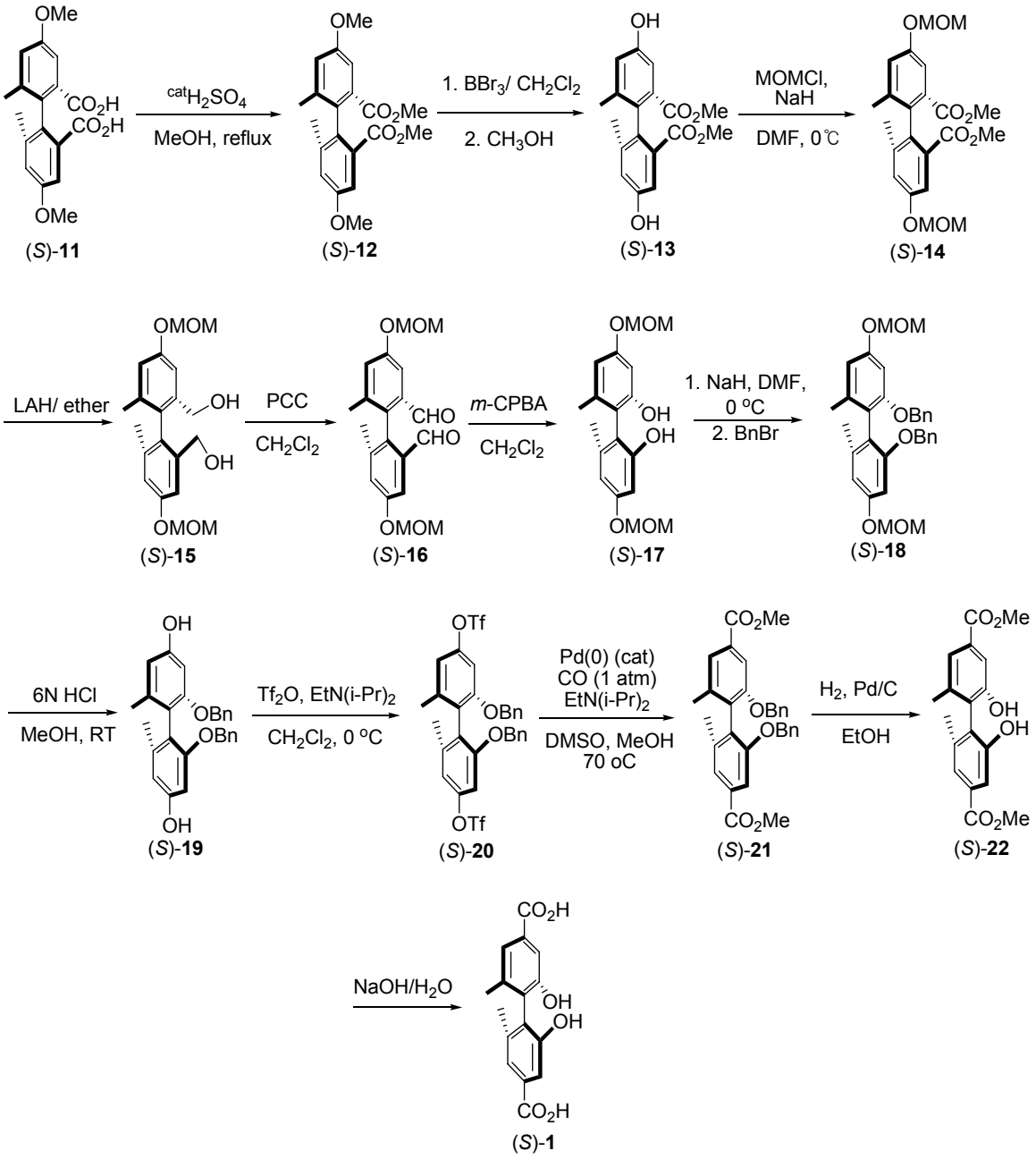
1.1. General consideration

Unless otherwise noted, all materials were obtained from commercial suppliers Aldrich and TCI, and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Toluene was distilled from calcium hydride and stored over 4Å molecular sieve. Evaporation of organic solvents was conducted using a Büchi rotary evaporator with a desktop vacuum pump. Thin layer chromatography plates (Silica gel 60 F254, Merck) were visualized by ultraviolet light and/or treatment with acidic *p*-anisaldehyde stain followed by gentle heating. Chromatographic purification of products were accomplished by flash chromatography by using Merck silica gel 60(230~400mesh) with a mixture of hexane and ethyl acetate as eluent. ^{1}H-NMR spectra were recorded on Varian Gemini 75 MHz spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to the methyl peak of TMS. High performance liquid chromatography (HPLC) was conducted using a Waters model 600 pumping system with a Waters model 2487 ultraviolet detector at 254nm. Infrared (IR) spectra were recorded on a Bomem 102 FT-IR spectrometer. Optical rotations were measured at the 589nm sodium D-Line with RUDOLPH AUTOPOL automatic polarimeter. Low- and High-resolution FAB mass spectra were obtained by JEOL JMS-AX505WA mass spectrometer. Melting points were measured with capillary melting point apparatus of Thomas Hoover and are uncorrected.

1.2. Preparation of (*S*)-**1**H_2

The synthesis was carried out according to the Scheme S1.



Scheme S1. Synthesis of chiral (*S*)-**1**H_2

(*S*)-4,4'-Dimethoxy-6,6'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylic acid ((*S*)-11)

A mixture of diacid (±)-**11** (3.7 g, 11.27 mmol) and brucine (4.2 g, 11.27 mmol) was dissolved in methanol (5 mL) and acetone (10 mL) at reflux. The solution was allowed to cool down slowly and the precipitated crystals were filtered off. The collected precipitates, (*S*)-**11**–brucine salt, were washed with cold methanol (2 mL) and then were placed in a reparatory funnel containing a 1:1 mixture of ethyl acetate/hydrochloric acid (1 M). After careful shaking, the organic layer was collected. Then the aqueous phases were extracted with ethyl acetate a couple of times more. The combined organic layers were washed with saturated aqueous solution of sodium bicarbonate (50 mL) and brine (3 × 50 mL), and then dried over anhydrous $MgSO_4$. After filtration of insoluble materials, the filtrate was concentrated *in vacuo* to yield 1.4 g of (*S*)-**11** (4.28 mmol, 38 %), IR and NMR spectra were identical to the literature data.

(*S*)-Dimethyl-4,4'-dimethoxy-6,6'-dimethy(1,1'-biphenyl)-2,2'-dicarboxylate ((*S*)-12)

To a solution of (*S*)-**11** (10.0 g, 30.27 mmol) in methanol (250 mL) was slowly added concentrated H_2SO_4 (96%, 2.5 mL), and the mixture was gently heated with stirring to reflux for 10 h. After cooling the reaction mixture to room temperature, the mixture was quenched with 6 N aqueous solution of Na_2CO_3 (100 mL). The volatiles were evaporated under vacuum. The residue was then dissolved in ethyl acetate (250 mL). The organic layer was washed with brine (3 × 200 mL) and dried over anhydrous $MgSO_4$. After filtration of insoluble materials, the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane/EA, 80:20 v/v) to give 10.3 g of (*S*)-**12** as a white solid (28.77 mmol, 95 %).

mp: 50 °C; TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.25; $[\alpha]_D$ = -108.5 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.57 (s, 6H), 3.83 (s, 6H), 6.96 (s, 2H), 7.32 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 51.6, 55.0, 111.6, 119.5, 130.4, 133.0, 138.4, 157.6, 167.2 ; IR (KBr): 2950, 1731 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}O_6$, 358.14; found, 358.28.

(*S*)-Dimethyl-4,4'-dihydroxy-6,6'-dimethy(1,1'-biphenyl)-2,2'-dicarboxylate ((*S*)-13)

To a solution of (*S*)-**12** (5.0 g, 13.95 mmol) in methylene chloride (28 mL) was added boron tribromide (7.3 g, 29.30 mmol) drop wise at -78 °C and the reaction mixture was stirred further for 1 h at -78 °C. The reaction mixture was slowly warmed to room temperature and then was quenched with methanol (20 mL). The reaction mixture was diluted with ether (150 mL), and the resultant mixture was washed with saturated aqueous $NaHCO_3$ (3 × 100 mL) and then brine (3 × 100 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under vacuum. The crude product was then purified by flash chromatography (*n*-Hexane/EA, 80/20 v/v) to give 4.2 g of (*S*)-**13** as a white solid (12.83 mmol, 92 %). mp: 111 °C; TLC (*n*-Hexane:EA, 50:50 v/v): R_f = 0.35; $[\alpha]_D$ = -28.6 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H), 3.89 (s, 3H), 7.51 (d, J = 3.3 Hz, 1H), 7.58 (d, J = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 19.4, 51.4, 113.7, 119.6, 130.1, 132.5, 138.6, 157.0, 166.8; IR (KBr): 3330, 2990, 1725 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{18}H_{18}O_6$, 330.1103; found, 330.1102.

(*S*)-Dimethyl-4,4'-bis(methoxymethoxy)-6,6'-dimethyl(1,1'-biphenyl)-2,2'-dicarboxylate ((*S*)-14)

To a solution of (*S*)-**13** (18.7 g, 56.61 mmol) in DMF (113 mL) was added sodium hydride (5.7 g, 141.52 mmol) slowly at 0 °C and the resultant mixture was stirred for 1 h. A solution of chloromethoxy methyl ether (10.7 mL, 141.52 mmol) in dichloromethane (10 mL) was added into the reaction mixture. The reaction mixture was allowed to be warmed to room temperature and then kept at room temperature for 2 h. The reaction mixture was quenched with water (50 mL) and then all the valitles materials including DMF were evaporated in vacuum. The residue was dissolved in ethyl

acetate (200 mL) then the organic layer was washed with brine (3 × 50 mL), dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated in vacuum. The crude product was purified by flash chromatography (*n*-Hexane/EA, 80:20 v/v) to give 23.5 g of (*S*)-**14** as a colorless oil. (56.04 mmol, 99 %).

TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.25; $[\alpha]_D$ = -36.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H), 3.43 (s, 3H), 3.89 (s, 3H), 5.12 (s, 2H), 7.01 (d, J = 3.3 Hz, 1H), 7.13 (d, J = 2.7 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 20.4, 55.4, 112.7, 121.6, 129.1, 134.5, 138.6, 158.0, 172.8; IR (KBr): 3030, 2990, 1730 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{22}H_{26}O_8$, 418.1628; found, 418.1628.

(*S*)-(4,4'-Bis(methoxymethyl)-6,6'-dimethyl(1,1'-biphenyl)-2,2'-dimethanol ((*S*)-15)

To a solution of (*S*)-**14** (23.4 g, 56.04 mmol) in THF (224 mL) was added lithium aluminum hydride (2 M solution in *n*-hexane, 28 mL, 56.04 mmol) slowly at 0 °C. The resultant mixture was stirred for 1 h at 0 °C. The reaction mixture was warmed to room temperature and then quenched with water. The reaction mixture was diluted with ethyl acetate (200 mL). And the organic layer was washed with saturated aqueous Na_2SO_4 solution (500 mL) and brine (3 × 20 mL) and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated in vacuum. The crude product was purified by recrystallization (*n*-hexane/ethyl acetate 90:10) to give 18.3 g of (*S*)-**15** as a white solid (50.40 mmol, 90 %).

mp: 105 °C; TLC (*n*-Hexane:EA, 50:50 v/v): R_f = 0.35; $[\alpha]_D$ = 8.6 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 3H), 3.05 (br, 1H), 4.07 (m, 3H), 5.18 (d, *J* = 2.2 Hz, 2H), 6.89 (d, *J* = 1.9 Hz, 1H), 7.00 (d, J = 2.2 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 20.4, 55.4, 112.7, 121.6, 129.1, 134.5, 138.6, 158.0, 172.8; IR (KBr): 3330, 2990 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{26}O_6$, 362.1729; found, 362.1729.

(*S*)-4,4'-Bis(methoxymethyl)-6,6'-dimethyl(1,1'-biphenyl)-2,2'-dicarbaldehyde ((*S*)-16)

To a solution of alcohol (*S*)-**15** (18.0 g, 49.67 mmol) was added PCC (11.7 g, 54.63 mmol) in dichloromethane (100 mL). The resultant mixture was stirred at room temperature for 45 minutes. Insoluble materials were filtered over silica gel pad with the aid of ethyl acetate/*n*-hexane 50/50 (1 L). The combined organic layer was concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane/EA, 80:20 v/v) to give 16.9 g of (*S*)-**16** as a white solid. (47.19 mmol, 95 %)

mp: 92 °C; TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.57; ^1H NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 3H), 3.52 (s, 3H), 5.26 (s, 2H), 7.24(d, J = 4.1 Hz, 1H), 7.52 (d, J = 2.4 Hz, 1H), 9.54(s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.1, 56.5, 94.5, 112.3, 124.2, 133.5, 136.2, 140.0, 157.3, 191.4; IR (KBr): 3030, 2991, 1716 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{20}H_{22}O_6$, 358.1416; found, 358.1416.

4,4'-Bis(methoxymethyl)-6,6'-dimethyl(1,1'-biphenyl)-2,2'-diol ((*S*)-17)

A solution of aldehyde (*S*)-**16** (268 mg, 0.75 mmol) and *m*-CPBA (1.3 g, 7.50 mmol) in dichloromethane (10 mL) was stirred at room temperature for 20 h. The excess of *m*-CPBA was reduced by addition of $Na_2S_2O_3$ (1 M, 10 mL). The reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 mL). The organic layer was stirred in Na_2CO_3 1 M (5 mL) for 30 minutes to hydrolyze the undesired formats at room temperature. The reaction mixture was extracted with dichloromethane (3 × 5 mL). The combined organic layer was washed with brine (3 × 20 mL) and dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated in vacuum. The crude product was purified by column chromatography (*n*-Hexane/EA, 60:40 v/v) to provide 86.9 mg (0.26 mmol, 35 %) of (*S*)-**17**.

mp: 90 °C; TLC (*n*-Hexane:EA, 50:50 v/v): R_f = 0.65; $[\alpha]_D$ = -30.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 11.94 (s, 3H), 3.45 (s, 3H), 5.11 (s, 2H), 5.17 (br, 1H), 6.54 (s, 1H), 6.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 55.9, 94.0, 100.9, 110.2, 113.0, 140.2, 155.0, 158.3; IR (KBr): 3330, 2990 cm^{-1}; HRMS (m/z): $[M + Na]^+$ calcd for $C_{18}H_{22}O_6$, 334.1416; found, 358.1411.

2,2'-Bis(benzyloxy)-4,4'-bis(methoxymethyl)-6,6'-dimethyl(1,1'biphenyl)((*S*)-18)

To a solution of (*S*)-**17** (1.6 g, 4.87 mmol) in dimethyl formamide (20 mL) was added sodium hydride (487 mg, 12.19 mmol) slowly at 0 °C. After stirring of the resultant mixture at 0 ^oC for 1 h, benzyl bromide (1.4 mL, 12.19 mmol) was added. And then the reaction mixture was warmed to room temperature, and kept at room temperature for 2 h. The reaction mixture was quenched with water (10 mL) and all the volatiles including DMF were evaporated in vacuum. The residue was dissolved in ethyl acetate (50 mL) and was washed with brine (3 × 50 mL). The organic layer was then dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated in vacuum. The crude product was purified by flash chromatography (*n*-Hexane/EA 80:20 v/v) to give 2.4 g of (*S*)-**18** as a white solid (4.82 mmol, 99 %).

mp: 53 °C; TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.52; $[\alpha]_D$ = -16.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 3.52 (s, 3H), 4.99 (s, 2H), 5.19 (s, 2H), 6.58 (d, *J* = 2.0 Hz, 1H), 6.56 (d, J = 1.9 Hz, 1H), 7.19 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.0, 55.9, 69.9, 94.6, 99.7, 109.5, 120.5, 126.3, 126.8, 127.0, 127.5, 128.1, 137.6, 139.3, 156.9, 157.0; IR (KBr): 3030, 2991 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{32}H_{34}O_6$, 514.2355; found, 514.2360.

2,2'-Bis(benzyloxy)-6,6'-dimethyl(1,1'-biphenyl)-4,4'-diol ((*S*)-19)

To a solution of (*S*)-**18** (4.5 g, 8.74 mmol) in methanol (17.5 mL) was added 6 N aqueous solution of HCl (8.8 mL) at 50 °C. The resultant mixture was stirred for 1 h at that temperature. The reaction mixture was then cooled to room temperature and then quenched with 6 N aqueous solution of Na_2CO_3 (10 mL). The volatiles were evaporated under vacuum. The residue was then dissolved in ethyl acetate (100 mL). The organic layer was washed with brine (3 × 100 mL) and dried over anhydrous $MgSO_4$. After filtration of insoluble materials, the filtrate was concentrated under vacuum. The crude product was purified by recrystallization (*n*-Hexane/EA, 90:10 v/v) to give 3.3 g of (*S*)-**19** as a white solid (7.86 mmol, 90 %).

mp: 85 °C; TLC (*n*-Hexane:EA, 50:50 v/v): R_f = 0.71; $[\alpha]_D$ = -27.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 1.94 (s, 3H), 4.73 (s, 1H), 4.93 (s, 2H), 6.33 (s, 1H), 6.38 (s, 1H), 7.19 (m, 5H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 19.8, 69.9, 98.6, 109.1, 119.2, 126.3, 127.2, 128.2, 137.5, 139.7, 155.1, 157.2; IR (KBr): 3330, 3030, 2991 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{28}H_{26}O_4$, 426.1831; found, 426.1832.

2,2'-Bis(benzyloxy)-6,6'-dimethylbiphenyl-4,4'-diylbis(trifluoromethanesulfonate)((*S*)-20)

To a solution of (*S*)-**19** (1.1 g, 2.67 mmol) and pyridine (1.3 mL, 16.02 mmol) in CH_2Cl_2 (27 mL) was added Tf_2O (0.9 mL, 5.61 mmol) drop wise at 0 °C and the mixture was stirred for 2 h at this temperature. Then, the reaction mixture was poured into water. After extraction with CH_2Cl_2 (3 × 30 mL), the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by column chromatography (*n*-Hexane/EA, 90:10 v/v) to give 1.7 g of (*S*)-**20** as a white solid (2.46 mmol, 92 %).

mp: 105 °C; TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.76; $[\alpha]_D$ = -12.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 1.93 (s, 3H), 4.91 (s, 2H), 6.30 (s, 1H), 6.36 (s, 1H), 7.19 (m, 5H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 19.8, 70.0, 98.6, 109.2, 119.1, 126.4, 127.2, 128.2, 137.4, 139.6, 155.1,

157.1; IR (KBr): 3031, 2991 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{30}H_{24}F_6O_8S_2$, 690.0817; found, 690.0858.

Dimethyl 2,2'-bis(benzyloxy)-6,6'-dimethyl(1,1'-biphenyl)-4,4'-dicarboxylate ((*S*)-21)

A mixture of (*S*)-**20** (547 mg, 0.91 mmol), $Pd(OAc)_2$ (40.9 mg, 0.18 mmol), dppp (75.1 mg, 0.18 mmol), *i*Pr_2NEt (0.7 mL, 4.01 mmol) in DMF/MeOH (v/v = 1/1) (5 mL) was charged with a CO gas (1 atm). The reaction mixture was heated with stirring to 100 °C for 12 h. After cooling the reaction mixture to room temperature, the whole mixture was poured into water (10 mL). Organic compounds were extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was then dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography (*n*-Hexane/EA, 80:20 v/v) to give 260.5 mg of (*S*)-**21** as a white solid (0.51 mmol, 56 %).

mp: 132 °C; TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.55; $[\alpha]_D$ = -54.0 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 3.93 (s, 3H), 5.04 (d, J = 3.0 Hz, 1H), 7.19 (m, 5H), 7.55 (s, 1H), 7.67 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ .3, 52.1, 69.9, 110.6, 123.9, 126.2, 127.3, 128.2, 130.0, 131.3, 136.8, 138.1, 155.6, 167,1; IR (KBr): 3030, 2991,1725 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{32}H_{30}O_6$, 510.2042; found, 510.2036.

Dimethyl 2,2'-dihydroxy-6,6'-dimethyl(1,1'-biphenyl)-4,4'-dicarboxylate ((*S*)-22)

A mixture of (*S*)-**21** (2.5 g, 4.90 mmol), Pd/C, in ethanol (30 mL) was charged with a H_2 gas (1 atm) and then the mixture was stirred at room temperature for 30 min. After filtration of insoluble materials by passing through Celite, the filtrate was concentrated in vacuum. The crude product was purified by recrystallization (*n*-Hexane/EA, 95:5 v/v) to give 1.6 g of (*S*)-**22** as a white solid (4.85 mmol, 99 %).

mp: 110 °C; TLC (*n*-Hexane:EA, 50:50 v/v): R_f = 0.63; $[\alpha]_D$ = -46.5 (c = 0.05 g cm^{-3} in MeOH); ^1H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H), 3.91 (s, 3H), 5.35 (br, 1H), 7.51 (s, 1H), 7.58 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.8, 52.5, 114.6, 123.1, 130.4, 131.2, 139.6, 155.8, 168.8; IR (KBr): 3330, 2991, 1726 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{18}H_{18}O_6$, 330.1122; found, 330.1121.

2,2'-Dihydroxy-6,6'-dimethyl(1,1'-biphenyl)-4,4'-dicarboxylic acid ((*S*)-1H_2)

A mixture of (*S*)-**22** (1.0 g, 3.03 mmol) in 6 N NaOH (15 mL), THF (15 mL) and MeOH (15 mL) was stirred for 5 h at room temperature. The reaction mixture was concentrated in vacuum and the residue was acidified with 1 N aqueous solution of HCl to pH 2 of the solution. The resultant white precipitate was extracted with ethyl acetate, and the organic layer washed with saturated solution of sodium bicarbonate (50 mL) and brine (3 × 50 mL), dried over anhydrous $MgSO_4$. After filtration, the filtrate was concentrated under vacuum. 906 mg of (*S*)-**1**H_2 was obtained as white crystals (3.00 mmol, 99 %).

mp: 145 °C; TLC (EA): R_f = 0.81; $[\alpha]_D$ = -108.0 (c = 0.03 g cm^{-3} in MeOH); ^1H NMR (300 MHz, DMSO-D_6): δ 1.90 (s, 3H), 7.32 (s, 2H), 9.42 (s, 1H); ^{13}C NMR (75 MHz, DMSO-D_6): δ 19.3, 113.4, 121.3, 128.8, 130.2, 137.6, 154.4, 167.4; IR (KBr): 3330, 1690 cm^{-1}; HRMS (m/z): $[M+H]^+$ calcd for $C_{16}H_{14}O_6$, 302.0790; found, 302.0771.

2. Preparation and characterization of (*S*)-KUMOF-1

2.1. Preparation of (*S*)-KUMOF-1

2.1.1 Synthesis of (*S*)-KUMOF-1

A reaction mixture in a small vial (4 mL) was prepared by dissolving of $Cu(NO_3)_2 \cdot 3H_2O$ (7.2 mg, 0.030 mmol) and (*S*)-**1**H_2 (9 mg, 0.030 mmol) in DEF/MeOH (1.5 / 1.5 mL). This vials, after capping with holes, was placed in a larger (20 mL capacity) vial filled with *N*,*N*-dimethylaniline (1.0 mL). The tightly-capped larger vial was placed in an oven at 65 ºC for 1 day. Blue cubic crystals were obtained in 35% yield based on the used ligand. The crystals were separated and rinsed with DEF/MeOH (3 / 3 mL) three times.

2.1.2 Formula determination of (*S*)-**KUMOF-1**: Based on the X-ray crystal structure, the framework of **(*S*)-KUMOF-1** has been formulated as $[(Cu_2((S)\text{-}\mathbf{1})_2(H_2O)_2]$ with Z = 6 in the unit cell. As the free guest species could not be determined by the current X-ray data, the identification of the included molecules were identified by elemental analyses of the evacuated crystals, ^{1}H-NMR analysis of the digested crystals, and thermogravimetric analysis (TGA) as shown in the following information. Based on the accumulated results, the formula used was calculated to $[(Cu_2((S)\text{-}\mathbf{1})_2(H_2O)_2](DEF)_{7.6}(MeOH)_{9.6}$.

2.1.3 Elemental analysis of the framework of (*S*)-**KUMOF-1***:* As the free guest molecules were evaporated before the conduction of the elemental analysis. Element Analysis: (%) calcd. for (*S*)-**KUMOF-1** $[Cu_2((S)\text{-}\mathbf{1})_2]\cdot(H_2O)_2 = C_{32}H_{28}O_{14}Cu_2$: C, 50.33; H, 3.70; found: C, 50.38; H, 3.75

2.1.4 IR (KBr) of (*S*)-**KUMOF-1**: 3407 (br), 2924 (w), 1655 (s), 1559 (s), 1414 (s), 1296 (w), 1248 (w), 1165 (w), 1103 (m), 1041 (m), 1000(m), 882 (w), 793 (m), 772 (m), 662(w)

2.1.5. ^{1}H NMR study to confirm the presence of ligand $1H_2$ after the dismantling of (*S*)-KUMOF-1:

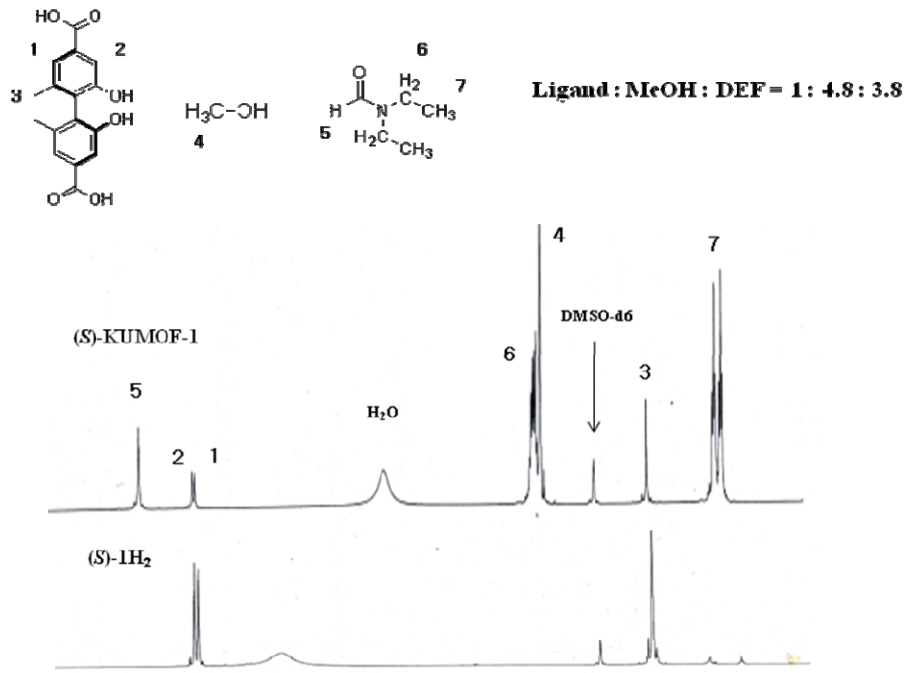


Figure S1. ^{1}H-NMR spectra of **KUMOF-1** (400 MHz, DCl/DMSO)

2.1.6 Thermogravimetric Analysis (TGA) of (*S*)-KUMOF-1: TGA was performed with TGA-S1000 (Scinco) under an ambient atmosphere. Sample (~13.8 mg) was loaded and the temperature was increased by 1°C/min from 25°C to 500°C. The first weight loss (– 63.5 %) is due to the evaporation of 7.6 DEFs, 9.6 MeOHs, and coordinating 2 H_2Os. The second step (–29.1 %) is for the decomposition of the (*S*)-**KUMOF-1** and the residue is attributed to CuO.

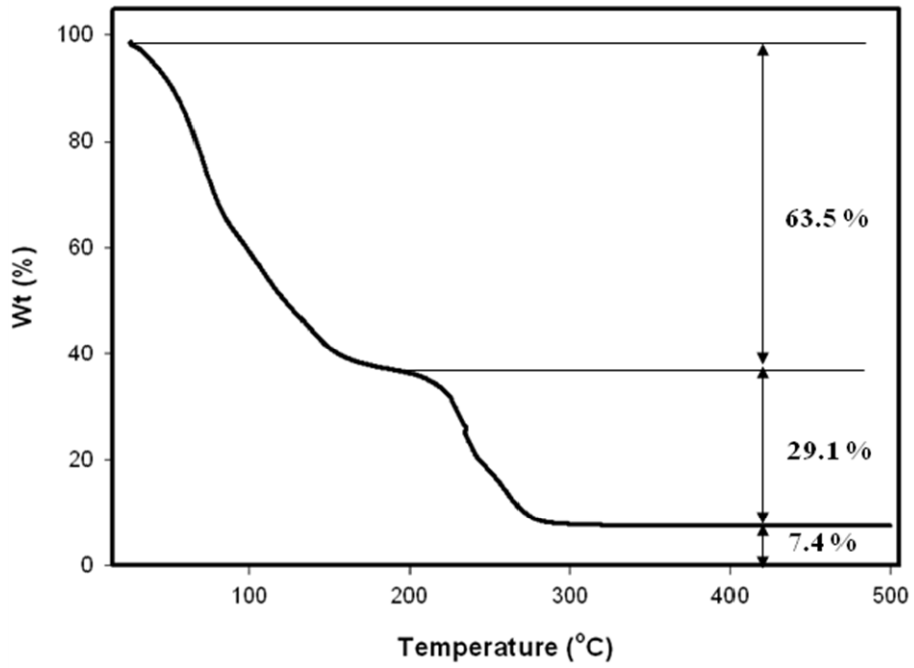


Figure S2. TGA thermogram of the (*S*)-**KUMOF-1** as-prepared.

2.2 Structure determination of (*S*)-**KUMOF-1**

2.2.1 Single Crystal Structure Determination

The diffraction data set from a blue block crystal sealed in a capillary was collected at 296 K on a Bruker APEX CCD diffractometer with CuKα radiation (λ = 1.54178 Å). Bruker SMART program[S1] was used for data collection, and SAINT[S2] was used for cell refinement, and reduction. Absorption correction was applied using SADABS[S3]. Crystal structure was solved using SHELX-TL software package[S4] with a chiral cubic space group, *I*432 (No. 211). An initial structure was obtained by direct methods using XS, and improved by subsequent refinements using XL. Both methyl and hydroxyl groups were disordered over two sites and almost overlapped with each other. Due to this disorder, it was not possible to define a right configuration of the organic ligand, and the resulting structure looked centrosymmetric. Therefore, the Flack's x parameter was meaningless in this structure. In fact, the crystal structure could be also solved with a centrosymmetric space group *Im*(-3)*m* (No. 225), and the structural feature of the cnetrosymmetric was identical with that of the *I*432 structure. Non-hydrogen atoms were refined anisotropically. An hydrogen atom bonded to C3 was placed in calculated positions and refined by applying a riding model. Hydrogen atoms for methyl and hydroxy groups were not included due their disorder. Water hydrogen atoms were also not generated for the final refinement process. Without including solvent molecules, the refinement converged to R1 = 0.1581 for 1152 reflections of $I > 2\sigma(I)$ and 0.2621 for all 3874 data. The large volume fraction of disordered solvents was calculated by PALTON SOLV CALC[S5] to 23971 Å^3 which corresponds to 87.1% of the unit cell volume. PALTON SQUEEZE[S5] routine calculated that 7298 electrons per unit cell were attributed to the disordered solvents. With a modified reflection data excluding the solvent contribution, the final refinement process converged to R1 = 0.0613, wR2 = 0.1891 ($I > 2\sigma(I)$). A part of the extended structure is in Figure S1, and crystal and refinement data are given in Table S1.

Table S1. Crystal data and structure refinement for (*S*)-**KUMOF-1**

Empirical formula	$C_{40}H_{54}Cu_2N_2O_{20}$	
Formula weight	1009.95	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Cubic	
Space group	*I*432 (No. 211)	
Unit cell dimensions	*a* = 30.1892(2) Å	α= 90°.
	b = 30.1892(2) Å	β= 90°.
	c = 30.1892(2) Å	γ = 90°.
Volume	27514.1(3) Å^3	
Z	6	
Density (calculated)	0.277 Mg/m^3	
Absorption coefficient	0.395 mm^{-1}	
F(000)	2340	
Crystal size	0.38 x 0.38 x 0.36 mm^3	
Theta range for data collection	2.07 to 64.63°.	
Index ranges	-32<=h<=26, -26<=k<=35, -26<=l<=27	
Reflections collected	53379	
Independent reflections	3874 [R(int) = 0.0471]	
Completeness to theta = 64.63°	99.6 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3874 / 19 / 68	
Goodness-of-fit on F^2	0.741	
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1891	
R indices (all data)	R1 = 0.1328, wR2 = 0.2227	
Absolute structure parameter	0.60(10)	
Largest diff. peak and hole	0.190 and -0.365 e.Å^{-3}	

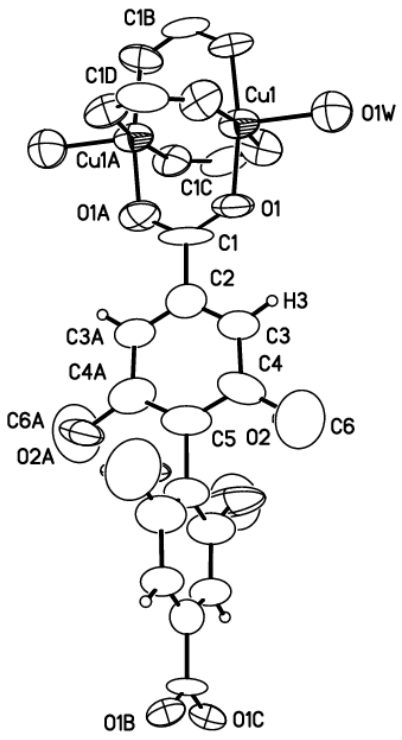


Figure S3. ORTEP drawing (20% probability) of a fragment in (*S*)-**1** ((*S*)-**KUMOF-1**) is displayed with selected atomic labels. C6 (-CH_3) and O2(-OH) atoms are disordered over two sites with a half-occupancy, respectively. Therefore, two atoms look superimposed onto same positions.

2.3. Activation and modification of (*S*)-**KUMOF-1**

2.3.1. Solvent exchange

The X-ray powder diffraction (XRPD) data of the evacuated (*S*)-**KUMOF-1** exhibited severe irreversible structural deformations under reduced pressure. Thus the occluded solvents in the MOF crystals were replaced by continuous washing with relatively inert solvents, such as toluene, THF, and/or dichloromethane. The replacement of the primary solvents, DEF and MeOH in most cases, was confirmed by the disappearance of the characteristic band for C=O stretching in the amides in the IR spectral measurements. The XRPD study confirmed that the MOF structure was intact after solvent exchange. After several treatments, including the azeotropic replacement of the solvents with toluene at reflux, the XRPD of the MOF confirmed that the structure remained unchanged.

The blue crystals were collected and rinsed with dry THF (3 × 5 mL) to remove DEF and MeOH. The MOF samples were rinsed with dry toluene (3 × 5mL) and soaked in dry THF for 3 days. THF-exchanged samples were rinsed with dry toluene (3 × 5mL) and placed in dry toluene (25mL). The residual THF and small quantity of MeOH were removed using dean-stock apparatus.

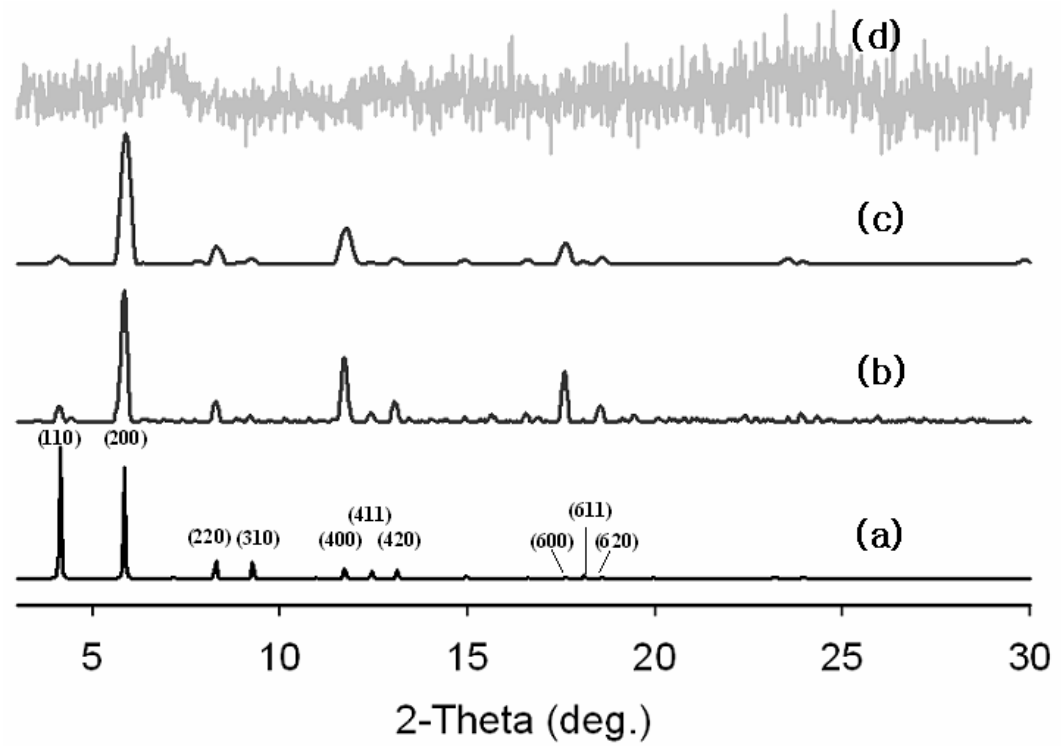


Figure S4. (a) XRPD patterns of the simulation based on the single-crystal structure of (*S*)-**KUMOF-1**, (b) the as-synthesized (*S*)-**KUMOF-1**, (c) solvent exchanged (*S*)-**KUMOF-1**, (d) dried (*S*)-**KUMOF-1.**

2.3.2. Modification of (*S*)-KUMOF-1 with dimethylzinc

2.3.2.1. Modification; To a solution of solvent exchanged (*S*)-**KUMOF-1** (102 mg, 0.27mmol) in dichloromethane (2 mL) was added dimethylzinc (0.41 mL, 2 M in dichloromethane, 0.81 mmol) at -78 °C and the solution was stirred for 3 h at this temperature. The newly obtained MOF was washed with dichloromethane and EA was measured after complete exacuation of dichloromethane by drying under vacuum for 1day.

elementary analysis: (%) calcd. for $[Cu_2((S)\text{-}\mathbf{1})_2]\cdot(H_2O)_{(3.8)}\cdot(Zn)_{(1.8)} = C_{32}H_{(27.6)}O_{(15.8)}Cu_2$: C, 42.25; H, 3.06; found: C, 42.79; H, 3.27.

2.3.2.2. Optical microscopic images and SEM–EDX of Crystals

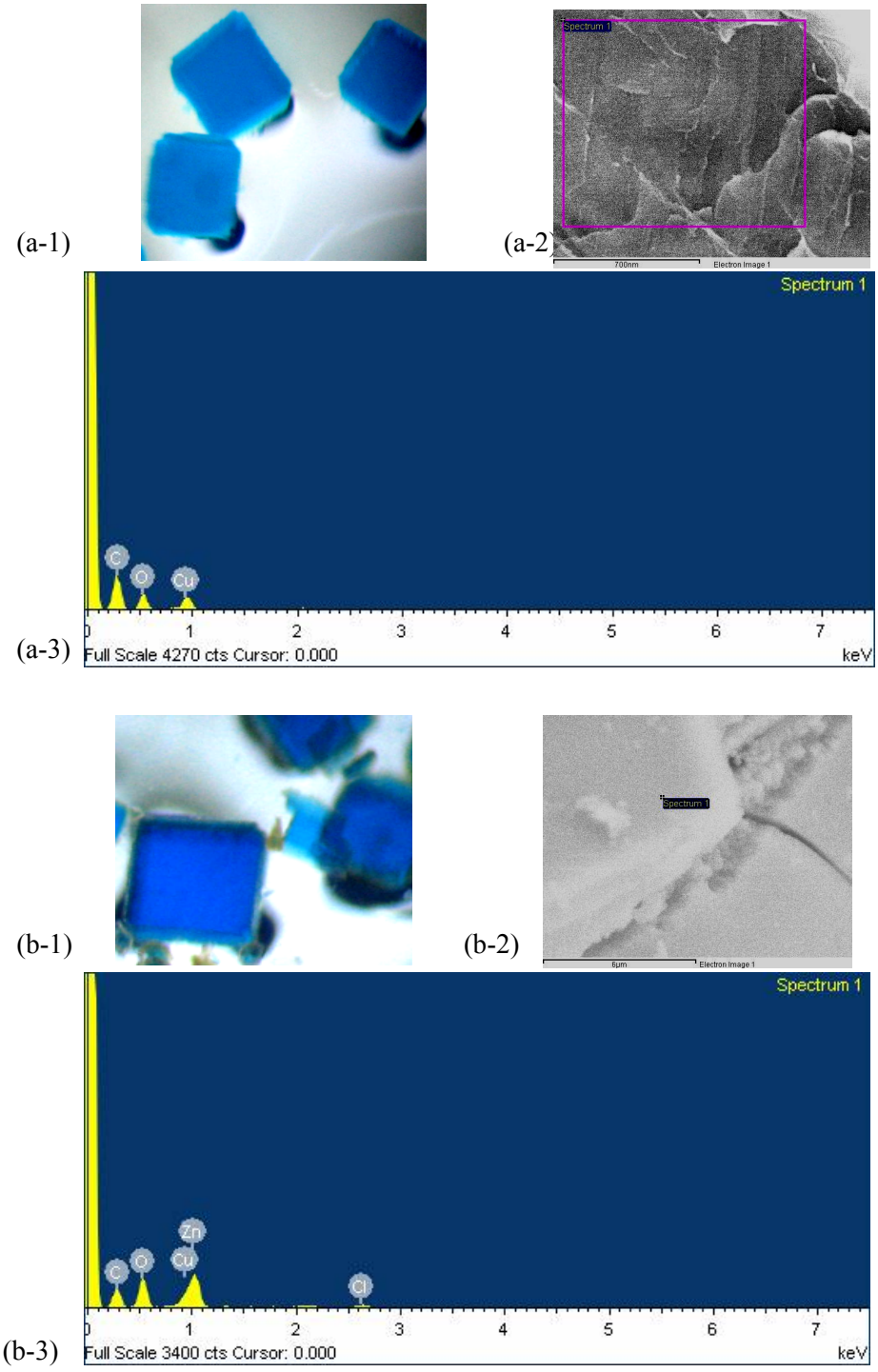


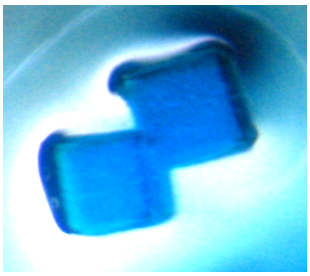
Figure S5. (a) (*S*)-**KUMOF-1** crystals: microscopic image (a-1), SEM image (a-2), and EDX spectrum of crystals (a-3). (b) After incubation of (*S*)-**KUMOF-1** with Me_2Zn in dichloromethane for 4h at 0 ^{o}C by shaking, instead of stirring with magnetic bar, not to destroy the appearance, the excess of Me_2Zn was removed by successive washing with toluene: microscopic image (b-1), SEM image (b-2), and EDX spectrum of crystals (b-3). SEM images are deformed in a certain degree since (*S*)-**KUMOF-1** out of the solvent and under vacuum are fragile as mentioned in the text.

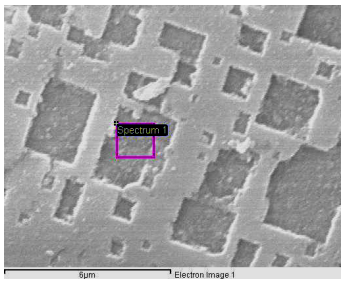
2.3.3. Modification of (*S*)-KUMOF-1 with titanium tetra-*iso*-propoxide

2.3.3.1. Modification; A mixture of (*S*)-**KUMOF-1** (24 mg, 0.063 mmol) and Ti(O-*i*Pr)$_4$ (0.19 mL, 1 M solution in toluene, 0.19 mmol) in toluene(1.5 mL) was stirred for 5 h at 25 °C. The newly obrained MOF was washed with cold toluene and EA was measured after complete exacuation of dichloromethane by drying under vacuum for 1day.

elementary analysis: (%) calcd. for $[Cu_2((S)\text{-}\mathbf{1})_2]\cdot(H_2O)_2\cdot(Ti)_2(O\text{-}iPr)_{(4.7)}$ = $C_{(46.1)}H_{(56.9)}O_{(18.7)}Cu_2$: C, 48.87; H, 5.06; found: C, 48.85; H, 5.44.

2.3.3.2. Optical microscopic images and SEM–EDX of Crystals

(a-1) 

(a-2) 

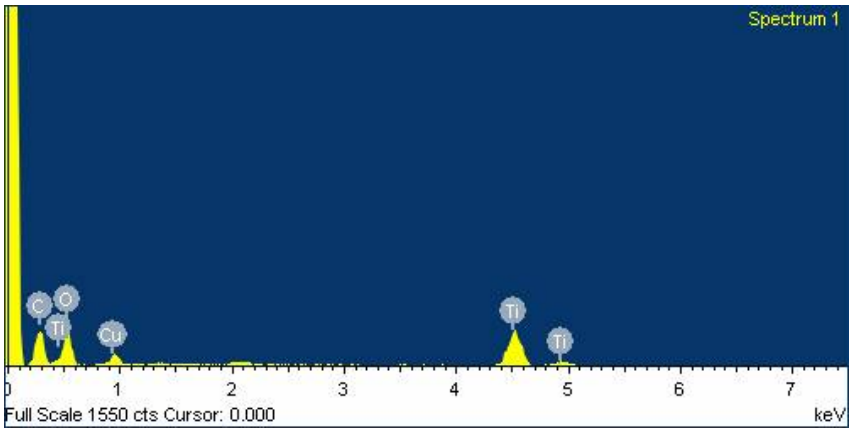
(a-3) 

Figure S6. After incubation of (*S*)-**KUMOF-1** with Ti(O-*i*Pr)$_4$ in toluene for 4h at 0 ^{o}C by shaking, instead of stirring with magnetic bar, not to destroy the appearance, the excess of Ti(O-*i*Pr)$_4$ was removed by successive washing with toluene: microscopic image (a), SEM image (b), and EDX spectrum of crystals (c). EDX data of crystals. SEM images are deformed in a certain degree since (*S*)-**KUMOF-1** out of the solvent and under vacuum are fragile as mentioned in the text.

3. Application to asymmetric heterogeneous catalyst

3.1. Carbonyl-Ene reaction

3.1.1. Preparation of substrate, 3-Methyl citronellal (2)

To slurry of cuprous iodide (4.0 g, 21 mmol) in diethyl ether (200 mL) at 0 °C was added methyl lithium (42 mL, 1 M in *n*-hexane, 42 mmol). After stirring at 0 °C for 10 min, the solution was cooled to -78 °C and the cuprate mixture previously prepared was slowly added to citral (3.0 g, 20 mmol) in diethyl ether (20 mL) at this temperature. The resulting mixture was stirred for 1 h at -78 °C and slowly warmed to room temperature. This mixture was poured into a cold-saturated NH_4Cl aqueous solution and extracted with ether. The combined organic layer was concentrated *in vacuo* and was purified by flash chromatography (*n*-hexane/ethyl acetate, 20/1) to give 1.6 g of **4** as a coloress oil (9.50 mmol, 45 %).

TLC (*n*-Hexane:EA, 90:10 v/v): R_f = 0.43; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H), 3.91 (s, 3H), 5.35 (br, 1H), 7.51 (s, 1H), 7.58 (s, 1H).; IR (KBr): 2910, 1705 cm^{-1}.

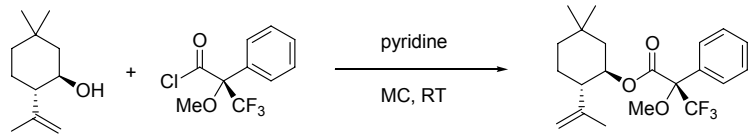
3.1.2. General procedure for the carbonyl-ene reaction; 5,5-dimethyl-2-(prop-1-en-2-yl)-cyclohexanol (3)

To a solution of (*S*)-**KUMOF-1** (102 mg, 0.27 mmol) in dichloromethane (2 mL) was added dimethyl zinc (0.4 mL, 2 M in dichloromethane, 0.80 mmol) at -78 °C. The resultant mixture was stirred for 3 h at this temperature. To this mixture was added **2** (15 mg, 0.089 mmol) in dichloromethane (0.1 mL) at -78 ^{o}C. The reaction mixture was warmed to 0 °C and stirred for 2 h at this temperature. The reaction mixture was quenched with aqueous solution of 6 N HCl (3 mL) and the resultant mixture was filtered through Celite. The filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography (*n*-hexane/ethyl acetate 5:1) to give **3** (13.8 mg, 92% yield)

TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.35; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92- 0.87 (m, 20H), 3.62 (ddd, J = 4.1, 1H), 4.84 (d, J = 12.3, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.2, 25.1, 26.3, 32.1, 32.9, 38.4, 46.7, 54.7, 67.5, 112.7, 146.

3.1.3. Preparation of Mosher ester (4) and ee Determination

Compound **3** was treated with (*S*)-(-)-MTPA-Cl (**23**) and pyridine in dichloromethane to give **6**, which would be a diastereomeric mixture and would be subjected to gas chromatography for determining optical purity.



3 **23** **4**

Scheme S2. Transformation of product **3** into a diastereomeric mixture of Mosher's esters **4**

(2*S*)-(1*S*,2*R*)-5,5-Dimethyl-2-(prop-1-en-2-yl)cyclohexyl 3,3,3-trifluoro-2-methoxy-2-phenylpropanoate (6) and its diastereomeric excess

A mixture of **3** (5 mg, 0.030 mmol), pyridine (0.03 mL, 0.37 mmol) and (*S*)-(-)-α-methoxy-(α-trifluoromethyl)phenylacetyl chloride ((*S*)-(-)-MTPA-Cl: 36 μL, 0.20 mmol) in dichloromethane (1 mL) was stirred for 1 h in the presence of a catalytic amount of 4-dimethylamlnopyridine at room temperature. The mixture was poured into l N HCl (3 mL) and extracted with dichloromethane. The combined organic layer was concentrated in vacuo and the residue was purified by flash chromatography to give **4** (7.5 mg, 65% yield). The diastereomeric ratio of MTPA esters was measured to be 74.8:25.2 by GLC (180 ^{o}C) (t, = 12.28 and 12.33 min).

TLC (*n*-Hexane:EA, 90:10 v/v): R_f = 0.72; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.95-2.18 (m, 17H), 3.52 (s, 3H), 4.60 (d, J = 10, 1H), 4.82 (s, 1H), 5.24 (ddd, J = 4.1, 1H), 7.37 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.7, 19.8, 24.6, 27.3, 27.5, 32.3, 32.4, 32.6, 32.6, 38.1, 43.6, 44.1, 50.4, 50.6, 55.4, 74.7, 75.0, 112.2, 121.4, 125.2, 127.3, 127.4, 128.1, 128.1, 129.3, 129.3, 132.4, 145.1, 146.0, 165.8, 166.0.

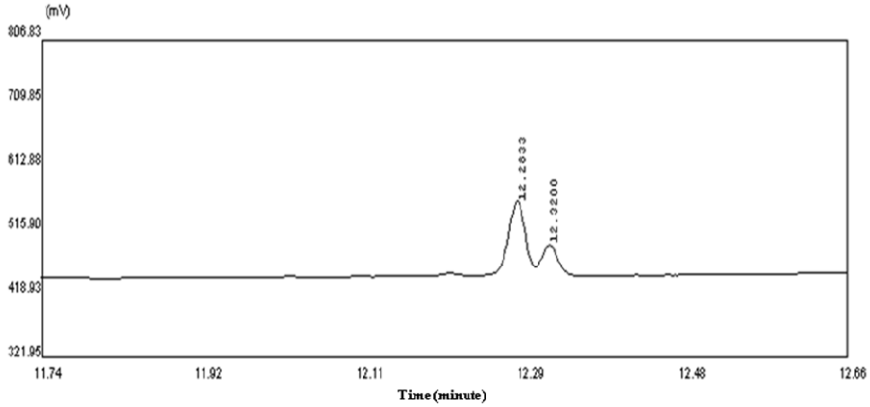
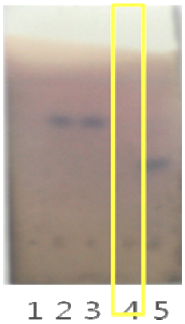


Figure S7. GLC Chromatogram for the determination of diastereomeric excess (50 % ee, t_1 = 12.28 min: t_2 = 12.32 min)

3.1.4.



1. The reaction mixture having (*S*)-**KUMOF-1**
2. Substrate **2** only
3. The reaction mixture right after the addition of **2**
4. The reaction mixture after 3h shaking
5. Product **3** only

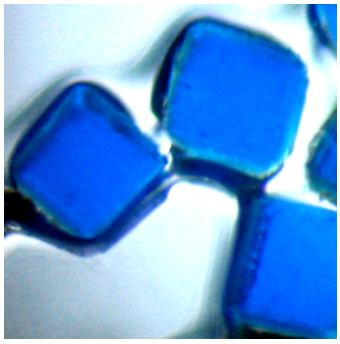


Figure S8. Thin layer chromatography for the reaction and Optical microscopic image of Zn/(*S*)-**KUMOF-1** after the complete disappearance of substrate **2**. There is no significant change in its appearance.

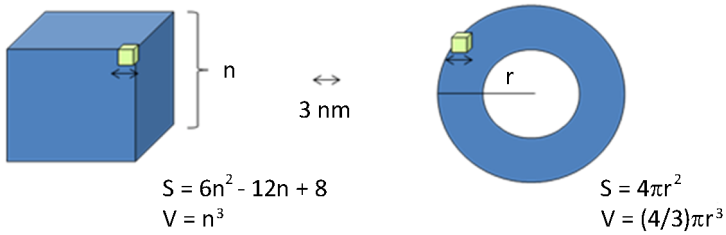
3.2. Calculation of the ratio between surface and whole volume

The notion, that the reaction occurred inside pore, could be proved by a simple mathematical treatment and measurement of particle size of MOF after the reaction.

In a previously mentioned carbonyl-ene reaction, when 3 equivalents of active sites were used, starting material **2** disappeared completely without indicating the formation of the product **3** on TLC. Product **3** is assumed to be entrapped inside the pore.

To rule out the possibility of trapping of **3** only by surface, the ratio of surface area *vs* whole volume was calculated. Assuming that powders have cubic structure, the particle size should be shorter than 10nm, if side of pore is 3 nm long, for that one third of ligand, an equivalent to **2** employed, were placed on the surface. And only in that case, all substrates or products were assumed to be trapped by the very first layer on the surface.

However, the average size of particles mechanically pulverized during the reaction was roughly, but conservatively, averaged to be >1μm by microscope (Fig S10). Same calculation shows that less than 2% of overall volume, in other word, is equivalent to 0.06eq of the amount of substrate **2,** would be exposed to environment which. This portion is far less to accommodate for all the substrate and product, and clearly indicated that the rest of substrates should be entrapped inside pore and transformed into the corresponding product at there.



S/V	n	MOF Size (nm)	S/V	n	MOF Size (nm)
1	2	6	1	3	6
0.50	10	30	0.30	10	30
0.27	20	60	0.20	20	60
0.18	30	90	0.10	30	90
0.12	50	150	0.06	50	150
0.06	100	300	0.03	100	300
0.017	333	1000	0.01	333	1000

Figure S9. Calculation for the ratio of Surface *vs* Volume

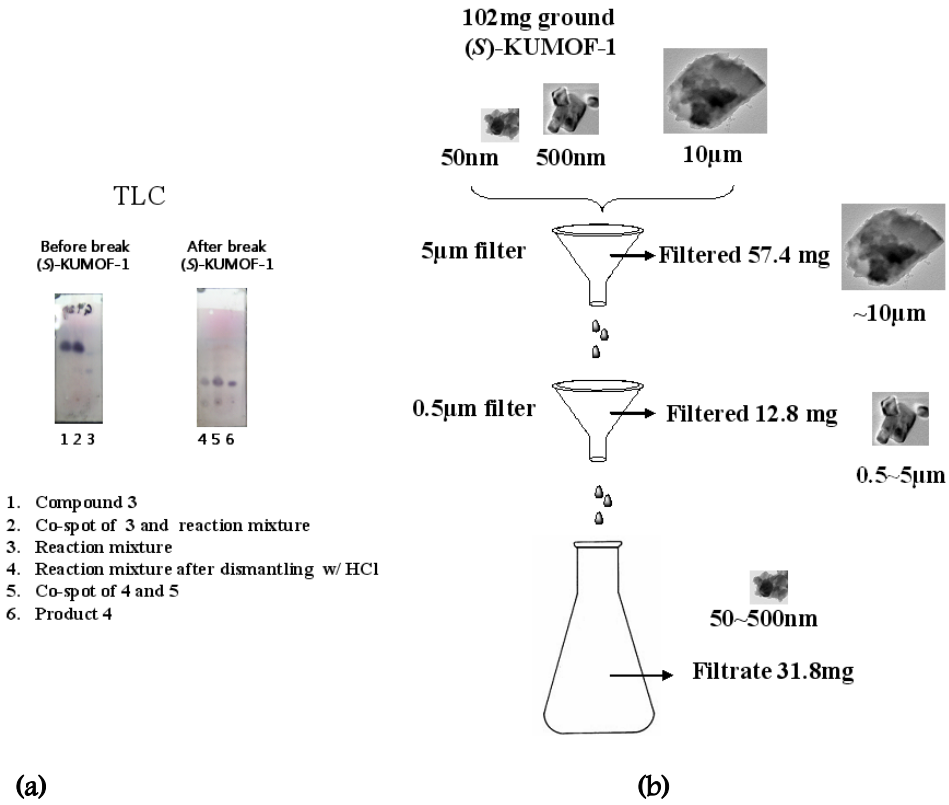


Figure S10. (a) TLC of carbonyl-ene reaction: All substrates disappeared on TLC before dismantling of MOF. (b) TEM image of grounded (*S*)-**KUMOF-1** after carbonyl-ene reaction; more than 50% of particles have average size greater than 10 μm.

3.3. Hetero Diels-Alder reaction

3.3.1. General Procedure for the hetero Diels-Alder reaction; (S)-2-Phenyl-2,3-dihydro-4H-pyran-4-one (9)

A mixture of (*S*)-**KUMOF-1** (24 mg, 0.063 mmol), $Ti(O\text{-}iPr)_4$ (0.19 mL, 1 M in toluene, 0.19 mmol) in toluene(1.5 mL) was stirred for 5 h at 25 °C. The mixture was cooled to 0 °C and to this mixture were added Danishefsky's diene **6** (41 μL, 0.21 mmol) and benzaldehyde **7** (21 μL, 0.21 mmol) sequentially. The mixture was allowed to stir at 0 °C for 3-5 days and the supernatant was transferred into a solution of TFA (5drops) in dichloromethane (1 mL) by syringe. After the mixture was stirred at 0 °C for another 15 min, a saturated aqueous solution of $NaHCO_3$ (1.5 mL) was added. The mixture was stirred for 10 min and then filtered through a plug of Celite. The organic layer was separated, and the aqueous layer was further extracted with EA (3 × 1 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate 5:1) to yield (*R*)-2-phenyl-2,3-dihydro-4*H*-pyran-4-one (**9**) (30.7 mg, 0.18 mmol, 84% yield) as a clear oil.

TLC (*n*-Hexane:EA, 75:25 v/v): R_f = 0.45; ^{1}H NMR (CD_3Cl_3, 300MHz) : δ 2.66 (dd, J = 17, 3.5 Hz, 1H), 2.90 (dd, J = 17, 14 Hz, 1H), 5.42 (dd, J = 15, 3.7 Hz 1H), 5.52 (d, J = 6.0 Hz, 1H), 7.3-7.4 (m, 5H), 7.48 (d, J = 6.0 Hz, 1H); ^{13}C NMR (CD_3Cl_3, 75MHz): δ 43.3, 81.0, 107.3, 126.0, 128.8, 128.9, 137.8, 163.1, 192.1; IR (KBr): 2990, 1680 cm^{-1}; HPLC, Daicel Chiralcel OD-H, *n*-hexane/*i*PrOH = 40/1, flow rate = 1.5 mL/min : *t*R = 17.5 min (*S*), *t*R = 21.5 min (*R*).

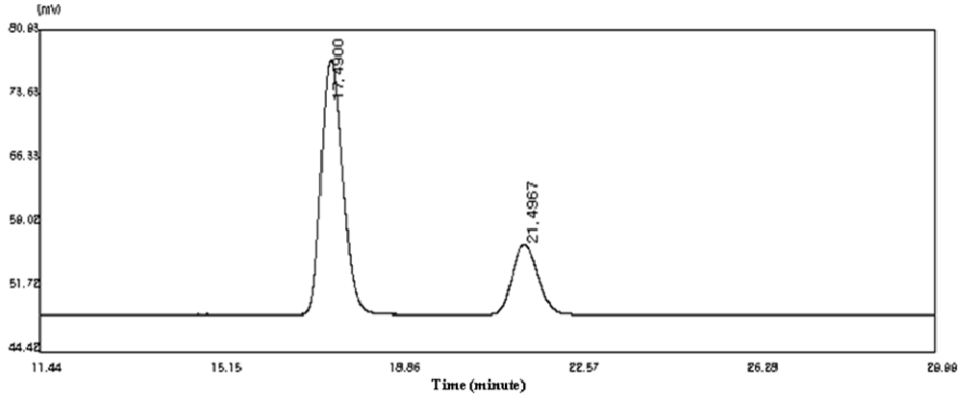


Figure S11. HPLC Chromatogram for the determination of enantiomeric excess of **9** (55% ee, t_1 = 17.49 min: t_2 = 21.49 min)

3.3.2. Recycling experiments

After first run of HDA reaction, the reaction mixture was diluted with fresh toluene (2 mL) and the all the soluble materials were removed by syringe and stored in a separate vial. This process was repeated five times to ensure the complete extraction of **9** from the reaction mixture. After this process, to the residue of Ti/(*S*)-**KUMOF-1,** was added a fresh toluene (1.5 mL) and the reaction mixture was charged with argon again. Additional Ti(O-*i*Pr)$_4$ (0.13 mL, 1 M in toluene, 0.13 mmol) was introduced to the mixture and stirred for 3 h at 25 °C. The mixture was cooled to 0 °C, and then Danishefsky's diene **7** (41 µL, 0.21 mmol) and benzaldehyde **8** (21 µL, 0.21 mmol) were added stepwise for the second run.

Meantime, the combined toluene layer was treated with 5 drops of TFA. After the mixture was stirred at 0 °C for 15 min, the reaction was quenched by treatment with a saturated aqueous $NaHCO_3$ solution (1.5 ml). After stirring for another 10 min, the reaction mixture was filtered through a plug of Celite. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (3 × 1 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash chromatography.

Table S2 Recycling of the MOFs catalyzed hetero Diels-Alder reaction

entry[a]		Additional Ti(O-*i*Pr)$_4$ (mol %)	*T* (°C)	*t* (d)	Yield of **10**[b] (%)	Ee of **10**[c] (%)
1	1st run	-	0	3	80	55
2	2nd run	90	0	3	72	54
3	3rd run	90	0	3	61	55

[a]Reaction condition: A mixture of the reused (*S*)-**KUMOF-1,** Ti(O-*i*Pr)$_4$ (0.13 ml, 1 M in toluene, 0.13 mmol) in toluene was stirred for 5 h at 25 °C. The mixture was cooled to 0 °C and then **7** (0.041 mL, 0.21 mmol) and **8** (21 mL, 0.21 mmol) were added stepwise. The mixture was stirred at 0 °C for 3-5 days and then treated with 5 drops of TFA.. [b] Isolated yield. [c]Determined by LC chromatography : Chiralcel OD-H, *n*-hexane/*i*PrOH = 40/1, flow rate = 1.5 mL/min

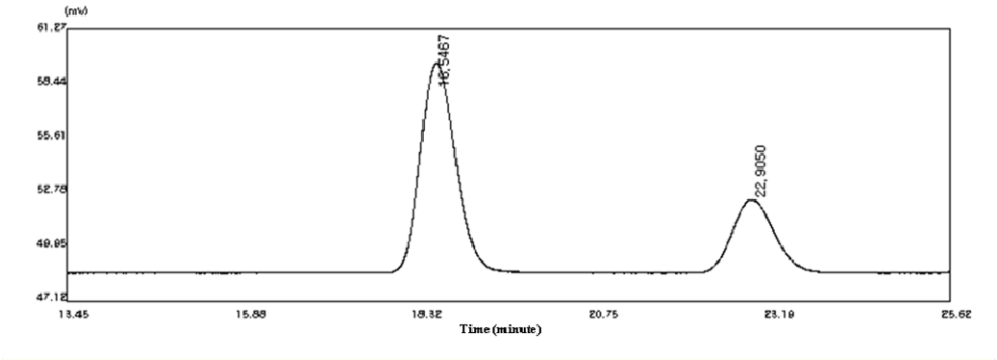


Figure S12. HPLC Chromatogram for the determination of enantiomeric excess of **9** obtained from the second run. (55% ee, t_1 = 16.54 min: t_2 = 22.9 min)

3.3.3 XPRD of Ti/(*S*)-KUMOF-1 after catalytic reaction.

All Powder X-ray diffraction (PXRD) data were collected using a Rigaku D/Max Ultima III (Cu Kα = 1.5418 Å; 1600 W, 40 kV, 40 mA)

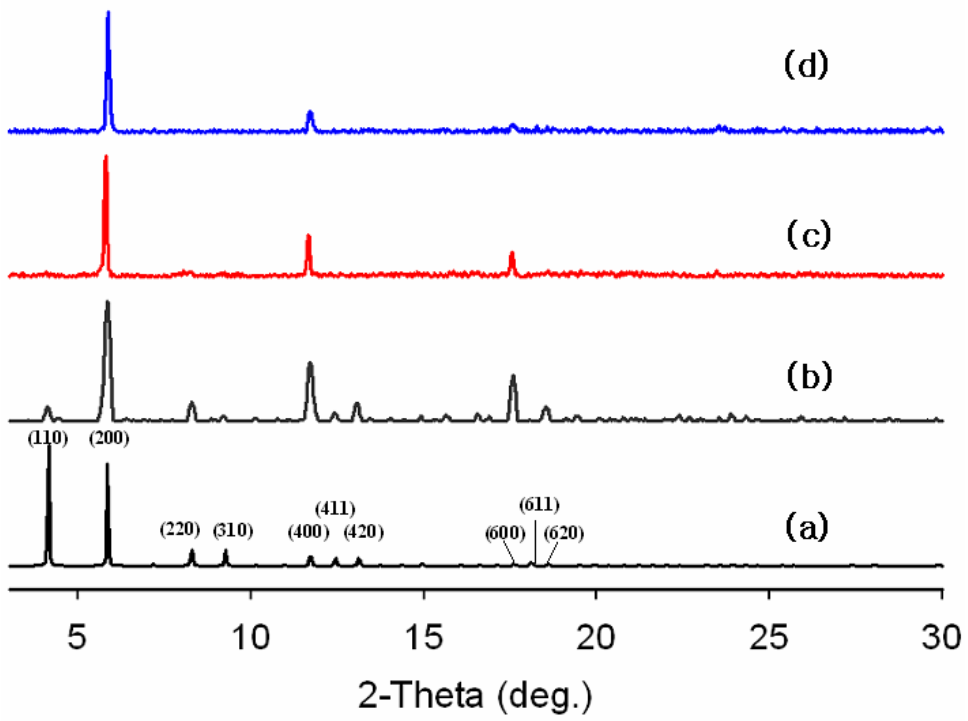


Figure S13. (a) XRPD patterns of the simulation based on the single-crystal structure of (*S*)-**KUMOF-1**, (b) the as-synthesized (*S*)-**KUMOF-1**, (c) after HDA reaction at 0 °C: MOF structure of Ti/(*S*)-**KUMOF-1** was retained and after carbonyl-ene reaction at 0 °C, (d) MOF structure of Ti/(*S*)-**KUMOF-1** was retained.

References

S1. Bruker SMART version 5.625, Area-Detector Software Package; Bruker AXS 1997-2001. Madison, WI, USA.

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