Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supporting information

## An isotetramolybdate-supported rhenium carbonyl derivative: synthesis, characterization, and catalysis for sulfoxidation

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## CONTENTS

## Section 1. Comments on previous reported typical organometallic derivatives of POMs:

Though carbonyl metal derivatives of POMs have attracted increasing interest in the recent years, the reports on new types of POM-based carbonyl metal derivatives are very rare. At the present time, the reported POM-supported tricarbonyl metal compounds are mainly dominated by Lindqvist-type polyoxoanions and Dawson-type $[P_2W_{15}Nb_3O_{62}]^{9-}$ polyoxoanions. The first POM-supported carbonyl metal compounds $[(OC)_3M(Nb_2W_4O_{19})]^{3-}$ (M = Mn, Re) were obtained by Klemperer' group in 1980.[1] Although they did not have crystal structure characterization, they forecasted their structures by the $^{17}O$ NMR study, and their structures was proved in 1985.[2] The $[M(CO)_3]^+$ (M = Mn, Re) group is bonded to three adjacent bridging oxygens of the $[Nb_2W_4O_{19}]^{4-}$ polyoxoanion. At the same time, Day and Klemperer reported a series of Lindqvist-polyoxoanion-supported carbonyl metal compounds.[3] A typical example is $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$,[3b] in which a $[M(CO)_3]^+$ unit is bonded to three bridging oxygen atoms of the $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})]^{3-}$ anion. It is worthwhile to note that the compound contains $[(\eta^5\text{-}C_5H_5)Ti]^{3+}$ and $[M(CO)_3]^+$ two organic groups. In 1997, Finke et al. prepared a few $[P_2W_{15}Nb_3O_{62}]^{9-}$-supported cabonyl metal compounds: $[(n\text{-}C_4H_9)_4N]_8[Re(CO)_3P_2W_{15}Nb_3O_{62}]\cdot(n\text{-}C_4H_9)_4NBF_4$, $[(n\text{-}C_4H_9)_4N]_8[Ir(CO)_2P_2W_{15}Nb_3O_{62}]$ and $[(n\text{-}C_4H_9)_4N]_8[Rh(CO)_2P_2W_{15}Nb_3O_{62}]$.[4] In 2001, Pope *et al.* found this type of compounds based on isoniobate or isotantalate: $K_7[M_6O_{19}M'(CO)_3]$ (M = Nb, Ta; M' = Mn, Re) and $[M_6O_{19}M'(CO)_3]^{6-}$ (M = Nb, Ta; M' = Mn, Re).[5] In 2003, Gouzerh et al. reported several compounds containing $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ and $[M(CO)_3]^+$ (M = Mn, Re) units.[6] Take $(nBu_4N)_2[Re(CO)_3(H_2O)]$ and $(nBu_4N)_3\{Na[Mo_5O_{13}(OMe)_4(NO)]_2[Mn(CO)_3]_2\}$ for instance, in the former, the $[Re(CO)_3]^+$ fragment is bonded to two adjacent axial oxygen atoms of the $[Mo_5O_{13}(OMe)_4(NO)]$ unit and a water molecule whereas the latter consists of two crystallographically independent $[\{Mo_5O_{13}(OMe)_4(NO)\}\{Mn(CO)_3\}]^{2-}$ units linked by a sodium cation. In 2008, our group synthesized a new compound $(n\text{-}Bu_4N)_2\{Mo_6O_{16}(OCH_3)_2[HOCH_2C(CH_2O)_3]_2[Mn(CO)_3]_2\}$.[7] Very recently our group discovered the novel octatungstate-supported tricarbonyl metal polyanions $[\{H_2W_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = $Mn^I$ and $Re^I$) with completely unprecedented structures;[8] the novel octamolybdate-supported tricarbonyl metal derivatives $[\{H_2Mo_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = $Mn^I$ and $Re^I$);[9] and a rarely reported isopentatungstate-supported $[\{Re(CO)_3\}_4\{(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})\}]^{5-}$.[10] In summary, the bonding of the $[M(CO)_3]^+$ (M = $Mn^I$ and $Re^I$) fragment, as a $d^6$-fac-$ML_3$ unit to a triangle of connecting three oxygen atoms, is common in POM-supported organometallic compounds.[1–12]

**Table 1** Summary of iso-POMs based on metal carbonyl compounds

| Formulas | Ref. |
|---|---|
| $[(\eta^5\text{-}C_5H_5)Ti(Mo_5O_{18})Mn(CO)_3]^{2-}$ | 3b |
| $[M_6O_{19}\{M'(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; M′ = Mn, Re; n = 1, 2) | 5 |
| $[M(CO)_3(H_2O)\{Mo_5O_{13}(OMe)_4(NO)\}]^{2-}$(M = Mn, Re) | 6 |
| $[Na\{Mo_5O_{13}(OMe)_4(NO)\}_2\{Mn(CO)_3\}_2]^{3-}$ | |
| $[Mn(H_2O)_2\{Mo_5O_{16}(OMe)_2\}\{Mn(CO)_3\}_2]^{4-}$ | |
| $[Mo_6O_{16}(OCH_3)_2\{HOCH_2C(CH_2O)_3\}_2\{Mn(CO)_3\}_2]^{2-}$ | 7 |
| $[\{H_2W_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = Mn, Re) | 8 |
| $[\{H_2Mo_8O_{30}\}\{M(CO)_3\}_2]^{8-}$ (M = $Mn^I$, $Re^I$) | 9 |
| $[\{Re(CO)_3\}_4\{(\mu_2\text{-}OH)(\mu_3\text{-}O)(W_5O_{18})\}]^{5-}$ | 10 |
| $[Mo_2O_5(OMe)_5\{M(CO)_3\}_2]^-$ (M = Re, Mn) | 11 |
| $[Mo_2O_4(OMe)_6\{Mn(CO)_3\}_2]$ | |
| $[Mo_2O_6(OMe)_4\{Re(CO)_3\}_2]^{2-}$ | |
| $[Mo_2O_4\{RC(CH_2O)_3\}_2\{Mn(CO)_3\}_2]$ (R = Me, $CH_2OH$) | |

[1] C. J. Besecker and W. G. Klemperer, *J. Am. Chem. Soc*., 1980, **102**, 7598.

[2] C. J. Besecker, V. W. Day, W. G. Klemperer and M. R. Thompson, *Inorg. Chem*., 1985, **24**, 44.

[3] (a) W. G. Klemperer and D. J. Main, *Inorg. Chem*., 1990, **29**, 2355; (b) V. W. Day, M. F. Fredrich, M. R. Thompson, W. G. Klemperer, R. S. Liu and W. Shum, *J. Am. Chem. Soc*., 1981, **103**, 3597; (c) W. G. Klemperer and B. Zhong, *Inorg. Chem*., 1993, **32**, 5821.

[4] T. Nagata, M. Pohl, H. Weiner and R. G. Finke, *Inorg. Chem*., 1997, **36**, 1366.

[5] A. V. Besserguenev, M. H. Dickman and M. T. Pope, *Inorg. Chem*., 2001, **40**, 2582.

[6] R. Villanneau, A. Proust, F. Robert and P. Gouzerh, *Chem. Eur. J*., 2003, **9**, 1982.

[7] J. P. Wang, J. L. Li and J. Y. Niu, *Chemical Research in Chinese University*, 2008, **24**, 675.

[8] J. Y. Niu, L. P. Yang, J. W. Zhao, P. T. Ma and J. P. Wang, *Dalton Trans*., 2011, **40**, 8298.

[9] D. D. Zhang, J. Zhao, Y. H. Zhang, X. J. Hu, L. S. Li, P. T. Ma, J. P. Wang and J. Y. Niu, *Dalton Trans*., 2013, **42**, 2696.

[10] J. Li, J. Guo, J. Jia, P. Ma, D. Zhang, J. Wang and J. Niu, *Dalton Trans.*, 2016, **45**, 6726.

[11] R. Villanneau, R. Delmont, A. Proust and P. Gouzerh, *Chem. – Eur. J*., 2000, 6, 1184.

[12] (a) V. W. Day and R. G. Klemperer, *Polyoxometalates: From Platonic Solids to Anti -Retroviral Activity* (Eds.: M. T. Pope and A. Müller), Kluwer, Dordrecht, 1994, pp. 87; (b) A. V. Besserguenev, M. H. Dickman and M. T. Pope, *Inorg. Chem*., 2001, **40**, 2582.

## Section 2. Structural figure

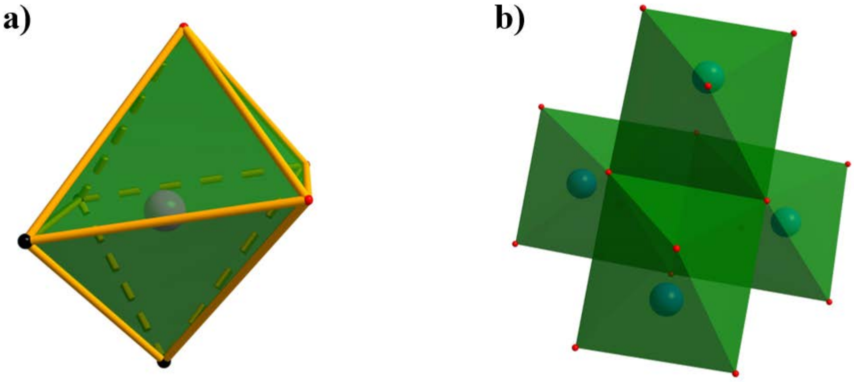


**Figure S1** a) The coordination environments of Re1. b) Polyhedral representation of $[Mo_4O_{16}]^{8-}$ unit. Colour code: Mo, mazarine; Re, purple; C, black; O, red; $MoO_6$ octahedral, green.

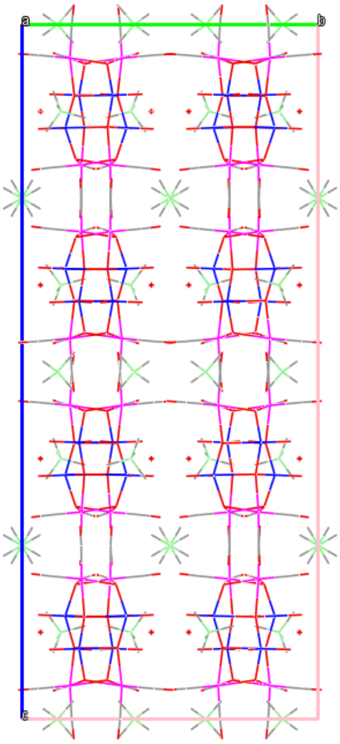


**Figure S2**. Packing diagram of **1** viewed along the a axis.

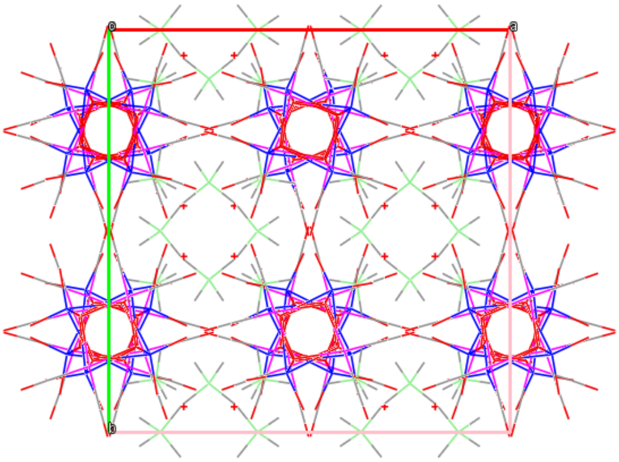


**Figure S3**. Packing diagram of **1** viewed along the c axis.

## Section 3 The BVS calculation results for all Mo atoms and O atoms on $[Mo_4O_{16}]^{8-}$

**Table S2** The BVS calculation results for all Mo atoms and O atoms on $[Mo_4O_{16}]^{8-}$

| Atom | Bond valence sum | Atom | Bond valence sum | Atom | Bond valence sum |
|---|---|---|---|---|---|
| Mo1 | 6.08 | O1 | -1.63 | O2 | -1.89 |
| O3 | -1.88 | O4 | -1.85 | O5 | -1.93 |
| O6 | -2.08 | O7 | -2.01 | O8 | -1.96 |
| O9 | -1.87 | O10 | -1.59 | O11 | -1.70 |
| O12 | -2.20 | O13 | -2.02 | O14 | -2.09 |
| O15 | -2.11 | O16 | -2.13 | | |

## Section 4. Selected bond angles and distances of 1

**Table S3** Selected band lengths (Å) for compound **1**

| | | | | | |
|---|---|---|---|---|---|
| Re(1)-C(2) | 1.853(14) | Re(1)-C(1) | 1.857(14) | Re(1)-C(3) | 1.859(16) |
| Re(1)-O(4) | 2.145(7) | Re(1)-O(4)$^{\#1}$ | 2.148(7) | Re(1)-O(2)$^{\#2}$ | 2.158(7) |
| Mo(1)-O(1) | 1.691(8) | Mo(1)-O(3) | 1.716(8) | Mo(1)-O(2) | 1.905(7) |
| Mo(1)-O(4) | 1.910(7) | Mo(1)-O(2)$^{\#3}$ | 2.410(7) | Mo(1)-O(2)$^{\#2}$ | 2.428(7) |
| O(2)-Re(1)$^{\#3}$ | 2.158(7) | O(2)-Mo(1)$^{\#2}$ | 2.410(7) | O(2)-Mo(1)$^{\#3}$ | 2.428(7) |
| O(4)-Re(1)$^{\#1}$ | 2.149(7) | O(5)-C(1) | 1.179(16) | O(6)-C(2) | 1.168(16) |
| O(7)-C(3) | 1.179(19) | | | | |

$^{\#1}$-X, 1-Y, -Z; $^{\#2}$-X, +Y, +Z; $^{\#3}$+X,1-Y, -Z.

**Table S4** Selected band angles (°) for compound **1**

| | | | |
|---|---|---|---|
| C(2)-Re(1)-C(1) | 85.8(6) | C(2)-Re(1)-C(3) | 85.4(5) |
| C(1)-Re(1)-C(3) | 87.8(5) | C(2)-Re(1)-O(4) | 100.2(5) |
| C(1)-Re(1)-O(4) | 173.4(4) | C(3)-Re(1)-O(4) | 95.4(4) |
| C(2)-Re(1)-O(4)$^{\#1}$ | 174.4(5) | C(1)-Re(1)-O(4)$^{\#1}$ | 99.0(5) |
| C(3)-Re(1)-O(4)$^{\#1}$ | 97.6(4) | O(4)-Re(1)-O(4)$^{\#1}$ | 74.9(3) |
| C(2)-Re(1)-O(2)$^{\#2}$ | 101.2(4) | C(1)-Re(1)-O(2)$^{\#2}$ | 100.3(4) |
| C(3)-Re(1)-O(2)$^{\#2}$ | 169.9(4) | O(4)-Re(1)-O(2)$^{\#2}$ | 76.0(3) |
| O(4)$^{\#1}$-Re(1)-O(2)$^{\#2}$ | 75.3(3) | O(1)-Mo(1)-O(3) | 105.0(4) |
| O(1)-Mo(1)-O(2) | 102.5(3) | O(3)-Mo(1)-O(2) | 103.2(3) |
| O(1)-Mo(1)-O(4) | 100.2(3) | O(3)-Mo(1)-O(4) | 101.0(3) |
| O(2)-Mo(1)-O(4) | 141.0(3) | O(1)-Mo(1)-O(2)$^{\#3}$ | 161.4(3) |
| O(3)-Mo(1)-O(2)$^{\#3}$ | 93.5(3) | O(2)-Mo(1)-O(2)$^{\#3}$ | 74.3(3) |
| O(4)-Mo(1)-O(2)$^{\#3}$ | 74.0(3) | O(1)-Mo(1)-O(2)$^{\#2}$ | 91.6(3) |
| O(3)-Mo(1)-O(2)$^{\#2}$ | 163.3(3) | O(2)-Mo(1)-O(2)$^{\#2}$ | 73.9(3) |
| O(4)-Mo(1)-O(2)$^{\#2}$ | 74.2(3) | O(2)$^{\#3}$-Mo(1)-O(2)$^{\#2}$ | 69.9(3) |
| Mo(1)-O(2)-Re(1)$^{\#3}$ | 154.0(4) | Mo(1)-O(2)-Mo(1)$^{\#2}$ | 101.7(3) |
| Re(1)$^{\#3}$-O(2)-Mo(1)$^{\#2}$ | 93.9(2) | Mo(1)-O(2)-Mo(1)$^{\#3}$ | 101.0(3) |
| Re(1)$^{\#3}$-O(2)-Mo(1)$^{\#3}$ | 92.9(2) | Mo(1)$^{\#2}$-O(2)-Mo(1)$^{\#3}$ | 110.1(3) |
| Mo(1)-O(4)-Re(1) | 110.2(3) | Mo(1)-O(4)-Re(1)$^{\#1}$ | 110.8(3) |
| Re(1)-O(4)-Re(1)$^{\#1}$ | 102.7(3) | O(6)-C(2)-Re(1) | 178.2(13) |
| O(5)-C(1)-Re(1) | 178.5(12) | O(7)-C(3)-Re(1) | 176.0(12) |

$^{\#1}$-X, 1-Y, -Z; $^{\#2}$-X, +Y, +Z; $^{\#3}$+X,1-Y, -Z.

## Section 5. The IR spectra of compound 1 and Re(CO)$_5$Cl

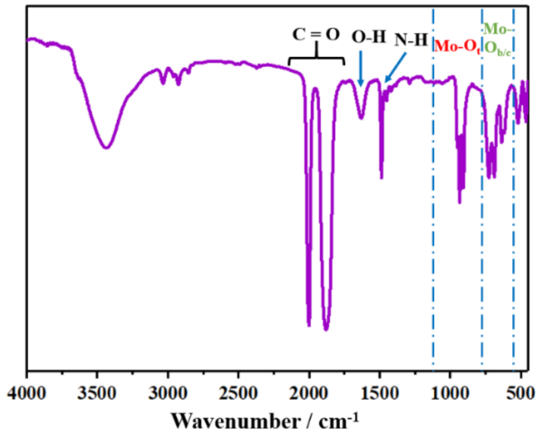


**Figure S4.** The IR spectrum of compound **1**

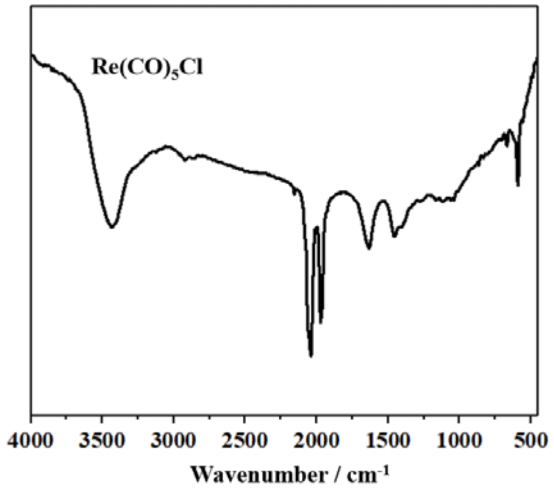


**Figure S5.** The IR spectrum of Re(CO)$_5$Cl

## Section 6. The UV−vis spectrum of 1

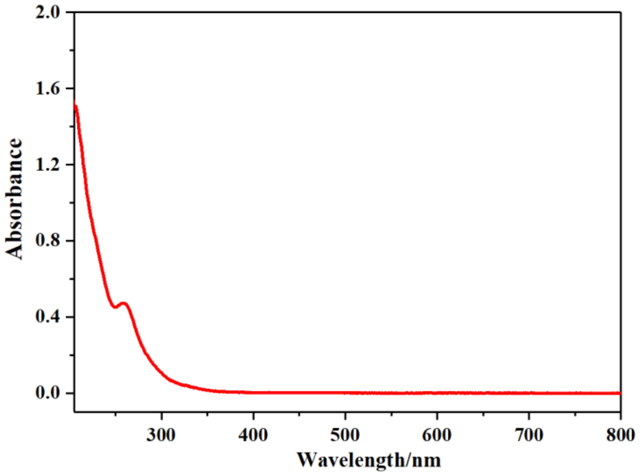


**Figure S6.** The UV−vis spectrum of **1**

## Section 7. The XPRD patterns

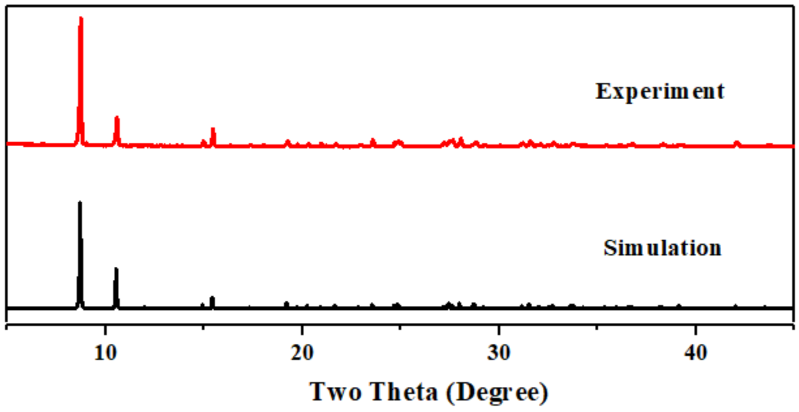


**Figure S7.** The XPRD patterns of **1**

## Section 8. Thermogravimetric analysis of 1

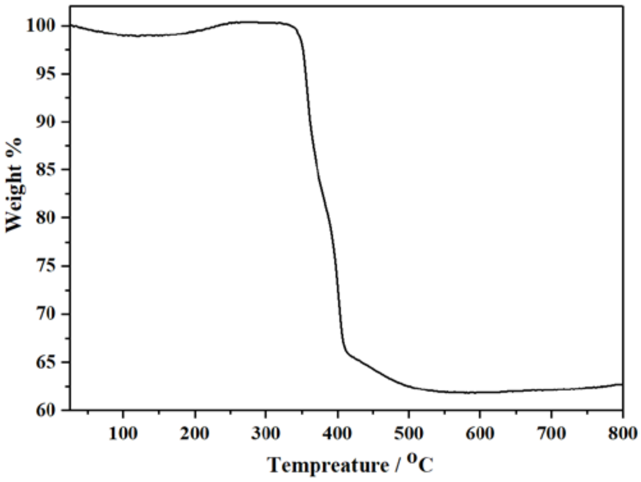


**Figure S8.** The thermogravimetric analysis curve of **1**

## Section 9. The ESI-MS spectrum of 1

These solutions were filtered and introduced to the spectrometer *via* direct injection at a flow rate of 15 μL $min^{-1}$ using a syringe pump. Moreover, the electrospray source was used with the dying nitrogen gas and the ion polarity for all MS data collections recorded was negative. The following parameters were consistent for all ESI-MS data collections as follows: ionspray voltage: -4500V, curtain gas flow, 25 PSI; ion source gas 1, 15 PSI; ion source gas 2, 15 PSI; ion energy 1, -1.1 V; pulser frequency, 11.332 KHz; pulse 1 duration, 3.902 μm; declustering potential, -10 V; collision energy, -5.0 V.

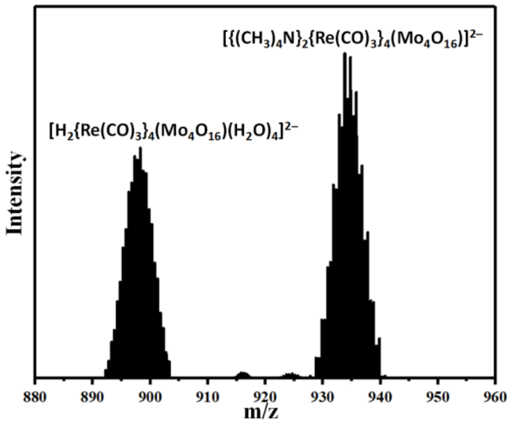


**Figure S9.** Negative-ion ESI-MS mass spectrum of **1a** in acetonitile.

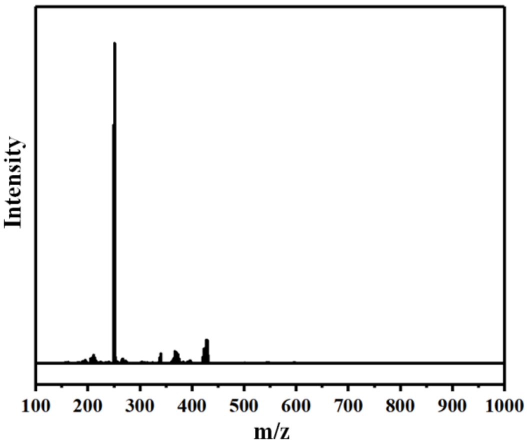
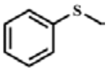


**Figure S10.** Negative-ion ESI-MS mass spectrum of **1a** against $H_2O_2$ in acetonitile.

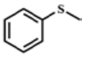
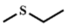
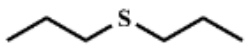
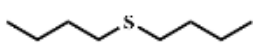
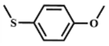
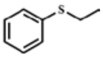
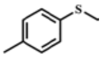
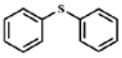
## Section 10. Catalytic properties

**Table S5** Oxidation of thioanisole with different catalysts [a]

| Entry | Substrate | Catalyst | Con.[b] (%)[c] | Sel. (%) (RR'SO) |
|---|---|---|---|---|
| 1 |  | – | 24 | 53 |
| 2 |  | $Re(CO)_5Cl$ | 37 | 56 |
| 3 |  | $Na_2MoO_4·2H_2O$ | 70 | 57 |
| 4 |  | Catalyst **1** | 99 | 93 |

[a] Reaction conditions: catalyst (5.5 μmol), substrate (1 mmol) and $H_2O_2$ (1.2 mmol) were mixed in 2 mL acetonitrile at 35 °C. [b] Determined by GC analyses based on initial substrate.

**Table S6** Oxygenation of various sulfides with $H_2O_2$ in $CH_3CN$ catalyzed by compound **1** [a]

| Entry | Substrate | $H_2O_2$[b] | Time (h) | Con.[c] (%) | Sel. (%) (RR'SO) | Sel. (%) ($RR'SO_2$) |
|---|---|---|---|---|---|---|
| 1 |  | 2.5 | 1 | >99 | 0 | 100 |
| 2 |  | 2.5 | 1 |  | 0 | 100 |
| 3 |  | 2.5 | 1 |  | 0 | 100 |
| 4 |  | 2.5 | 1 |  | 3 | 97 |
|  |  | 2.5 | 1.5 |  | 4 | 96 |
| 5 |  | 2.5 | 2 |  | 3 | 97 |
| 6 |  | 2.5 | 1.5 |  | 5 | 95 |
| 7 |  | 2.5 | 1.5 |  | 24 | 76 |

[a] Reaction conditions: catalyst (11.1 mg, 5.5 μmol), substrate (1 mmol) and $H_2O_2$ were mixed in 2 mL acetonitrile at 35 °C. [b] $H_2O_2$/substrate ratio. [c] Determined by GC analyses based on initial substrate.