

Supporting Information

N-Oxides Rescue Ru(V) in Catalytic Griffith-Ley (TPAP) Alcohol Oxidations

Timothy J. Zerk, Peter W. Moore, Craig M. Williams* and Paul V. Bernhardt*

School of Chemistry and Molecular Biosciences, University of Queensland, Brisbane 4072, Australia

Experimental

N-Methylmorpholine *N*-oxide monohydrate (NMO) was obtained by evaporating an aqueous solution of commercial *N*-methylmorpholine *N*-oxide (50 wt%, obtained from Sigma Aldrich) under reduced pressure. Pyridine *N*-oxide was purchased from Alfa Aesar. Sodium periodate was obtained from AJAX Finechemical Pty Ltd. Ruthenium(III) trichloride hydrate was obtained from Precious Metals Online. Acetonitrile was dried with an anhydrous purification system from John Morris Scientific. Melting point measurements are uncorrected measurements recorded in duplicate using a Digimelt MPA161 SRS apparatus. Infra-red spectra were recorded using a Perkin Elmer FT-IR spectrometer (spectrum 2000). Benchtop UV-vis spectroscopy was performed using an Agilent 8453 spectrophotometer. Microanalyses were performed by the University of Queensland Microanalytical Service. High resolution accurate mass measurements were recorded in positive or negative ion modes on a Bruker MicroTOF-Q (quadrupole – Time of flight) instrument with a Bruker ESI source.

Tetra-*n*-propylammonium perruthenate (NPr₄[RuO₄], TPAP) Synthesis

This synthesis was a modification of the method reported by Griffith *et al.*,^[1] using the apparatus shown below. Round bottomed flask A was filled with tetra-*n*-propylammonium hydroxide solution (1.0 M, 1.25 mL), deionized water (2.5 mL) and sodium hydroxide solution (1.0 M, 10.0 mL). In flask B sodium periodate (375 mg, 1.43 mmol) was dissolved in deionized water (10.0 mL) then treated with ruthenium trichloride solution (374.0 mg in 2.5 mL of deionized water). The reaction flasks were stoppered, and the reaction stirred at room temperature for 16 h. During the course of the reaction RuO₄ formed in flask B (*caution* RuO₄ is a strong and highly volatile oxidant) diffused into flask A where it oxidised hydroxide to form perruthenate. A dark green solid of NPr₄[RuO₄] formed in flask A, which was filtered off, washed with water (5 mL) and dried under vacuum (147 mg, 33%).

M.p. (Dec): 165.2 °C ; HRMS: m/z for ¹⁰²RuO₄⁻, calcd: 165.8846, found: 165.8849; HRMS: m/z for C₁₂H₂₈N⁺, calcd: 186.2216, found: 186.2213; UV-Vis: λ_{\max} (MeCN) = 316, 385 nm; IR: ν_{\max} 2969, 2940, 2879, 1476, 1457, 1390, 1039, 982, 968, 823, 750 cm⁻¹; Anal. Calcd for C₁₂H₂₈NO₄Ru: C, 41.01; H, 8.03; N, 3.99. Found: C, 41.12; H, 8.01; N, 3.98.

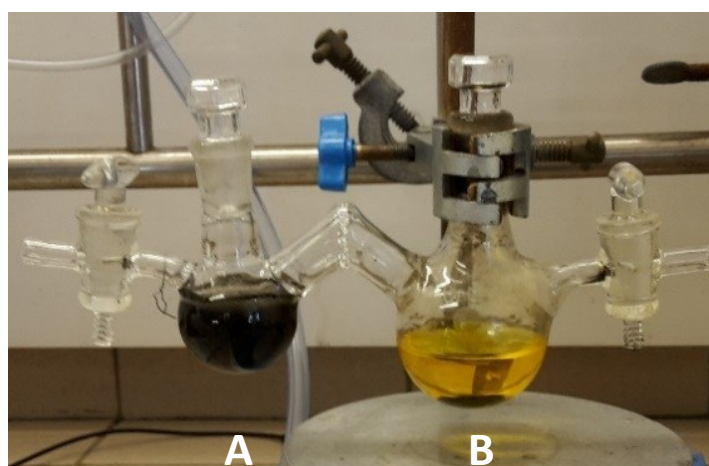


Figure S1: TPAP synthetic apparatus after reaction. Flask A contains TPAP in solution.

Cyclic Voltammetry

Cyclic voltammetry was performed on a BAS100B/W potentiostat employing a glassy carbon working electrode, platinum auxiliary electrode and a non-aqueous Ag/Ag⁺ reference electrode in acetonitrile. Ferrocene (Fc) was used as a standard and all potentials are cited versus the Fc⁺⁰ couple. The supporting electrolyte was 0.1 M NBu₄·BF₄ and all solutions were purged with argon before measurement. Between each measurement the electrode was polished using alumina (50 nm), washed and carefully. For experiments in which *N*-oxide was added to the perruthenate solution, this was undertaken by titrating from a bulk solution of the relevant *N*-oxide, which was made up in acetonitrile and dried over 3Å molecular sieves for 12 h.

Spectroelectrochemistry

Spectral measurements were made using an Ocean Optics USB 2000 spectrometer and DT-MINI-2-GS Miniature deuterium/tungsten/halogen UV-Vis-NIR Light Source coupled to the already mentioned potentiostat. A BAS EF-1350 spectroelectrochemical cell (1 mm optical path length) was used comprising an Au flag working electrode (situated in the spectrometer beam), platinum auxiliary electrode and non-aqueous Ag/Ag⁺ reference electrode. All measurements were recorded under a nitrogen atmosphere (< 10 ppm O₂) in a Belle Technology glovebox. The cuvette contained 2.0 mL of 1.0 mM TPAP in anhydrous MeCN with 0.1 M NBu₄·BF₄ as the supporting electrolyte. Reduction of perruthenate was achieved by poisoning the working electrode potential at -2300 mV vs Fc⁺⁰. Spectra were recorded every 2 seconds until a time of 200 seconds.

References

- [1] W.P. Griffith, S.V. Ley, G.P. Whitcombe, A.D. White, *J. Chem. Soc., Chem. Commun.* **1987**, 1625-1627.

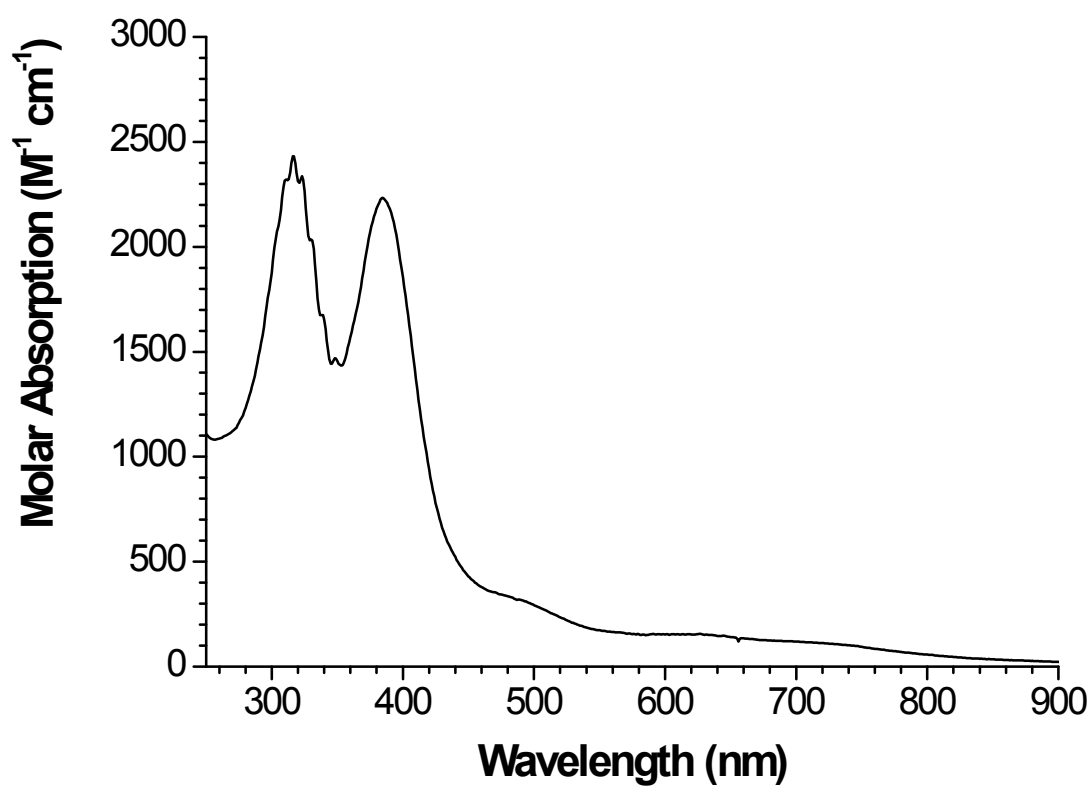


Figure S2. UV-vis spectrum of $\text{NPr}_4[\text{RuO}_4]$ in MeCN.

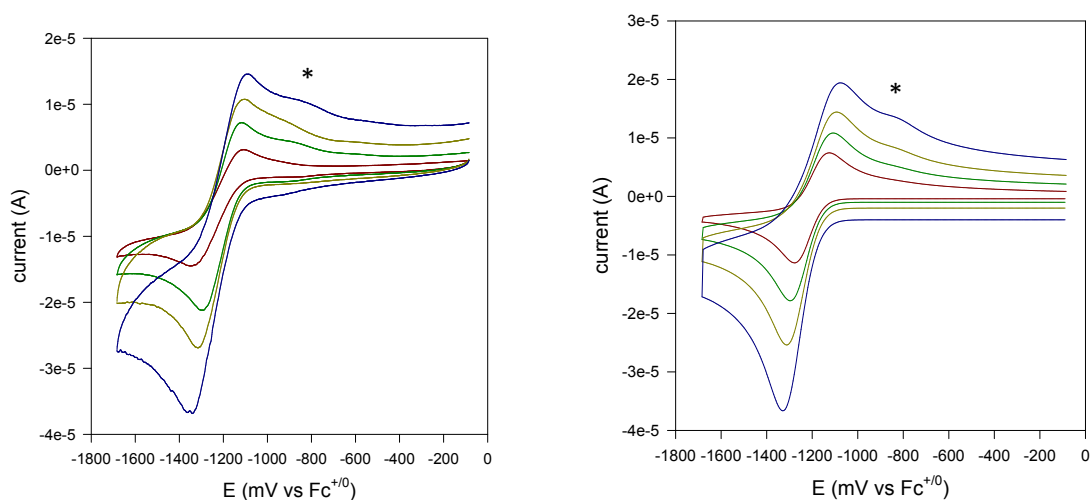
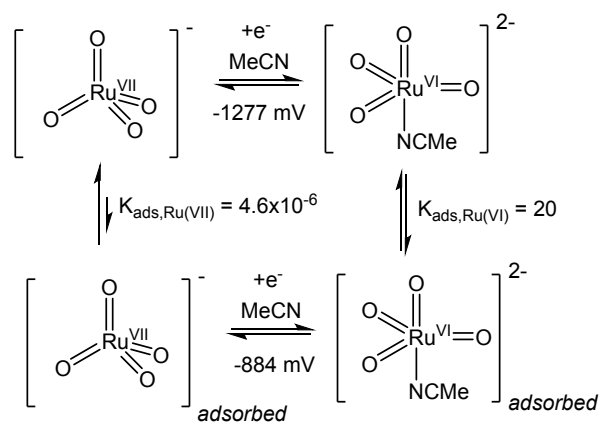


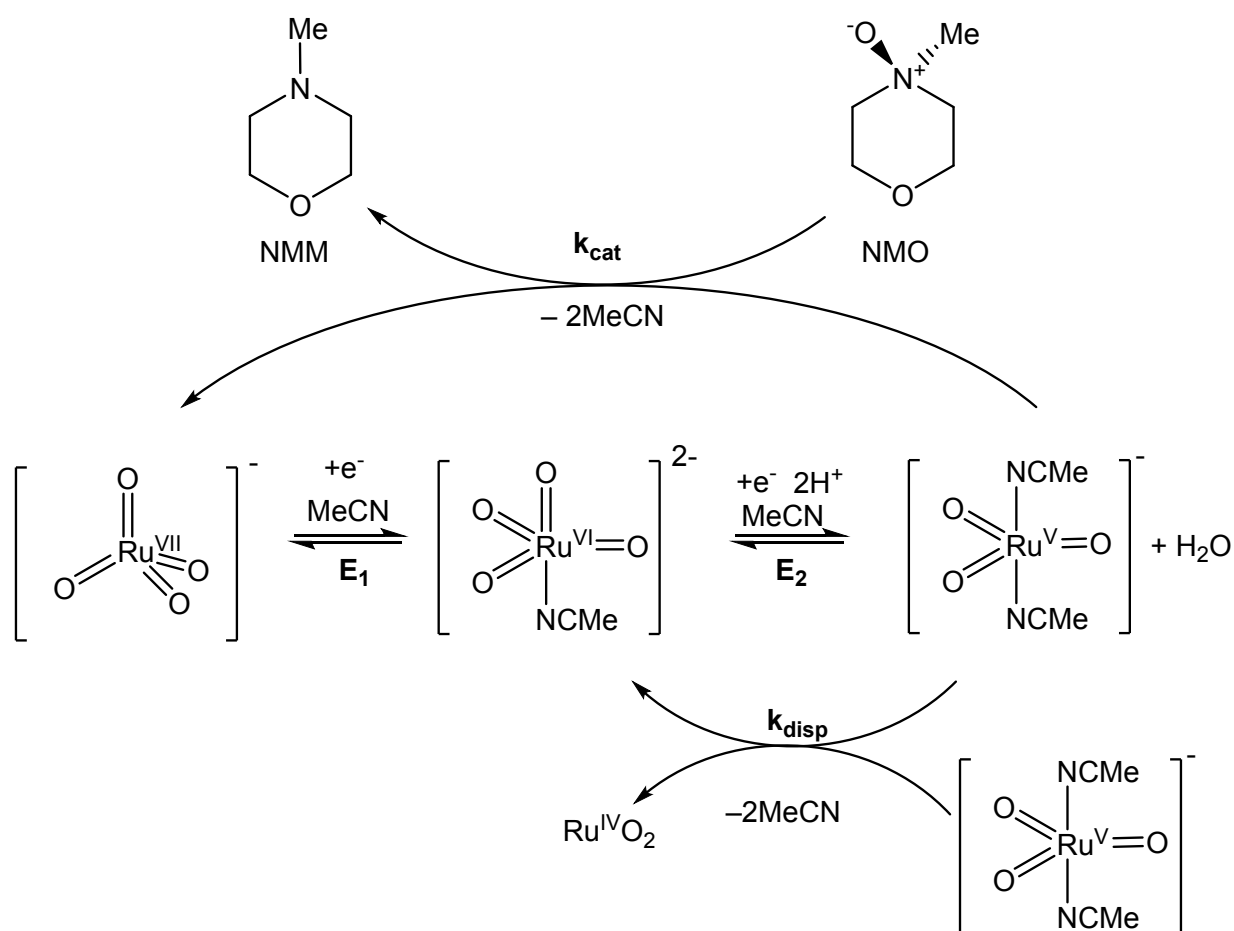
Figure S3. Experimental (left) and simulated (right) voltammetry of 1.0 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4) in the vicinity of the $\text{Ru}^{\text{VII/VI}}$ couple: 20 (red), 50 (green), 100 (yellow) and 200 mVs^{-1} (blue). The potential was initially swept in the negative direction. The response from the adsorbed Ru^{VI} species is indicated with an asterisk.



Scheme S1. The mechanism describing the $\text{Ru}^{\text{VII/VI}}$ couple in Figure S3 including both diffusing and surface-adsorbed redox components.

Table S1. Parameters obtained from voltammetric simulation; see Scheme S2 for definitions.

Electrochemical Steps		Chemical Reactions	
E_1 (mV vs $\text{Fc}^{+/0}$)	-1277	$K_{\text{cat}} (k_{\text{cat}}/k_{-\text{cat}})$	200
α_1	0.5	$k_{\text{cat}} (\text{M}^{-1}\text{s}^{-1})$	3×10^3
$k_{s,1}$ (cm s^{-1})	0.05	$K_{\text{disp}} (k_{\text{disp}}/k_{\text{comp}})$	100
E_2 (mV vs $\text{Fc}^{+/0}$)	-1677	$k_{\text{disp}} (\text{M}^{-1}\text{s}^{-1})$	3×10^6
α_2	0.5	$D_o (\text{cm}^2 \text{s}^{-1})$	4×10^{-5}
$k_{s,2}$ (cm s^{-1})	10^{-3}		



Scheme S2.

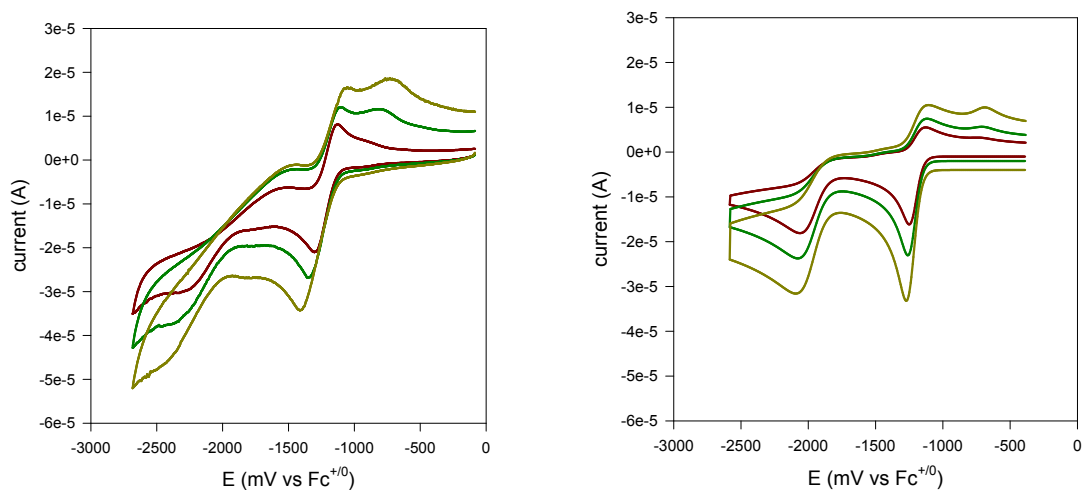


Figure S4. Experimental (left) and simulated (right) voltammetry of 0.8 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4). Sweep rate 50 (red); 100; (green) and 200 mV s^{-1} (yellow). The potential was initially swept in the negative direction. Note the sloping baseline at the negative end of the range of the experimental CVs was due to the onset of a reduction process at low potential (< -2600 mV) and this was not modelled.

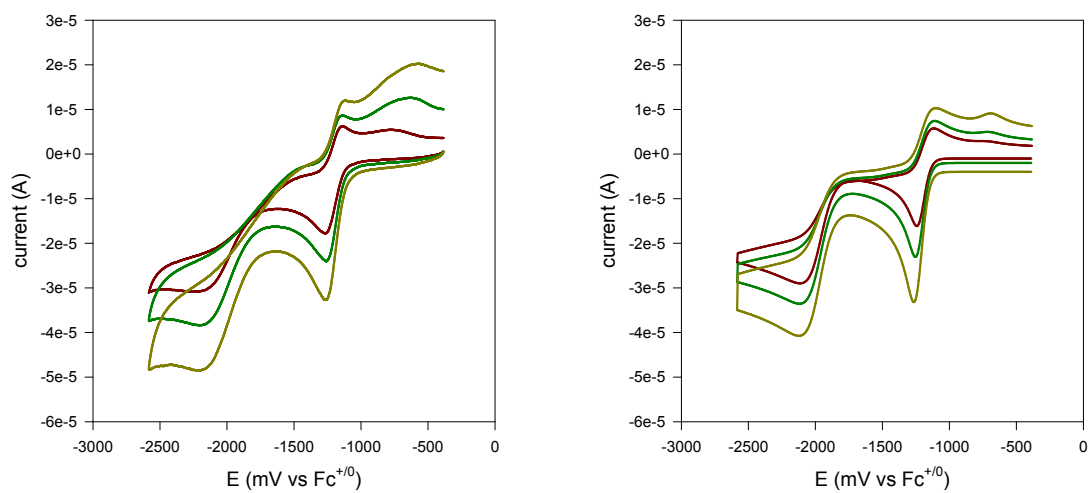


Figure S5. Experimental (left) and simulated (right) voltammetry of 0.8 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4) and 10 mM NMO. Sweep rate 50 (red); 100; (green) and 200 mV s^{-1} (yellow). The potential was initially swept in the negative direction.

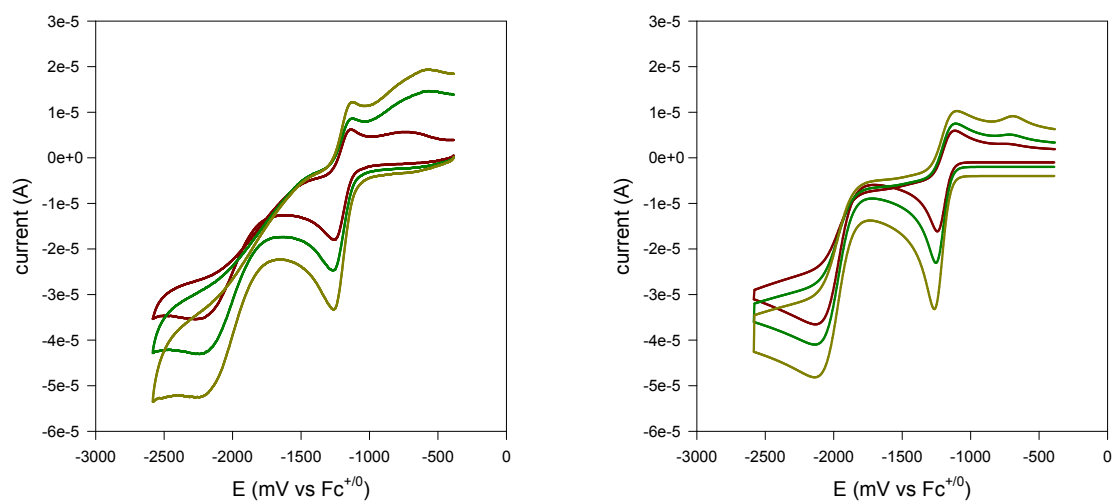


Figure S6. Experimental (left) and simulated (right) voltammetry of 0.8 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4) and 20 mM NMO. Sweep rate 50 (red); 100; (green) and 200 mV s^{-1} (yellow). The potential was initially swept in the negative direction.

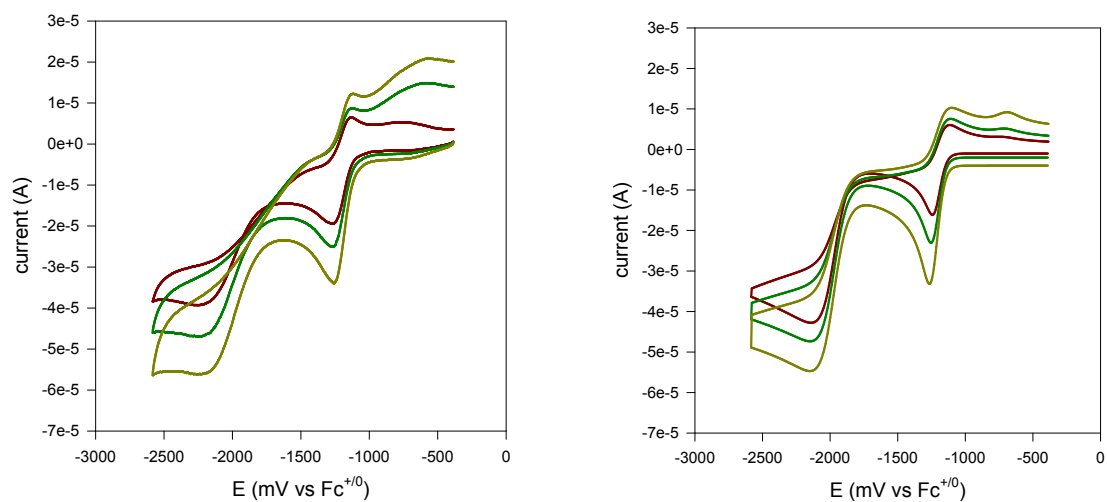


Figure S7. Experimental (left) and simulated (right) voltammetry of 0.8 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4) and 30 mM NMO. Sweep rate 50 (red); 100; (green) and 200 mV s^{-1} (yellow). The potential was initially swept in the negative direction.

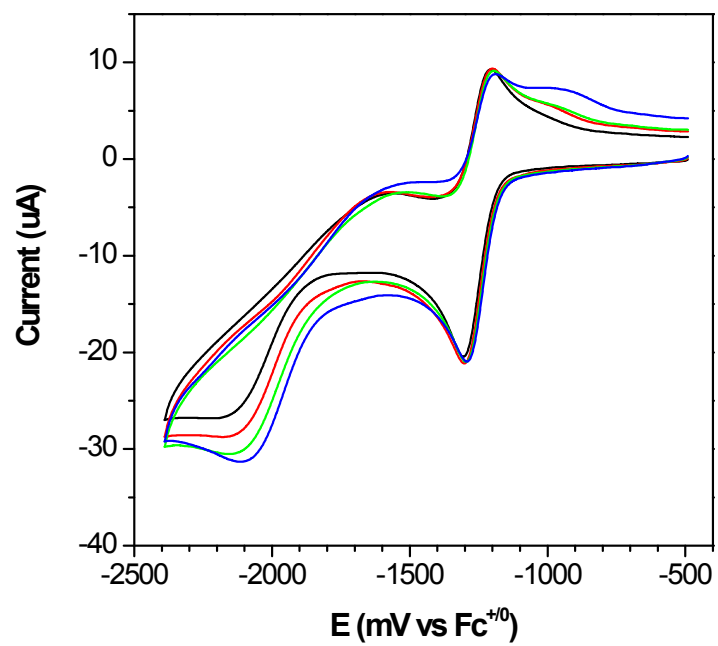


Figure S8. Cyclic voltammetry of 1 mM $\text{NPr}_4[\text{RuO}_4]$ in MeCN (0.1 M NBu_4BF_4) with 0 mM (black), 10 mM (red), 20 mM (green) and 30 mM (blue) pyridine *N*-oxide. Sweep rate 50 mVs^{-1} . No significant catalysis is apparent.