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Supplementary Information

Metal-Organic Frameworks with Designed Chiral Recognition Sites

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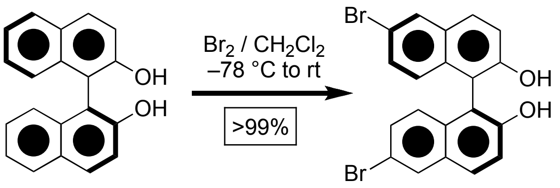
General Experimental (Strut)

Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl radical under an atmosphere of N_2. Anhydrous dichloromethane and acetonitrile were obtained from an EMD Chemicals DrySolv® system. Anhydrous *p*-dioxane was purchased from Aldrich and handled under an atmosphere of argon. $CDCl_3$, C_6D_6, CD_2Cl_2 and $(CD_3)_2CO$ were purchased from Aldrich and used without further purification. All other reagents were purchased from commercial sources and were used without further purification, unless indicated otherwise. All reactions were carried out under an atmosphere of N_2 in flame-dried flasks using freshly distilled or anhydrous solvents, unless indicated otherwise. Thin-layer chromatography (TLC) was carried out using glass plates, precoated with silica gel 60 with fluorescent indicator (Whatman LK6F). The plates were inspected by UV light (254 nm) and/or potassium permanganate stain. Column chromatography purifications were carried out using the flash technique using silica gel 60F (230- 400 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX500 (500 MHz) spectrometer. The chemical shifts (δ) for ^1H spectra are given in ppm are referenced to the residual proton signal of the deuterated solvent. The chemical shifts (δ) for ^{13}C spectra are referenced relative to the signal from the carbon of the deuterated solvent. High-resolution mass spectra were measured on a Finnigan LCQ iontrap mass spectrometer (HR-ESI). The general experimental details for the preparation and analysis of (*SS*)-MOF-1020 and (*RR*)-MOF-1020 can be found on page S16.

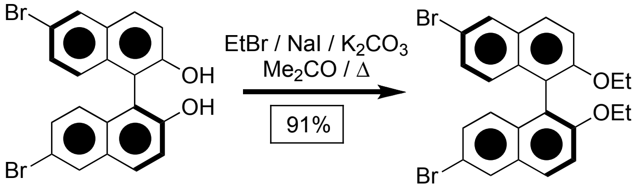
Synthetic Procedures

The synthesis and characterization of all intermediates *en route* to (*SS*)-**2** are provided. The synthesis of (*RR*)-**2** was performed in a similar fashion.



(S)-**4** (S)-**S1**

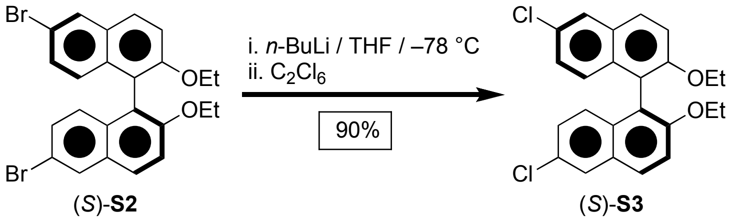
(S)-6,6'-Dibromo-1,1'-binaphthyl-2,2'-diol [(*S*)-**S1**].[S1] A solution of bromine (4.7 mL, 92.6 mmol) in CH_2Cl_2 (40 mL) was added dropwise over 30 min to a solution of (*S*)-1,1'-binaphthyl-2,2'-diol ((*S*)-**3**, 9.8 g, 34.2 mmol) in CH_2Cl_2 (200 mL) at –78 °C. The resulting reaction mixture was stirred for an additional 2 h at –78 °C before being warmed gradually to rt. The reaction mixture was stirred for an additional 2 h at rt before quenching the excess bromine by slow addition of a saturated aqueous $NaHSO_3$ solution. The organic layer was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to provide 15.1 g of (*S*)-**S1** (>99%) as a beige powder that required no further purification. ^1H NMR (500 MHz, $CDCl_3$) δ = 8.08 (d, *J* = 2.0 Hz , 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.42 (d, *J* = 9.0 Hz, 2H), 7.39 (dd, *J* = 9.0, 2.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 5.32 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 153.0, 132.0, 130.8, 130.5, 130.5, 130.4, 126.0, 119.1, 117.9, 111.0.



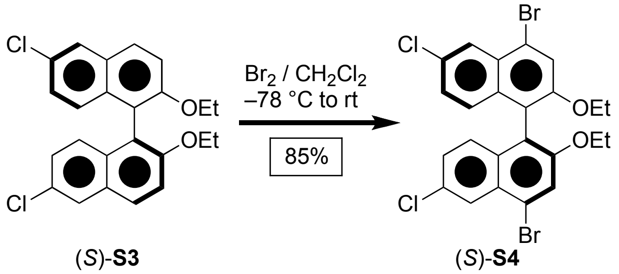
(S)-**S1** (S)-**S2**

(S)-6,6'-Dibromo-2,2'-diethoxy-1,1'-binaphthyl [(*S*)-**S2**].[S1] Solid NaI (250 mg, 1.7 mmol) and K_2CO_3 (18.2 g, 131.5 mmol) were added to a solution of (*S*)-**S1** (14.6 g, 32.9 mmol) in Me_2CO (160 mL). The reaction mixture was warmed to reflux, after which bromoethane (14.7 mL, 197.2 mmol) was added portion-wise over 8 h (~ 3.5 mL every 2 h). The resulting mixture was stirred overnight before being cooled to rt, filtered through a pad of celite and the filtrate was concentrated *in vacuo*. Pentane was added to the solid residue, and the resulting heterogeneous mixture was stirred and sonicated sequentially so

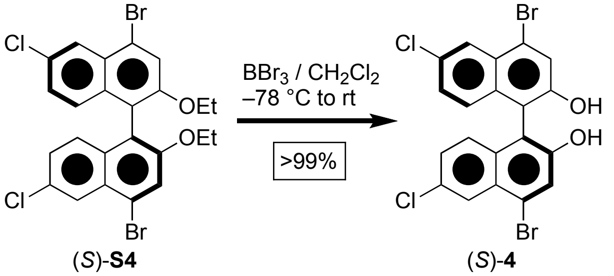
as to disperse the solid finely. The solid was subsequently filtered and rinsed with fresh pentane to provide 14.9 g of (*S*)-**S2** (91%) as a white powder that required no further purification. $[\alpha]_{23}^{D} = -15.8°$ ($CHCl_3$, *c* = 0.18 g/100mL). ^1H NMR (500 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 1.5 Hz , 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 9.0 Hz, 2H), 7.28 (dd, *J* = 9.0, 1.5 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 4.10–4.04 (m, 4H), 1.09 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.7, 132.7, 130.4, 130.0, 129.6, 128.6, 127.3, 120.1, 117.4, 116.6, 65.2, 15.1.



(S)-6,6'-Dichloro-2,2'-diethoxy-1,1'-binaphthyl [(*S*)-**S3**].[S2] A solution of *n*-BuLi (6.0 mL, 15.0 mmol, 2.5 M solution in hexanes) was added dropwise to a solution of (*S*)-**S2** (2.5 g, 5.0 mmol) in THF (25 mL) at –78 °C. The reaction mixture was stirred for an additional 30 min at –78 °C before adding slowly a solution of hexachloroethane (2.4 g, 5.0 mmol) in THF (5 mL). The reaction was stirred for an additional 1 h at –78 °C before gradually warming to rt and stirring overnight. The reaction was quenched with a saturated aqueous NH_4Cl solution and extracted with EtOAc (2×100 mL). The combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo*. The solid residue was suspended in a minimal amount of pentane and the resultant suspension was filtered to provide 1.85 g of (*S*)-**S3** (90%) as a white powder that required no further purification. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 9.0 Hz , 2H), 7.85 (d, *J* =2.0 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.17 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.05 (d, *J* = 9.0 Hz, 2H), 4.10–4.04 (m, 4H), 1.08 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.6, 132.5, 129.8, 129.3, 128.6, 127.2, 127.1, 126.7, 120.2, 116.7, 65.3, 15.1.

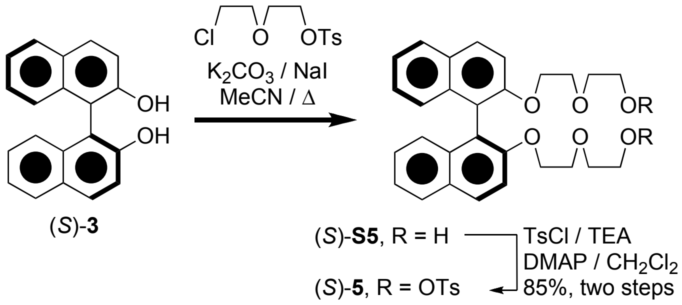


(*S*)-4,4'-Dibromo-6,6'-dichloro-2,2'-diethoxy-1,1'-binaphthyl [(*S*)-**S4**].[S1] A solution of bromine (18.4 mL, 357.0 mmol) in CH_2Cl_2 (100 mL) was added dropwise to a solution of (*S*)-**S3** (9.8 g, 23.8 mmol) in CH_2Cl_2 (450 mL) at –78 °C over 30 min. The reaction mixture was stirred for an additional 30 min at –78 °C before being warmed gradually to rt. The reaction was stirred for an additional 2 h at rt before quenching the excess of bromine by slow addition of a saturated aqueous $NaHSO_3$ solution. The organic layer was separated, and the aqueous layer was extracted with fresh CH_2Cl_2. The combined organic layers were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The solid residue was taken up in a minimum amount of Me_2CO (20 mL) followed by hexanes (150 mL) and the resultant suspension was filtered to provide 11.6 g of (*S*)-**S4** (85%) as a white powder that was used without further purification. Note, a trace (<5%) impurity is present that is of no consequence in the next reaction. $[\alpha]_{23}^{D} = -63.4°$ ($CHCl_3$, *c* = 0.517 g/100mL). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 2.5 Hz , 2H), 7.73 (s, 2H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 4.08–4.02 (m, 4H), 1.08 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.4, 133.1, 131.4, 128.7, 128.4, 127.6, 126.5, 122.8, 120.7, 119.5, 65.7, 15.2.



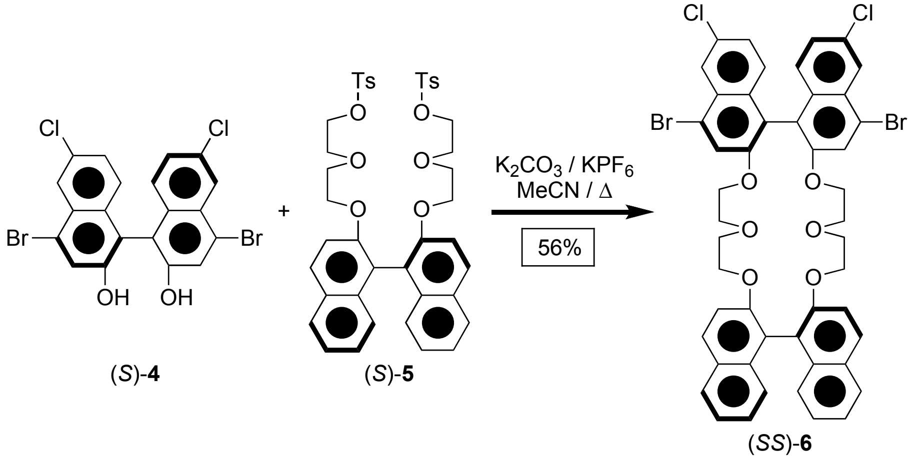
(S)-4,4'-Dibromo-6,6'-dichloro-1,1'-binaphthyl-2,2'-diol [(*S*)-**3**].[S1] BBr_3 (50.4 mL, 50.4 mmol, 1.0 M solution in CH_2Cl_2) was added to a solution of (*S*)-**S4** (11.5 g, 20.2 mmol) in CH_2Cl_2 (135 mL) at –78 °C. The reaction mixture was stirred for 2 h at –78 °C and

then was gradually warmed to rt and stirred overnight before quenching with saturated aqueous $NaHCO_3$. The organic layer was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to provide 10.3 g of (*S*)-**3** (>99%) as a beige powder that required no further purification. $[\alpha]_{23}^{D} = +29.6°$ ($CHCl_3$, c = 0.30 g/100mL). ^1H NMR (500 MHz, $CDCl_3$) δ = 8.31 (d, J = 2.5 Hz , 2H), 7.78 (s, 2H), 7.32 (dd, J = 9.0, 2.5 Hz, 2H), 7.05 (d, J = 9.0 Hz, 2H), 5.15 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.8, 132.5, 132.2, 129.7, 129.3, 127.2, 126.5, 125.2, 123.4, 110.7.

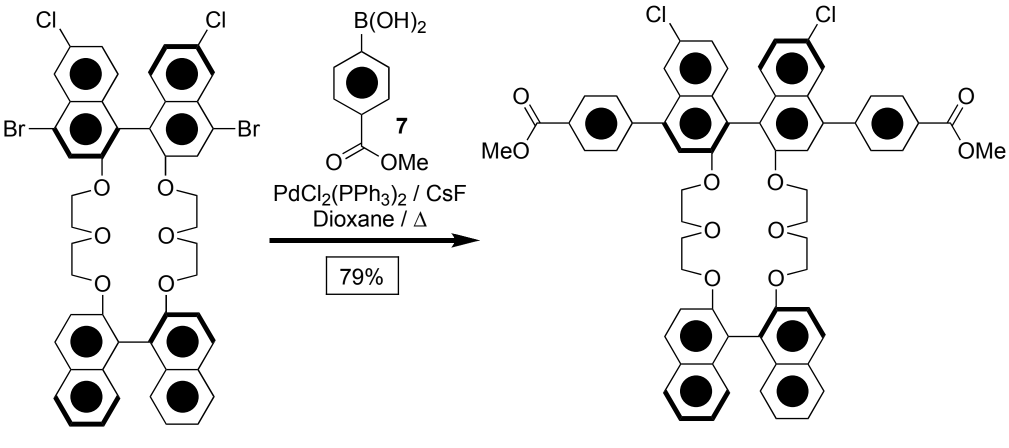


(*S*)-5. K_2CO_3 (3.86 g, 28.0 mmol), NaI (0.42 g, 2.79 mmol) and 2-(2-chloroethoxy)ethanol (1.56 mL, 14.7 mmol) were added to a solution of (*S*)-1,1'-binaphthyl-2,2'-diol ((*S*)-**4**, 2.00 g, 7.0 mmol) in MeCN (35 mL) at rt. The reaction mixture was warmed to reflux and stirred for 6 h before adding an additional portion of 2-(2-chloroethoxy)ethanol (2.00 mL, 19.0 mmol). The reaction was heated under reflux overnight before adding an additional portion of 2-(2-chloroethoxy)ethanol (3.00 mL, 28.5 mmol) and stirring for a further 7 h, after which time the reaction was shown to be complete by TLC analysis. The reaction mixture was cooled to rt and filtered through a pad of celite which was washed further with fresh EtOAc. The filtrate was concentrated *in vacuo* to provide crude (*S*)-**S5** as a yellow oil (9.69 g). The crude material was taken up in CH_2Cl_2 (100 mL) and *p*-toluenesulfonyl chloride (24.0 g, 130 mmol), triethylamine (35.8 mL, 250 mmol) and 4-(dimethylamino)pyridine (510 mg, 4.2 mmol) were added successively. The resulting mixture was allowed to stir overnight at rt before being quenched with 1 M HCl (200 mL). The organic layer was isolated, washed with an additional portion of HCl (200 mL), brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo.* The crude material was taken up in a minimal amount of CH_2Cl_2 and loaded onto a pad of silica gel, flushing with CH_2Cl_2 until the first two impurities eluted (excess of

TsCl (R_f = 1.0, CH_2Cl_2) and 2-(2-chloroethoxy)ethyl *p*-toluenesulfonate (R_f = 0.6, CH_2Cl_2)). The desired product was then eluted using a 10% EtOAc in CH_2Cl_2 mobile phase (R_f = 1.0, 10 % EtOAc in CH_2Cl_2), to provide 13.8 g of (*S*)-**5** (85%) as a viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 9.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.74–7.71 (m, 4H), 7.37 (d, *J* = 9.0 Hz, 2H), 7.33–7.29 (m, 6H), 7.20 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H) 7.15–7.12 (m, 2H), 4.08–3.98 (m, 4H), 3.66–3.32 (m, 4H), 3.41–3.37 (m, 4H), 3.03–2.90 (m, 4H), 2.44 (s, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 154.0, 144.7, 133.4, 133.0, 129.8, 129.4, 129.3, 127.9, 127.9, 126.4, 125.4, 123.8, 120.3, 115.2, 70.0, 69.5, 69.2, 68.5, 21.7.

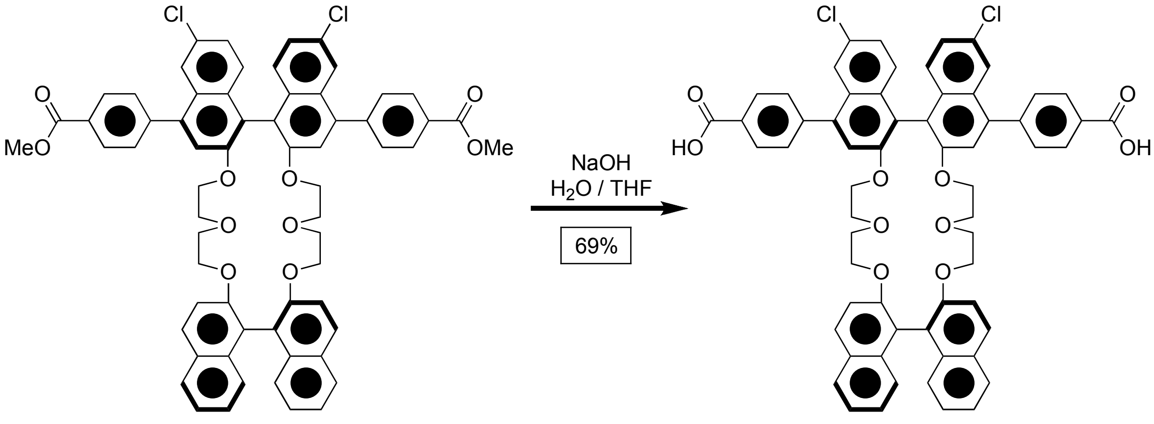


(*SS*)-**6**. K_2CO_3 (7.3 g, 52.6 mmol) and KPF_6 (2.4 g, 12.9 mmol) were added to a solution of the strut (*S*)-**3** (6.0 g, 11.7 mmol) and (*S*)-**5** (9.0 g, 11.7 mmol) in MeCN (780 mL). The resulting mixture was warmed to relfux and stirred overnight. The reaction was cooled to rt and filtered through a pad of celite that was washed further with fresh EtOAc. The filtrate was concentrated *in vacuo* before redissolving the residue in fresh EtOAc. The organic layer was washed twice with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The solid residue was suspended in Me_2CO, and the resulting heterogeneous mixture was stirred and sonicated sequentially so as to create a fine solid dispersion, which was subsequently filtered and rinsed with fresh Me_2CO until the washing ran clear, providing 6.45 g of (*SS*)-**6** (56%) as a white powder that required no further purification. $[\alpha]_{23}^{D}$ = –112.2° ($CHCl_3$, *c* = 0.257 g/100mL). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.31 (d, *J* = 2.0 Hz , 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.75 (s, 2H), 7.43 (d, *J* = 9.0 Hz, 2H), 7.36 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.25–7.21 (m, 4H), 7.06 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.10–3.96 (m, 2H), 3.94–3.89 (m, 4H), 3.88–3.83 (m, 2H), 3.34–3.28 (m, 4H), 3.21–3.15 (m, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 154.5, 154.4, 134.5, 133.2, 131.5, 129.7, 129.6, 128.8, 128.6, 128.3, 127.7, 126.7, 126.4, 125.6, 124.0, 122.8, 120.6, 120.3, 119.4, 115.3, 70.1, 69.7, 69.6, 69.3. ESI-MS: *m*/*z* = 954.0589 $[M + NH_4]^+$.



(*SS*)-**S6**

(*SS*)-**S6**. *p*-Dioxane (130 mL) was added to a flask was charged with (*SS*)-**6** (6.0 g, 6.4 mmol), 4-(methoxycarbonyl)phenylboronic acid (3.5 g, 19.2 mmol), cesium fluoride (5.8 g, 38.3 mmol) and bis(triphenylphosphine)palladium(II) dichloride (448 mg, 0.64 mmol). The mixture was warmed to 90 °C and stirred overnight. The reaction mixture was cooled to rt and filtered through a pad of celite which was washed further with fresh EtOAc. The filtrate was concentrated in vacuo and the residue was purified by column chromatography on silica gel (R_f = 0.40; 10% EtOAc, 30% CH_2Cl_2, 60% hexanes) to give (*SS*)-**S6** which contained trace impurities. The solid residue was suspended in acetone–2-propanol co-solvent (1:3) and the resulting heterogeneous mixture was stirred and sonicated sequentially so as to create a fine solid dispersion, which was subsequently filtered and rinsed with fresh 2-propanol to provide 5.3 g of (*SS*)-**S6** (79%) as a white powder that required no further purification. $[\alpha]_{23}^{D}$ = –94.0° ($CHCl_3$, *c* = 0.20 g/100mL). ^{1}H NMR (500 MHz, CD_2Cl_2) δ = 8.14 (d, *J* = 8.0 Hz, 4H), 7.78 (d, *J* = 2.0 Hz, 2H), 7.72 (t, *J* = 8.0 Hz, 4H), 7.62 (d, *J* = 8.5 Hz, 4H), 7.33 (s, 2H), 7.22 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.12 (dd, *J* = 9.0, 2.5 Hz, 2H), 7.09 (ddd, *J* = 8.5, 7.0, 1.0 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 3.99–3.94 (m, 2H), 3.92 (s, 6H), 3.92–3.88 (m, 2H), 3.87–3.83 (m, 2H), 3.82–3.78 (m, 2H), 3.34–3.27 (m, 4H), 3.24–3.16 (m, 4H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 167.1, 154.5, 154.4, 145.0, 140.5, 134.5, 133.2, 130.6, 130.4, 130.2, 129.7, 129.6, 128.3, 128.2, 127.8, 127.7, 126.7, 125.5, 125.1, 124.0, 120.5, 119.9, 117.7, 115.5, 69.9, 69.7, 69.7, 69.6. ESI-MS: *m*/*z* = 1071.2693 [*M* + Na]$^+$ and 1066.3113 [*M* + NH_4]$^+$ and 1049.2842 [*M* + H]$^+$.



(*SS*)-**S6**

(*SS*)-**2**

(*SS*)-**2**. A solution of NaOH (0.76 g, 18.9 mmol) in H_2O (25 mL) was added to a solution of (*SS*)-**S6** (1.32 g, 1.26 mmol) in THF (25 mL). The reaction mixture was vigorously stirred overnight at rt before removing the THF *in vacuo*. The resulting white suspension was acidified with 1 M (HCl) until pH ~ 1.0, filtered, and washed with ample H_2O. The wet solid material was dissolved in Me_2CO and concentrated to dryness *in vacuo*. The solid residue was then suspended in pentane–Me_2CO co-solvent (1:1, 15 mL), filtered, washed with additional pentane–acetone (1:1, 10 mL) and dried *in vacuo* to provide 0.89 g of (*SS*)-**2** (69%) as a white powder. The filtrate was concentrated *in vacuo* to provide 0.16 g of impure (*SS*)-**2** (> 90% purity based on ^{1}H NMR spectroscopy) as a beige solid. $[\alpha]_{23}^{D}$ = –111.3° (Me_2CO, *c* = 0.450 g/100mL). ^{1}H NMR (500 MHz, $(CD_3)_2CO$) δ = 8.30 (d, *J* = 8.0 Hz, 4H), 7.89 (d, *J* = 2.0 Hz, 2H), 7.87–7.82 (m, 8H), 7.65 (s, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.32 (dd, *J* = 9.0, 2.0 Hz, 2H), 7.30 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 7.21 (d, *J* = 9.0 Hz, 2H), 7.19 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 4.23–4.17 (m, 2H), 4.13–4.07 (m, 2H), 4.06–4.00 (m, 2H), 3.95–3.89 (m, 2H), 3.43–3.37 (m, 4H), 3.30–3.23 (m, 4H). ^{13}C NMR (125 MHz, $(CD_3)_2CO$) δ = 167.4, 155.3, 155.2, 145.4, 141.0, 135.1, 133.9, 131.2, 131.0, 130.9, 130.4, 130.3, 130.0, 128.8, 128.6, 128.5, 128.0, 127.0, 125.9, 125.3, 124.3, 120.9, 120.4, 118.6, 116.1, 70.3, 70.1, 70.0, 69.9. ESI-MS: m/z = 1043.2385 $[M + \mathrm{Na}]^+$ and 1038.2803 $[M + \mathrm{NH_4}]^+$.

^{1}H NMR Binding Studies

Synthesis of (*S*)-α-methylbenzylammonium perchlorate: A solution of HCl in dioxane (11.3 mL, 4.0 M) was added to a solution of (*S*)-α-methylbenzylamine (5.0 g, 41.3 mmol) in dioxane (5 mL). The reaction mixture was stirred for 5 min and concentrated *in vacuo* to provide (*S*)-α-methylbenzylammonium chloride as a light yellow solid. The residue was suspended in EtOAc and the resulting heterogeneous mixture was stirred and sonicated sequentially so as to create a fine solid dispersion, which was subsequently filtered and rinsed with fresh EtOAc. The white solid was collected and dried *in vacuo*. Anion exchange was accomplished according to a procedure adapted from Cram and co-workers.[S3] Solid NH_4ClO_4 (2.35 g, 20 mmol) was added to a solution of (*S*)-α-methylbenzylammonium chloride (3.16 g, 20 mmol) in $CHCl_3/CH_3CN$ (1:1, 100 mL total). The reaction mixture was stirred for 24 h, after which the insoluble material (NH_4Cl) was removed by filtration. The filtrate was concentrated *in vacuo* to provide (*S*)-α-methylbenzylammonium perchlorate as a colorless viscous oil.

Binding studies: Stock solutions of the host dimethyl ester (*SS*)-**S6** (10 mM, 31.5 mg in 3.0 mL of CD_2Cl_2) and the guest (*S*)-α-methylbenzylammonium perchlorate (10 mM, 11.1 mg in 5.0 mL of CD_2Cl_2) were prepared. Samples for analysis by ^{1}H NMR were prepared to a final volume of 500 μL with varying ratios of (*SS*)-**S6** and (*S*)-α-methylbenzylammonium perchlorate (Table S1). All spectra were recorded at 298 K and referenced to the residual proton signal of the deuterated solvent.

Table S1. Sample preparation volumes of (*SS*)-**S6** (host) and (*S*)-α-methylbenzylammonium perchlorate (guest) for analysis by ^{1}H NMR spectroscopy.

Sample	1	2	3	4	5	6	7	8	9	10	11
Host Solution 10 mM (μL)	500	450	400	350	300	250	200	150	100	50	0
Guest Solution 10 mM (μL)	0	50	100	150	200	250	300	350	400	450	500
Host:Guest Ratio	10:0	9:1	8:2	7:3	6:4	5:5	4:6	3:7	2:8	1:9	0:10

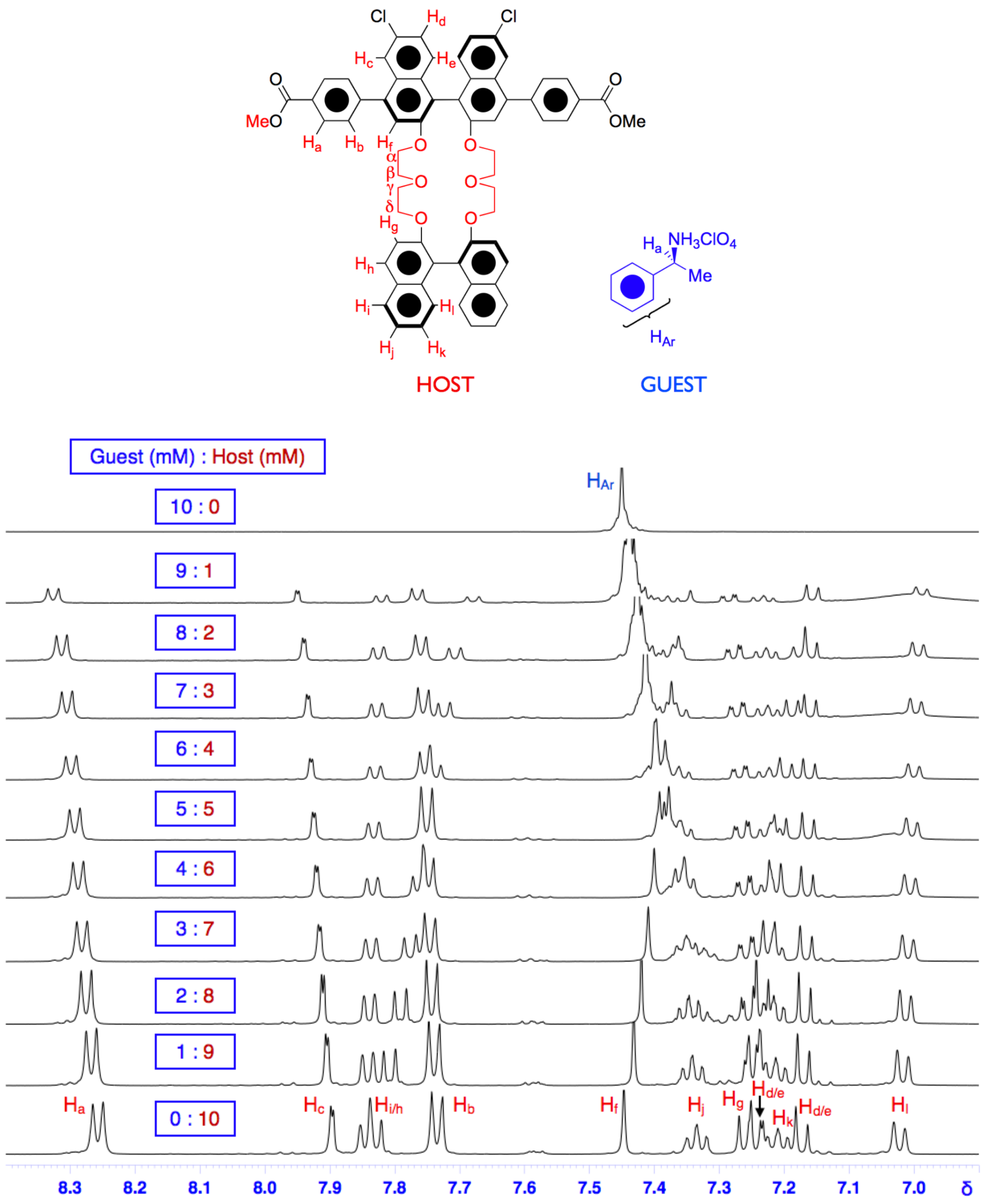


Figure S1. Partial (aromatic region) annotated ^{1}H NMR spectrum for (*SS*)-**S6** and (*S*)-α-methylbenzylammonium perchlorate, and varying combinations of each of these species in CD_2Cl_2 at 298 K and 500 MHz. Gradual upfield and downfiled shifts in the ^{1}H resonances is observed on account of the association of the guest ammonium salt with the host dilocular macrocycle.

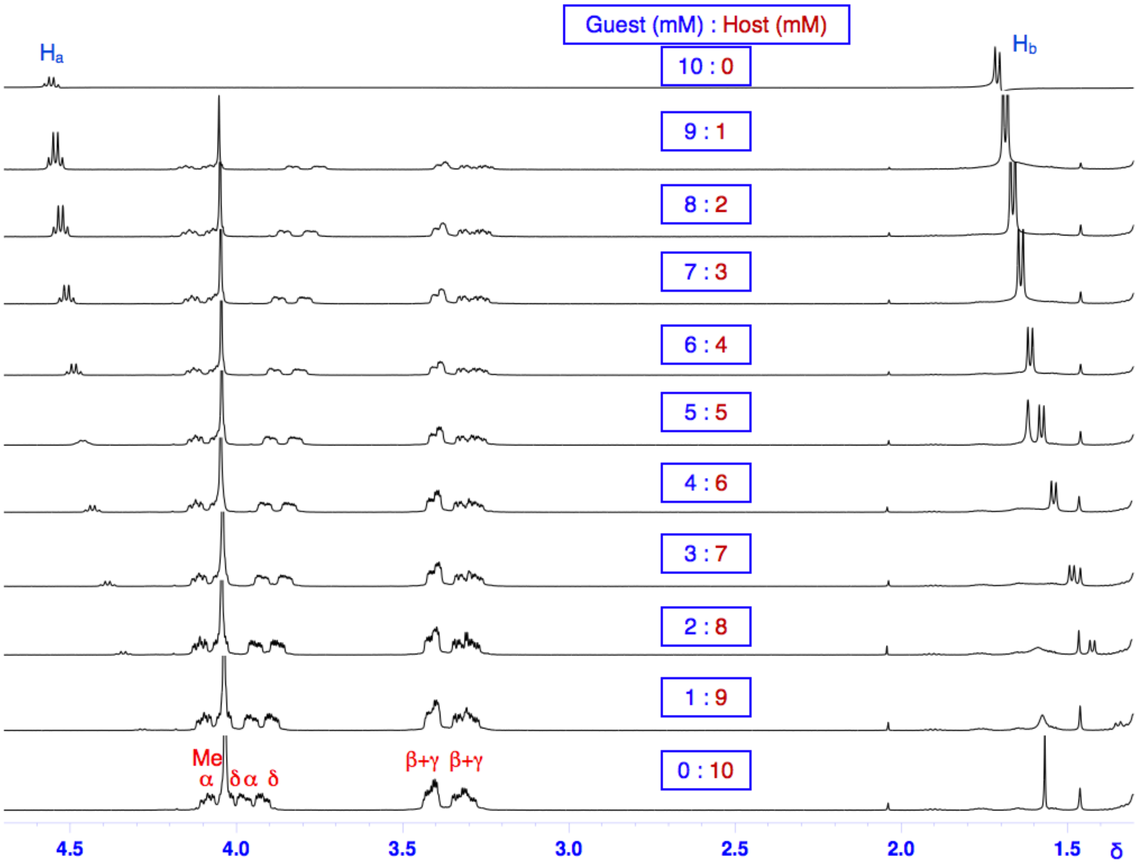


Figure S2. Partial (aliphatic region) annotated ^{1}H NMR spectrum for (*SS*)-**S6** and (*S*)-α-methylbenzylammonium perchlorate, and varying combinations of each of these species in CD_2Cl_2 at 298 K and 500 MHz. Gradual upfield and downfiled shifts in the ^{1}H resonances is observed on account of the to association of the guest ammonium salt with the host dilocular macrocycle.

Crystal Growth Conditions for (*SS*)-2

Colourless crystals of (*SS*)-**2** were grown by slow vapor diffusion of pentane into a solution of (*SS*)-**2** in tetrahydrofuran (16 mg/mL) under ambient conditions over 24 h.

Data Collection

A colourless block crystal of C78 H78 Cl2 O14 having approximate dimensions of 0.22 x 0.15 x 0.13 mm was mounted using oil (Infineum V8512) on a glass fiber. All measurements were made on a Bruker APEX-II CCD detector with graphite monochromated Cu-*K*α radiation (λ = 1.54178 Å). Cell constants and an orientation matrix for data collection corresponded to a triclinic cell (see Table S2 for dimensions).

For $Z = 1$ and FW = 1310.30, the calculated density is 1.243 g/cm^3. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P1$. The data were collected at a temperature of 100(2)K with a θ range for data collection of 3.0–64.8°. Data were collected in 0.5° oscillations with 10 second exposures. The crystal-to-detector distance was 40.0 mm.

Data Reduction

Of the 13176 reflections which were collected, 6750 were unique ($R_{\mathrm{int}} = 0.0214$). Data were collected using Bruker APEX-II detector and processed using SAINTPLUS from Bruker. The linear absorption coefficient, mu, for Cu-$K\alpha$ radiation is 1.359 mm^{-1}. A numerical absorption correction was applied. Minimum and maximum transmission factors were: 0.8559 and 0.9120, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods and expanded using Fourier techniques[S4]. The non-hydrogen atoms were refined anisotropically. Rigid bond restraints (delu) were imposed on the displacement parameters as well as restraints on similar amplitudes (simu) separated by less than 1.7 Å. Hydrogen atoms were included in idealized positions, but not refined. The final cycle of full-matrix least-squares refinement[S5] on F^2 was based on 6750 reflections and 894 variable parameters and converged (largest parameter shift was 0.001 times its esd) with unweighted and weighted agreement factors of:

$$R_1 = \Sigma|\,|F_o|-|F_c|\,|/\Sigma|F_o| = 0.0599$$

$$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1785$$

The weighting scheme was calc $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + 0.0000P]$ where $P = (F_o^2+2F_c^2)/3$. The standard deviation of an observation of unit weight[S6] was 0.851. The weighting scheme was based on counting statistics and included a factor to downweight the intense reflections. Plots of $\Sigma\, w\, (|F_o| - |F_c|^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.653 and –0.474 eV/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber[S7]. Anomalous dispersion effects were included in Fcalc[S8]; the values for Df' and Df" were those of Creagh and McAuley[S9]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[S10]. All calculations were performed using the Bruker SHELXTL3 crystallographic software package.

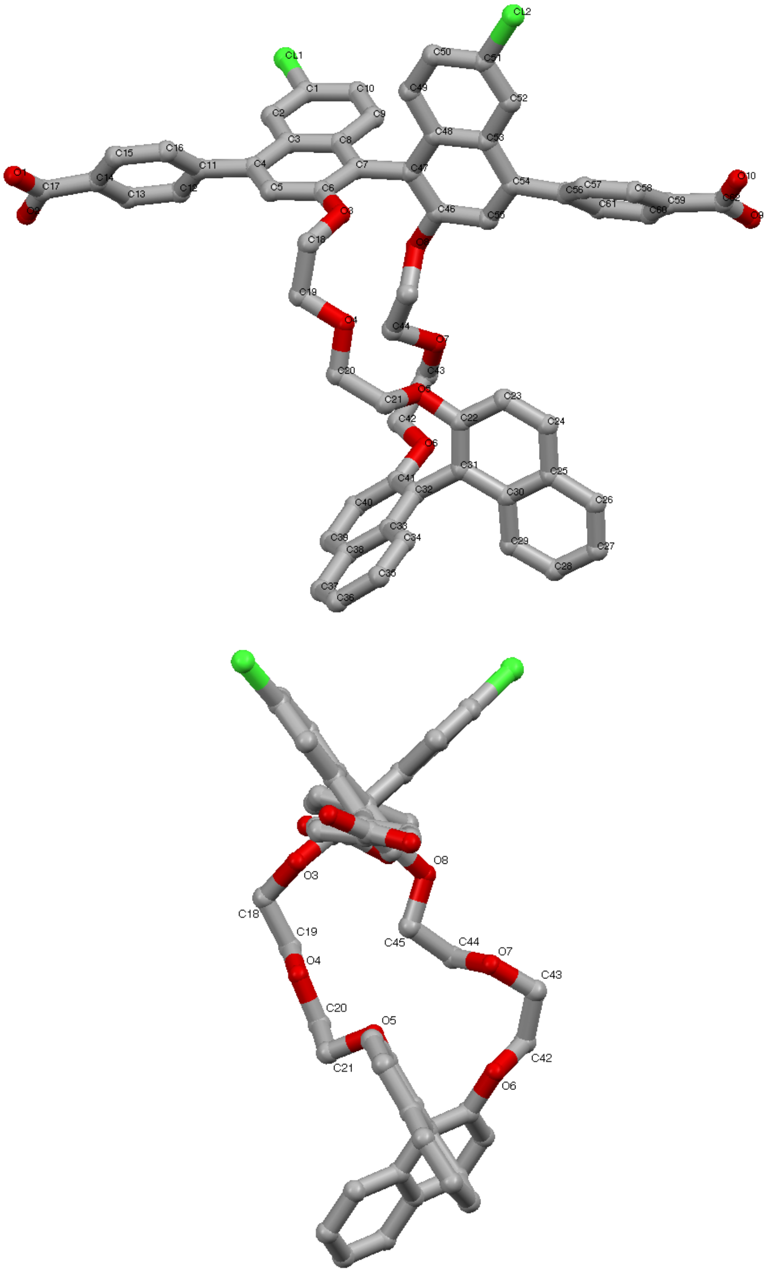


Figure S3. Stick representation for the front (top) and side (bottom) views of the crystal structure of (*SS*)-**2**. Solvent molecules and hydrogen atoms have been omitted for clarity. C, grey; O, red; Cl, green.

Table S2. Crystal data and structure refinement for (*SS*)-**2**.

Empirical formula	C78 H78 Cl2 O14
Formula weight	1310.30
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 8.40020(10) Å α = 101.548(1)° b = 14.2660(2) Å β = 92.220(1)° c = 15.2820(3) Å γ = 101.720(1)°
Volume	1750.84(5) Å^3
Z	1
Calculated density	1.243 Mg/m^3
Absorption coefficient	1.359 mm^{-1}
F(000)	692
Crystal size	0.22 x 0.15 x 0.13 mm^3
Theta range for data collection	2.96 to 64.83 °
Limiting indices	-9<=h<=6, -14<=k<=16, -17<=l<=17
Reflections collected / unique	13176 / 6750 [R(int) = 0.0214]
Completeness to theta = 64.83°	96.2 %
Absorption correction	Numerical
Max. and min. transmission	0.9120 and 0.8559
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6750 / 929 / 894
Goodness-of-fit on F^2	0.891
Final *R* indices [I>2sigma(I)]	R_1 = 0.0599, wR_2 = 0.1785
R indices (all data)	R_1 = 0.0620, wR_2 = 0.1838
Absolute structure parameter	-0.004(15)
Largest diff. peak and hole	0.653 and -0.474 e-/Å^{-3}

General Experimental (MOF)

N,N-Dimethylformamide (DMF) and zinc nitrate tetrahydate were purchased from Fisher Scientific, and used as received. Elemental analysis was performed by Quantitative Technologies, Inc. Thermal gravimetric analyses (TGA) were measured using TA Instruments Q-500 series thermal gravimetric analyzer with samples held in platinum pans in a continuous airflow atmosphere. Samples were heated at a constant rate of 5 ºC/min to 600 °C during all TGA experiments. Powder X-ray diffraction (PXRD) data were collected using a Bruker D8-Discover θ–2θ diffractometer in reflectance Bragg-Brentano geometry. Cu-*K*α radiation (λ = 1.5406 Å; 1,600 W, 40 kV, 40 mA) was focused using a planar Gobel Mirror riding the *K*α line. A 0.6 mm divergence slit was used for all measurements. Diffracted radiation was detected using a Vantec line detector (Bruker AXS) (6° 2θ sampling width) equipped with a Ni monochromator. All samples were mounted on a glass slide or a zero background quartz plate fixed on a sample holder by dropping crystals and then leveling the sample surface with a wide blade spatula. The best counting statistics were achieved by using a 0.02º 2θstep scan from 2–50º with an exposure time of 0.4s per step. Single-crystal X-ray diffraction (SXRD) data were collected on a Bruker SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1200 W power (40 kV, 30 mA) to generate Cu *Ka* radiation (λ = 1.5418 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals were mounted in a flame sealed borosilicate capillarys containing a small amount of mother liquor to prevent desolvation during data collection.

Synthesis of (SS)-MOF-1020 ($Zn_4O(C_{62}H_{44}Cl_2O_{10})_3$): DMF (10 mL, Fisher) was added to a solid mixture of (*SS*)-**2** (20 mg, 0.0196 mmol) and zinc nitrate tetrahydate (20 mg, 0.0672 mmol) in a 20 mL scintillation vial. The vial was capped tightly and the mixture was sonicated for 3 min to dissolve all solid material. The resulting homogeneous solution was placed in a programmable oven, with a temperature step program of 65 °C, 75 °C and 85 °C for 24 h each (72 h in total). The reaction mixture was cooled to room temperature and then the block-shaped crystals were washed with fresh DMF (3 × 1 mL).

Elemental analysis (evacuated): Calcd: C 66.94 %, H 3.99 %, Cl 6.37 %; Found: C 65.63 %, H 3.96 %, Cl 5.96 %.

Synthesis of (*RR*)-MOF-1020 ($Zn_4O(C_{62}H_{44}Cl_2O_{10})_3$): The exact procedure employed for the preparation of (*SS*)-MOF-1020 was carried out, with the exception that (*RR*)-**2** was used in place of (SS)-**2**.

Activation of (*SS*)-MOF-1020

The rinsed crystals were further washed with Me_2CO (3x 1 mL) and then immersed in the same solvent to exchange out the DMF molecules in the pore. Fresh Me_2C was replenished three times during the two-day period of the solvent-exchange process. The fully exchanged compound was then activated using Samdri-PVT-3D Critical-Point Dryer, and subsequently the thermal gravimetric analysis was performed to ensure the compound was fully activated.

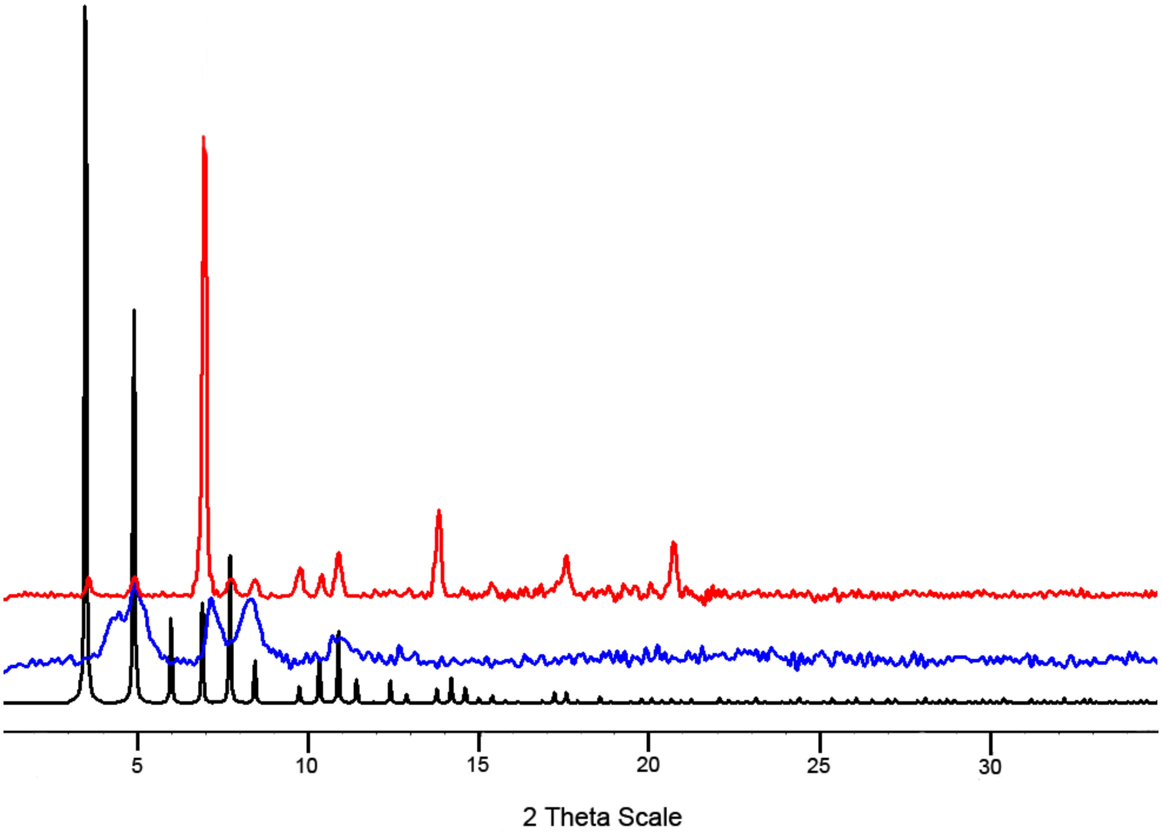


Figure S4. A comparison of powder X-ray diffraction patterns for simulated (black), activated (blue) and re-solvated (red) (*SS*)-MOF-1020. Crystallinity of the MOF appears to be lost upon evacuation of guest solvent molecules, however, it is partially restored upon resolvation with fresh DMF.

Thermal Gravimetric Analysis

Samples were held in platinum pans in a continuous airflow atmosphere. Samples were heated at a constant rate of 5 ºC/min to 600 °C during all TGA experiments.

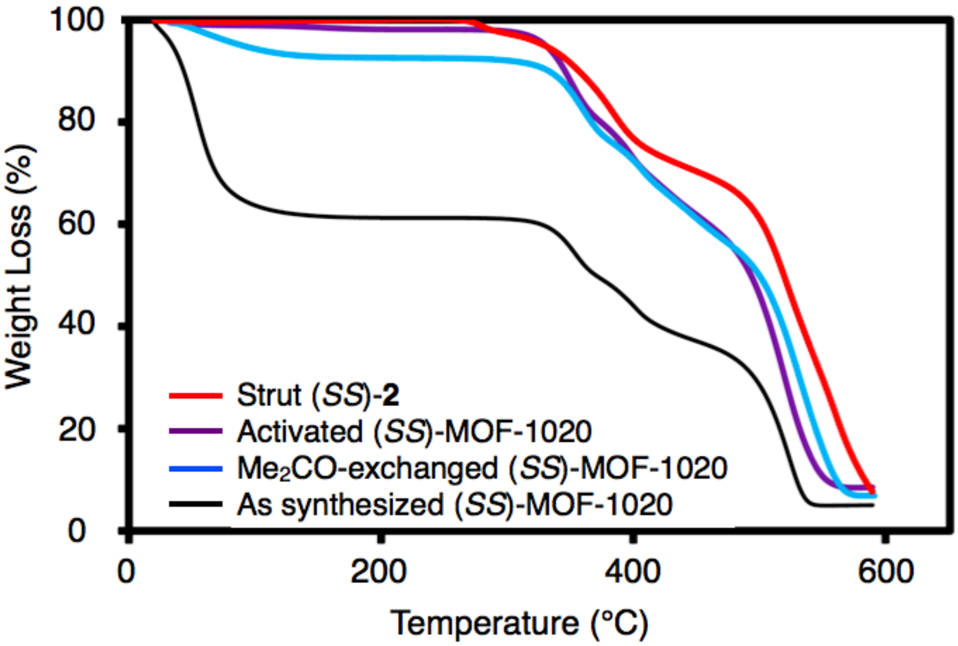


Figure S5. Thermal gravimetric analysis traces for as-synthesized (black), acetone-exchanged (blue) and activated (red) (*SS*)-MOF-1020 as well as the organic strut (*SS*)-**2** (purple).

Single Crystal Data Collection

A colorless cubic crystal (0.2 × 0.2 × 0.2 mm^3) of (*SS*)-MOF-1020 was placed in a 0.4 mm diameter borosilicate capillary along with a small amount of mother liquor. The capillary was flame sealed and mounted on a SMART APEX-II three-circle diffractometer equipped with a CCD area detector and operated at 1200 W power (40 kV, 30 mA) to generate Cu $K\alpha$ radiation (λ = 1.5418 Å) while being cooled to 258(2) K in a liquid N_2 cooled stream of nitrogen. After a preliminary unit cell check of parameters, the data collection strategy for MOF-1020 was refined by the *APEX2* software suite for the desired completeness and redundancy (desired completeness: 100%, desired redundancy: 4). In total, 2591 frames were collected with overlapping φ and ω scans at different detector (2θ) settings. A total of 37116 reflections were collected, of which 2189 were unique and 1275 of these were greater than 2σ(*I*). The range of *θ* was from 1.72 to 33.39°.

Because of the highly disordered crown ethers and solvent molecules in the void spaces in the crystal and from the capillary used to mount the crystal contributes to the background noise and the 'washing out' of high angle data. For this reason, a complete structural solution was not obtained. However, a preliminary backbone of the structure was obtained by direct methods using the *SHELXTL '97* software suite, where the space group *P23* was the outcome. The Zn_4O inorganic secondary building unit (SBU), carbon and oxygen atoms of the carboxylate group and the first two carbon atoms of the first phenylene ring attached to the carboxylate were located.

Table S3. Atomic coordinates for (*SS*)-MOF-1020. Crystal system: Cubic; Space group: *P*23 (No. 195); Unit cell parameters: *a* = 25.7527(6) Å.

	x	y	z	s.o.f
Zn1	0.043496	0.043496	0.043496	0.33333
O1	0.029385	0.030149	0.116740	1.00000
O2	0.000000	0.000000	0.000000	0.08333
C1	0.000000	0.000000	0.127752	0.50000
C2	0.000000	0.000000	0.190054	0.50000
C3	0.027273	0.027600	0.217129	1.00000
C4	0.030494	0.030913	0.293016	1.00000
C5	0.000000	0.000000	0.312165	0.50000
C25	-0.077627	0.082127	0.467165	1.00000
C30	0.017719	-0.015773	0.372925	1.00000
C31	-0.012938	0.017816	0.454744	1.00000

Crystal Structure Modeling

The model for (*SS*)-MOF-1020, including cell parameters and atomic positions was generated using Materials Studio[S10] chemical structure-modeling software employing the Crystal Building module based on the SXRD dataset. The structure of (*SS*)-MOF-1020 was generated using the space group *P*23, the cell parameters were used as obtained from SXRD data. The constructed structure was minimized with the Forcite module using the Geometry Optimization option with the Universal Force Field (UFF)[S11, S12]. The simulated powder X-ray pattern was extracted from here to compare with the experimental patterns.

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S5. Full-Matrix Least-Squares refinement on F^2: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

S6. GooF = $S = \{S[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$ where n = number of reflections and p = total number of reflections refined.

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S11. Materials Studio version 5.0.0.0, Copyright © 2009, Accelrys Software Inc.

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