

Supporting Information

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Mechanistic Complexity in Organo–SOMO Activation**

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¹H NMR of **5** S16

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Procedure for drying of reagents

Octanal, NaHCO₃, CAN, and **3** were dried by azeotroping with benzene. Compound was added to a round bottom flask. Benzene was added. The benzene was removed via rotary evaporation at 50 °C employing just enough vacuum to evaporate the solvent. The compound was further dried to constant weight under high vacuum.

Allyltrimethylsilane was dried using activated 3A molecular sieves.

DME was dried using sodium benzophenone ketyl. The dried solvent was distilled into a flame-dried round bottom flask.

All dried compounds were stored in an Ar atmosphere dry box.

Procedure for SOMO Reaction Progress Kinetic Analysis.

A 100 mL round bottom flask equipped with magnetic stir bar was charged with **3**, CAN, and NaHCO₃. 20 mL of DME was added to the flask and it was sealed with a rubber septum. The slurry was cooled to -78 °C and evacuated with vigorous stirring for several minutes. The flask was back-filled with Ar. H₂O was added to the flask. The flask was then evacuated and back-filled with Ar two more times with vigorous stirring. **2** and **1** were added via syringe. The reaction was warmed to -20 °C and stirred under Ar. This process required approximately 15 m.

After reaching -20°C, 0.5 mL aliquots were drawn from the reaction during its course and quenched in 1.5 mL cooled diethyl ether containing biphenyl as a standard. The resultant supernatant was analyzed via GC.

Table S1: Conditions for Anhydrous SOMO Same Excess experiment.

Run	[1]	[CAN]	[CAN]ex	[NaHCO3]	[NaHCO3]ex	[2]	[2]ex	[3]	[4]
Run 1 - 0%	0.250	0.600	0.100	0.375	0.125	0.625	0.375	0.050	0.000
Run 1 - 50%	0.125	0.350	0.100	0.250	0.125	0.500	0.375	0.050	0.125
Run 2	0.125	0.350	0.100	0.250	0.125	0.500	0.375	0.050	0.000

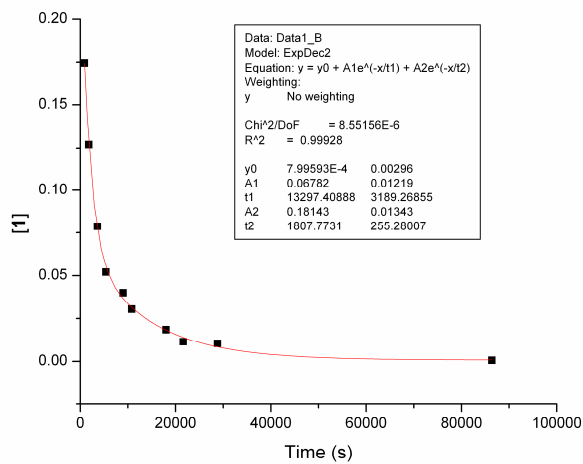


Figure S1: Decay data for Run 1

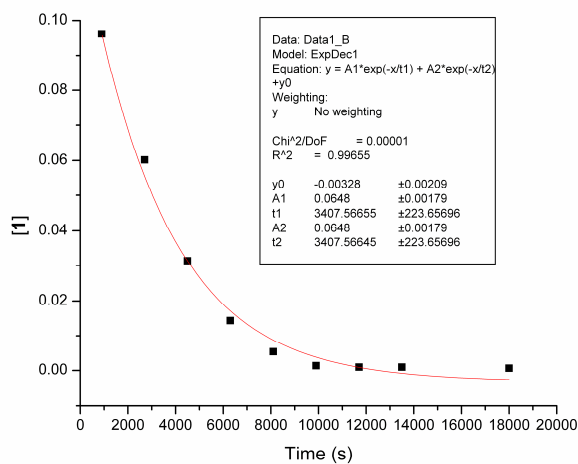


Figure S2: Decay data for Run 2

Math for conversion of decay data

1. The raw data as a plot of [I] vs. time (s) was fitted as a second order exponential decay in the cases of Runs 1 and 2 and as a first order exponential decay in the cases of the remaining runs.
2. The fits given as

$$[I] = y_0 + A_1 e^{\frac{-time}{t_1}} + A_2 e^{\frac{-time}{t_2}}$$

for Runs 1 and 2, and

$$[1] = y_0 + A_0 e^{\frac{-time}{\tau_1}}$$

for the remaining data. The expressions for [1] were then converted to their derivatives

$$-\frac{d[1]}{dt} = \frac{A_1 e^{\frac{-time}{\tau_1}}}{-\tau_1} + \frac{A_2 e^{\frac{-time}{\tau_2}}}{-\tau_2}$$

for Runs 1 and 2, and

$$-\frac{d[1]}{dt} = \frac{A_1 e^{\frac{-time}{\tau_1}}}{-\tau_1}$$

for the remaining data.

3. The RPKA was then plotted using the derivative to determine the rate and the fit to determine [1].
4. For 2nd order exponential decay, error bars for [1] were calculated using

$$\sigma_x = A_1 e^{\frac{-time}{\tau_1}} \sqrt{\left(\frac{-e^{\frac{-time}{\tau_1}} time}{\tau_1 \sigma_{\tau_1}}\right)^2 + \left(\frac{\sigma_{A_1}}{A_1}\right)^2} + A_2 e^{\frac{-time}{\tau_2}} \sqrt{\left(\frac{-e^{\frac{-time}{\tau_2}} time}{\tau_2 \sigma_{\tau_2}}\right)^2 + \left(\frac{\sigma_{A_2}}{A_2}\right)^2} + y_0$$

5. For 2nd order exponential decay, error bars for rate were calculated using

$\tau_{[1]}$

6. For 1st order exponential decay, error bars for [1] were calculated using

$$\sigma_x = A_1 e^{\frac{-time}{\tau_1}} \sqrt{\left(\frac{-e^{\frac{-time}{\tau_1}} time}{\tau_1 \sigma_{\tau_1}}\right)^2 + \left(\frac{\sigma_{A_1}}{A_1}\right)^2} + y_0$$

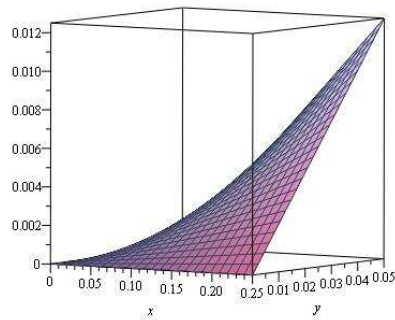
7. For 1st order exponential decay, error bars for rate were calculated using

$$\sigma_y = A_1 e^{\frac{-time}{\tau_1}} \sqrt{\left(\frac{-e^{\frac{-time}{\tau_1}} time}{\tau_1 \sigma_{\tau_1}}\right)^2 + \left(\frac{\sigma_{A_1}}{A_1}\right)^2 + \left(\frac{\sigma_{\tau_1}}{\tau_1}\right)^2}$$

Mathematical Modeling

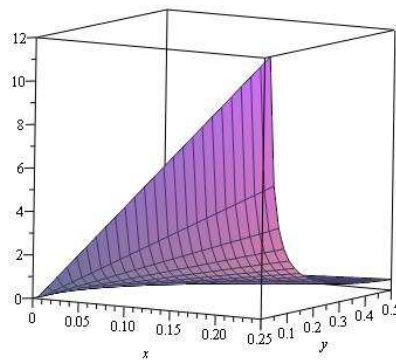
Using Maple 13:

$$-\frac{d[\mathbf{1}]}{dt} = k[\mathbf{1}][\mathbf{3}]$$



where $k=1$, $[\mathbf{1}]=x=0-0.25$, and $[\mathbf{3}]=y=0-0.05$. This shows the effect of change in concentration of **3** or CAN on the RPKA results. This concave up shape is consistent with observed deactivation of **3**.

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k[\mathbf{1}]}{[H_2O]}$$



Where $k=1$, $[1]=x=0-0.25$, and $[H_2O]=0-0.5$. If the $[H_2O]$ was changing over the course of the reaction, the RPKA plots would show a concave down shape, which is not present in the RPKA results.

Table S2: Conditions for SOMO Same Excess experiment with 2 equiv H_2O .

Run	[1]	[CAN]	[NaHCO ₃]	[2]	[H ₂ O]	[3]	[4]
Run 3 - 0%	0.250	0.600	0.375	0.625	0.500	0.050	0.000
Run 3 - 50%	0.125	0.350	0.250	0.500	0.500	0.050	0.125
Run 4	0.125	0.350	0.250	0.500	0.500	0.050	0.000

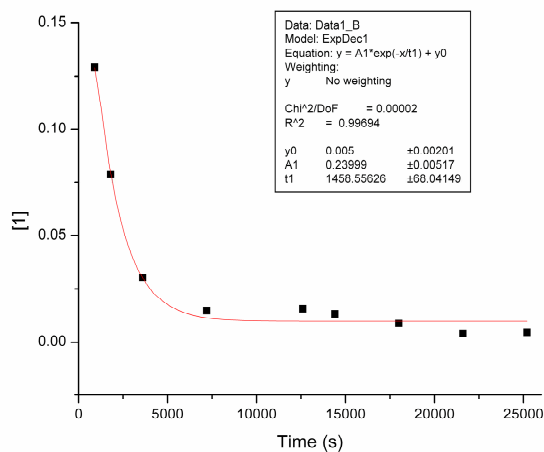


Figure S3: Decay data for Run 3

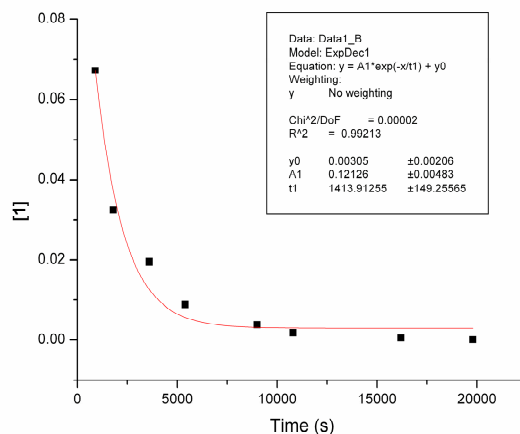


Figure S4: Decay data for Run 4

Table S3: Conditions for determination of the effect of H₂O.

Run	[Octanal]	[CAN]	[NaHCO ₃]	[AllylTMS]	[H ₂ O]	[Catalyst]
Run 5	0.250	0.600	0.375	0.625	1.000	0.050
Run 6	0.125	0.350	0.250	0.500	1.000	0.050

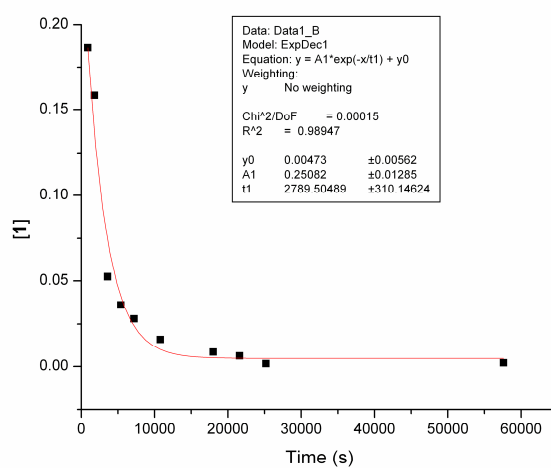


Figure S5: Decay data for Run 5

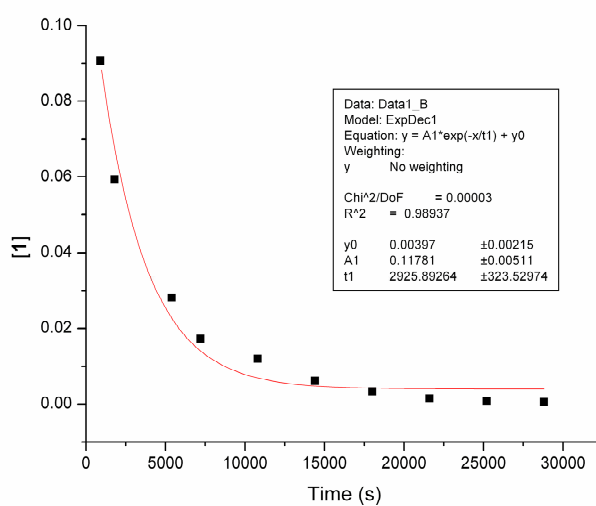


Figure S6: Decay data for Run 6



Figure S7. SOMO reaction at $-78\text{ }^{\circ}\text{C}$.



Figure S8. SOMO reaction at $-20\text{ }^{\circ}\text{C}$ with 0 equiv H_2O . In the absence of **1**, $[\text{CAN}] = 0.03\text{ M}$.



Figure S9. SOMO reaction at $-20\text{ }^{\circ}\text{C}$ with 2 equiv H_2O . In the absence of **1**, $[\text{CAN}] = 0.39\text{ M}$.

Table S4: Conditions for SOMO Different Excess experiment for rate order of CAN.

Run	[1]	[CAN]	[CAN]ex	[NaHCO ₃]	[2]	[H ₂ O]	[3]
0.35 M CAN	0.125	0.350	0.100	0.250	0.500	0.500	0.050
0.6 M CAN	0.125	0.600	0.350	0.250	0.500	0.500	0.050

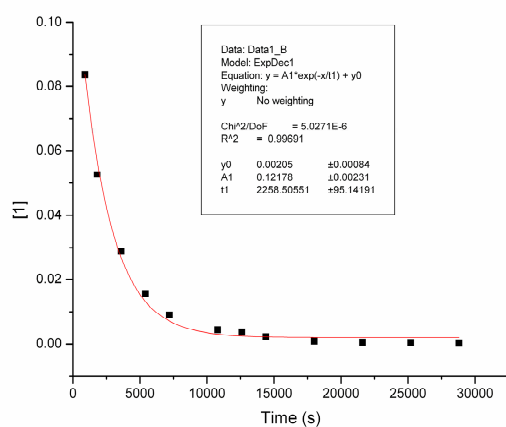


Figure S10: Decay data for CAN different excess run

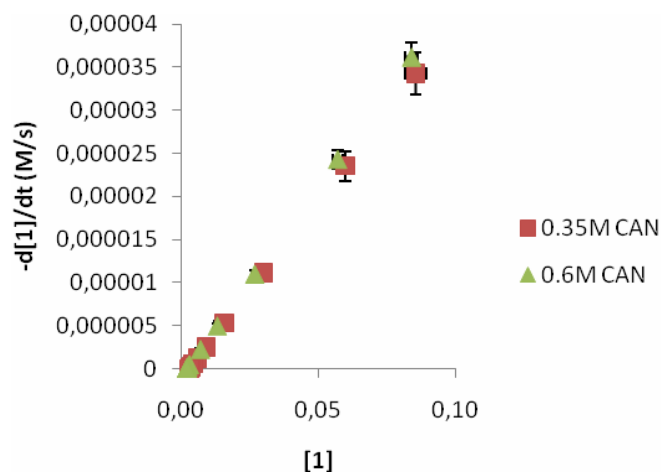


Figure S11: Plot of rate vs. [1] for the rate order of CAN

Table S5: Conditions for SOMO Different Excess experiment for rate order of NaHCO_3 .

Run	[1]	[CAN]	[NaHCO_3]	[NaHCO_3]ex	[2]	[H_2O]	[3]
0.25 M NaHCO_3	0.125	0.350	0.250	0.125	0.500	0.500	0.050
0.5 M NaHCO_3	0.125	0.350	0.500	0.375	0.500	0.500	0.050

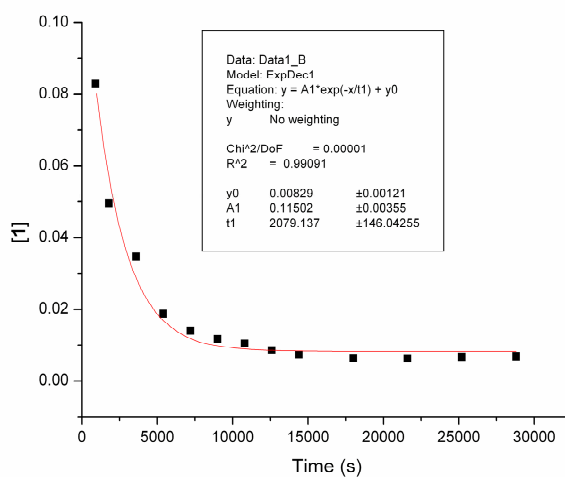


Figure S12: Decay data for NaHCO_3 different excess run

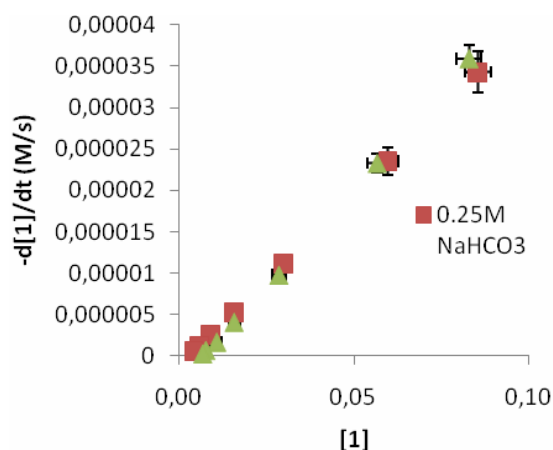


Figure S13: Plot of rate vs. [1] for the rate order of NaHCO₃.

Procedure for reaction with 0 NaHCO₃

Using conditions similar to Run 3, a 100 mL round bottom flask equipped with magnetic stir bar was charged with **3** and CAN. No NaHCO₃ was added to the flask. 20 mL of DME was added to the flask and it was sealed with a rubber septum. The slurry was cooled to -78 °C and evacuated with vigorous stirring for several minutes. The flask was back-filled with Ar. H₂O was added to the flask. The flask was then evacuated and back-filled with Ar two more times with vigorous stirring. **2** and **1** were added via syringe. The reaction was warmed to -20 °C and stirred under Ar. This process required approximately 15 m.

After reaching -20°C, 0.5 mL aliquots were drawn from the reaction during its course and quenched in 1.5 mL cooled diethyl ether containing biphenyl as a standard. The resultant supernatant was analyzed via GC.

The reaction did not go to completion as a result of protonation the catalyst due to an increase in pH.

Table S6: Conditions for SOMO Different Excess experiment for rate order of **3**.

Run	[1]	[CAN]	[NaHCO ₃]	[2]	[H ₂ O]	[3]
0.05 M 3	0.125	0.350	0.250	0.500	0.500	0.050
0.025 M 3	0.125	0.350	0.250	0.500	0.500	0.025

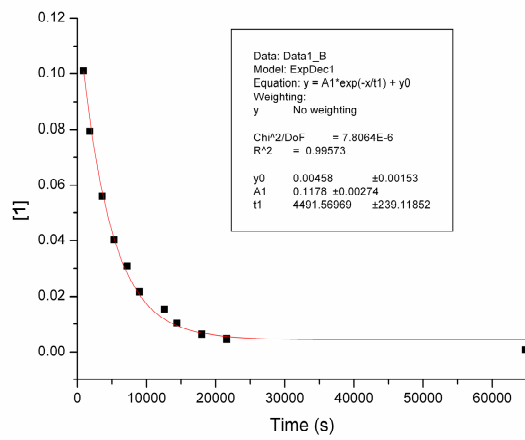


Figure S14: Decay data for different **3** loading run

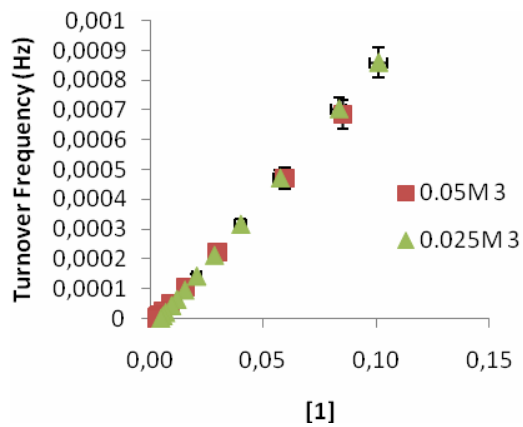


Figure S15: Plot of rate/[**3**] vs. [**1**] for the rate order of **3**.

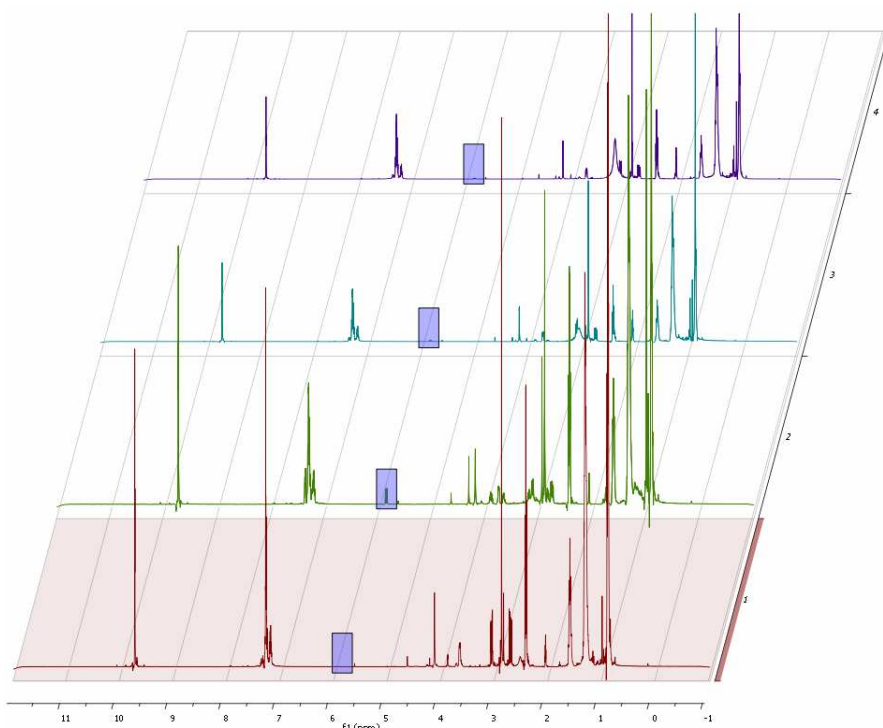
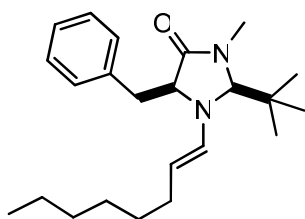


Figure S16: NMR analysis on the effect of H₂O and CAN on formation of **5**: (1) **1** and **3** in deuterated acetone, (2) **1** and **3** with 3 mol% CAN, (3) 2 equiv H₂O, and (4) 4 equiv H₂O. Blue box denotes proton exclusive to **5**.

Procedure for synthesis of **5**



In a 100 mL round bottom flask, CAN (33 mg, 60 μ mol) was dissolved in 40 mL anhydrous MeCN. **3** (0.49 g, 2 mmol) and **1** (311 μ L, 2 mmol) were added and the reaction was stirred for 15 min. The reaction was concentrated via rotary evaporation. Purification by Teledyne ISCO CombiFlash Rf (silica gel pretreated with 1% Et₃N/EtOAc followed by Hexanes, 0-100% EtOAc/Hexanes) afforded **5** (0.1663, 23% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.21 (m, 4H), 7.19-7.14 (m, 1H), 5.63 (d, J=14 Hz, 1H), 4.10 (s; 1H), 3.80 (dt; J=13.9 Hz, 6.9 Hz; 1H), 3.70 (dd; J=8.5 Hz, 4.5 Hz; 1H), 3.19 (dd; J=13.6 Hz, 4.6 Hz; 1H), 2.92 (s; 3H), 2.85 (dd; J=14.1 Hz, 6.6 Hz, 1H),

1.72-1.62 (m; 2H), 1.29-1.20 (m; 4H), 1.19-0.97 (m; 6H), 0.93 (s; 9H), 0.85 (t; J=7.7 Hz; 3H). ¹³C (125 MHz, CDCl₃) δ 172.5, 138.8, 138.6, 129.7, 128.4, 126.4, 102.5, 88.4, 66.0, 39.8, 37.5, 31.7, 31.3, 30.8, 30.2, 28.5, 26.2, 22.7, 14.2. HRMS (ESI+) exact mass calculated for [M+H]⁺ (C₂₃H₃₇N₂O) requires *m/z* 357.2906, found *m/z* 357.2887.

Rate law derivation

A. From Scheme 1, Therefore, the rate of oxidation of **5** is given by

$$-\frac{d[\mathbf{1}]}{dt} = k_2[\mathbf{5}][\mathbf{CAN}]$$

where **5** is assumed to be at steady state

$$-\frac{d[\mathbf{5}]}{dt} = 0 = k_1[\mathbf{1}][\mathbf{3}] - k_{-1}[\mathbf{5}][\mathbf{H}_2\mathbf{O}] - k_2[\mathbf{5}][\mathbf{CAN}]$$

Solving for **5** provides

$$[\mathbf{5}] = \frac{k_1[\mathbf{1}][\mathbf{3}]}{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}]}$$

which can then be substituted into rate expression giving.

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1 k_2 [\mathbf{1}][\mathbf{CAN}]}{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}][\mathbf{3}]}$$

For the case of a catalytic cycle, a mass balance is needed to add up the species that the original catalyst, [3]_{total}, partitions into

$$[\mathbf{3}]_{\text{total}} = [\mathbf{3}] + [\mathbf{5}] = [\mathbf{3}] \left(1 + \frac{k_2[\mathbf{1}]}{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}]} \right)$$

The expression above makes use of the equation describing the steady-state concentration of **5**. We can now manipulate this equation to solve for the concentration of **3** in the cycle, as a function of the total amount of **3** added:

$$[\mathbf{3}] = \frac{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}]}{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}] + k_1[\mathbf{1}]} [\mathbf{3}]_{\text{total}}$$

The overall steady-state catalytic rate expression becomes:

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1 k_2 [\mathbf{1}][\mathbf{CAN}]}{k_{-1}[\mathbf{H}_2\mathbf{O}] + k_2[\mathbf{CAN}] + k_1[\mathbf{1}]} [\mathbf{3}]_{\text{total}}$$

If we assume that oxidation is rate limiting and that $k_1[\mathbf{1}] \ll [\mathbf{1}]$, the catalytic rate expression becomes eq 3

$$-\frac{d[\mathbf{1}]}{dt} = K_{eq} k_2 \frac{[\mathbf{1}][\mathbf{CAN}]}{[\mathbf{H}_2\mathbf{O}]} [\mathbf{3}]_{total}$$

Procedure for Optimized SOMO Reaction.

In the dry box, a flame-dried 100 mL round bottom flask equipped with magnetic stir bar was charged with azeotroped **3** (0.246 g, 1 mmol), azeotroped CAN (6.6 g, 12 mmol), and azeotroped NaHCO₃ (0.64 g, 7.5 mmol). 20 mL of DME dried with sodium benzophenone ketyl was added to the flask and it was sealed with a rubber septum. The slurry was cooled to -78 °C and evacuated with vigorous stirring for several minutes. The flask was back-filled with Ar. H₂O (18 μL, 10 mmol) was added to the flask. The flask was then evacuated and back-filled with Ar two more times with vigorous stirring. **2** dried with 3A molecular sieves (2 mL, 12.5 mmol) and azeotroped **1** (0.78 mL, 5 mmol) were added via syringe. The reaction was warmed to -20 °C and stirred under Ar for 8 h. The reaction was then poured into 150 mL diethyl ether and shaken vigorously. The solution was filtered through a bed of Celite. The filtrate was dried with MgSO₄ and concentrated via rotary evaporation giving **4** as a yellow oil (0.748 g, 89% yield, 86% ee). ¹H NMR (500 MHz, CDCl₃) δ 9.56 (d, J=2.4 Hz, 1H), 5.74-5.65 (m, 1H), 5.06-4.98 (m, 2H), 2.39-3.28 (m, 2H), 2.23-2.16 (m, 2H), 1.65-1.56 (m, 2H), 1.49-1.39 (m, 2H), 1.34-1.16 (m, 6H), 0.84 (bt, J=7.4 Hz, 3H). ¹³C (125 MHz, CDCl₃) δ 204.5, 136.4, 117.0, 51.7, 33.5, 32.2, 29.9, 28.8, 27.4, 23.1, 14.1. Enantiopurity was determined by GLC using a Varian Chirasil-Dex-CB (25 m x 0.25 mm) column (100 °C isotherm); (*S*) isomer *t*_r = 23.2 min and (*R*) isomer *t*_r = 23.8 min.

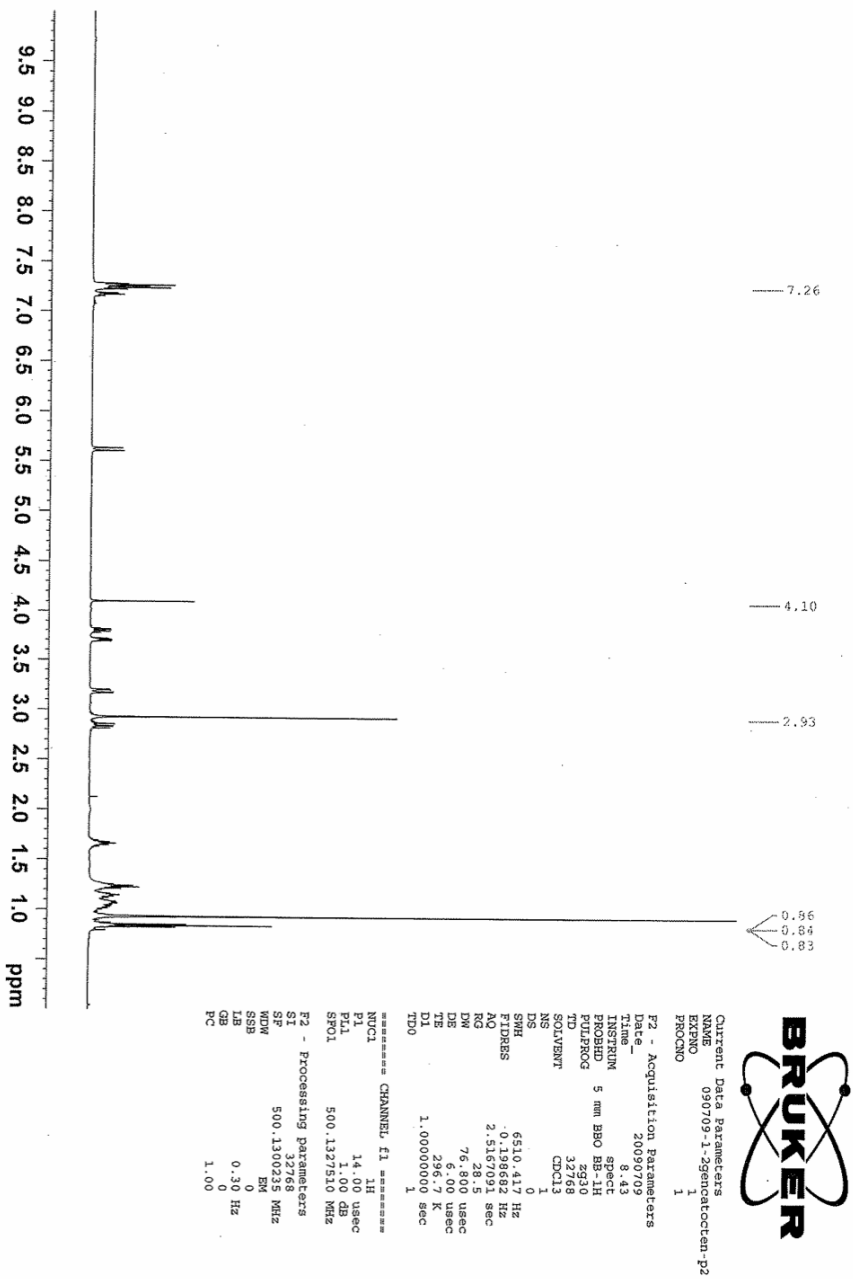


Figure S17: ^1H NMR of 5.

