

## Supporting Information for:

### A reusable catalytic system for sulfide oxidation and epoxidation of allylic alcohols in water catalyzed by poly(dimethyl diallyl) ammonium/polyoxometalate

Wei Zhao<sup>\*</sup>, Chunxia Yang, Zhiguo Cheng, Zhenghui Zhang

*College of Chemistry and Pharmaceutical Engineering, Nanyang Normal University, Nanyang, China*

#### 1. Experimental

##### 1.1 Preparation of catalyst (PDDA-SiV<sub>2</sub>W<sub>10</sub>)

Firstly, an aqueous solution of  $[\gamma\text{-}1,2\text{-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  was prepared according to reference [11a, 12]. The anion was then connected and precipitated from the solution by Poly(diallyldimethylammonium chloride) (PDDA).

$\text{K}_8[\text{SiW}_{10}\text{O}_{36}] \cdot 12\text{H}_2\text{O}$  [12b] (1.6 g) was quickly dissolved in 1 M HCl (5.6 mL),  $\text{NaVO}_3$  (0.5 M, 2.2 mL) was added, and the mixture was gently stirred for 5 min. A clear solution was obtained after filtration, and poly (diallyldimethylammonium chloride) (2.0 g, average Mw 100000-200000, 20 wt. % in water) was added. After stirred for 0.5 h, acetone (100-150 mL) was added. The resulting yellow precipitate was collected by filtration and then dried in air (denoted as PDDA-SiV<sub>2</sub>W<sub>10</sub>). IR spectrum (KBr,  $\text{cm}^{-1}$ ): 1634, 1474, 1386, 1201, 1041, 967, 918, 871, 794, 702, 544, 403.

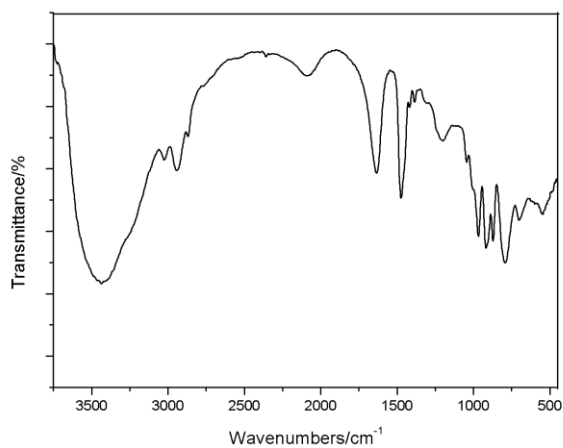
##### 1.2 Catalytic reaction

Catalytic oxidation of sulfides: catalyst (50 mg), substrate (2 mmol),  $\text{H}_2\text{O}_2$  (30% aq., 10 mmol) and  $\text{H}_2\text{O}$  (2 mL) were charged in the reaction flask. The mixture was then stirred at room temperature (298 K) for 2-8 h. The reaction was detected by GC. After reaction, the organic products were separated from the aqueous phase by extraction with ethyl acetate and analyzed by GC. The yields of products were calculated from the peak areas by using an internal standard method. The products were identified by GC-MS. The aqueous phase containing the catalyst after extraction was carried out for the next oxidation cycle.

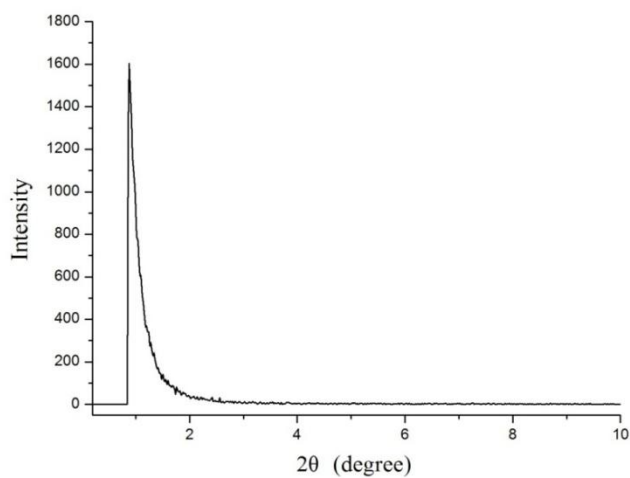
Catalytic epoxidation of allylic alcohols: catalyst (50 mg), substrate (5 mmol),  $\text{H}_2\text{O}_2$  (30% aq.,

5 mmol) and H<sub>2</sub>O (1 mL) were charged in the reaction flask. The mixture was then stirred at 308 K for 1-7 h. The reaction was detected by GC. After reaction, the organic products were separated from the aqueous phase by extraction with ethyl acetate and analyzed by GC. The yields of products were calculated from the peak areas by using an internal standard method. The products were identified by GC-MS. The aqueous phase containing the catalyst after extraction was carried out for the next oxidation cycle.

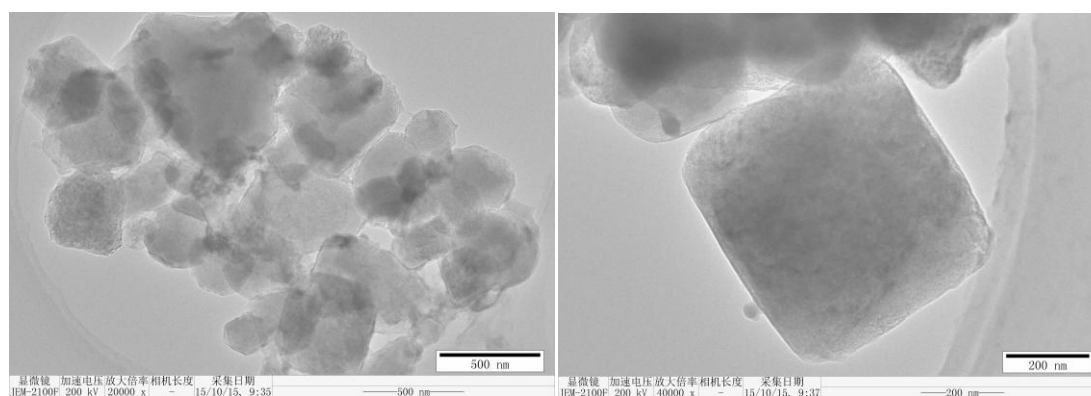
## 2. IR spectrum of the catalyst



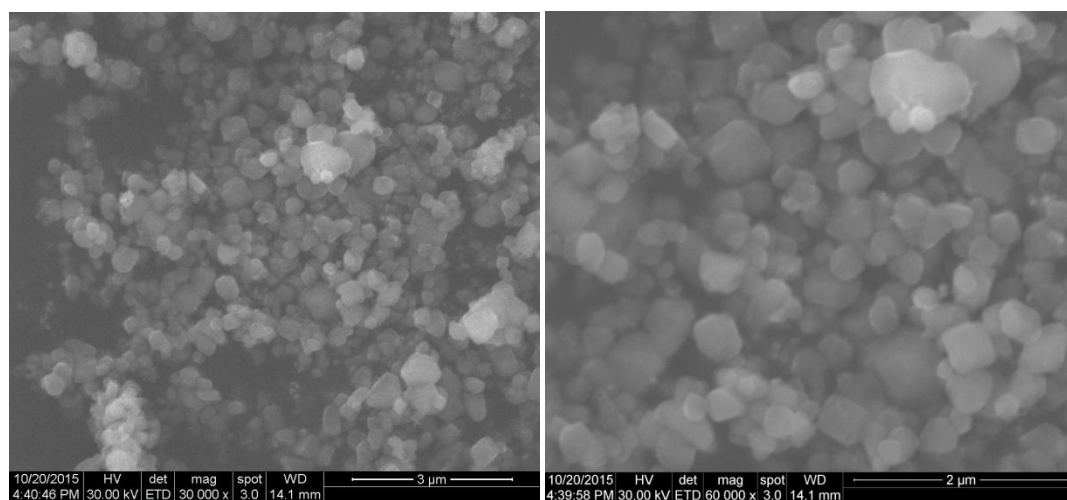
## 3. XRD analysis of prepared catalyst



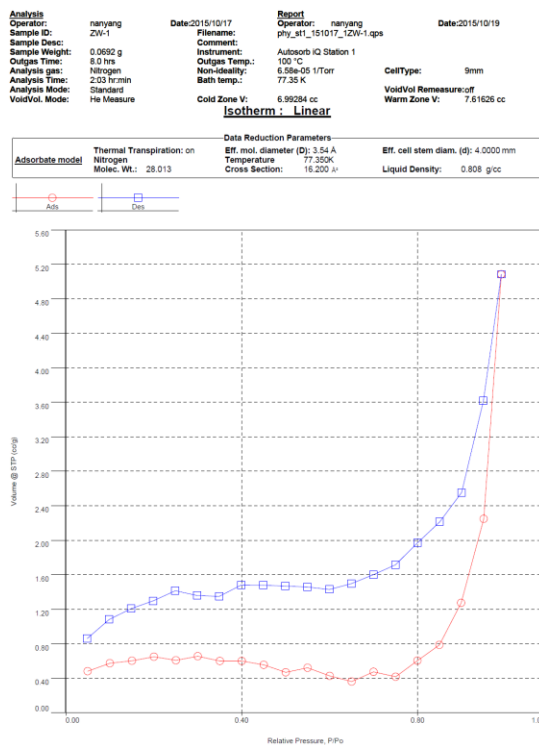
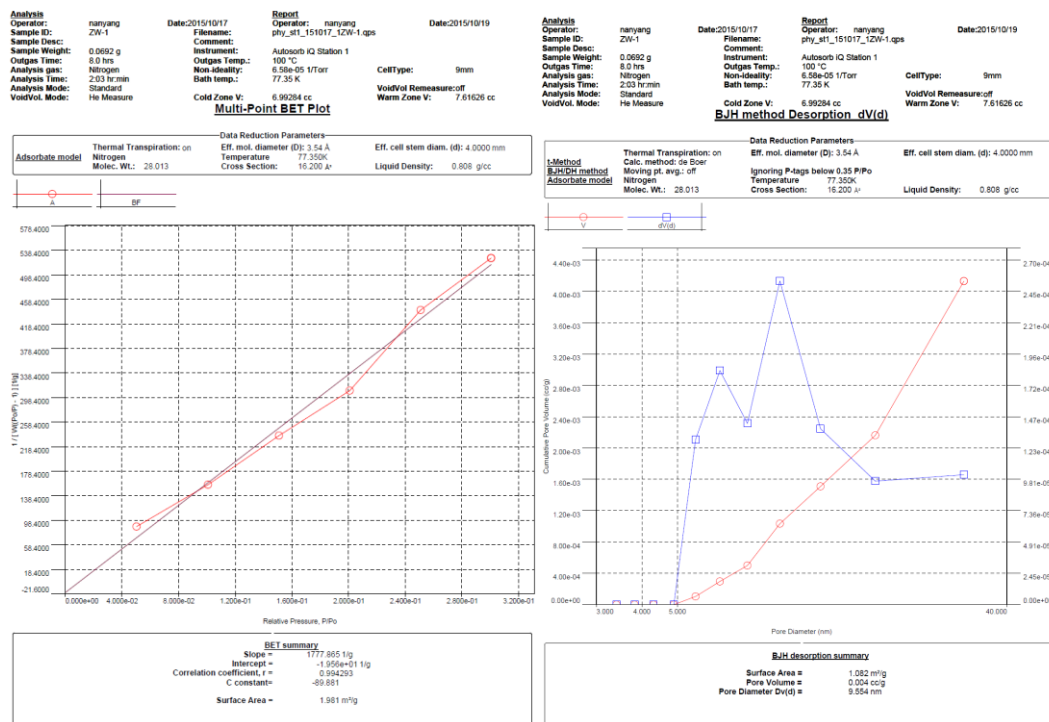
#### 4. TEM images of prepared catalyst



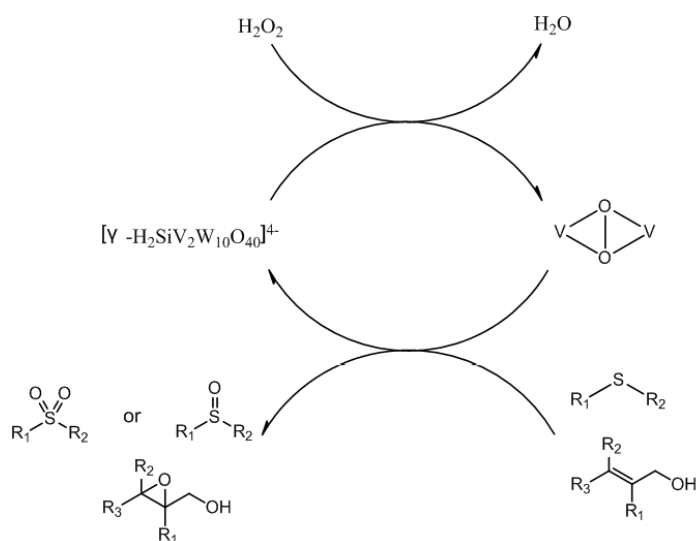
#### 5. SEM images of prepared catalyst



## 6. BET, pore size and particle size distribution characterizations of the catalyst



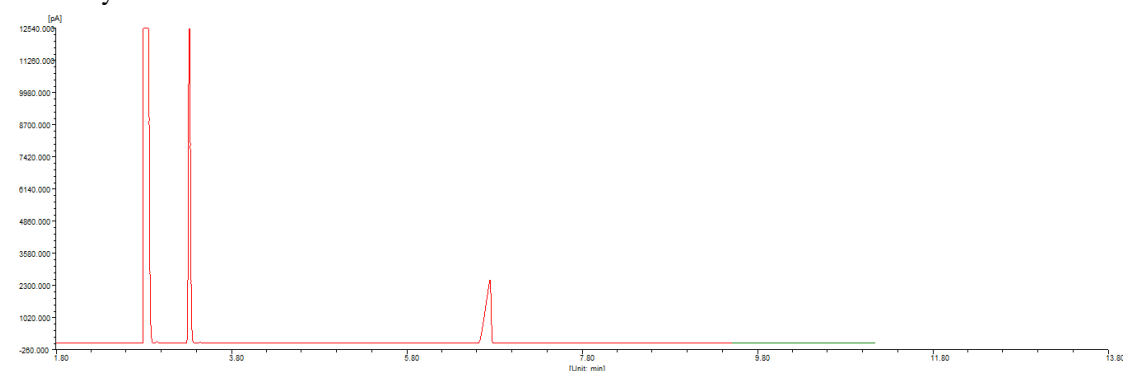
## 7. Proposed mechanism



Consult to reference (*Inorg. Chem.*, 2007, **46**, 1727-1736)

## 8. Gas chromatograms of standard samples to draw the calibration plot

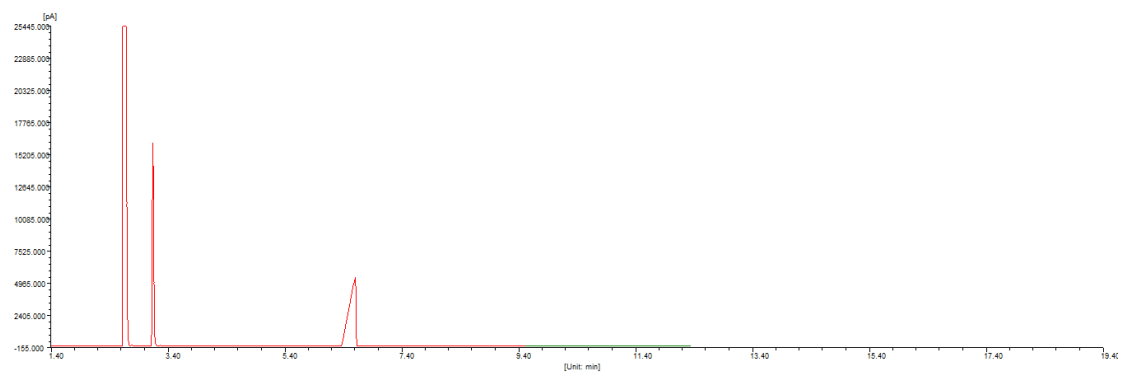
(A) 1 mmol of Methyl phenyl sulfone+ 2 mmol of Chlorobenzene (internal standard) in 6 mL ethyl acetate



Compound Name	Ret. Time	Area (%)
Chlorobenzene	3.319	11.3456
Methyl phenyl sulfone	6.756	5.9808

Concentration of Methyl phenyl sulfone / Concentration of Chlorobenzene = 0.53

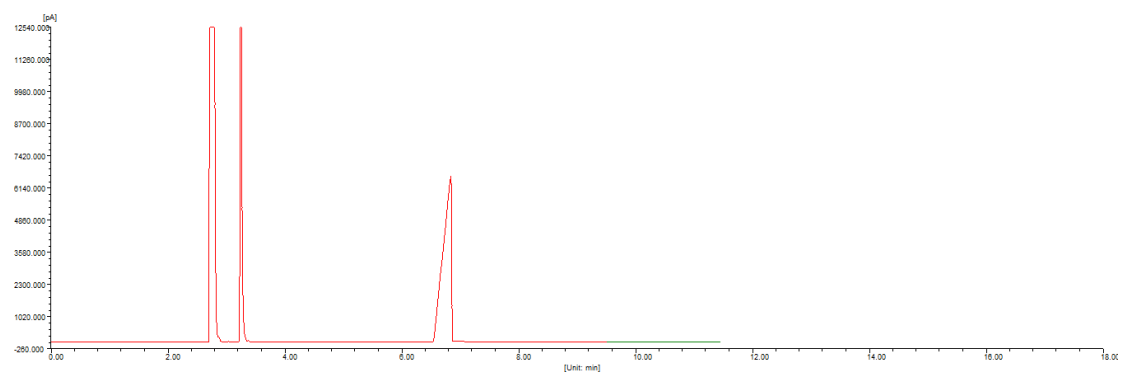
(B) 2 mmol of Methyl phenyl sulfone+ 2 mmol of Chlorobenzene (internal standard) in 6 mL ethyl acetate



Compound Name	Ret. Time	Area (%)
Chlorobenzene	3.144	10.0285
Methyl phenyl sulfone	6.616	14.5728

Concentration of Methyl phenyl sulfone / Concentration of Chlorobenzene = 1.45

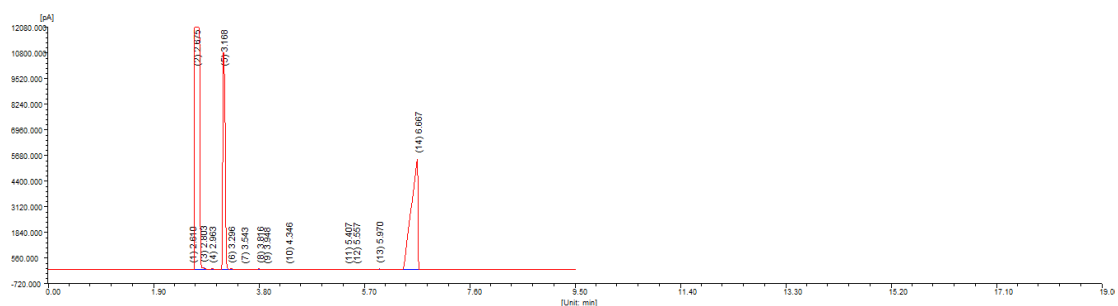
(C) 3 mmol of Methyl phenyl sulfone+ 2 mmol of Chlorobenzene (internal standard) in 6 mL ethyl acetate



Compound Name	Ret. Time	Area (%)
Chlorobenzene	3.253	10.5135
Methyl phenyl sulfone	6.842	23.1260

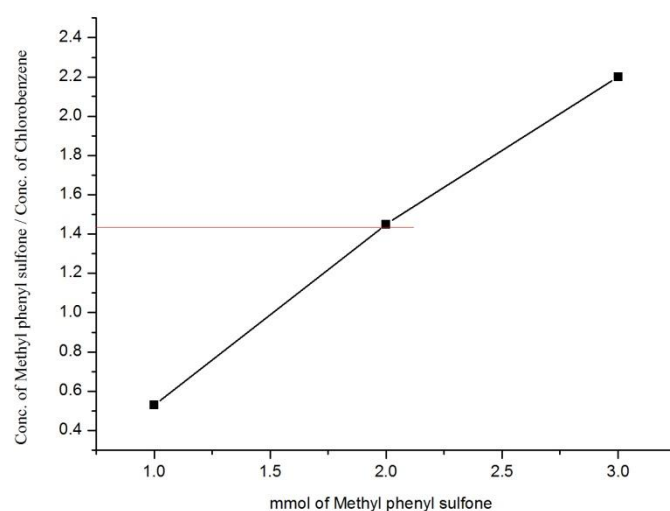
Concentration of Methyl phenyl sulfone / Concentration of Chlorobenzene = 2.2

(D) Reaction system (2 mmol substrate of methyl phenyl sulfide) + 2 mmol of Chlorobenzene (internal standard)



Compound Name	Ret. Time	Area (%)
Chlorobenzene	3.168	10.4540
Methyl phenyl sulfone	6.667	15.0458

Concentration of Methyl phenyl sulfone / Concentration of Chlorobenzene = 1.44



Calibration curve to find out unknown concentration of Methyl phenyl sulfone after reaction

From the calibration plot, the concentration of Methyl phenyl sulfone in the oxidation of methyl phenyl sulfide using PDDA-SiV<sub>2</sub>W<sub>10</sub> in water with hydrogen peroxide displays 99% sulfone.

## 9. The data (GC retention) of the products

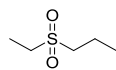


GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature

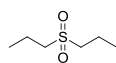
(338 K, 2 min), final column temperature (423 K), progress rate (15 K/min), injection temperature (493 K), detection temperature (523 K), retention time (7.1 min).



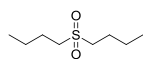
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (338 K, 2 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (7.2 min).



GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (353 K, 1 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (6.1 min).



GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (423 K, 2 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.0 min).



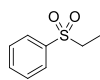
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (423 K, 2 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (5.4 min).



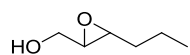
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (423 K, 2 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (6.7 min).



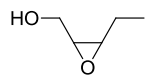
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (423 K, 2 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.6 min).



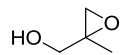
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (423 K, 2 min), final column temperature (473 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (5.8 min).



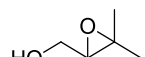
GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (373 K, 2 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.1 min).



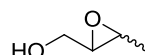
: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (358 K, 2 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.3 min).



: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (328 K, 3 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.8 min).



: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (338 K, 2 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.8 min).



: GC (SE-54 capillary column, 0.32 mm×30 m): carrier gas (N<sub>2</sub>), initial column temperature (338 K, 2 min), final column temperature (423 K), progress rate (20 K/min), injection temperature (493 K), detection temperature (523 K), retention time (4.1 min).