Supporting Information for

A metalloporphyrin functionalized metal-organic framework for selective oxidization of styrene

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Experimental Section

Materials and General Procedures. All of the chemicals were obtained from commercial sources and were used without further purification. The determinations of the unit cells and data collections for the crystals of compounds **1**, **1a**, **1b** and **1c** were performed on a CrysAlisPro, Oxford Diffraction Ltd. The data were collected using graphite–monochromatic enhanced ultra Cu radiation (λ = 1.54178 Å) at 293 K. The data sets were corrected by multi-scan absorption correction using spherical harmonics, and implemented in SCALE3 ABSPACK scaling algorithm.[1] All structures were solved by direct methods, and were refined by full-matrix least-square methods with the **SHELX-97** program package.[2] The solvent molecules in compounds **1**, **1b** and **1c** are highly disordered, and attempts to locate and refine the solvent peaks were not reasonable. SQUEEZE subroutine of the PLATON software suit was used to remove the scattering from the highly disordered guest molecules.[3] The resulting new files were used to further refine the structures. IR spectrum was recorded from KBr pellet on a FTS-40 spectrophotometer. Powder X-ray diffraction (PXRD) were recorded on a RIGAKU D/MAX 2550/PC for Cu-Kα (λ = 1.5406 Å). Thermogravimetric analysis (TGA) was carried out under N_2 on a NETZSCH STA 409 PC/PG instrument at a heating rate of 10 °C/min. ^{1}H NMR spectra were recorded on a 500 MHz spectrometer in $CDCl_3$ solution and the chemical shifts were reported relative to the internal standard TMS (0 ppm).

*Synthesis of $[Cd_{1.25}(Pd\text{-}H_{1.5}TCPP)(H_2O)]\cdot 2DMF$ (**1**)*: Heating a mixture of

Pd-H_4TCPP (75 mg, 0.084 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (0.50 g, 1.62 mmol) in a mixed solvent of DMF (40 mL), MeOH (20 mL) and acetic acid (15 mL) at 80 ^oC for ten days afforded dark brown crystals, which were isolated by filtration, washed with DMF, EtOH and Et_2O, and dried at room temperature. Yield: 38 mg (37.8%, based on Pd-H_4TCPP). IR (KBr): ν = 1605 (m), 1586 (m), 1541 (m), 1401 (s), 1351 (w), 1177 (w), 1102 (w), 1014 (s), 871 (w), 853 (w), 795 (w), 777 (w), 715 (w), 495 (w) cm^{-1}.

*A Typical procedure for the Selective oxidation of styrene catalyzed by solid **1**:* Solid **1** (0.01 mmol), styrene (0.2 mmol), $HClO_4$ (70%, 0.01 mmol) and H_2O_2 (30%, 0.6 mmol) in CH_3CN (6 mL) were stirred at 55 ^oC for 12 h. The mixture was subsequently cooled down to room temperature, which was filtered, extracted with ether, dried over sodium sulfate, and subjected to GC-MS analysis. ^1H NMR (500 MHz, $CDCl_3$, TMS) for acetophenone: δ_H = 7.25-7.36 (5H, m), 3.86-3.87 (1H, dd, J = 4.5, 2.4 Hz), 3.14-3.16 (1H, dd, J = 4.5, 5.4 Hz), 2.80-2.81 (1H, dd, J = 5.4, 2.4 Hz). MS: m/z calcd. 120, found 120 [M^+].

References:

1. Oxford Diffraction Ltd. *CrysAlisPro*, Version 1.171.33.56, 2010.

2. G. M. Sheldrick, *Program for Structure Refinement*: University of Göttingen, Germany, 1997.

3. A. L. Spek, *J. Appl. Crystallogr.,* 2003, **36**, 7.

Figures:

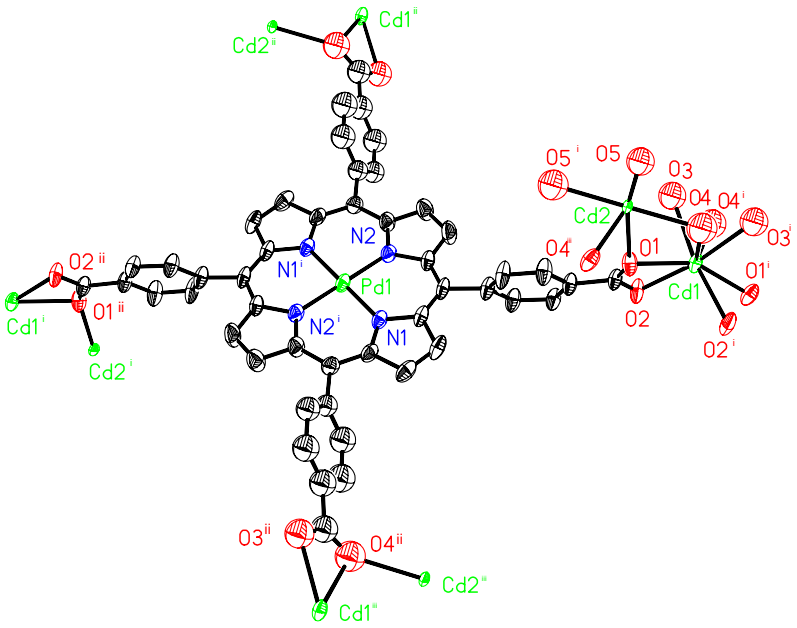

Fig. S1. ORTEP representation of the symmetry expanded local structure for **1** (30% probability ellipsoids).

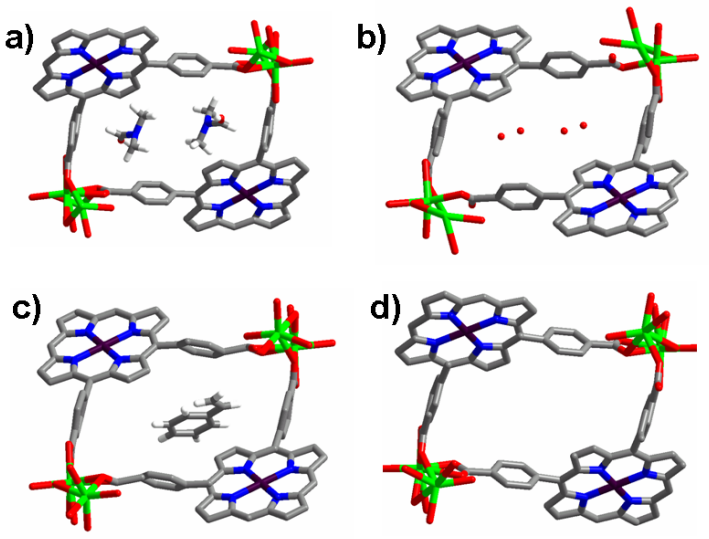

Fig. S2. A view of the solvent guests occupied 1D opening channels in **1** (a), **1b** (b) and **1c** (c), and the solvent free 1D opening channel in **1a** (d).

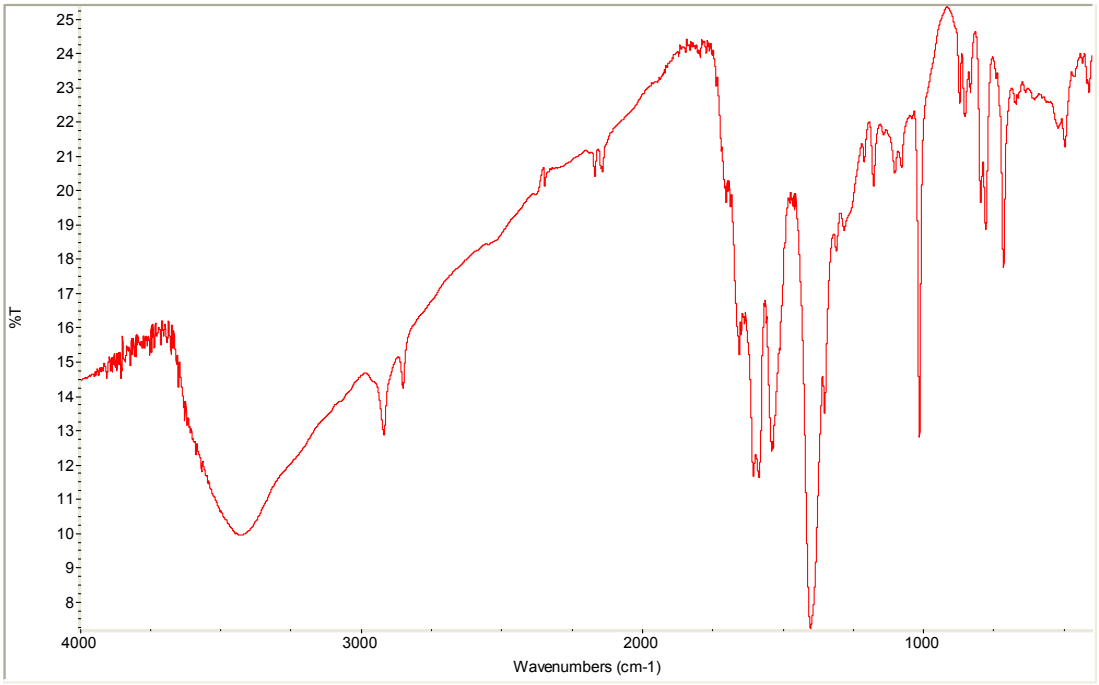

Fig. S3. IR spectrum of **1**.

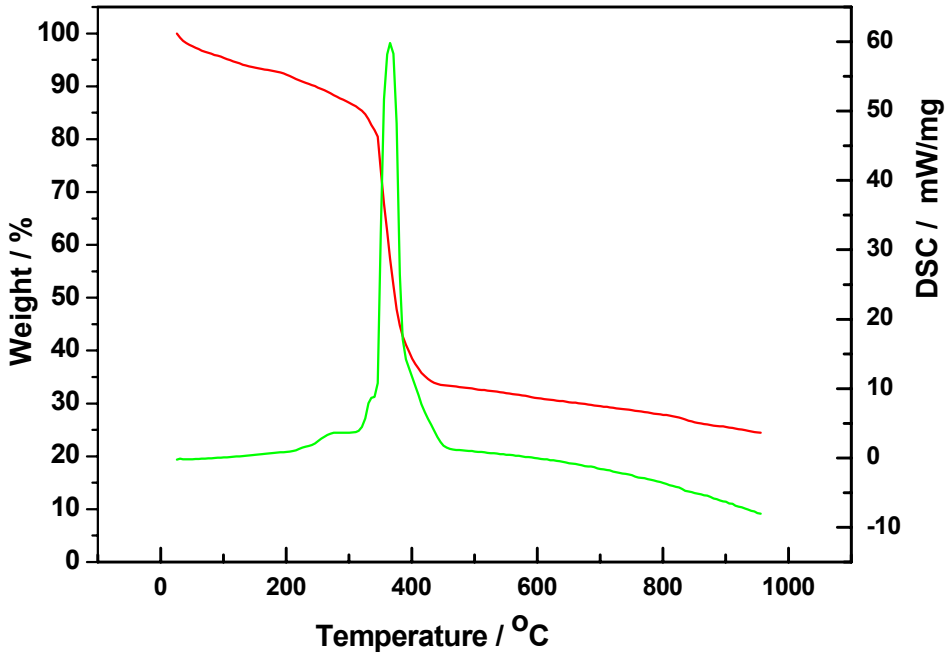

Fig. S4. TGA results of **1**.

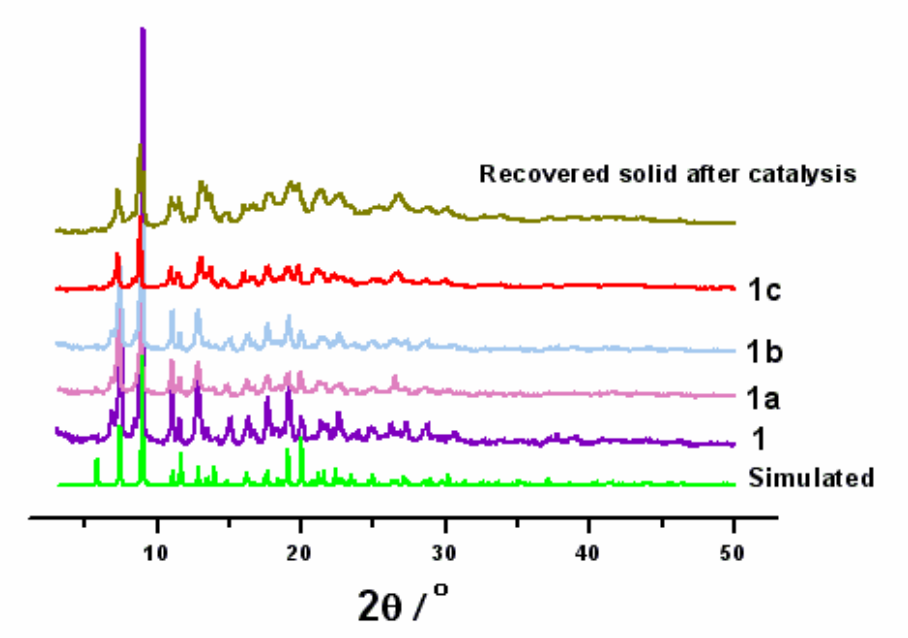

Fig. S5. Powder X-ray diffraction patterns for compounds **1**, **1a**, **1b**, **1c** and the recovered solid after catalysis of **1**.

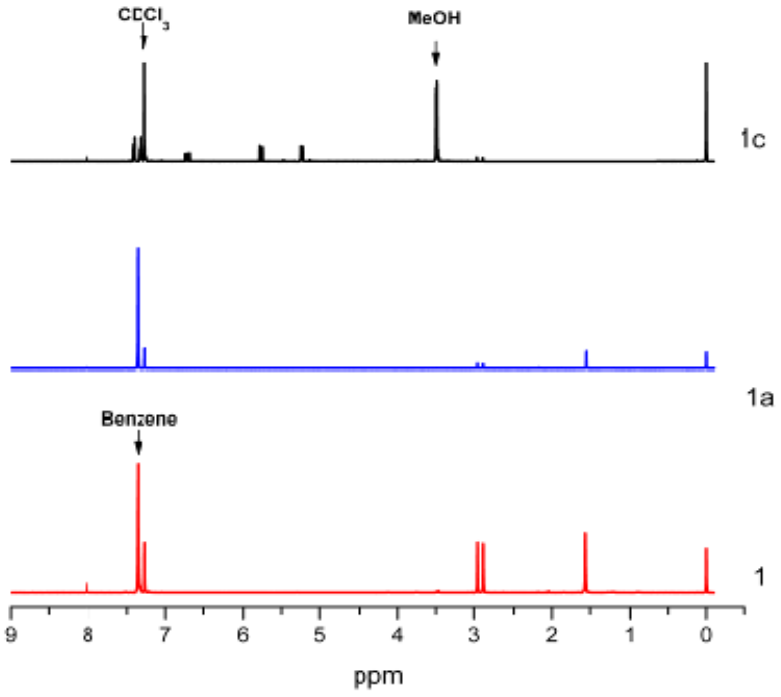

Fig. S6. NMR spectra for the samples of **1**, **1a** and **1c**.

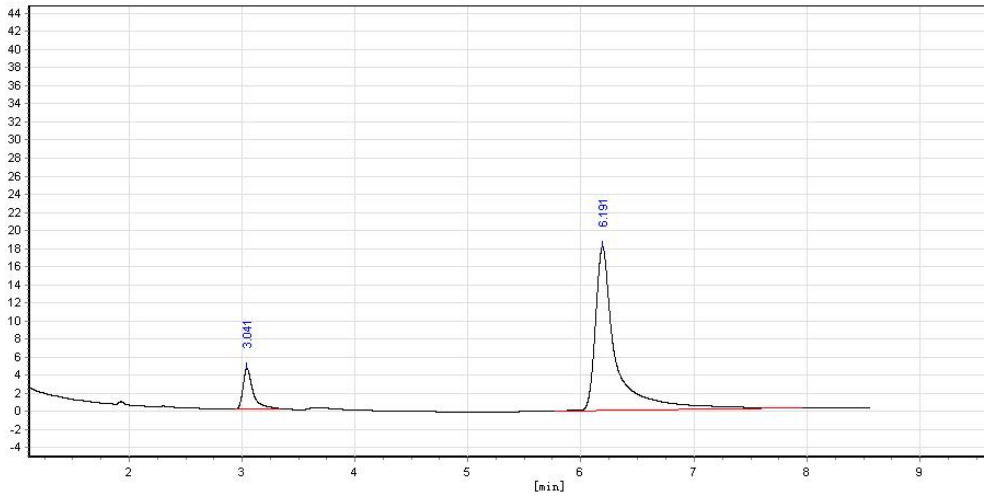

Fig. S7. GC trace of the catalytic results for the selective oxidation of styrene catalyzed by solid **1**.

Fig. S8. MS spectrum for the product at 3.041 min.

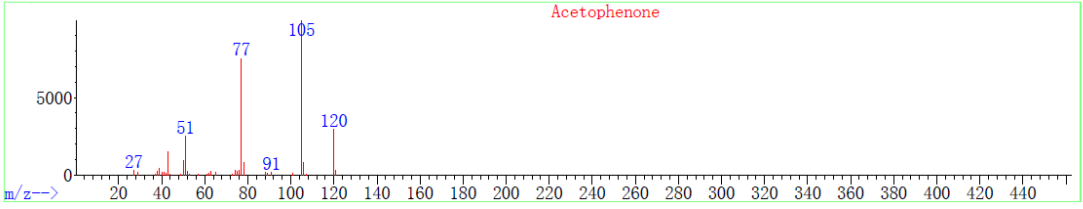

Fig. S9. MS spectrum for the product at 6.191 min.

Tables:

Table S1. Crystal data and structure refinements for **1** and **1a**.

Compound	**1**	**1a**
Formula	$C_{54}H_{41.5}Cd_{1.25}N_6O_{11}Pd$	$C_{48}H_{25.5}Cd_{1.25}N_4O_8Pd$
Formula weight	1197.33	1033.12
Crystal color	Dark brown	Dark brown
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a (Å)	7.2953(1)	7.2172(15)
b (Å)	25.5761(7)	25.613(5)
c (Å)	30.7597(6)	30.660(3)
β (^{o})	96.361(2)	96.392(13)
Volume (Å^3)	5704.0(2)	5632.5(17)
Z	4	4
Calculated density (g·cm^{-3})	1.394	1.218
F(000)	2406	2046
Temperature (K)	293(2)	293(2)
Wavelength (Å)	1.54178	1.54178
Absorption coefficient (mm^{-1})	6.756	6.713
θ for data collection (^{o})	3.46 to 58.91	2.90 to 58.91
Limiting indices	-6≤h≤8, -28≤k≤27, -34≤l≤33	-8≤h≤7, -28≤k≤19, -34≤l≤31
Reflections collected	15512 [R(int) = 0.0332]	7339 [R(int) = 0.0585]
Data / parameters	4054 / 284	3942 / 275
Goodness-of-fit on F^2	1.024	0.908
R1 (wR2) [$I > 2\sigma(I)$]	0.0776 (0.1837)	0.0886 (0.1752)
R1 (wR2) (all data)	0.0852 (0.1904)	0.1648 (0.2164)
Largest diff. peak and hole (e·Å^3)	1.065 and -0.493	0.481 and -0.329

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

Table S2. Crystal data and structure refinements for **1b** and **1c**.

Compound	**1b**	**1c**
Formula	$C_{48}H_{47.5}Cd_{1.25}N_4O_{19}Pd$	$C_{64}H_{41}Cd_{1.25}N_4O_{8.5}Pd$
Formula weight	1231.30	1248.91
Crystal color	Dark brown	Dark brown
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a (Å)	7.1564(9)	7.2751(3)
b (Å)	25.080(4)	25.5905(15)
c (Å)	31.192(3)	30.7749(11)
β (°)	96.287(11)	96.478(4)
Volume (Å^3)	5564.7(12)	5692.9(5)
Z	4	4
Calculated density (g·cm^{-3})	1.470	1.457
F(000)	2486	2508
Temperature (K)	293(2)	293(2)
Wavelength (Å)	1.54178	1.54178
Absorption coefficient (mm^{-1})	7.036	6.754
θ for data collection (°)	6.71 to 58.91	3.45 to 58.93
Limiting indices	-7≤h≤7, -27≤k≤24, -34≤l≤34	-7≤h≤8, -28≤k≤28, -34≤l≤32
Reflections collected	8511 [R(int) = 0.0783]	9346 [R(int) = 0.0417]
Data / parameters	3941 / 284	4037 / 280
Goodness-of-fit on F^2	0.788	1.070
R1 (wR2) [$I > 2\sigma(I)$]	0.0938 (0.2092)	0.0969 (0.2234)
R1 (wR2) (all data)	0.1608 (0.2562)	0.1136 (0.2323)
Largest diff. peak and hole (e·Å^3)	0.524 and -0.437	0.877 and -0.488

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