Electronic Supplementary Information

An Organometallic Catalase Mimic with Exceptional Activity, H_2O_2 Stability, and Catalase/Peroxidase Selectivity

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Synthetic Procedures

General synthetic considerations. Complex **Ru1** was prepared as previously described.[1-4] All other materials were of reagent quality and used as received. All solvents used were HPLC grade. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using a Bruker 500 MHz spectrometer. Chemical shifts δ (in ppm) for ^{1}H and ^{13}C NMR are referenced to $SiMe_4$ using the residual protio-solvent as an internal standard. For ^{1}H NMR: $CDCl_3$, 7.26 ppm; DMSO-d_6, 2.50 ppm. For ^{13}C NMR: $CDCl_3$, 77.16 ppm; DMSO-d_6, 39.52 ppm. Coupling constants (*J*) are expressed in hertz (Hz). Fourier transform high-resolution mass spectrometery with electrospray ionization (ESI-MS) were acquired on a Thermo q-Exactive Plus instrument via direct injection (100% CH_3CN) using an Thermo Ultimate 3000 HPLC at a flow rate of 0.2L/min. A resolving power of 140,000 was used for the data acquisition, and the instrument was calibrated immediately prior to use yielding better than 5 ppm mass accuracy. All reactions were performed under an inert atmosphere under an N_2 atmosphere using standard Schlenk or glovebox techniques with the exclusion of light. All subsequent manipulations were performed under ambient conditions using standard benchtop techniques without the exclusion of light. When required, solvents were dried and deoxygenated using an Innovative Technologies solvent purification system, and then stored over molecular sieves (3 Å) in a drybox.

Spectroscopic and Kinetic Analysis Procedures

General spectroscopic considerations. UV–visible absorption spectra were acquired on a Varian Cary 50 Bio spectrometer equipped with a water-cooled Quantum Northwest TC-125 peltier temperature controller. All solution measurements were performed at 25.0 ± 0.1 °C in matched gas-tight quartz cuvettes (Precision Scientific) with 1 cm path lengths and 3.0 mL analyte solution volumes. Absorption spectra were acquired from 950 to 200 nm with a scanning speed of 300 nm min^{-1} and a resolution of 0.5 nm. Each kinetic analysis experiment (5 second intervals) was performed in quadruplicate on four different days. Stock solutions were prepared fresh daily and filtered (0.2 μm PTFE) immediately prior to use.

General procedure for kinetic analysis of H_2O_2 disproportionation by Ru1 in PBS. To a cuvette was added 2940 μL of PBS (pH 7.4), and this solution was allowed to equilibrate at 25 °C for 10 min. Next, a 30 μL aliquot of **Ru1** (from a 1.0 mM stock solution in CH_3CN) was added to the cuvette, the cuvette was covered and mixed via repeated inversion for 3 s, then placed back in the spectrometer, and an absorbance spectrum was acquired. The data acquisition mode was then switched to single-wavelength kinetics, the absorbance was set to zero, single-wavelength absorbance data collection was started, and the solution was allowed to equilibrate at 25 °C for 5 min. Next, a 30 μL aliquot of H_2O_2 (from a 2.0 M stock solution in H_2O) was added, the cuvette was covered and mixed via repeated inversion for 3 s, then placed back in the spectrometer, and the kinetics program was allowed to continue. After the kinetics program had completed, another absorbance spectrum was acquired to confirm H_2O_2 consumption. Standard conditions (unless specified otherwise): [**Ru1**]$_0$ = 20 μM; [H_2O_2]$_0$ = 20 mM; PBS (pH 7.4), 25 °C. The [H_2O_2] was determined from absorbance at 240 nm (ε = 43.6 M^{-1} cm^{-1}), and [ABTS$^{•-}$] was determined from absorbance at 734 nm (ε = 1.5 × 10^4 M^{-1} cm^{-1}).[5]

Rate law experiments. The concentrations of **Ru1** and H_2O_2 employed in the rate law experiments (cf. Figures 3 and 4) were obtained using this general kinetic procedure by varying stock solution concentration and holding aliquot volume constant. The H^+ concentrations were obtained using PBS adjusted to different pH values before the addition of any aliquots. The temperatures were obtained by allowing the working solution to equilibrate at different temperatures before the addition of **Ru1**.

Headspace Gas Analysis. The headspace of the reaction vessel was analyzed using He flow (~0.7 mL sec^{-1}) that went from the reaction vessel and fed an autosampling valve on the Thermo Trace GC with thermal conductivity detector. The autosampling valve made headspace injections onto the column (Restek packed column, ShinCarbon ST 80/100) every four and then two minutes, in a repeating cycle over 75 minutes total. The carrier flow was 22 mL min^{-1} and the oven was set at 25 °C.

Derivation of General Rate Law for Proposed Mechanism

Proposed mechanism. Adapted from Scheme 2. The intermediates [L$_n$Ru–OH], [L$_n$Ru–OH$_2$]$^{1+}$, [L$_n$Ru–(H$_2$O$_2$)]$^{1+}$, [L$_n$Ru–OOH], [L$_n$Ru–H], and [L$_n$Ru–O–O–RuL$_n$] have been abbreviated as [**RuA**], [**RuB**], [**RuC**], [**RuD**], [**RuH**], and [**RuE**], respectively, for clarity.

Equation S1: Our previous studies into **Ru1**-catalyzed ABTS$^{\bullet-}$ reduction revealed that formation of the Ru–H intermediate was the turnover-limiting step. For our current studies into **Ru1**-catalyzed H$_2$O$_2$ disproportionation, we hypothesized that Ru–H formation would likewise be the turnover-limiting step in our proposed mechanism (step 3). Thus, completion of the catalytic cycle would be limited by how quickly the Ru–H intermediate formed *and then* reacted with H$_2$O$_2$:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k_4[\text{H}_2\text{O}_2][\textbf{RuH}]$$

Equation S2: The sum of the concentrations of the Ru-containing species leading up to the turnover-limiting step is equal to $[\textbf{Ru1}]_0$, which is the total concentration of **Ru1** added at the beginning of the reaction:

$$[\textbf{Ru1}]_0 = [\textbf{RuA}] + [\textbf{RuB}] + [\textbf{RuC}] + [\textbf{RuD}] + [\textbf{RuH}] + [\textbf{RuE}]$$

Equation S3: Using the assumption that steps 1, 2, 5, and 6 achieve equilibrium rapidly (compared to turnover):

$$K_1 = \frac{[\textbf{RuC}]}{[H_2O_2][\textbf{RuB}]}$$

$$K_2 = \frac{[H^+][\textbf{RuD}]}{[\textbf{RuC}]}$$

$$K_5 = \frac{[\textbf{RuB}]}{[H^+][\textbf{RuA}]}$$

$$K_6 = \frac{[H^+][\textbf{RuE}]}{[\textbf{RuB}][\textbf{RuD}]}$$

Equation S4: Rearranging allows us to express the concentration of each Ru-containing species relative to an equilibrium counterpart:

$$[\textbf{RuA}] = \left(\frac{1}{K_5[H^+]}\right)[\textbf{RuB}]$$

$$[\textbf{RuB}] = \left(\frac{1}{K_1[H_2O_2]}\right)[\textbf{RuC}]$$

$$[\textbf{RuC}] = \left(\frac{[H^+]}{K_2}\right)[\textbf{RuD}]$$

$$[\textbf{RuE}] = \left(\frac{K_6}{[H^+]}\right)[\textbf{RuB}][\textbf{RuD}]$$

Equation S5: Using the assumptions that (*i*) steady-state for steps 3-4 is rapidly achieved, (*ii*) $k_4 \gg k_3$, (*iii*) $k_4 \gg k_{-3}$, and (*iv*) $k_{-4} \approx 0$ given that $[\textbf{RuB}] \gg [\textbf{RuA}]$:

$$-\frac{d[\textbf{RuH}]}{dt} = k_3[\textbf{RuD}] - k_4[H_2O_2][\textbf{RuH}] = 0$$

$$[\textbf{RuD}] = \left(\frac{k_4[H_2O_2]}{k_3}\right)[\textbf{RuH}]$$

Equation S6: We can substitute the various Ru-containing terms in **Equation S2** with the relationships derived in **Equations S5-S6**, which will ultimately result in an equation describing $[\textbf{Ru1}]_0$ as a function of *only* $[\textbf{RuH}]$:

$$[\textbf{Ru1}]_0 = \left(\frac{1}{K_5[H^+]} + 1\right)[\textbf{RuB}] + [\textbf{RuC}] + [\textbf{RuD}] + [\textbf{RuH}] + [\textbf{RuE}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{1}{K_1K_5[H^+][H_2O_2]} + \frac{1}{K_1[H_2O_2]} + 1\right)[\textbf{RuC}] + [\textbf{RuD}] + [\textbf{RuH}] + [\textbf{RuE}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{\cancel{[H^+]}}{K_1K_2K_5\cancel{[H^+]}[H_2O_2]} + \frac{[H^+]}{K_1K_2[H_2O_2]} + \frac{[H^+]}{K_2} + 1\right)[\textbf{RuD}] + [\textbf{RuH}] + [\textbf{RuE}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{k_4\cancel{[H_2O_2]}}{k_3K_1K_2K_5\cancel{[H_2O_2]}} + \frac{k_4[H^+]\cancel{[H_2O_2]}}{k_3K_1K_2\cancel{[H_2O_2]}} + \frac{k_4[H^+][H_2O_2]}{k_3K_2} + \frac{k_4[H_2O_2]}{k_3} + 1\right)[\textbf{RuH}] + [\textbf{RuE}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{k_4}{k_3K_1K_2K_5} + \frac{k_4[H^+]}{k_3K_1K_2} + \frac{k_4[H^+][H_2O_2]}{k_3K_2} + \frac{k_4[H_2O_2]}{k_3} + 1\right)[\textbf{RuH}] + \left(\frac{K_6}{[H^+]}\right)[\textbf{RuB}][\textbf{RuD}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{k_4}{k_3K_1K_2K_5} + \frac{k_4[H^+]}{k_3K_1K_2} + \frac{k_4[H^+][H_2O_2]}{k_3K_2} + \frac{k_4[H_2O_2]}{k_3} + 1\right)[\textbf{RuH}] + \left(\frac{K_6}{K_1[H^+][H_2O_2]}\right)[\textbf{RuC}][\textbf{RuD}]$$

$$[\textbf{Ru1}]_0 = \left(\frac{k_4}{k_3K_1K_2K_5} + \frac{k_4[H^+]}{k_3K_1K_2} + \frac{k_4[H^+][H_2O_2]}{k_3K_2} + \frac{k_4[H_2O_2]}{k_3} + 1\right)[\textbf{RuH}] + \left(\frac{K_6\cancel{[H^+]}}{K_1K_2\cancel{[H^+]}[H_2O_2]}\right)[\textbf{RuD}]^2$$

$$[\mathbf{Ru1}]_0 = \left(\frac{k_4}{k_3 K_1 K_2 K_5} + \frac{k_4 [\mathrm{H}^+]}{k_3 K_1 K_2} + \frac{k_4 [\mathrm{H}^+][\mathrm{H}_2\mathrm{O}_2]}{k_3 K_2} + \frac{k_4 [\mathrm{H}_2\mathrm{O}_2]}{k_3} + 1 \right) [\mathbf{RuH}] + \left(\frac{k_4^2 K_6 [\mathrm{H}_2\mathrm{O}_2]^{\mathbf{\color{red}2}}}{k_3^2 K_1 K_2 {\color{red}[\mathrm{H}_2\mathrm{O}_2]}} \right) [\mathbf{RuH}]^2$$

$$[\mathbf{Ru1}]_0 = \left(\frac{k_4^2 K_6 [\mathrm{H}_2\mathrm{O}_2]}{k_3^2 K_1 K_2} \right) [\mathbf{RuH}]^2 + \left(\frac{k_4}{k_3 K_1 K_2 K_5} + \frac{k_4 [\mathrm{H}^+]}{k_3 K_1 K_2} + \frac{k_4 [\mathrm{H}^+][\mathrm{H}_2\mathrm{O}_2]}{k_3 K_2} + \frac{k_4 [\mathrm{H}_2\mathrm{O}_2]}{k_3} + 1 \right) [\mathbf{RuH}]$$

Equation S7:   To simplify the visual presentation of this equation, we can replace the coefficient for the $[\mathbf{RuH}]^2$ term with $F_1\{H_2O_2\}$, to note that this coefficient is a function of $[\mathrm{H}_2\mathrm{O}_2]$, and is not just a collection of invariant constants:

$$[\mathbf{Ru1}]_0 = F_1\{H_2O_2\} \bullet [\mathbf{RuH}]^2 + \left(\frac{k_4}{k_3 K_1 K_2 K_5} + \frac{k_4 [\mathrm{H}^+]}{k_3 K_1 K_2} + \frac{k_4 [\mathrm{H}^+][\mathrm{H}_2\mathrm{O}_2]}{k_3 K_2} + \frac{k_4 [\mathrm{H}_2\mathrm{O}_2]}{k_3} + 1 \right) [\mathbf{RuH}]$$

Equation S8:   With the coefficient for the $[\mathbf{RuH}]$ term, we can find the lowest common denominator and combine the numerators:

$$[\mathbf{Ru1}]_0 = F_1\{H_2O_2\} \bullet [\mathbf{RuH}]^2 + \left(\frac{k_4}{k_3 K_1 K_2 K_5} + \frac{k_4 K_5 [\mathrm{H}^+]}{k_3 K_1 K_2 K_5} + \frac{k_4 K_1 K_5 [\mathrm{H}^+][\mathrm{H}_2\mathrm{O}_2]}{k_3 K_1 K_2 K_5} + \frac{k_4 K_1 K_2 K_5 [\mathrm{H}_2\mathrm{O}_2]}{k_3 K_1 K_2 K_5} + \frac{k_3 K_1 K_2 K_5}{k_3 K_1 K_2 K_5} \right) [\mathbf{RuH}]$$

$$[\mathbf{Ru1}]_0 = F_1\{H_2O_2\} \bullet [\mathbf{RuH}]^2 + \left(\frac{k_4 + k_4 K_5 [\mathrm{H}^+] + k_4 K_1 K_5 [\mathrm{H}^+][\mathrm{H}_2\mathrm{O}_2] + k_4 K_1 K_2 K_5 [\mathrm{H}_2\mathrm{O}_2] + k_3 K_1 K_2 K_5}{k_3 K_1 K_2 K_5} \right) [\mathbf{RuH}]$$

Equation S9:   To simplify the visual presentation of this equation, we can replace the coefficient for the $[\mathbf{RuH}]$ term with $F_2\{H^+, H_2O_2\}$ to note that this coefficient is a function of both $[\mathrm{H}^+]$ and $[\mathrm{H}_2\mathrm{O}_2]$, and is not just a collection of invariant constants:

$$[\mathbf{Ru1}]_0 = F_1\{H_2O_2\} \bullet [\mathbf{RuH}]^2 + F_2\{H^+, H_2O_2\} \bullet [\mathbf{RuH}]$$

Equation S10: We need to use the quadratic formula to solve for [**RuH**], thus we need to subtract [**Ru1**]$_0$ from both sides:

$$0 = F_1\{H_2O_2\} \bullet [\textbf{RuH}]^2 + F_2\{H^+, H_2O_2\} \bullet [\textbf{RuH}] + (-[\textbf{Ru1}]_0)$$

Equation S11: W we can abbreviate $F_1\{H_2O_2\}$ and $F_2\{H^+, H_2O_2\}$ with F_1 and F_2, respectively, to make the quadratic formula less cluttered:

$$0 = F_1 \bullet [\textbf{RuH}]^2 + F_2 \bullet [\textbf{RuH}] + (-[\textbf{Ru1}]_0)$$

Equation S12: Using the quadratic formula to solve **Equation S11** for [**RuH**], we obtain:

$$[\textbf{RuH}] = \frac{-F_2 \pm \sqrt{F_2^2 + 4F_1 \bullet [\textbf{Ru1}]_0}}{2 \bullet F_1}$$

Equation S13: F_1 and F_2 contain rate and equilibrium constants, which cannot be negative. In addition, the only operators in F_1 and F_2 are addition and multiplication, thus there are the hard constraints that $F_1 > 0$ and $F_2 > 0$. Thus, $-F_2$ can only be negative and the square root term can only be positive. As a result, subtracting the positive square root term from $-F_2$ would always afford a negative number for [**RuH**], and concentrations cannot be negative. We can therefore replace $\pm$ with simply $+$:

$$[\textbf{RuH}] = \frac{-F_2 + \sqrt{F_2^2 + 4F_1 \bullet [\textbf{Ru1}]_0}}{2 \bullet F_1}$$

Equation S14: Now that we have a unique expression for [**RuH**], we can solve **Equation S1** by plugging **Equation S13** into it:

$$-\frac{d[H_2O_2]}{dt} = k_4 \bullet [H_2O_2] \bullet \left(\frac{-F_2 + \sqrt{F_2^2 + 4F_1 \bullet [\textbf{Ru1}]_0}}{2 \bullet F_1} \right)$$

Equation S15: Recalling that F_1 is a function of $[H_2O_2]$, we can rearrange this equation to collect similar terms:

$$-\frac{d[H_2O_2]}{dt} = k_4 \bullet \left(\frac{[H_2O_2]}{2 \bullet F_1}\right) \bullet \left(-F_2 + \sqrt{F_2^2 + 4F_1 \bullet [\textbf{Ru1}]_0}\right)$$

Equation S16: Expanding F_1 into its full expression results in both $[H_2O_2]$ terms canceling out, leaving behind only rate and equilibrium constants, which we will abbreviate as G_1:

$$\left(\frac{[H_2O_2]}{2 \bullet F_1}\right) = k_4 \bullet \cancel{[H_2O_2]} \bullet \left(\frac{k_3^2 K_1 K_2}{2k_4^2 K_6 \cancel{[H_2O_2]}}\right) = \left(\frac{k_3^2 K_1 K_2}{2k_4 K_6}\right) = G_1$$

Equation S17: The rate of **Ru1**-catalyzed H_2O_2 disproportionation can thus be described using the equation below, where G_1 is a constant, F_1 is a function of $[H_2O_2]$, and F_2 is a function of both $[H^+]$ and $[H_2O_2]$:

$$-\frac{d[H_2O_2]}{dt} = G_1 \bullet \left(-F_2 + \sqrt{F_2^2 + 4F_1 \bullet [\textbf{Ru1}]_0}\right)$$

Equation S18: If our reaction rate data are acquired very early in the reaction (i.e., the initial reaction rate, v_0), assuming that steady-state has still been achieved, then the concentrations of H^+ and H_2O_2 will not have yet deviated significantly from their initial values. We can therefore replace the unknown, time-dependent concentration terms $[H^+]$ and $[H_2O_2]$ with the known, initial concentration values $[H^+]_0$ and $[H_2O_2]_0$, respectively:

$$F_1 = \frac{k_4^2 K_6 [H_2O_2]_0}{k_3^2 K_1 K_2}$$

$$F_2 = \frac{k_4 + k_4 K_5 [H^+]_0 + k_4 K_1 K_5 [H^+]_0 [H_2O_2]_0 + k_4 K_1 K_2 K_5 [H_2O_2]_0 + k_3 K_1 K_2 K_5}{k_3 K_1 K_2 K_5}$$

Equation S19:   To explore the relationship between v_0 and $[\mathbf{Ru1}]_0$, v_0 is measured as $[\mathbf{Ru1}]_0$ is varied but $[H^+]_0$ and $[H_2O_2]_0$ are held constant. Within these constraints, F_1 and F_2 simplify to:

$$F_1 = a_1$$

$$F_2 = b_1$$

Equation S20:   Plugging **Equation S19** into **Equation S17** will give the relationship between v_0 and $[\mathbf{Ru1}]_0$ that is predicted by the proposed mechanism:

$$v_0 = G_1 \bullet \left(-b_1 + \sqrt{b_1^2 + 4a_1 \bullet [\mathbf{Ru1}]_0} \right)$$

Equation S21:   If the proposed mechanism is correct, then a plot of measured v_0 vs. $[\mathbf{Ru1}]_0$ (y and x, respectively) will be accurately fit by:

$$y = G_1 \bullet \left(-b_1 + \sqrt{b_1^2 + 4a_1 \bullet x} \right)$$

Equation S22:   Because G_1 is just a constant, we can replace it with (c). For a simpler equation, we can drop the subscripts for a and b, with the understanding that a, b, and c here are not the same as in **Equation S26** or **Equation S30**.

$$y = (c) \bullet \left[-b + (b^2 + 4ax)^{1/2} \right]$$

Equation S23:   To explore the relationship between v_0 and $[H_2O_2]_0$, v_0 is measured as $[H_2O_2]_0$ is varied but $[H^+]_0$ and $[\mathbf{Ru1}]_0$ are held constant. Within these constraints, F_1 and F_2 simplify to:

$$F_1 = a_2 \bullet [H_2O_2]_0$$

$$F_2 = b_2 \bullet [H_2O_2]_0 + c_2$$

Equation S24: Plugging **Equation S23** into **Equation S17** will give the relationship between v_0 and $[H_2O_2]_0$ that is predicted by the proposed mechanism:

$$v_0 = G_1 \bullet \left\{ -b_2[H_2O_2]_0 - c_2 + \sqrt{(b_2 \bullet [H_2O_2]_0 + c_2)^2 + 4a_2 \bullet [\textbf{Ru1}]_0 \bullet [H_2O_2]_0} \right\}$$

Equation S25: If the proposed mechanism is correct, then a plot of measured v_0 vs. $[H_2O_2]_0$ (y and x, respectively) will be accurately fit by:

$$y = G_1 \bullet \left\{ -b_2 x - c_2 + \sqrt{(b_2 x + c_2)^2 + 4a_2[\textbf{Ru1}]_0 \bullet x} \right\}$$

Equation S26: Because G_1 is just a constant, we can replace it with (d). For a simpler equation, we can drop the subscripts for a, b, and c, with the understanding that a, b, and c here are not the same as in **Equation S22** or **Equation S30**. In this equation, $[\textbf{Ru1}]_0$ is an invariant constant (2.0×10^{-5} M).

$$y = (d) \bullet \left[-bx - c + \{(bx + c)^2 + 4a[\textbf{Ru1}]_0 \bullet x\}^{1/2} \right]$$

Equation S27: To explore the relationship between v_0 and $[H^+]_0$, v_0 is measured as $[H^+]_0$ is varied but $[H_2O_2]_0$ and $[\textbf{Ru1}]_0$ are held constant. Within these constraints, F_1 and F_2 simplify to:

$$F_1 = a_3$$

$$F_2 = b_3 \bullet [H^+]_0 + c_3$$

Equation S28: Plugging **Equation S27** into **Equation S17** will give the relationship between v_0 and $[H^+]_0$ that is predicted by the proposed mechanism:

$$v_0 = G_1 \cdot \left\{ -b_3[H^+]_0 - c_3 + \sqrt{(b_3 \cdot [H^+]_0 + c_3)^2 + 4a_3 \cdot [\text{Ru1}]_0} \right\}$$

Equation S29: If the proposed mechanism is correct, then a plot of measured v_0 vs. $[H^+]_0$ (y and x, respectively) will be accurately fit by:

$$y = G_1 \cdot \left\{ -b_3 x - c_3 + \sqrt{(b_3 x + c_3)^2 + 4a_3[\text{Ru1}]_0} \right\}$$

Equation S30: Because G_1 is just a constant, we can replace it with (d). For a simpler equation, we can drop the subscripts for a, b, and c, with the understanding that a, b, and c here are not the same as in **Equation S22** or **Equation S26**. In this equation, $[\text{Ru1}]_0$ is an invariant constant (2.0×10^{-5} M).

$$y = (d) \cdot \left[-bx - c + \{(bx + c)^2 + 4a[\text{Ru1}]_0\}^{1/2} \right]$$

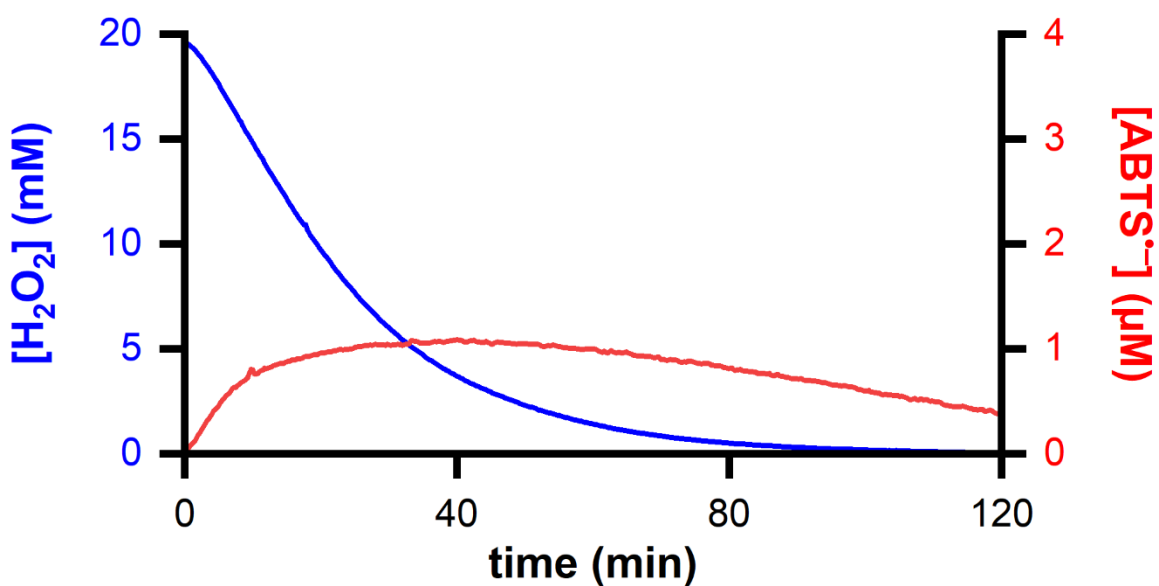**Figure S1.** Plot of absorbance vs. time for H_2O_2 disproportionation (blue trace) and $ABTS^{2-}$ oxidation (red trace) by **Ru1**. Conditions: $[H_2O_2]_0$ = 20 mM (blue trace) or 5 μM (red trace), $[ABTS^{2-}]_0$ = 0 μM (blue trace) or 200 μM (red trace), $[\mathbf{Ru1}]_0$ = 10 μM, PBS (pH 7.4), 25 °C.; $[H_2O_2]$ determined from absorbance at 240 nm (ε = 43.6 M^{-1} cm^{-1}), and $[ABTS^{\bullet-}]$ determined from absorbance at 734 nm (ε = 1.5 × 10^4 M^{-1} cm^{-1}).
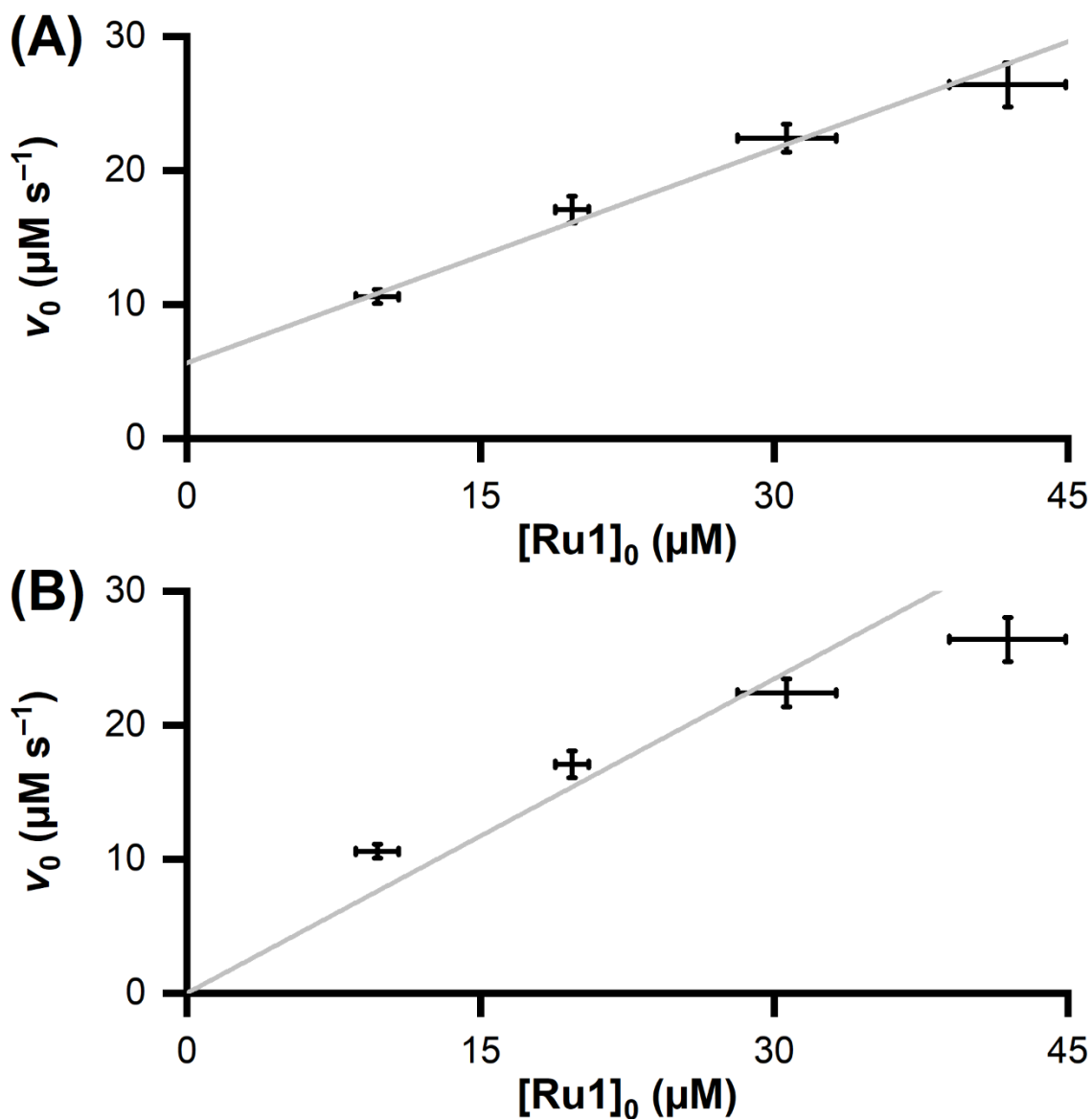
Figure S2. Plot of initial rate (v_0) of **Ru1**-catalyzed H_2O_2 disproportionation vs. $[\text{Ru1}]_0$ which shows that (**A**) the unforced linear fit predicts an uncatalyzed reaction rate of 5 $\mu M\ s^{-1}$ and (**B**) forcing the linear fit to have a y-intercept $= 0$ does not adequately model the experimental data. Conditions: $[\text{Ru1}]_0 = 10, 20, 30, \text{or } 40\ \mu M$; $[H_2O_2]_0 = 20\ mM$; PBS (pH 7.4), 25 °C.

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