# Remarkable enhancement of catalytic activity of a 2:1 complex between a non-planar Mo(V)-porphyrin and a ruthenium-substituted Keggin-type heteropolyoxometalate in catalytic oxidation of benzyl alcohols 

Atsutoshi Yokoyama, ${ }^{a, b}$ Kei Ohkubo, ${ }^{a}$ Tomoya Ishizuka, ${ }^{c}$ Takahiko Kojima, ${ }^{*}{ }^{c}$ and Shunichi Fukuzumi* ${ }^{*, b}$<br>${ }^{a}$ Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), 2-1 Yamada-oka, Suita, Osaka 565-0871, Japan. E-mail: fukuzumi@chem.eng.osaka-u.ac.jp<br>${ }^{b}$ Department of Bioinspired Chemistry (WCU), Ewha Womans University, Seoul 120-750, Korea<br>${ }^{c}$ Department of Chemistry, Graduate School of Pure and Applied Science, University of Tsukuba,<br>1-1-1 Tennoudai, Tsukuba, Ibaraki 305-8571, Japan. E-mail: kojima@chem.tsukuba.ac.jp

(a)

(b)


Fig. S1. MALDI-TOF-MS spectra in the negative mode: (a) $\mathbf{3}$ before the oxidation reaction; (b) after the oxidation reaction of benzylalcohol by $\mathbf{3}$ and PhIO in $\mathrm{CDCl}_{3}$. The peaks at $m / Z=5499$ and $m / Z=5268$ were assigned to that of $\{\mathbf{3}+\mathrm{ClO}\}^{-}$(calcd. 5497) and that of $\{3-2 \mathrm{Ph}-\mathrm{O}\}^{-}$(calcd. 5275), respectively.


Fig. S2 A Hammett plot for the pseudo-first-order rate constants of oxidations of benzyl alcohol derivatives by $\mathbf{3}$ and PhIO in $\mathrm{CDCl}_{3}$. The $\sigma$ values were adopted from S. H. Pine, in Organic Chemistry (5th Ed.), McGraw-Hill, New York, 1987.

