Supporting information available for

The oxidative properties of a manganese(IV) hydroperoxide moiety and its relationships with the corresponding manganese(IV) oxo and hydroxo moieties

Yujuan Wang, Song Shi, Dajian Zhu, Guochuan Yin*

School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

1. Mass spectrometry experiment to detect the manganese(IV) hydroperoxide intermediate

To be consistent with the catalytic conditions applied in the manganese(IV) hydroperoxide mediated oxidations, the ESI-MS experiments were also conducted in t-butanol/water (4:1) at pH 1.5 containing 5 mM $Mn(Me_2EBC)Cl_2$ catalyst to detect the manganese(IV) hydroperoxide intermediate, and 30% H_2O_2 were added in excess. In ms spectrum, the dominant ms peak at m/z = 342.0 is corresponding to the $Mn(Me_2EBC)(O)(OH)^+$ species which dominate under the oxidative conditions. The minor ms peak at m/z = 358.1 is corresponding to the $Mn(Me_2EBC)(O)(OOH)^+$ species.

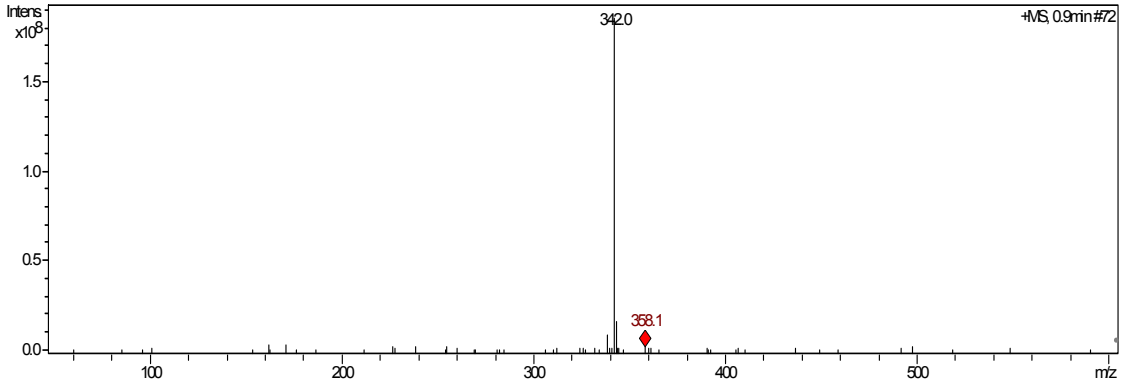


Fig. S1 ESI-MS spectrum of the manganese(IV) hydroperoxide intermediate (m/z = 358.1) in t-butanol/water (4:1) at pH 1.5

2. The attempts to detect the hydroxyl radical by ESR in t-butanol/water (4:1) containing $Mn(Me_2EBC)Cl_2$ catalyst and H_2O_2 at pH 1.5

In order to detect the potential hydroxyl radical in the catalytic hydrogen abstraction and oxygenation solutions containing the $Mn(Me_2EBC)Cl_2$ catalyst with H_2O_2, the ESR experiments were conducted under various catalytic conditions which have been used in the text. First, the $FeSO_4$/DTPA/H_2O_2 system (DTPA: diethylene triamine penlaacetic acid) in aqueous solution was tested to display the typical 4-line ESR signal of the hydroxyl radical with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the hydroxyl radical scavenger, then the Fe/DTPA/H_2O_2 system in t-butanol/water (4:1) at pH 1.5 to demonstrate the ESR signal of the hydroxyl radial has been significantly reduced. Finally, a list of the catalytic conditions for the manganese(IV) hydroperoxide mediated oxidations, including normal hydrogen abstraction, normal oxygenation, and ^{18}O-labeling experiments for mechanistic studies, were tested to detect the potential hydroxyl radical with DMPO scavenger. However, as shown in the following figures (Fig S3-S8), there is only DMPOX singal, an oxidation product of DMPO, was observed with no typical 4-line signal of the hydroxyl radical in all cases.

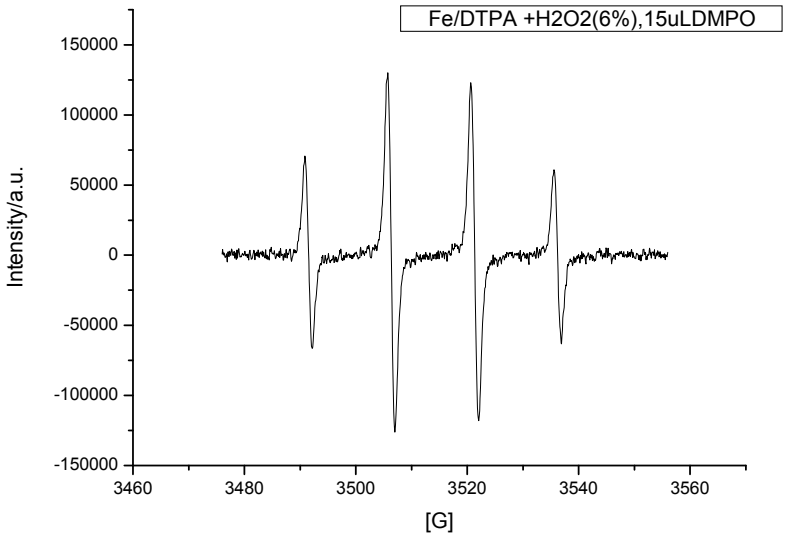


Fig. S2 The ESR spectrum of $FeSO_4$/DTPA with 6% H_2O_2 in aqueous solution.

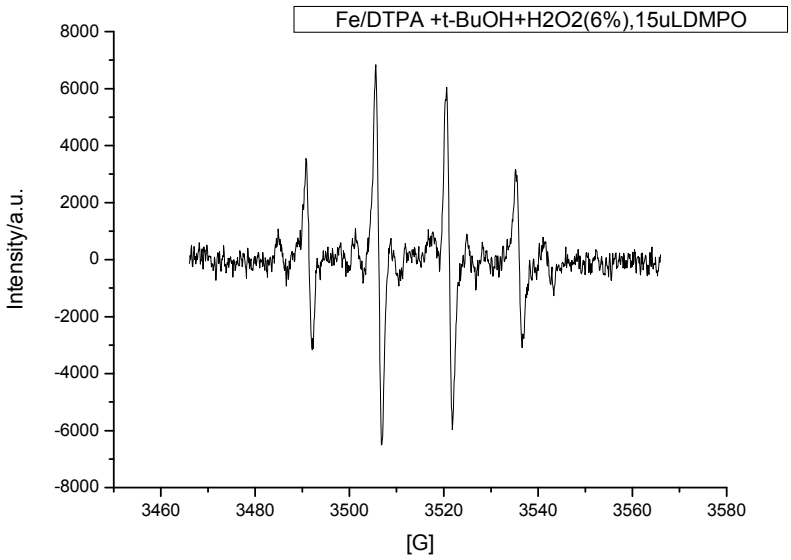


Fig. S3 The ESR spectrum of $FeSO_4$/DTPA with 6% H_2O_2 in t-butanol/water (4: 1) at pH 1.5.

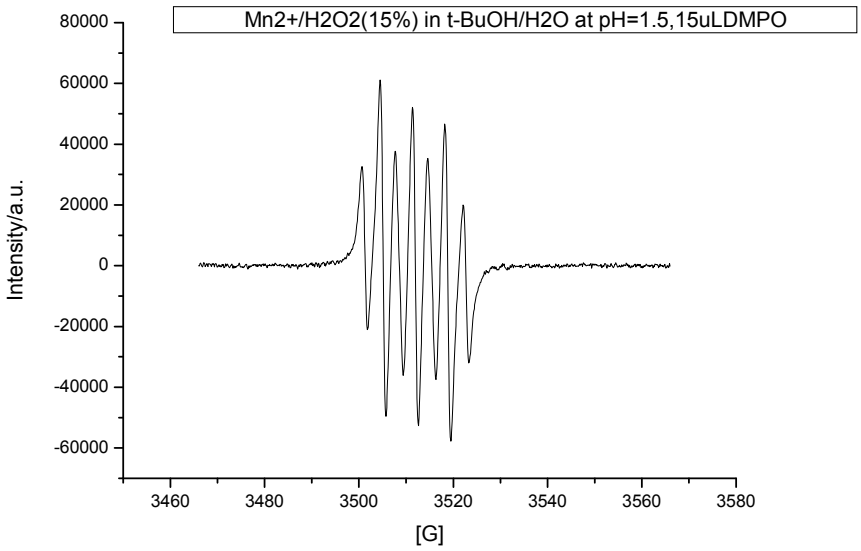


Fig. S4 The ESR spectrum of $Mn(Me_2EBC)Cl_2$ catalyst with 15% H_2O_2 in t-butanol/water (4: 1) at pH 1.5.

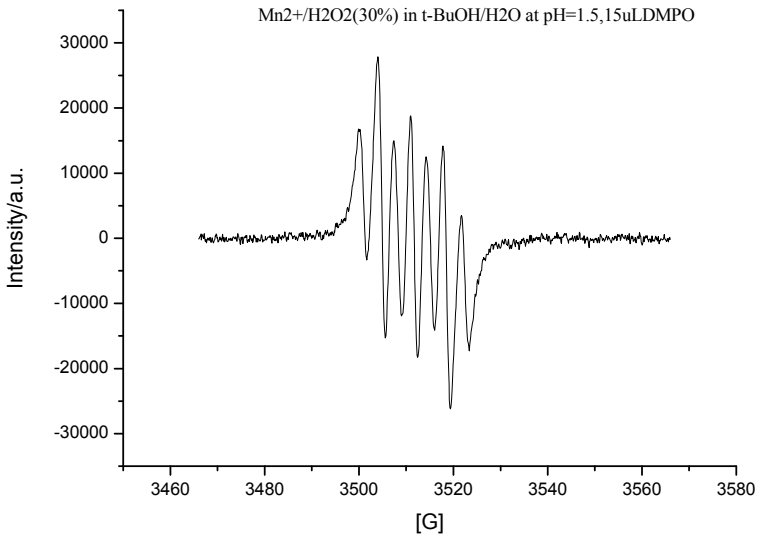


Fig. S5 The ESR spectrum of $Mn(Me_2EBC)Cl_2$ catalyst with 30% H_2O_2 in t-butanol/water (4: 1) at pH 1.5.

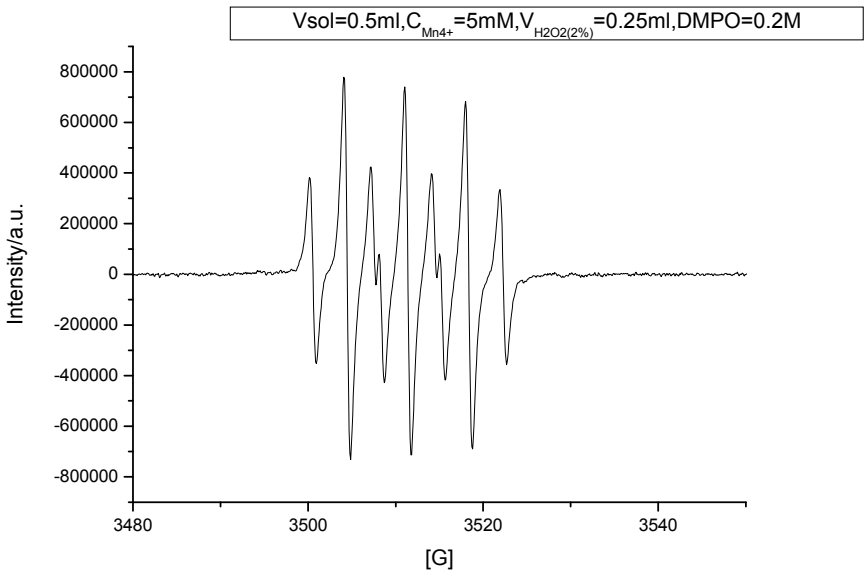


Fig. S6 The ESR spectrum of $Mn(Me_2EBC)Cl_2$ catalyst under the conditions for hydrogen abstraction from ethylbenzene with 2% $H_2{}^{18}O_2$ in t-butanol/water (4: 1) at pH 1.5.

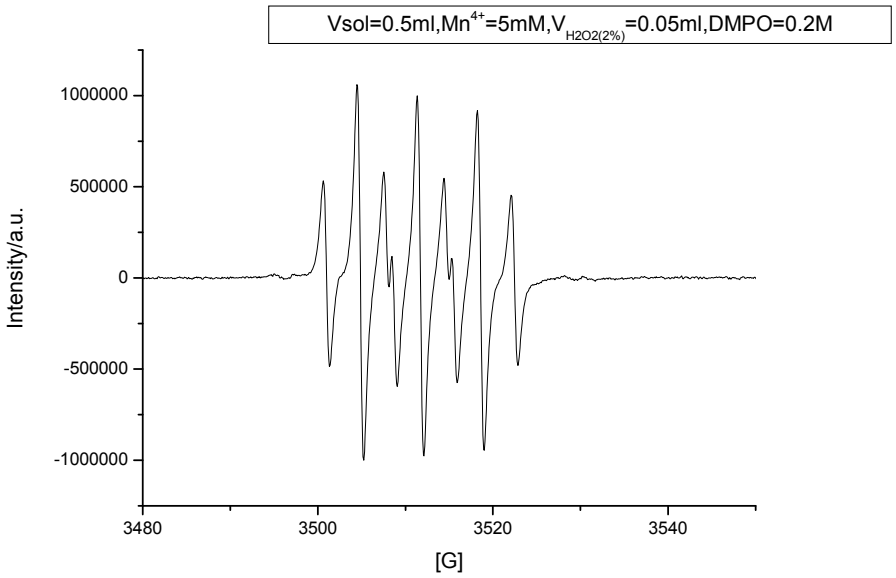
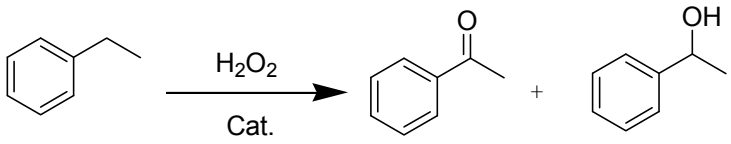


Fig. S7 The ESR spectrum of $Mn(Me_2EBC)Cl_2$ catalyst with normal 2% H_2O_2 under the conditions for diphenyl sulfide oxygenation with 2% $H_2{}^{18}O_2$ in t-butanol/water (4: 1) at pH 1.5.

5. **GC-MS results for the ^{18}O-Isotope labeling experiments for hydrogen abstraction and oxygenation reactions**

a) **Reaction conditions:** t-BuOH/$H_2{}^{18}O$ (4:1) 2.5 mL, pH 1.5, $Mn(Me_2EBC)Cl_2$ 5 mM, ethylbenzene 0.1 M, 30% H_2O_2 0.5 mL, stirred at 323 K for 4.5 h.



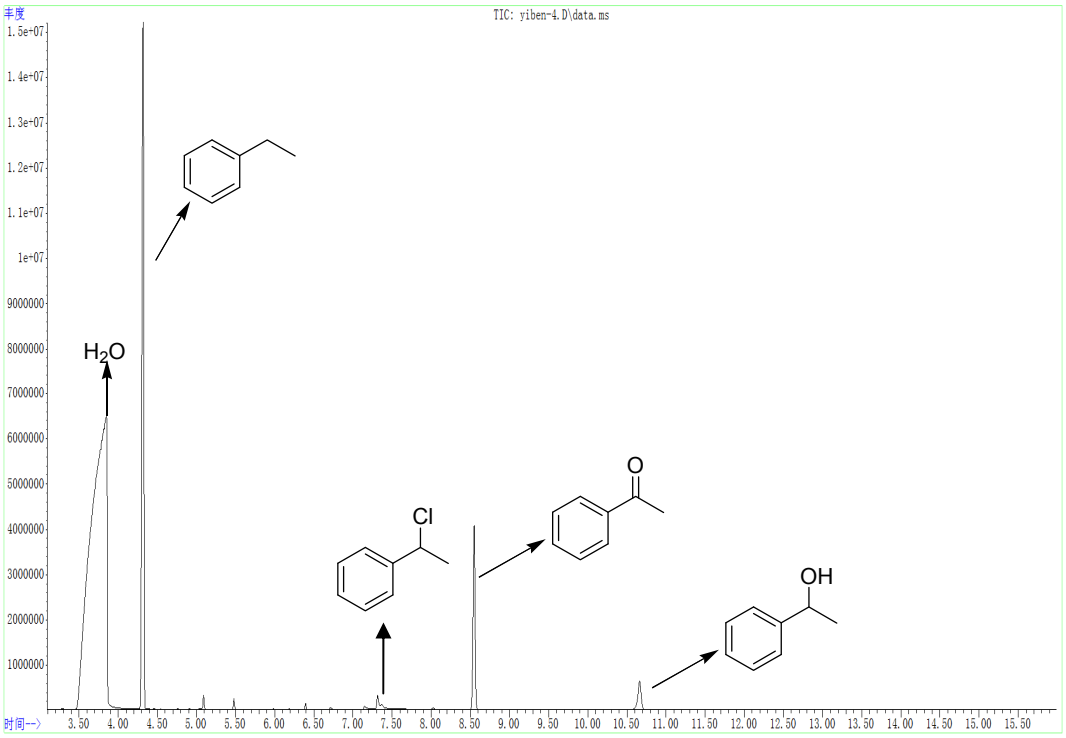


Fig. S8 GC-MS graph for catalytic hydrogen abstraction from ethylbenzene with ^{18}O-water.

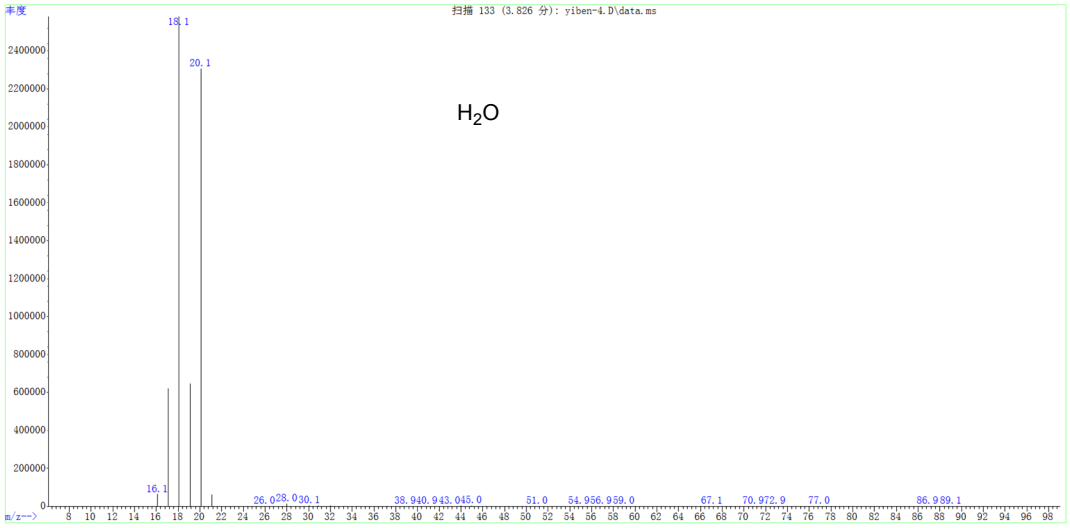


Fig. S8-1 MS graph of water in catalytic hydrogen abstraction from ethylbenzene with ^{18}O-water.

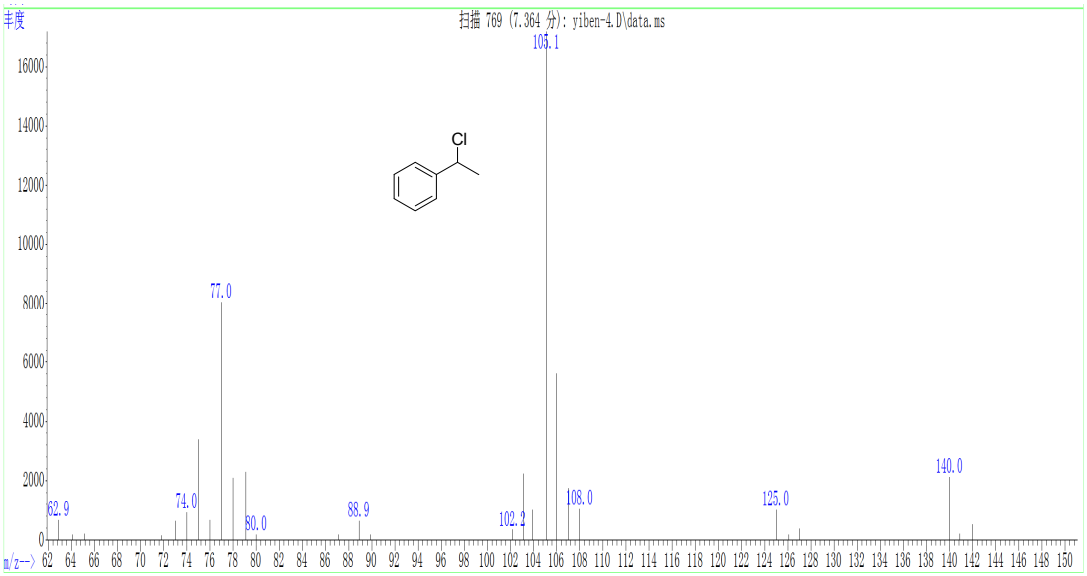


Fig. S8-2 MS graph of 1-phenylethyl chloride in catalytic hydrogen abstraction from ethylbenzene with ^{18}O-water.

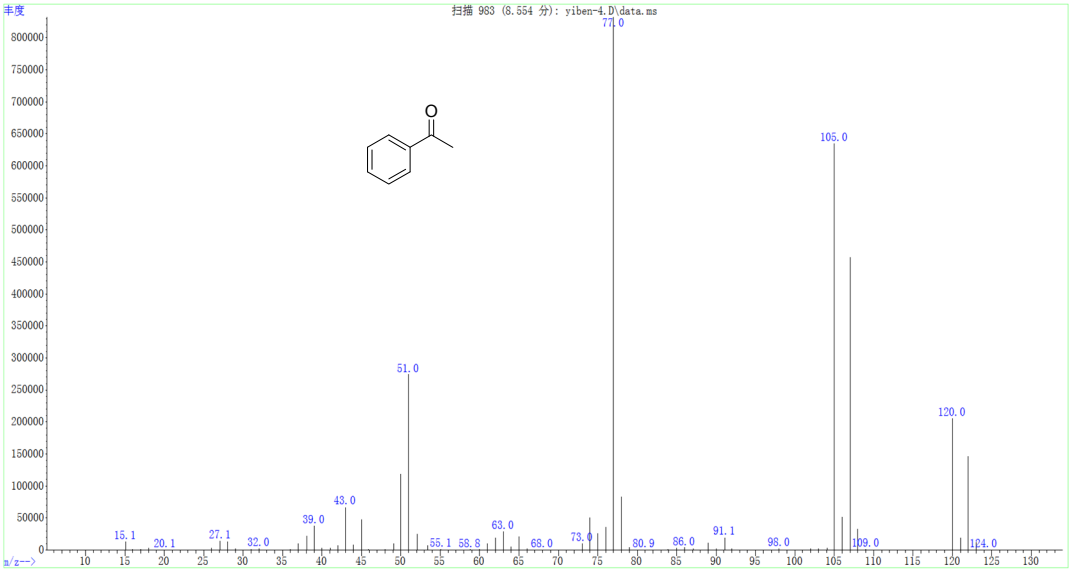


Fig. S8-3 MS graph of acetonphenone product in catalytic hydrogen abstraction from ethylbenzene with ^{18}O-water.

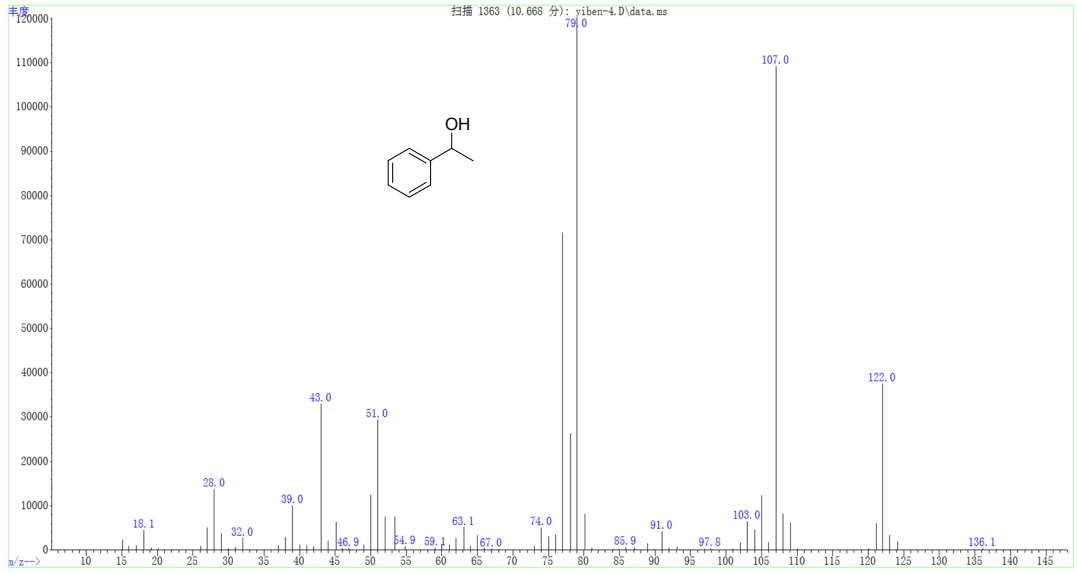
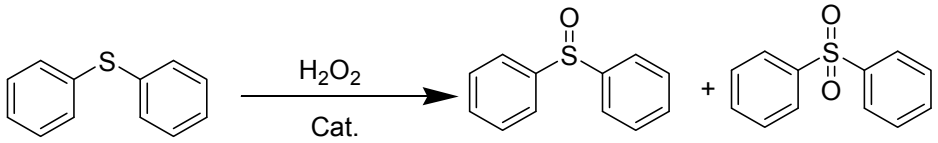


Fig. S8-4 MS graph of 1-phenylethanol in catalytic hydrogen abstraction from ethylbenzene with ^{18}O-water.

b) Reaction conditions: t-BuOH/$H_2{}^{18}O$ (4:1) 2.5 mL, pH 1.5, $Mn(Me_2EBC)Cl_2$ 5 mM, diphenyl sulfide 0.1M, H_2O_2 (30%) 0.03 mL, stirred at 278 K for 20 min.



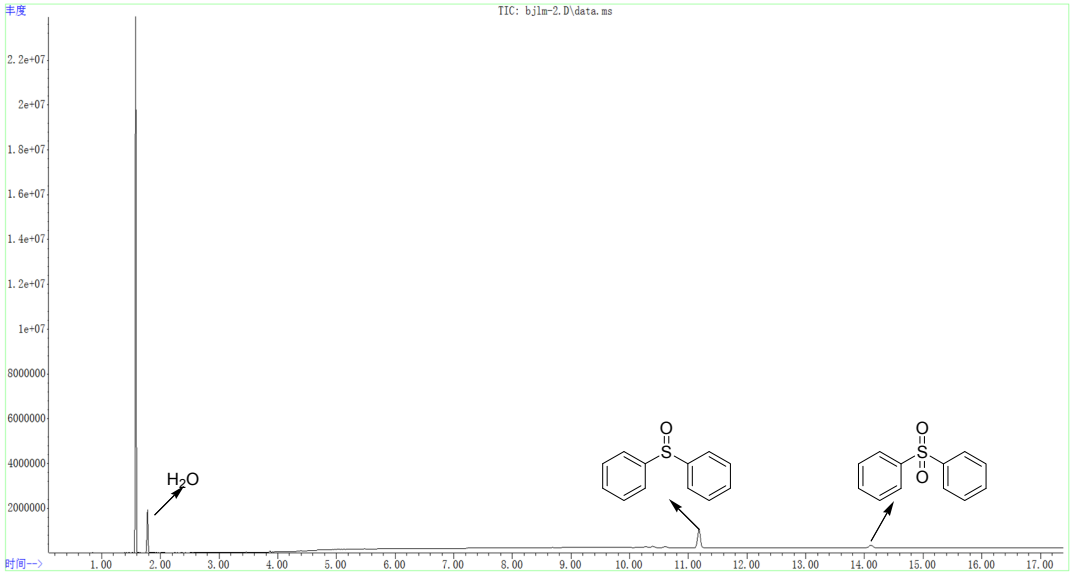


Fig. S9 GC-MS graph for catalytic oxygenation of diphenyl sulfide with ^{18}O-water.

Fig. S9-1 MS graph of water in catalytic oxygenation of diphenyl sulfide with ^{18}O-water.

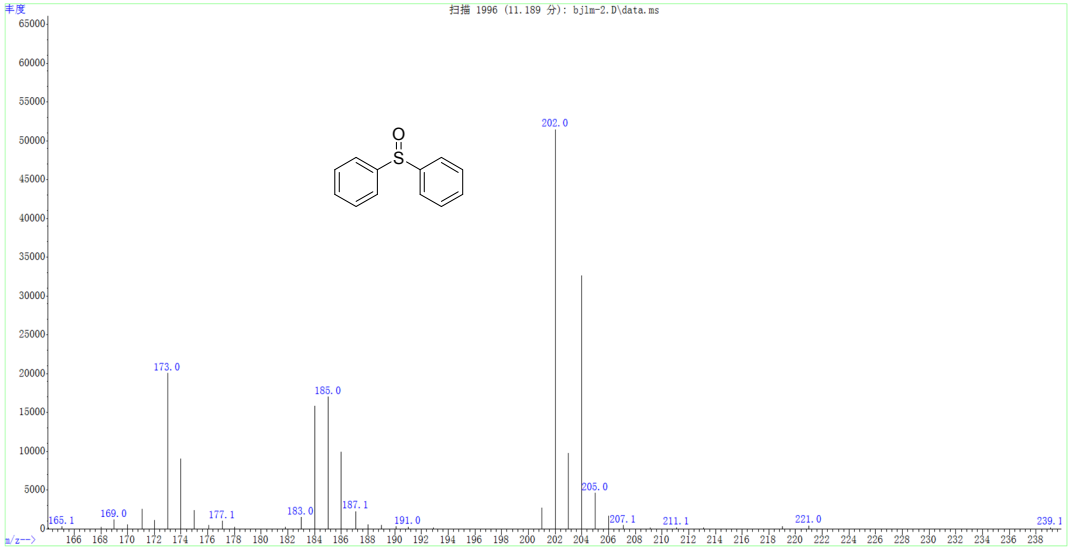


Fig. S9-2 MS graph of diphenyl sulfoxide in catalytic oxygenation of diphenyl sulfide with ^{18}O-water.

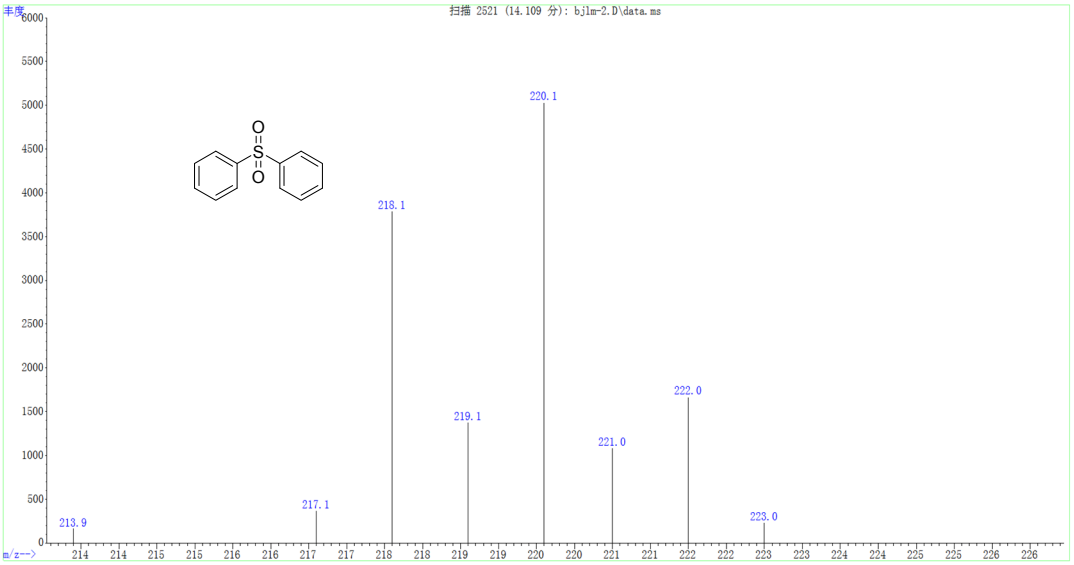
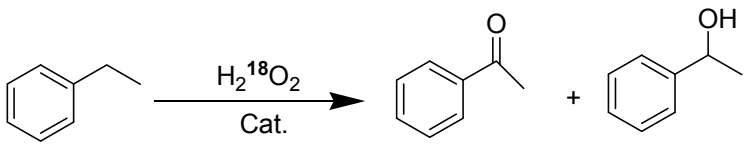


Fig. S9-3 MS graph of diphenyl sulfdioxide in catalytic oxygenation of diphenyl sulfide with ^{18}O-water.

c) Reaction conditions: t-BuOH/H_2O (4:1) 1.0 mL, pH 1.5, $Mn(Me_2EBC)Cl_2$ 5 mM, ethylbenzene 0.35 M, $H_2{}^{18}O_2$ (2%) 0.5 mL, stirred at 323 K for 24 h.



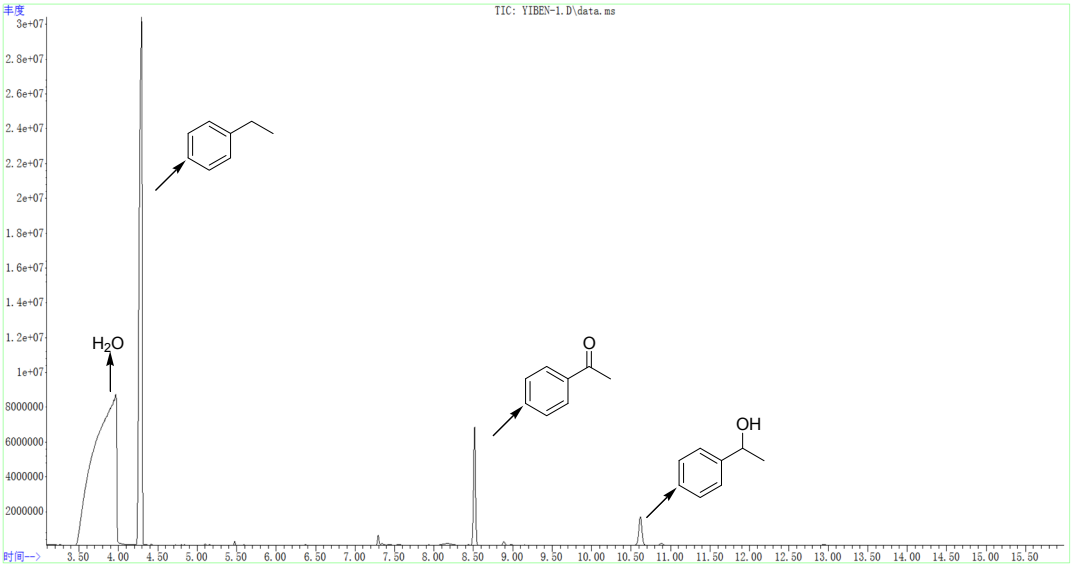


Fig. S10 GC-MS graph for catalytic hydrogen abstraction from ethylbenzene with $H_2{}^{18}O_2$.

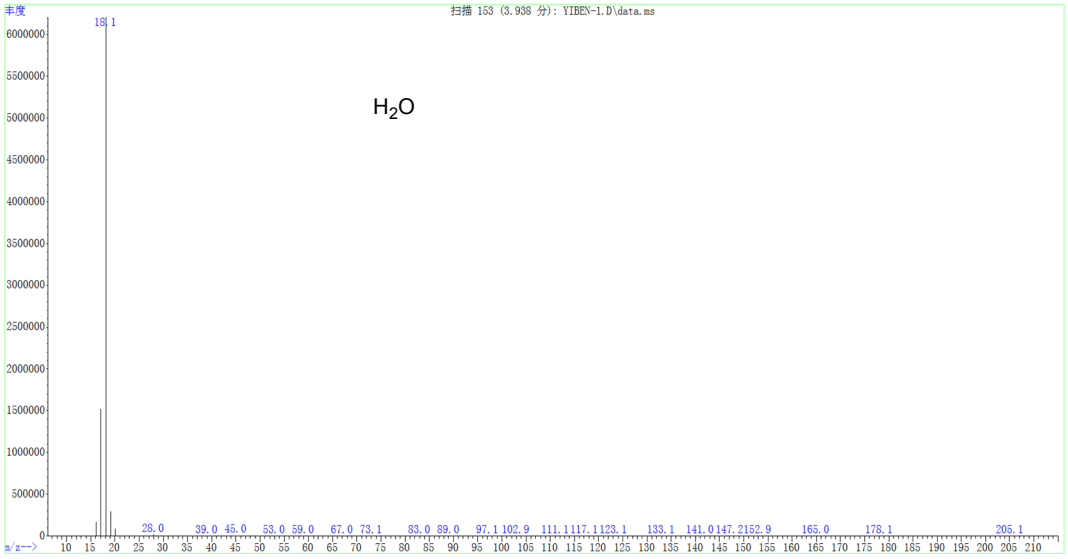


Fig. S10-1 MS graph of water in catalytic hydrogen abstraction from ethylbenzene with $H_2{}^{18}O_2$.

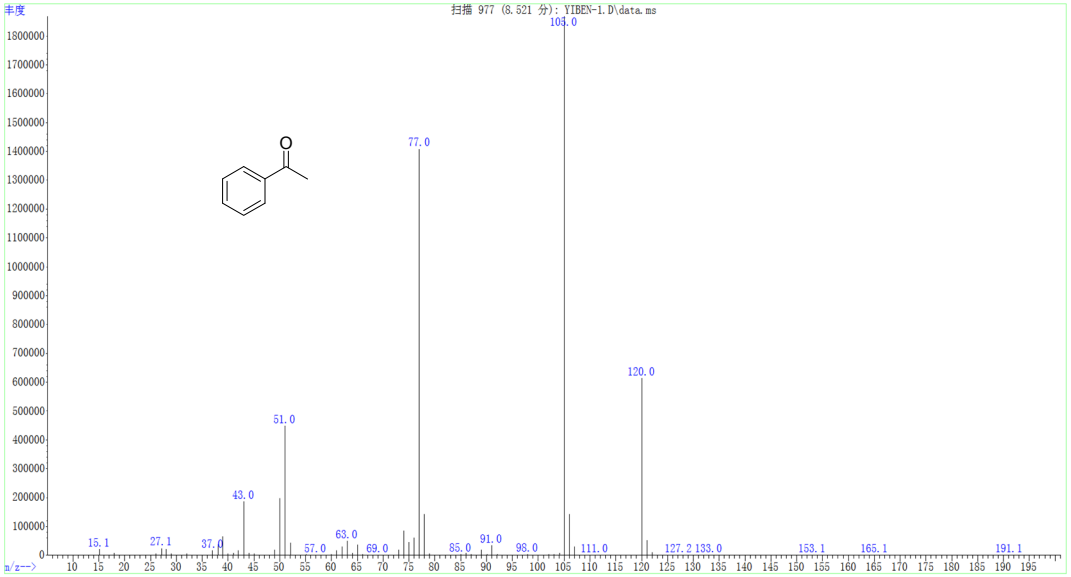


Fig. S10-2 MS graph of acetonphenone in catalytic hydrogen abstraction from ethylbenzene with $H_2{}^{18}O_2$.

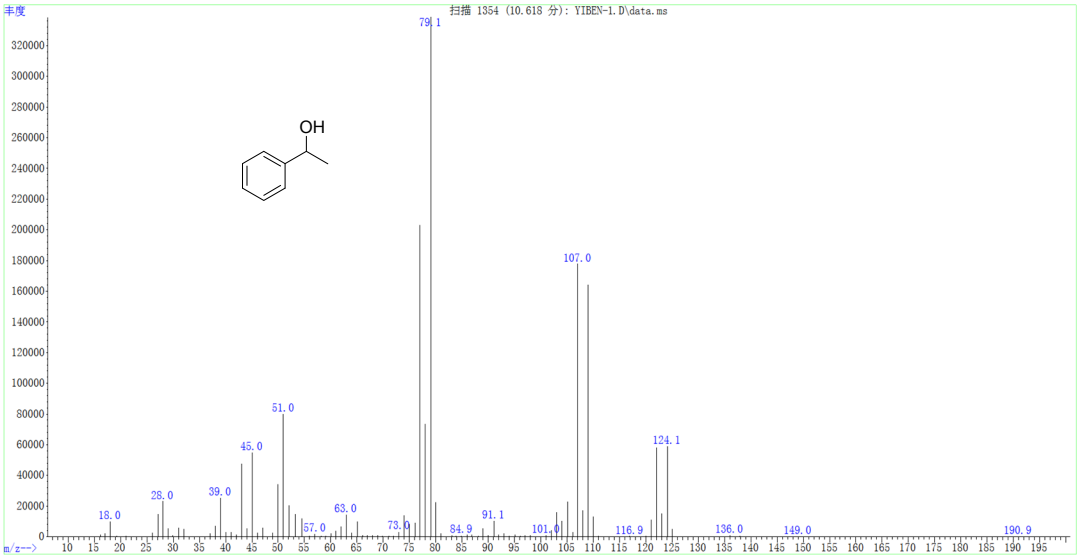
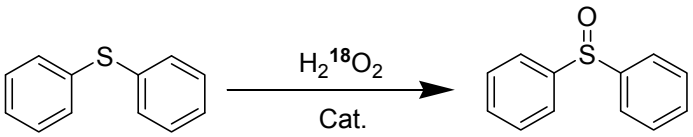


Fig. S10-3 MS graph of 1-benzylehtanol in catalytic hydrogen abstraction from ethylbenzene with $H_2{}^{18}O_2$.

d) **Reaction conditions:** t-BuOH/H_2O (4:1) 1.0 mL, pH 1.5, $Mn(Me_2EBC)Cl_2$ 5 mM, diphenyl sulfide 0.26 M, $H_2{}^{18}O_2$ (2%) 0.1 mL, stirred at 278 K for 24 h.



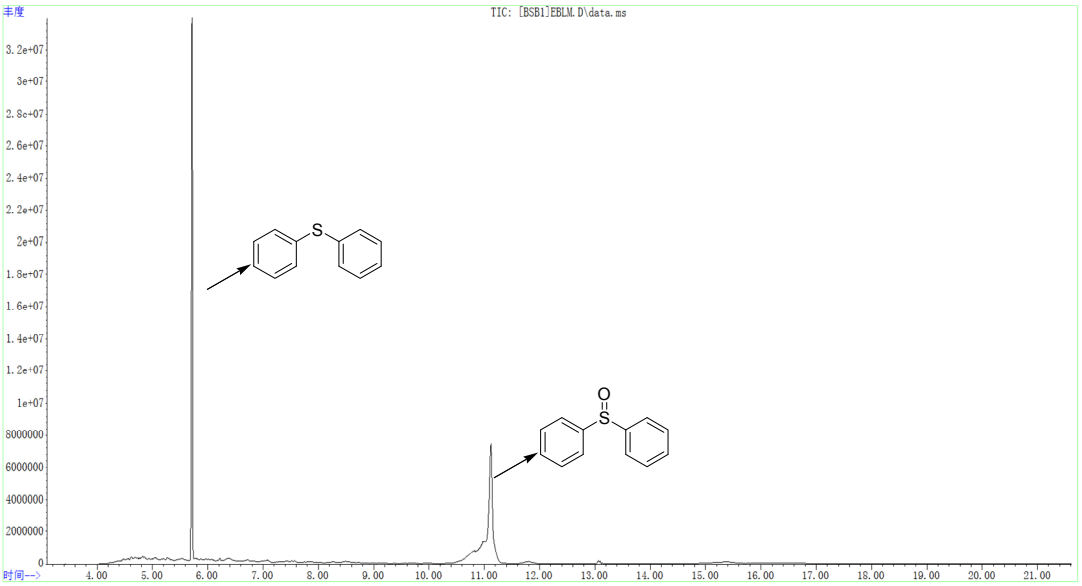


Fig. S11 GC-MS graph for catalytic oxygenation of diphenyl sulfide with $H_2{}^{18}O_2$.

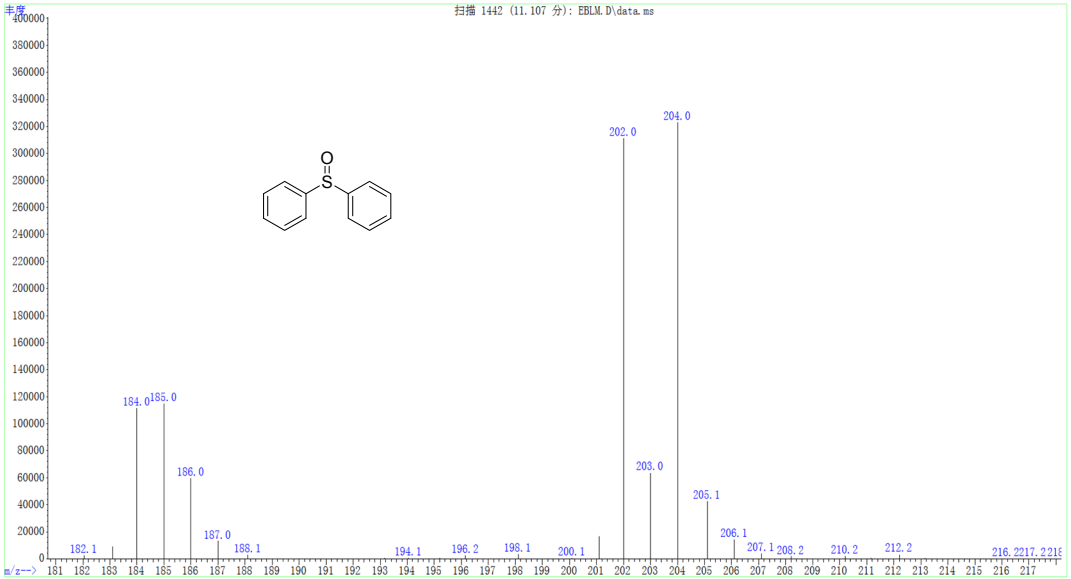


Fig. S11-1 MS graph of diphenyl sulfoxide in catalytic oxygenation of diphenyl sulfide with $H_2{}^{18}O_2$.

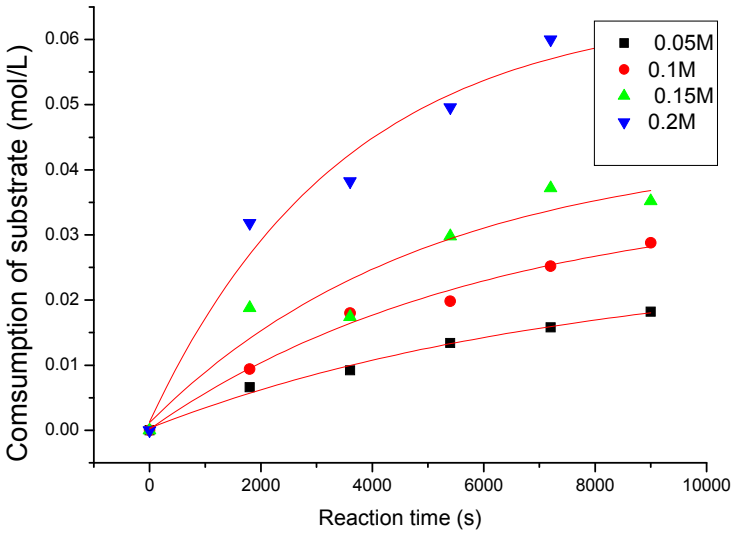


Fig. 12 Substrate dependent kinetics of catalytic hydrogen abstraction. Conditions: acetone/water(4:1), pH 1.5, 30 % H_2O_2 1 mL, $Mn(Me_2EBC)Cl_2$ 5 mM, 50 °C.

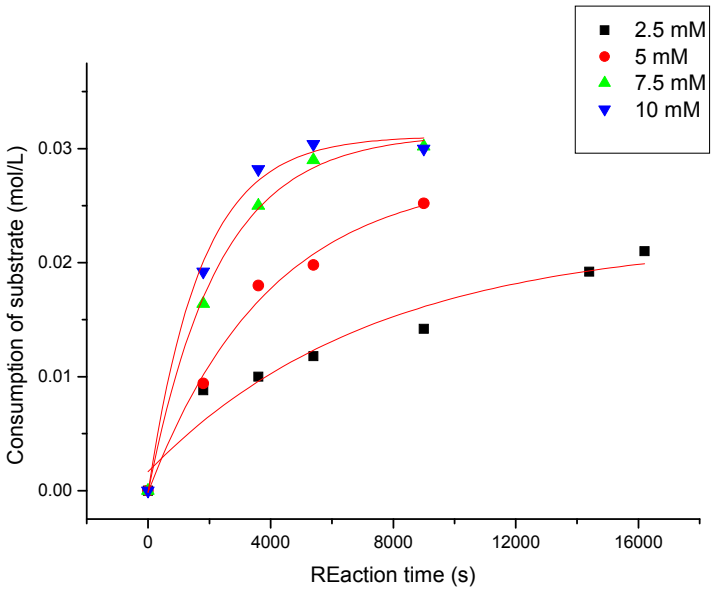


Fig. 13 Catalyst dependent kinetics of catalytic hydrogen abstraction. Conditions: acetone/water(4:1), pH 1.5, 30 % H_2O_2 1 mL ethylbenzene 0.1 M, 50 °C.