Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2021

Supporting Information

Selective Photocatalyst for Styrene Epoxidation with atmospheric O_2 by Covalent Organic Frameworks

Defa Gu[a,†], Nianjie Liang[a,†], Qiaosheng Li[a,†], Guangwen Li[b,*], Dongdong Yu[a], Yuzhou Liu[a,c,d*]

a.School of Chemistry, Beihang University, 37 Xueyuan Rd, Beijing, 100191, China.

b. Research Institute of Petroleum Processing, SINOPEC, Beijing 100083, China.

c.Beijing Advanced Innovation Center for Biomedical Engineering, Beihang University, 37 Xueyuan Rd, Beijing, 100191, China.

d.Beijing Shenyun Zhihe Technology Co., Ltd., 2 Yongcheng North Rd, Beijing, 100094, China.

†These authors contributed equally.

E-mail: liuyuzhou@buaa.edu.cn (Y.Z.L.)

Abstract: Biomimetic catalysis has been widely concerned due to environmentally friendly nature. In this work, **Fe@POG-OH** comprising a plurality of iron-catechols like catechol dioxygenases was synthetized and used to photo-catalyze styrene epoxidation with high selectivity and high conversion at room temperature. According to various spectroscopic and experimental results, it was revealed that **Fe@POG-OH** enables the activation of atmospheric O_2 to $O_2^{\bullet-}$ playing crucial roles in the effective and selective oxidation of styrene to styrene oxide (100% yield and 94% selectivity). A possible mechanism for the oxidation of styrene was proposed and also investigated using **DFT** calculations to better understand reaction path. The occurrence of spin crossing makes it possible to catalyze the cycle under light. The main path to generate styrene oxide is more energy-efficient than the side path to generate benzaldehyde and formaldehyde, which is consistent with the experimental results. This article reports the influence of the difference in spin multiplicity on the ring formation of the side pathway for the first time, which provides guidance for the investigation of the catalytic calculation of Fe coordination unsaturated complexes.

S1 Materials and Methods

S1-1:Materials and Equipment.

Unless otherwise mentioned, all commercials were purchased through Beijing InnoChem technology co., ltd and then used without any further purification. High resolution transmission electron microscopy (HR-TEM) experiments were recorded on a Hitachi 7650 electron microscope JEM-2100UHR. Products of epoxidation were analysed with a GC-MS (SHIMADZU,GCMS-QP2010 SE). Both the conversion and selectivity were obtained through the internal standard method according to the GC-MS data. Electron paramagnetic resonance (EPR) were collected on a BRUKER E500 electron paramagnetic resonance spectrometer under visible-light irradiation. High angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) images were obtained by a JEOL JEM-ARM200F microscope incorporated with a spherical aberration correction system for STEM. Energy-dispersive X-ray spectroscopy (EDS) mapping was performed using a 100 mm^2 JEOL Centurio SDD EDS detector. As a light source, LED flow reactor WP-TEC-1020HSL was used. Solid UV-vis absorption spectra were recorded on a SolidSpec-3700. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) were collected on a Agilent 725 ES.

S1-2: Synthesis of Fe@POG-OH.

POG-OH (100 mg) was dispersed in ethanol (200 mL) and sonicated for 30 minutes, and then aqueous NaOH solution (0.1 M, 10 ml) was added. The mixture was sonicated for 60 minutes and then filtered, followed by copious wash by excessive water to remove excessive NaOH. After washing, the black solids was treated with $FeCl_2 \cdot 4H_2O$ (18 mg, 5 wt% Fe compared to **POG-OH**) in 200 mL ethanol and sonicated for 60 minutes. The mixed solution was stirred for 12 hours at room temperature under Ar. Afterwards, the sample was filtrated and washed with ethanol, and then was heated at 100^oC for 24 hours under vacuum to obtain **Fe@POG-OH** as a black solid.

S1-3: Photoelectrochemical Measurements.

Photocurrent measurements were conducted with a CHI 760E electrochemical workstation (Chenhua Instrument, Shanghai, China) in a standard three-electrode system with the photocatalyst-coated FTO as the working electrode, Pt plate as the counter electrode, and an Ag/AgCl as a reference electrode. A 300 W xenon lamp was used as the light source. EIS was performed with a CHI 760E electrochemical workstation (Chenhua Instrument, Shanghai, China) in a conventional three electrode

cell, using a Pt plate as the counter electrode and Ag/AgCl electrode as the reference electrode. The electrolyte was a 0.1 M Na2SO4 solution. The 2 mg of catalyst was added into 1 mL of isopropanol and 20 μL of Nafion mixed solution. Then a 1mL suspension was dropped on the surface of a FTO glass and dried at room temperature for photocurrent measurements, and the signals were recorded under chopped light at 0.325 V. EIS was performed on the working electrode in a frequency range from 10−1 to 105 Hz with a bias potential of −0.7 V.

S1-4: Photocatalytic Activity Test.

In a typical activity test, a 10 mL Pyrex glass bottle was used as the reactor, after a mixture of Fe@POG-OH (1 mol%, in terms of Fe element) , styrene (0.1 mmol) and n-dodecane (0.1 mmol, a GC-MS internal standard) was dissolved in the solvent (1 mL)of N,N-Dimethylformamide (DMF). The reaction tube was then stirred magnetically for 8 hours at room temperature and irradiated with a LED fluorescent tubes (8 W). The temperature was kept constant using a water circulating system during the whole reaction. Products of epoxidation were analysed with a GC-MS (SHIMADZU,GCMS-QP2010 SE). Both the conversion and selectivity were obtained through the internal standard method according to the GC-MS data.

S1-5: Preparation-scale reaction.

A 100 mL Quartz pool was used as the reactor, after a mixture of Fe@POG-OH (50.48mg) , styrene (520 μL) and n-dodecane (510 μL, a GC-MS internal standard) was dissolved in the solvent (45 mL)of N,N-Dimethylformamide (DMF). The reaction tube was then stirred magnetically for 8 hours at room temperature and irradiated with a Xenon lamp (195 W). Products of epoxidation were analysed with a GC-MS (SHIMADZU,GCMS-QP2010 SE). Both the conversion and selectivity were obtained through the internal standard method according to the GC-MS data.

S1-6: EPR Detection.

The reactive oxygen species generated by **Fe@POG-OH** have been detected by EPR in the presence of DMPO. 10 μL of DMPO in DMF (1 mg/mL) was mixed with 50 μL of **Fe@POG-OH** in H_2O or DMF suspension. The formed mixture (60 μL) was added into the EPR tube. EPR measurements were carried out during the light irradiation with a 300 W xenon lamp (λ > 380 nm) under the air conditions.

S1-7: Computational methods.

All calculations were performed with Gaussian 16 software[S1]. The PBEPBE functional[S2, S3] was used in conjunction with the basis set B for geometry optimizations. B is a combination of the 6-31G* basis set[S4] for C, H, O and Cl atoms and the SDD effective core potential basis set[S5] for Fe atom. Harmonic vibration frequency calculations were performed at the same level of geometry optimizations in order to identify the local minima and the transition states. Thermal corrections were obtained from the frequency calculations. Intrinsic reaction coordinate (IRC)[S6,S7] calculations confirmed that the transition states connect two relevant minima. Single-point energy calculations were performed with the double-hybrid functional revDSD-PBEP86-D3[S8] and the def2-TZVPP basis set[S9]. Dispersion corrections were calculated by the Grimme's D3 correction with the Becke-Johnson (BJ) damping function[S10, S11]. The Gibbs free energy values were the sum of the thermal corrections obtained by the frequency calculations and the electronic energies obtained by the single-point energy calculations.

S2 Figures and Tables

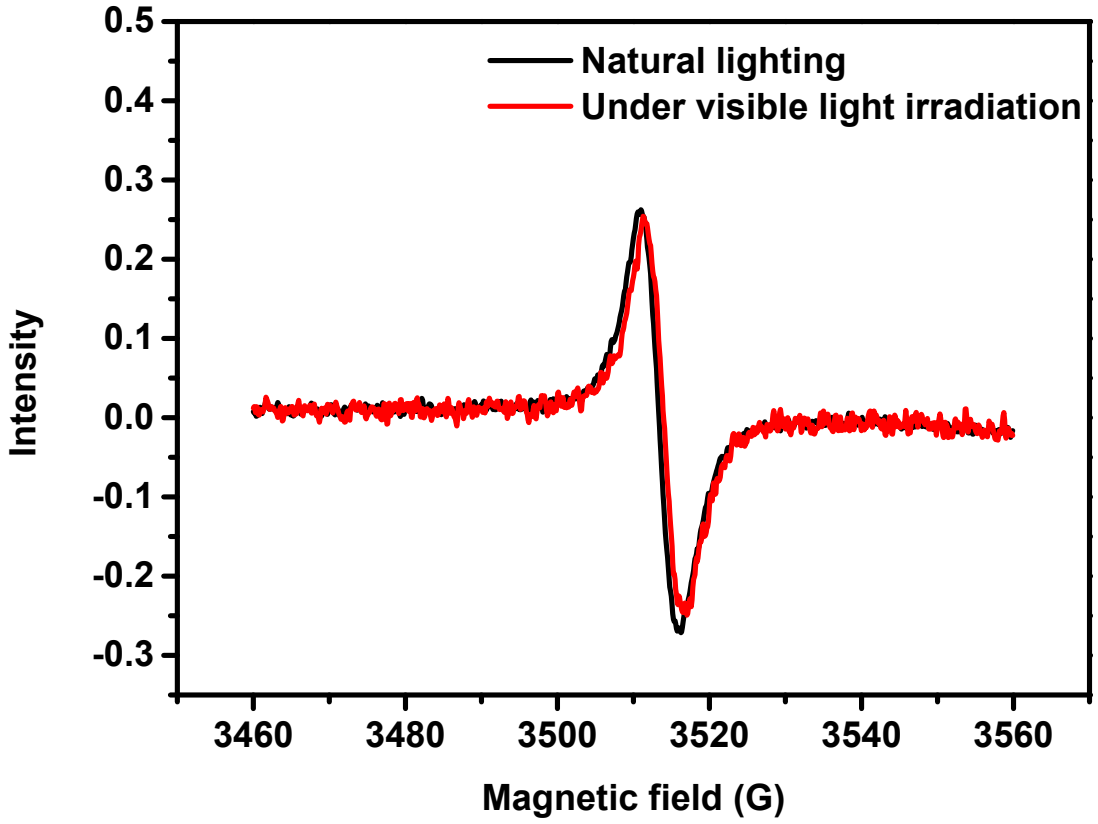


Figure S1. EPR spectra of **Fe@POG-OH** in the presence of DMPO, H_2O and air;

Table S1. Summary of Gibbs Free Energy of Different Structures (The above table represents the spin state, TS represents the transition state.)

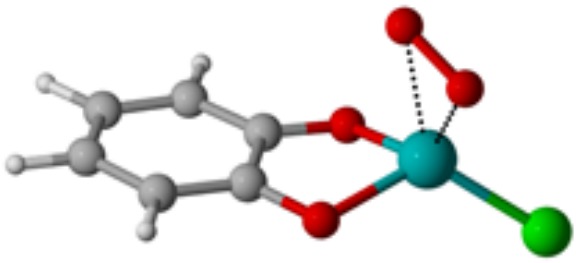
	Thermodynamic correction (Hartree)	Single-point energy (Hartree)	Total energy (Hartree)
1^4	0.046967	-2103.923065	-2103.876098
2^4	0.051109	-2254.122026	-2254.070917
$TS1^4$	0.048860	-2254.093661	-2254.044801
3^4	0.050540	-2254.119725	-2254.069185
4^4	0.169574	-2563.228442	-2563.058868

$TS2^4$	0.171305	-2563.230204	-2563.058899
5^4	0.173790	-2563.262352	-2563.088562
6^4	0.171408	-2563.288289	-2563.116881
$TS3^4$	0.170452	-2563.188914	-2563.018462
7^4	0.174709	-2563.322991	-2563.148282
8^4	0.177144	-2488.193784	-2488.016640
$TS4^4$	0.172063	-2488.220033	-2488.047970
9^4	0.172307	-2488.241796	-2488.069489
10^4	0.165991	-2563.272385	-2563.106394
$TS5^4$	0.168962	-2563.183370	-2563.014408
11^4	0.170740	-2563.238612	-2563.067872
12^4	0.170741	-2563.238614	-2563.067873
$TS6^4$	0.172041	-2563.287810	-2563.115769
13^4	0.176519	-2563.335031	-2563.158512
14^4	0.177392	-2563.356230	-2563.178838
$TS7^4$	0.171942	-2563.341655	-2563.169713
15^4	0.165692	-2563.440088	-2563.274396
1^6	0.047238	-2103.983959	-2103.936721
2^6	0.047554	-2254.150172	-2254.102618
$TS1^6$	0.048621	-2254.145641	-2254.097020
3^6	0.050424	-2254.128387	-2254.077963
4^6	0.164481	-2563.263577	-2563.099096
$TS2^6$	0.168390	-2563.236379	-2563.067989
5^6	0.171034	-2563.281553	-2563.110519
6^6	0.171034	-2563.281552	-2563.110518
$TS3^6$	0.170331	-2563.236835	-2563.066504
7^6	0.169342	-2563.296718	-2563.127376
8^6	0.171300	-2488.234580	-2488.063280
$TS4^6$	0.170213	-2488.233026	-2488.062813
9^6	0.171243	-2488.267058	-2488.095815
10^6	0.165869	-2563.300475	-2563.134606
$TS5^6$	0.170673	-2563.262427	-2563.091754

11^6	0.175764	-2563.291275	-2563.115511
12^6	0.170896	-2563.284820	-2563.113924
$TS8^6$	0.172640	-2563.287483	-2563.114843
16^6	0.174615	-2563.319332	-2563.144717
17^6	0.173936	-2563.315736	-2563.141800
$TS9^6$	0.173434	-2563.307437	-2563.134003
18^6	0.169287	-2563.424915	-2563.255628
O_2	-0.016406	-150.152168	-150.168574
styrene	0.098677	-309.140819	-309.042142
epoxy styrene	0.103309	-384.262211	-384.158902

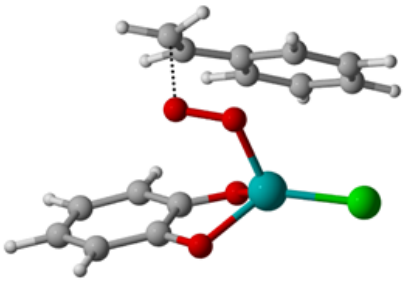
All geometric structures in ESI were shown through CYLview[S12]. Gray, white, red, cyan and green balls represent carbon, hydrogen, oxygen, iron and chlorine atoms, respectively.

Table S2. Graphic and geometric structure information of $TS1^4$.



C	3.69865000	-0.58528800	0.47426300
C	2.51907500	-1.11713700	0.98180600
C	1.28909100	-0.68818500	0.42563900
C	1.28967400	0.24808600	-0.70253800
C	2.51069900	0.77701800	-1.18806400
C	3.69592100	0.35385700	-0.59980400
H	4.65570700	-0.88633300	0.91091000
H	2.50940600	-1.83045200	1.81002000
H	2.49104100	1.48543100	-2.02034400
H	4.65047600	0.74068800	-0.96852400
O	0.11251800	0.48800300	-1.23841500
O	-1.83539100	1.79060000	0.54436600
Fe	-1.26003900	0.02033900	0.02856600
Cl	-3.05325500	-1.06259400	-0.52879100
O	-0.84331700	1.83462200	1.39157400
O	0.10882300	-1.10124600	0.82333100

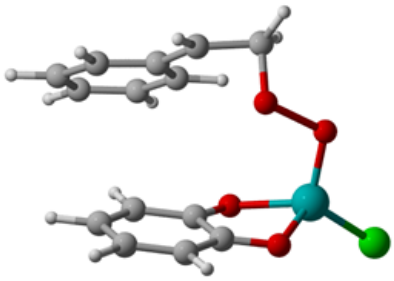
Table S3. Graphic and geometric structure information of TS2[4].



C	-3.14134900	2.11497500	-0.91290700
C	-1.81912600	1.75827700	-1.14721600
C	-1.41659600	0.41852600	-0.90831700
C	-2.39548200	-0.56033600	-0.42383800
C	-3.73198300	-0.15287100	-0.18117800
C	-4.08872400	1.16665800	-0.42982000
H	-3.46682200	3.14259300	-1.10253700
H	-1.08045000	2.46908800	-1.52739900
H	-4.45076000	-0.89067200	0.18553100
H	-5.11975900	1.48886100	-0.25406400
O	-1.95636600	-1.78986900	-0.27791500
O	0.01223200	-1.08310500	1.70493500
Fe	-0.02497400	-1.66209200	-0.08230300
Cl	1.48571500	-3.17762800	-0.51226700
O	-0.86509700	-0.12056800	2.00836300
C	3.67444700	1.14538400	-1.16774500
C	3.47021900	0.37632300	-0.00874800
C	1.58610700	1.80819000	0.62736400
C	2.45263900	0.70683500	0.88619000
C	1.82204700	2.57999600	-0.54414800
C	2.85196700	2.25644500	-1.42493800
H	4.47242600	0.87955600	-1.86760600
H	4.10430800	-0.49223600	0.19205200
H	2.30500900	0.09511300	1.77955400
H	1.16923200	3.43540400	-0.75115400
H	3.01157000	2.85977100	-2.32393800
C	0.45748800	2.12567600	1.45931400
H	-0.21425400	2.91012900	1.09239200
C	0.06816300	1.41633800	2.60336400
H	-0.76322600	1.80491700	3.19898200

O	-0.20491200	-0.03877600	-1.12328600
H	0.79913600	0.82758600	3.16557000

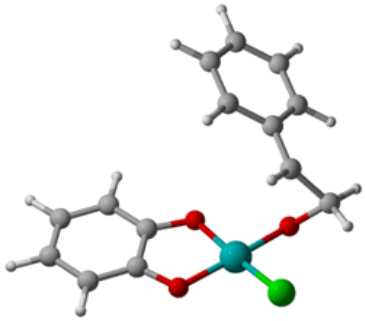
Table S4. Graphic and geometric structure information of TS3[4].



C	1.70433400	2.78497600	-0.47338700
C	1.22327300	1.60710500	-1.02880800
C	-0.08736000	1.17841000	-0.69860300
C	-0.90382900	1.98016000	0.21876200
C	-0.37074900	3.17146800	0.77845200
C	0.91342600	3.56210200	0.42498000
H	2.71327600	3.12660400	-0.72536600
H	1.82472000	0.99688200	-1.70666700
H	-0.98864300	3.75241900	1.46847600
H	1.33244200	4.48356000	0.84124600
O	-2.10634300	1.52975100	0.46113600
O	-1.75264800	-1.33874000	1.22914700
Fe	-2.24452900	-0.34423700	-0.10243000
Cl	-4.00214500	-1.02642500	-1.20866300
O	-0.26196700	-0.72922000	1.90196100
C	3.81966400	-1.09967600	-1.75000600
C	2.61298500	-1.81549500	-1.64099300
C	2.38985600	-1.10149000	0.68708100
C	1.90475500	-1.82545700	-0.44083600
C	3.59654800	-0.35596000	0.54612700
C	4.30804100	-0.36845300	-0.65159800
H	4.37442200	-1.10513000	-2.69337300
H	2.22193800	-2.36326700	-2.50337100
H	0.95624000	-2.36350200	-0.37442300
H	3.96471500	0.21902400	1.40229300
H	5.24117600	0.19627600	-0.73927300
C	1.74231900	-1.12473300	1.95870000
H	2.13804600	-0.46611100	2.73974900

C	0.49887700	-1.86553200	2.26963900
H	0.36496600	-2.15694900	3.32729600
O	-0.64889500	0.09361700	-1.17163700
H	0.29691800	-2.72824100	1.61193800

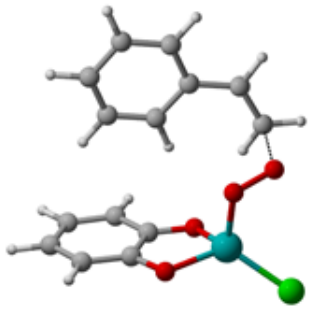
Table S5. Graphic and geometric structure information of TS4[4].



C	-2.87955900	3.23060300	-0.29606100
C	-1.69504300	2.58964400	-0.69200600
C	-1.60066600	1.20476000	-0.49496000
C	-2.67601400	0.47518000	0.08104100
C	-3.85768700	1.11981800	0.47398700
C	-3.94494300	2.50654200	0.27787000
H	-2.97655400	4.31173500	-0.43615000
H	-0.86085000	3.13697100	-1.14043200
H	-4.67464800	0.54309800	0.91645100
H	-4.85639900	3.03368300	0.57600200
O	-2.43791500	-0.84775600	0.18480800
O	-0.54273500	0.43603900	-0.81755600
Fe	-0.74366100	-1.33131400	-0.30863700
Cl	-0.91026100	-3.30231400	0.64222600
O	0.95166900	-1.65790800	-1.04140800
C	4.31818800	1.52702500	-0.58600100
C	3.68090500	0.28968200	-0.50880700
C	2.61265000	0.09212600	0.40484100
C	2.20177800	1.17591700	1.22606700
C	2.84431900	2.41029800	1.14477900
C	3.90370100	2.58829800	0.23877700
H	5.14081300	1.67262300	-1.29231800
H	4.00141500	-0.53022600	-1.15740600
H	1.36082800	1.03223500	1.91220700
H	2.51682200	3.23963700	1.77832000

H	4.40595800	3.55828000	0.17065700
C	1.93918800	-1.16617300	0.54892100
H	1.22242500	-1.27132800	1.37463800
C	2.01127800	-2.32863600	-0.36239600
H	2.89645800	-2.41023400	-1.01119800
H	1.71665200	-3.29647800	0.07286800

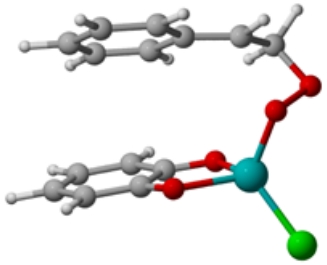
Table S6. Graphic and geometric structure information of TS5[4].



C	-0.61851400	3.71724200	1.10040700
C	-0.08406600	2.55410300	1.65590300
C	0.68105700	1.69515400	0.83483700
C	0.89614500	2.03558900	-0.56231600
C	0.32643900	3.20942800	-1.10360600
C	-0.41803800	4.04106500	-0.26796800
H	-1.20465600	4.39396600	1.72983700
H	-0.23777600	2.29091500	2.70624500
H	0.49144900	3.44327700	-2.15889500
H	-0.85185100	4.96186100	-0.66941300
O	1.63660900	1.18180500	-1.24919700
O	0.61317600	-1.56672400	-0.94196800
Fe	1.94720900	-0.43675600	-0.28738400
Cl	3.90775700	-1.37518700	-0.09595100
O	0.64035500	-2.72299800	-0.28488900
C	-4.08540100	0.45362200	-0.76415100
C	-2.87555300	0.74354400	-0.10955100
C	-2.53314500	-1.64235000	0.33118400
C	-2.11172400	-0.28697900	0.43675000
C	-3.76619100	-1.91138400	-0.32493900
C	-4.52974000	-0.87742100	-0.86457000
H	-4.68429300	1.26338200	-1.19256200
H	-2.52462000	1.77657600	-0.02261900
H	-1.18443700	-0.04875000	0.96016100
H	-4.10320400	-2.94992600	-0.41339000
H	-5.47306100	-1.10312200	-1.37138100
C	-1.75111600	-2.73877200	0.83982400
H	-2.17716600	-3.74100300	0.70903200
C	-0.45461700	-2.64637400	1.34355200
H	0.01276200	-3.53261200	1.78107500

O	1.21777400	0.55624300	1.23897800
H	-0.03899000	-1.68613500	1.66954100

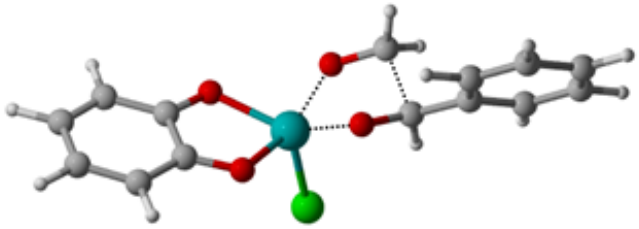
Table S7. Graphic and geometric structure information of TS6[4].



C	-2.33993100	2.99084700	1.15154700
C	-1.21312700	2.38202400	1.69254400
C	-0.31064300	1.70878900	0.82919800
C	-0.59573600	1.63923000	-0.61162600
C	-1.76123600	2.27938600	-1.12382100
C	-2.60949000	2.94244400	-0.24987600
H	-3.03247900	3.52733400	1.80782300
H	-0.99067700	2.42154400	2.76298300
H	-1.95672100	2.22613200	-2.19846200
H	-3.50494800	3.44026400	-0.63520000
O	0.23287100	0.95291700	-1.33699500
O	1.76718100	-1.58118200	-0.17176000
Fe	1.80553200	0.29742500	-0.24362800
Cl	3.68728600	1.12161100	-1.00371100
O	2.25298300	-1.91348900	1.22261900
C	-3.53639200	-1.31364000	-0.83257700
C	-2.97957400	-0.75370600	0.33146700
C	-1.06423700	-2.26595400	0.15100400
C	-1.76288200	-1.22170400	0.82223700
C	-1.65389100	-2.82963000	-1.01796800
C	-2.87125700	-2.35639300	-1.50234100
H	-4.48703900	-0.93425800	-1.21974900
H	-3.48742700	0.06789200	0.84470100
H	-1.33552900	-0.76396500	1.71698900
H	-1.12357200	-3.63108400	-1.54299600
H	-3.30559800	-2.79243100	-2.40690500
C	0.22965700	-2.71620800	0.55239400
H	0.62724900	-3.60800100	0.05644900
C	0.98285500	-2.27558800	1.77580800

H	1.14675100	-3.08172600	2.51634500
O	0.77459800	1.10111100	1.23759500
H	0.51654500	-1.40636300	2.27581800

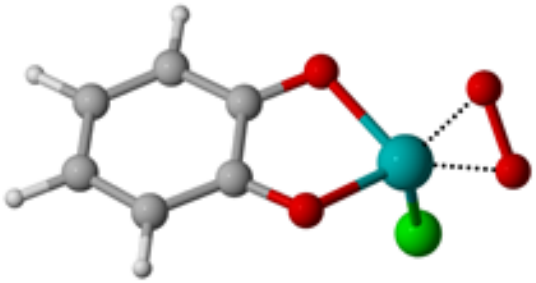
Table S8. Graphic and geometric structure information of TS7[4].



C	5.49468800	1.01228300	0.64022900
C	4.57154100	0.15806400	1.22183900
C	3.26570200	0.08745700	0.66319900
C	2.92576000	0.90220100	-0.51657600
C	3.90569200	1.77009000	-1.07858700
C	5.16389400	1.81232900	-0.50154200
H	6.50385000	1.08291700	1.05770200
H	4.81115100	-0.45757900	2.09289100
H	3.64163600	2.37104500	-1.95282600
H	5.93148200	2.46800800	-0.92418100
O	1.71973600	0.76435400	-0.96376100
O	-0.97352600	0.36959200	-0.29363200
Fe	0.65823200	-0.66108600	0.00740500
Cl	0.61882900	-2.34239600	-1.44209800
O	-0.40350900	-1.36965400	1.48699300
C	-5.91985600	1.45264300	-0.00509000
C	-4.76666600	2.24595600	0.12953200
C	-3.37851200	0.26139900	-0.08631600
C	-3.50119700	1.65532500	0.09680700
C	-4.53972700	-0.53005000	-0.21954800
C	-5.80474300	0.06376000	-0.17958900
H	-6.90992600	1.91839400	0.02650100
H	-4.86069000	3.32842500	0.26140700
H	-2.59089700	2.25399300	0.19511100
H	-4.44022900	-1.61229700	-0.36282700
H	-6.70240400	-0.55241900	-0.28936600
C	-2.04923600	-0.38615200	-0.08782900
H	-2.02750100	-1.38825500	-0.56909600
C	-1.67691800	-1.04940100	1.59116500
H	-2.38848100	-1.89052800	1.69946400
O	2.30428600	-0.64934000	1.12853200

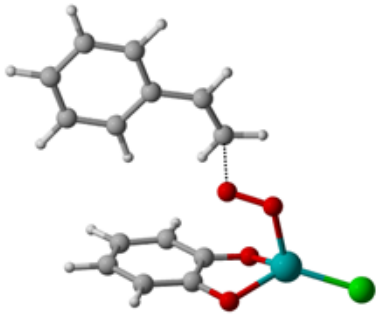
H	-1.92053600	-0.16778900	2.21713900

Table S9. Graphic and geometric structure information of TS1[6].



C	3.65191100	0.35087300	-0.61776200
C	2.47462100	0.50341800	-1.33048700
C	1.26606700	0.02323300	-0.75434800
C	1.27430100	-0.54463000	0.61132000
C	2.50723300	-0.68509500	1.30303000
C	3.66664700	-0.23990900	0.68745200
H	4.59747600	0.68396000	-1.05573100
H	2.44556200	0.94737300	-2.32888400
H	2.50708500	-1.11926000	2.30613500
H	4.62281700	-0.32939500	1.21202500
O	0.11556700	-0.88761500	1.09199700
O	-2.98330500	-1.10793600	0.21407900
Fe	-1.32086200	-0.09171600	-0.02626400
Cl	-1.61936100	1.98527500	0.53535300
O	-2.42039900	-1.50574000	-0.93131800
O	0.11987700	0.00190700	-1.36812200

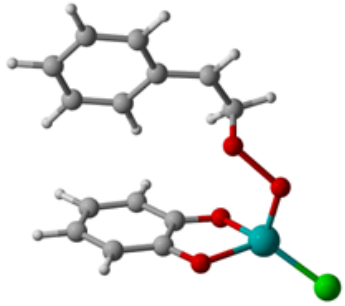
Table S10. Graphic and geometric structure information of TS2[6].



C	-0.84881200	2.79268800	0.89461500
C	0.06761300	1.97843200	1.55462000
C	1.10936600	1.36900100	0.80913000
C	1.20891100	1.61817400	-0.63206100
C	0.23253900	2.42362300	-1.27391400
C	-0.77385200	3.00336500	-0.51145700
H	-1.64438100	3.28190400	1.46603800
H	0.02412900	1.81293400	2.63528800
H	0.31076400	2.58472100	-2.35248800
H	-1.52016500	3.64060000	-0.99560600
O	2.24773200	1.09211100	-1.24226700
O	1.30796800	-1.55323400	-0.59511900
Fe	2.80268100	-0.40100300	-0.13899800
Cl	4.73550500	-1.39558400	-0.10917000
O	0.14337100	-0.93224400	-0.49988000
C	-5.53614200	0.11843000	-0.54547500
C	-4.40798400	0.81676900	-0.07769500
C	-3.21984200	-1.29410700	0.25758500
C	-3.26579300	0.12566400	0.32202300
C	-4.36403800	-1.98116800	-0.22979700
C	-5.50802800	-1.28453800	-0.62056900
H	-6.43159600	0.66640300	-0.85474100
H	-4.42201700	1.91049100	-0.03053300
H	-2.39042400	0.68350100	0.66524000
H	-4.33683600	-3.07439900	-0.29431000
H	-6.38097000	-1.83165900	-0.98959500
C	-2.05513200	-2.05223800	0.65088500
H	-2.08872900	-3.12934000	0.44538500
C	-0.88806600	-1.52857700	1.18432700
H	-0.08870100	-2.20008500	1.50627800

O	2.04336400	0.60397300	1.33632400
H	-0.84826300	-0.51202700	1.58312500

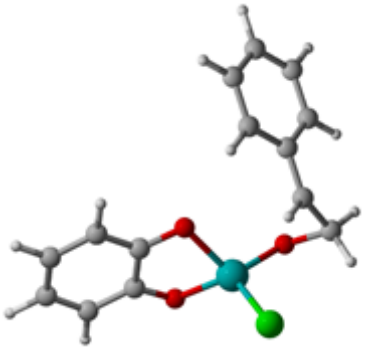
Table S11. Graphic and geometric structure information of TS3[6].



C	0.94791300	3.14278800	-0.91908100
C	0.04245400	2.29662700	-1.55164300
C	-0.82642100	1.49954800	-0.75987700
C	-0.75291800	1.58182600	0.70412000
C	0.19176400	2.45217900	1.31096800
C	1.02398600	3.21639200	0.50314800
H	1.61485600	3.76752900	-1.52176700
H	-0.02929800	2.23329500	-2.64129200
H	0.23883900	2.49733800	2.40235300
H	1.75121700	3.89300200	0.96284300
O	-1.59665100	0.84330800	1.37126000
O	-1.66205400	-1.87498500	0.19441000
Fe	-2.56224000	-0.40497700	0.17936600
Cl	-4.69817900	-0.79995900	0.24804200
O	0.05363400	-1.72006600	0.14808800
C	4.99130700	0.20059400	0.52446500
C	3.82318700	0.75952000	-0.02606800
C	2.83885800	-1.47035400	-0.22298400
C	2.76041900	-0.05750800	-0.40134500
C	4.02360100	-2.01610300	0.35293400
C	5.08676000	-1.19090000	0.71116800
H	5.82388300	0.84863800	0.81529400
H	3.73789900	1.84260100	-0.15581100
H	1.85038700	0.39316100	-0.80487600
H	4.08813600	-3.09887700	0.50368800
H	5.99219400	-1.62448700	1.14635500
C	1.78140600	-2.34541600	-0.60867000
H	1.86296900	-3.40552500	-0.34982100

C	0.49146400	-1.90307900	-1.18668100
H	-0.06511400	-2.70226100	-1.70452400
O	-1.72110500	0.68472800	-1.25478400
H	0.48805300	-0.97625300	-1.78717100

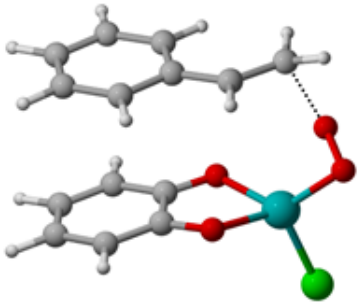
Table S12. Graphic and geometric structure information of TS4[6].



C	-3.73983100	2.57283400	0.57065700
C	-2.45411300	2.15224900	0.91051300
C	-1.88222800	1.05046000	0.23491200
C	-2.64774500	0.35731100	-0.79328700
C	-3.95014900	0.79970100	-1.10737300
C	-4.48210000	1.90020200	-0.43203000
H	-4.18391600	3.43018400	1.08595200
H	-1.86896700	2.65564500	1.68608600
H	-4.51443900	0.26916700	-1.87963600
H	-5.49012700	2.24828800	-0.67863100
O	-2.04521400	-0.66030300	-1.40205600
O	-0.65592400	0.59737400	0.46682900
Fe	-0.60010000	-1.24674500	-0.24382700
Cl	-0.94858900	-2.74727000	1.37005000
O	1.06803300	-1.71492700	-1.09266600
C	4.54055300	1.47240900	-0.86817700
C	3.88849000	0.25517600	-0.69438900
C	2.81657000	0.14454700	0.23598900
C	2.41317900	1.29863800	0.96743100
C	3.07162100	2.51334400	0.78310100
C	4.13605900	2.60185800	-0.12994600
H	5.36649900	1.55297300	-1.58090600
H	4.20024000	-0.62006100	-1.27092300
H	1.55539400	1.22093800	1.64115800
H	2.75249100	3.39799800	1.34156400

H	4.65152300	3.55653300	-0.27454200
C	2.13873100	-1.08564600	0.48378200
H	1.42573900	-1.11747000	1.32009900
C	2.14984900	-2.29654000	-0.36998500
H	3.02911200	-2.44278800	-1.01803100
H	1.87656400	-3.22884700	0.15240600

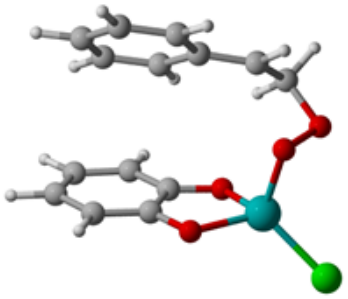
Table S13. Graphic and geometric structure information of TS5[6].



C	-2.35695100	2.50634400	0.64064500
C	-1.47998500	1.69479100	1.34171100
C	-0.37017600	1.12536500	0.65847100
C	-0.18674100	1.40766400	-0.77731800
C	-1.11065600	2.24572300	-1.45980700
C	-2.17150000	2.78667500	-0.74984900
H	-3.20991100	2.95486500	1.15945900
H	-1.61028300	1.47728800	2.40478800
H	-0.95035300	2.45550000	-2.52108000
H	-2.88442600	3.44378400	-1.25743100
O	0.85283800	0.85438100	-1.33858900
O	2.84089700	-1.58785300	-0.75089900
Fe	2.09192400	0.06993300	-0.02406200
Cl	3.68360900	1.42341100	0.64099700
O	2.12274400	-2.02067600	0.34567300
C	-4.00338500	-0.63165600	0.55026200
C	-3.19677300	-1.39389400	1.41960600
C	-1.53882000	-1.69875700	-0.35485700
C	-1.98469400	-1.91774800	0.98042600
C	-2.35628800	-0.90370600	-1.20574800
C	-3.57517800	-0.38698000	-0.76209100
H	-4.95748600	-0.22763700	0.90255600
H	-3.52370800	-1.57474300	2.44837100
H	-1.36507600	-2.49865300	1.66926100

H	-2.02197900	-0.71911000	-2.23181500
H	-4.18709100	0.21809800	-1.43745500
C	-0.33383300	-2.27057700	-0.89634700
H	-0.12174200	-2.02561200	-1.94429300
C	0.58247800	-3.09510100	-0.24126100
H	1.26363700	-3.70187900	-0.84211200
O	0.51757200	0.35979900	1.21250700
H	0.37966800	-3.47220200	0.76581000

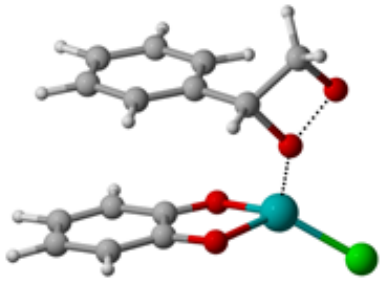
Table S14. Graphic and geometric structure information of TS8[6].



C	1.87551400	-3.09533500	0.99127300
C	0.82100100	-2.38479700	1.57522300
C	-0.07583400	-1.68078100	0.74335000
C	0.09726200	-1.71469500	-0.69543700
C	1.17865100	-2.42557400	-1.25779500
C	2.05622700	-3.10979300	-0.41264200
H	2.56647300	-3.65526400	1.62972200
H	0.66457600	-2.37154800	2.65826200
H	1.29707300	-2.43674700	-2.34501800
H	2.88915300	-3.67484700	-0.84253400
O	-0.82587000	-1.07728100	-1.40239200
O	-1.29073200	1.71969600	-0.47329800
Fe	-2.00847500	-0.05830800	-0.26984400
Cl	-4.17472700	-0.20234200	-0.53574400
O	-1.77843600	2.14631800	0.87039100
C	4.10043000	0.68431100	-0.56564700
C	3.31229400	0.13610000	0.46072200
C	1.68318200	1.94325700	0.17973000
C	2.12016500	0.75098000	0.83558400
C	2.50581100	2.48541800	-0.85803200
C	3.69453800	1.86453900	-1.22142000
H	5.03097200	0.19009700	-0.86148600

H	3.61554200	-0.79044200	0.95488100
H	1.51784000	0.30928500	1.63086800
H	2.17412200	3.39362400	-1.37201200
H	4.31090000	2.28694500	-2.02049000
C	0.45728300	2.58415300	0.47887500
H	0.24004100	3.52917400	-0.03079700
C	-0.51655900	2.20973300	1.56081700
H	-0.61604400	2.98165500	2.34824600
O	-1.11362300	-0.97935900	1.18800800
H	-0.29043100	1.23378400	2.02467600

Table S15. Graphic and geometric structure information of TS9[6].



C	3.26173400	-2.01272100	0.32789300
C	2.19169500	-1.70127600	1.17327200
C	0.92422200	-1.45363100	0.61468600
C	0.75215800	-1.51792200	-0.82691900
C	1.85292900	-1.83756600	-1.65869600
C	3.09595500	-2.08236200	-1.07739400
H	4.24706100	-2.21118300	0.76164500
H	2.31308300	-1.64517700	2.25848400
H	1.69752800	-1.88977600	-2.74046700
H	3.95191000	-2.33620600	-1.71009400
O	-0.46272000	-1.27452900	-1.28784700
O	-1.71765500	1.01836100	-0.56566000
Fe	-1.66999500	-0.79698100	0.19507200
Cl	-3.67444000	-1.61577600	0.48910200
O	-2.48257600	2.32918000	-0.01641700
C	3.03135800	1.73367100	1.09508200
C	1.83170800	2.03284200	1.76251600
C	0.62096300	1.85900900	-0.33926300
C	0.63130000	2.10045600	1.04998000
C	1.82301000	1.54528000	-0.99813000
C	3.02746100	1.49222100	-0.28471500

H	3.96925100	1.67957000	1.65663000
H	1.83331300	2.20954800	2.84238300
H	-0.30919700	2.32169500	1.56610200
H	1.81083800	1.33508700	-2.07277900
H	3.95572900	1.23629400	-0.80324900
C	-0.65632900	1.93227500	-1.11167600
H	-0.50589200	1.66912800	-2.16978500
C	-1.59365400	3.11849000	-0.83904700
H	-2.10643500	3.49870100	-1.74161100
O	-0.16093100	-1.18294500	1.33321400
H	-1.14783400	3.94889000	-0.26572600

REFERENCES

S1 Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A., Jr Montgomery,. J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S2 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

S3 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 1997, **78**, 1396.

S4 L. Olcari, *Inorg. Chim. Acta* 1986, **119**, 234.

S5 M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* 1987, **86**, 866.

S6 C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* 1990, **94**, 5523.

S7 C. Gonzalez, H. Schlegel, *J. Chem. Phys.* 1989, **90**, 2154.

S8 G. Santra, N. Sylvetsky, J. M. L. Martin, *J. Phys. Chem. A* 2019, **123**, 5129.

S9 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297.

S10 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 2010, **132**, 154104.

S11 S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* 2011, **32**, 1456.

S12 C. Y. Legault, CYLview, 1.0b, Université de Sherbrooke, 2009.