Supporting Information

for

Highly Efficient Oxidation of Sulfides with Hydrogen Peroxide Catalyzed by $[SeO_4\{WO(O_2)_2\}_2]^{2-}$

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General. GC analyses were performed on Shimadzu GC-17A with a flame ionization detector equipped with a InerCap Pure-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). Mass spectra were recorded on Shimadzu GCMS-QP2010 equipped with a TC-5HT capillary column (internal diameter = 0.25 mm, length = 30 m). NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H, 270.0 MHz; ^{13}C, 67.80 MHz; ^{29}Si, 53.45 MHz; ^{31}P, 109.25 MHz; ^{51}V, 70.90 MHz, ^{77}Se, 51.30 MHz; ^{183}W, 11.20 MHz) by using 5 mm tubes (for ^{1}H, ^{13}C, and ^{31}P) or 10 mm tubes (for ^{29}Si, ^{77}Se, and ^{183}W). Chemical shifts (δ) were reported in ppm downfield from $SiMe_4$ (solvent, $CDCl_3$) for ^{1}H, ^{13}C, and ^{29}Si NMR spectra, 85% H_3PO_4 for ^{31}P NMR spectra, Me_2Se for ^{77}Se NMR spectra, and 2 M Na_2WO_4 (solvent, D_2O) for ^{183}W NMR spectra, respectively. IR spectra were measured on Jasco FT/IR-460 Plus using KCl disks. UV-vis spectra were recorded on a Jasco V-570 spectrometer. CSI-MS spectra were recorded on a JMS-T100LC spectrometer. Typical measurements were as follows: Olifice voltage (90 V for positive ions), sample flow (0.05 mL·min^{-1}), solvent (CH_3CN), concentration (0.3 mM), spray temp. (263 K), and ion source temp. (room temp.). Acetonitrile (Kanto Chemical) was purified by The Ultimate Solvent System (GlassContour Company).[S1] The other solvents and sulfides were obtained from TCI or Aldrich (reagent grade) and purified prior to the use.[S2]

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[SeO_4\{WO(O_2)_2\}_2]$ (I). The TBA salt derivative of $[SeO_4\{WO(O_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.[S3] In 15% aqueous H_2O_2 (9.25 mL, 42 mmol), H_2WO_4 (1.75 g, 7 mmol) was suspended and the resulting suspension was stirred at 305 K for 30 min until a pale yellow solution was obtained. The solution was filtered to remove insoluble materials followed by addition of 80% H_2SeO_4 (2.1 mL, 28 mmol). After stirring the solution for 60 min at 273 K, an excess amount of TBA·NO_3 (3.05 g, 10 mmol) was added in a single step. After stirring the solution for 30 min at 273 K, the resulting white precipitate (1.07 g) was collected by the filtration and then washed with an excess amount of H_2O and diethyl ether. After the dryness, acetonitrile solution (1 mL) containing the crude product (0.2 g) and a drop of H_2O_2 was cooled to 277 K. The colorless plate-like crystalline solid was obtained by vapor diffusion of diethyl ether into the acetonitrile solution. Yield: 0.11 g (55% based on the crude product). ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -569.2$ ($\Delta\nu_{1/2}$ = 3.9 Hz); ^{77}Se NMR (51.30 MHz,

CD_3CN, 298 K, $(CH_3)_2Se$): δ = 1168.9 ($\Delta\nu_{1/2}$ = 3.7 Hz); UV/Vis (CH_3CN) λ_{max} (ε) 256.2 nm (1258 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 972, 915, 884, 864, 847, 831, 779, 739, 698, 654, 593, 576, 520, 463, 393, 371 cm^{-1}; Raman: ν = 987, 974, 922, 884, 868, 838, 783, 599, 583, 542, 398, 336, 306, 264 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1398 $[(TBA)_3SeO_4\{WO(O_2)_2\}_2]^+$; 2554 $[(TBA)_5\{SeO_4\{WO(O_2)_2\}_2\}_2]^+$; 3709 $[(TBA)_7\{SeO_4\{WO(O_2)_2\}_2\}_3]^+$; elemental analysis calcd (%) for $C_{32}H_{72}N_2O_{14}SeW_2$ ($(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$): C 33.26, H 6.28, N 2.42, Se 6.83, W 31.82; found: C 33.21, H 6.30, N 2.48, Se 6.53, W 31.21.

Procedure for Catalytic Oxidation of Sulfide. The catalytic oxidation of various sulfides was carried out in a 30-mL glass vessel containing a magnetic stir bar. All products were identified by the comparison of GC retention time, mass spectra, and NMR spectra with those of the authentic samples. A typical procedure for the catalytic oxidation was as follows: **1a** (1 mmol), acetonitrile (5.9 mL), and 30% aqueous H_2O_2 (1 mmol) were charged in the reaction vessel. The reaction was initiated by the acetonitrile solution containing **I** (1 μmol; [**I**] = 10 mM, 0.1 mL) and the reaction solution was periodically analyzed. Before the GC analysis, the remaining H_2O_2 was decomposed at 273 K by the addition of $Ru(OH)_x/Al_2O_3$.[S4] It was confirmed that the oxidation of **1a** did not proceed at all in the presence of $Ru(OH)x/Al_2O_3$ during the decomposition of H_2O_2. The sulfoxides and sulfone were identified by comparison of their ^{1}H and ^{13}C NMR signals with the literature data.

A Larger-Scale (100 mmol scale) Production of Sulfoxide. Into a glass reactor were successively placed **I** (0.005 mol% with respect to **1a** and H_2O_2), **1a** (100 mmol, 12.42 g), 30% aqueous H_2O_2 (100 mmol), and acetonitrile (40 mL). The reaction mixture was stirred at 293 K. The GC yield of **2a** and **3a** reached 94% and 3% for 240 min, respectively. Then, acetonitrile was removed by evaporation. Into the resulting solution, the aqueous solution saturated with NaCl was added followed by the extraction of the products with dichloromethane (3×20 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. *n*-Hexane/ethyl acetate (50 mL, 60/40, v/v) was added to the concentrated solution. The isolation of **2a** was carried out by column chromatography on silica gel (Silica Gel 60N, spherical, neutral, 63−210 μm, Kanto, Cat. No. 37565-79) using *n*-hexane/ethyl acetate (60/40, v/v) as an eluent, giving 12.73 g of pure **2a** (91% yield, 99% purity by ^{1}H NMR).

Synthesis and Characterization of $[(n\text{-}C_6H_{13})_4N]_3[AsO_4\{WO(O_2)_2\}_4]$. The tetra-*n*-hexylammonium (THA) salt derivative of $[AsO_4\{WO(O_2)_2\}_4]^{3-}$ was synthesized according to the literature procedure.[S5] Yield: 2.41 g (43%). ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): δ = −567.5 ($\Delta\nu_{1/2}$ = 5.0 Hz); UV/Vis (CH_3CN) λ_{max} (ε) 255.2 nm (1184 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 978, 917, 892, 876, 845, 756, 729, 647, 590, 574, 520, 485, 435 cm^{-1}; Raman: ν = 990, 924, 900, 862, 843, 653, 597, 580, 534, 386, 336, 328, 303, 232 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 2613 $[(THA)_4AsO_4\{WO(O_2)_2\}_4]^+$; elemental analysis calcd (%) for $C_{72}H_{156}N_3O_{24}AsW_4$ ($(THA)_3[AsO_4\{WO(O_2)_2\}_4]$): C 38.29, H 6.96, N 1.86, As 3.32, W 32.56; found: C 38.06, H 6.99, N 1.80, As 3.13, W 32.39.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[SO_4\{WO(O_2)_2\}_2]$: The TBA salt derivative of $[SO_4\{WO(O_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.[S6] Yield: 1.39 g (54%). ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): δ = −587.2 ($\Delta\nu_{1/2}$ = 2.6 Hz); UV/Vis (CH_3CN) λ_{max} (ε) 254.1 nm (1270 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 988, 974, 962, 922, 887, 858, 850, 739, 679, 655, 646, 599, 594, 575, 540, 526, 487 cm^{-1}; Raman: ν = 994, 970, 915, 883, 865, 806, 750, 662, 600, 582, 547, 409, 336, 311, 289, 266 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1351 $[(TBA)_3SO_4\{WO(O_2)_2\}_2]^+$; elemental analysis calcd (%) for $C_{32}H_{72}N_2O_{14}SW_2$ ($(TBA)_2[SO_4\{WO(O_2)_2\}_2]$): C 34.67, H 6.55, N 2.53, W 33.16; found: C 34.69, H 6.59, N 2.44, W 34.16.

Synthesis and Characterization of $[(n\text{-}C_6H_{13})_4N]_3[PO_4\{WO(O_2)_2\}_4]$. The THA salt derivative of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ was synthesized according to the literature procedure.[S7] Yield: 1.39 g (50%). ^{31}P NMR (109.25 MHz, CD_3CN, 298 K, H_3PO_4): $\delta = 4.5$ ($^2J_{W\text{-}P} = 18.5$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -588.2$ ($^2J_{W\text{-}P} = 18.4$ Hz, $\Delta\nu_{1/2} = 7.3$ Hz); UV/Vis (CH_3CN) λ_{max} (ε) 254.2 nm (1268 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 977, 853, 843, 797, 757, 728, 660, 649, 603, 591, 573, 549, 525, 444 cm^{-1}; Raman: ν = 990, 864, 821, 655, 597, 580, 543, 391, 333, 305, 266, 237 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 2569 $[(THA)_4PO_4\{WO(O_2)_2\}_4]^+$; elemental analysis calcd (%) for $C_{72}H_{156}N_3O_{24}PW_4$ ($(THA)_3[PO_4\{WO(O_2)_2\}_4]$): C 39.05, H 7.10, N 1.90, P 1.40, W 32.22; found: C 38.82, H 6.97, N 1.36, P 1.36, W 33.28.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[HAsO_4\{WO(O_2)_2\}_2]$. The tetra-*n*-butylammonium (TBA) salt derivative of $[HAsO_4\{WO(O_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.[S8] Yield: 2.60 g (49%). ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -603.9$ ($\Delta\nu_{1/2} = 5.0$ Hz); UV/Vis (CH_3CN) λ_{max} (ε) 252.1 nm (1330 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): ν = 968, 932, 871, 843, 814, 777, 739, 664, 584, 575, 569, 527, 512, 495, 457, 385, 366 cm^{-1}, Raman: ν = 983, 914, 889, 859, 821, 651, 580, 531, 464, 391, 315, 264, 237 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1395 $[(TBA)_3HAsO_4\{WO(O_2)_2\}_2]^+$, 2548 $[(TBA)_5\{HAsO_4\{WO(O_2)_2\}_2\}_2]^+$; elemental analysis calcd (%) for $C_{32}H_{73}N_2O_{14}AsW_2$ ($(TBA)_2[HAsO_4\{WO(O_2)_2\}_2]$): C 33.35, H 6.38, N 2.43, As 6.50, W 31.90; found: C 33.08 H 6.33, N 2.39, As 6.35, W 31.44.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[HPO_4\{WO(O_2)_2\}_2]$. The TBA salt derivative of $[HPO_4\{WO(O_2)_2\}_2]^{2-}$ was synthesized according to the literature procedure.[S9] Yield: 1.70 g (60%). ^{31}P NMR (109.25 MHz, CD_3CN, 298 K, H_3PO_4): $\delta = 2.8$ ($^2J_{W\text{-}P} = 17.3$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -626.4$ ($^2J_{W\text{-}P} = 17.1$ Hz, $\Delta\nu_{1/2} = 5.8$ Hz); UV/Vis (CH_3CN) λ_{max} (ε) 251.5 nm (1294 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 1019, 996, 963, 882, 853, 843, 800, 737, 646, 625, 584, 569, 538, 487 cm^{-1}; Raman: ν = 977, 915, 887, 862, 807, 652, 582, 536, 335, 319, 300, 262, 239 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1351 $[(TBA)_3HPO_4\{WO(O_2)_2\}_2]^+$; elemental analysis calcd (%) for $C_{32}H_{73}N_2O_{14}PW_2$ ($(TBA)_2[HPO_4\{WO(O_2)_2\}_2]$): C 34.67, H 6.64, N 2.53, P 2.79, W 33.17; found: C 34.50, H 6.54, N 2.33, P 2.75, W 33.48.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[Ph_2SiO_2\{WO(O_2)_2\}_2]$: The TBA salt derivative of $[Ph_2SiO_2\{WO(O_2)_2\}_2]^{2-}$ was synthesized by the modification of the reported method; tetraphenylphosphonium $[Ph_4P]^+$ was replaced by tetra-*n*-butylammonium $[(n\text{-}C_4H_9)_4N]^+$.[S10] Yield: 1.70 g (40%). ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): $\delta = 7.77$ (m, 4H, *m*-), 7.36 (m, 6H, *o*-, *p*-); ^{13}C NMR (67.80 MHz, $ClCD_2CD_2Cl$, 298 K, TMS): δ = 135.5, 130.0, 128.3; ^{29}Si NMR (53.45 MHz, CD_3CN, 298 K, TMS): $\delta = -34.6$ ($^2J_{Si\text{-}C} = 2.9$ Hz, $\Delta\nu_{1/2} = 1.0$ Hz); ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = 651.6$ ($\Delta\nu_{1/2} = 3.9$ Hz); IR (KBr): ν = 974, 965, 933, 881, 850, 840, 746, 712, 701, 638, 582, 563, 505, 480, 437 cm^{-1}; Raman: ν = 1006, 983, 940, 915, 886, 858, 646, 626, 588, 573, 531, 518, 403, 341, 325, 306, 262, 204 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1469 $[(TBA)_3PhSiO_2\{WO(O_2)_2\}_2]$; elemental analysis calcd (%) for $C_{44}H_{82}N_2O_{12}SiW_2$ ($(TBA)_2[Ph_2SiO_2\{WO(O_2)_2\}_2]$): C 43.07, H 6.74, N 2.28, Si 2.29, W 29.97; found: C 43.00, H 6.89, N 2.08, Si 2.00, W 27.28.

Synthesis and Characterization of $[(n\text{-}C_4H_9)_4N]_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$. The tetra-*n*-butylammonium (TBA) salt derivative of $[\{WO(O_2)_2\}_2(\mu\text{-}O)]^{2-}$ was synthesized according to the literature procedure.[S11] Yield: 0.2 g (12%). ^{183}W NMR (11.20 MHz, CD_3CN, 298 K, Na_2WO_4): $\delta = -587.5$ ($\Delta\nu_{1/2} = 24.3$ Hz); IR (KCl): ν = 962, 955, 848, 835, 655, 631, 615, 571, 554, 543, 524 cm^{-1}; Raman: ν = 970, 961, 858, 844, 801, 786, 662, 624, 597, 572, 470, 328, 308, 275, 259 cm^{-1}; positive ion MS (CSI, CH_3CN): *m/z*: 1270.3

$[(TBA)_3\{WO(O_2)_2\}_2(\mu\text{-}O)]^+$; elemental analysis calcd (%) for $C_{32}H_{72}N_2O_{11}W_2$ ($(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$): C 37.37, H 7.06, N 2.72, W 35.75; found: C 37.24, H 7.13, N 2.69, W 35.28.

Data of Products

Methyl phenyl sulfoxide (2a): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.64 (s, 3H), 7.51−7.55 (m, 3H), 7.61−7.64 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 44.2, 124.3, 130.1, 131.6, 147.6; MS (70 eV, EI): *m/z* (%): 140 (100) [M^+], 125 (100), 124 (25), 109 (13), 97 (62), 94 (18), 91 (14), 78 (15), 77 (51), 65 (16), 51 (45), 50 (19), 45 (11).

Methyl phenyl sulfone (3a): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 3.04 (s, 3H), 7.59−7.70 (m, 3H), 7.91−7.93 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 44.4, 128.0, 130.2, 134.5, 141.9; MS (70 eV, EI): *m/z* (%): 156 (36) [M^+], 141 (33), 94 (42), 77 (100), 51 (28).

Methyl *p*-methoxyphenyl sulfoxide (2b): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.63 (s, 3H), 3.82 (s, 3H), 7.04−7.09 (m, 2H), 7.55−7.60 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 50.0, 58.7, 121.0, 129.2, 139.3, 165.3; MS (70 eV, EI): *m/z* (%): 170 (21) [M^+], 155 (100), 154 (12), 139 (16), 123 (11).

Methyl *p*-methylphenyl sulfoxide (2c): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.36 (s, 3H), 2.62 (s, 3H) 7.32−7.35 (m, 2H), 7.48−7.52 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 21.0, 43.4, 124.3, 130.6, 142.4, 124.8; MS (70 eV, EI): *m/z* (%): 154 (66) [M^+], 139 (100), 138 (19), 111 (12), 91 (36), 77 (28), 67 (13), 65 (20), 63 (11).

***p*-Fluorophenyl methyl sulfoxide (2d):** ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.66 (s, 3H), 7.23−7.33 (m, 2H), 7.65−7.71 (m, 2H); MS (70 eV, EI): *m/z* (%): 158 (58) [M^+], 143 (100), 142 (18), 127 (16), 115 (41), 112 (14), 95 (27), 83 (19), 75 (23).

***p*-Chlorophenyl methyl sulfoxide (2e):** ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.64 (s, 3H), 7.48−7.52 (m, 2H), 7.55−7.60 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 43.5, 126.1, 130.1, 137.1, 144.9; MS (70 eV, EI): *m/z* (%): 176 (17), 175 (11), 174 (48) [M^+], 161 (34), 160 (28), 159 (100), 158 (54), 145 (12), 143 (39), 131 (36), 128 (18), 127 (12), 125 (12), 112 (15), 111 (22), 108 (32), 76 (11), 75 (35), 74 (17), 69 (14), 63 (11), 50 (24), 45 (32).

***p*-Bromophenyl methyl sulfoxide (2f):** ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.63 (s, 3H), 7.48−7.53 (m, 2H), 7.63−7.68 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 43.4, 125.4, 126.3, 133.0, 145.5; MS (70 eV, EI): *m/z* (%): 281 (19), 220 (62) [M^+], 218 (67), 205 (98), 204 (100), 203 (92), 202 (77), 189 (28), 187 (28), 177 (26), 175 (20), 171 (24), 131 (23), 122 (20), 108 (72), 96 (46), 86 (11), 82 (21), 77 (29), 76 (47), 75 (27), 74 (34), 69 (25), 63 (23), 59 (10), 58 (18), 56 (21), 51 (28), 50 (56), 45 (14), 43 (15).

4-(Methylsulfinyl)-acetophenone (2g): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.57 (s, 3H), 2.70 (s, 3H), 7.69−7.73 (m, 2H), 8.05−8.08 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 26.8, 43.2, 124.5, 129.6, 139.5, 151.1 198.7; MS (70 eV, EI): *m/z* (%): 182, (63) [M^+], 168 (10), 167 (100), 152 (73), 151 (12), 139 (22), 124 (12), 121 (13), 76 (12), 50 (13).

4-Methyl sulfinyl benzonitrile (2h): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.68 (s, 3H), 7.52−7.59 (m, 2H), 7.81−7.86 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 43.1, 114.5, 118.5, 125.0, 133.7, 151.7; MS (70 eV, EI): *m/z* (%): 165 (89) [M^+], 150 (100), 149 (24), 122 (60), 119 (18), 116 (13), 102 (29), 90 (11), 76 (16), 75 (26), 51 (14), 50 (13), 45 (10).

***p*-Nitrophenyl methyl sulfoxides (2i):** ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.73 (s, 3H), 7.84 (d, J = 8.1 Hz, 2H), 8.34 (d, J = 7.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN,

298 K, TMS): δ = 43.8, 125.1, 125.8, 150.1, 152.8, 150.3, 154.5; MS (70 eV, EI): *m/z* (%): 185 (100) [M^+], 170 (45), 140 (22), 124 (12), 112 (14), 96 (10), 92 (10), 84 (10), 76 (17), 75 (11), 63 (14).

Ethyl phenyl sulfoxide (2j): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 1.08 (t, *J* = 7.3 Hz, 3H), 2.66−2.97 (m, 2H), 7.51−7.62 (m, 5H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 5.8, 50.1, 124.8, 130.0, 131.7, 143.5; MS (70 eV, EI): *m/z* (%):154 (26) [M^+], 126 (64), 125 (17), 97 (12), 78 (100), 77 (21), 51 (22).

Benzyl methyl sulfoxide (2k): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ 2.40 (t, *J* = 7.3 Hz, 3H), 3.8−4.0 (m, 2H), 7.2−7.4 (m, 5H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 37.3, 59.4, 128.7, 129.2, 130.8, 131.3; MS (70 eV, EI): *m/z* (%):154 (1) [M^+], 106 (1), 105 (2), 92 (8), 91 (100), 89 (2), 78 (1), 77 (7), 65 (10), 63 (2), 51 (5).

Diphenyl sulfoxide (2l): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 7.43−7.53 (m, 6H), 7.65−7.65 (m, 4H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 125.1, 130.3, 132.0, 147.3; MS (70 eV, EI): *m/z* (%): 203 (15) [M^++1], 202 (100) [M^+], 186 (14), 185 (22), 174 (15), 173 (21), 155 (11), 154 (83), 153 (23), 152 (12), 141 (13), 125 (11), 109 (84), 97 (36), 77 (48), 65 (33).

Diphenyl sulfone (3l): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 7.54−7.65 (m, 6H), 7.93−7.95 (m, 4H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 128.3, 130.5, 134.4, 142.5; MS (70 eV, EI): *m/z* (%): 218 (28) [M^+], 153 (4), 152 (6), 127 (5), 126 (8), 125 (100), 97 (17), 77 (35), 51 (25).

Methyl octyl sulfoxide (2m): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 0.97 (t, *J* = 7.3 Hz, 3H), 1.60−1.69 (m, 12H), 2.40 (s, 3H), 2.61−2.68 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 14.1, 22.9, 23.0, 29.0, 29.4, 29.5, 32.2, 38.1, 52.3; MS (70 eV, EI): *m/z* (%): 177 (10) [M^++1], 112 (11), 107 (17), 94 (13), 91 (13), 85 (11), 84 (17), 83 (27), 82 (13), 81 (100), 80 (25), 79 (11), 77 (10), 71 (41), 70 (20), 69 (24), 57 (63), 56 (29), 55 (30), 53 (10), 43 (48), 42 (10), 41 (50).

Methyl octyl sulfone (3m): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 0.86 (t, *J* = 5.9 Hz, 3H), 1.27−1.78 (m, 12H), 2.83 (s, 3H), 2.96−3.02 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 14.1, 22.9, 23.0, 28.7, 29.4, 29.5, 32.2, 40.5, 54.8; MS (70 eV, EI): *m/z* (%): 193 (3) [M^++1], 177 (6), 175 (4), 112 (11), 107 (11), 84 (12), 83 (21), 81 (100), 80 (24), 71 (49), 70 (17), 69 (21), 57 (64), 56 (23), 55 (34).

Ethyl propyl sulfoxide (2n): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 1.03 (t, *J* = 7.4 Hz, 3H), 1.22 (t, *J* = 7.5 Hz, 3H), 1.63−1.78 (m, 2H), 2.56−2.74 (m, 4H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 6.7, 13.2, 16.6, 45.4, 53.2; MS (70 eV, EI): *m/z* (%): 120 (43) [M^+], 103 (13), 78 (100), 77 (12), 63 (51), 50 (21), 43 (82), 41 (58).

Diallyl sulfoxide (2o): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 3.32−3.54 (m, 4H), 5.31−5.40 (m, 4H), 5.77−5.92 (m, 2H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 54.6, 123.6, 127.1; MS (70 eV, EI): *m/z* (%): 130 (16) [M^+], 113 (5), 100 (12), 89 (8), 82 (16), 81 (100), 80 (23), 79 (14), 73 (12), 68 (33), 67 (12).

Diallyl sulfones (3o): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 3.74 (d, *J* = 7.0 Hz 2H), 5.39−5.47 (m, 2H), 5.79−5.95 (m, 1H); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 56.6, 124.9, 125.8; MS (70 eV, EI): *m/z* (%): 146 (0.1) [M^+], 105 (6), 97(2), 82 (2), 81 (20), 79 (2), 68 (6), 67 (100), 54 (49).

Di(2-hydroxylethyl)sulfoxide (2p): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 2.93−3.09 (m, 2H), 3.89 (t, *J* = 4.9 Hz); $^{13}C\{^1H\}$ NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 55.2, 123.4, 127.7; MS (70 eV, EI): *m/z* (%): 138 (3) [M^+], 104 (3), 96 (4), 94 (70), 91 (3), 76 (100), 63 (44), 61 (14).

Phenyl vinyl sulfoxide (2q): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 5.83 (d, J = 4.7 Hz, 1H), 6.09 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 4.9, 8.2 Hz, 1H), 7.36–7.62 (m, 5H); ^{13}C{^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 120.7, 125.2, 130.4, 132.0, 144.3, 144.7; MS (70 eV, EI): *m/z* (%): 152 (19) [M^+], 136 (8), 124 (13), 123 (16), 109 (31), 104 (100), 97 (14), 91 (11), 78 (42), 77 (31), 65 (15), 51 (32), 50 (11).
Phenyl vinyl sulfone (3q): ^{1}H NMR (270 MHz, CD_3CN, 298 K, TMS): δ = 6.10 (d, J = 5.0 Hz, 1H), 6.37 (d, J = 8.2 Hz, 1H), 6.80 (d, J = 5.0, 8.2 Hz, 1H), 7.62–7.73 (m, 2H), 7.85–7.89 (m, 3H); ^{13}C{^{1}H} NMR (67.5 MHz, CD_3CN, 298 K, TMS): δ = 128.3, 129.0, 130.3, 134.6, 139.2, 140.5; MS (70 eV, EI): *m/z* (%): 168 (21) [M^+], 125 (100), 97 (13), 78 (11), 77 (100), 65 (12), 51 (35).

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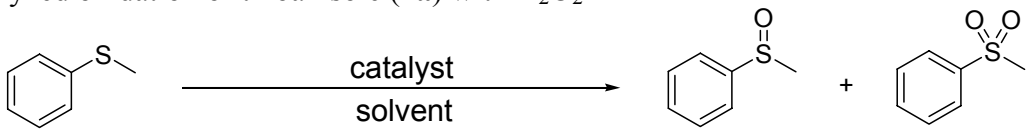
Table S1 Transition-metal-catalyzed oxidation of thioanisole (**1a**) with H_2O_2[a]



1a **2a** **3a**

entry	catalyst	Sub/Ox/Cat	solvent	temp (K)	time (min)	yield (%)	select. to **2a** (%)	TON	TOF (h^{-1})	ref.
1	***I***	*20000/20000/1*	*CH_3CN*	*293*	*240*	*99*	*97*	***19500***	***70800***	*this work*
2	$[WO_4]^{2-}$/LDH	27/54/1	CH_3CN	303	30	91	15	49	98	S12
3	$[WO_4]^{2-}$/LDH	22/68/1	water	rt	30	35	88	24	43	S13
4	$[PO_4\{WO(O_2)_2\}_4]^{3-}$-dendrimer	284/800/1	$CDCl_3$	303	10	71	0	568	3400	S14
5	WO_3/SiO_2	208/313/1	water	rt	5	66	100	208	2496	S15
6	$[W_2O_3(O_2)_4]^{2-}$/Im-SiO_2	67/73/1	$MeOH/CH_2Cl_2$	281	150	92	–	62	25	S16
7[b]	$[PhPO_3\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]^{2-}$/CP·Cl	200/400/1	$CHCl_3$	rt	120	64	72	256	128	S17
8	$[WO(O_2)(HMPT)(H_2O)]/CH_3SO_3H$	363/367/1	EtOH/water	298	–	96	–	348	200–380	S18
9	$[WO_4]^{2-}/NH^+SiO_2$	50/150/1	CH_2Cl_2/MeOH	rt	90	30	100	41	27	S19
10	WO_3/MCM-48	100/110/1	MeOH	rt	240	96	94	106	27	S20
11	$[PW_{12}O_{40}]^{3-}$/poly(*N*-isopropylacrylamide)	500/2000/1	–	323	240	49	3	985	246	S21
12	$Na_2WO_4/PhPO_3H_2/[CH_3(n\text{-}C_8H_{17})_3N]HSO_4$	2000/2000/1	–	308	1080	99	99	1980	110	S22
13[b]	$(CP)_3[PW_{12}O_{40}]$	200/400/1	$CHCl_3$	rt	120	49	93	195	97	S23
14[c,d]	$(NH_4)_3PMo_{12}O_{40}$/FAP /UHP	38/43/1	–	313	1800	96	91	41	1	S24
15	$(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$/imidazole	100/100/1	CH_3CN	296	180	100	100	100	33	S25
16	$[\gamma\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$/Im-$SiO_2$	250/250/1	CH_3CN/*t*-BuOH	298	360	99	92	248	41	S26
17	$(Bu_4N)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$	125/125/1	CH_3CN	305	120	97	95	121	61	S27
18	$(Bu_4N)_5[PznMo_2W_9O_{39}]\cdot 3H_2O$	20/24/1	CH_3CN	rt	30	92	–	18	37	S28
19	$(Bu_4N)_7[(PtiW_{11}O_{39})_2OH]$	2000/400/1	CH_3CN	298	–	–	–	–	65	S29
20	$PyH_3PMo_{11}VO_{40}$	70/200/1	CH_3CN	rt	30	34	–	67	134	S30
21	$[WZnMn(II)_2(ZnW_9O_{34})_2]^{12-}$ /methyltricaprylammonium	1000/2000/1	$ClCH_2CH_2Cl$	rt	–	43	79	700	–	S31

22	$(Bu_4N)_8[\{\gamma\text{-}SiTi_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-}O)_2]$	500/100/1	CH_3CN	305	90	83	>99	83	55	S32
23	cinchonine salt of $[PMo_{12}O_{40}]^{3-}$/UHP	100/200/1	CH_3CN	293	120	48	–	95	48	S33
24	$HNbMoO_6$	57/57/1	CH_3OH	rt	180	99	100	57	19	S34
25[e,d]	*cis*-$[MoO_2(phox)_2]$/UHP	40/40/1	CH_2Cl_2/CH_3OH	rt	20	95	100	38	114	S35
26[b]	$(CP)_3[PO_4\{MoO(O_2)_2\}_4]$	55/28/1	$CHCl_3$/EtOH	253	–	–	–	–	83	S36
27	MoO_2Cl_2	67/70/1	acetone/water	rt	5	92	–	64	772	S37
28	TiO_2	8/23/1	CH_3CN	298	180	61	4	15	3	S38
29	TiO_2-SiO_2	38/76/1	CH_3CN	313	60	100	0	76	320	S39
30	Ti-MCM-48	49/147/1	CH_3CN	313	30	33	74	48	96	S40
31	Ti-MMM-2	61/74/1	CH_3CN	293	35	99	74	74	100	S41
32[f]	Ti-Ge-MCM-41	82/164/1	[emim][BF_4]	313	30	26	90	42	85	S42
33	Ti-β	240/240/1	*t*-BuOH	303	120	86	93	206	288	S43
34	$Ti_4[(OCH_2)_3CMe]_2(i\text{-}PrO)_{10}$	20/30/1	CH_3OH	rt	30	67	81	20	40	S44
35	Ti-SBA-15	50/55/1	CH_3CN	293	60	56	72	31	31	S45
36	Ti-triphenolate amino ligand	100/100/1	CD_3OD	301	–	99	90	99	1700	S46
		10000/1000/1	CD_3OD	301	–	80	99	8000	800	S46
37[g]	VO(OiPr)(L)·iPrOH	200/220/1	CH_3CN	rt	5	99	83	220	2640	S47
38[h]	$VO(acac)_2$-resin	17/18/1	water	rt	10	98	100	16	98	S48
39[i]	$[VO(sal\text{-}oaba)(H_2O)]$-Y	650/650/1	CH_3CN	rt	180	96	97	624	598	S49
40	silica-vanadia gel	233/233/1	CH_3OH	rt	30	99	97	233	698	S50
41	VS-2	343/343/1	CH_3CN	333	30	100	84	343	686	S51
42	VCl_3	20/20/1	THF	rt	5	98	–	20	240	S52
43[j]	$[VO_2(sal\text{-}aebmz)]$	111/111/1	CH_3CN	rt	180	93	98	103	30	S53
44	V-triphenolate amino ligand	1000/1000/1	CD_3OD	301	20	98	97	980	8000	S54
		10000/10000/1	CD_3OD	301	255	99	98	9900	2667	S54
45[k]	$[(VO)_3(\mu\text{-tpip})_3(\mu\text{-}O)_3]$	100/117/1	CH_2Cl_2	rt	60	73	90	80	80	S55
46	VO-alkyl phosphate/SiO_2	31/62/1	CH_3CN	rt	60	50	99	31	31	S56
47	Nb(salen)	500/3500/1	CH_2Cl_2	313	120	16	83	559	280	S57
48[l]	Ta-MCM-41	1000/2000/1	[bmim][NTf_2]	313	15	22	92	432	1728	S58
49	$Sc(OTf)_3$	5/6/1	CH_2Cl_2/EtOH	rt	360	84	97	5	<1	S59
50	$C_5H_8N_2H[CrO_3F]$	100/200/1	–	rt	30	75	–	75	150	S60
51	CH_3ReO_3	100/110/1	EtOH	rt	60	92	97	101	101	S61

52[d]	$Re(PPh_3)_2OCl_3$/UHP	58/55/1	CH_3CN	rt	1080	92	–	53	3	S62
53	CH_3ReO_3	100/100/1	$CDCl_3$	293	1440	83	97	85	4	S63
54	$HAuCl_4 \cdot 4H_2O$	10000/20000/1	CH_3OH	298	720	94	99	9400	783	S64
55[m]	Cu(salan)/TEMPO	100/200/1	CH_3CN	293	270	99	99	99	22	S65
56[d,n]	Mn(*N*-OPh-sal)(acac)(EtOH)/imidazole/UHP	10/20/1	CH_2Cl_2/CH_3OH	rt	1	60	72	12	2700	S66
57[d,e]	$[Mn(phox)_2(CH_3OH)_2]ClO_4$/imidazole/UHP	10/20/1	CH_2Cl_2/CH_3OH	rt	5	57	74	11	420	S67
59[p]	$[(tmtacn)_2Mn^{IV}_2(\mu\text{-}O)_3](PF_6)_2$	400/2000/1	acetone	298	–	19	84	372	–	S68
60[p]	$Mn(OAc)_3 \cdot 2H_2O$/tmtacn	500/4000/1	acetone	273	120	34	59	1363	682	S69
61	Mn(salen)	33/267/1	AcOH	rt	25	14	86	38	90	S70
62[q]	Mn(Phth)/imidazole	43/238/1	EtOH	rt	5	70	–	30	361	S71
63[r]	$[(TBP_8Cz)Fe^{III}]$/dmap	333/367/1	THF	296	1	98	–	326	19580	S72
64[d,s]	[Fe(L)(acac)(EtOH)]/UHP	20/40/1	CH_2Cl_2/CH_3OH	rt	15	49	93	20	78	S73
65[t]	$(F_{20}TPP)Fe$	3333/3333/1	EtOH	rt	4	96	–	3200	47995	S74
66[u]	$[Ru(L5pyr)(CH_3CN)][PF_6]_2$	600/15/1	acetone	rt	540	90	–	14	2	S75
67[v]	$Ru\text{-}L_2(Me)_2$	100/250/1	CH_3OH	rt	5	41	93	102	1220	S76
	$Ru\text{-}L_2Me\text{-}MCM\text{-}41$	143/357/1	CH_3OH	rt	270	43	90	154	34	S76
68[w]	$[Ru(dmp)_2(Py@LUS)Cl]Cl$	600/15/1	acetone	rt	200	89	90	13	10	S77
69	$NH_4Ho(SO_4)_2 \cdot H_2O$	39/118/1	$ClCH_2CH_2Cl$	343	180	20	90	24	8	S78
70[x]	$[Pt(dppmO)_2][BF_4]_2$	50/55/1	$ClCH_2CH_2Cl$	298	–	17	99	10	–	S79
71	$ZrCl_4$	0.7/3.5/1	CH_3OH	rt	1	19	99	<1	41	S80
72	sodium dodecyl sulfate/HCl	20/160/1	–	rt	5	12	99	18	216	S81
73	Tf_2O	2/4/1	EtOH	rt	5	48	–	2	4	S82
74	Carbon-based solid acid	2/2/1	$ClCH_2CH_2Cl$	reflux	10	94	–	2	12	S83
75	–	1/1/*	–	343	60	97	–	–	–	S84
76	flavin	200/200/1	CH_3OH	rt	360	98	99	198	33	S85
77	β-cyclodextrin	5/20/1	water	318	240	23	93	5	1	S86
78	L-proline	10/25/1	CH_3CN	rt	90	41	95	10	7	S87

[a] Yield (%) = (**2a** (mol) + **3a** (mol) × 2)/H_2O_2 used (mol) × 100. TON = (**2a** (mol) + **3a** (mol) × 2)/catalyst used (mol). [b] CP = cetylpyridinium. [c] FAP = fluoroapatite. [d] UHP = urea hydrogen peroxide adduct. [e] Hphox = 2-(2'-hydroxyphenyl)oxazoline. [f] [emim][BF_4] = 1-ethyl-3-methylimidazolium tetrafluoroborate. [g] H_2L = 3-[(2-Hydroxyphenylimino)methyl]biphenyl-2,2′-diol. [h] Hacac = acetylacetone. [i] H_2(sal-oaba) = *o*-aminobenzyl alcohol. [j] Hsal-ambmz = Schiff base obtained by the condensation of salicylaldehyde and 2-aminomethylbenzimidazole. [k] tpip = tetraphenylimidodiphosphinate. [l] [bmim][NTf_2] = 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide. [m] TEMPO = 2,2,6,6-tetramethylpiperidine 1-oxyl. [n] *N*-HOPh-Hsal =

N-hydroxyphenyl-salicyldienamine. [o] TPP = *meso*-tetraphenyl porphyrin. The values in parentheses were reported in the literature. [p] tmtacn = 1,4,7-trimethyl-1,4,7-triazacyclononane. [q] Phth = phtalocyanine. [r] TBP_8Cz = β-octakis-4-tert-butylphenylcorrolazinato, dmap = *N*,*N*-(dimethylamino)pyridine. [s] L = salicylidene benzoyl hydrazine. [t] $F_{20}TPP$ = tetrakis-(pentafluorophenyl)porphyrin. [u] L5pyr = 2,6-bis-(6-ethyl-2,2′-bipyridyl)-pyridine. [v] L_2Me = (1*S*,2*S*)-*N*,*N*'-bis-pyridin-2-ylmethyl-cyclohexane-1,2-diamine. [w] dmp = 2,9-dimethyl-1,10-phenantroline, LUS = Laval University Silica (2D hexagonal porous mesostructured silica). [x] dppmO = $Ph_2PCH_2P(O)Ph_2$.

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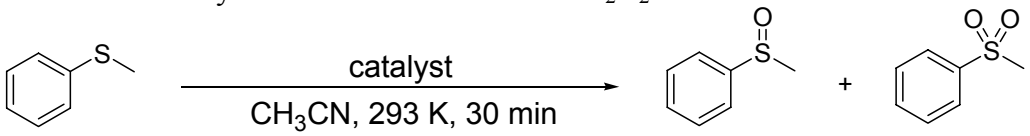
Table S2 Effect of catalysts on oxidation of **1a** with H_2O_2[a]



1a **2a** **3a**

entry	catalyst	yield (%)	selectivity (%)		R_0 (mM min^{-1})
			2a	**3a**	
1	**I**	90	95	5	25.0
2	without	<1	–	–	–
3[b]	H_2SeO_4	1	99	1	<0.1
4[c]	SeO_2	12	93	7	0.4
5	H_2WO_4	1	44	56	<0.1
6	$H_2SeO_4 + H_2WO_4$	4	92	8	0.2
7	$(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$	45	87	13	3.1
8	$(TBA)_2[SO_4\{WO(O_2)_2\}_2]$	73	92	8	16.0
9[d]	$(THA)_3[AsO_4\{WO(O_2)_2\}_4]$	83	92	8	15.8
10[d]	$(THA)_3[PO_4\{WO(O_2)_2\}_4]$	61	92	8	7.7
11	$(TBA)_2[HAsO_4\{WO(O_2)_2\}_2]$	61	87	13	4.1
12	$(TBA)_2[HPO_4\{WO(O_2)_2\}_2]$	52	89	11	3.7
13	$(TBA)_2[Ph_2SiO_2\{WO(O_2)_2\}_2]$	11	86	14	0.5

[a] Reaction conditions: Catalyst (W: 0.2 mol% relative to **1a** and H_2O_2), **1a** (1 mmol), 30% aqueous H_2O_2 (1 mmol), CH_3CN (6 mL), 293 K, 30 min. Yield was determined by GC. R_0 values were determined from the reaction profiles at low conversions (≤20%) of both **1a** and H_2O_2. [b] H_2SeO_4 (0.1 mol%). [c] SeO_2 (0.1 mol%). [d] THA = $[(n\text{-}C_6H_{13})_4N]^+$.