Supporting information

**$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]/H_2O_2$/Ethyl Acetate/Alkene：A Recyclable and Environmentally Benign Alkenes Epoxidation Catalytic System**

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**Full Experimental Section**

**Instruments**

Infrared spectra were recorded on a Nocolet FTIR-360 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding. $^{31}P$ MAS NMR spectra were recorded at 9.4T on a Bruker Avance-400 wide bore spectrometer. The $^{31}P$ MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz with BB MAS probe head using 4 mm $ZrO_2$ rotors and 3.8 μs pulse and 2s repetition time and 4096 scans, with samples spun at 10 kHz and referenced to 85% $H_3PO_4$. $^{31}P$ NMR spectra were recorded on a Varian Unity-300MHz NMR spectrometer, using dichloromethane as the solvent; $^{31}P$ chemical shifts are referenced to 85% $H_3PO_4$ as an external standard. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded on a Bruker AM-400 and Varian mercury 300 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent unless otherwise noted.

UV-vis spectra were recorded on a VARIAN CARY 100 Conc spectrometer. Visible Raman spectra were obtained on a Nicolet Raman 950. GC analyses were performed on Shimadzu GC-9AM with a flame ionization detector equipped with SE-54 capillary (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter = 0.25 mm, film thickness = 0.25μm, length = 30m). Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (IRIS ER/S), and C, H, and N contents were measured on a German Elementar Vario EL spectrometer. X-ray powder diffraction was recorded on D/Max 2400 Rigaku X-ray diffractometer with Cu-Kα radiation, λ=0.1542 nm.

**Syntheses and characterization of polyoxometalates.**

**Catalyst of $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$ ( I )**

To a solution of cetylpyridinium chloride (1.1 g, 3.1 mmol) in 30% $H_2O_2$ (40 mL) was dropwise added $H_3PW_{12}O_{40}$ (3.0 g, ca. 1.0 mmol) in 30% $H_2O_2$ (10 mL) with intense stirring over about 30 min, and the mixture was stirred at 40 °C for 5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After filtration, the precipitate was washed repeatedly with water and dried under air. Analytically pure cat I was obtained as a white powder. Yield: 1.9g (87%). Anal. calcd for $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$ : C,34.51; H, 5.20; N, 1.92; P,1.42; W, 33.57; O,23.38; Found: C, 36.16; H, 5.59; N, 1.74; P, 1.23; W, 32.33; O, 22.95; Raman spectra ($cm^{-1}$): 213, 235, 324, 556, 647, 862, 953, 988, 1006, 1029, 1064, 1174, 1217, 1299, 1440, 1582, 1633. IR spectrum (KBr, $cm^{-1}$): 2920, 2851, 2334, 1711, 1633, 1484, 1173, 1088, 1060, 984, 915, 846, 773, 723, 683, 650, 572, 549, 526, 440. UV-vis spectrum (in dichloromethane) showed shoulder bands at 227 nm, 260 nm. $^{31}P$ MAS NMR: 3.5, 0.7, -15.8 ppm. $^{31}P$ NMR (dichloromethane): 3.1, -14.2 ppm.

**Catalyst I of cycle 1**: After the first reaction, the white precipitate catalyst was appeared and was filtered from the solvent. Then the recovered catalyst was dried overnight in an oven at 40 $^oC$ to wait for a next cycle reaction.

IR spectrum (KBr, $cm^{-1}$): 2923, 2851, 2363, 1707, 1631, 1490, 1455, 1374, 1312, 1217, 1174, 1096, 1047, 948, 891, 865, 810, 784, 737, 684, 639, 584, 519, 405. UV-vis spectrum (in dichloromethane) showed shoulder bands at 205, 210, 227,261 nm. $^{31}P$ MAS NMR: 6.3, 2.2, -11.1, -11.9 ppm

**Catalyst I of cycle 2**: After the second reaction, the white precipitate catalyst was appeared and was filtered from the solvent. Then the recovered catalyst was dried overnight in an oven at 40 $^oC$ to wait for a next cycle raction.

IR spectrum (KBr, $cm^{-1}$): 2924, 2851, 2365, 1708, 1631, 1596, 1554, 1489, 1458, 1371, 1309, 1214, 1176, 1100, 1047, 947, 894, 862, 812, 786, 740, 684, 585, 538,. UV-vis spectrum (in dichloromethane) showed shoulder bands at 203, 210, 226,261 nm. $^{31}P$ MAS NMR: 5.9, 1.5, -11.4, -12.2 ppm

**$[\pi\text{-}C_5H_5N(CH_2)_{11}CH_3]_3$-Cat**

To a solution of 1-dodecylpyridinium chloride (0.43 g, 1.5 mmol) in 30% $H_2O_2$ (20 mL) was dropwise added $H_3PW_{12}O_{40}$ (1.5 g, ca. 0.5mmol) in 30% $H_2O_2$ (5 mL) with intense stirring over about 30 min, and the mixture was stirred at 40 $^oC$ for 5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After filtration, the precipitate was washed repeatedly with water and dried under air.

IR spectrum (KBr, $cm^{-1}$): 2925, 2853, 2328, 1707, 1633, 1582, 1556, 1487, 1464, 1376, 1319, 1214, 1175, 1079, 1029, 951, 895, 843, 823, 775, 720, 686, 646, 630, 571, 549, 524, 448. $^{31}P$ MAS NMR: 4.8, 1.8, -7.6, -15.9 ppm

**$\{[CH_3(CH_2)_3]_4N\}_3$-Cat**

To a solution of tetra-butyl ammomium chloride (0.843 g, 1.5 mmol) in 30% $H_2O_2$ (20 mL) was dropwise added $H_3PW_{12}O_{40}$ (1.5 g, ca. 0.5mmol) in 30% $H_2O_2$ (5 mL) with intense stirring over about 30 min, and the mixture was stirred at 40 $^{o}$C for 5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After filtration, the precipitate was washed repeatedly with water and dried under air.

IR spectrum (KBr, cm$^{-1}$): 2964, 2875, 2365, 1646, 1484, 1382, 1152, 1085, 1054, 975, 896, 844, 818, 741, 651, 621, 596, 576, 549, 522, 457. $^{31}$P MAS NMR: 3.4, 2.5, -15.5 ppm

**$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3$-Cat**

To a solution of cetylpyridinium bromide (0.59 g, 1.5 mmol) in 30% $H_2O_2$ (20 mL) was dropwise added $H_3PW_{12}O_{40}$ (1.5 g, ca. 0.5mmol) in 30% $H_2O_2$ (5 mL) with intense stirring over about 30 min, and the mixture was stirred at 40 $^{o}$C for 5 h. The suspended mixture was cooled to room temperature until a white precipitate was produced. After filtration, the precipitate was washed repeatedly with water and dried under air.

IR spectrum (KBr, cm$^{-1}$): 2923, 2851, 1633, 1580, 1486, 1463, 1374, 1315, 1212, 1173, 1078, 978, 896, 809, 760, 679, 596, 521. $^{31}$P MAS NMR: 6.3, -1.6, -5.7, -13.0, -15.2, -16.1 ppm

**$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_{12}O_{40}]$**

To a solution of cetylpyridinium bromide (5.2mmol) in 70 ml of distilled water was added dropwise to $H_3PW_{12}O_{40}$ (1.7mmol) in 10 ml of distilled water with stirring at ambient temperature to form a white precipitate immediately. After being stirred continuously for 3.5 h, the resulting mixture was filtered, washed several times with distilled water, and then dried at room temperature under vacuum for ca.12h. UV-visible spectrum in acetonitrile at 298K: $\lambda$ =266nm. Infrared spectra (KBr): 3425, 2923, 2851, 1633, 1486, 1464, 1173, 1080, 978, 896, 830-740, 678, 522 cm$^{-1}$. $^{31}$P MAS NMR: -15.5 ppm

**Xi' catalyst preparation**

$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$ was synthesized by a modification of the method reported in ref.[12a] as follows:

A suspension of tungstic acid 2.5 g (10 mmol) in 24.3 ml of aqueous $H_2O_2$ (30%) was stirred and heated to 60 $^{\circ}$C until a colorless solution was obtained. This solution was filtered and then cooled to 25 $^{\circ}$C. Forty percent (w/v) $H_3PO_4$ (0.62 ml, 2.5 mmol) was added to the solution, and then was diluted to 30 ml with water. An amount equal to 1.80 g of cetylpyridiniumammonium chloride (5 mmol) in dichloromethane (40 ml) was added dropwise with stirring in 2 min, and the stirring was continued for an additional 15 min. The organic phase was then separated, dried with anhydrous $Na_2SO_4$, filtered and evaporated under atmospheric pressure at 50–60 °C (bath) and about 2.5 g (85%, based on the quaternary ammonium salt charged ) of the dried yellow powder was obtained by further evacuation.

IR spectrum (KBr, $cm^{-1}$): 2923, 2851, 2359, 1633, 1579, 1489, 1462, 1374, 1318, 1214, 1175, 1087, 1032, 942, 884, 835, 776, 719, 686, 625, 582, 543. $^{31}P$ MAS NMR: 4.9, -2.8, -10.1 ppm. Anal. Calcd for $C_{63}H_{114}O_{16}PN_3W_4$: C, 39.08; H, 5.95; N, 2.17. Found: C, 39.08; H, 5.73; N, 1.90.

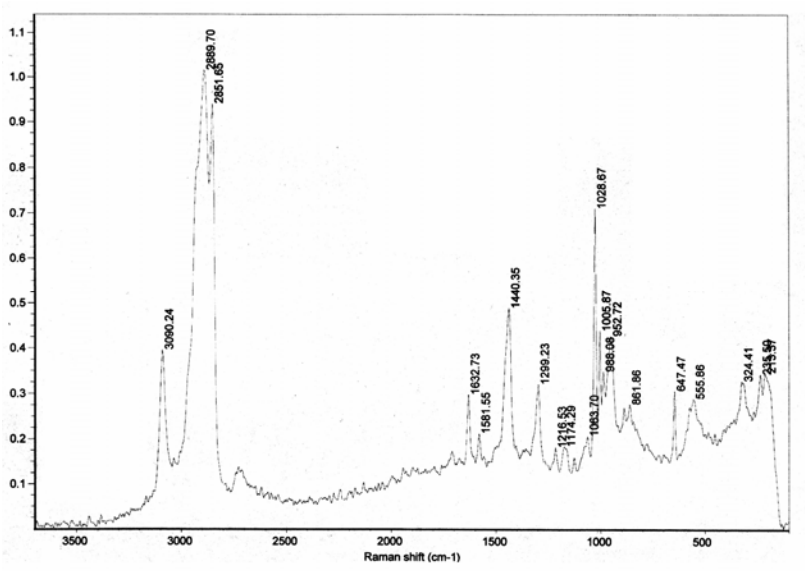



**Fig S1** Raman spectrum of the fresh catalyst $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$

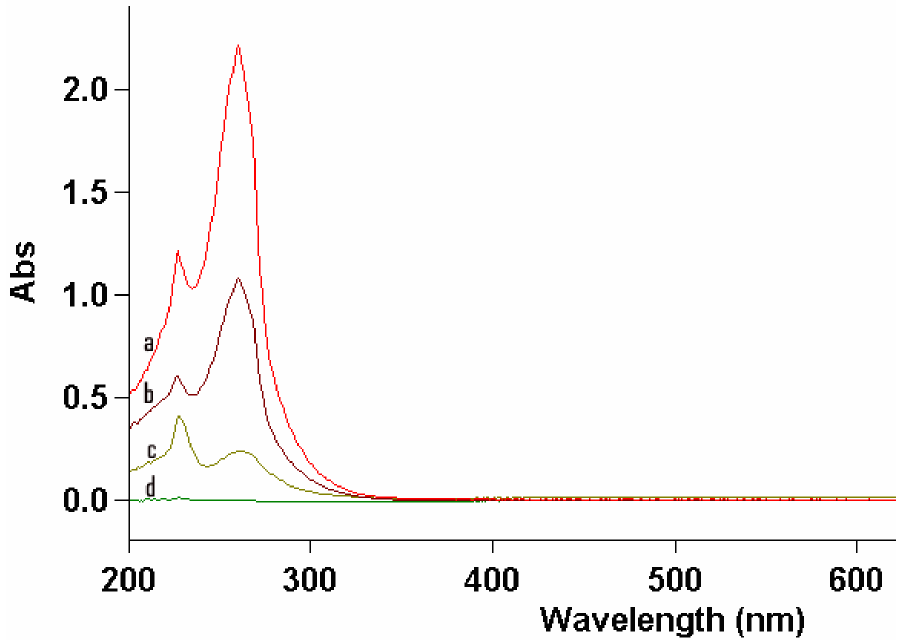



**Fig S2** UV-vis absorption spectra of catalyst [π-$C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$in dichloromethane :

(a) the fresh catalyst [π-$C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$; (b) the catalyst I treated with $H_2O_2$; (c) the used catalyst for cycle 1; (d) the reaction solution after epoxidation (catalyst has precipitated from the solvent)

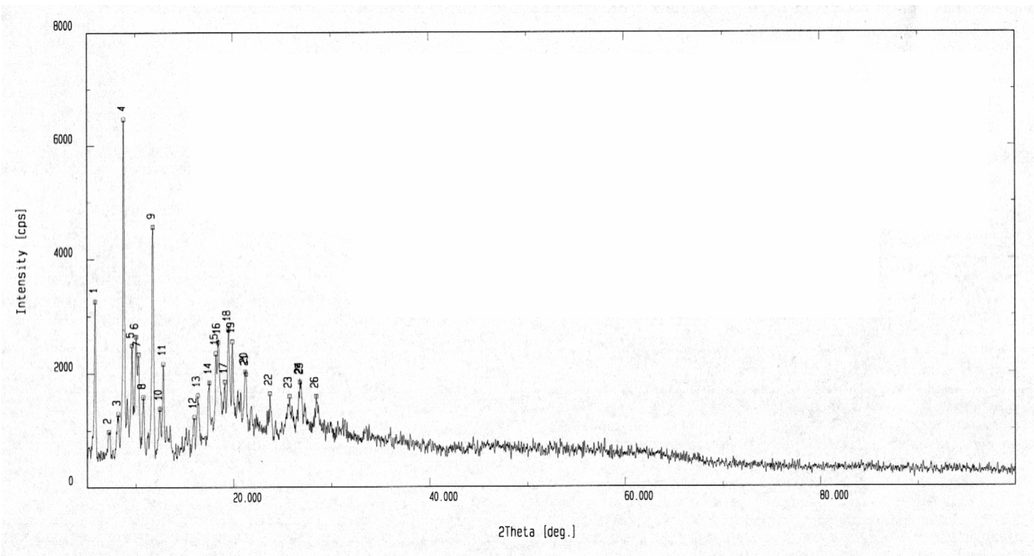



**Fig S3** XRD pattern of fresh catalyst of [π-$C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$

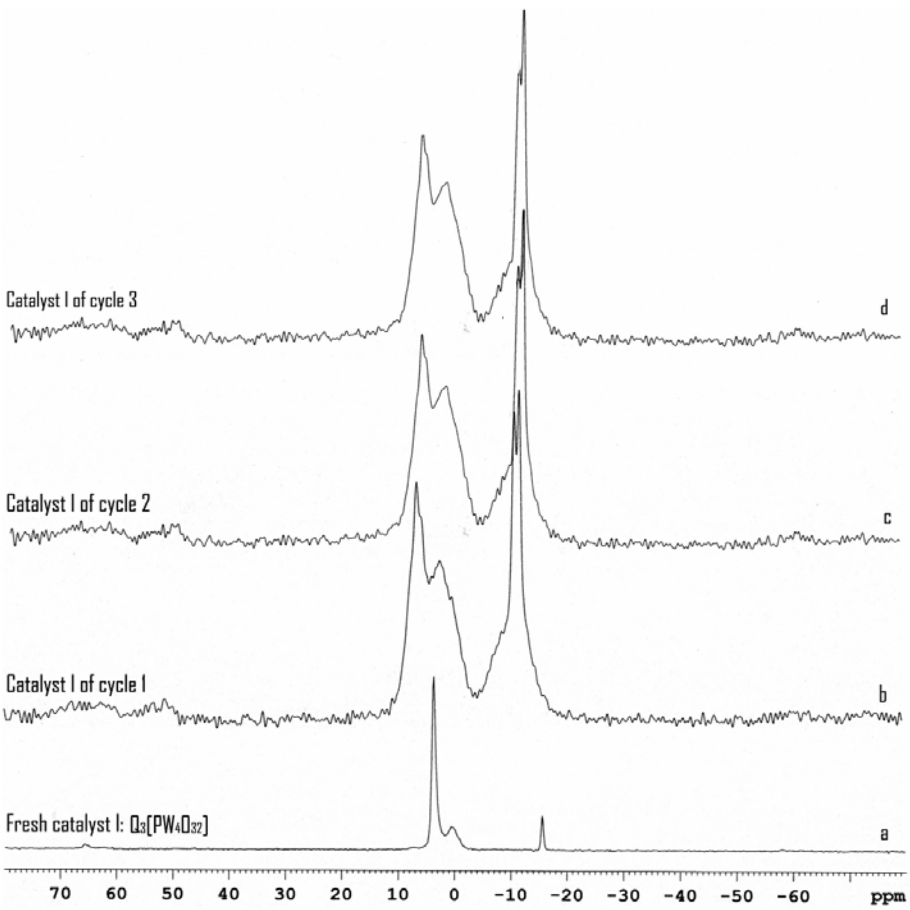



**Fig S4** $^{31}$P MAS NMR spectra of : a) the fresh catalyst of [π-$C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$; b) the catalyst of cycle 1; c) the catalyst of cycle 2; d) the catalyst of cycle 3.

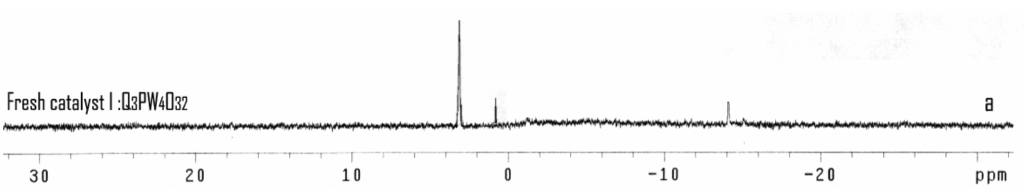



**Fig S5** $^{31}$P NMR spectra of the fresh catalyst [π-$C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$ in dichloromethane;

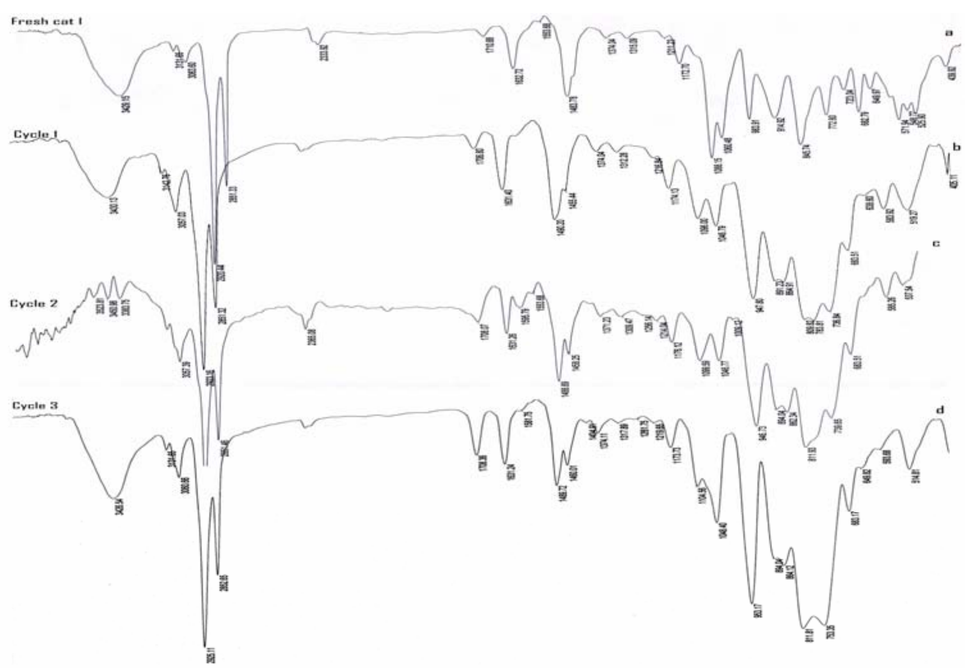


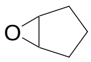
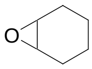
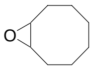
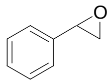
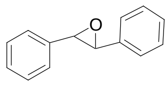
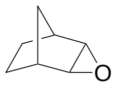
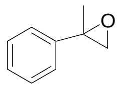
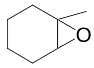
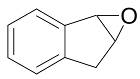
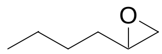
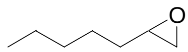
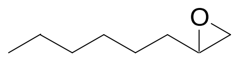
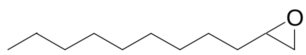
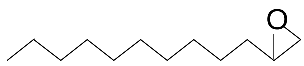
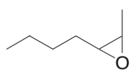

**Fig S6**. Infrared spectra of: a) fresh catalyst of $[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{32}]$; b) the catalyst of cycle 1; c) the catalyst of cycle 2;d) the catalyst of cycle 3

The catalytic reactions were performed in a 25 ml two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. The epoxidation was carried out as follows: catalyst (30mg), solvent (3ml), substrate (3mmol), and $H_2O_2$ (30% aq., 0.75mmol) were charged in the reaction flask. The reaction was carried out at 338K and detected by TLC accompanied with GC. After the reaction was over, the organic layer was analyzed by GC. The yield of products were calculated from the peak areas by using an internal standard method. The products were identified by GC/MS (Finnigan Trace DSQ). The carbon balance in each experiment was in the range of 95-100%. The amount of $H_2O_2$ remaining after the reaction was analyzed by a normal iodometric methods. Internal standard compound is bromobenzene in the quantitative analysis of epoxides by GC.

The characterization products of dienes as follows:

The precipitate was removed by centrifugation and filtration, and the filtrate extracted with EtOAc (30ml x 3), the organic layer was collected and washed with water and brine, then dried with anhydrous $Na_2SO_4$. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography with eluent (petroleum ether/ethyl acetate10/1) to give epoxides as colorless oil. The structure of the epoxides were determined by $^{1}$H NMR, $^{13}$ C NMR, MS (EI).

Table 1 The internal standard compounds and GC response factor

| Product | Internal substance | GC response factor |
|---|---|---|
|  | bromobenzene | 1.08 |
|  | bromobenzene | 1.06 |
|  | bromobenzene | 0.98 |
|  | bromobenzene | 0.97 |
|  | bromobenzene | 0.90 |
|  | bromobenzene | 0.98 |
|  | bromobenzene | 0.95 |
|  | bromobenzene | 1.0 |
|  | bromobenzene | 0.96 |
|  | n-heptane | 1.05 |
|  | n-heptane | 1.0 |
|  | n-heptane | 0.97 |
|  | n-decane | 1.0 |
|  | n-dodecane | 1.0 |
|  | n-heptane | 1． 08 |

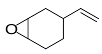
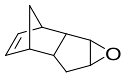
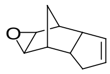
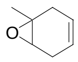
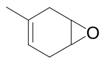
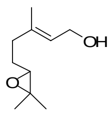
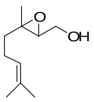
| | | |
|---|---|---|
|  | bromobenzene | 0.95 |
|  | bromobenzene | 0.8 |
|  | bromobenzene | 0.8 |
|  | bromobenzene | 1.05 |
|  | bromobenzene | 1.05 |
|  | bromobenzene | 1.14 |
|  | bromobenzene | 1.14 |

Table 2 Experiment for the leaching of W after each catalytic run [a]

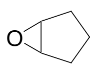
| Entry | Cycle times | Concentration of W in reaction solvent (ppm) |
|---|---|---|
| 1 | 1 | 46 |
| 2 | 2 | 50 |
| 3 | 3 | 44 |
| 4 | 4 | 51 |
| 5 | 5 | 42 |

[a] Reaction conditions: 3mmol 1-octene; 0.75mmol $H_2O_2$; 30mg catalyst; 3ml ethyl acetate; reaction temperature: 65$^{o}$C, reaction time: 2h.

Leaching was measured with ICP analysis and checked by filtration experiments

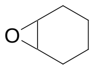
**Characterization of oxidation products:**

The data (GC retention time, mass, and NMR) of epoxides were listed below:

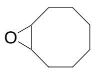


cyclopentene oxide

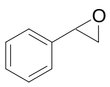
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (100 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.3 min). MS (70 eV, EI): m/z (%): 84 (10) [$M^+$], 83 (38) [M$^+$-], 69 (13), 56 (42), 55 (100), 41(54), 39 (30), 27(22). The data of $^1$H NMR and $^{13}$C NMR see reference 1.


Cyclohexene oxide

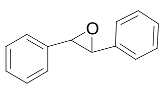
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (110 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.8 min).MS (70 eV, EI): m/z (%): 98 (18) [M$^+$], 83 (100), 70 (28), 69 (35), 57 (45), 54(58), 42 (60), 39(43). The data of $^1$H NMR and $^{13}$C NMR see reference 2.


Cyclooctene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (110 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.5min).MS (70 eV, EI): m/z (%): 126 (4) [M$^+$], 97 (22), 83 (28), 67 (60), 57 (53), 55(100), 54(41), 41(75). The data of $^1$H NMR and $^{13}$C NMR see reference 2.

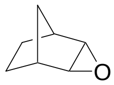

Styrene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.9min).MS (70 eV, EI): m/z (%): 120 (44) [M$^+$], 119 (22), 92 (31), 91 (100), 90 (29), 89(28), 65(17), 63(10). The data of $^1$H NMR and $^{13}$C NMR see reference 2.

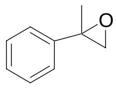

trans-Stilbene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), initial column temperature (130 °C), final column temperature

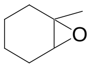
(200 °C), progress rate (20 °C/min), injection temperature (240 °C), detection temperature (240 °C), retention time (8.1min). MS (70 eV, EI): m/z (%): 196 (100) [$M^+$], 195 (70), 178 (31), 167 (85), 90 (66), 89(63). The data of $^1H$ NMR and $^{13}C$ NMR see reference 3.


Norbornene oxide

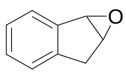
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.9min).MS (70 eV, EI): m/z (%): 110 (10) [$M^+$], 109 (7), 95 (19), 92 (15), 82 (29), 81(100), 79(65), 67(40), 55(43), 54(31), 39(25). The data of $^1H$ NMR and $^{13}C$ NMR see reference 3


a-Methylstyrene oxide

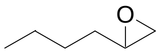
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (2.8min).MS (70 eV, EI): m/z (%): 134 (37) [$M^+$], 133(65), 105 (100), 103(40), 91 (15), 77 (29), 51(14). The data of $^1H$ NMR and $^{13}C$ NMR see reference 2


1-Methylcyclohexene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.4min).MS (70 eV, EI): m/z (%): 112 (18) [$M^+$], 97(82), 83 (17), 69(25), 55(48), 43 (100), 41(50). The data of $^1H$ NMR and $^{13}C$ NMR see reference 2

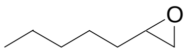

Indene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (180 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (4.2min).MS (70 eV, EI): m/z (%): 132 (30) [$M^+$], 104(100), 103 (27), 78(27), 77(17), 63 (13), 52 (12), 51(29). The data of $^{1}H$ NMR and $^{13}C$ NMR see reference 2.



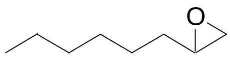
1-Hexene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.3min).MS (70 eV, EI): m/z (%): 100 (3) [$M^+$], 85(2), 71 (100), 58(32), 55(41), 42(65), 41 (71), 39(33). The data of $^{1}H$ NMR and $^{13}C$ NMR see reference 2.



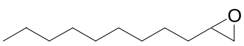
1,2-epoxyheptane

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.3min).MS (70 eV, EI): m/z (%): 114 (7) [$M^+$], 85(10), 71 (100), 58(40), 56(50), 55(41), 43(34), 41 (50). The data of $^{1}H$ NMR and $^{13}C$ NMR see reference 4 and 5.



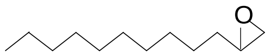
1-Octene oxide

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.7min).MS (70 eV, EI): m/z (%): 128 (4) [$M^+$], 85 (19), 81 (30), 71(100), 69(29), 58(41), 55(65), 41 (70). The data of $^{1}H$ NMR and $^{13}C$ NMR see reference 2.

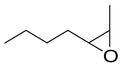


, 2-nonyloxirane

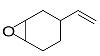
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (180 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.5min).MS (70 eV, EI): m/z (%): 170 (5) [$M^+$], 126(11), 110 (15), 96(25), 82(50), 71(100), 55(75), 43 (90), 41(82), 29(50). The data of $^1$H NMR and $^{13}$C NMR see reference 6.


, 1,2-Epoxydodecane

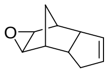
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (180 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.7min).MS (70 eV, EI): m/z (%): 184 (2) [$M^+$], 95(21), 82(35), 71(82), 69 (46), 55(78), 43(75), 41 (100), 29(30). The data of $^1$H NMR sees reference 7, $^{13}$C NMR sees reference 1.


, *cis*-2,3-Epoxyheptane

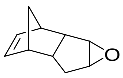
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.8min). MS (70 eV, EI): m/z (%):114 (9) [$M^+$], 85(87), 71 (54), 57(72), 55 (86), 45 (100), 42 (96), 41 (80), 29(60). The data of $^1$H NMR and $^{13}$C NMR see reference 8.


, 4-vinyl-1,2-epoxycyclohexanes

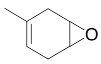
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (2.3min). MS (70 eV, EI): m/z (%): 124 (4) [$M^+$], 123(6), 109(8), 107(14), 95 (20), 79 (64), 55 (89), 41(100). Colorless liquid, $^1$H NMR (300MHz, $CDCl_3$): δ = 5.34-5.51 (m, 1H), 4.61-4.71 (tt, J=9.3Hz, 2H), 2.81-2.89 (m, 2H), 1.86-1.92 (m, 1H), 1.02-1.75 (m, 6H). The data of $^1$H NMR and $^{13}$C NMR see reference 9.



GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.2min).MS (70 eV, EI): m/z (%):148 (5) [$M^+$], 120(13), 92 (13), 91(26), 82 (79), 81 (100), 79(23), 66(43), 39(27). $^1$H NMR (300MHz, $CDCl_3$): δ = 5.58-5.66 (m, 2H), 2.94 (d, J=3.9Hz, 2H), 2.51(m, 2H), 2.68(m, 2H), 2.28(m, 2H), 1.38(d, J=9.6Hz, 1H), 0.78(t, 1H). The data of $^1$H NMR and $^{13}$C NMR see reference 10.

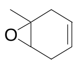


GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.5min).MS (70 eV, EI): m/z (%):148 (7) [$M^+$], 91(10), 83(10), 82(10), 81 (15), 77 (7), 66(100), 39(17), 27(6). $^1$H NMR (300MHz, $CDCl_3$): δ = 6.10 (d, 2H), 3.19 (m, 1H), 3.02 (d, 1H), 2.75(d, 2H), 2.50(m, 2H), 1.80(m, 1H), 1.58(m, 2H), 1.26(d, 1H). The data of $^1$H NMR and $^{13}$C NMR see reference 10.



1-Methyl-4,5-epoxy-1-cyclohexene

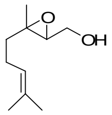
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.8min). MS (70 eV, EI): m/z (%): 110 (100) [$M^+$], 95 (86), 91 (25), 82 (19), 81 (98), 80 (21), 79 (91),77 (38). $^1$H NMR (300MHz, $CDCl_3$): δ = 5.01-5.07 (m, 1H), 4.09 (d, J = 6.9Hz, 2H), 2.46-2.51(m, 2H), 1.94-2.09 (m, 2H), 1.56( s, 3H). The data of $^{13}$C NMR see reference 11.



1-Methyl-1,2-epoxy-4-cyclohexene

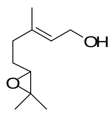
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /$cm^2$), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.5min). MS (70 eV, EI): *m*/*z* (%): 110

[$M^+$] (4), 95 (8), 91 (10), 81(42), 67 (28), 50 (17), 43 (100). $^1$H NMR (300MHz, $CDCl_3$): δ = 5.33-5.36 (t, 2H), 2.95 (m,1H), 2.50-2.17 (m, 2H), 1.90-2.14 (m, 2H), 1.22 ( s, 3H). The data of $^1$H NMR and $^{13}$C NMR see reference 12.



2,3-Epoxy-3,7-dimethyloct-6-en-1-ol

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), initial column temperature (130 °C), final column temperature (180 °C), progress rate (20 °C/min), injection temperature (220 °C), detection temperature (220 °C), retention time (2.7min).MS (70 eV, EI): m/z (%):170 (2) [$M^+$], 111(21), 94(40), 93(25), 81 (15), 68 (40), 59(100), 55(48), 43(60), 41(31). $^1$H NMR (400 MHz, $CDCl_3$): 5.08 (t, $J$ = 1.2 Hz, 1H), 3.80-3.83 (m, 1H), 3.64-3.69 (m, 1H), 2.97-2.99 (m, 1H), 2.59(s, br, 1H), 2.05-2.11 (m, 2H), 1.64-1.70 (m, 4H), 1.61(s, 3H), 1.43-1.51 (m, 1H), 1.30 (s, 3H). $^{13}$ C NMR (100 MHz, $CDCl_3$): 132.04, 123.29, 63.07, 61.32, 61.14, 38.43, 25.56, 23.60, 17.55, 16.66. The data of $^1$H NMR and $^{13}$C NMR see reference 13.



6,7-Epoxy-3,7-dimethyloct-2-en-1-ol

GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation) carrier gas ($N_2$, 1.2kg /cm$^2$), initial column temperature (130 °C), final column temperature (180 °C), progress rate (20 °C/min), injection temperature (220 °C), detection temperature (220 °C), retention time (2.9min). $^1$H NMR (400 MHz, $CDCl_3$): 5.45 (t, $J$ =8.8 Hz, 1H), 4.15 (d, $J$ = 9.6 Hz, 2H), 2.72 (t, $J$ = 8.4 Hz, 1H), 2.09-2.24 (m, 2H), 1.86 (s, br, 1H), 1.70 (s, 3H), 1.63-1.67(m, 2H), 1.31 (s, 3H), 1.27 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): 138.28, 124.04, 63.99, 59.09, 58.36, 36.16, 27.04, 24.75, 18.65, 16.16. The data of $^1$H NMR and $^{13}$C NMR see reference 13

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