

Supplementary Information

Infinite Building Blocks for Directed Self-Assembly of A Supramolecular Polyoxometalate-Cyclodextrin Framework for Multifunctional Oxidative Catalysis

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1. Materials

$\text{Na}_7[\text{MnV}_{13}\text{O}_{38}] \cdot 18\text{H}_2\text{O}$ ^[1], $\text{Na}_9[\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ ^[2] and $\text{K}_5\text{PW}_{10}\text{V}_2\text{O}_{40}$ ^[3] were synthesized according to the literature. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was purchased from Admas-beta, $\alpha\text{-CD}$ was purchased from Rhawn, Ltd, respectively. All reagents were of A.R. grade and used without further purification.

2. Instrumentation

Crystallography: Single-crystal X-ray diffraction data of **1** was collected at 150 K at Donghua University (Shanghai) using Mo-K α ($\lambda = 0.71073 \text{ \AA}$) Bruker D8 venture X-ray single crystal diffractometer for several times, and the best dataset was chosen to be indexed, integrated and scaled using the APEX 3 program^[4]. The structure was solved by the direct methods with ShelXT^[5] and refined with ShelXL^[6] using OLEX 2^[7]. All non-hydrogen atoms are anisotropic refined by the least square method, and the hydrogen atoms are determined by the ideal geometry by the theoretical hydrogenation method. CCDC-2209404 (**1**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Element Analyses: C, N and H content were determined by VARIDEL III Elemental Analyzer. The contents of Mn, V, Ce, P, W and Na were determined from Prodigy-ICP plasma spectrometer by dissolving 2 mg of **1** in 10 mL of 1M HNO_3 solution.

Thermogravimetric Analysis (TGA): Thermogravimetric analysis was performed on a METTLER TOLEDO TG8000 Thermogravimetric Analyzer under nitrogen flow at a typical heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$.

Powder X-ray Diffraction (PXRD): Powder XRD was recorded on a Haoyuan DX-2700B

diffractometer equipped with monochromatized Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation in the range of $3^\circ \leq 2\theta \leq 50^\circ$, with a scanning rate of $0.04^\circ \text{ s}^{-1}$.

Fourier-transform infrared (FT-IR) spectroscopy: The samples were prepared as a KBr pellet and the FT-IR spectrum was collected in transmission mode in the range of 500-4000 cm^{-1} using a NEXUS-670 spectrometer. Wavenumbers are given in cm^{-1} . Intensities are denoted as w = weak, m = medium, s = strong, vs = very strong, br = broad.

GC mass spectra: GC-Mass analysis was carried out on Agilent 8860 GC system and 5977B GC/MSD system with EI mode

Nuclear Magnetic Resonance Spectroscopy: All the NMR spectra were recorded on Bruker AVANCE III HD 600MHz spectrometer. The experimental details are described as bellow: **1** (30mg) was added to a solution of 800 μL 1M DCl and sonicated for 10 minutes to make a clear solution. After filtration, the liquid is transferred to 5 mm NMR tube for ^1H NMR and ^{31}P NMR test at Larmor frequencies of 600.0 and 162.0 MHz, respectively. The solid-state ^{13}C NMR and ^{31}P NMR spectra were collected on the 600MHz spectrometer utilizing a 1.9 mm Bruker HXY probe at a MAS frequency of 30 kHz with sample loading of 200 mg.

3. Synthesis

Synthesis of $\text{H}_2\text{Ce}_3(\text{H}_2\text{O})_{13}(\text{MnV}_{12}\text{O}_{38})_{0.5}(\text{PW}_{10}\text{V}_2\text{O}_{40})(\text{C}_{36}\text{H}_{60}\text{O}_{30}) \cdot 20\text{H}_2\text{O}$. (**1**)

$\text{Na}_7[\text{MnV}_{13}\text{O}_{38}] \cdot 18\text{H}_2\text{O}$ (0.01 mmol, 18 mg), $\text{Na}_9[\alpha\text{-PW}_9\text{O}_{34}] \cdot 7\text{H}_2\text{O}$ (0.02 mmol, 48.2 mg) and $\alpha\text{-CD}$ (0.056 mmol, 54.5 mg) were dissolved in H_2O (2 mL) (Solution A), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in H_2O (0.5 mL)(Solution B), then add solution B to solution A under stirring conditions, stir at room temperature for a few minutes. The resultant solution was heated at 40°C for 2 hours. After cooled to room temperature, The solution was filtered in a 10ml small glass bottle and volatilized at room temperature, Yellow rod crystals were obtained after two weeks. (yield: 41.00 mg, 40.36 % based on $\text{Na}_7[\text{MnV}_{13}\text{O}_{38}] \cdot 18\text{H}_2\text{O}$). Anal. Calcd for

$\text{H}_2\text{Ce}_3(\text{H}_2\text{O})_{13}(\text{MnV}_{12}\text{O}_{38})_{0.5}(\text{PW}_{10}\text{V}_2\text{O}_{40})(\text{C}_{36}\text{H}_{60}\text{O}_{30}) \cdot 20\text{H}_2\text{O}$ (MW = 5236.74), EA(%): Mn: 0.52; V: 7.78; Ce: 8.02; P: 0.59; W: 35.10; Na: 0.00; C: 8.25; H: 2.46; found: Mn: 0.59; V: 8.04; Ce: 8.27; P: 0.59; W: 35.45; Na: 0.02; C: 8.34; H: 2.45. IR (KBr pellet, 4000 - 500 cm^{-1}): 3310, 2923, 1617, 1340, 1150, 1076, 1029, 952, 916, 792, 599, 514, 423.

Synthesis of **1-CL**_{0.5}

Compound **1** was immersed in anhydrous THF for solvent exchange and then vacuated at 120 °C for 24 hours to remove guest water molecules. The dried **1** (0.02 mmol, 105 mg) was then added into a 10ml three neck flask, followed by addition of hexamethylene diisocyanate (0.18 mmol, 32 μ L, 0.5 equivalent of 18 hydroxyl groups on α -cyclodextrin) and dry DMF (2 mL). The mixture was then heated at 70 °C for 24h, filtered and washed by isopropyl alcohol to afford **1-CL**_{0.5} as yellow powder. (yield: 103.00 mg, 75.79 % based on compound **1**). Anal. Calcd for $\text{H}_2\text{Ce}_3(\text{H}_2\text{O})_{13}(\text{MnV}_{12}\text{O}_{38})_{0.5}(\text{PW}_{10}\text{V}_2\text{O}_{40})(\text{C}_{36}\text{H}_{60}\text{O}_{30})(\text{HDI})_9(\text{DMF})_6$ (MW = 6826.739), EA(%): Mn: 0.40; V: 5.97; Ce: 6.16; P: 0.45; W: 26.93; C: 22.15; H: 3.45; N: 4.92; found: Mn: 0.48; V: 6.04; Ce: 6.34; P: 0.41; W: 27.15, C: 22.42; H: 3.65; N: 4.66. IR (KBr pellet, 4000 - 500 cm^{-1}): 3320, 2929, 2854, 1616, 1569, 1253, 1049, 912, 794, 599, 514, 423.

4. Crystallographic data and crystal structures of **1**

Table S1 Crystallographic Details for **1**

Compound	1
Empirical formula	C ₃₆ H ₁₃₈ Ce ₃ Mn _{0.50} O ₁₂₇ PV ₈ W ₁₀
Formula weight	5328.28
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2
a /Å	30.250(9)
b /Å	36.327(10)
c /Å	17.050(4)
α/°	90
β/°	90
γ/°	90
V /Å ³	18736(9)
Z	4
ρ calc /g·cm ⁻³	1.889
μ(MoKα) /mm ⁻¹	7.332
F(000)	9982
2θ range /°	1.885 to 25.326
	-36<=h<=36
Index ranges	-43<=k<=43
	-20<=l<=20
Reflections collected	298878
Data / restraints / parameters	34151 / 45 / 1453
R ₁ /wR ₂ (I>2σ(I)) ^a	0.0460/0.1134
R ₁ /wR ₂ (all data)	0.0502/0.1165
GooF (all data) ^b	1.044
Data completeness	99.9%

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$$

$$^b \text{GooF} = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / (n-p) \}^{1/2}$$

5. Bond valence sum (BVS) calculations of Mn, Ce and V atoms in 1

Table S2 Bond valence sum (BVS) calculations of Mn, Ce and V atoms in compound 1.

compound 1	BVS calc. for Mn (III)	BVS calc. for Mn (IV)
Mn1	3.8456	4.0248

compound 1	BVS calc. for Ce (III)	BVS calc. for Ce (IV)
Ce1	3.263	2.740
Ce2	3.265	2.756
Ce3	3.265	2.864

compound 1	BVS calc. for V (IV)	BVS calc. for V (V)
V1	4.694	4.995
V2	4.790	5.097
V3	4.593	4.888
V4	4.593	4.888
V5	4.694	4.995

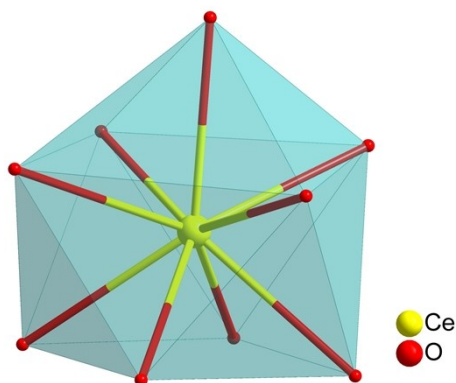


Figure S1 Mono-capped square antiprism configuration of Ce³⁺ in compound 1

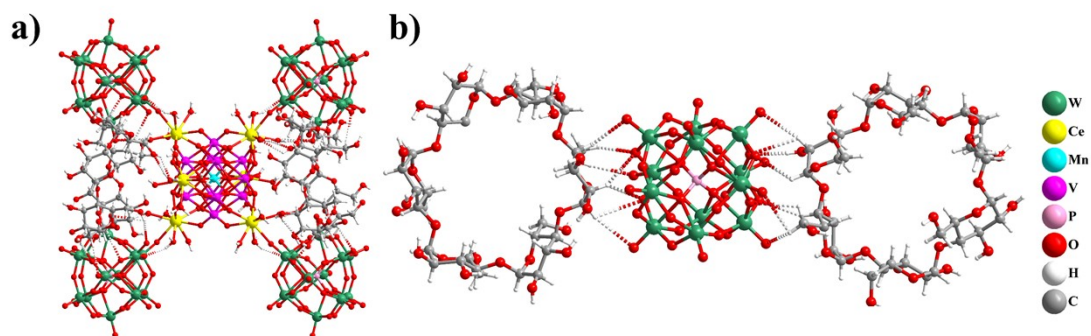


Figure S2 Multiple hydrogen bonding between coordinated H₂O on Ce centers (a), {PW₁₀V₂} (b) and α -CD in compound **1**

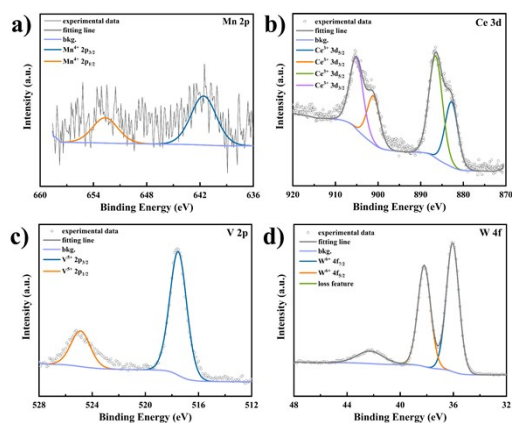


Figure S3 The XPS analysis of a) Mn; b) Ce; c) V; d) W in compound **1**

6. NMR spectra of **1** and α -CD

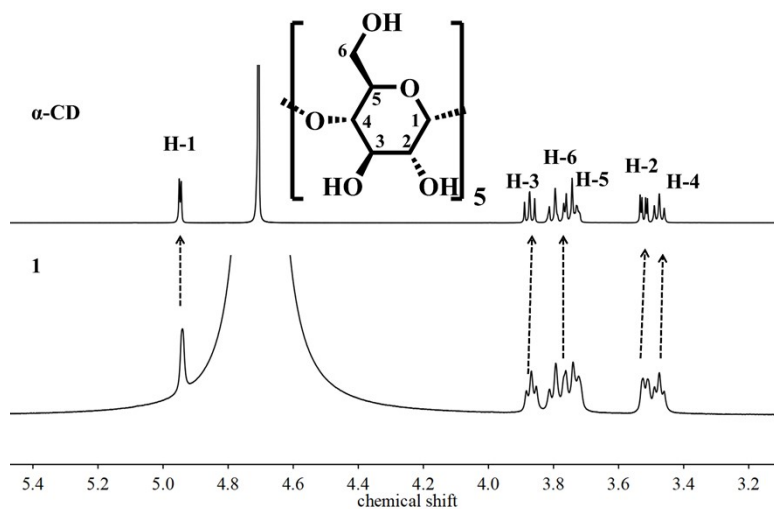


Figure S4 ¹H NMR spectra of **1** and α -CD in a mixture of DCl and D₂O

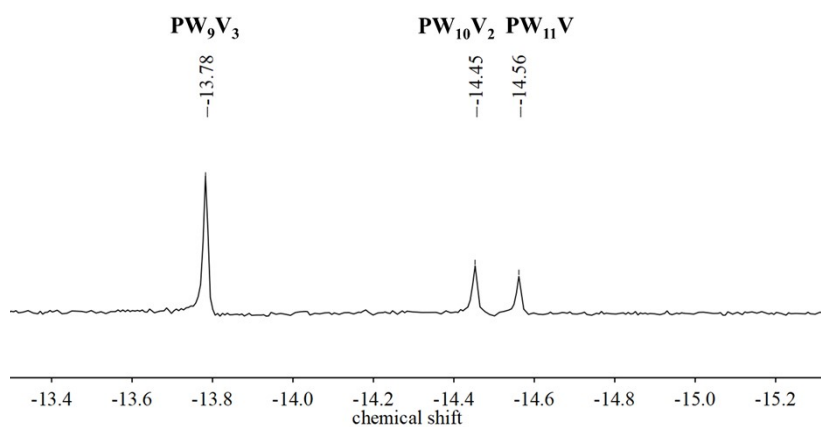


Figure S5 ^{31}P NMR spectrum of **1** in a mixture of DCl and D₂O, {PW₉V₃} (δ 13.78 ppm), {PW₁₀V₂} (δ 14.45 ppm) and {PW₁₁V} (δ 14.56 ppm)

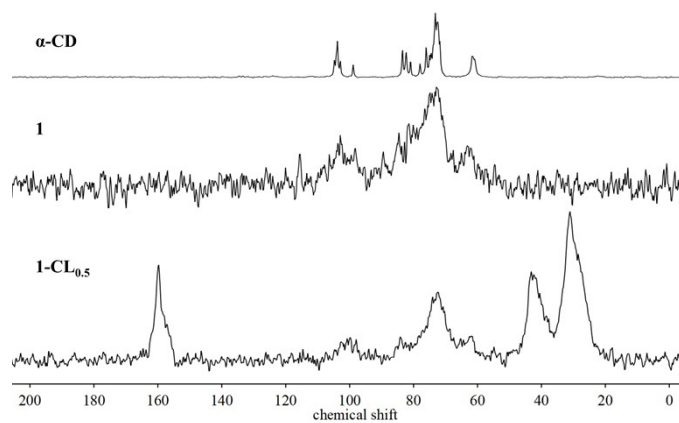


Figure S6 Solid-state ^{13}C NMR spectra of α -CD, **1** and **1-CL_{0.5}**

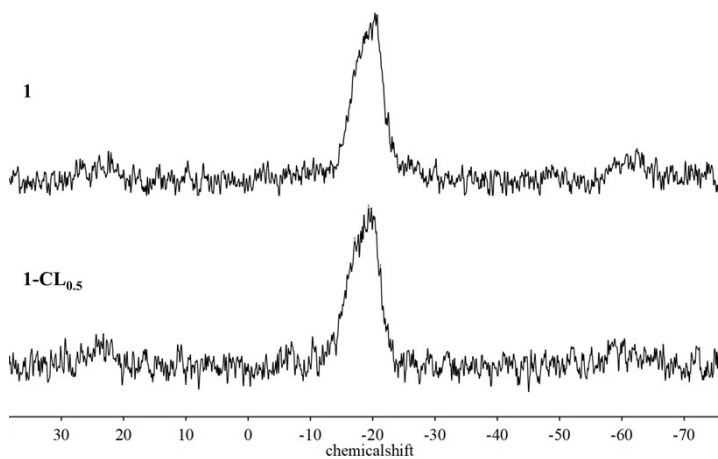


Figure S7 Solid-state ^{31}P NMR spectra of **1** and **1-CL_{0.5}**

7. FT-IR spectra of $\{\text{MnV}_{13}\}$, $\{\text{PW}_{10}\text{V}_2\}$, $\alpha\text{-CD}$ and **1**

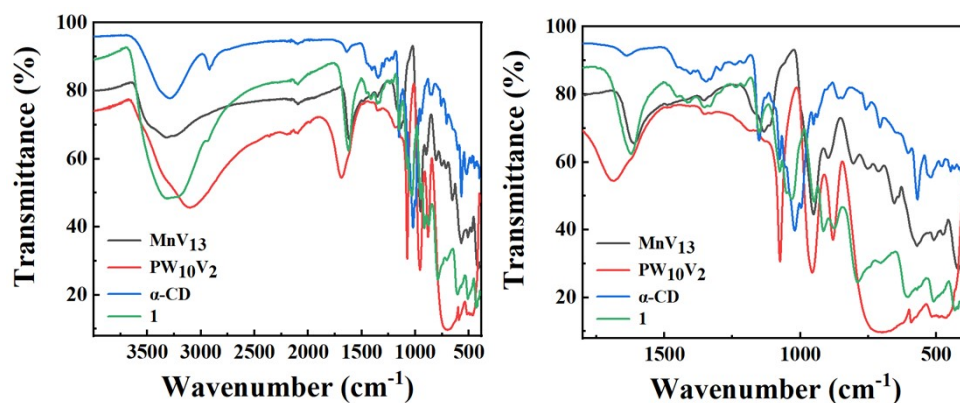


Figure S8 The FT-IR spectra of $\text{Na}_7[\text{MnV}_{13}]\cdot 18\text{H}_2\text{O}$ ($\{\text{MnV}_{13}\}$), $\text{K}_5\text{PW}_{10}\text{V}_2\text{O}_{40}$ ($\{\text{PW}_{10}\text{V}_2\}$), $\alpha\text{-CD}$ and **1**.

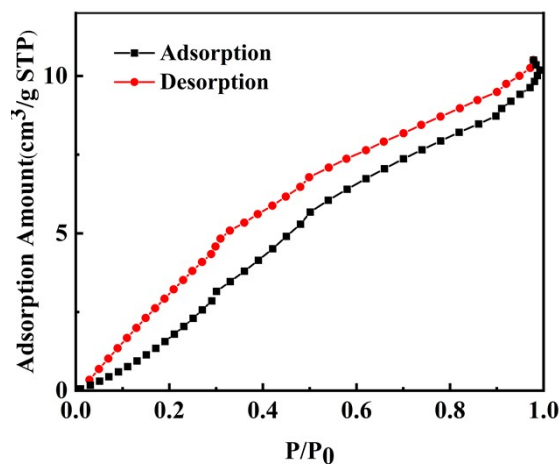


Figure S9 N₂ adsorption of **1**.

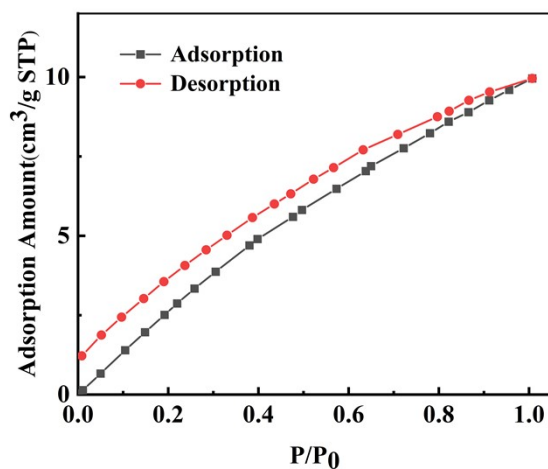


Figure S10 CO₂ adsorption of **1**.

8. Dye adsorption by 1 and 1-CL_{0.5}

Preparation of the working curves of Dyes: The standard solutions of rhodamine B (RB) and methylene blue (MB) were prepared in a sequential concentration of 1mg/L, 5mg/L, 10mg/L, 15mg/L and 20mg/L, respectively. These standard solutions were then tested by Uv-Vis spectrometer to make working curves based on the relationship between absorption and concentration.

Dye adsorption experiment: Taking 3 mL of 20mg/L standard solution (RB/MB) into a 50 mL glass bottle, 3 mg 1/1-CL_{0.5} was subsequently added and stirred for 24 hours. The solution was then filtered and used for testing its absorbance with a spectrometer. The amount of absorbed dye molecules per formula was evaluated by comparing their absorbances with the working curves.

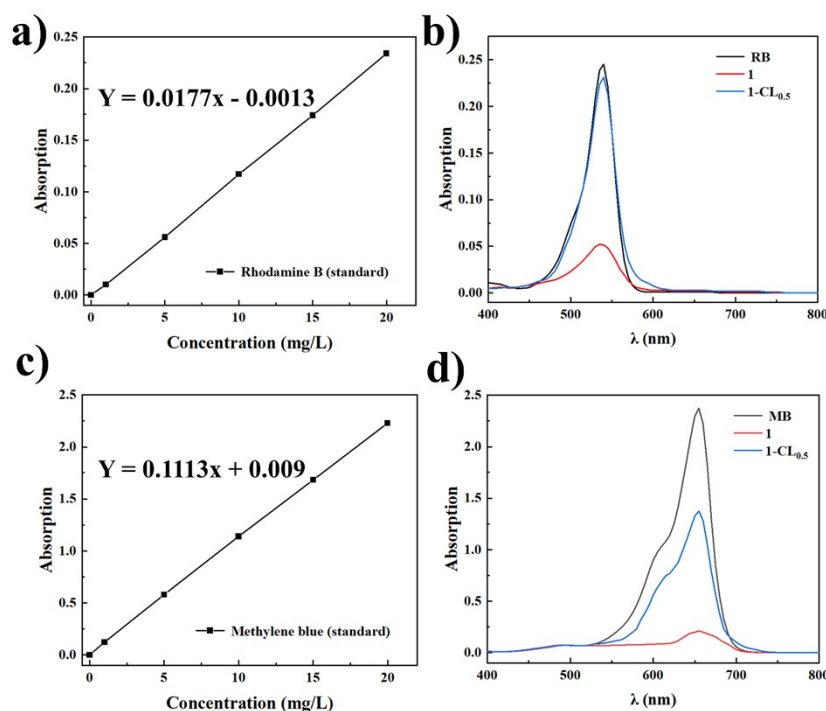


Figure S11 UV-Vis absorption spectra of Rhodamine B (RB) and methylene blue (MB) solution before and after adsorption by 1 and 1-CL_{0.5}. RB/MB (20 mg/L, 3 mL), 1/1-CL_{0.5} (3 mg), 24 h.

9 PXRD spectra of 1 and 1-CL_{0.5}

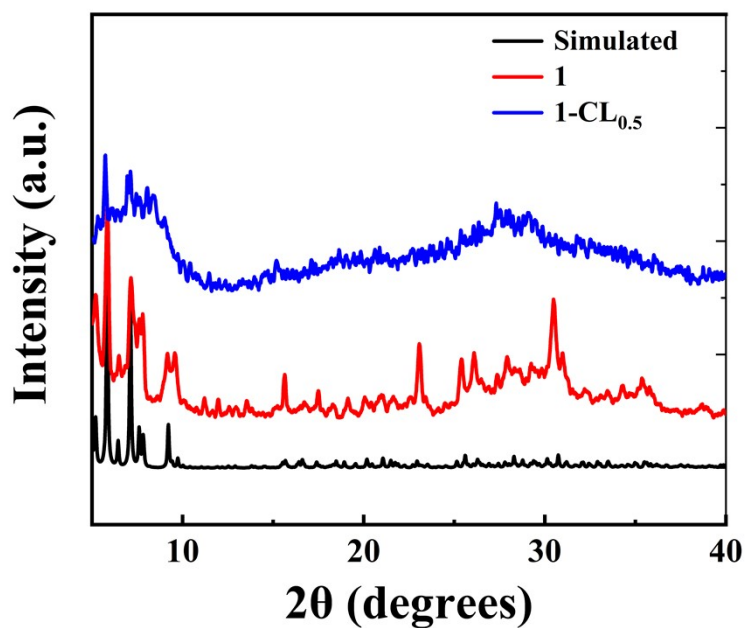


Figure S12 Experimental and simulated PXRD patterns of 1 and 1-CL_{0.5}.

10. TGA result of 1 and 1-CL_{0.5}

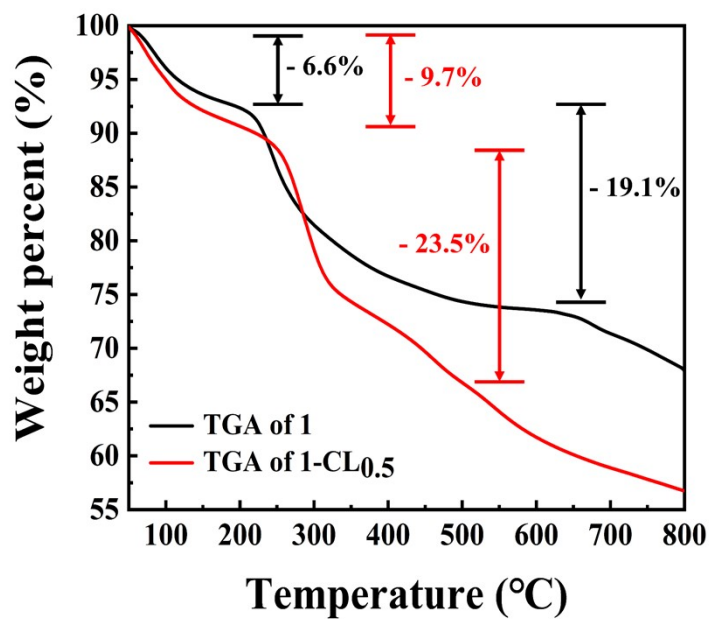


Figure S13 TGA curve for 1 and 1-CL_{0.5}.

11. FT-IR spectra of 1, 1-CL_{0.5} and HDI

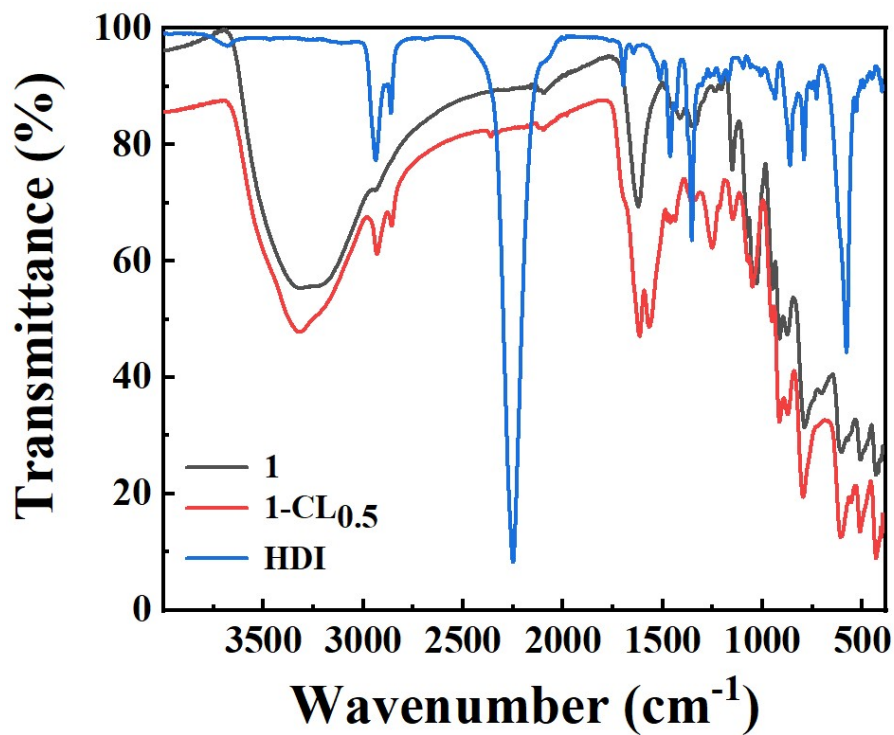


Figure S14 The FT-IR spectra of 1, 1-CL_{0.5} and hexamethylene diisocyanate(HDI)

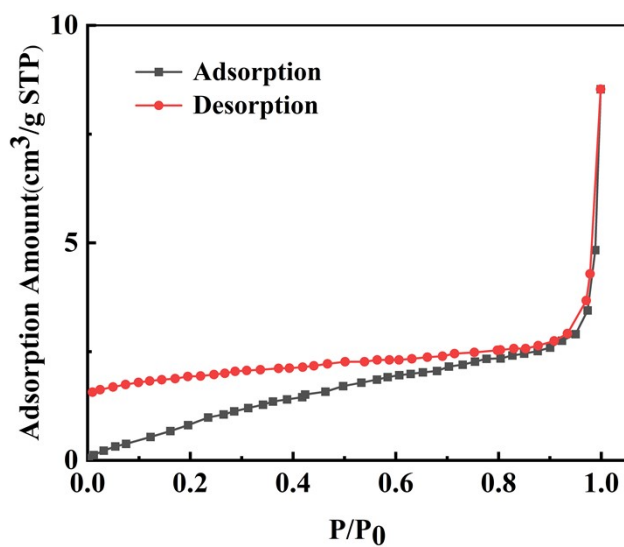


Figure S15 N_2 adsorption of 1-CL_{0.5}

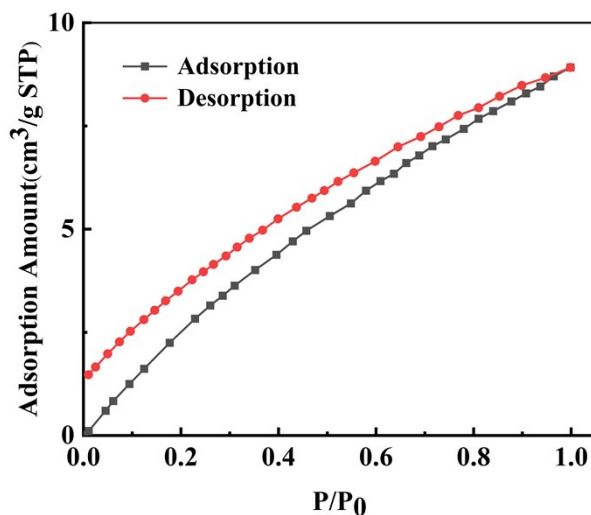
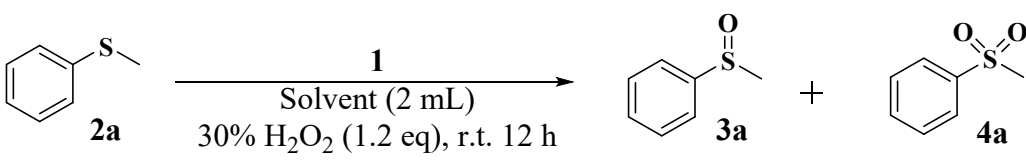


Figure S16 CO₂ adsorption of **1-CL_{0.5}**

12. The general procedure of sulfoxidation by **1**

Compound **1** (0.4 mol%), sulfide (0.2 mmol), H₂O₂ (1.05 eq), internal standard (mesitylene 0.2 mmol) and solvent (2 mL) are added into the test tube (φ20 mm × 170 mm), and the magnetic stir bar coated with PTFE is added for stirring at room temperature for certain time. After the reaction, the reaction solution is tested by GC-MS, and the products are confirmed by comparison of their GC-Mass spectra with those of authentic data, and the yield is calculated according to the internal standard. Thioanisole is taken as a model compound. Similarly, we screen solvent, the amount of catalyst and H₂O₂. After the reaction, the catalyst is deposited at the bottom of the centrifuge tube by centrifugation, which is conducive to the recovery of the catalyst. The recovered catalyst is washed with methanol and dried.

Table S3 Screening the solvents for catalytic oxidation of sulfides^a

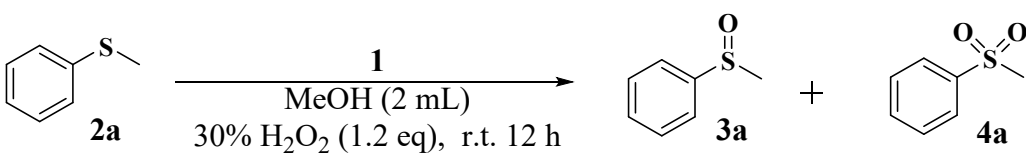


Entry	solvent	Yields (%) ^b	
		3a	4a
1	Methanol	83	17
2	Ethanol	45	25
3	Acetonitrile	25	5
4	Ethyl ether	24	39
5	Ethyl acetate	22	41
6	Acetone	10	n.d.
7	2-Butanone	37	11
8	Dichloromethane	38	7
9	(trifluoromethyl)benzene	10	45
10	Tetrahydrofuran	26	4
11	Trichloromethane	41	18
12	N,N-Dimethylformamide	25	n.d.
13	Dimethyl sulfoxide	n.d.	n.d.

^aReaction conditions: 2a (0.2 mmol), **1** (0.4 mol%), 30% H₂O₂ (1.2 eq), r.t., methanol (2 mL), 12 h.

^bYields are determined by GC-MS using mesitylene as an internal standard. The “n.d.” means “not detected”.

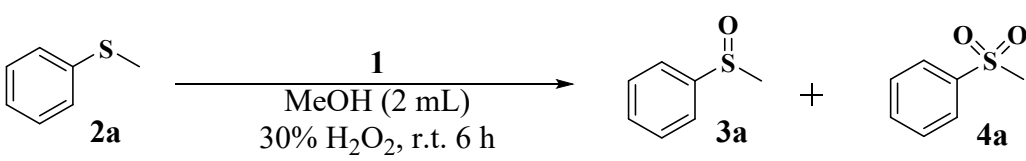
Table S4 Screening the amount of catalyst for catalytic oxidation of sulfides^a



Entry	Amount of catalyst (mol%)	Yields (%) ^b	
		3a	4a
1	0.1	90	3
2	0.2	92	8
3	0.4	95	5
4	0.6	87	13

^aReaction conditions: 2a (0.2 mmol), 30% H₂O₂ (1.2 eq), r.t., methanol (2 mL), 12 h. ^bYields are determined by GC-MS using mesitylene as an internal standard.

Table S5 Screening the amount of H₂O₂ for catalytic oxidation of sulfides^a



Entry	Oxidant/substrate (eq)	Yields (%) ^b	
		3a	4a
1	1.00	86	n.d.
2	1.05	95	5
3	1.10	94	2
4	1.20	93	4
5	1.30	93	7
6	1.40	90	10

^aReaction conditions: 2a (0.2 mmol), **1** (0.4 mol%), 30% H₂O₂, r.t., methanol (2 mL), 6 h. ^bYields are determined by GC-MS using mesitylene as an internal standard. The “n.d.” means “not detected”.

Table S6 Catalytic oxygenation of 2a using various catalysts and methanol as solvent^a

Entry	Catalyst	Yields (%) ^b	
		3a	4a
1	1	95	5
2 ^c	—	7	n.d.
3 ^d	Na ₇ [MnV ₁₃]·18H ₂ O	60	40
4 ^e	K ₅ PW ₁₀ V ₂ O ₄₀	30	n.d.
5 ^f	Ce(NO ₃) ₃ ·6H ₂ O	55	Trac e
6 ^g	α-cyclodextrin	n.d.	n.d.
7	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀	83	14
8	Na ₇ [MnV ₁₃]·18H ₂ O, Ce(NO ₃) ₃ ·6H ₂ O	83	17
9	Na ₇ [MnV ₁₃]·18H ₂ O, α-cyclodextrin	88	12
10	K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O	83	12
11	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O	88	7
12	K ₅ PW ₁₀ V ₂ O ₄₀ , α-cyclodextrin	24	Trac e
13	Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	48	3
14	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , α-cyclodextrin	89	10
15	Na ₇ [MnV ₁₃]·18H ₂ O, Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	91	9
16	K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	81	7
17	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	88	10

^aReaction conditions: 2a (0.2 mmol), **1** (0.4 mol%), 30% H₂O₂ (1.05 eq), r.t., methanol (2 mL), 6 h.

^bYields are determined by GC-MS using mesitylene as an internal standard. ^cNo catalyst.

^dNa₇[MnV₁₃]·18H₂O (0.4 mol%). ^eK₅PW₁₀V₂O₄₀ (0.8 mol%). ^fCe(NO₃)₃·6H₂O (2.4 mol%). ^gα-cyclodextrin (0.8 mol%). The “n.d.” means “not detected”.

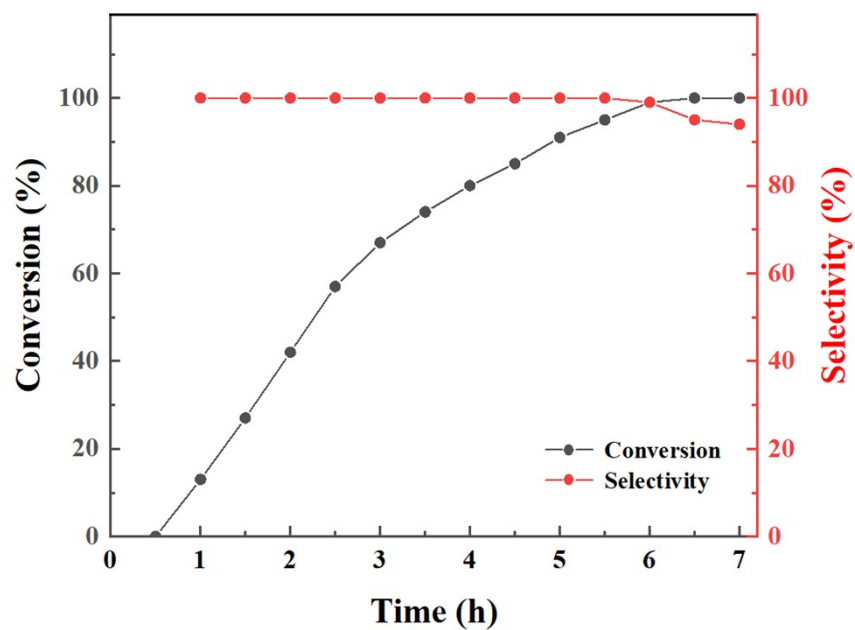


Figure S17 Relationship between conversion and selectivity of sulfoxidation of thioanisole over time

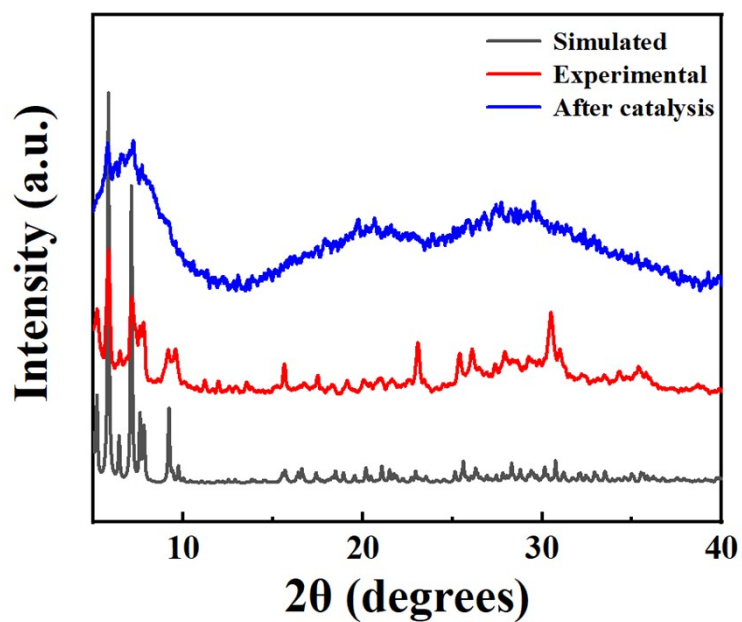


Figure S18 Comparison of the PXRD patterns of 1 before and after sulfoxidation

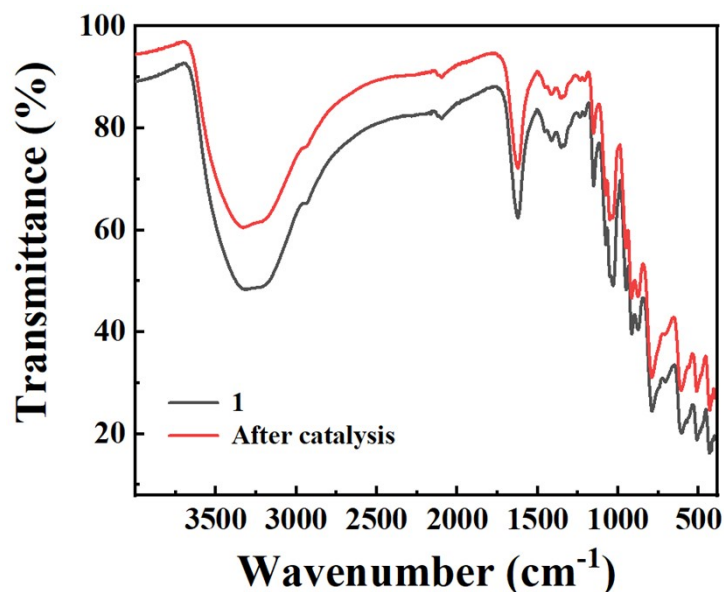


Figure S19 The FT-IR spectra of **1** before and after catalysis.

Table S7 Elemental Analysis of **1** after Catalysis

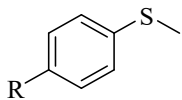
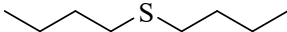
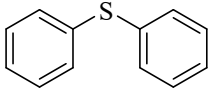
Element	Mn	V	Ce	P	W	C	H
Calculated value (%)	0.52	7.78	8.02	0.59	35.10	8.25	2.46
Actual value (%)	0.59	8.04	8.27	0.59	35.45	8.34	2.45
After catalysis (%)	0.59	7.94	8.19	0.62	35.78	8.15	2.59
Mother liquor after catalyst filtration (%)	0.01	0.13	0.13	0.02	0.55	-	-

13. The general procedure of sulfoxidation by **1-CL_{0.5}** at r.t.

1-CL_{0.5} (0.4 mol%), sulfide (0.2 mmol), H₂O₂ (1.05 eq), internal standard (mesitylene 0.2 mmol) and solvent (2 mL) are added into the test tube (φ20 mm × 170 mm), and the magnetic stir bar coated with PTFE is added for stirring for 19h at room temperature. After the reaction, the reaction solution is tested by GC-MS, and the products are confirmed by comparison of their GC-Mass spectra with those of authentic data, and the yield is calculated according to the internal standard. After the reaction, the catalyst is deposited at the bottom of the centrifuge tube by centrifugation, which is conducive to the recovery of the catalyst. The recovered catalyst is washed with methanol and dried.

Table S8 Substrate scope of catalytic oxidation of sulfides^a

$$\begin{array}{ccc} \text{R}_1-\text{S}-\text{R}_2 & \xrightarrow[\text{30\% H}_2\text{O}_2 \text{ (1.05 eq), r.t. 19 h}]{\text{1-CL}_{0.5} \\ \text{MeOH (2 mL)}} & \text{R}_1-\overset{\text{O}}{\parallel}{\text{S}}-\text{R}_2 + \text{R}_1-\overset{\text{O}}{\parallel}{\text{S}}(\text{O})-\text{R}_2 \\ \mathbf{2} & & \mathbf{3} \quad \quad \quad \mathbf{4} \end{array}$$

Entry	Substrate		Yields (%) ^b
1		R=H	3a/4a=80/5
2		R=CH ₃	3b/4b=83/5
3		R=Cl	3c/4c=63/2
4			3d/4d=94/6
5			3e/4e=59/5

^aReaction conditions: 2a (0.2 mmol), **1-CL_{0.5}** (0.4 mol%), 30% H₂O₂ (1.05 eq), r.t., methanol (2 mL), 19 h. ^bYields are determined by GC-MS using mesitylene as an internal standard.

14. The general procedure of sulfoxidation by **1-CL_{0.5}** at 40 °C.

1-CL_{0.5} (0.4 mol%), sulfide (0.2 mmol), H₂O₂ (1.10 eq), internal standard (mesitylene 0.2 mmol) and solvent (2 mL) are added into the test tube (φ20 mm × 170 mm), and the magnetic stir bar coated with PTFE is added for stirring for 6h at 40 °C. After the reaction, the reaction solution is tested by GC-MS, and the products are confirmed by comparison of their GC-Mass spectra with those of authentic data, and the yield is calculated according to the internal standard. After the reaction, the catalyst is deposited at the bottom of the centrifuge tube by centrifugation, which is conducive to the recovery of the catalyst. The recovered catalyst is washed with methanol and dried.

Table S9 Screening the temperature for catalytic oxidation of sulfides^a

Entry	Temperature (°C)	Yields (%) ^b	
		3a	4a
1	r.t.	48	n.d.
2	40	88	4
3	50	79	2
4	60	80	4

^aReaction conditions: 2a (0.2 mmol), 1-CL_{0.5} (0.4 mol%), 30% H₂O₂, methanol (2 mL), 6 h. ^bYields are determined by GC-MS using mesitylene as an internal standard. The “n.d.” means “not detected”.

Table S10 Screening the amount of H₂O₂ for catalytic oxidation of sulfides at 40

°C^a

Entry	Oxidant/substrate (eq)	Yields (%) ^b	
		3a	4a
1	1.05	87	4
2	1.10	95	5
3	1.15	91	9
4	1.20	85	15

^aReaction conditions: 2a (0.2 mmol), 1-CL_{0.5} (0.4 mol%), 30% H₂O₂, 40 °C, methanol (2 mL), 6 h.

^bYields were determined by GC-MS using mesitylene as an internal standard.

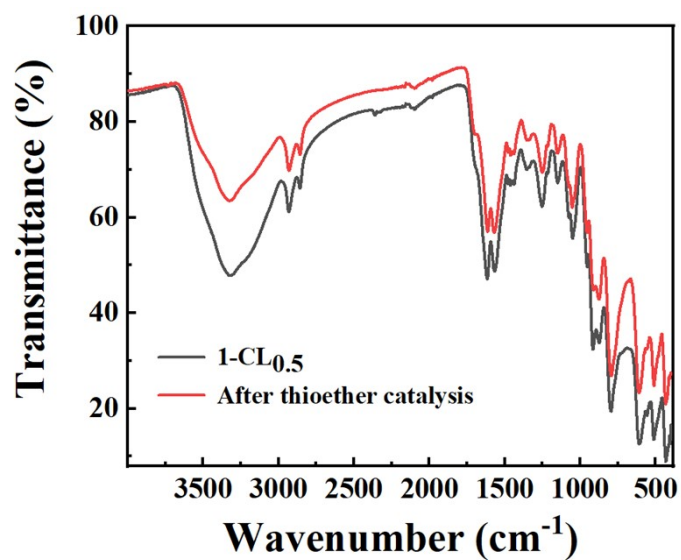


Figure S20 The FT-IR spectrum of **1-CL_{0.5}** before and after thioether catalysis

Table S11 Elemental Analysis of **1-CL_{0.5}** after Catalysis

Element	Mn	V	Ce	P	W	C	H	N
Calculated value (%)	0.40	5.97	6.16	0.45	26.93	22.15	3.45	4.92
Actual value (%)	0.48	6.04	6.34	0.41	27.15	22.42	3.65	4.66
After catalysis (%)	0.40	6.15	5.94	0.47	27.27	22.46	3.53	4.60
Mother liquor after catalyst filtration (%)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-

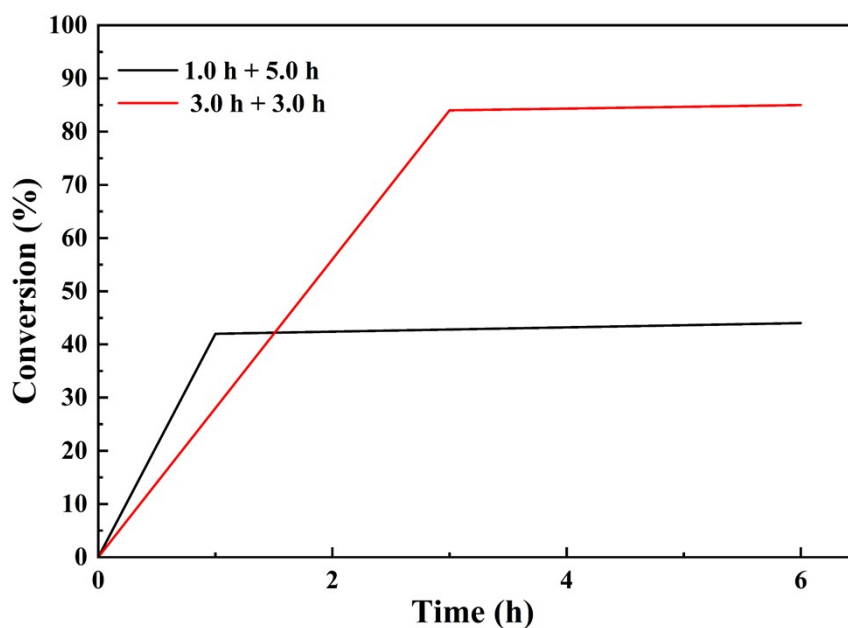
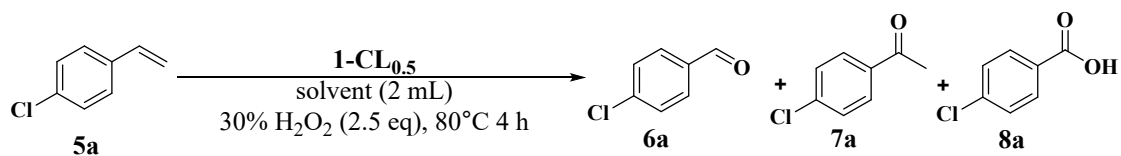


Figure S21 Hot filtration experiment using **1-CL_{0.5}** for the catalytic oxidation of benzyl sulfide.

15. General process of oxidative cleavage of alkenes by **1-CL_{0.5}**

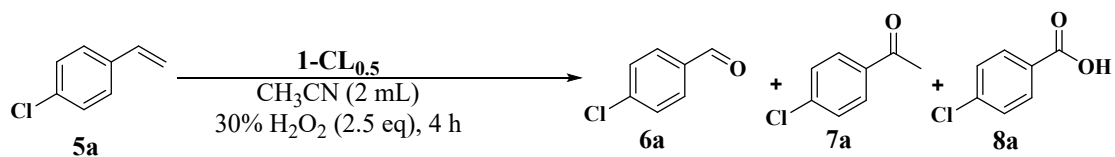
1-CL_{0.5} (0.3 mol%), alkene compounds (0.6 mmol), H₂O₂ (2.5 eq), internal standard (mesitylene/n-Hexadecane 0.2 mmol) and solvent (2 mL) are added into the seal tube, and the magnetic stir bar coated with PTFE is added for stirring at room temperature. After the reaction, the reaction solution is tested by GC-MS, and the products are confirmed by comparison of their GC-Mass spectra with those of authentic data, and the yield is calculated according to the internal standard. 4-Chlorostyrene is taken as a model compound. Similarly, we screen solvent, the amount of catalyst and H₂O₂. After the reaction, the catalyst is deposited at the bottom of the centrifuge tube by centrifugation, which is conducive to the recovery of the catalyst. The recovered catalyst is washed with methanol and dried.

Table S12 Screening the solvents for alkene compounds to aldehydes^a



Entry	solvent	Yields (%) ^b		
		6a	7a	8a
1	Acetonitrile	83	7	7
2	Ethyl acetate	72	9	9
3	Methanol	53 ^c	6	22 ^d
4	Ethanol	70 ^e	4	10 ^f
5	Tetrahydrofuran	16	13	n.d.
6	Acetone	65	14	5
7	1,4-Dioxane	34	4	2
8	N,N-Dimethylformamide	21	8	4
9	Dimethyl sulfoxide	10	n.d.	n.d.
10	Dichloromethane	n.d.	n.d.	n.d.
11	Dichloroethane	n.d.	n.d.	n.d.
12	Trichloromethane	n.d.	n.d.	n.d.
13	Toluene	n.d.	n.d.	n.d.

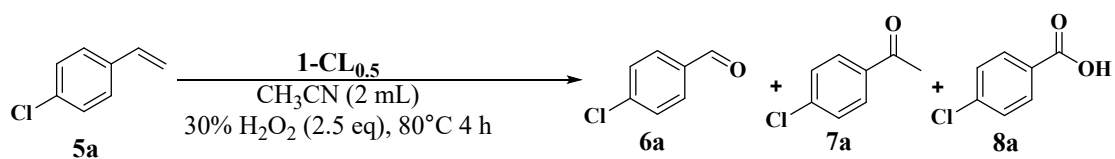
^aReaction conditions: 5a (0.6 mmol), 1-CL_{0.5} (0.05 mol%), 30% H₂O₂ (2.5 eq), 80 °C, 4 h. ^bYields are determined by GC-MS using mesitylene as an internal standard. ^cYields include aldehydes and acetals. ^dThe yield of methyl benzoate. ^eYields include aldehydes and acetals. ^fThe yield of ethyl benzoate. The “n.d.” means “not detected”.

Table S13 Screening the temperature for alkene compounds to aldehydes^a

Entry	Temperature (°C)	Yields (%) ^b		
		6a	7a	8a
1	70	84	5	6
2	80	88	5	7
3	90	85	4	6

^aReaction conditions: 5a (0.2 mmol), 1-CL_{0.5} (0.05 mol%), 30% H₂O₂, acetonitrile (2 mL), 4 h.

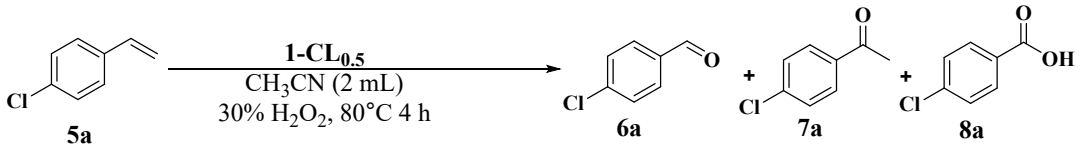
^bYields are determined by GC-MS using mesitylene as an internal standard.

Table S14 Screening the amount of catalyst for alkene compounds to aldehydes^a

Entry	Amount of catalyst (mol%)	Yields (%) ^b		
		6a	7a	8a
1	0.025	74	8	4
2	0.050	88	5	7
3	0.100	75	8	10

^aReaction conditions: 5a (0.6 mmol), 30% H₂O₂ (2.5 eq), 80 °C, acetonitrile (2 mL), 4 h. ^b Yields are determined by GC-MS using mesitylene as an internal standard.

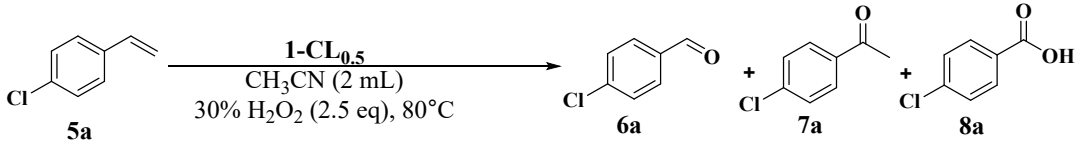
Table S15 Screening the amount of H₂O₂ for alkene compounds to aldehydes ^a



Entry	Oxidant/substrate (eq)	Yields (%) ^b		
		6a	7a	8a
1	2.0	71	7	2
2	2.2	75	7	5
3	2.3	86	5	4
4	2.4	86	2	7
5	2.5	88	5	7
6	2.6	85	5	9
7	2.8	71	6	23
8	3.0	65	6	28

^aReaction conditions: 5a (0.2 mmol), 1-CL_{0.5} (0.05 mol%), 30% H₂O₂, 80 °C, acetonitrile (2 mL), 4 h. ^bYields are determined by GC-MS using mesitylene as an internal standard.

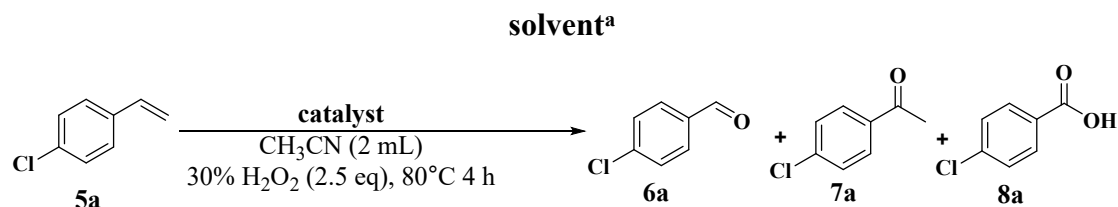
Table S16 Screening time for alkene compounds to aldehydes ^a



Entry	Time (h)	Yields (%) ^b		
		6a	7a	8a
1	2.0	76	5	n.d.
2	3.0	84	6	n.d.
3	3.5	82	5	4
4	4.0	88	5	7
5	4.5	85	5	9

^aReaction conditions: 5a (0.2 mmol), 1-CL_{0.5} (0.05 mol%), 30% H₂O₂ (2.5 eq), 80 °C, acetonitrile (2 mL). ^bYields were determined by GC-MS using mesitylene as an internal standard. The “n.d.” means “not detected”.

Table S17 catalytic oxygenation of 5a using various catalysts and acetonitrile as



Entry	Catalyst	Yields (%) ^b		
		6a	7a	8a
1	1-CL _{0.5}	88	5	7
2 ^c	—	25	5	n.d.
3 ^d	Na ₇ [MnV ₁₃]·18H ₂ O	51	2	n.d.
4 ^e	K ₅ PW ₁₀ V ₂ O ₄₀	24	10	n.d.
5 ^f	Ce(NO ₃) ₃ ·6H ₂ O	28	3	n.d.
6 ^g	α-cyclodextrin	15	4	n.d.
7	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀	26	2	n.d.
8	Na ₇ [MnV ₁₃]·18H ₂ O, Ce(NO ₃) ₃ ·6H ₂ O	63	10	14
9	Na ₇ [MnV ₁₃]·18H ₂ O, α-cyclodextrin	34	5	n.d.
10	K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O	25	8	n.d.
11	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O	68	21	2
12	K ₅ PW ₁₀ V ₂ O ₄₀ , α-cyclodextrin	27	12	n.d.
13	Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	6	3	n.d.
14	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , α-cyclodextrin	38	11	n.d.
15	Na ₇ [MnV ₁₃]·18H ₂ O, Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	8	4	n.d.
16	K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	58	21	n.d.
17	Na ₇ [MnV ₁₃]·18H ₂ O, K ₅ PW ₁₀ V ₂ O ₄₀ , Ce(NO ₃) ₃ ·6H ₂ O, α-cyclodextrin	68	11	5

^aReaction conditions: 5a (0.6 mmol), **1-CL_{0.5}** (0.05 mol%), 30% H₂O₂ (2.5 eq), 80 °C, acetonitrile (2 mL), 4 h. ^bYields are determined by GC-MS using mesitylene/n-Hexadecane as an internal standard. ^cNo catalyst. ^dNa₇[MnV₁₃]·18H₂O (0.05 mol%). ^eK₅PW₁₀V₂O₄₀ (0.1 mol%). ^fCe(NO₃)₃·6H₂O (0.3 mol%). ^gα-cyclodextrin (0.1 mol%). The “n.d.” means “not detected”.

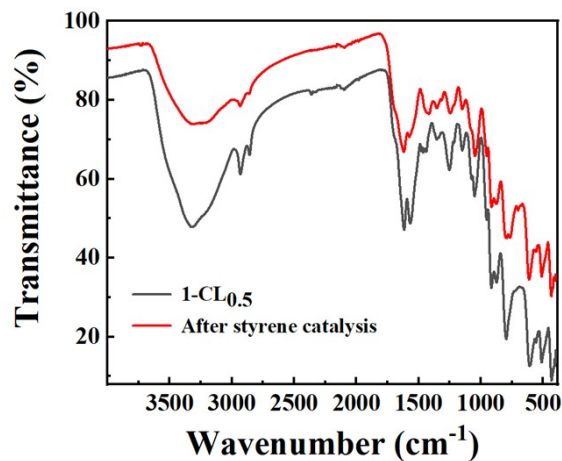


Figure S22 The FT-IR spectra of **1-CL_{0.5}** and after styrene catalysis

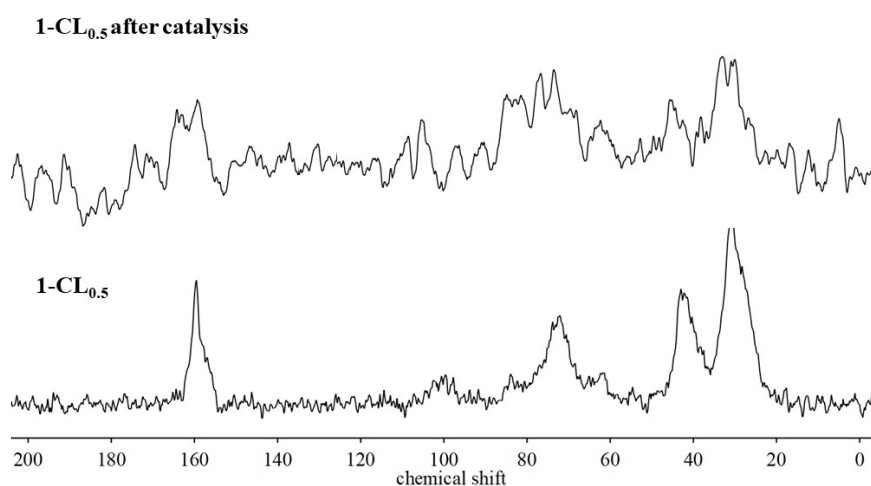


Figure S23 ¹³C solid-state NMR spectrum of **1-CL_{0.5}** and after styrene catalysis

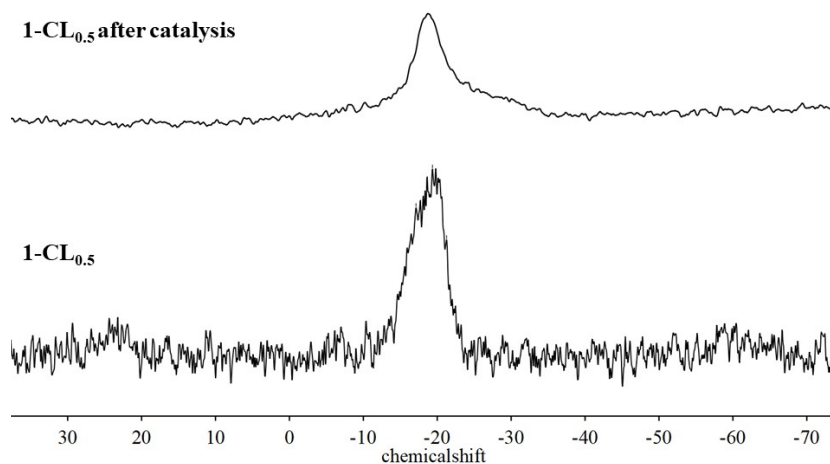


Figure S24 ^{31}P solid-state NMR spectrum of **1-CL_{0.5}** and after styrene catalysis

Table S18 Elemental Analysis of 1-CL_{0.5} after Catalysis

Element	Mn	V	Ce	P	W	C	H	N
Calculated value (%)	0.40	5.97	6.16	0.45	26.93	22.15	3.45	4.92
Actual value (%)	0.48	6.04	6.34	0.41	27.15	22.42	3.65	4.66
After catalysis (%)	0.41	6.14	5.92	0.44	27.38	22.39	3.34	4.70
Mother liquor after catalyst filtration (%)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	-	-	-

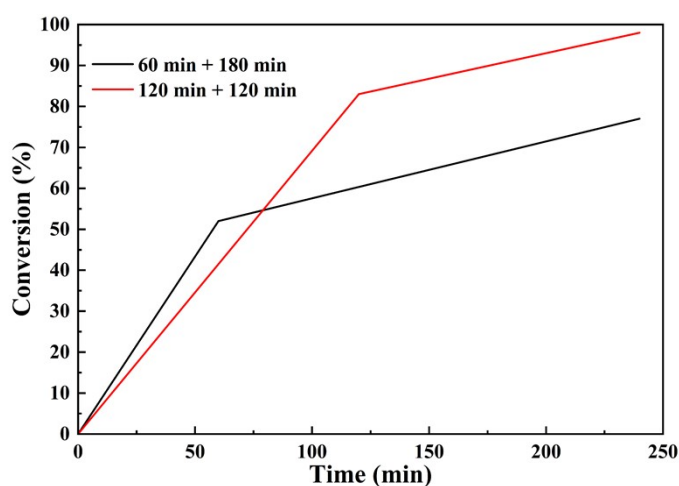


Figure S25 Hot filtration experiment using **1-CL_{0.5}** for the catalytic oxidation of p-chlorostyrene.

16. Recycling experiments.

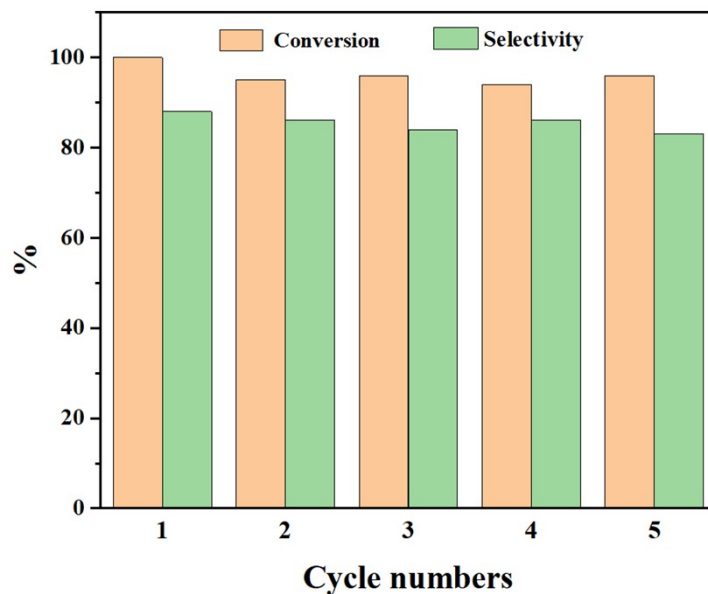


Fig. S26 Recycling experiments for the catalytic oxidation of 4-Chlorostyrene.

17. References

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