

Supporting Information

Highly Efficient Oxidation of Various Thioethers Catalyzed by Organic Ligand Modified Polyoxomolybdates

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I . Supplementary experiments

Materials and methods

We used chemicals that were commercially purchased without further purification ($\text{Na}_2\text{MoO}_4/\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}/\text{PABA}/\text{CoCl}_2 \cdot 6\text{H}_2\text{O}/\text{MnCl}_2 \cdot 2\text{H}_2\text{O}/\text{NiCl}_2 \cdot 6\text{H}_2\text{O}/\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and CsCl were purchased from Energy Chemical and J&K Chemicals; Methyl phenyl/1-Methyl-4-(methylthio)benzene/1-Methoxy-4-(methylthio)benzene/4-Chlorothioanisole/4-Fluorothioanisole/benzyl sulfide/phenyl sulfide and 2-chloroethyl ethyl sulfide were purchased from Aladdin and Sigma-Aldrich). Elemental analyses (H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; P, Mo, Co, Mn and Cs were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. We detected the IR spectra using KBr pellets as the background in the range $400\text{--}4000\text{ cm}^{-1}$ on an Alpha Centaur FT/IR spectrophotometer. TG analyses were performed in flowing N_2 at a heating rate of $10^\circ\text{C min}^{-1}$ on a Perkin-Elmer TGA7 instrument. The PXRD patterns of the samples were recorded on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromatized Cu-K α radiation ($\lambda = 0.154\text{ nm}$) and 2θ varying from 5° to 50° . The diffuse reflectivity spectra were performed on finely ground samples with a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere, which were measured from 200 to 800 nm. The GC analysis was performed with an Agilent HP6890 spectrometer with a flame ionization detector, which was used to monitor the conversion and selectivity. GC-MS at the final time point was used to confirm the identity of the products. The

GC–MS spectra were measured on an Agilent HP6890/5973MSD spectrometer. ¹HNMR spectroscopy was also used to monitor conversation and ascertain the product. And ¹HNMR spectra were collected on a 500 MHz Bruker Avance III system in CDCl₃.

CAUTION: The simulant of CWAs CEES, is highly toxic and must be handled only by trained personnel using applicable safety procedures in a closed system or in a hood under good ventilation.

Synthesis of Cs₃[AsMo₆O₂₁(PABA)₃]·nH₂O (5)

The synthetic procedure was similar to that used for **1** but without metal cations. The filtrate was kept undisturbed for two weeks under ambient conditions, and then light yellow crystals were isolated. FTIR data (cm⁻¹): 3367 (s), 1603 (s), 1539 (s), 1411 (s), 1278 (m), 1173(m), 1076(w), 926(m), 890 (w), 779 (m), 675 (s), 568(w), 448 (w).

Synthesis of {CoAsMo₆(PABA)₃}

The synthetic procedure was similar to that used for **1**, with the central hetero material Na₂HPO₃·5H₂O (0.0216 g, 0.1 mmol) alone instead of As₂O₃ (0.0197 g, 0.1 mmol). The filtrate was kept undisturbed for two weeks under ambient conditions, and then pink crystals were isolated. FTIR data (cm⁻¹): 3360 (s), 1607 (s), 1548 (s), 1413 (w), 1271 (m), 1178(m), 923(m), 894(s), 777 (w), 678 (m), 620(w), 512 (m).

Synthesis {CoTeMo₆(PABA)₃}

The synthetic procedur was similar to that used for **1**, with the central hetero material Na₂HPO₃·5H₂O (0.0216 g, 0.1 mmol) alone instead of Na₂TeO₃ (0.022 g, 0.1

mmol). The filtrate was kept undisturbed for two weeks under ambient conditions, and then pink crystals were isolated. FTIR data (cm⁻¹): 3385 (s), 1604 (s), 1533 (s), 1406 (s), 1281 (w), 1178(m), 903(s), 768 (w), 728 (w), 637(s), 513 (w).

X-ray crystallography

A Bruker Smart CCD diffractometer with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) was used to collect the crystallographic data of four compounds at 293 K or 220 K by θ and ω scan modes. The method of empirical absorption correction was adopted. SHELXTL-97 software was used to solve the structures of **1** and **2** and refine the data.¹ In **1** and **2**, most non-H atoms are refined anisotropically, and only some of water molecules were excepted. H atoms linked to the C and N atoms were fixed in their ideal positions. To get reasonable thermal parameters and atom sites, some commands such as “isor” and “dfix” were utilized. Table S8 S9 summarizes the structural determination and crystallographic data for **1** and **2**.

The CCDC reference numbers for compounds **1** and **2** are 1949665 and 1949666.

II. Supplementary structure figures

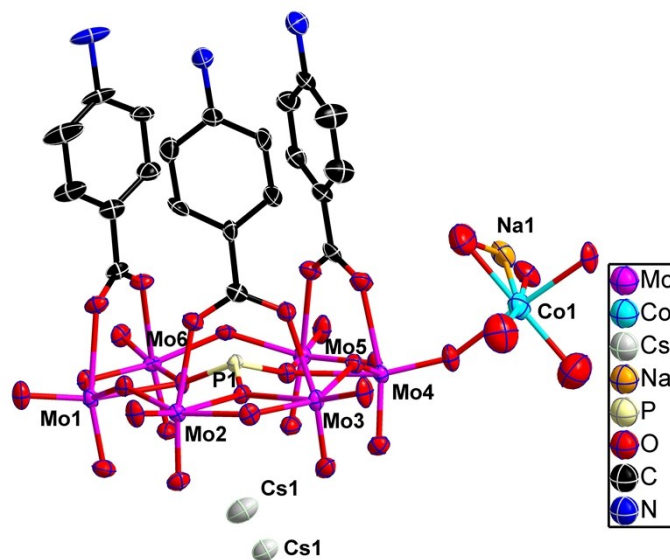


Fig. S1. ORTEP drawing of **1** with thermal ellipsoids at 50% probability. Free water molecules are omitted for clarity. (color code: Co light blue, Mo purple, P light yellow, O red, N blue, C black).

III. FT-IR spectroscopy

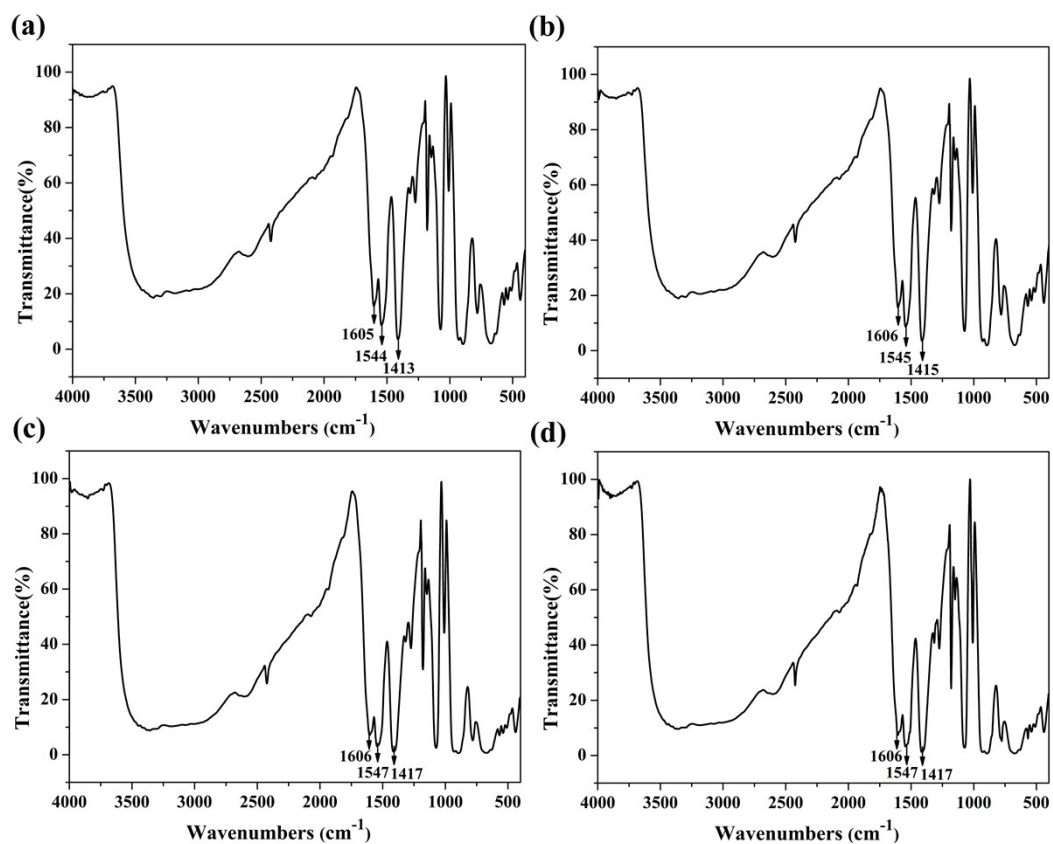


Fig. S2. IR spectra for compounds 1-4.

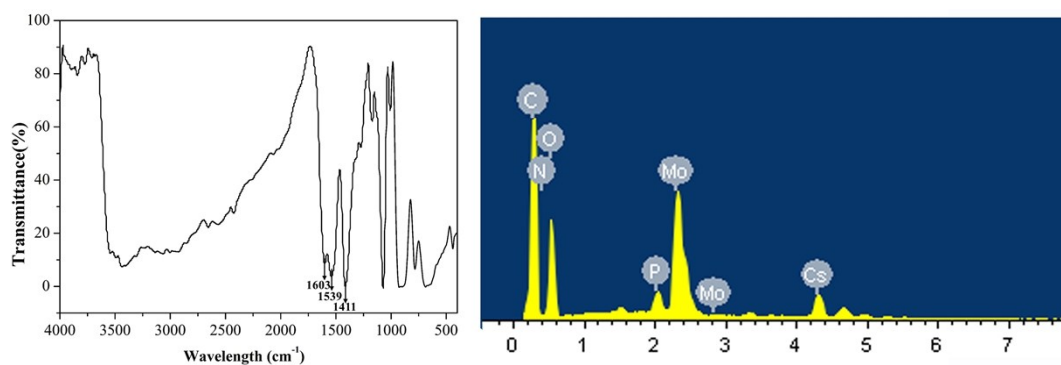


Fig. S3. IR spectrum and EDS data for compound 5.

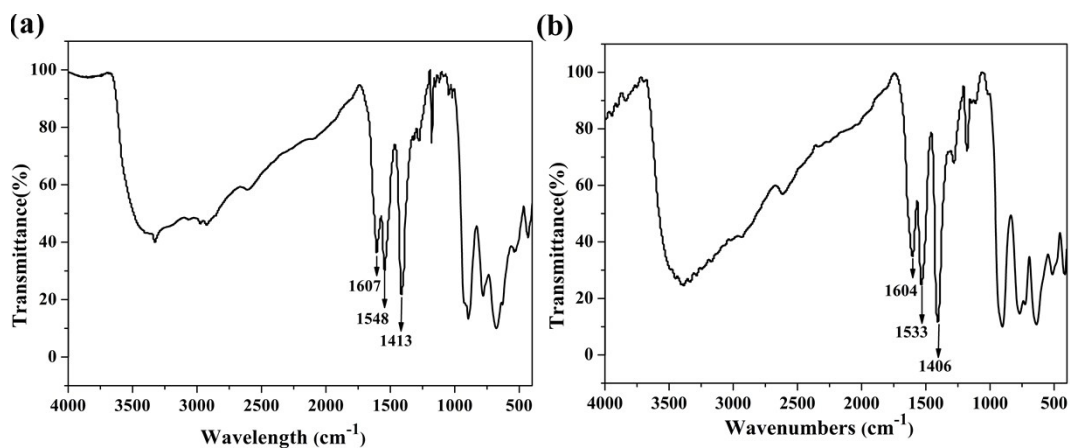


Fig. S4. a) IR spectra for $\{\text{CoAsMo}_6(\text{PABA})_3\}$; b) IR spectra for $\{\text{CoTeMo}_6(\text{PABA})_3\}$.

IV. UV-Vis spectroscopy

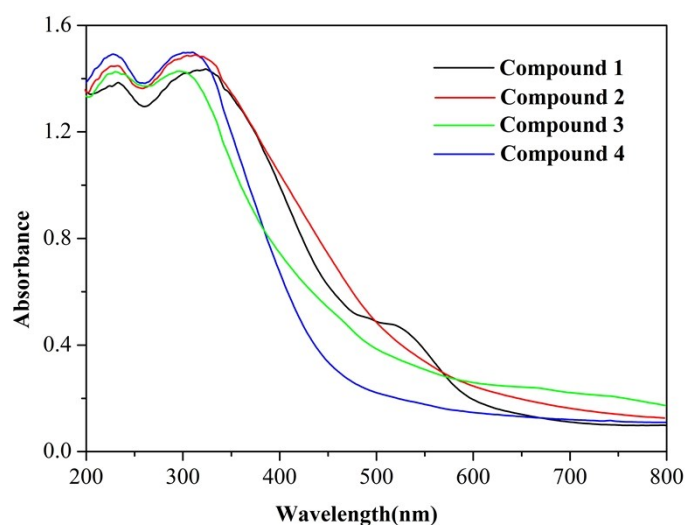


Fig. S5. UV-vis diffuse reflectance spectra of compounds 1-4.

V. TG analysis and PXRD

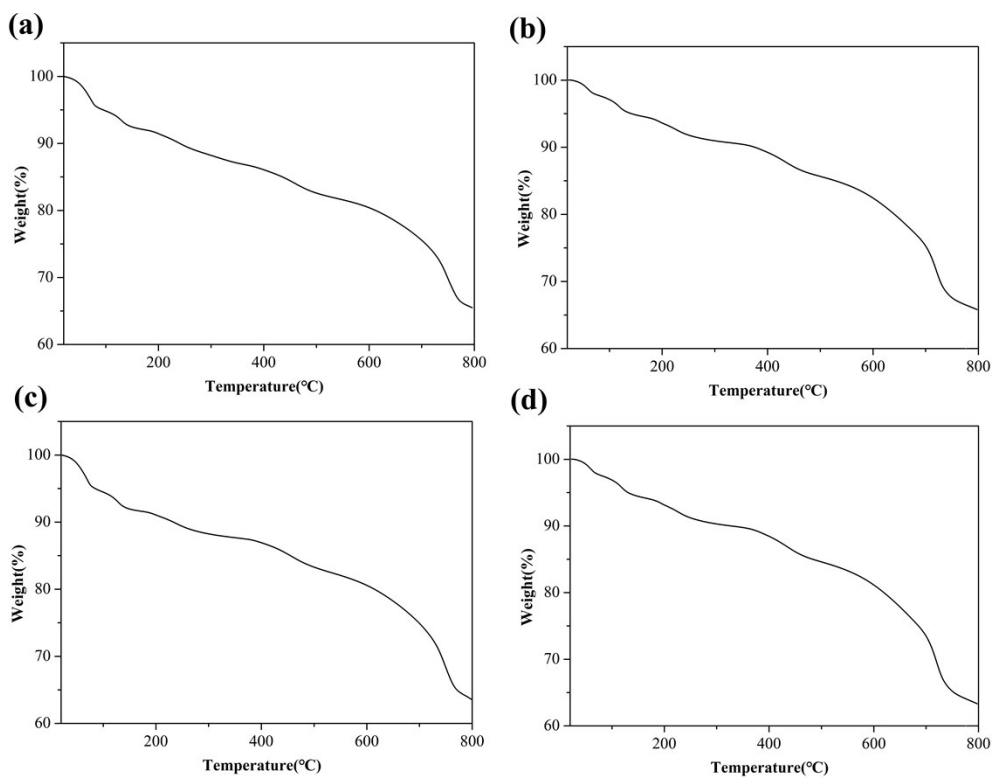


Fig. S6. Thermogravimetric plots of compounds 1-4.

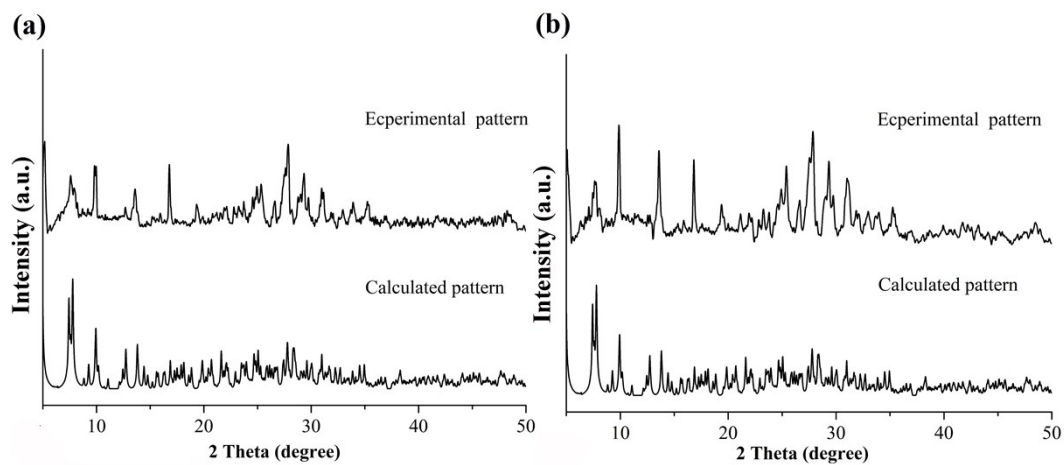


Fig. S7. a, b) The calculated and experimental PXRD patterns for compounds 1 and 2.

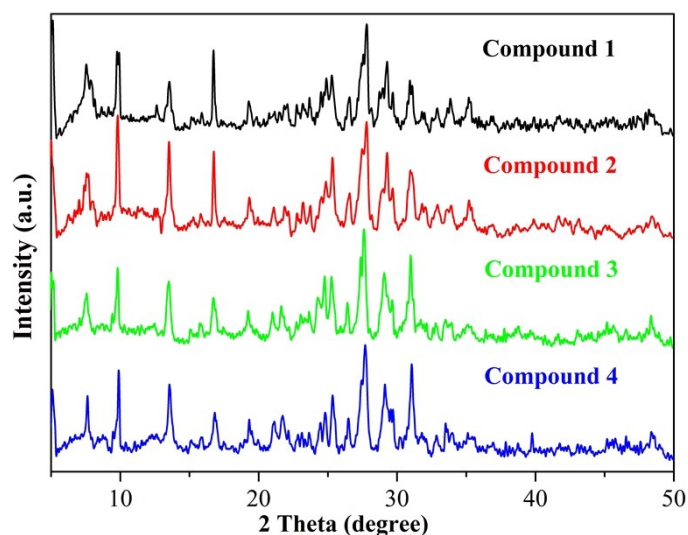


Fig. S8. The comparison of the experimental PXRD among compounds 1-4.

VI. Kinetics Study

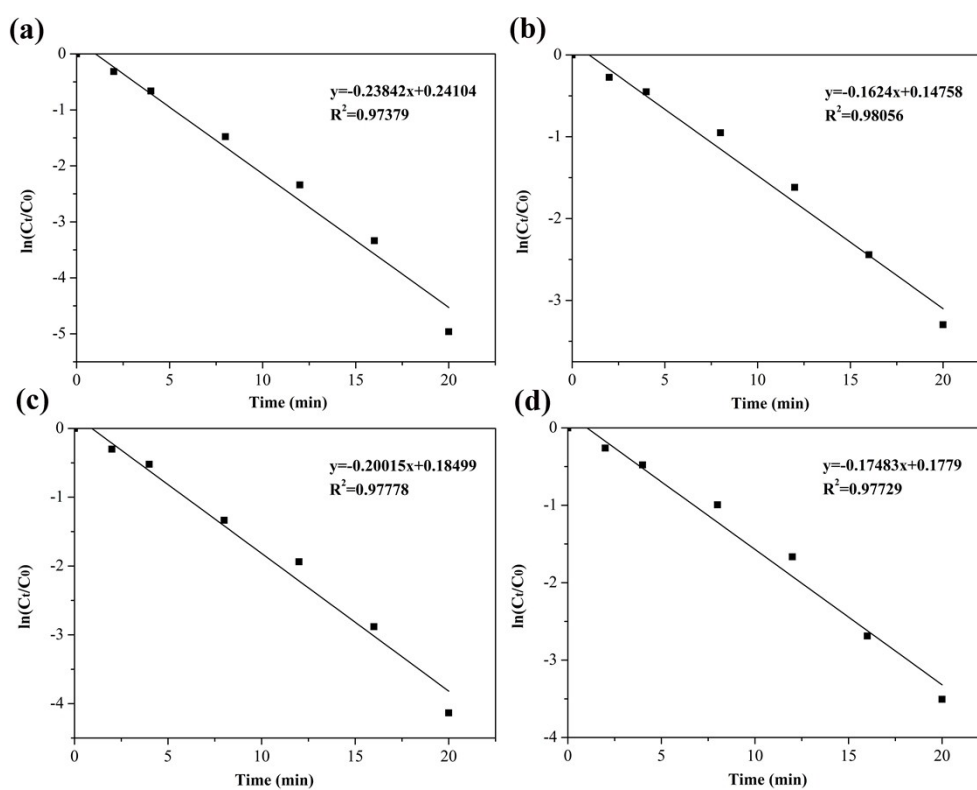


Fig. S9 a, b, c, d) Kinetic analysis of methyl phenyl sulfide oxidation for compounds 1-4 ($\ln(C_t/C_0)$ versus reaction time, C_t and C_0 represent the concentration of methyl phenyl sulfide at some time and at the starting time).

VII. ¹H NMR Data

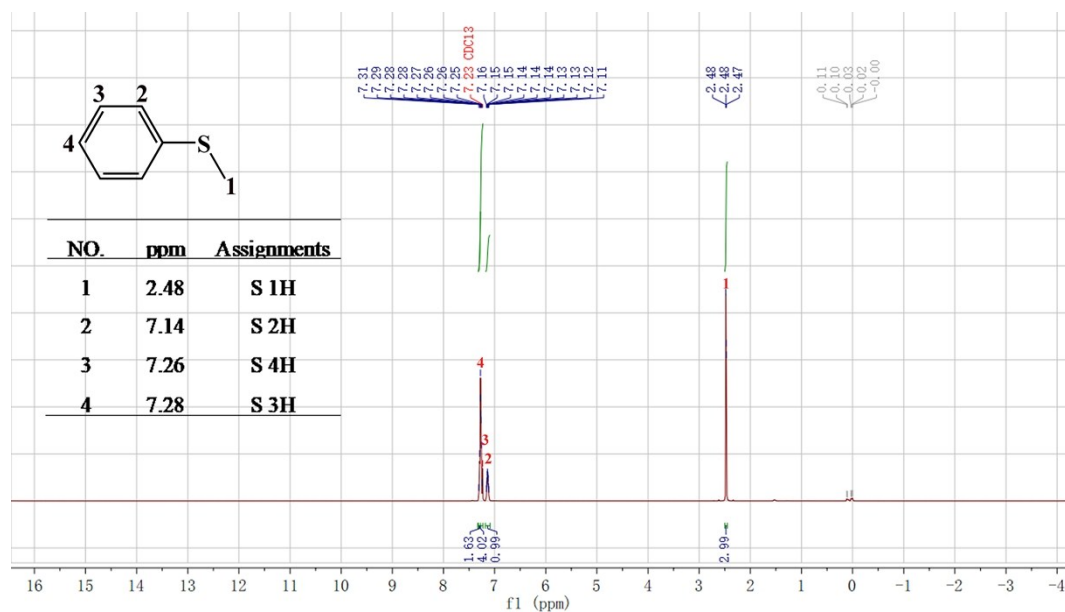


Fig. S10 ¹H NMR Data for methyl phenyl sulfide.

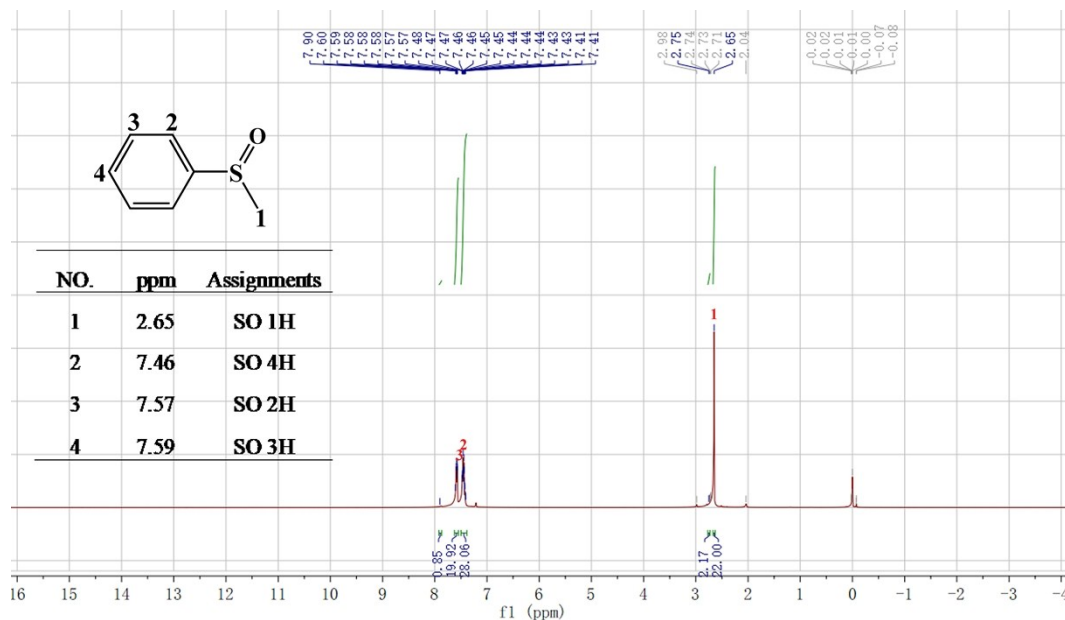


Fig. S11 ¹H NMR Data for methyl phenyl sulfoxide.

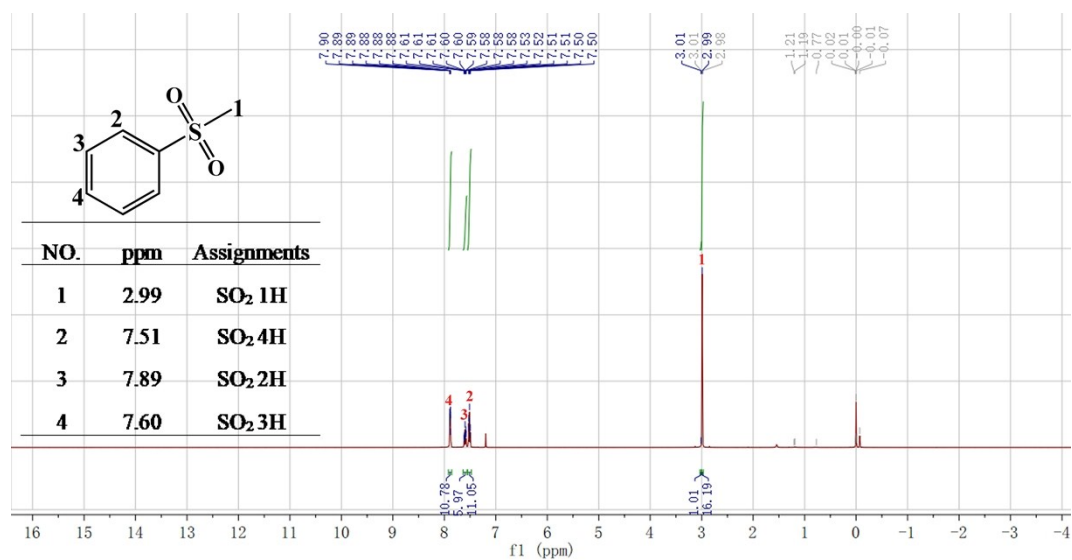


Fig. S12 ¹H NMR Data for methyl phenyl sulfone.

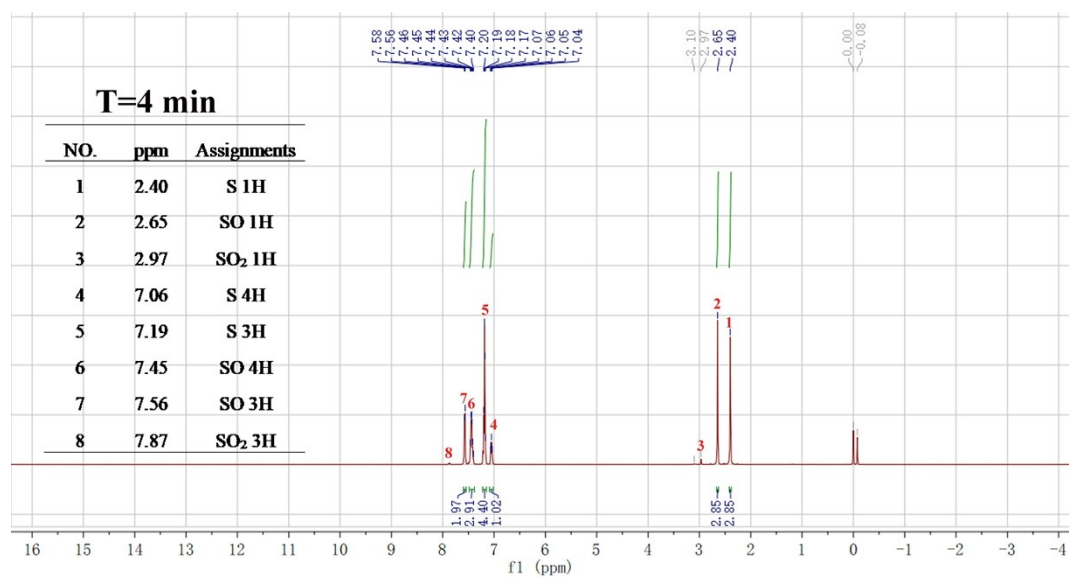


Fig. S13 ¹H NMR Data for oxidation of methyl phenyl sulfide at 4 min.

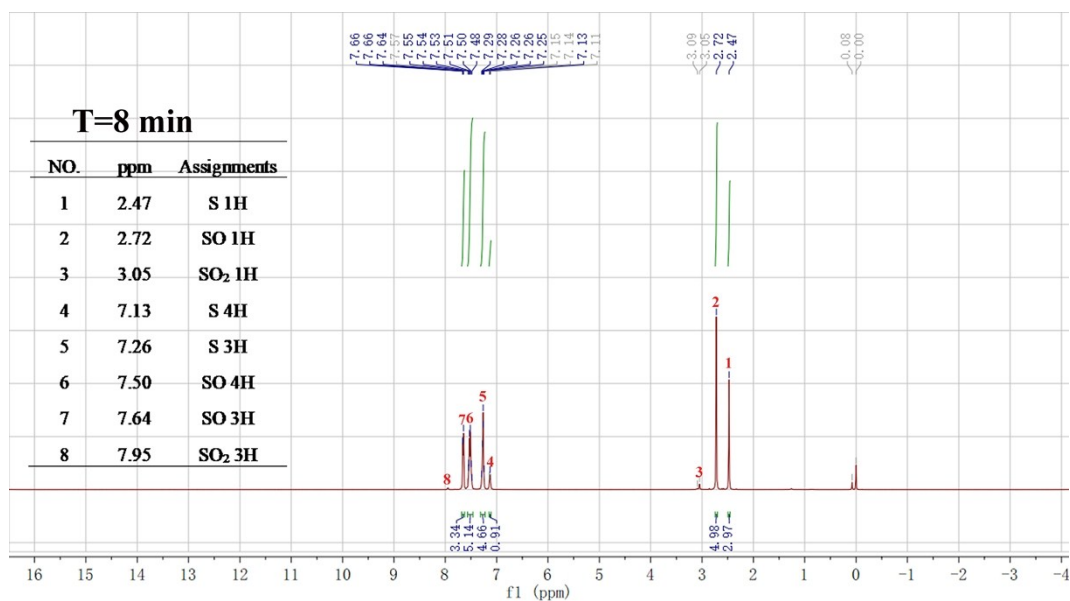


Fig. S14 ¹H NMR Data for oxidation of methyl phenyl sulfide at 8 min.

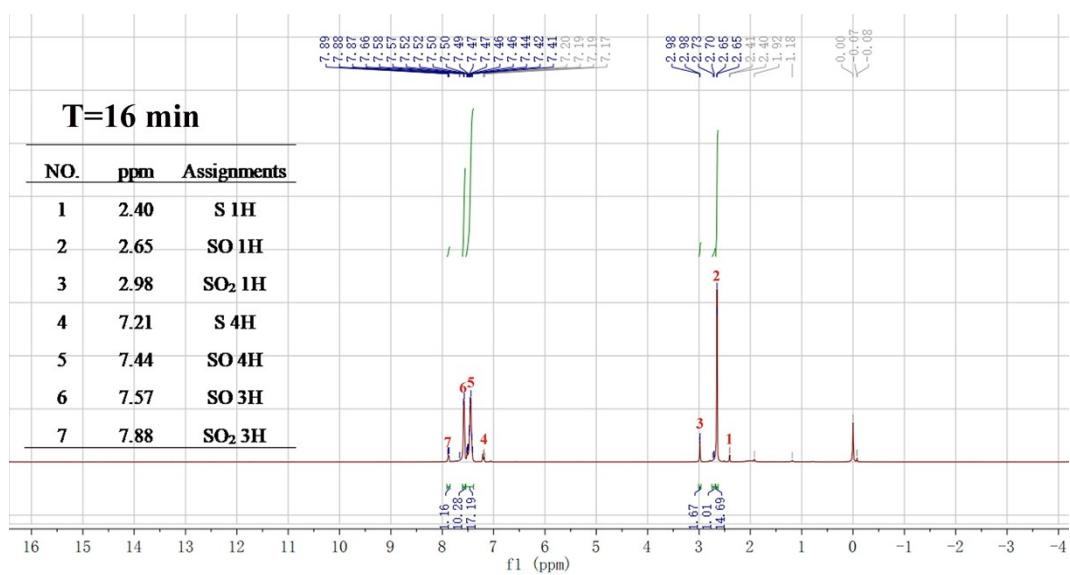


Fig. S15 ¹H NMR Data for oxidation of methyl phenyl sulfide at 16 min.

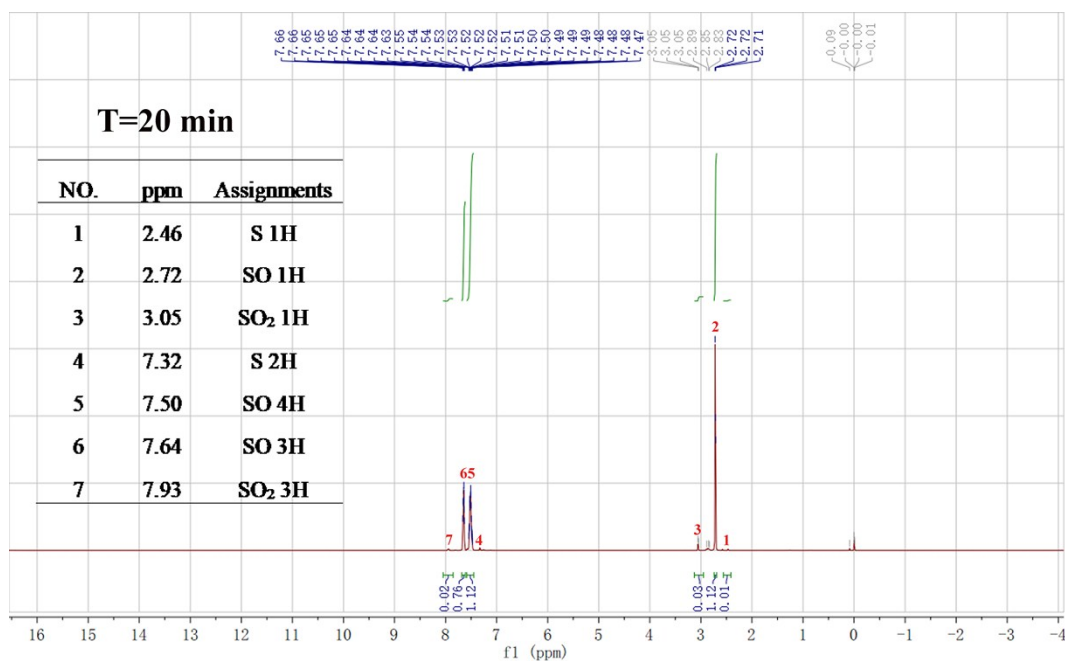


Fig. S16 ¹H NMR Data for oxidation of methyl phenyl sulfide at 20 min.

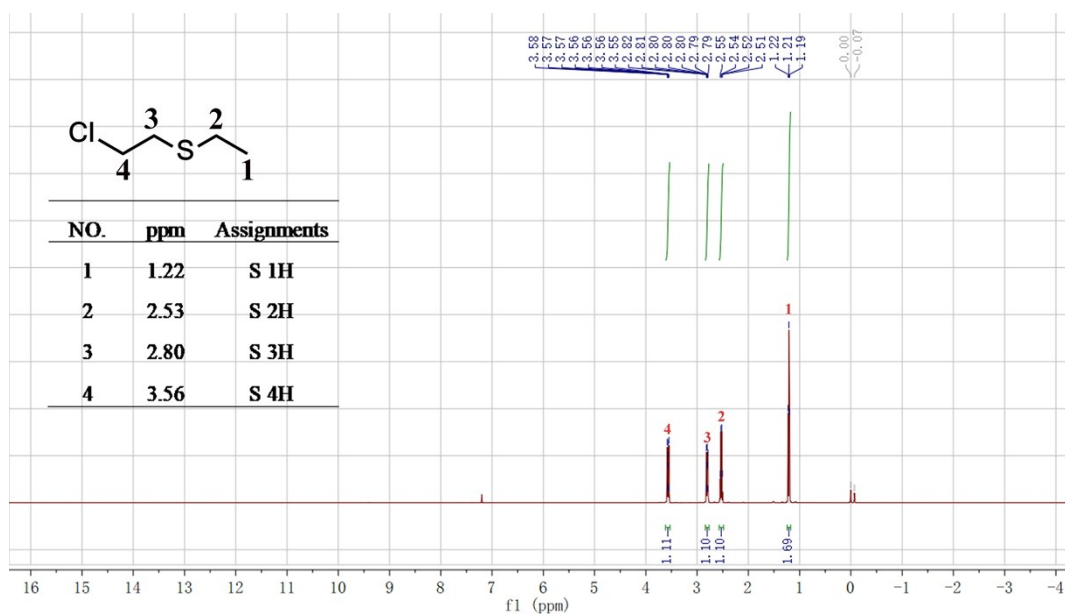


Fig. S17 ¹H NMR Data for CEES.

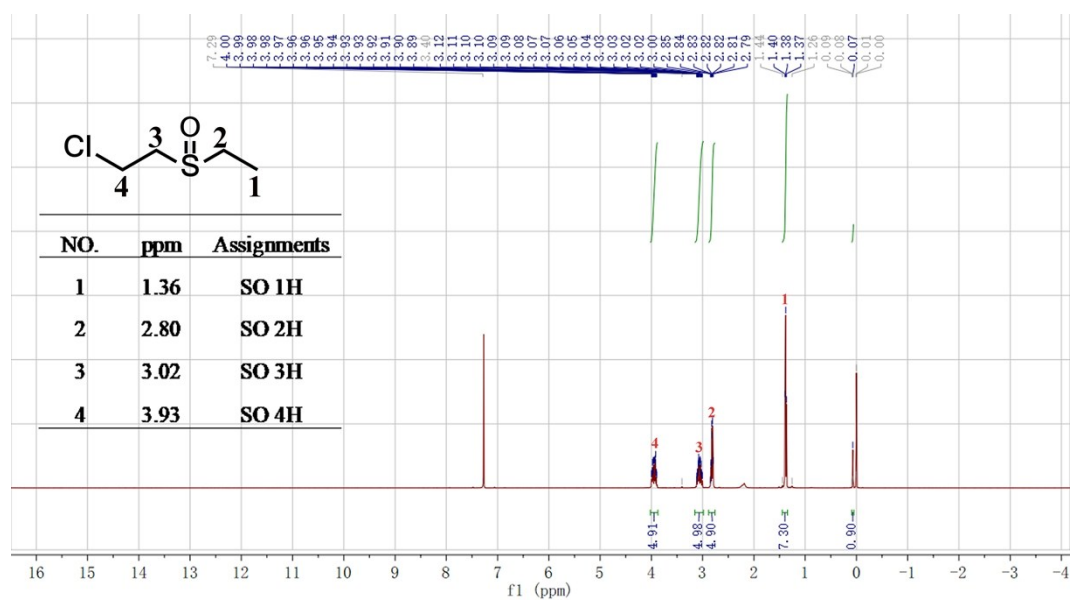


Fig. S18 ¹H NMR Data for CEESO.

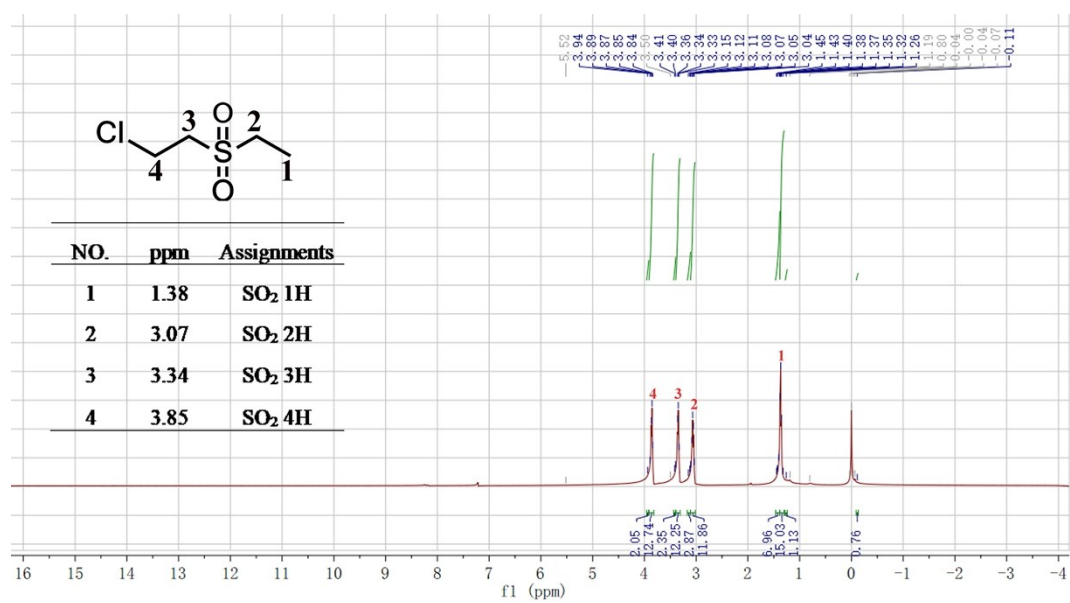


Fig. S19 ¹H NMR Data for CEESO₂.

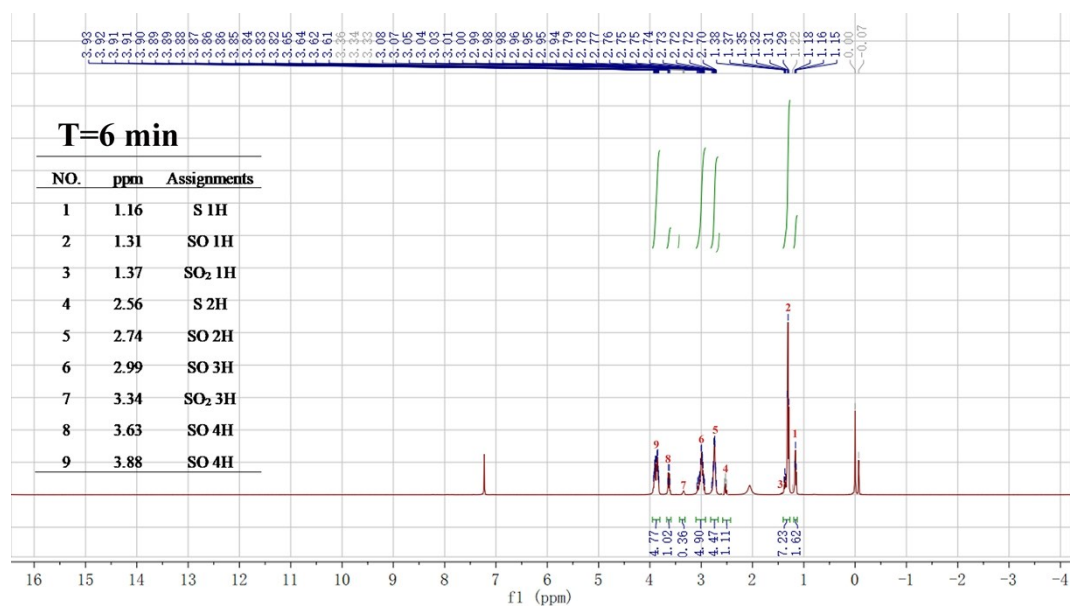


Fig. S20 ¹H NMR Data for oxidation of CEES at 6 min.

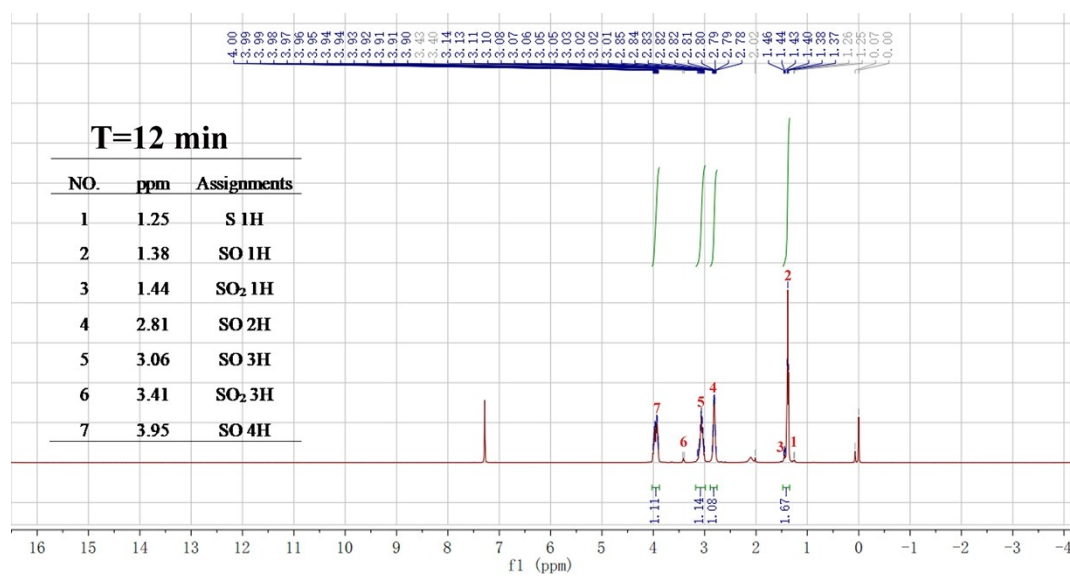


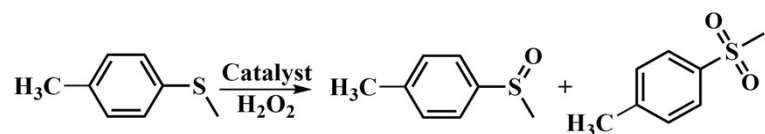
Fig. S21 ¹H NMR Data for oxidation of CEES at 12 min.

VIII. Catalytic oxidation study for various organic sulfides

Table S1. Comparison of methyl phenyl sulfide oxidation in heterogeneous manner by different materials based on POMs in recent years

catalysts	Time (min)	Oxidant	Temperature (°C)	Conversion (%)	Sulfoxide selectivity (%)	refs
1	20	H ₂ O ₂	25	99	98.0%	This work
2	20	H ₂ O ₂	25	96.3	97.1%	This work
3	20	H ₂ O ₂	25	98.3	97.6%	This work
4	20	H ₂ O ₂	25	97.3	97.4%	This work
{Cu ₃ (ptz) ₄ (Co ₂ Mo ₁₀)}	240	TBHP	40	99	100	33
{[Cu(mIM) ₄]V ₂ O ₆ }	240	UHP	40	98.7	100	34
V ^V ₁₇ V ^{IV} ₁₂ (C ₆ H ₈ O ₄) ₈	60	TBHP	25	98	91	30
P ₂ W ₁₅ -Al ₂ O ₃	35	H ₂ O ₂	25	95	99	25a
PW ₁₂ @Al-MCF _{en}	45	H ₂ O ₂	25	100	92	19
{As ₄ W ₄₀ O ₁₄₀ (Ru ₂ (Ac) ₂)}	60	H ₂ O ₂	50	97.4	87	29a
SBA-15/K ₆ P ₂ W ₁₈ O ₆₂	60	H ₂ O ₂	25	96.9	98	20
PDDA-SiV ₂ W ₁₀	300	H ₂ O ₂	25	100	91	24

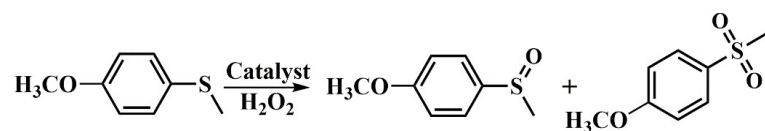
Table S2. Oxidation of 1-Methyl-4-(methylthio)benzene to the corresponding sulfoxide and sulfone. ^aSelectivity to sulfoxides, the byproduct was sulfone



Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	98.4	97.5
{CoAsMo ₆ (PABA) ₃ }	20	96.2	91.4
{CoTeMo ₆ (PABA) ₃ }	20	95.1	92.6

Reaction conditions: 0.25 mmol 1-Methyl-4-(methylthio)benzene, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

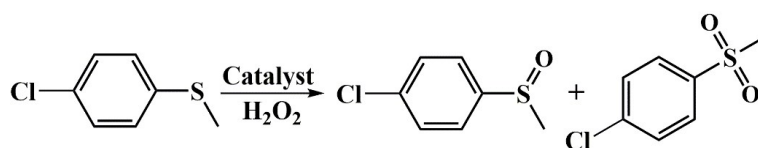
Table S3. Oxidation of 1-Methoxy-4-(methylthio)benzene to the corresponding sulfoxide and sulfone. ^aSelectivity to sulfoxides, the byproduct was sulfone



Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	98	96.5
{CoAsMo ₆ (PABA) ₃ }	20	95.4	92.1
{CoTeMo ₆ (PABA) ₃ }	20	95	91.1

Reaction conditions: 0.25 mmol 1-Methoxy-4-(methylthio)benzene, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

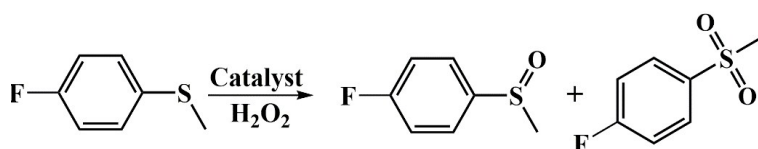
Table S4. Oxidation of 4-Chlorothioanisole to the corresponding sulfoxide and sulfone. ^aSelectivity to sulfoxides, the byproduct was sulfone



Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	97.8	95.7
{CoAsMo ₆ (PABA) ₃ }	20	95.1	92
{CoTeMo ₆ (PABA) ₃ }	20	96	90

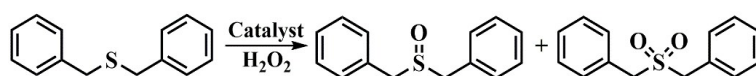
Reaction conditions: 0.25 mmol 4-Chlorothioanisole, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

Table S5. Oxidation of 4-Fluorothioanisole to the corresponding sulfoxide and sulfone. ^aSelectivity to sulfoxides, the byproduct was sulfone



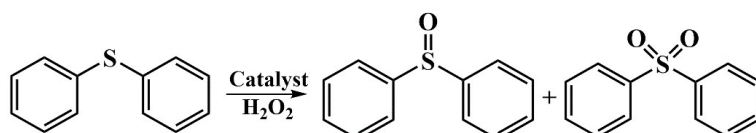
Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	98.6	96.5
{CoAsMo ₆ (PABA) ₃ }	20	94	89.0
{CoTeMo ₆ (PABA) ₃ }	20	93.1	88.8

Reaction conditions: 0.25 mmol 4-Fluorothioanisole, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

Table S6. Oxidation of benzyl sulfide to the corresponding sulfoxide and sulfone.^aSelectivity to sulfoxides, the byproduct was sulfone

Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	98.1	94.3
{CoAsMo ₆ (PABA) ₃ }	20	95.1	87.9
{CoTeMo ₆ (PABA) ₃ }	20	94.4	86.9

Reaction conditions: 0.25 mmol benzyl sulfide, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

Table S7. Oxidation of phenyl sulfide to the corresponding sulfoxide and sulfone.^aSelectivity to sulfoxides, the byproduct was sulfone

Compound	Time (min)	Con.(%)	Sel.(%) ^a
1	20	95.1	92.9
{CoAsMo ₆ (PABA) ₃ }	20	90.7	87.5
{CoTeMo ₆ (PABA) ₃ }	20	90	87

Reaction conditions: 0.25 mmol phenyl sulfide, 2.5 μmol material, 0.25 mmol naphthalene (internal standard), 0.3 mmol H₂O₂ and 0.5 mL ethanol at room temperature for 20 min

IX. X-Ray Single Crystallography Result

Table S8. Crystal data and structure refinement for **1** and **2**

Complex	1	2
formula	C ₄₂ H ₉₉ N ₆ O ₈₃ Mo ₁₂ Cs ₄ CoP ₂ Na ₂	C ₄₂ H ₁₀₃ N ₆ O ₈₅ Mo ₁₂ Cs ₄ MnP ₂
formula weight	3866.04	3852.10
T (K)	293(2)	293(2)
crystal system	Triclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> -1
a (Å)	11.6777(7)	11.7189(5)
b (Å)	12.4217(7)	12.3672(5)
c (Å)	18.5662(12)	18.6001(8)
α (°)	74.791(4)	74.667(2)
β (°)	85.539(4)	85.523(2)
γ (°)	84.253(4)	84.148(2)
U (Å ³)	2582.0(3)	2582.54(19)
Z	1	1
μ (mm ⁻¹)	2.486	2.477
reflections collected	9055	9064
independent reflections	7296	7449
R(int)	0.0391	0.0338
GOF on F ²	1.010	1.028
R ₁ ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0483	0.0540
wR ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1208	0.1509
R ₁ (all data)	0.0625	0.0657
wR ₂ (all data)	0.1300	0.1613

Table S9. Selected distances (Å) and angles (°) for **1** and **2**

Compound 1			
Mo(1)-O(14)	1.706(5)	Mo(2)-O(15)	2.230(6)
Mo(3)-O(18)	1.706(6)	Mo(4)-O(1)	2.311(6)
Mo(5)-O(9)	1.917(6)	Mo(6)-O(3)	2.300(5)
Co(1)-O(18)	2.150(7)	Co(1)-O(19)	2.137(7)
O(1)-P(1)-O(22)	110.5(3)	O(1)-P(1)-O(3)	109.5(3)
Compound 2			
Mo(1)-O(4)	1.709(7)	Mo(2)-O(21)	2.346(6)
Mo(3)-O(3)	1.717(7)	Mo(4)-O(1)	2.322(6)
Mo(5)-O(2)	2.308(6)	Mo(6)-O(21)	2.329(6)
Mn(1)-O(3)	2.127(8)	Mn(1)-O(4)	2.186(8)
O(21)-P(1)-O(2)	110.3(3)	O(1)-P(1)-O(2)	110.1(3)

X. References

- 1 a) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997*; b) G. M. Sheldrick, *SHELXL 97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997*.