Supporting Information for

From one to three: a serine derivate manipulated homochiral metal-organic framework

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Experimental Section

Materials and General Procedures. All of the chemicals were obtained from commercial sources and used without further purification. The determinations of the unit cell and data collection for the crystal of compound **1** were performed on a Siemens SMART CCD APEX II. The data were collected using graphite–monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The data sets were corrected by **SADABS** program.[1] The structure was solved by direct method, and refined by full-matrix least-square method with the **SHELXTL-97** program package.[2] H atoms on C and N atoms were generated geometrically. The H-atoms of the water molecule were clearly visible in a different map and were handled in the subsequent refinement with fixed isotropic displacement parameters. All of the reactions and manipulations were carried out under Nitrogen with the use of standard inert atmosphere and Schlenk techniques. Solvents used in all the reactions were dried by standard procedures.[3] ^{1}H NMR spectra were recorded on 400 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported relative to internal standard TMS (0 ppm). The following abbreviations are used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Substituted substrates were synthesized according to literature method.[4]

Biginelli reaction of benzaldehyde, urea and ethyl acetoacetate with solid catalyst 1. A mixture of benzaldehyde (0.1 mmol), urea (0.1 mmol), ethyl acetoacetate (0.1 mmol), solid **1** (0.01 mmol) and CH_2Cl_2 (2mL) was stirred at 40 ^oC for 12 h in a Schlenk flask. DMF was added to dissolve the produced white precipitation. The mixture was filtered, extracted with ether, dried over sodium sulfate and concentrated in vacuum. The residue was subjected to chromatography on silica gel to give the isolated yield.

A typical procedure for 1,2-addition of Grignard reagent to α, β-unsaturated ketones with solid catalyst 1. To a 5 mL Schlenk flask, solid catalyst **1** (0.01 mmol) was added, after pump dried under vacuum at 70°C for 2 h, α, β-unsaturated ketone (0.1 mmol) was added, and then dried THF (2 ml) was added by syringe, followed by adding Grignard reagent (0.12 mmol) dropwise under N_2 at 0 ^{o}C. The reaction mixture was stirred and allowed to warm to ambient temperature over 12 h, and then quenched with saturated ammonium chloride solution (2 ml). The mixture was extracted with ether, dried over sodium sulfate and concentrated in vacuum to give crude product. An aliquot was analyzed on GC to give the conversion and *ee*% values.

5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one: ^{1}H NMR($CDCl_3$): δ9.18 (1H, s), 7.82 (1H, s), 7.24-7.35 (5H, m), 5.26 (1H, d, J = 3.2Hz), 2.29 (3H, s), 2.10 (3H, s). HPLC condition: (Chiralcel AD-H column, eluent: 2-Propanol : Hexane = 20 : 80, flow rate: 1 mL/min): t_1 = 8.5 min; t_2 = 10.4 min.

2-cyclohexyl-4-phenylbut-3-en-2-ol (Table 1, entry 1): ^{1}H NMR($CDCl_3$): δ7.24-7.42 (5H, m), 6.59 (1H, d, J=16 Hz), 6.31 (1H, d, J = 16.4 Hz), 1.55-1.82 (4H, m), 1.43-1.49 (1H, m), 1.37 (3H, s), 1.03-1.28 (6H, m). GC condition: (Supelco β-Dex 120, 30 m × 0.25 mm × 0.25 μm, Detector t: 250 ^{o}C, Ejector t: 250 ^{o}C, Column t: 220 ^{o}C, support gas: N_2 0.1mL/min): t_1 = 9.3 min, t_2 = 9.8 min.

1-cyclohexyl-3-phenylprop-2-en-1-ol (Table 1, entry 5): ^{1}H NMR($CDCl_3$): δ7.25-7.41 (5H, m), 6.55 (1H, d, J=16 Hz), 6.24 (1H, q, J = 7.7 Hz), 4.02 (1H, m), 1.67-1.77 (4H, m), 1.50-1.53 (1H, m), 1.04-1.29 (6H, m). GC condition: (Supelco β-Dex 120, 30 m × 0.25 mm × 0.25 μm, Detector t: 250 ^{o}C, Ejector t: 250 ^{o}C, Column t: 220 ^{o}C, support gas: N_2 0.1mL/min): t_1 = 9.8 min, t_2 = 11.0 min.

2-cyclohexyl-4-p-tolylbut-3-en-2-ol (Table 1, entry 6): ^{1}H NMR($CDCl_3$): δ7.28 (1H, d, J=8.4 Hz), 7.12 (1H, d, J=7.6 Hz), 6.59 (1H, d, J=16.4 Hz), 6.31 (1H, d, J = 16.4 Hz), 2.33 (3H, s), 1.76-1.87 (4H, m), 1.39-1.45 (1H, m), 1.34 (3H, s), 0.97-1.26 (6H, m). GC condition: (Supelco β-Dex 120, 30 m × 0.25 mm × 0.25 μm, Detector t: 250 °C, Ejector t: 250 °C, Column t: 220 °C, support gas: N_2 0.1mL/min): t_1 = 11.9 min, t_2 =12.9 min.

4-(4-chlorophenyl)-2-cyclohexylbut-3-en-2-ol (Table 1, entry 7): ^{1}H NMR($CDCl_3$): δ7.27-7.34 (5H, m), 6.61 (1H, d, J=16 Hz), 6.35 (1H, d, J = 16 Hz), 1.77-1.87 (4H, m), 1.60-1.61 (1H, m), 1.56 (3H, s), 0.86-1.25 (6H, m). GC condition: (Supelco β-Dex 120, 30 m × 0.25 mm × 0.25 μm, Detector t: 250 °C, Ejector t: 250 °C, Column t: 220 °C, support gas: N_2 0.1mL/min): t_1 = 12.3 min, t_2 = 12.8 min.

References:

1. G. M. Sheldrick, **SADABS**; *Siemens Analytical X-ray Instrument Division*: Madison, WI, **1995**.
2. G. M. Sheldrick, *Program for Structure Refinement*: University of Göttingen, Germany, **1997**.
3. W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals.* 5th Edition, Butterworth Heinemann.
4. A. Isleyen, O. Dogan, *Tetrahedron: Asym.* **2007**, *18*, 679.

Figures

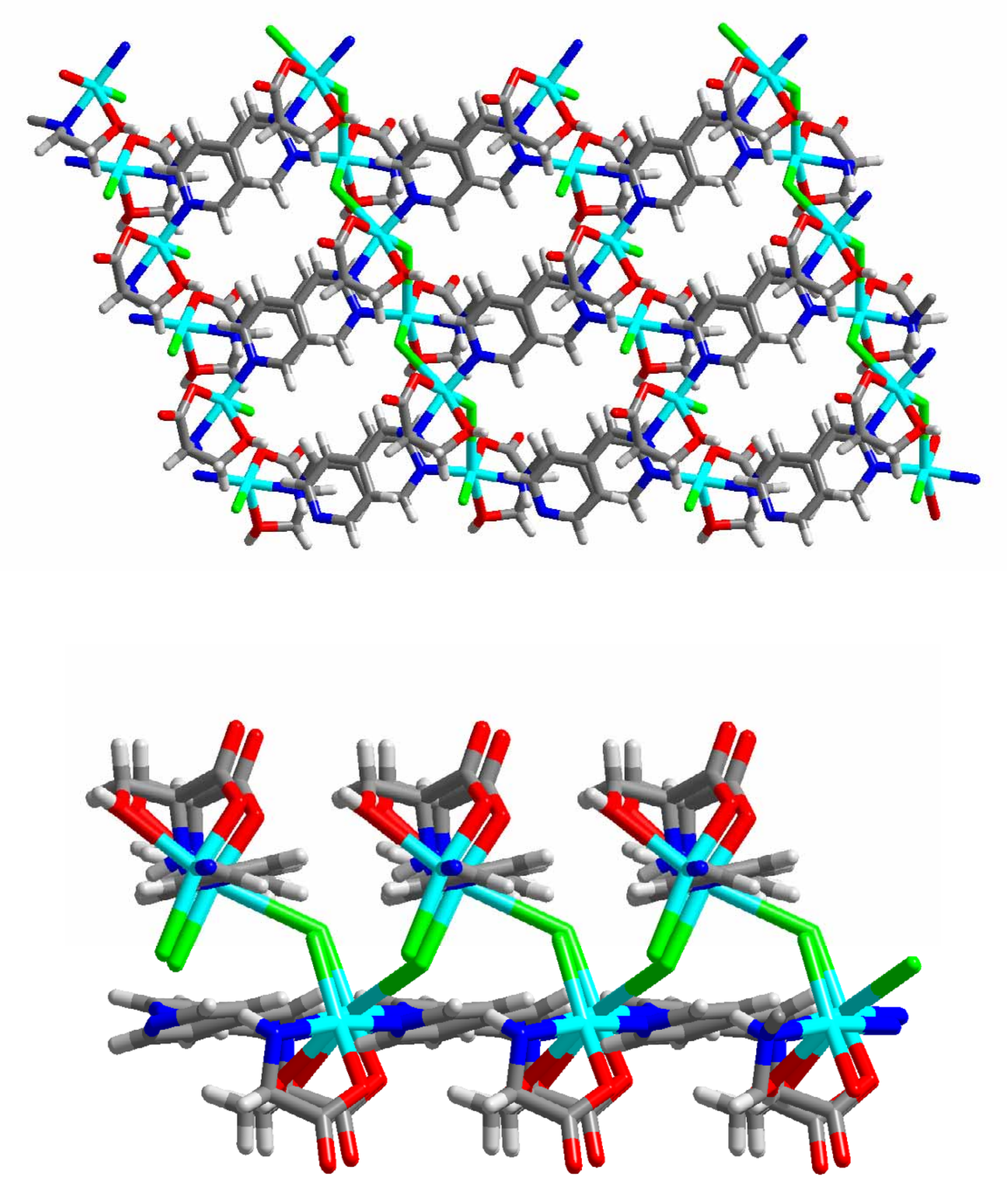

Figure S1. Top and side views of the double-Layer framework of **1**.

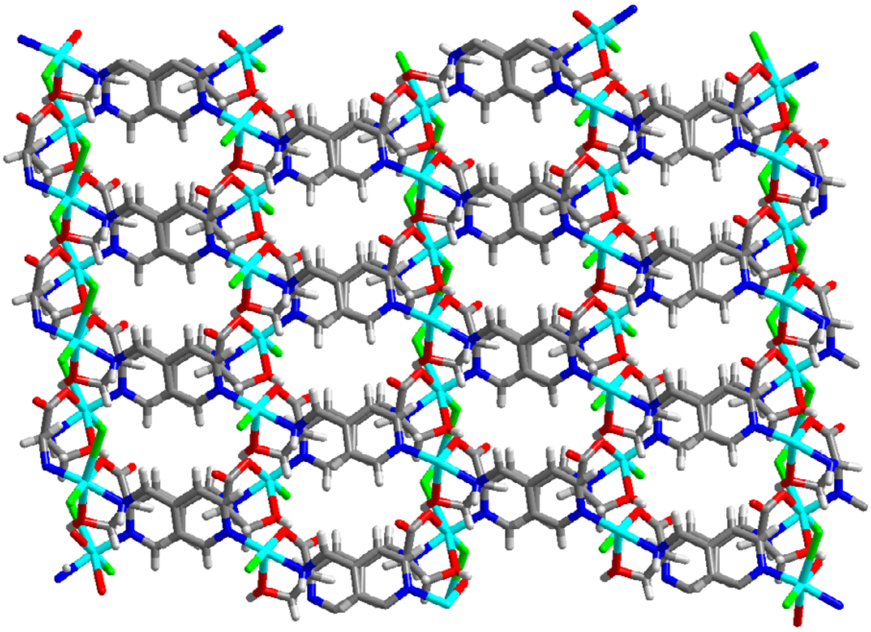

Figure S2. Packing diagram of **1** viewed down the *a* axis.

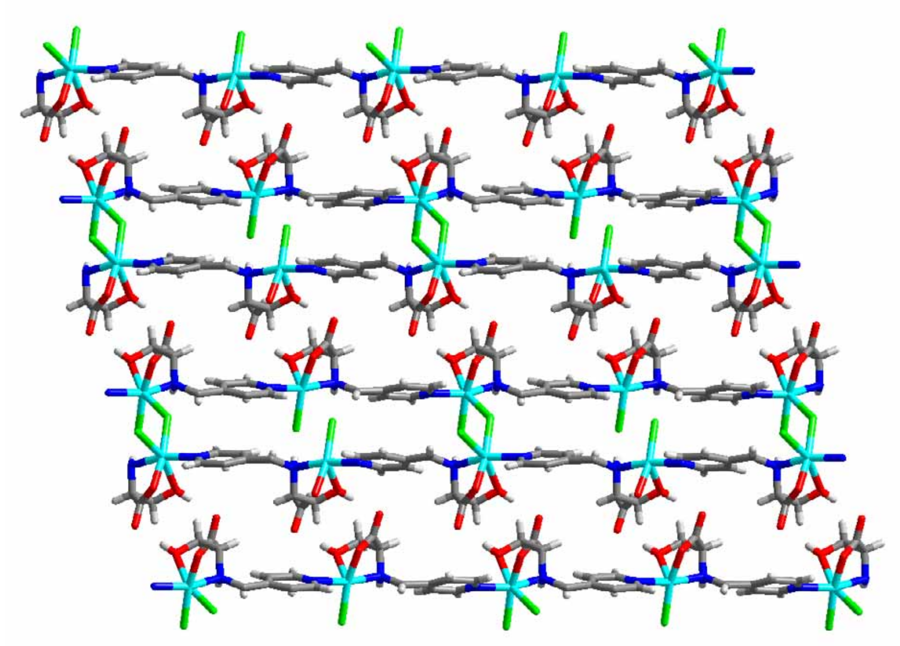

Figure S3. Packing diagram of **1** viewed down the *b* axis.

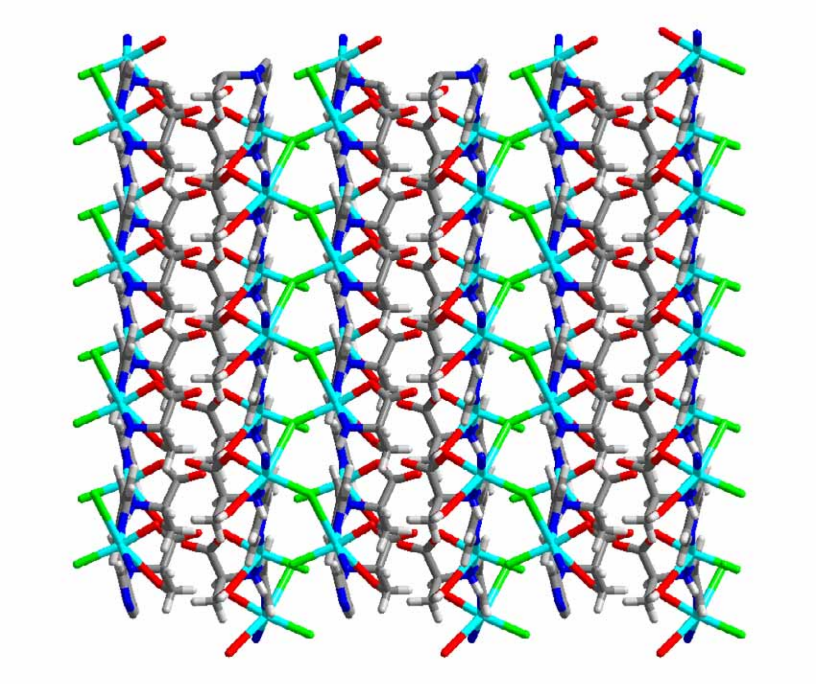

Figure S4. Packing diagram of **1** viewed down the *c* axis.

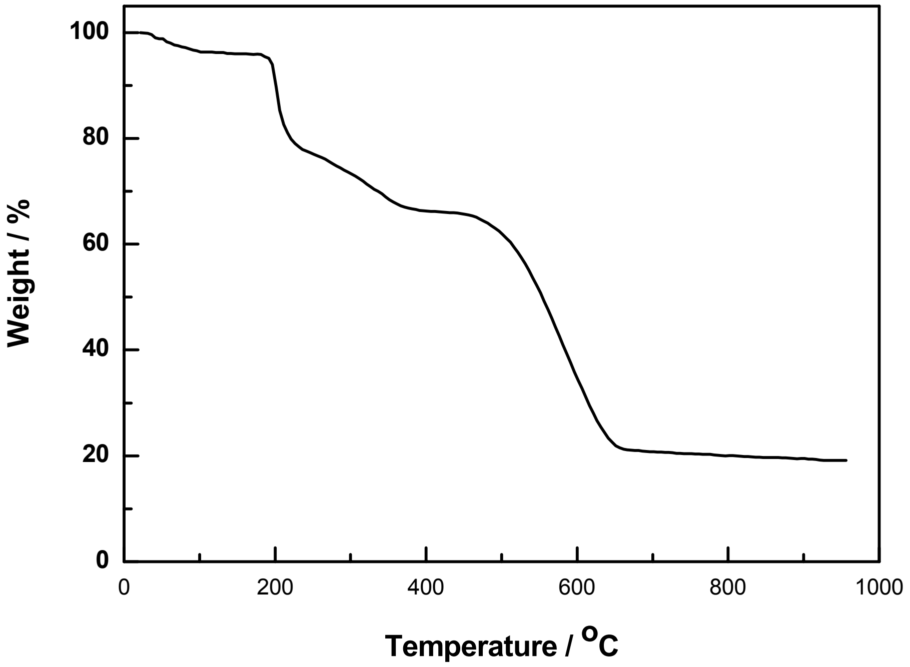

Figure S5. Thermogravimetric analysis curve of **1**.

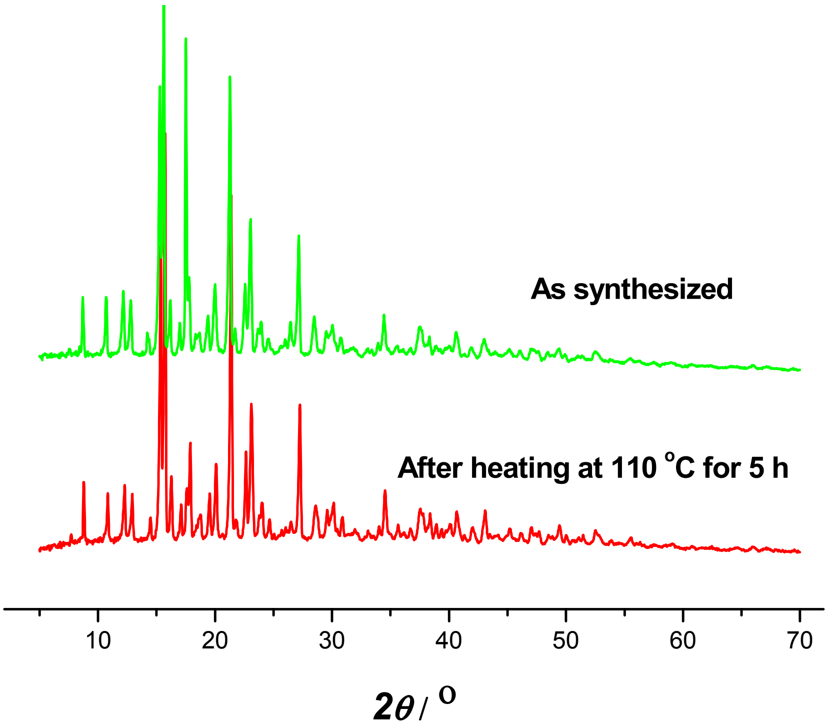

Figure S6. Powder X-ray diffraction patterns for compound **1**.

Tables

Table S1. Crystal data and structure refinements for $[Cu_2\mathbf{L}_2Cl_2]\cdot H_2O$ (**1**)

	1
Formula	C18 H22 Cl2 Cu2 N4 O7
Formula weight	604.38
Crystal size (mm^3)	0.07 × 0.10 × 0.15
Crystal color	Blue
Crystal system, Space group	Monoclinic, $P2_1$
a (Å)	10.3787(2)
b (Å)	6.6130(1)
c (Å)	16.8336(2)
β (°)	103.344(1)
Volume (Å^3)	1124.17(3)
Z	2
Calculated density (g·cm^{-3})	1.785
F(000)	612
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Absorption coefficient (mm^{-1})	2.178
θ for data collection (°)	1.24 to 27.56
Limiting indices	$-13\leq h\leq 13$, $-8\leq k\leq 8$, $-21\leq l\leq 21$
Reflections collected	9767 [R(int) = 0.0262]
Data / parameters	4669 / 304
Goodness-of-fit on F^2	0.989
R1 (wR2) [$I > 2\sigma(I)$]	0.0371 (0.0682)
R1 (wR2) (all data)	0.0541(0.0746)
Flack parameter	0.017(12)
Largest diff. peak and hole (e·Å^3)	0.445 and -0.375

$R1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$.

Table S2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths	(Å)	Bond angles	(°)	Bond angles	(°)
Cu(1)-O(5)	1.973(3)	O(2)-Cu(2)-N(3)	90.6(1)	O(5)^{i}-Cu(1)-N(1)	91.0(1)
Cu(1)-N(1)	1.989(3)	O(2)-Cu(2)-N(2)	82.3(1)	O(5)^{i}-Cu(1)-N(4)^{i}	81.6(1)
Cu(1)-N(4)^{i}	2.016(3)	N(3)-Cu(2)-N(2)	163.7(1)	N(1)-Cu(1)-N(4)^{i}	171.0(1)
Cu(1)-Cl(1)	2.263(1)	O(2)-Cu(2)-Cl(2)	169.9(1)	O(5)^{i}-Cu(1)-Cl(1)	167.3(1)
Cu(1)-O(6)^{i}	2.392(3)	N(3)-Cu(2)-Cl(2)	94.2(1)	N(1)-Cu(1)-Cl(1)	94.2(1)
Cu(2)-O(2)	1.957(3)	N(2)-Cu(2)-Cl(2)	95.2(1)	N(4)^{i}-Cu(1)-Cl(1)	94.1(1)
Cu(2)-N(3)	1.981(3)	O(2)-Cu(2)-Cl(2)^{ii}	81.4(1)	O(5)^{i}-Cu(1)-O(6)^{i}	84.2(1)
Cu(2)-N(2)	2.023(3)	N(3)-Cu(2)-Cl(2)^{ii}	93.0(1)	N(1)-Cu(1)-O(6)^{i}	98.9(1)
Cu(2)-Cl(2)	2.263(1)	N(2)-Cu(2)-Cl(2)^{ii}	100.3(1)	N(4)^{i}-Cu(1)-O(6)^{i}	75.3 (1)
Cu(2)-Cl(2)^{ii}	3.001(1)	Cl(2)-Cu(2)-Cl(2)^{ii}	89.4(1)	Cl(1)-Cu(1)-O(6)^{i}	106.4(1)

Symmetry transformations used to generate equivalent atoms: i) x, y-1, z+1; ii) -x-2, y+1/2, -z.