Supporting Information for

Factors Influencing Conversion Kinetics of Triply-Bridged (μ-η^1:η^1-Peroxo)Diiron(III) Intermediates to Doubly-Bridged (μ-η^1:η^1-Peroxo)Diiron(III) Intermediates

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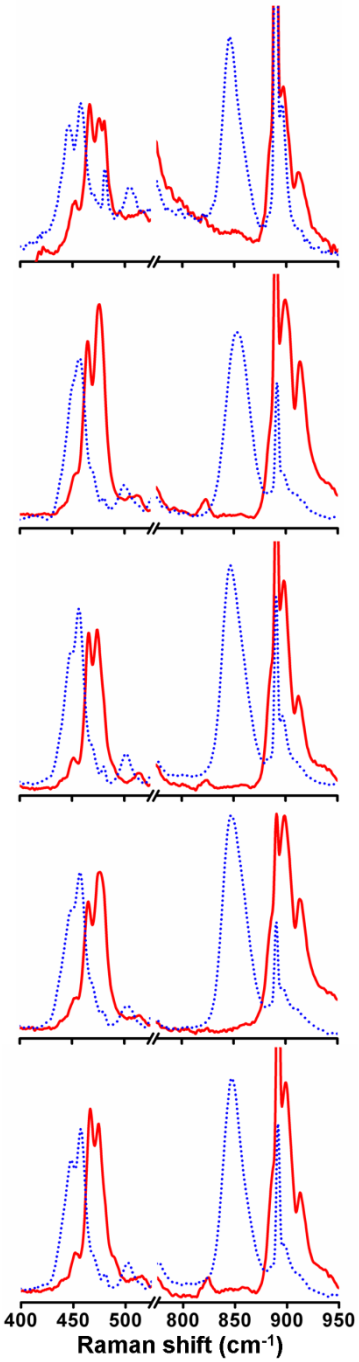

Figure S1. From top to bottom, resonance Raman spectra of **3**•O_2CCMe_3, **3**•$O_2CC_6H_2$-3,4,5-$(OMe)_3$, **3**•$O_2CC_6H_3$-3,4-$(OMe)_2$, **3**•$O_2CC_6H_3$-3,5-$(OMe)_2$, and **3**•$O_2CC_6H_4$-4-OMe (solid red line = $^{16}O_2$, dotted blue line = $^{18}O_2$).

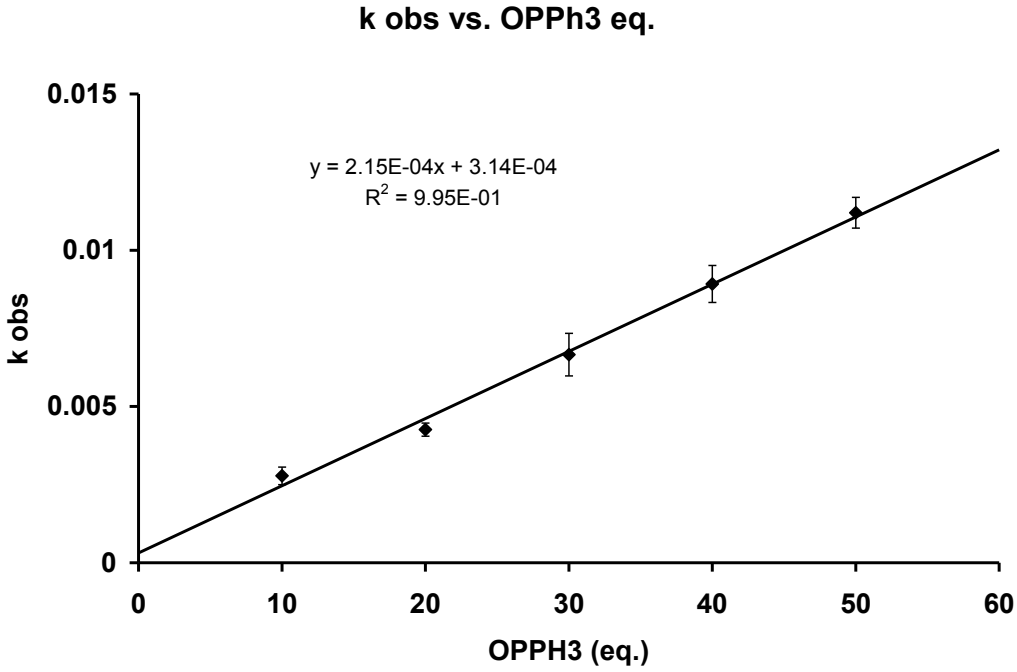

Figure S2. k_{obs} for the conversion of **2**•O_2PPh_2 to **3**•O_2PPh_2 in CH_2Cl_2 at -40 °C was determined by finding the y-intercept produced by finding k_{obs} for the conversion induced by addition of varying equivalents of $OPPh_3$.

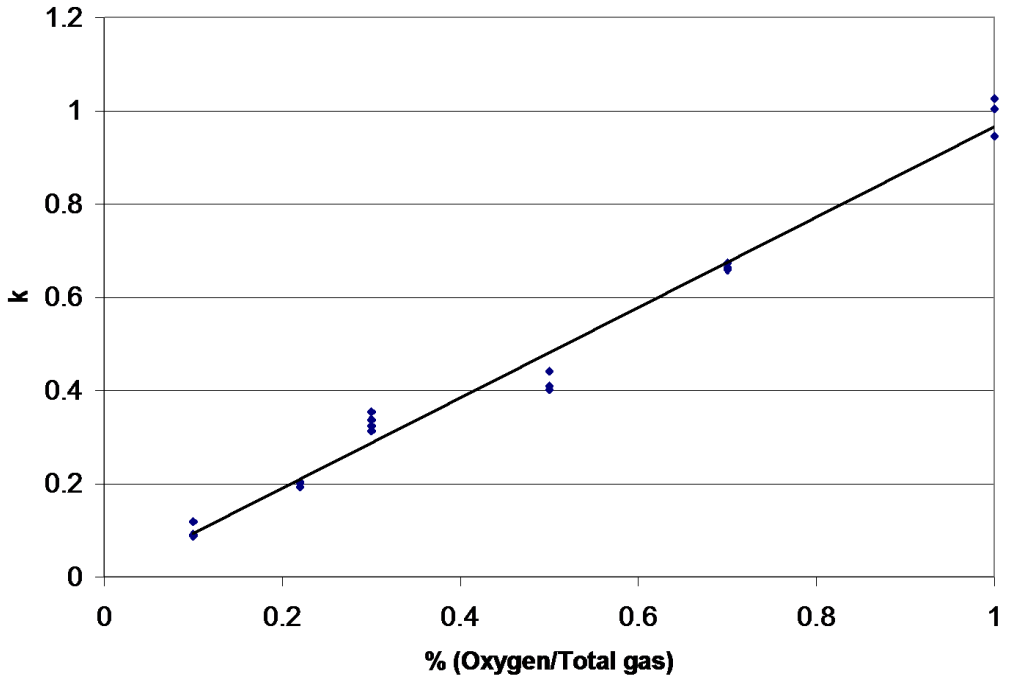

Figure S3. Rate constant for formation of **2**•O_2PPh_2 from 0.34 mM **1**•O_2PPh_2 in CH_2Cl_2 as a function of O_2. Absorbance measured at 690 nm at -50 °C. Solid lines represent fits of $R_i = a[O_2] + b$ to the data where a = 0.9692 and b = 0.0033.

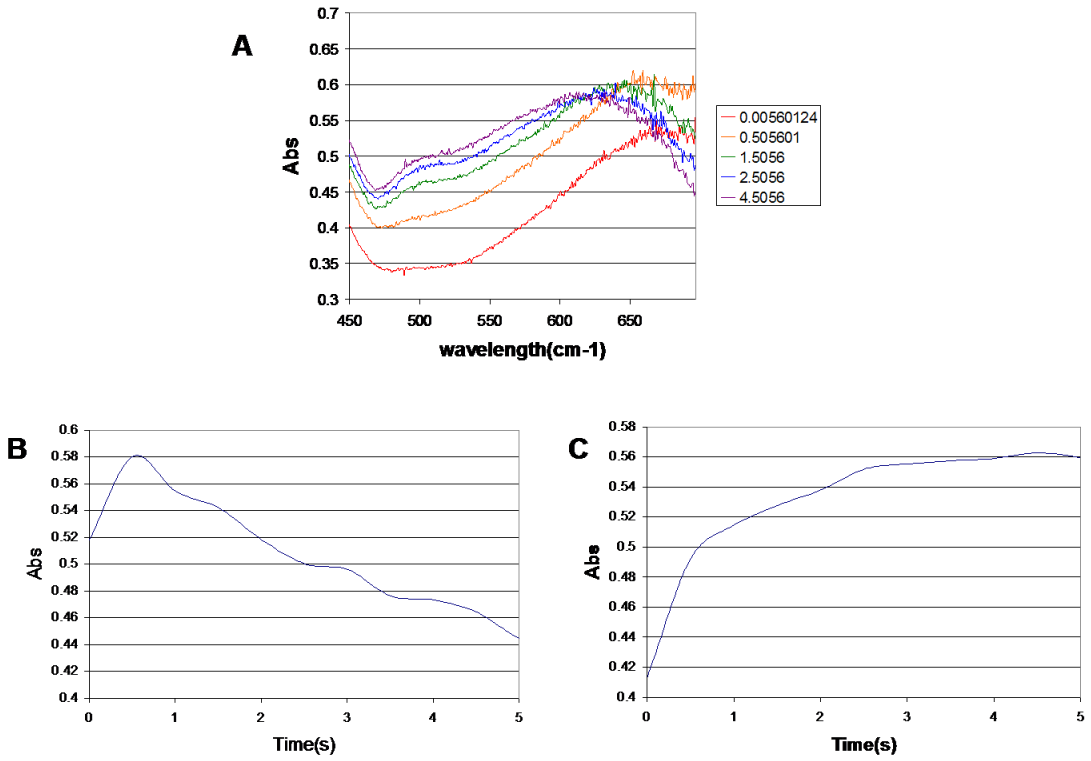

Figure S4. Time resolved spectra acquired by stopped-flow technique during the reaction of **1**•O_2PPh_2 (0.364 mM) with O_2 in MeCN at -10 °C (diode array mode, arc lamp). A) Multi-wavelength spectra between 0-5 s. B) Absorbance between 0-5s at 690 nm. C) Absorbance between 0-5 s at 580 nm. Similar absorbance changes were observed in single-wavelength experiments, but the time scale of the decomposition of **2**•O_2PPh_2 was longer, and the absorbance changes were smaller, indicating partial photodecomposition of **2**•O_2PPh_2 upon illumination with intense white light in diode-array measurements.

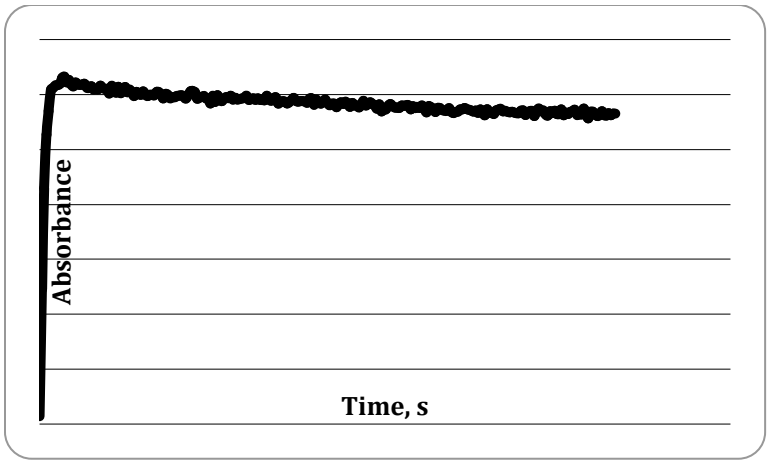

Figure S5. (A) Oxygenation of **1**•O_2CPh in CH_2Cl_2 at -70 ˚C (single-wavelength measurements at 580 nm; 100% O_2).

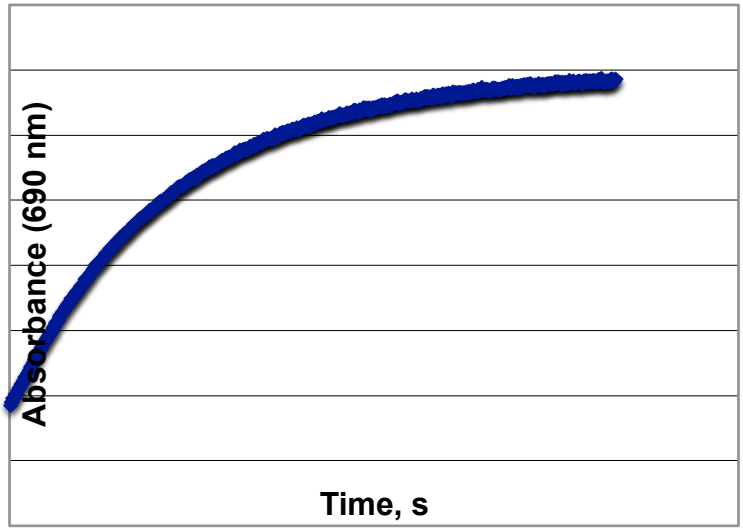

Figure S5 (B). Oxygenation of **1**•O_2CPh in CH_2Cl_2 at -70 ˚C (single-wavelength measurements at 580 nm; 100% O_2).