Supplementary Information

Highly efficient electro-epoxidation of olefins coupling with bromine recycling

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Preparation of electrodes: The carbon paper (1 cm×2 cm) and graphite (1 cm×2 cm) were ultrasonically cleaned with acetone and then deionized water for 10 minutes each before reaction. DSA (Ti/Ru-IrO_2 and Ti/Sn-SbO_2) and Pt electrode were purchased from Suzhou Sinero Technology CO., LTD (Suzhou, China). The electrodes were cleaned by deionized water and ethanol in preparation for electrochemical measurements.

Gas chromatography (GC): Yields were determined using a Fuli GC-9790II equipped with an AE SE-54 column (Lanzhou Institute of Chemical Physics, 30 m length, 0.33 mm diameter, 0.5μm film thickness). Samples of 0.4 μl were injected with a micro-sampler (1μl, Shanghai Gaoge industry and trade CO., LTD). Products were identified on a gas chromatography-mass spectrometry (GC-MS Agilent 8890-5977B) with an Agilent J&W SE-54 column. GC method: Inlet temperature: 220℃. Injection gases: Split (100:1). Detection: flame ionization detector (FID), temperature 280℃.
Oven heating:
0~1 mins Hold at 70 ℃
1~15 mins Ramp to 280 ℃ at 15 ℃/min
15~16 mins Hold at 280 ℃ for 1 min

Inductively coupled plasma-Mass Spectrometry (ICP-MS): The concentration and total amounts of Br were determined using an Agilent 7800(MS). Testing parameters were listed below:
Pump rate: 20 r/min;
Nebulizer flow: 1 L/min; Auxiliary gas: 1 L/min;
Sample flush time: 40 s;
RF power: 1550 W.

In this experiment, 2 ml of aqueous phase obtained by extraction was digested by HNO_3 and HCl, then diluted to a final volume of 10 ml prior to testing. The sample was further diluted 1000 times and injected using the Agilent SPS 4 autosampler.

Scanning electron microscope (SEM): Scanning electron microscope images were taken using a Zeiss sigma 300 scanning electron microscope operating at 3 KV EHT.

Product analysis

The products were analyzed by GC and GC-MS to determine conversion, selectivity and Faradaic efficiency.

The conversions of substrate were calculated as follow:

$$Conversion(\%) = \frac{n_{con}}{n_{initial}} \times 100\%$$

Where n_{con} is converted substrate mole, n_{inital} is initial substrate mole.

The yield of epoxide was calculated as follow:

$$Yield(\%) = \frac{n_{target\ product}}{n_{initial}} \times 100\%$$

Where $n_{target\ product}$ is target product mole, n_{inital} is initial substrate mole.

The selectivity of epoxides was calculated as follow:

$$Selectivity(\%) = \frac{Yield\ (\%)}{Conversion\ (\%)} \times 100\%$$

The Faradaic efficiency was calculated as follow:

$$FE(\%) = \frac{n_{target\ product} \times 2F}{Q} \times 100\%$$

$$Q = \int_0^{T_{end}} I \times t$$

Where $n_{target\ product}$ is target products moles; 2 moles of electrons were transferred for per mole of epoxides in this reaction; F is Faradaic constant of 96485 C/mol; Q is the total passed charge, T_{end} is reaction time; In constant current electrochemical reaction, I is constant current and total passed charge is $Q = I_{const} \times t$.

Standard curve calculation:

The moles of target product ($n_{target\ product}$) were determined by GC using ethylbenzene as internal standard.

Standard curve of styrene oxide was calculated as followed:

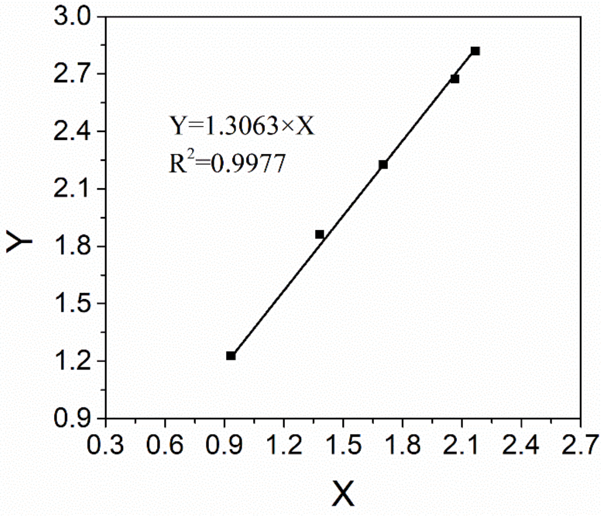

Fig.S1 Standard curve of styrene oxide

Standard curve of styrene oxide

$$Y = 1.3063X$$

Where X was square of styrene oxide minus divided by square of ethylbenzene; Y was moles of styrene oxide divided by moles of ethylbenzene. Five solutions with various concentration of styrene oxide were carried out for linear fitting of standard curve.

$$Y_i = \frac{n_{i,styrene\ oxide}}{n_{i,ethylbenzene}}\ i = 1,2,3,4,5$$

Where $n_{i,styrene\ oxide}$ was the moles of styrene oxide in the ith solution; $n_{i,ethylbenzene}$ was the moles of ethylbenzene in the ith solution.

$$X_i = \frac{S_{i,styrene\ oxide}}{S_{i,ethylbenzene}}\ i = 1,2,3,4,5$$

Where $S_{i,styrene\ oxide}$ was the square of styrene oxide in the ith solution obtained from GC; $S_{i,ethylbenzene}$ was the moles of ethylbenzene in the ith solution.

The standard curve was obtained by linear fitting of five data points (X_i, Y_i), $i = 1,2,3,4,5$.

Standard curve of Thioanisole was calculated as followed:

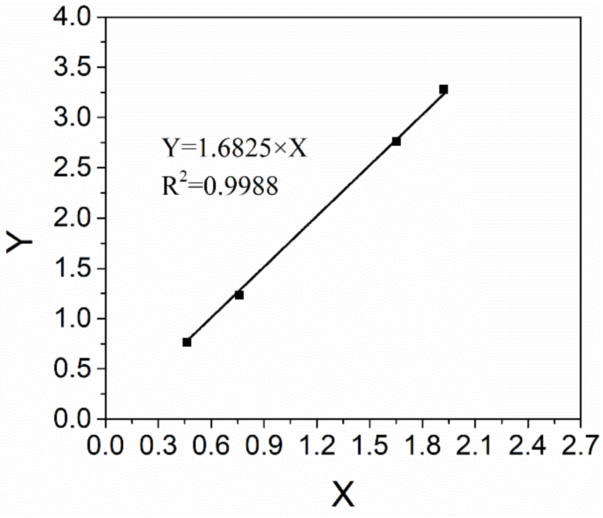

Fig. S2 Standard curve of Thioanisole

An example for calculating the yield of styrene oxide was as followed:

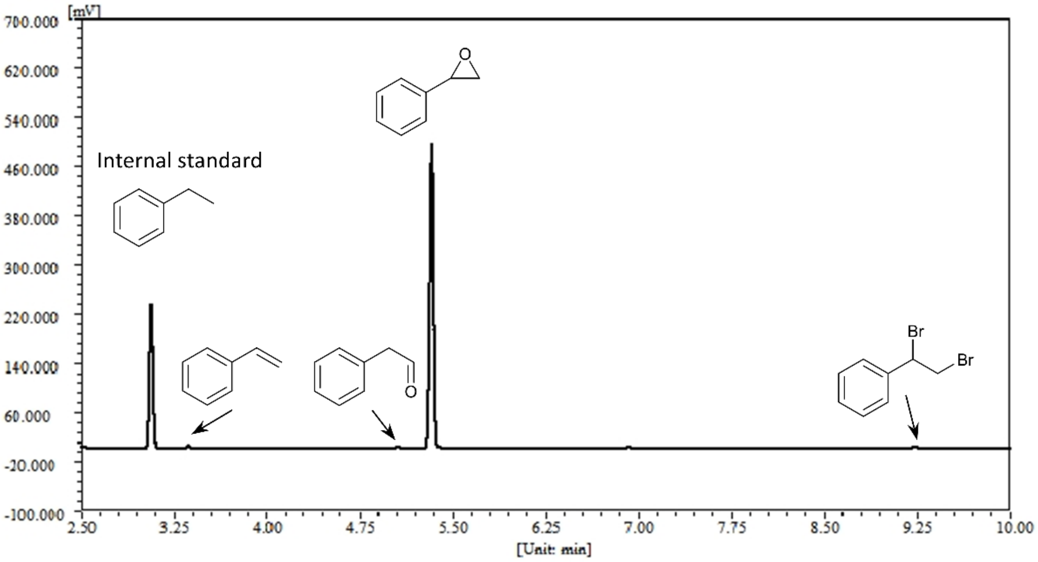

Fig.S3 GC curve of products after post-processing using ethylbenzene as internal standard

The peak area of ethylbenzene and styrene oxide was 821099.6 UV*S and 1799666.6 UV*S, respectively. 0.0181 g ethylbenzene was added in the solution after reaction. The mole of styrene oxide was calculated as followed:

$$n_{i,styrene\ oxide} = \frac{0.0181\ g}{106.16\ g/mol} \times 1.3063 \times \frac{1799666.6}{821099.6} = 0.000488\ mol$$

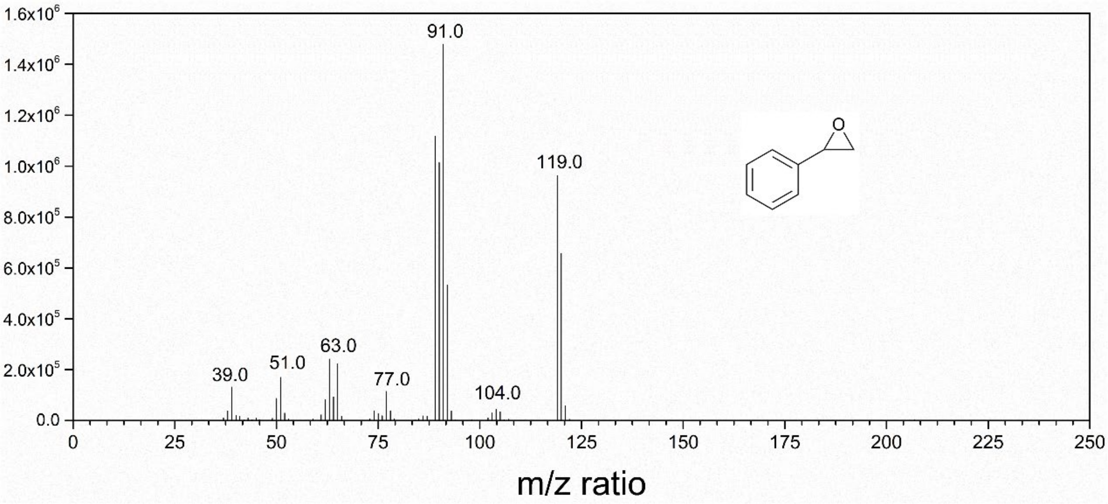

Fig. S4 a GC-MS of styrene oxide

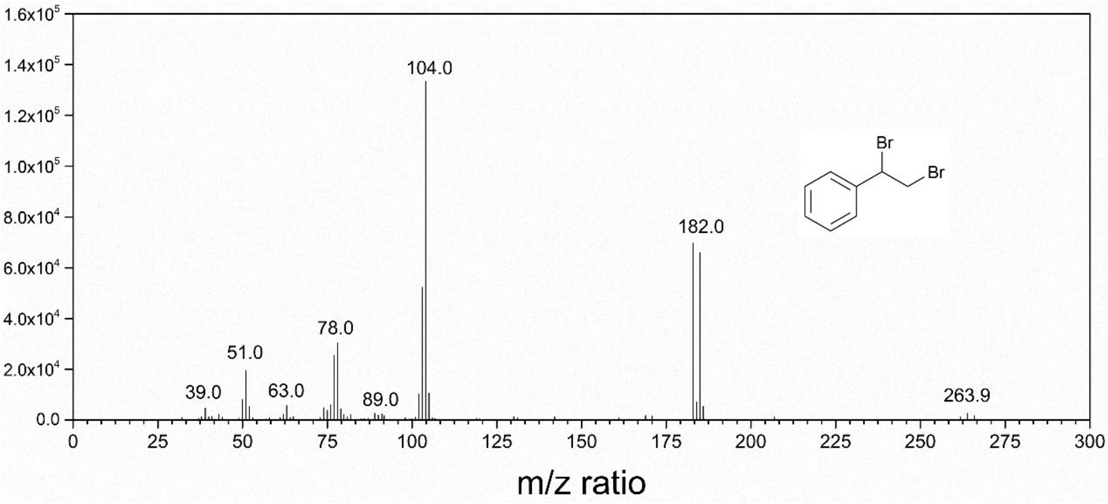

Fig.S4 b GC-MS of (1,2-Dibromoethyl) benzene

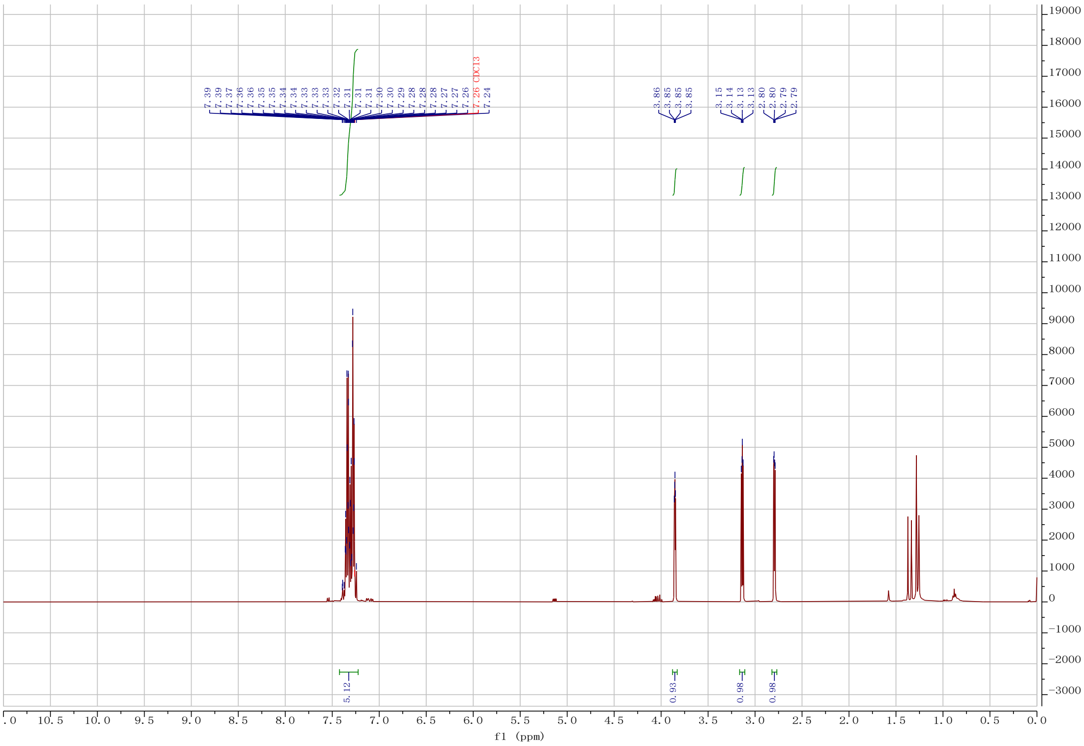

Fig.S5 H NMR of styrene oxide

^{1}H NMR (500 MHz, CDCl3) δ 7.53, 7.39, 7.39, 7.39, 7.37, 7.36, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.33, 7.32, 7.31, 7.31, 7.31, 7.30, 7.30, 7.29, 7.28, 7.28, 7.28, 7.27, 7.27, 7.26, 7.26, 7.24, 4.06, 4.05, 4.03, 4.01, 3.86, 3.85, 3.85, 3.85, 3.15, 3.14, 3.13, 3.13, 2.80, 2.80, 2.79, 2.79.

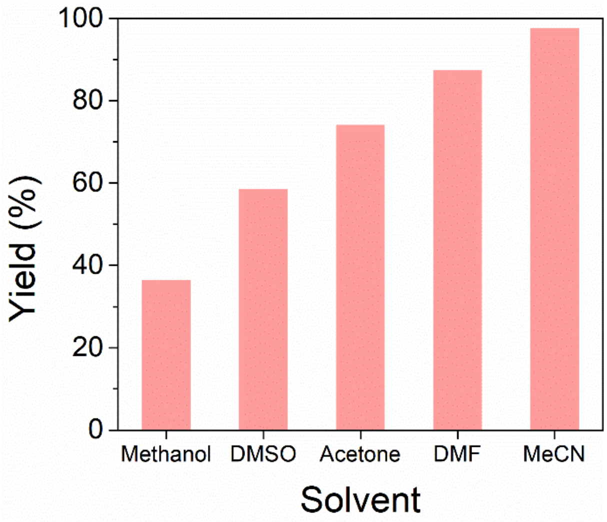

Figure.S6 Yield of styrene oxide in different organic solvents (Methanol, DMSO, Acetone, DMF, MeCN) and water with the same ratio of 50:50 vol%.

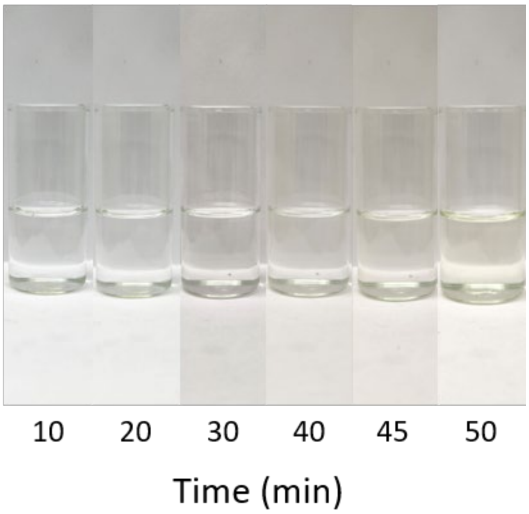

Figure.S7 The reaction solutions at various time points.

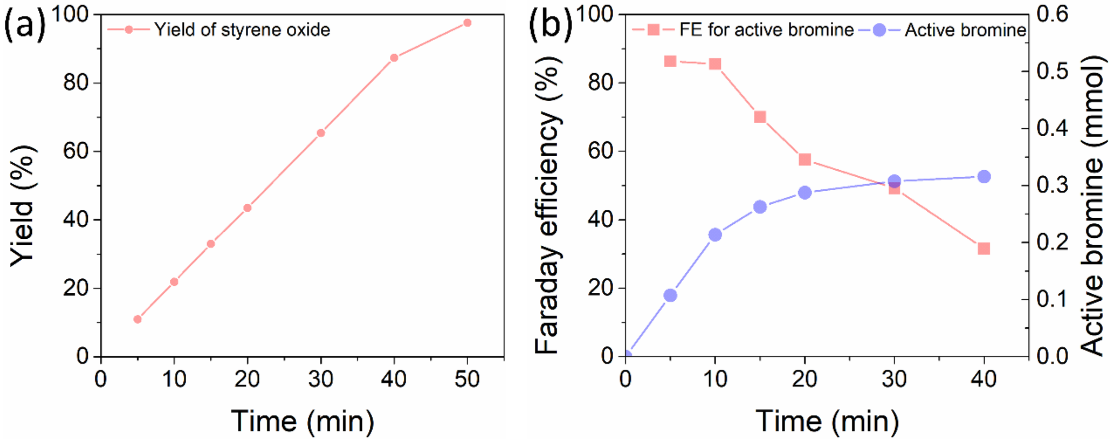

Figure.S8 (a) Yield of styrene oxide t different time-course of reaction. (b)Faraday efficiency and total amounts of active bromine at different time-course of reaction without substrates.

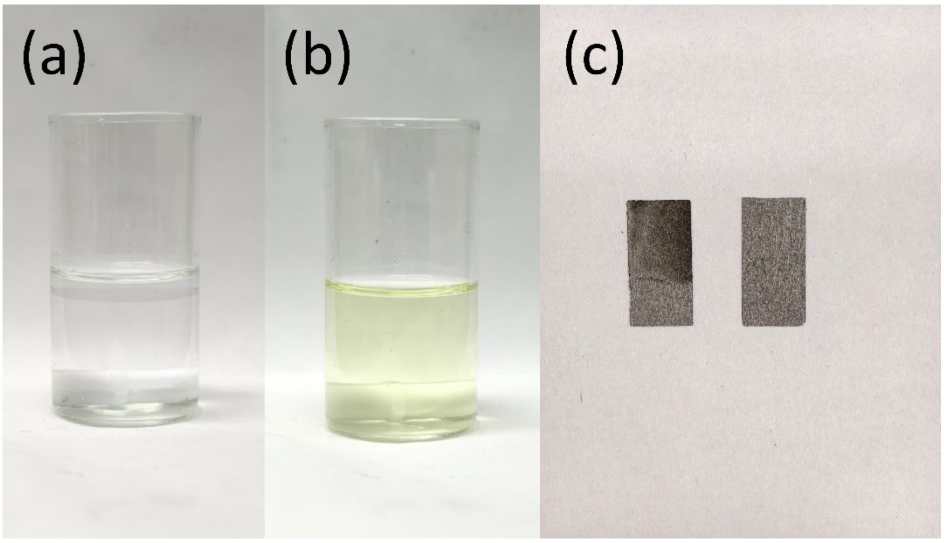

Figure.S9 Photograph of a 50:50 vol% MeCN-H_2O mixture containing an initial concentration of 150 mM styrene (a), along with the solution after reaction (b). (c) Photograph of carbon paper after reaction in 150 mM styrene system(left) and in 66 mM styrene system(right).

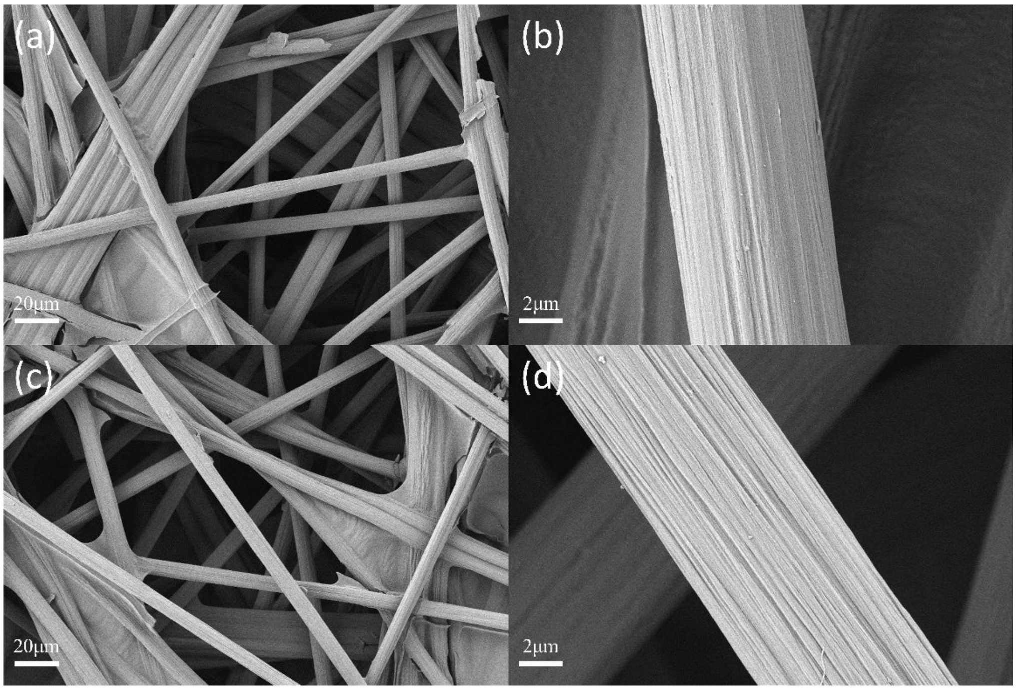

Figure.S10 SEM of carbon paper before (a, b) and after 23 runs (c, d).

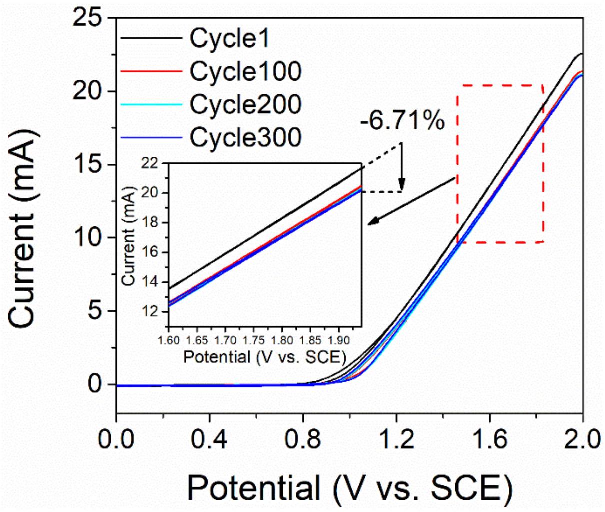

Figure.S11 Cyclic voltammogram (300 cycles) of the bromine evolution reaction at a CP anode in the reaction solution containing 1mmol styrene.

Analysis of main products by GC-MS for electrochemical epoxidation of **4-Fluorostyrene (1b), 4-Clorostyrene (1c), 4-Bromostyrene (1d), 3-Fluorostyrene (1e), 4-Methylstyrene (1h), Allylbenzene (1j), 1-Octene (2a), 1-Decene (2b), Cyclohexene (2c), Thioanisole (3a)** mentioned in Fig.4. Method was as followed:

Inlet temperature: 220 ℃.

Injection gases: Split (100:1).

Detection: flame ionization detector (FID), temperature 280℃.

0~1 mins Hold at 70 ℃

1~15 mins Ramp to 280 ℃ at 15 ℃/min

15~16 mins Hold at 280 ℃ for 1 min

Analysis of main products by GC-MS for electrochemical epoxidation of **4-*tert*-Butyl-styrene (1f), 4-Methoxystyrene (1g), 2-Vinylnaphthalene (1i), 4-(trifluoromethyl) styrene (1k), *cis*-Stilbene (1l), Phenyl sulfide (3b)** mentioned in Fig.4. Method was as followed:

Inlet temperature: 280 ℃.

Injection gases: Split (100:1).

Detection: flame ionization detector (FID), temperature 280℃.

0~1 mins Hold at 70 ℃

1~8 mins Ramp to 280 ℃ at 30 ℃/min

8~11 mins Hold at 280 ℃ for 3 mins

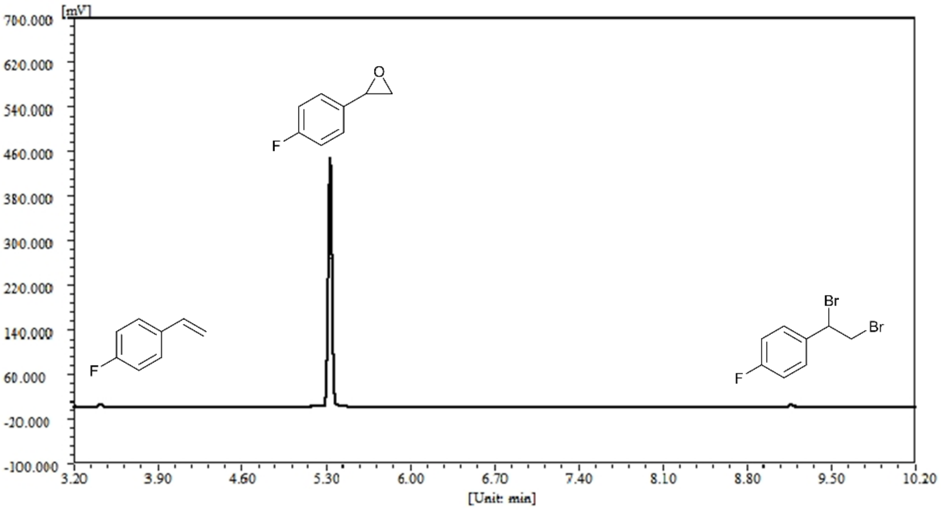

Figure.S12 Product analysis by GC-MS for epoxidation of **4-Fluorostyrene (1b)**.

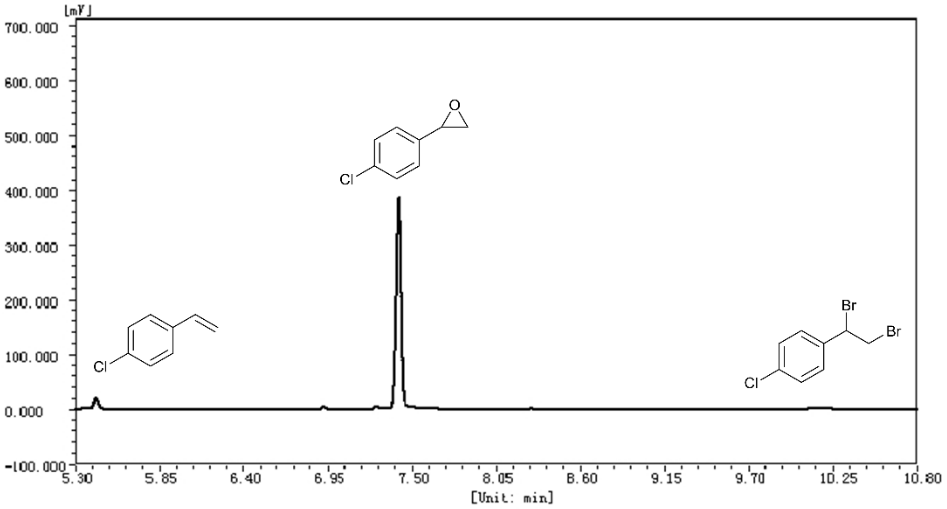

Figure.S13 Product analysis by GC-MS for epoxidation of **4-Clorostyrene (1c)**.

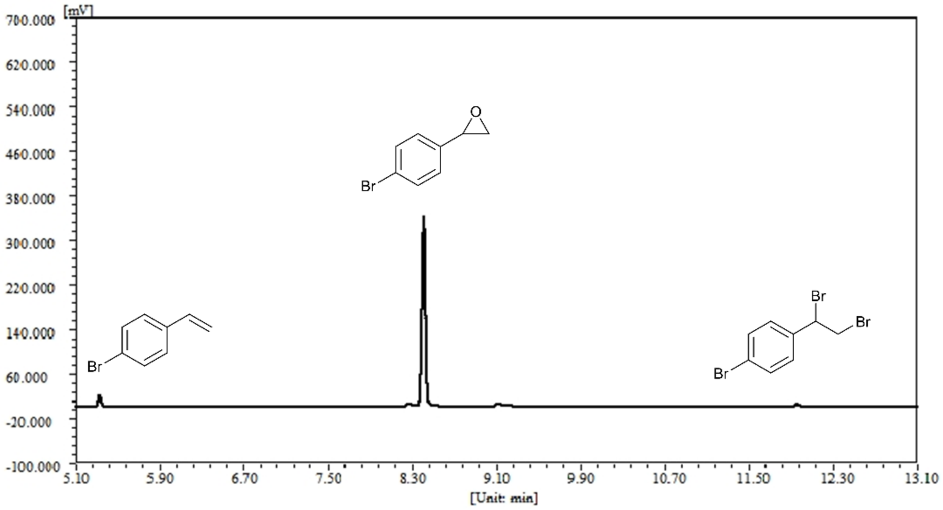

Figure.S14 Product analysis by GC-MS for epoxidation of **4-Bromostyrene (1d)**.

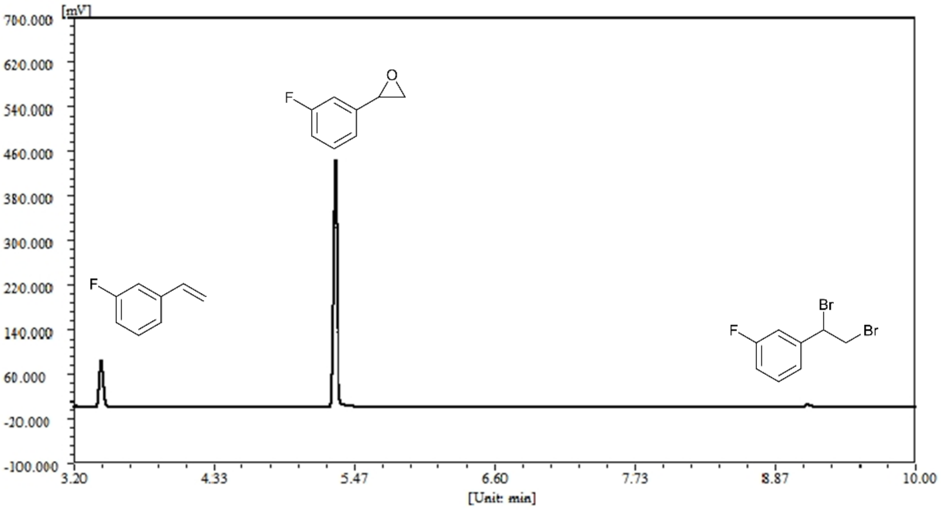

Figure.S15 Product analysis by GC-MS for epoxidation of **3-Fluorostyrene (1e)**.

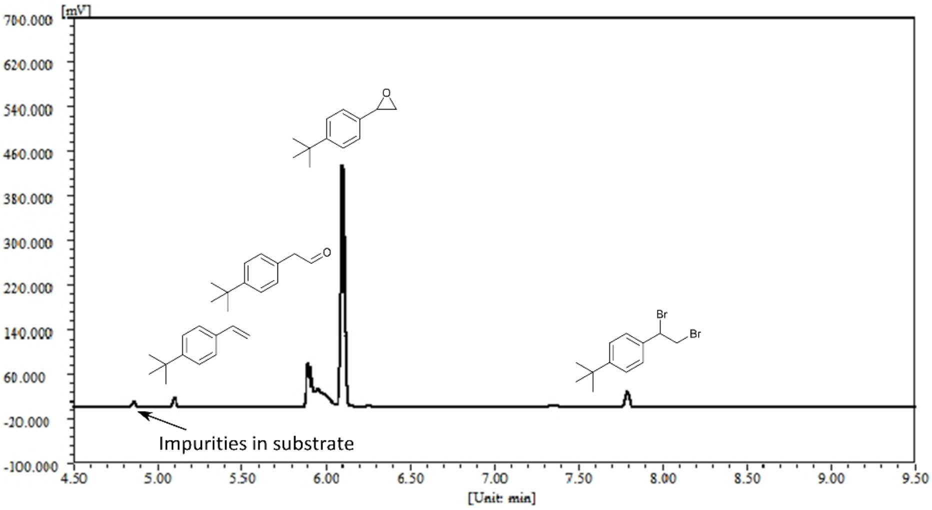

Figure.S16 Product analysis by GC-MS for epoxidation of **4-*tert*-Butylstyrene (1f)**.

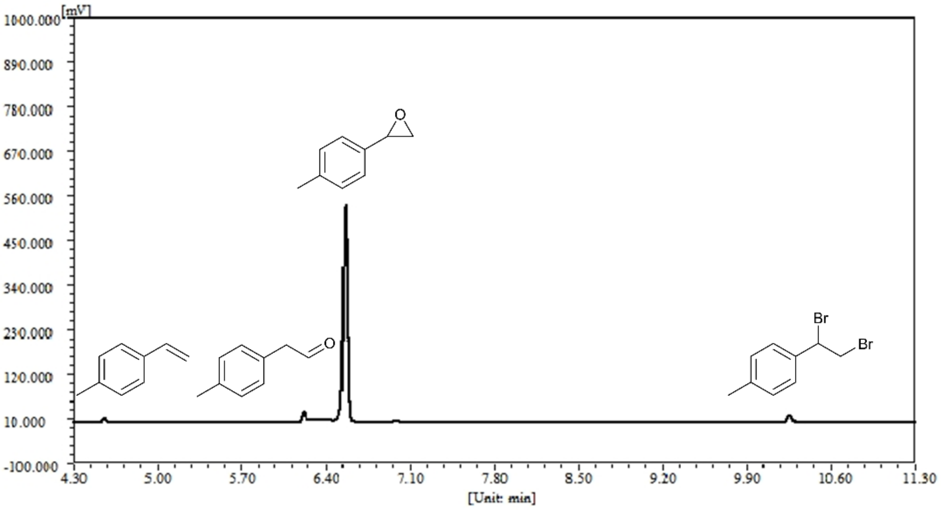

Figure.S17 Product analysis by GC-MS for epoxidation of **4-Methylstyrene (1h)**.

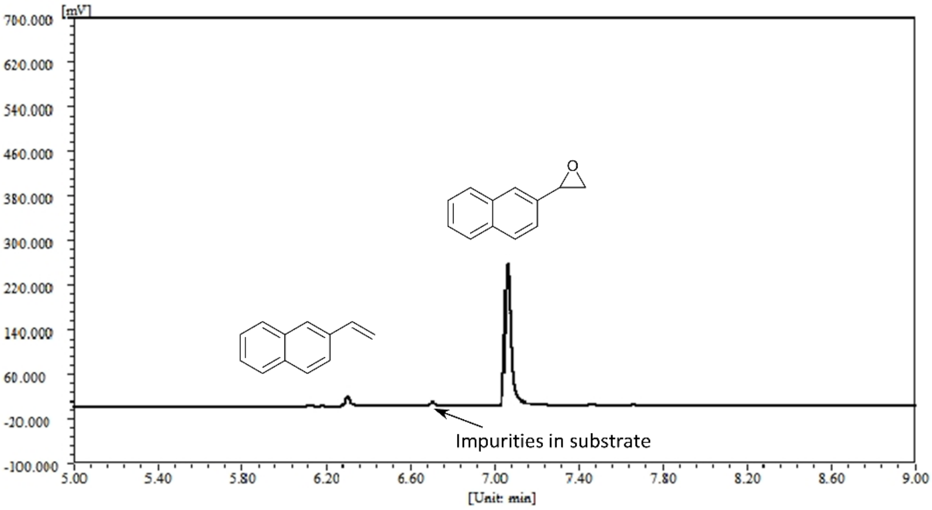

Figure.S18 Product analysis by GC-MS for epoxidation of **2-Vinylnaphthalene (1i)**.

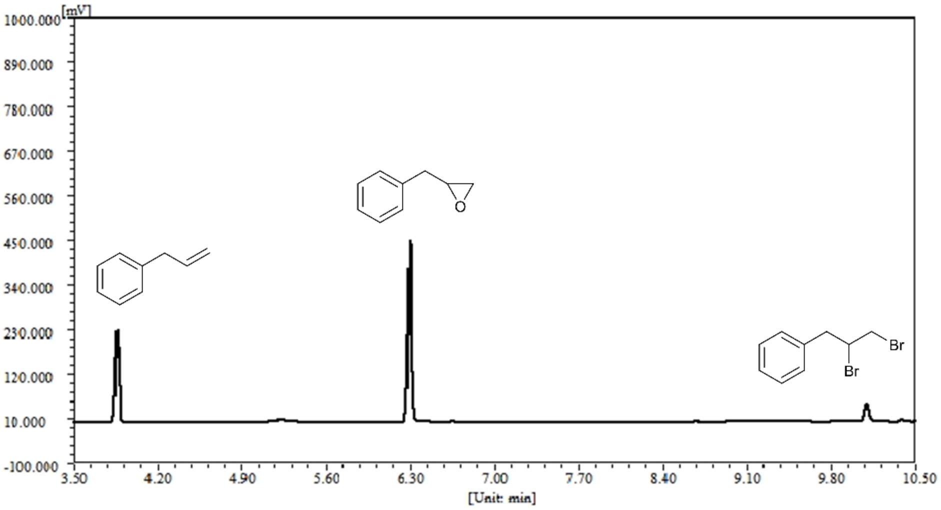

Figure.S19 Product analysis by GC-MS for epoxidation of **Allylbenzene (1j)**.

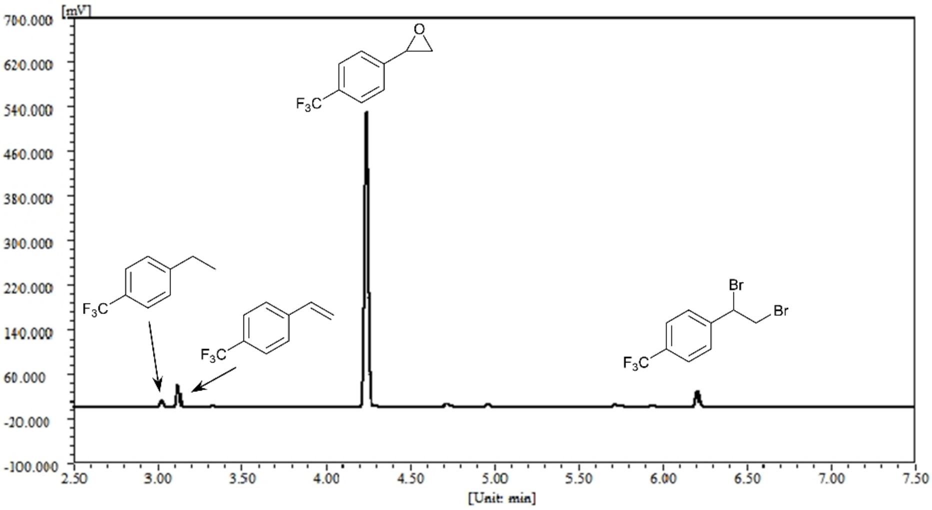

Figure.S20 Product analysis by GC-MS for epoxidation of **4-(trifluoromethyl) styrene (1k)**.

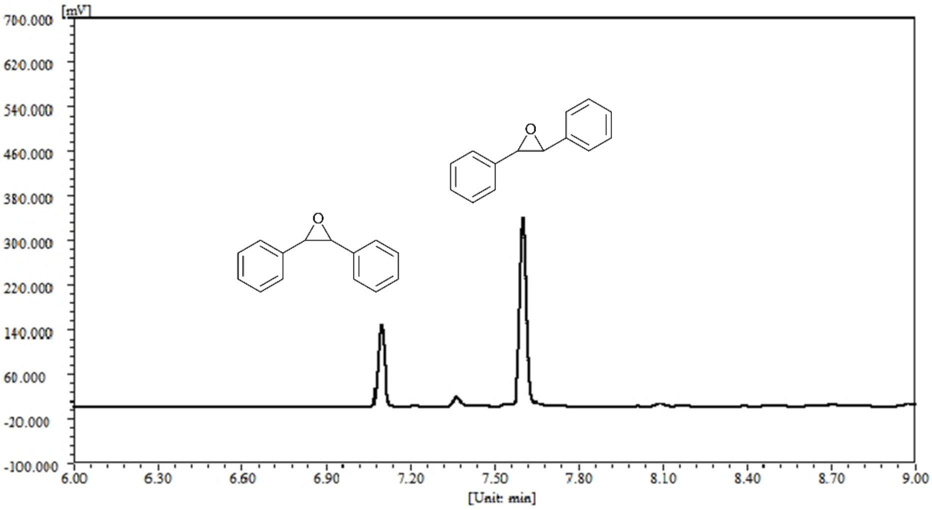

Figure.S21 Product analysis by GC-MS for epoxidation of ***cis*-Stilbene (1l)**.

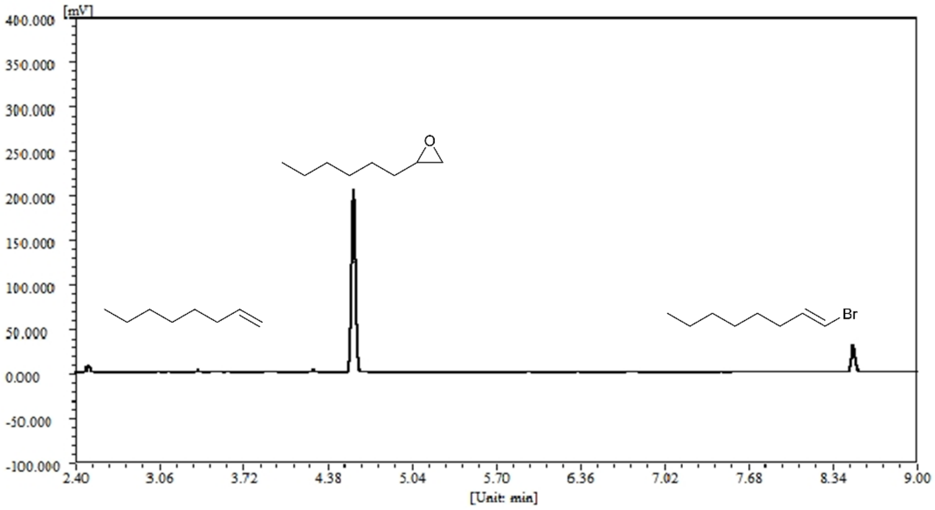

Figure.S22 Product analysis by GC-MS for epoxidation of **1-Octene (2a)**.

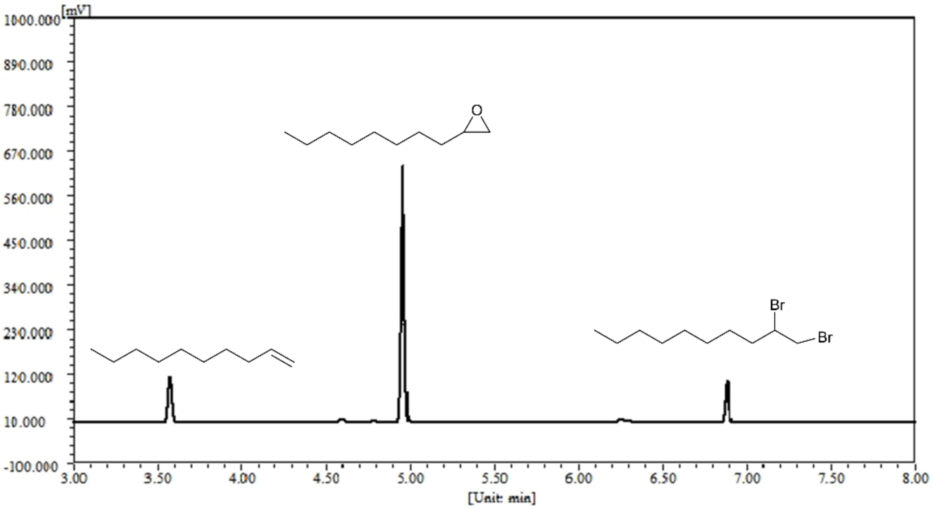

Figure.S23 Product analysis by GC-MS for epoxidation of **1-Decene (2b)**.

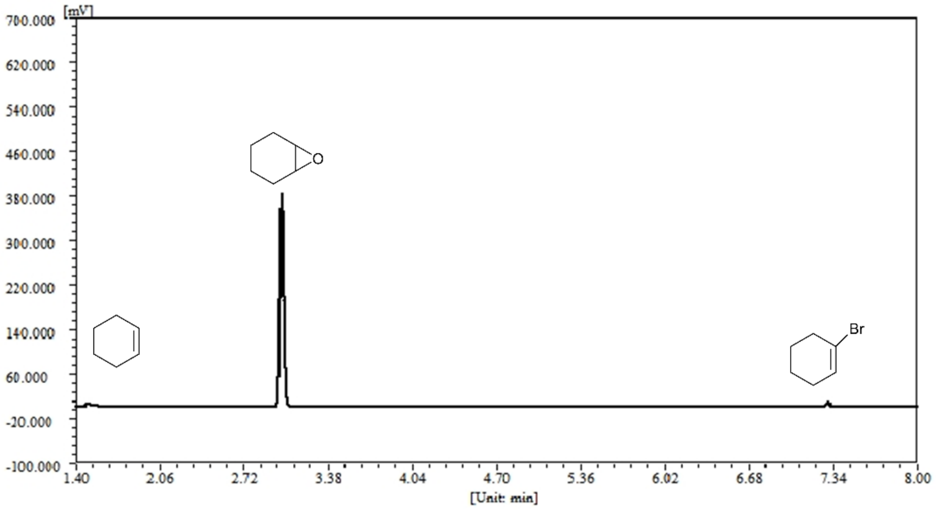

Figure.S24 Product analysis by GC-MS for epoxidation of **Cyclohexene (2c)**.

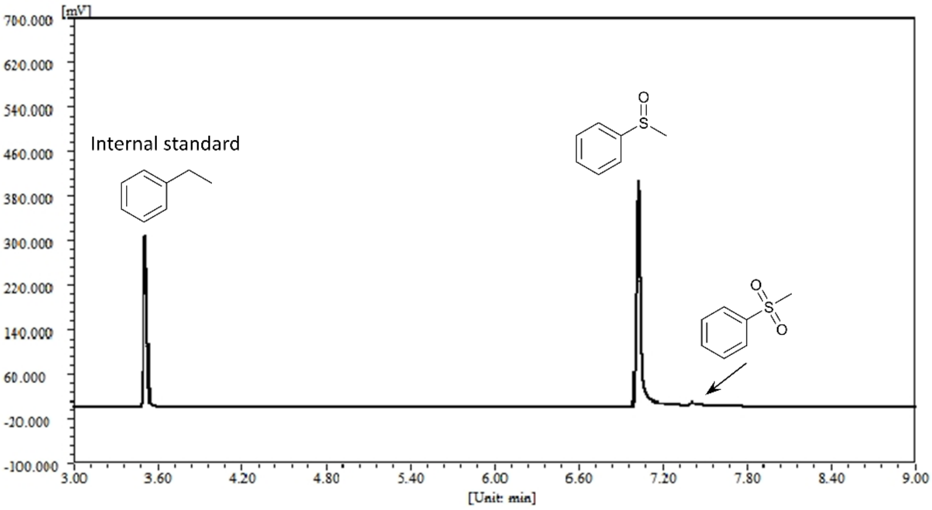

Figure.S25 Product analysis by GC-MS for epoxidation of **Thioanisole (3a)**.

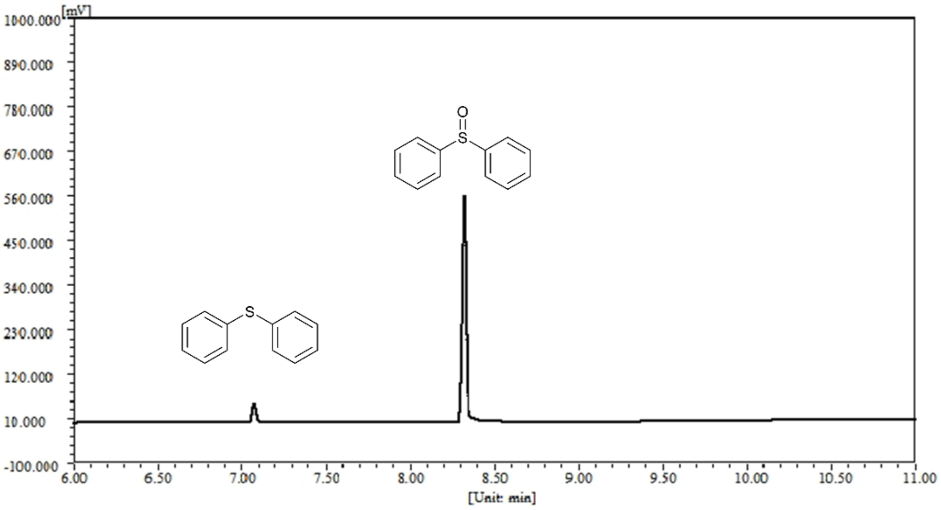

Figure.S26 Product analysis by GC-MS for epoxidation of **Phenyl sulfide (3b)**.