Electronic supporting information

Pre-constructed multi-peroxotungstic centers for highly efficient and recyclable organophosphorus-tungstic catalysts in styrene epoxidation

Chang Xu[a,b], Yuequn Li[a,b], Lin Tang[a,b], Weiqiang Yuan[a,c], Wenxi Chen[c], Jingjing Chen[a,b*],
Haohong Li[a,d*], Huidong Zheng[a,b*]

[a]*Engineering Research Center of Advanced Manufacturing Technology for Fine Chemicals (Fujian Province University), College of Chemical Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China*

[b]*Qingyuan Innovation Laboratory, Quanzhou, Fujian, 362801, China*

[c]*Huazhi Engineering Technology Co., LTD. Fuzhou, Fujian, 350108, China*

[d]*College of Chemistry, Fuzhou University, Fuzhou, Fujian, 350108, China*

*Corresponding authors: jing_chem@fzu.edu.cn (J. Chen), youngman@fzu.edu.cn (H. Zheng)

1. Experimental section

1.1 Reagents and characterization

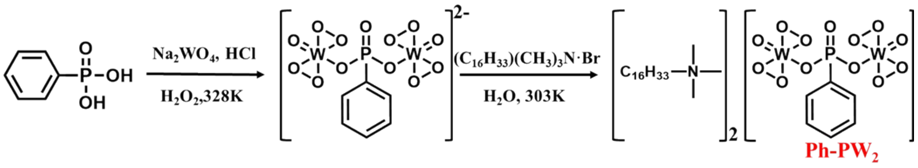
The chemicals used in this work, including phenylphosphonic acid ($PhP{=}O(OH)_2$) (AR), *p*-xylylenebisphosphonic acid ($Ph(p\text{-}CH_2P{=}O(OH)_2)_2$, 97%), H_3PO_4 (85%), $(C_{16}H_{33})(CH_3)_3N\cdot Br$ (HTMA·Br) (AR), $(C_{18}H_{37})_2(CH_3)_2N\cdot Cl$ (DMDOA·Cl) (AR), Na_2SO_4 (99%), Na_2WO_4 (98%), H_2O_2 (30%), styrene (98%), limonene (95%), 1-octene (99%), cyclohexene (98%), cyclooctene (99%), styrene oxide (99%), toluene (AR), ethyl acetate (AR), N, N-dimethylformamide (DMF, AR), $C_2H_4Cl_2$ (AR) and $CHCl_3$ (AR) were obtained from commercial resource and used without further purification.

FT-IR spectra were recorded on a Thermo Scientific Nicolet iS50 spectrophotometer in the range of 400–4000 cm^{-1} via KBr model. Raman spectra were analyzed on a Renishaw OPTIMA 8000 in the range of 200~1000 nm. Elemental analysis of C, H, N, O were obtained from a

Elementar Vario EL cube apparatus. P and W contents were determined by a Thermoi CAP7400 ICP spectrometer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DRK-400 apparatus in $CDCl_3$. X-ray diffraction (XRD) patterns were obtained on a Philips X'Pert-MPD diffractometer (Cu Kα radiation, λ=1.54056 Å) in the scanning range of 5~60°. X-ray photoelectron spectroscopy (XPS) were measured through the Thermo Fisher Scientific ESCALAB 250X system. The element mapping of catalysts was scanned by ultra-high-resolution SEM (Helios G4 CX). The concentrations in the reacting system were determined by a gas chromatograph (GC-2014C) equipped with an InerCap-5 capillary column. And the qualitative analysis of the products and by-products were performed by a GC-MSQP2020 NX GC-MS equipped with a Rtx-5MS column.

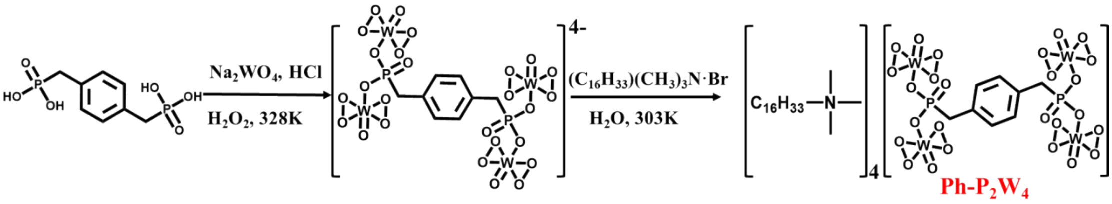
1.2 Catalysts preparation

$[(C_{16}H_{33})(CH_3)_3N]_2\cdot\{PhPO_3[W{=}O(O_2)_2]_2\}$ (labelled as Ph-PW$_2$) : Ph-PW$_2$ was prepared by reference of literature method (Scheme S1).[S1] In a 50 mL three-neck flask, Na_2WO_4 (5.9 g, 20 mmol) was dissolved in 10 mL deionized water, then HCl (2 g, 20 mmol, 36%) was dropped. The mixture was stirred for 5 min at 35°C to produce yellow solids. H_2O_2 (9.1 g, 80 mmol, 30 wt%) was added at 55°C and stirred for 10 min, during which the yellow precipitation was dissolved to obtained yellow transparent solution. In another flask, phenylphosphonic acid (0.8 g, 5 mmol) and $(C_{16}H_{33})(CH_3)_3N\cdot Br$ (3.65 g, 5 mmol) were dissolved in 100 mL deionized water under ultrasound. The latter solution was added into the former yellow solution and stirred for 1h at 600 rpm to yield yellow precipitation. The solids were separated by centrifuged, which were washed with water and dried under vacuum for 12 h. Yield: 5.0 g, 79.87% based on W. IR (KBr, cm^{-1}, Fig. S1a): 3438(s), 2920(s), 2850(s), 2360(w), 1629(m), 1487(s), 1469(s), 1146(s), 1126(m), 1051(s), 940(s), 907(s), 820(m), 729(s), 705(s), 594(w), 562(m). Elemental analysis: Cal. C 42.18%; H 7.16%; N 2.24%; O 16.60%; P 2.47%; W 29.35%; found: C 40.24%; H 7.01%; N 2.12%; O 15.61%; P 2.91%; W 32.11%.



Scheme S1 Synthetic procedure for the catalyst Ph-PW$_2$

$[(C_{16}H_{33})(CH_3)_3N]_4\cdot Ph\{CH_2PO_3[W{=}O(O_2)_2]_2\}_2$ (labelled as Ph-P$_2$W$_4$): Ph-P$_2$W$_4$ was synthesized via the same procedure with that of Ph-PW_2 (Scheme S2), except that phenylphosphonic acid was replaced by *p*-xylylenebisphosphonic acid (0.66 g, 2.5 mmol). Yellow solids (4.6 g) were obtained with yield of 74.92% based on W. IR (KBr, cm^{-1}, Fig. S1b): 3453(s), 2923(s), 2850(s), 2363(s), 2330(m), 1645(s), 1489(s), 1472(s), 1263(s), 1103(m), 1050(m), 950(s), 861(m), 804(s), 720(w), 701(w), 616(w), 585(w), 555(m). Elemental analysis: Cal. C 41.09%; H 7.22%; N 2.28%; O 16.94%; P 2.52%; W 29.95%; found: C 40.88%; H 7.53%; N 2.65%; O 17.16%; P 2.33%; W 29.45%.



Scheme S2 Synthetic procedure for the catalyst Ph-P_2W_4

$[(C_{18}H_{37})_2(CH_3)_2N]_3\cdot PO_4[WO(O_2)_2]_4$ (labelled as DMDOA-PW_4): DMDOA-PW_4 was prepared according to literature method .[S2] Firstly, in a 100 mL three-neck flask, Na_2WO_4 (5.9 g, 20 mmol) was dissolved in 15 mL H_2O to obtain clear solution, into which HCl (4.05 g, 40 mmol, 36%) was dropped. This mixture was stirred for 5 min at 35°C and then heated to 55°C, at this temperature H_2O_2 (15.88 g, 140 mmol) was added. The obtained yellow-green suspension was stirred for 30 min and centrifuged at rate of 8000 rpm for 5 min. The supernatant was moved into 85 mL H_3PO_4 aqueous solution (H_3PO_4: 5 mmol, 0.58 g H_3PO_4) and kept stirring of 10 min. 50 mL CH_2Cl_2 containing $(C_{18}H_{37})_2(CH_3)_2N\cdot Cl$ (8.80 g, 15 mmol) was added dropwise into the above yellow-green solution. The resultant emulsion was stirred for 1h at 600 rpm at room temperature. Finally, the organic phase was separated to obtain bright yellow-green solution. $CHCl_2$ was removed by rotating evaporation at 30~40°C to yield the yellow-green powders, which was labelled as DMDOA-PW_4. Yield: 12.20g, 87.02%. IR (KBr, cm^{-1}, Fig. S1b): 3440(s), 2920(s), 2850(s), 2363(w), 2330(w), 1640(m), 1470(s), 1370(m), 1080(s), 953(s), 885(m), 819(m), 804(s), 720(s),608(w), 550(m).

2.3 Styrene epoxidation reaction

In a 50 mL flask, styrene (2.1 g, 20 mmol) and catalyst Ph-PW_2 (0.5 g, 0.4 mmol) were dissolved in 8 mL $CHCl_3$, and the solution was heated to 40°C. After catalyst was dissolved completely, 30% H_2O_2 (2.3 g, 20 mmol) aqueous solution containing Na_2SO_4 (0.85 g, 6 mmol) was added dropwise and kept reacting for 2h, during which the elevating temperature must be controlled by cooling water. $CHCl_3$ was eliminated in the solvent-free reaction, during which styrene acted as not only solvent but also reactant. The usage of H_2O_2 and Na_2SO_4 were half amount of solvent-present ones. The products were extracted from reaction system at certain intervals, which was separated by centrifugation and toluene was used as internal standard for GC-MS analysis. H_2O_2 concentration during the reaction was determined by iodometric titration method. The styrene conversion (X_1), conversion in solvent-free reaction (X_2), styrene epoxide yield (Y), selectivity (S) in organic solvents and concentration of H_2O_2 were defined as follows:

$$X_1 = \frac{C_{\mathrm{styrene}\,*} - C_{styrene}}{C_{\mathrm{styrene}\,*}} \times 100\% \quad Y = \frac{C_{\mathrm{epoxide}}}{C_{\mathrm{epoxide}\,*}} \times 100\% \quad S = \frac{Y}{X_1} \times 100\%$$

$$X_2 = \frac{M_{\mathrm{styrene}\,*} - M_{\mathrm{styrene}}}{M_{\mathrm{hydrogen\ peroxide}\,*}} \times 100\%$$

$$c(H_2O_2) = \frac{V(Na_2S_2O_2) \times c(Na_2S_2O_2) \times M(H_2O_2)}{2000 \times m(H_2O_2)} \times 100\%$$

Here, $C_{\mathrm{styrene}*}$ was the initial concentration of styrene, C_{styrene} was the concentration of styrene at certain reacting times. $C_{\mathrm{epoxide}*}$ was the theoretical concentration of styrene oxide, and C_{epoxide} was the real-time concentrations of styrene oxide at certain reacting times. $M_{\mathrm{styrene}*}$ was the initial moles of styrene, M_{styrene} was the moles of styrene at certain reacting time, $M_{\mathrm{hydrogen\ peroxide}*}$ was the initial moles of H_2O_2. $V(Na_2S_2O_2)$: volume of standard $Na_2S_2O_3$ solution (mL), $c(Na_2S_2O_2)$: molar concentration of standard $Na_2S_2O_3$ (mol/L), $M(H_2O_2)$: 34.01, $m(H_2O_2)$: mass of H_2O_2.

2.4 Catalyst recovering procedure

After the styrene epoxidation was completed, the emulsion suspension was centrifuged at rate of 8000 rpm for 5 min. The obtained yellow oil phase was dissolved in equal volume of acetonitrile, then the mixture was cooled to -10°C to generate solids. Styrene oxide can be obtained by removing acetonitrile using rotating evaporation. The raw solids were washed with acetonitrile for three times and dried under vacuum. The mass recovery yields of **Ph-PW$_2$** and **Ph-P$_2$W$_4$** were 65% and 60%, respectively. Na_2SO_4 can be recovered in water phase. The recovered catalysts and Na_2SO_4 can be used in the next epoxidation reaction. Due to some mass loss of the catalysts, the recovered catalysts from previous identical reactions were combined and used in the subsequent catalytic run in the recycled reactions.

2. Additional Tables

Table S1 Element analysis of Ph-PW_2 based on formula of $[C_{16}H_{33}(CH_3)_3N]_2[C_6H_5PO_3\{WO(O_2)_2\}_2]$

Element	Atomic number	Weight/%
N	1.90	2.12
C	41.96	40.24
H	87.10	7.01
O	12.22	15.61
P	1.18	2.91
W	2.19	32.11

Table S2 Condition setting during the reaction optimization of **Ph-PW_2** catalyzed styrene epoxidation

	Optimized items	Reaction conditions
Solvent-present in Fig.2	Solvent optimization in Fig.2a	0.4 mmol Ph-PW_2, 20 mmol styrene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 100 mmol solvent, 40°C, 21 h, 500 rpm
	Reaction time optimization in Fig.2b	0.4 mmol Ph-PW_2, 20 mmol styrene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 100 mmol $CHCl_3$, 40°C, 500 rpm
	Reaction temperature optimization in Fig.2c	0.4 mmol Ph-PW_2, 20 mmol styrene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 100 mmol $CHCl_3$, 10 h, 500 rpm
	Catalyst dosage optimization in Fig.2d	20 mmol styrene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 100 mmol $CHCl_3$, 40°C, 10 h, 500 rpm
	Styrene concentration optimization in Fig.2e	0.4 mmol Ph-PW_2, 20 mmol styrene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 40°C, 10 h, 500 rpm
	Oxidant dosage optimization in Fig.2f	0.4 mmol Ph-PW_2, 20 mmol styrene, 100 mmol $CHCl_3$, 40°C, 10 h, 500 rpm, molar ratio of Na_2SO_4 and H_2O_2 3:10
Solvent-present in Fig.3	Catalytic performances of recovered catalysts in five cycles in Fig. 3c	0.4 mmol Ph-PW_2, 20 mmol styrene, 30 mmol H_2O_2, 9 mmol Na_2SO_4, 100 mmol $CHCl_3$, 10 h, 40°C, 500 rpm
Solvent-free in Fig.3	Reaction temperature optimization in Fig.3a	0.4 mmol Ph-PW_2, 20 mmol styrene, 10 mmol H_2O_2, 3 mmol Na_2SO_4, 2 h, 500 rpm
	Oxidant dosage optimization in Fig.3b	0.4 mmol Ph-PW_2, 20 mmol styrene, 2 h, 40°C, 500 rpm, molar ratio of Na_2SO_4 and H_2O_2 3:10
	Catalytic stability in solvent-free system in Fig. 3d	0.4 mmol Ph-PW_2, 20 mmol styrene, 10 mmol H_2O_2, 3 mmol Na_2SO_4, 2 h, 40°C, 500 rpm

Table S3 Catalytic performance comparison of styrene epoxidation with literatures

Catalysts	Oxidant/Solvent	$n_{Oxidant}$:$n_{Styrene}$	Temperature /time (°C/h)	Conversion/%	Selectivity/%	Ref.
$[(C_8H_{17})_3CH_3N]_3[(PO_4)\{WO(O_2)_2\}_4]$	H_2O_2/none	0.5:1	50/1	50.0	93.0	S3
$[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$	H_2O_2/ethyl acetate	0.2:1	60/3	23.8	92.0	S4
$\{[(C_8H_{17})(CH_3)_2N]_2(CH_2)_3\}_{1.5}\{PO_4[WO(O_2)_2]_4\}$	H_2O_2/CH_3CN	0.5:1	35/20	37.9	86.6	S5
$[(C_{18}H_{37})_2(CH_3)_2N]_7[PW_{11}O_{39}]$	H_2O_2/ethyl acetate	3:1	85/1	90.1	90.5	S6
$H_3PW_{12}O_{40}$	H_2O_2/isooctane-H_2O	2:1	70/8	78.0	74.0	S7
$PMo \subset Mo_{72}Fe_{30}$	H_2O_2/H_2O	0.4:1	25/5	33.4	99.0	S8
$Cs_7[PW_{10}Cu_2(H_2O)O_{38}]$	TBHP/none	1.5:1	60/8	77.9	51.6	S9
$[Cu(en)_2]_2[Cu(en)_2(H_2O)_2]_4[SiNb_{12}V_2O_{42}]\cdot 7H_2O$	TBHP/CH_3CN	2:1	80/4	82.1	48.6	S10
$C_{66}H_{54}Cu_6N_{12}O_{77}P_2W_{18}$	TBHP/CH_3CN	2:1	808	95.9	86.0	S11
$[Cu_2(4,4'\text{-bipy})_3(H_2O)_2(\mu_2\text{-}OH)_2(H_4PMo_9V_3O_{40})]\cdot 4H_2O$	O_2/CH_3CN	/	35/4	100.0	70.9	S12
$[Co_2(H_2O)_4(BBTZ)_3][HPW_{10}V_2O_{40}]$	O_2/CH_3CN	/	25/4	89	70	S13
$WO(O_2)_2(2,2'\text{-bpy})$	H_2O_2/CH_3CN	1.7:1	70/24	76.0	40.0	S14
Ph-PW_2	H_2O_2/$CHCl_3$	1.5:1	40/10	92.8	92.5	This work
Ph-PW_2	H_2O_2/none	0.5:1	40/2	93.4	94.5	This work
Ph-P_2W_4	H_2O_2/$CHCl_3$	1.5:1	40/6	93.9	95.5	This work

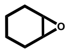
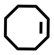
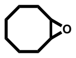
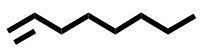
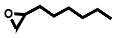
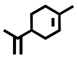
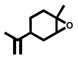
Table S4 P and W elemental analysis of aqueous/organic phases for **Ph-PW_2** after reaction

Element	Relative content/ wt%	absolute content/ g	relative content/ wt%	absolute content/ g

	aqueous phase		organic phase	
P	2.34	0.00073	96.33	0.029
W	2.52	0.0093	96.66	0.36

Reaction conditions: 1 mmol **Ph-PW$_2$**, 50 mmol styrene, 75 mmol H_2O_2, 22 mmol Na_2SO_4, 250 mmol $CHCl_3$, 10 h, 40°C, 500 rpm

Table S5 Catalytic epoxidation of different olefins to the corresponding epoxides by Ph-PW$_2$ and Ph-P$_2$W$_4$

Entry	Substrate	Product	Time/ h	Conv. in %$^{a/b}$	Sel. in %$^{a/b}$
1			2/2	95.0/95.1	94.8/99.0
2			2/2	96.8/97.0	98.5/98.7
3			21/21	89.4/92.1	93.8/94.2
4			4/3	87.8/92.3	89.1/86.1

^{a}: Catalyst: **Ph-PW$_2$**, 20 mmol alkene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 0.4 mmol Ph-PW$_2$, 40°C, 500 rpm, without solvent; ^{b}: Catalyst: **Ph-P$_2$W$_4$,** 20 mmol alkene, 20 mmol H_2O_2, 6 mmol Na_2SO_4, 0.2 mmol Ph-P$_2$W$_4$, 40°C, 500 rpm,70 mmol $CHCl_3$.

Table S6 Element analysis of Ph-P$_2$W$_4$ based on formula of $[C_{16}H_{33}(CH_3)_3N]_4[C_8H_8(PO_3)_2\{WO(O_2)_2\}_4]$

Element	Atomic number	Weight/%
N	4.65	2.65
C	83.65	40.88
H	184.91	7.53
O	26.36	17.16
P	1.84	2.33
W	3.93	29.45

Table S7 Condition setting during the reaction optimization of **Ph-P$_2$W$_4$** catalyzed styrene epoxidation reaction

Optimized items	Reaction conditions
Catalytic performance of recovered catalysts in five cycles in Fig. 4e	0.2 mmol Ph-P$_2$W$_4$, 20 mmol styrene, 30 mmol H_2O_2, 9mmol Na_2SO_4, 70 mmol $CHCl_3$, 6 h, 40°C, 500 rpm
Catalytic stability in solvent-free system in Fig. 4f	0.2 mmol Ph-P$_2$W$_4$, 20 mmol styrene, 12 mmol H_2O_2, 3.6 mmol Na_2SO_4, 2 h, 40°C, 500 rpm
Optimization of reaction time in Fig. S6a	0.2 mmol Ph-P$_2$W$_4$, 20 mmol styrene, 30 mmol H_2O_2, 9 mmol Na_2SO_4, 70 mmol $CHCl_3$, 40°C, 500 rpm

Optimization of reaction temperature Fig. S6b	0.2 mmol Ph-P_2W_4, 20 mmol styrene, 20 mmol H_2O_2, 6mmol Na_2SO_4, 70 mmol $CHCl_3$, 6 h, 500 rpm
Optimization of oxidant dosage in Fig. S6c	0.2 mmol Ph-P_2W_4, 20 mmol styrene, 70 mmol $CHCl_3$, 40°C,6 h, 500 rpm, molar ratio of Na_2SO_4 and H_2O_2 3:10;
Optimization of catalyst dosage Fig. S6d	20 mmol styrene, 30 mmol H_2O_2, 9 mmol Na_2SO_4, 70 mmol $CHCl_3$, 40°C, 6 h, 500 rpm

3. Additional Figures

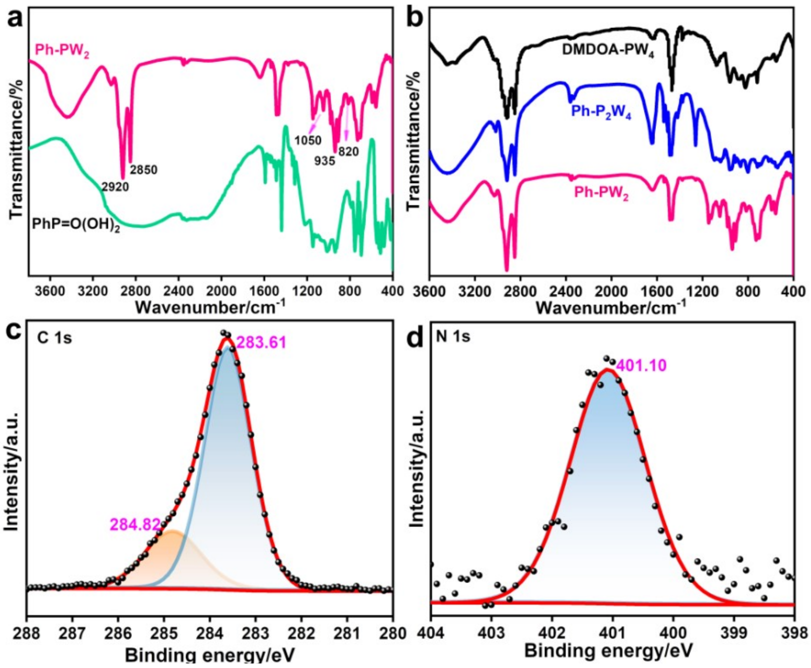


Fig. S1. (a) FT-IR spectra of **Ph-PW$_2$** catalyst and organic ligand; (b) FT-IR spectra of three catalysts in this work; (c) high-resolution XPS C 1s spectrum; (d) N 1s XPS spectrum

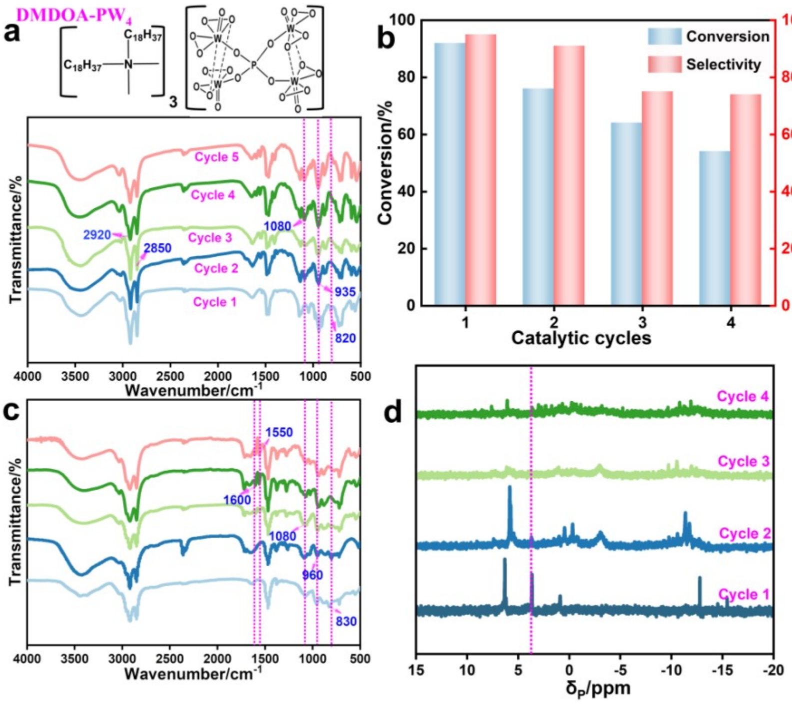


Fig. S2. (a) FT-IR spectra of recovered catalysts in five catalytic cycles together with structure of **DMDOA-PW$_4$**; (b) catalytic performances of recovered **DMDOA-PW$_4$** catalyst in four cycle (reaction condition: 0.2 mmol DMDOA-PW$_4$, 20 mmol styrene, 10 mmol H_2O_2, 3 mmol Na_2SO_4, 2 h, 30°C, 500 rpm); (c, d) FT-IR and ^{31}P NMR spectra of recovered **DMDOA-PW$_4$** catalyst in four cycles

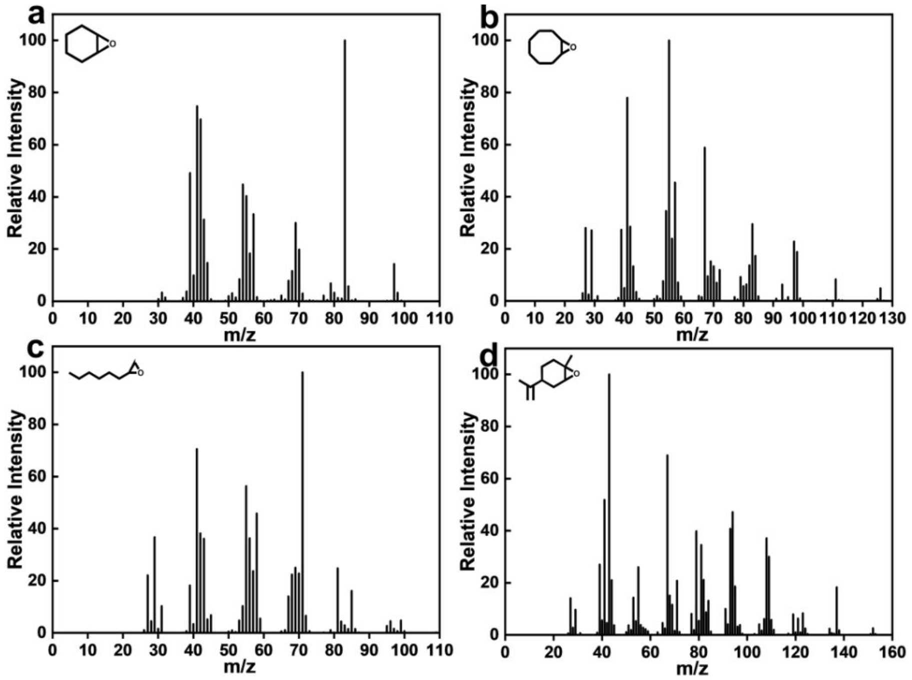


Fig. S3. Mass spectra of epoxide products in substrate scope under **Ph-PW$_2$** catalyst: (a) cyclohexene epoxide; (b),2-epoxyoctane; (c) 1,2-epoxyoctane; (d) limonene epoxide

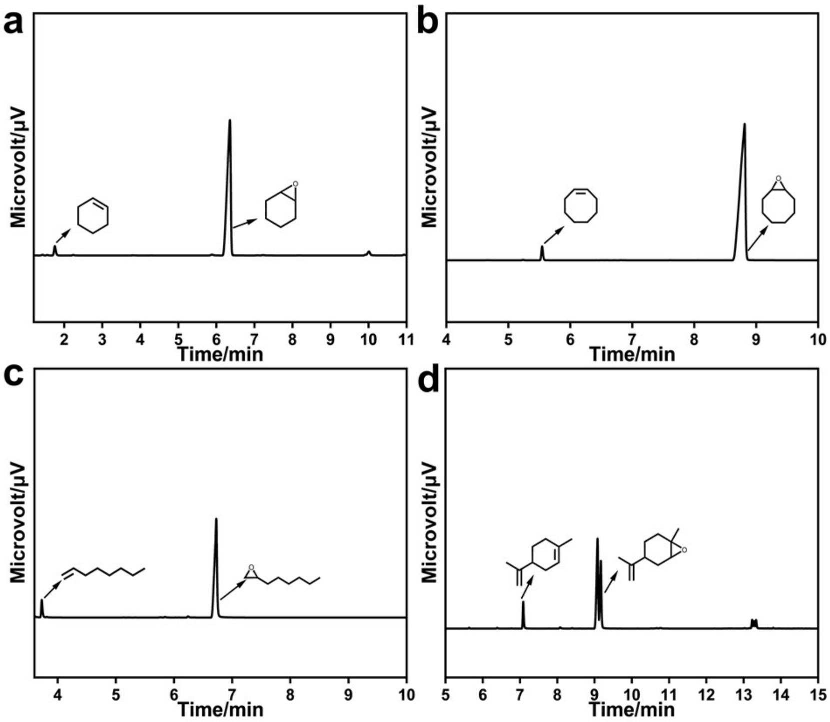


Fig. S4. GC of epoxide products in substrate scope under **Ph-PW$_2$** catalyst: (a) cyclohexene epoxide; (b),2-epoxyoctane; (c) 1,2-epoxyoctane; (d) limonene epoxide

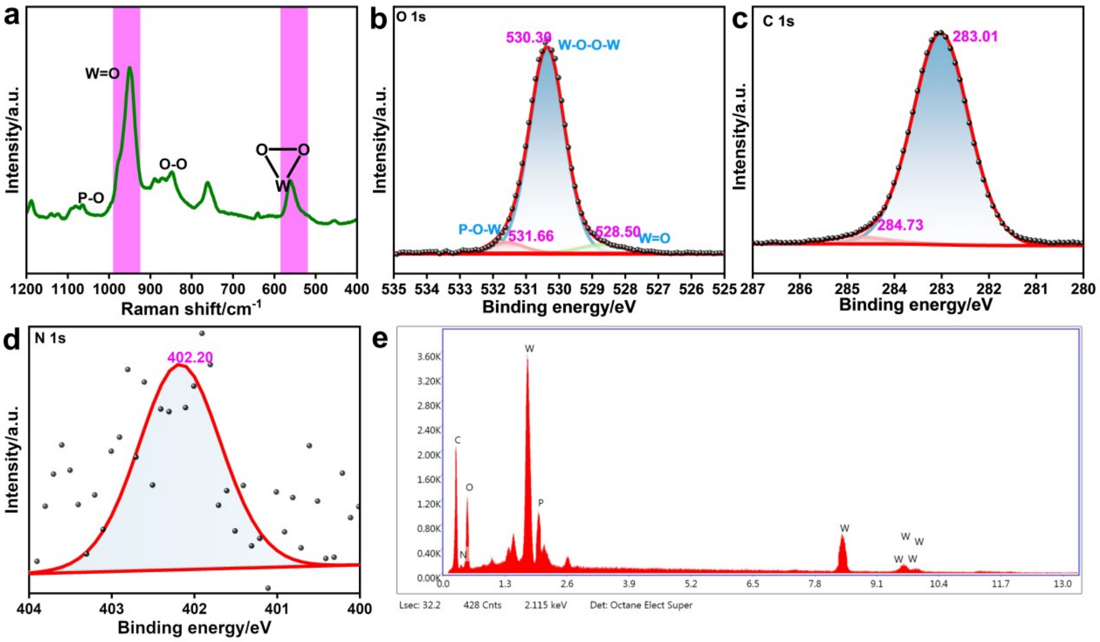


Fig. S5. Characterizations of **Ph-P$_2$W$_4$**: (a) Raman spectrum; high-resolution XPS spectra: (b) O 1s; (c) C 1s; (d) N 1s; (e) EDS spectrum

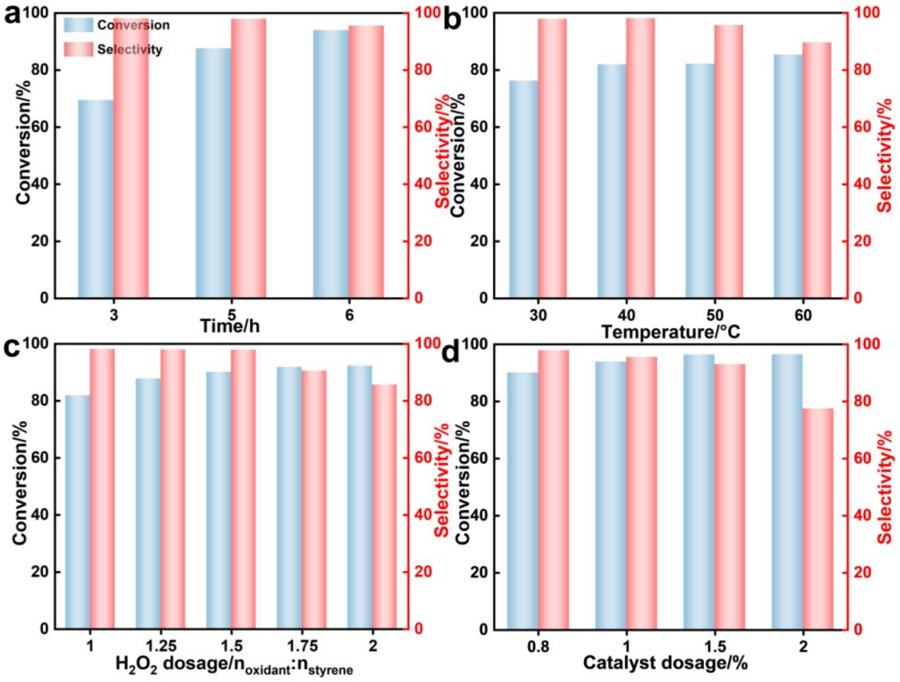


Fig. S6. Catalytic reaction optimization of **Ph-P$_2$W$_4$** on styrene epoxidation: (a) reaction time; (b) reaction temperature; (c) oxidant dosage; (d) catalyst dosage

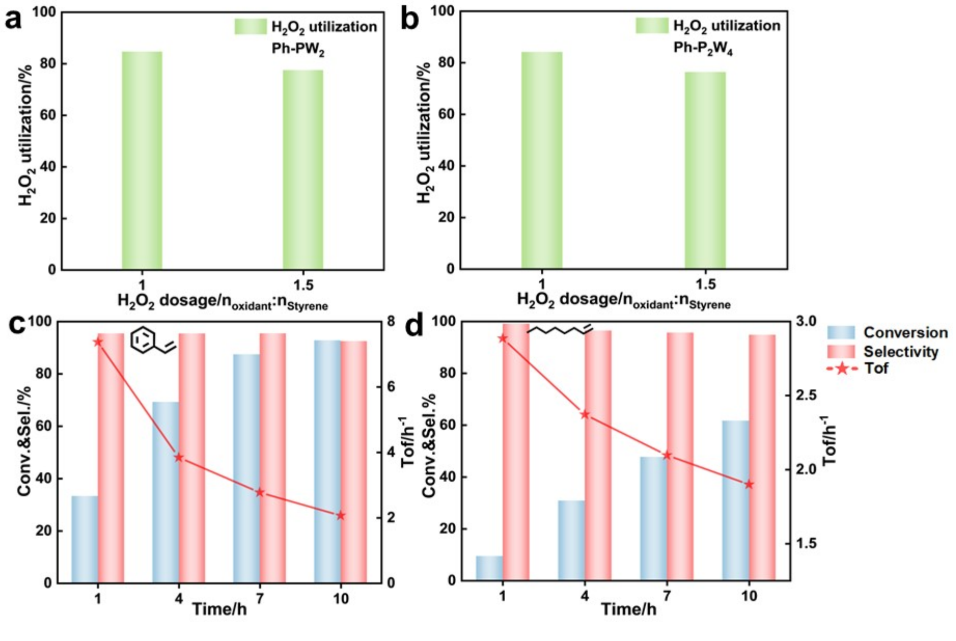


Fig. S7. H_2O_2 utilization efficiency: (a) **Ph-PW$_2$** and **Ph-P$_2$W$_4$** (reaction conditions correspond to the optimal parameters for **Ph-PW$_2$** and **Ph-P$_2$W$_4$**); TOF comparison (c) styrene and (d) 1-octene (reaction conditions: 0.4 mmol **Ph-PW$_2$**, 20 mmol styrene or 1-octene, 30 mmol H_2O_2, 9 mmol Na_2SO_4, 100 mmol $CHCl_3$, 10 h, 40°C, 500 rpm).

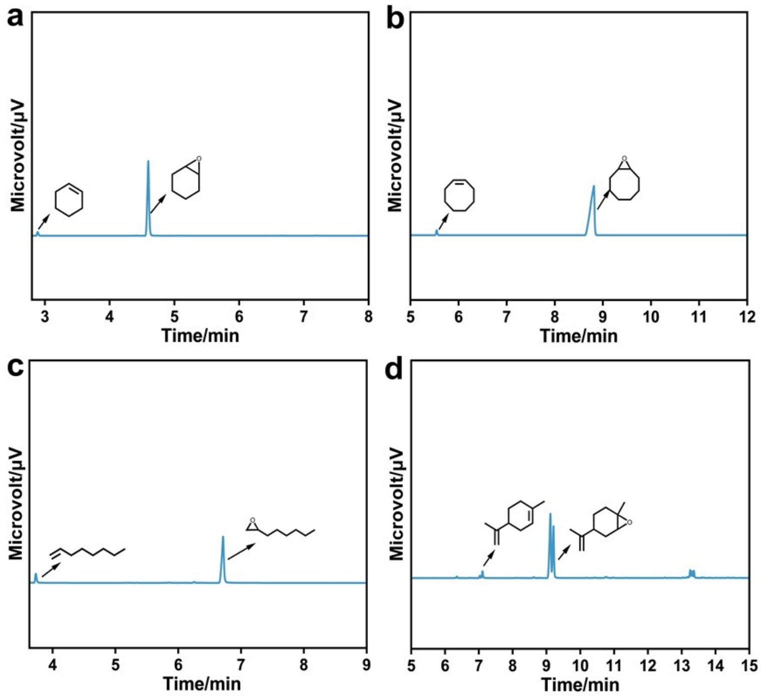


Fig. S8. Catalytic performance of **Ph-P_2W_4** and its substrate scope judged from GC: (a) cyclohexene epoxide; (b) 2-epoxyoctane; (c) 1,2-epoxyoctane; (d) limonene epoxide

References

S1 G. S. Girolami and A. P. Sattelberger, Inorg. Synth., 2014, **36**, 147.

S2 W. B. Cunningham, J. D. Tibbetts, M. Hutchby, K. A. Maltby, M. G. Davidson, U. Hintermair, P. Plucinski and S. D. Bull, *Green Chem.*, 2020, **22**, 513–524.

S3 Q. N. Xiao, Y. Y. Jiang, W. Q. Yuan, J. J. Chen, H. H. Li and H. D. Zheng, *Chin. J. Chem. Eng.*, 2022, **55**, 192–201.

S4 B. C. Ma, W. Zhao, F. M. Zhang, Y. S. Zhang, S. Y. Wu and Y. Dong, *RSC Adv.*, 2014, **4**, 32054–32062.

S5 Z. J. Zhang, Q. Y. Zha, Y. Liu, Z. B. Zhang, J. Liu and Z. Zhou, *Chin. J. Chem. Eng.*, 2023, **58**, 146–154.

S6 Y. X. Wu, Z. Chen, Y. D. Wang and J. H. Xu, *Ind. Eng. Chem. Res.*, 2022, **61**, 10747–10755.

S7 A. G. Sathicq, L. R. Pizzio, P. G. Vázquez, P. Tundo, F. Aricò and G. P. Romanelli, *Sustainable Chem. Pharm.*, 2020, **15**, 100201.

S8 R. Fareghi-Alamdari, S. M. Hafshejani, H. Taghiyar, B. Yadollahi and M. R. Farsani, *Catal. Commun.*, 2016, **78**, 64–67.

S9 R. Sadasivan, A. Patel and A. Ballabh, *Inorg. Chim. Acta*, 2019, **487**, 345–353.

S10 T. T. Zhang and X. B. Cui, *Polyhedron*, 2023, **243**, 116532.

S11 Y. Liu, X. Zhang, X. B. Cui and J. Q. Xu, *Inorg. Chem.*, 2018, **57**, 11123–11134.

S12 Y. F. Liu, X. Bai, Y. X. Zhang, M. C. Zhu, B. Li and S. X. Liu, *Inorg. Chem. Commun.*, 2025, **176**, 114172.

S13 C. Y. Sun, Y. X. Zhang, M. C. Zhu, Y. F. Liu, A. G. Zhang, S. Y. Wang, Y. Liu and S. X. Liu, *Inorg. Chim. Acta*, 2026, **589**, 122881.

S14 T. R. Amarante, M. M. Antunes, A. A. Valente, F. A. Almeida Paz, M. Pillinger and I. S. Gonçalves, *Inorg. Chem.*, 2015, **54**, 9690–9703.