Supplementary information for

Mechanistic Investigation of cyclohexane oxidation by a binuclear non-heme iron model complex: Evidence of product inhibition by low-temperature stopped-flow studies

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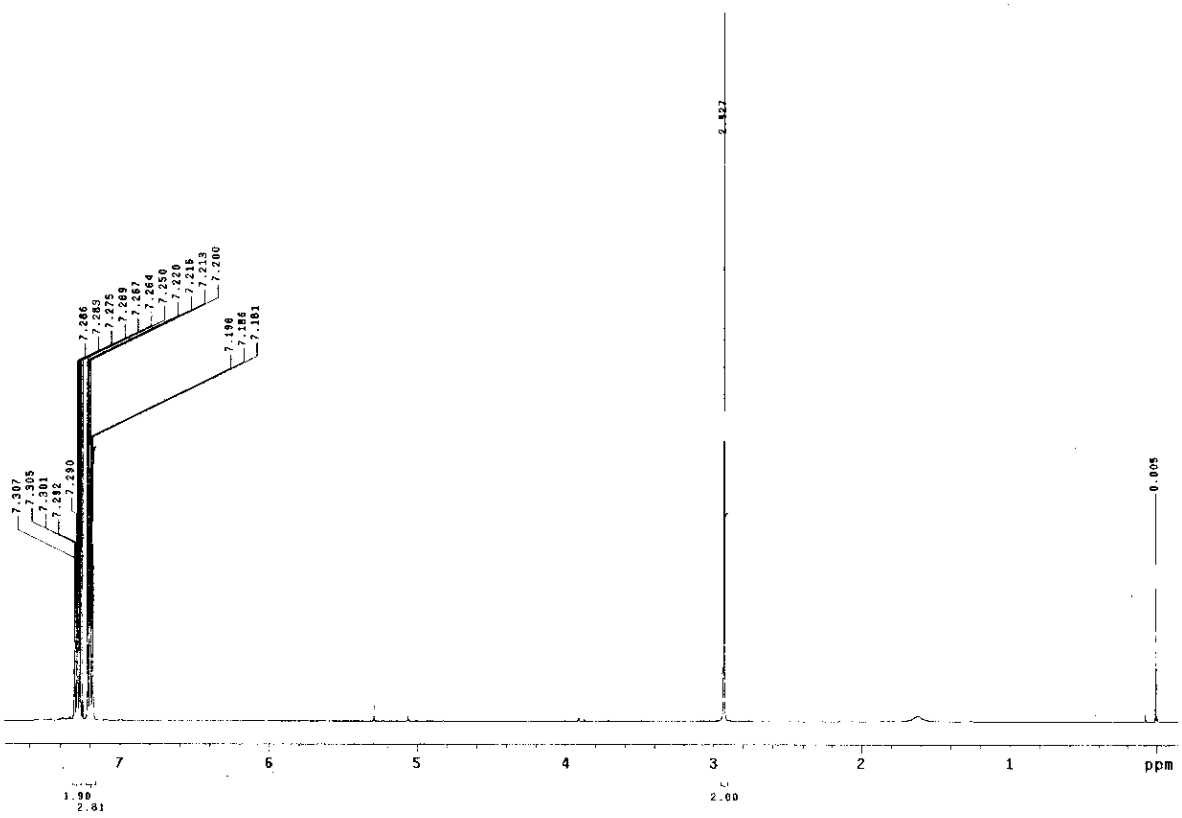

Figure S1: 400 MHz ^{1}H-NMR spectrum of MPP-OL-Cl_6 in $CDCl_3$.

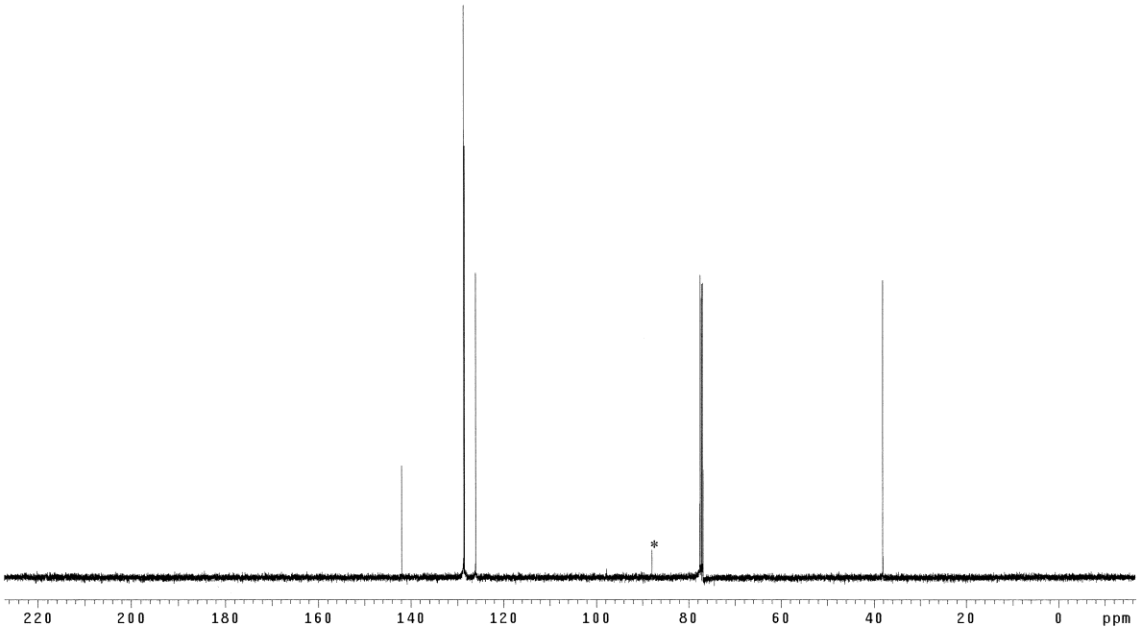

Figure S2: 400 MHz ^{13}C-NMR Spectrum of MPP-OL-Cl_6 in $CDCl_3$. Starred peak indicates signal from residual hexachloroacetone starting material.

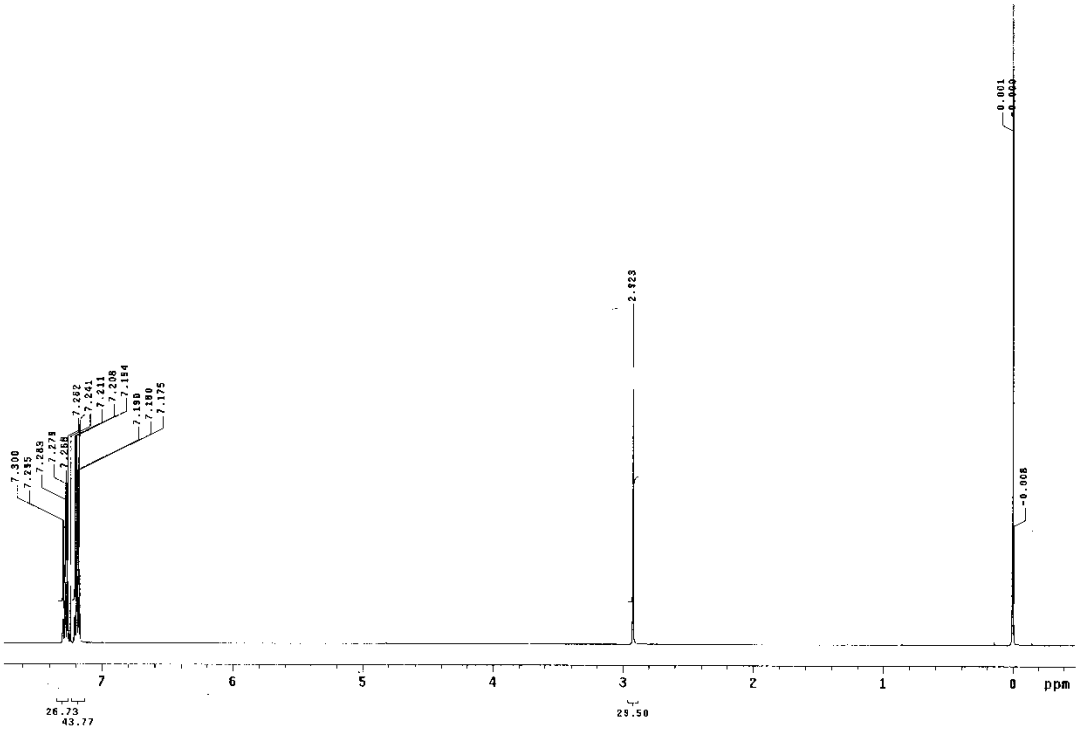

Figure S3: 400 MHz ^{1}H-NMR Spectrum of MPPH-Cl_6 in $CDCl_3$.

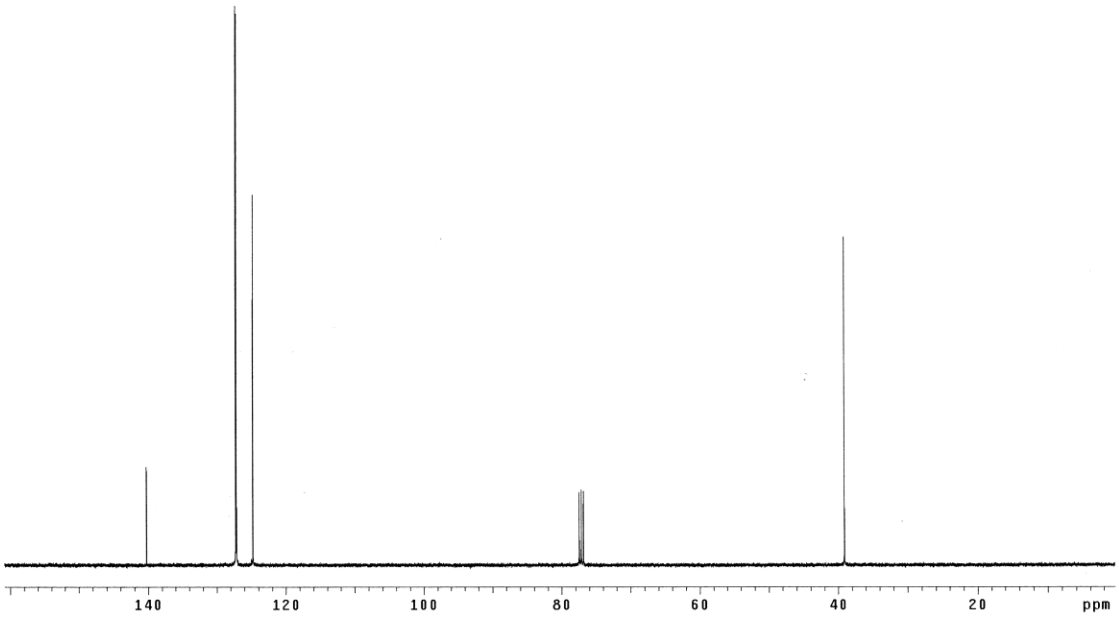

Figure S4: 400 MHz ^{13}C-NMR Spectrum of MPPH-Cl_6 in $CDCl_3$.

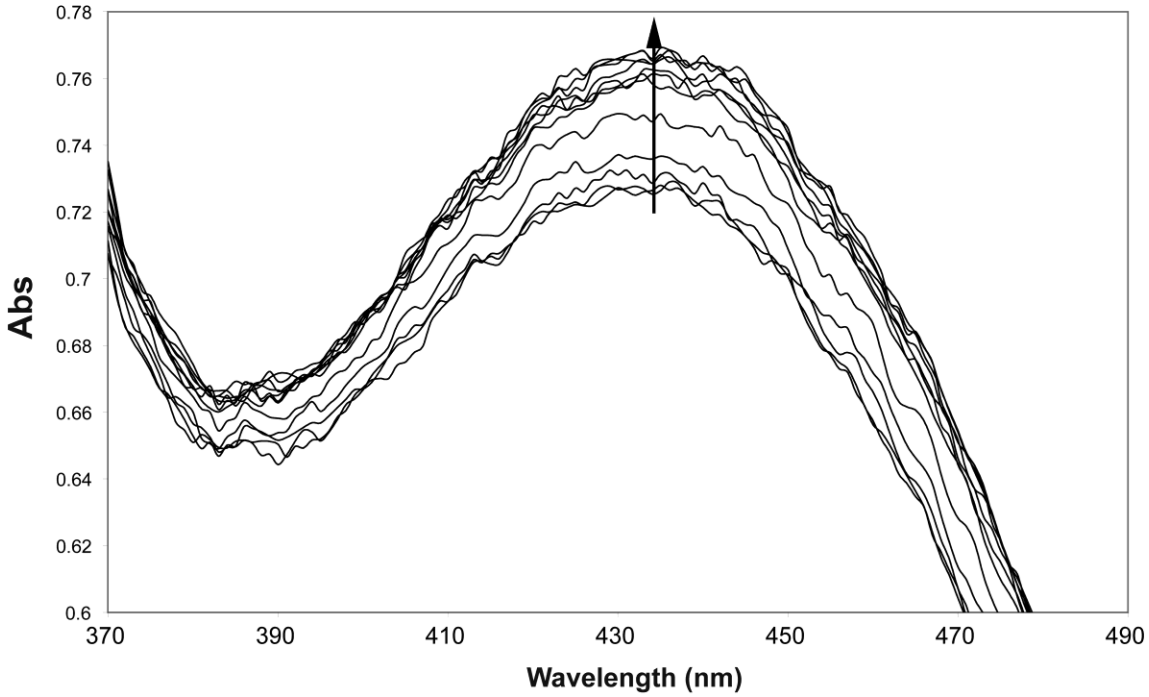

Figure S5: Diode-array mode stopped-flow spectra of the reaction of **1** with MPPH-Cl_6 at -75°C. Data represents the first second of the reaction time. [**1**] = 0.21 mM and [MPPH-Cl_6] = 53 mM. Scans acquired every 10 ms for a total of 108 samples. 12 scans across the entire time regime displayed here for clarity.

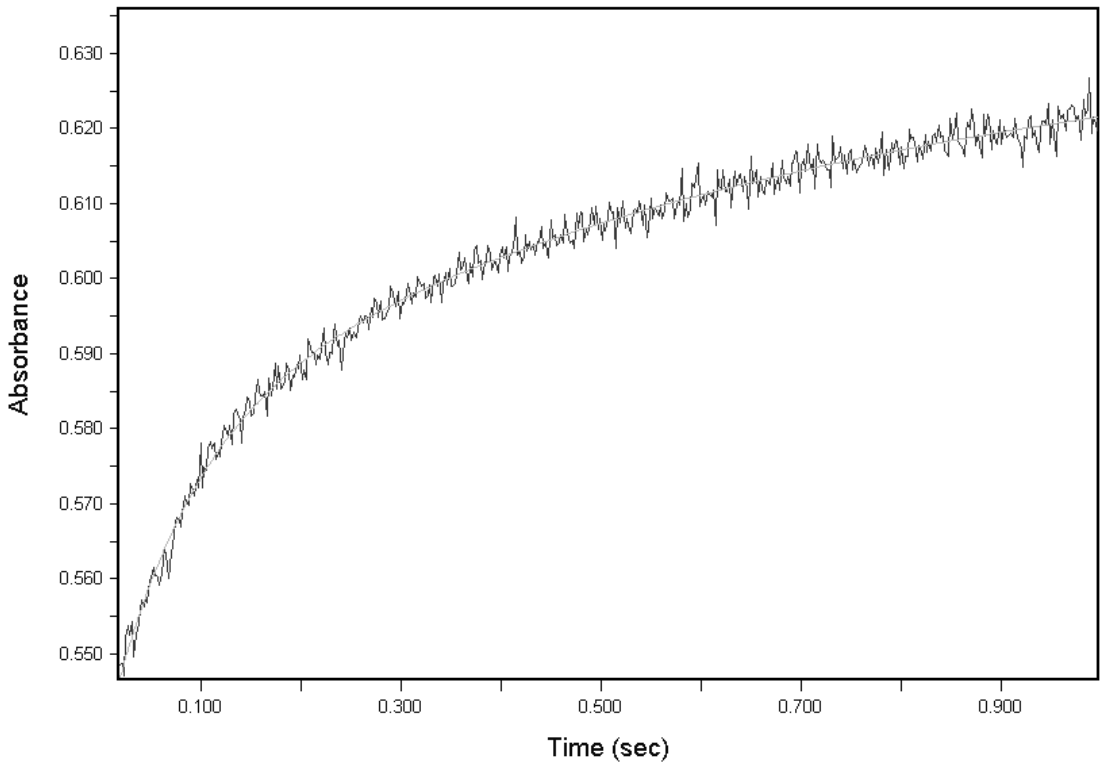

Figure S6: Single-wavelength-mode stopped-flow absorbance (438 nm) versus time for the first second of the reaction of MPPH-Cl_6 with **1** at -75°C. [**1**] = 0.21 mM and [MPPH-Cl_6] = 53 mM.

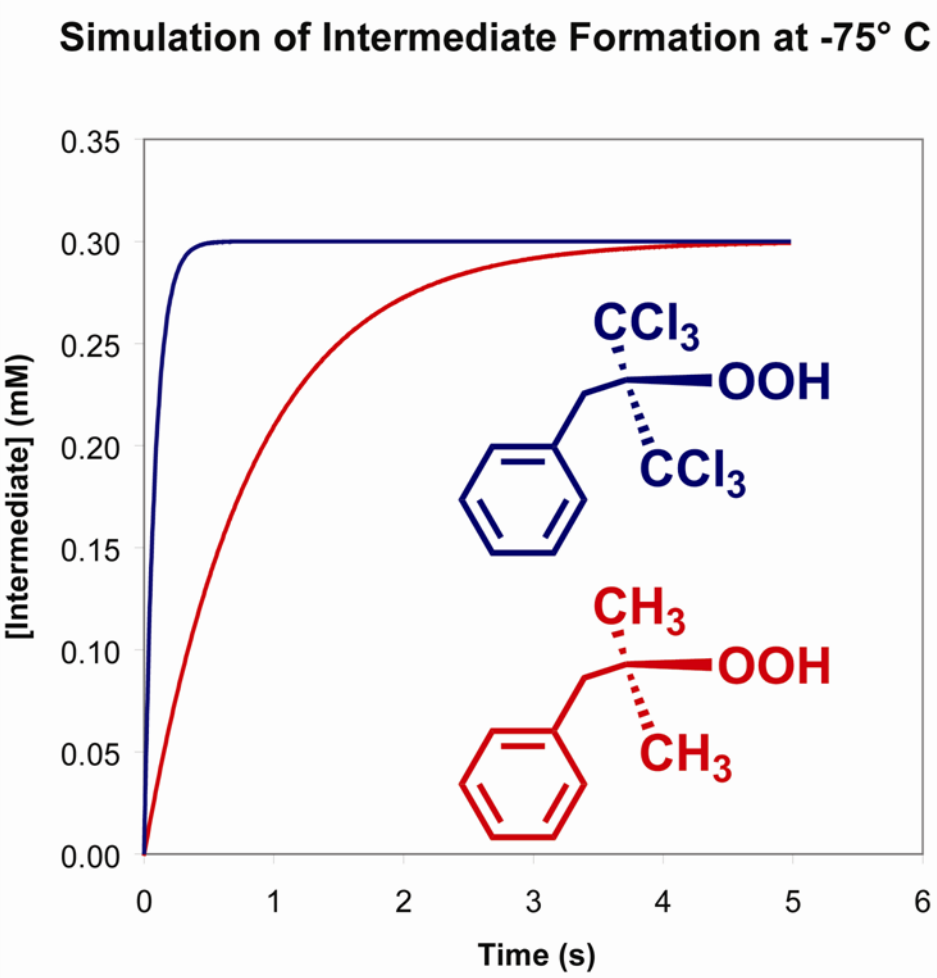

Figure S7: Simulation of k_1 reaction using the second order rate constants determined for 1+MPPH and 1+MPPH-Cl_6 reactions measure at -75°C. [**1**] = 0.3 mM and [R-OOH] = 50 mM.

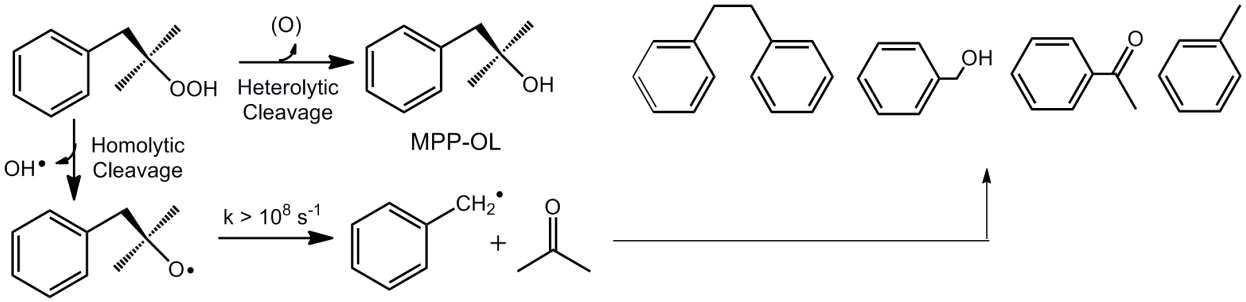

Figure S8: Heterolytic/homolytic decomposition pathways of MPPH

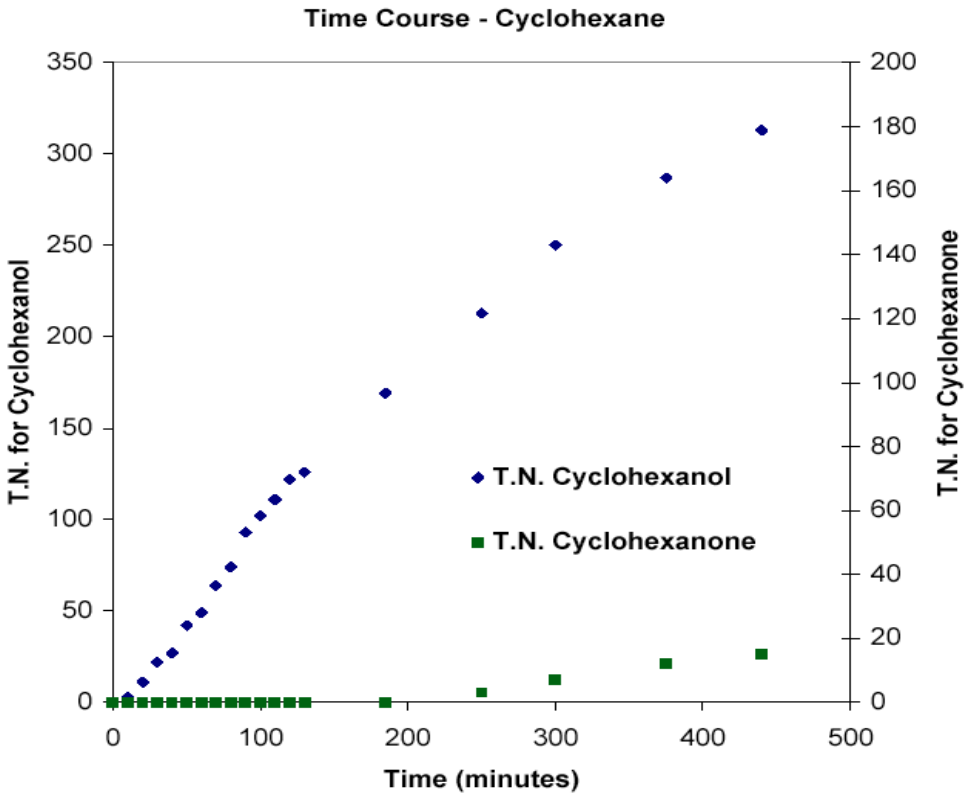

Figure S9: Time course reactivity of **1** with MPPH as oxidant and cyclohexane as substrate.

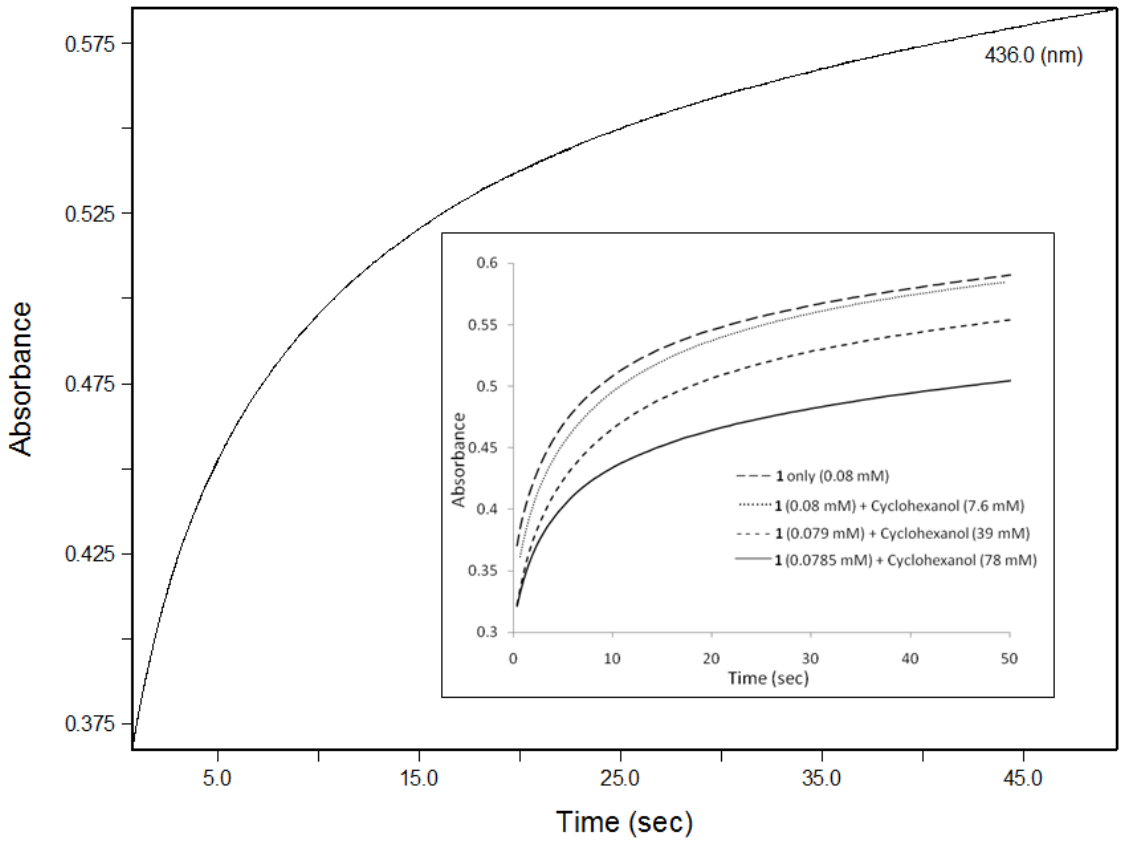

Figure S10: Single wavelength data and kinetic fit for **1** (0.08 mM) and MPPH (9.2 mM) with cyclohexanol (7.6 mM). Inset: Effect of single-wavelength data by addition of cyclohexanol

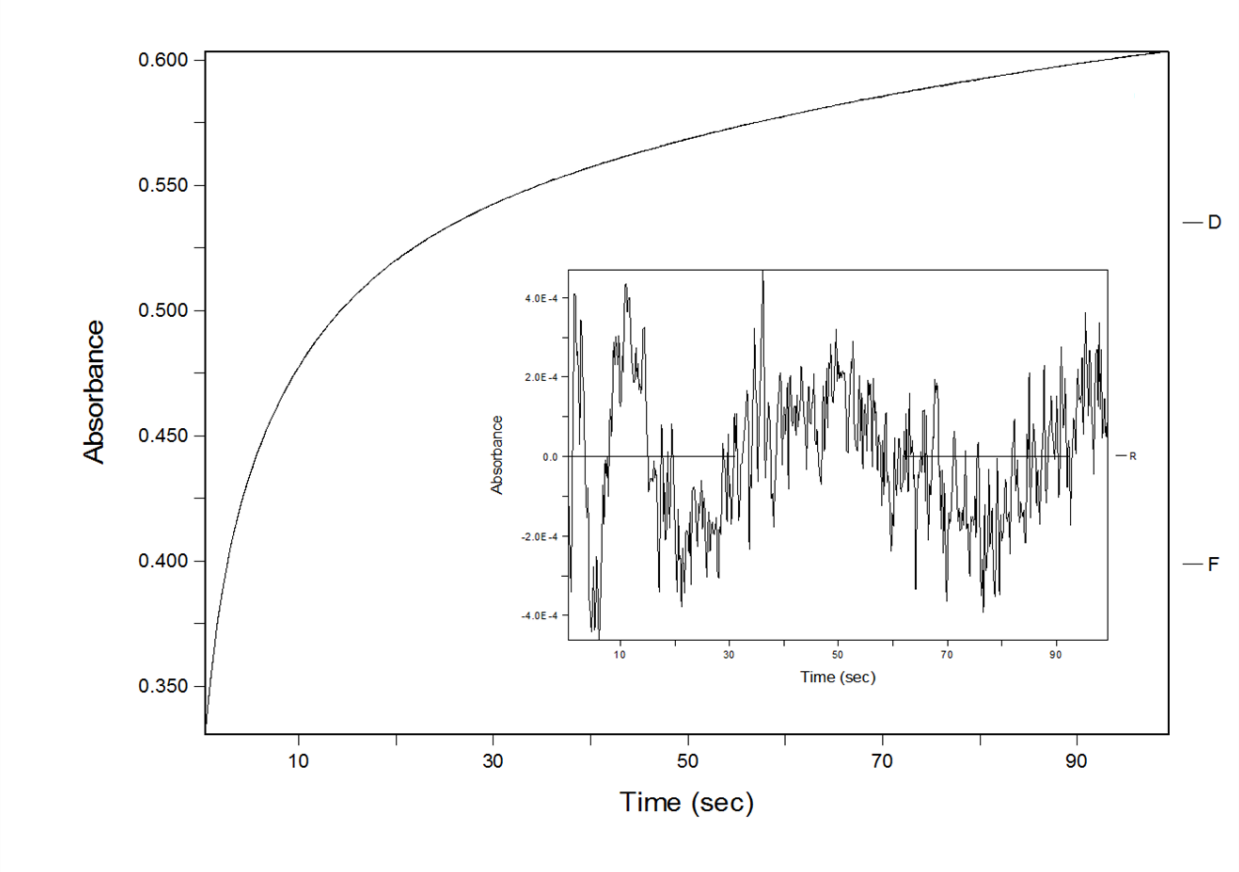

Figure S11: Kinetic data at 438 nm and overlay of fit for the reaction of **1** (0.079 mM) and cyclohexanol (78 mM) and 2-methyl-1-phenylprob-2-yl hydroperoxide (9.2 mM) at 193 K. Inset: residuals from fit.

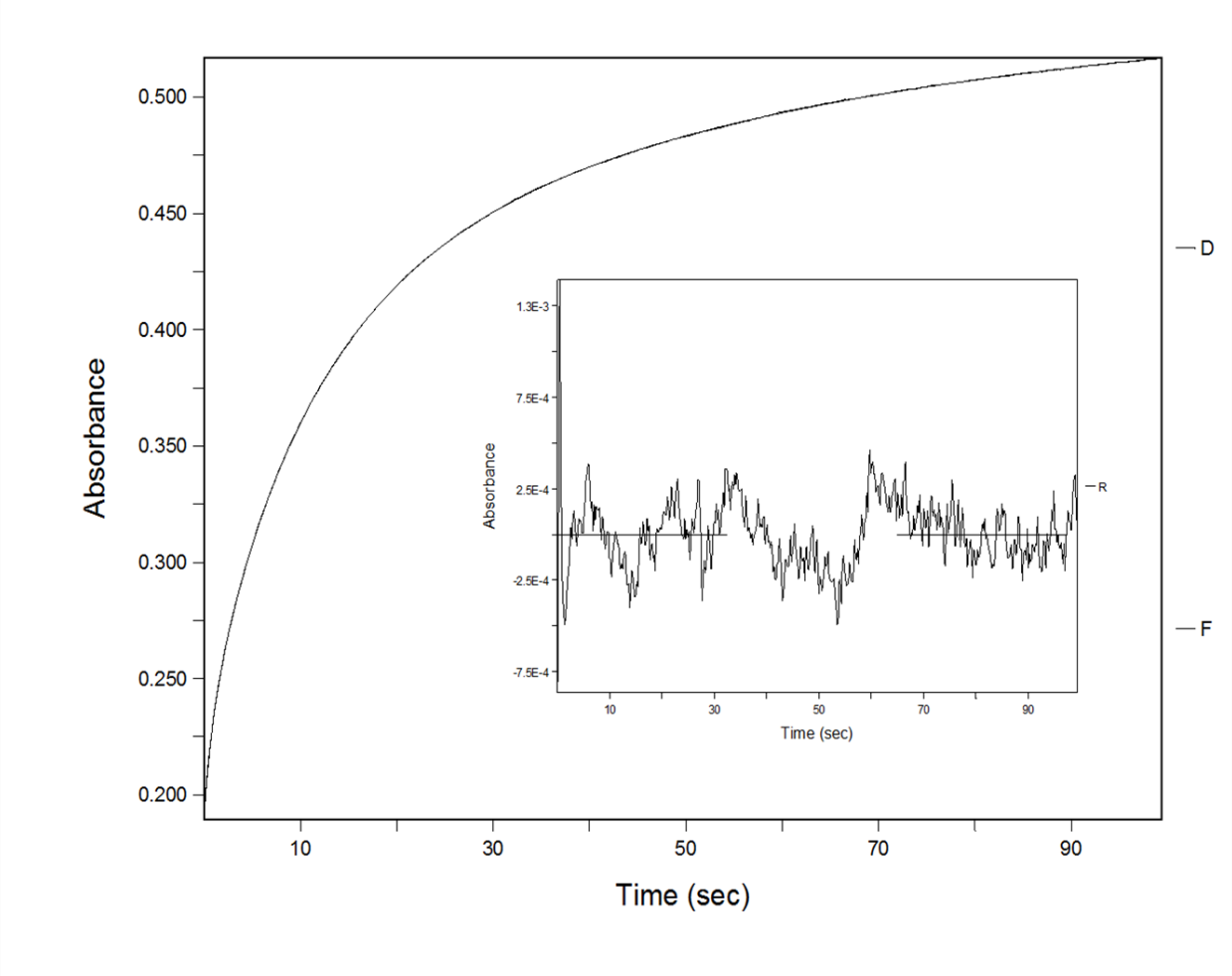

Figure S12: Kinetic data at 438 nm and overlay of fit for the reaction of **1** (0.11 mM) and methanol (11 mM) and 2-methyl-1-phenylprob-2-yl hydroperoxide (12.3 mM) at 193 K. Inset: residuals from fit.

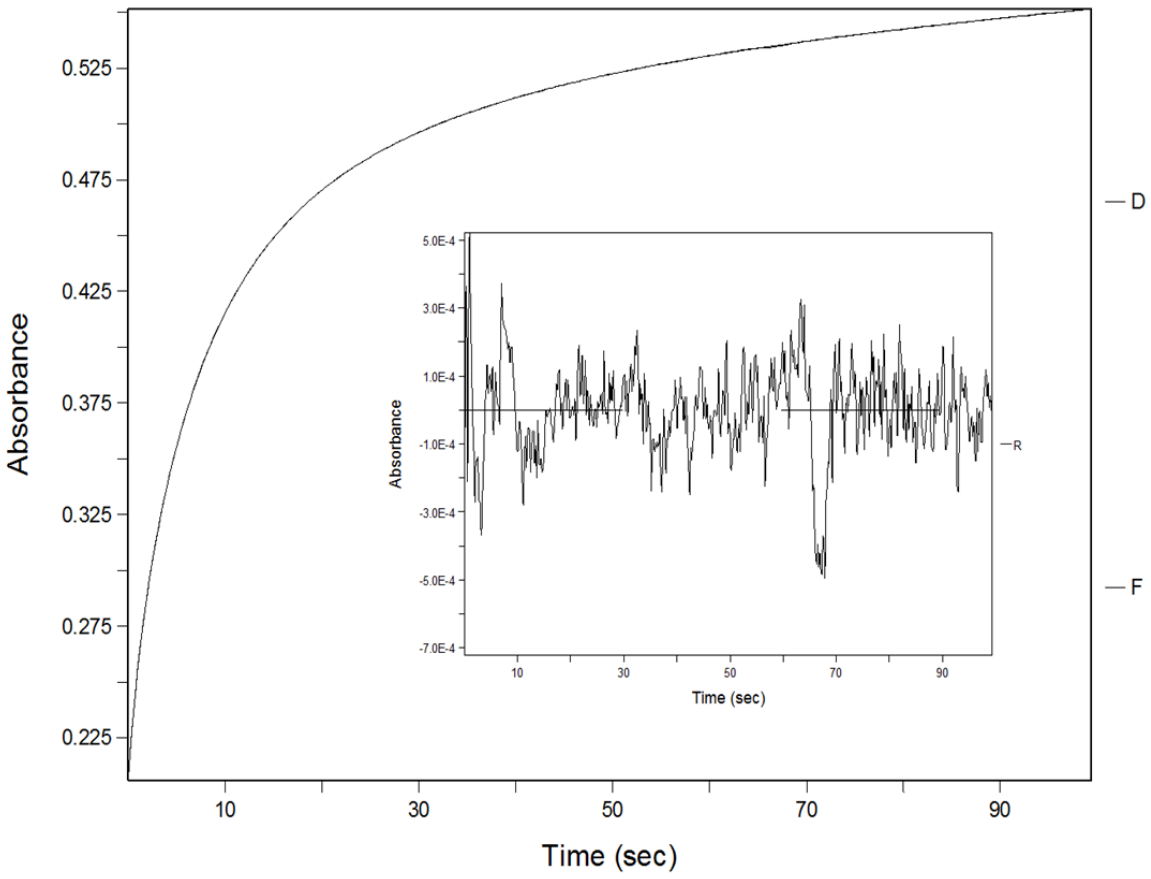

Figure S13: Kinetic data and overlay of fit for the reaction of **1** (0.11 mM) and MPP-OL (10.8 mM) and 2-methyl-1-phenylprob-2-yl hydroperoxide (12.1 mM) at 193 K. Inset: residuals from fit.

Table S1: Rate data for cyclohexanol

Step	Experiment A	Experiment B	Experiment C	Average
k_f ($M^{-1}s^{-1}$)	4.326	9.110	4.4894	
k_r (s^{-1})	0.04688	0.04814	0.04578	
k_1 (s^{-1})	0.15 (fixed)	0.15 (fixed)	0.15 (fixed)	
$k_1^{inhib}{}_{obs}$ (s^{-1})	2.36×10^{-7}	3.564×10^{-9}	9.93×10^{-9}	
k_1^{inhib} ($M^{-1}s^{-1}$)	2.65×10^{-5}	3.874×10^{-7}	1.014×10^{-6}	
k_2 (s^{-1})	0.1260	0.1167	0.1109	
k_3(s^{-1})	0.006601	0.004545	0.00634	
K_{eq}	**92.7**	**189**	**98.1**	**127**

Experimental conditions:

A. [**1**] = 0.08 mM, [cyclohexanol] = 7.6 mM, [MPPH] = 9.2 mM
B. [**1**] = 0.079 mM, [cyclohexanol] = 39 mM, [MPPH] = 9.2 mM
C. [**1**] = 0.078 mM, [cyclohexanol] = 78 mM, [MPPH] = 9.2 mM

Table S2: Rate data for methanol

	Experiment D	**Experiment E**	**Experiment F**	**Average**
k_f ($M^{-1}s^{-1}$)	7.9634	4.238	0.707	
k_r (s^{-1})	0.0115	0.005659	0.001241	
k_1 (s^{-1})	0.15 (fixed)	0.15 (fixed)	0.15 (fixed)	
$k_1^{inhib}{}_{obs}$ (s^{-1})	1.194×10^{-4}	6.994×10^{-5}	1.038×10^{-4}	
k_1^{inhib} ($M^{-1}s^{-1}$)	0.009710	0.005868	0.00844	
k_2 (s^{-1})	0.1283	0.143	0.1332	
k_3(s^{-1})	0.00536	0.0067	0.00521	
$\boldsymbol{K_{eq}}$	**692**	**748**	**707**	**716**

Experimental Conditions:

D. [**1**] = 0.11 mM, [CH_3OH] = 11 mM, [MPPH] = 12.3 mM
E. [**1**] = 0.1095 mM, [CH_3OH] = 54 mM, [MPPH] = 12.3 mM
F. [**1**] = 0.109 mM, [CH_3OH] = 109 mM, [MPPH] = 12.3 mM

Table S3: Rate data for MPP-OL

	Experiment G	**Experiment H**	**Experiment I**	**Average**
k_f ($M^{-1}s^{-1}$)	8.9281	3.69	2.866	
k_r (s^{-1})	0.0452	0.0144	0.011	
k_1 (s^{-1})	0.15 (fixed)	0.15 (fixed)	0.15 (fixed)	
$k_1^{inhib}{}_{obs}$ (s^{-1})	1.579×10^{-4}	4.610×10^{-4}	3.398×10^{-4}	
k_1^{inhib} ($M^{-1}s^{-1}$)	0.01305	0.0381	0.02808	
k_2 (s^{-1})	0.1156	0.1383	0.1306	
k_3(s^{-1})	0.0062	0.0063	0.003712	
K_{eq}	**197**	**235**	**260**	**230**

Experimental Conditions:

G. [**1**] = 0.11 mM, [MPP-OL] = 10.8 mM, [MPPH] = 12.1 mM
H. [**1**] = 0.108 mM, [MPP-OL] = 53.5 mM, [MPPH] = 12.1 mM
I. [**1**] = 0.106 mM, [MPP-OL] = 106 mM, [MPPH] = 12.1 mM

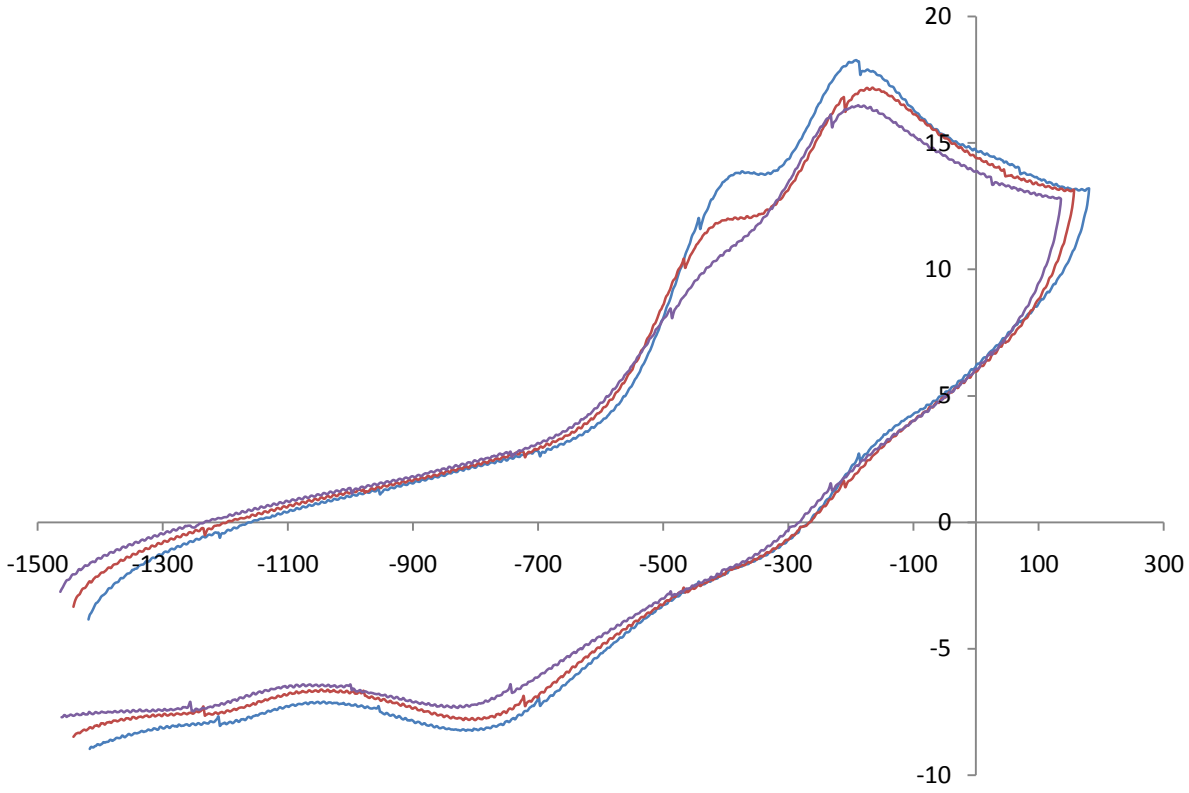

Figure S14: Electrochemistry (blue trace) of **1** (0.1 mM) in Electrochemistry (red trace) of **1** (0.098 mM) and cyclohexanol (309 mM). Electrochemistry (purple trace) of **1** (0.091 mM) and cyclohexanol (870 mM). All electrochemistry in DMF with electrolyte (10 mM) and referenced externally to Fc/Fc^{+} vs. NHE under anaerobic conditions.

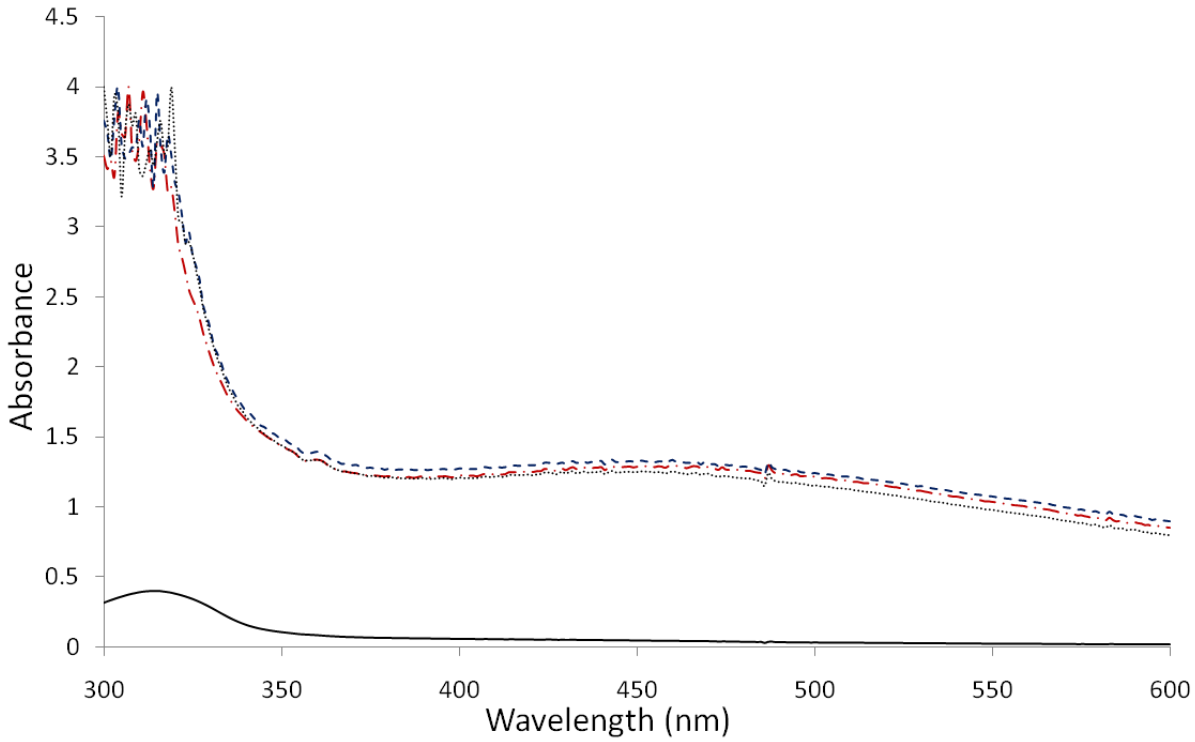

Figure S15: UV-vis spectrum of a solution of **1** (0.19 mM) in 70:30 DCM:DMF (v/v) (black line) at -74ºC. A solution of hydroxyurea (0.19 mM) was added to **1** causing a shift in chromophore (red line) followed by the addition of *p*-CN-DMANO (11 mM) (blue line) and no chromophore of **4** observed after 20 minutes (black dashed line)

Equations used in kinetic models and fits for the reaction of **1** with MPPH (X) in the presence of ROH (S1-S5, S8) and in the absence of substrate (S6, S7, S9-S11, S13):

$$\mathbf{1} + MPPH \leftrightarrow \mathbf{5} \quad \text{(S1)}$$

$$\mathbf{5} \xrightarrow{k1inhib} \mathbf{6} \quad \text{(S2)}$$

$$\frac{-d[\mathbf{1}]}{dt} = \frac{d[\mathbf{5}]}{dt} = kf[\mathbf{1}][\mathrm{ROH}] \quad \text{(S3)}$$

$$\frac{-d[\mathbf{5}]}{dt} = \frac{d[\mathbf{1}]}{dt} = kr[\mathbf{5}] \quad \text{(S4)}$$

$$\frac{-d[\mathbf{5}]}{dt} = \frac{d[\mathbf{6}]}{dt} = k1inhib[\mathbf{5}] \quad \text{(S5)}$$

$$1 + MPPH \xrightarrow{k1} \mathbf{2} + MPPH \quad \text{(S6)}$$

$$\mathbf{2} \xrightarrow{k2} \mathbf{3} \quad \text{(S7)}$$

$$\mathbf{6} \xrightarrow{k2} \mathbf{3} \quad \text{(S8)}$$

$$\mathbf{3} \xrightarrow{k3} \mathbf{4} \quad \text{(S9)}$$

$$\frac{-d[\mathbf{1}]}{dt} = \frac{d[\mathbf{2}]}{dt} = k1[\mathbf{1}][MPPH] \quad \text{(S10)}$$

$$\frac{-d[\mathbf{2}]}{dt} = \frac{d[\mathbf{3}]}{dt} = k2[\mathbf{2}] \quad \text{(S11)}$$

$$\frac{-d[\mathbf{6}]}{dt} = \frac{d[\mathbf{3}]}{dt} = k2[\mathbf{6}] \quad \text{(S12)}$$

$$\frac{-d[\mathbf{3}]}{dt} = \frac{d[\mathbf{4}]}{dt} = k3[\mathbf{3}] \quad \text{(S13)}$$

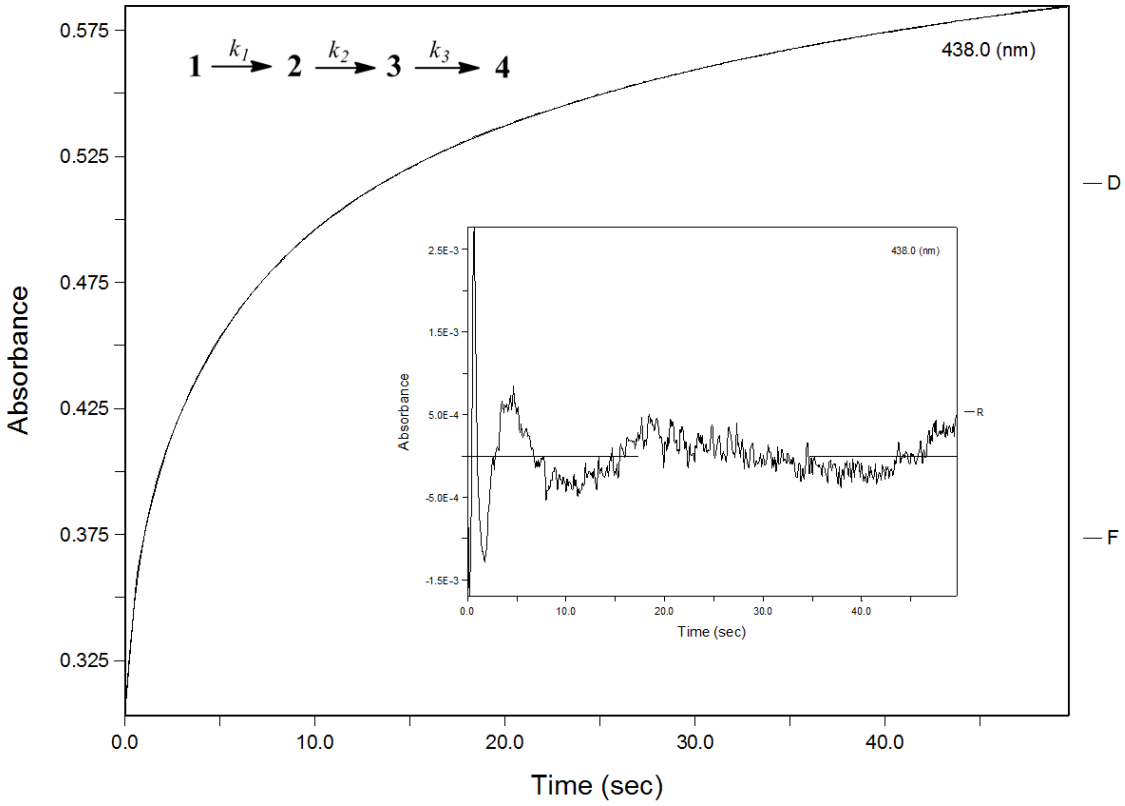

Figure S16: Kinetic fit and residuals (Inset) for models that did not resutl in adequate fits to the data.

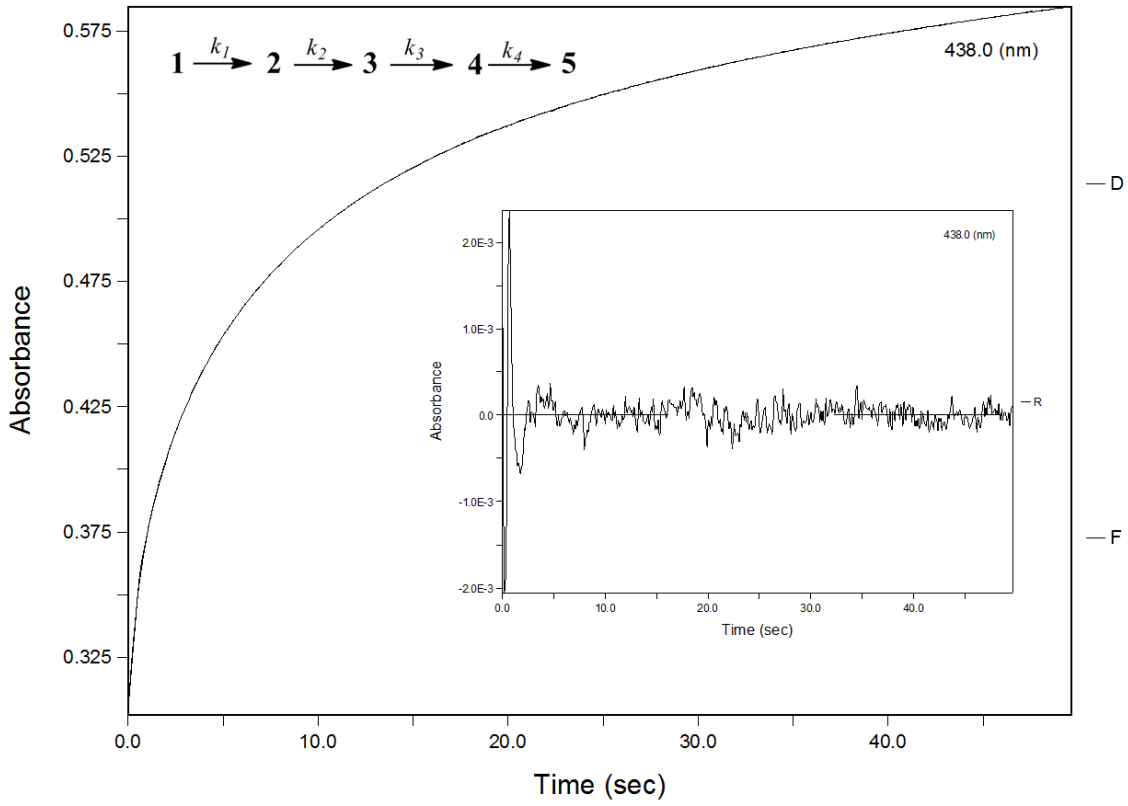

Figure S17: Kinetic fit and residuals (Inset) for models that did not resutl in adequate fits to the data.

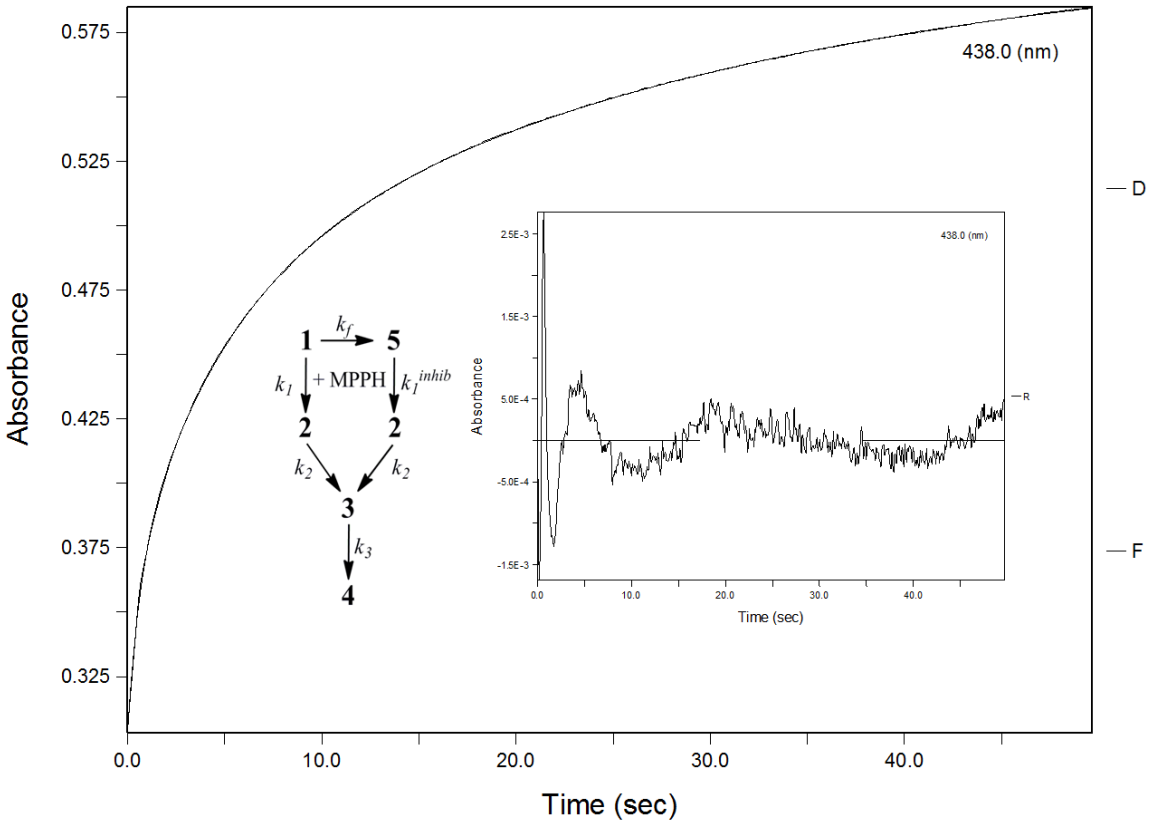

Figure S18: Kinetic fit and residuals (Inset) for models that did not resutl in adequate fits to the data.

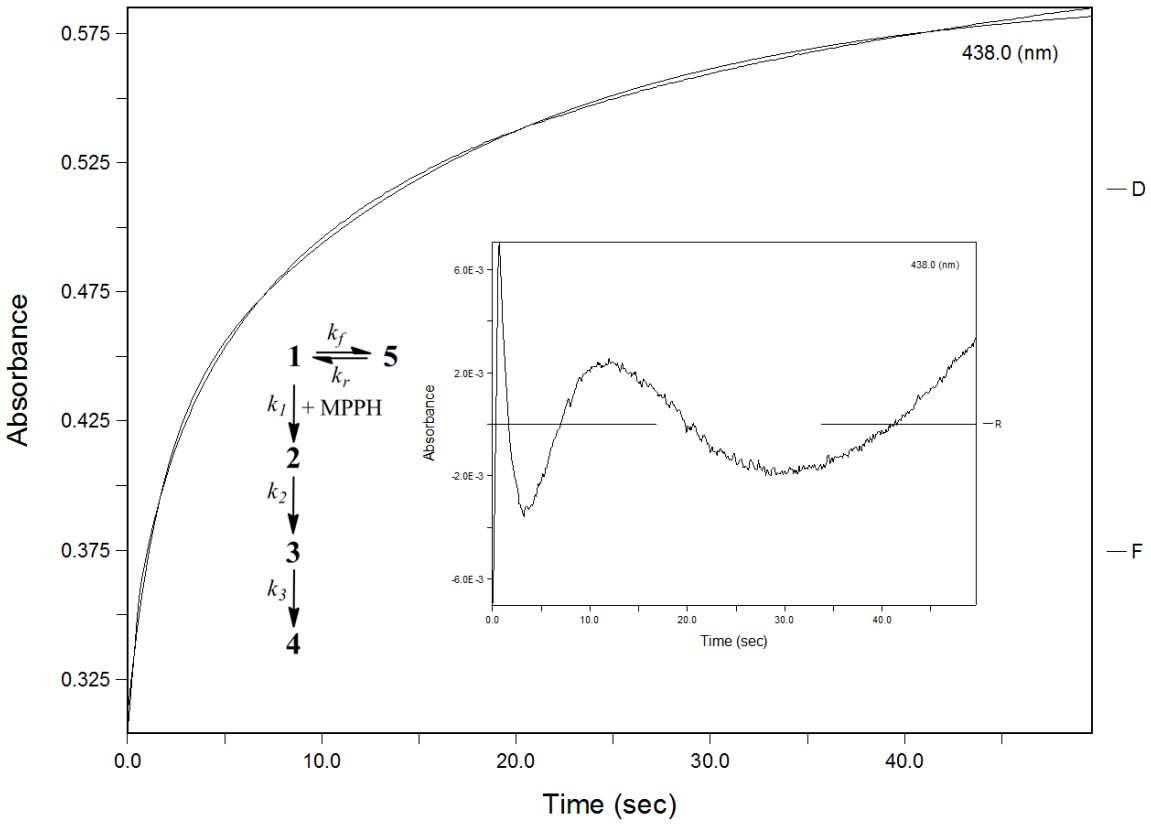

Figure S19: Kinetic fit and residuals (Inset) for models that did not resutl in adequate fits to the data.

References:

S1. S. Mukerjee, A. Stassinopoulos and J. P. Caradonna, *Journal of the American Chemical Society*, 1997, **119**, 8097-8098.

S2. T. L. Foster and J. P. Caradonna, *Journal of the American Chemical Society*, 2003, **125**, 3678-3679.

S3. R. R. Hiatt and W. M. J. Strachan, *Journal of Organic Chemistry*, 1963, **28**, 1893-1894.

S4. G. T. Rowe, C. E. Rogge, E. V. Rybak-Akimova and J. P. Caradonna, *Chemistry--A European Journal*, 2008, **14**, 8303-8311.

S5. D. A. Skoog, D. M. West, and F. J. Holler. *Fundamentals of Analytical CHemistry;* 7th ed.; Harcourt Brace & Company: Orlando, 1996.