**Experimental Supplemental Information**

**Formation of persulphate from sodium sulphite and molecular oxygen catalysed by H$_5$PV$_3$Mo$_{10}$O$_{40}$ - aerobic epoxidation and hydrolysis**

**Experimental Details.**

**Materials:** Solvents and substrates available from commercial sources were of the highest purity available and were used without further purification. Alkenes were purified on a neutral alumina column in order to remove peroxides and other impurities. N-tert-butyl-alpha-phenylnitrone was purified on an activated carbon column to remove paramagnetic impurities. H$_5$PV$_3$Mo$_{10}$O$_{40}$ was prepared according to a literature method. Sodium sulphite (98%) was purchased from Sigma-Aldrich.

**Instruments:** The IR spectra were measured on a Nicolet 6700 FTIR using KBr pellets. EPR spectra were recorded on a Bruker ELEXSYS 500 X-band spectrometer equipped with a Bruker ER4102ST resonator in a J-young 3 mm tube at room temperature. The EPR spectra were simulated with home written Matlab program using EasySpin subroutines. Raman spectra were acquired on Renishaw Micro Raman In Via Imaging Microscope using a 633 nm laser. Samples were obtained by evaporation of the solvent. UV-Visible spectra were measured on Agilent 89090A spectrophotometer using 1.0 cm quartz cuvettes at the given concentrations.

**Oxidation reactions:** Catalytic oxidation reactions were carried out in 25 mL ace glass pressure tubes. The tubes were charged with the catalyst, sodium sulphite, substrate and solvent in the specified amounts; air was purged and then pressurized with O$_2$ and heated in a temperature controlled oil bath. At each relevant time period, a 50 µL aliquot was taken, dissolved in 0.2 mL DCM and then analyzed by GC-FID/GC-MS. The separation was carried out using a 5% phenylmethylsilicone 0.32 mm i.d., 0.25 µm coating, 30 m long column using He as eluent.

**Figure S1:** Raman spectra obtained by mixing H$_5$PV$_3$Mo$_{10}$O$_{40}$, sodium sulphite and $^{16}$O$_2$ (black trace) / $^{18}$O$_2$ 97% (green trace) 1 bar in AcOH at 65 °C. small impurities, <2% are observable.
Figure S2: Rate of cyclododecene epoxidation as a function of O$_2$ pressure. Cyclododecene (0.43 mmol), Na$_2$SO$_3$ (0.43 mmol), 1 mol % H$_5$PV$_2$Mo$_{10}$O$_{40}$ (4.3 µmol) in 1 mL AcOH, O$_2$ pressure (0.21-3 bar), 110 °C.

\[ y = 0.0715x - 0.7264 \]