Supporting Information For

Substrate-Triggered Activation of a Synthetic [$Fe_2(\mu\text{-}O)_2$] Diamond Core for C–H Bond Cleavage

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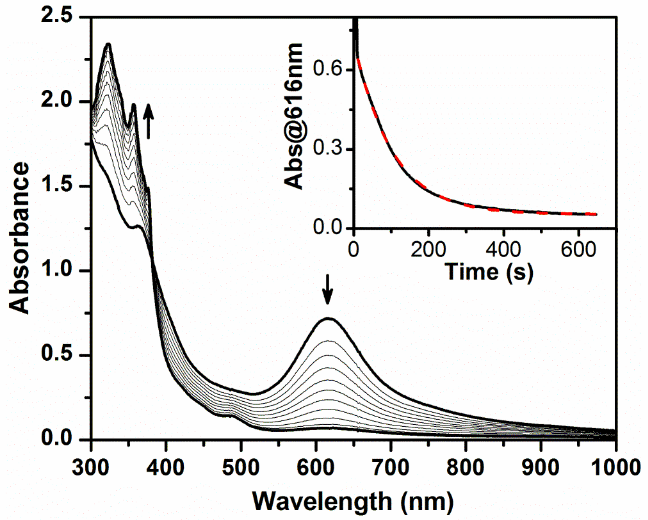

Figure S1. Time-resolved spectral changes during the oxidation of 10 mM DHA by **1** at -30 ºC in MeCN in the presence of 1.0 M H_2O. Inset: time trace at 616 nm (black solid line) together with the fit (red dashed line) using a first-order rate constant of 0.0099 s^{-1}.

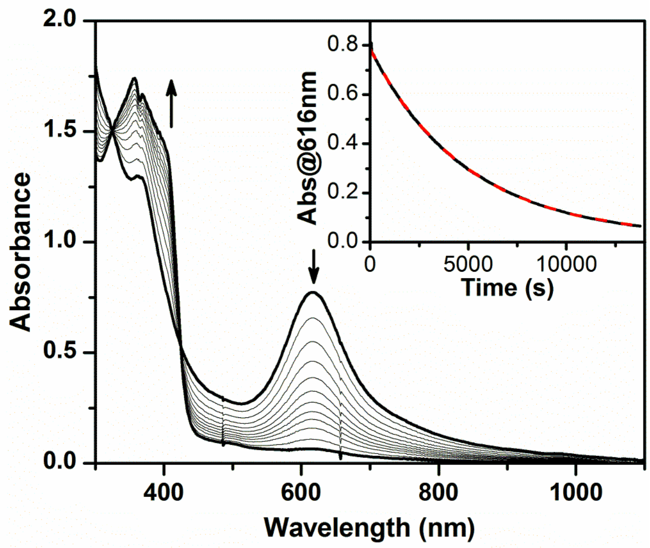

Figure S2. Time-resolved spectral changes during the oxidation of 1.0 mM CH_3OH by **1** at -30 ºC in MeCN in the presence of 50 mM H_2O. Inset: time trace at 616 nm (black solid line) together with the fit (red dashed line) using a first-order rate constant of 2.0×10^{-4} s^{-1}.

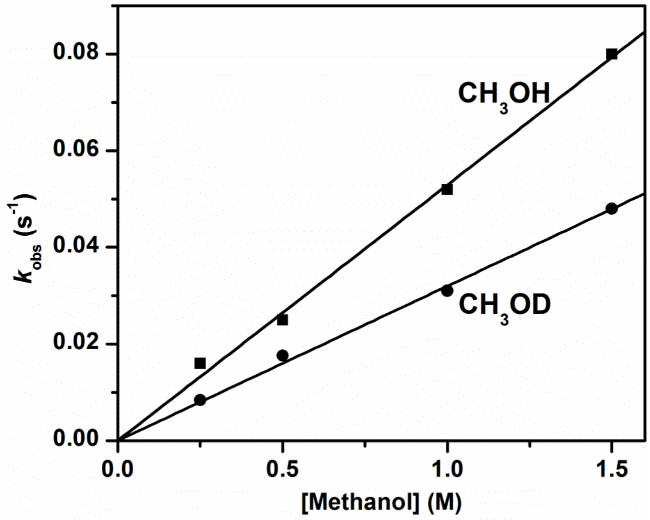

Figure S3. k_{obs}-vs-[substrate] plots for oxidation of CH_3OH (squares) or CH_3OD by **1** in MeCN in the presence of 10 mM 2,6-lutidine. The corresponding second order rate constants (k_2) are 0.053 M^{-1} s^{-1} and 0.032 M^{-1} s^{-1}, and KIE is 1.6. The reaction rates were measured under Ar at -30 ºC.

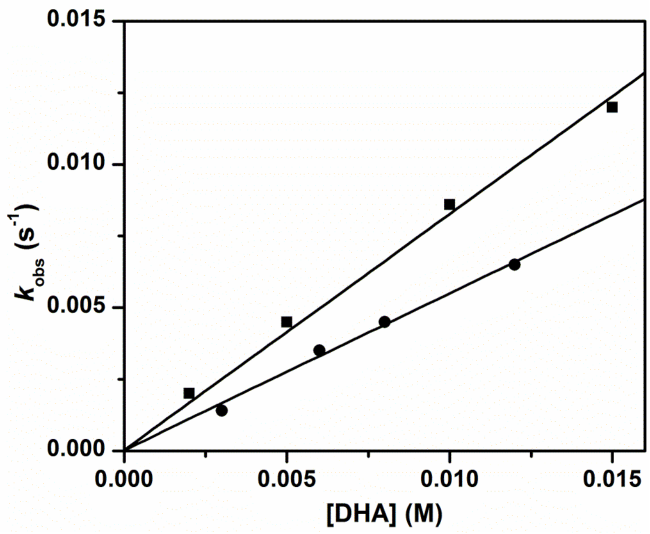

Figure S4. k_{obs}-vs-[DHA] plots for oxidation by 1 in MeCN in the presence of 1.0 M H_2O (squares) or D_2O (circles). The corresponding second order rate constants (k_2) are 0.82 M^{-1} s^{-1} and 0.56 M^{-1} s^{-1}, and KIE is 1.5. The reaction rates were measured under Ar at -30 ºC.

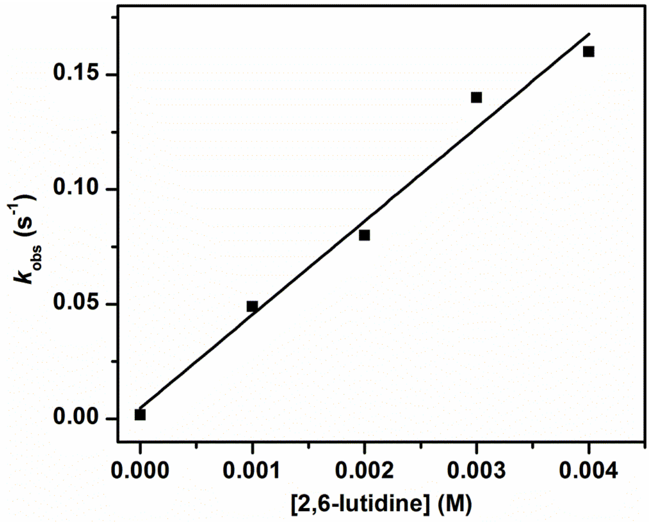

Figure S5. k_{obs}-vs-[2,6-lutidine] plot for oxidation of 2.0 mM DHA by **1** in MeCN with 1.0 M H_2O at -30 C under Ar. See Table S5 for list of data in the plot.

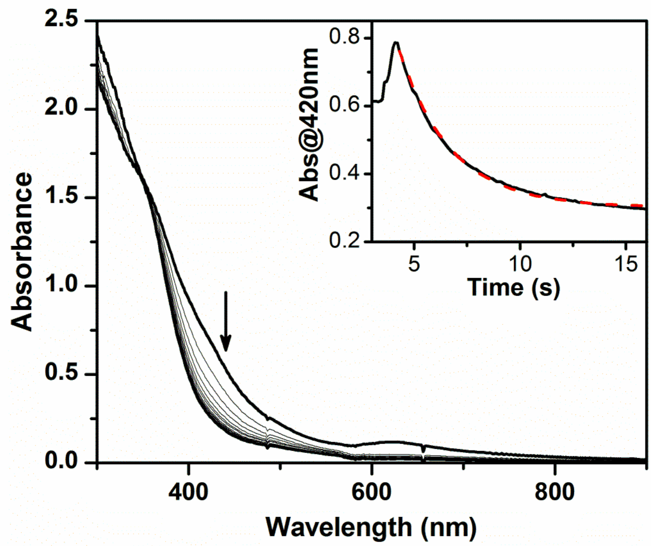

Figure S6. Time resolved spectral changes during self-decay of **1**-OCH_3 at -50 ºC in 3:1 CH_2Cl_2-MeCN. Inset: time trace at 420 nm (black solid line, one data point per 0.1 second) together with the fit (red dashed line) using a first order rate constant of 0.40 s^{-1}.

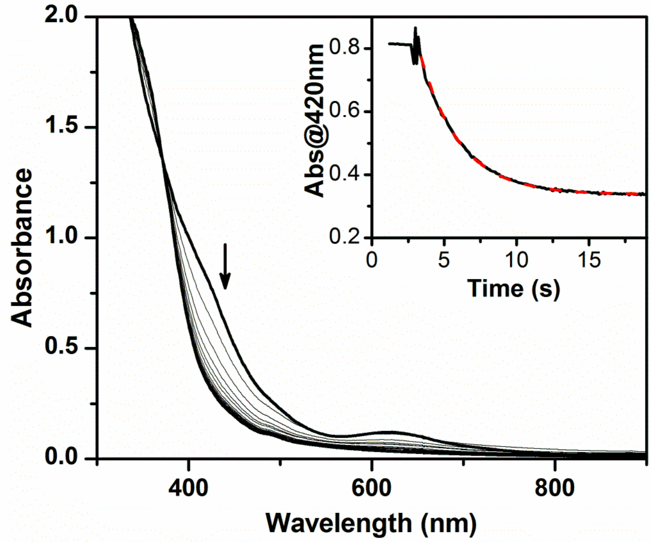

Figure S7. Time-resolved spectral changes during the oxidation of DHA by **1**-OCD_3 at -80 ºC in 3:1 CH_2Cl_2-MeCN. Inset: time trace at 420 nm (black solid line, one data point per 0.1 second) together with the fit (red dashed line) using a first order rate constant of 0.36 s^{-1}.

Table S1. Summary of k_2’ values for substrate oxidations by **1** and **3** at -30 ºC under Ar.

Substrate	BDE kcal mol^{-1}	k_2’ (M^{-1} s^{-1}) by **3** in MeCN	k_2’ (M^{-1} s^{-1}) by **1** in MeCN with 0.05 M H_2O	k_2’ (M^{-1} s^{-1}) by **1** in MeCN with 1.0 M H_2O
xanthene	75.5[1]	ND	4.8×10^{-2}	0.84
DHA	78[1]	1.2	7.0×10^{-3}	0.20
fluorene	80[1]	0.22	4.1×10^{-3}	0.16
triphenylmethane	81[2]	0.16	ND	ND
diphenylmethane	82[2]	ND	ND	6.5×10^{-3}
tetralin	85[2]	0.10	6.9×10^{-5}	1.4×10^{-3}
ethylbenzene	87[1]	2.7×10^{-3}	ND	1.0×10^{-4}
toluene	90[1]	ND	ND	4.0×10^{-5}
benzhydrol	79[3]	ND	4.7×10^{-3}	ND
benzyl alcohol	85[4]	0.047	5.0×10^{-4}	1.7×10^{-3}
2-hexanol	90[4]	2.2×10^{-3}	2.1×10^{-5}	ND
1-hexanol	93[4]	3.6×10^{-4}	1.5×10^{-4}	ND
isobutanol	93[4]	ND	2.0×10^{-5}	ND
ethanol	93[4]	ND	1.4×10^{-4}	ND
methanol	96[5]	2×10^{-5}	6.0×10^{-5}	6.3×10^{-5}

Table S2. Rate constants for methanol (1.0 M) oxidation by **1** in MeCN at -30 ºC under Ar (Figure 6). For the k_{obs} versus pK_a experiments, 10 mM bases were added to mixture of **1** and methanol.

[2,6-lutidine] / mM	0	2.0	4.0	6.0	8.0	10	20	50
k_{obs} (x 10^{-3} s^{-1})	0.20	1.6	2.6	3.8	4.1	5.7	11	23
[2,4,6-collidine] / mM	0	2.0	4.0	6.0	10			
k_{obs} (x 10^{-3} s^{-1})	0.20	3.2	6.0	9.2	14			
pK_a	5.17	5.97	6.51	6.77	7.48			
k_{obs} (x 10^{-3} s^{-1})	0.23	0.80	1.4	5.7	14			

Table S3. Comparison of the rates for the oxidation of DHA[a] and methanol[b].

Oxidant	T/Solvent	Rate constants
DHA oxidation[a]		
1 + 1 M H_2O	-30 °C/CH_3CN	0.80 M^{-1} s^{-1}
2 + 1 M H_2O	-30 °C/CH_3CN	0.15 M^{-1} s^{-1}
2	-80 °C/3:1 CH_2Cl_2:CH_3CN	10^{-5} M^{-1} s^{-1}
4	-80 °C/3:1 CH_2Cl_2:CH_3CN	10^{-4} M^{-1} s^{-1}
2-OH	-80 °C/3:1 CH_2Cl_2:CH_3CN	28 M^{-1} s^{-1}
2-OCD_3	-80 °C/3:1 CH_2Cl_2:CH_3CN	360 M^{-1} s^{-1}
Methanol oxidation[b]		
1 (+ 2.0 M CH_3OH)	-30 °C/CH_3CN	4.0 x 10^{-4} s^{-1}
2 (+ 2.0 M CH_3OH)	-30 °C/CH_3CN	3.3 x 10^{-5} s^{-1}
4 (+ 2.0 M CH_3OH)	-30 °C/CH_3CN	5 x 10^{-6} s^{-1}

[a] DHA oxidation rates by **2**, **4** and **2**-OH were reported from ref 6. [b] Only first order rate constants for the oxidation of 2 M CH_3OH are listed, because the reaction rates for **2** and **4** at lower methanol concentrations were too slow to allow second order rate constants to be obtained.

Table S4. Rate constants measured for the Eyring plot for the self-decay of **2**-OCH_3 (Figure 9, inset). All k_{obs} values are averages of data from three measurements.

T (ºC)	-85	-80	-75	-70	-65	-60	-55	-50
$k_{obs}/(s^{-1})$	0.012	0.024	0.040	0.080	0.13	0.33	0.44	0.78

Table S5. Rate constants for DHA (2 mM) oxidation by **1** in the presence of 1 M H_2O and varying amounts of 2,6-lutidine in MeCN at -30 ºC under Ar (Figure S5).

[2,6-lutidine]/mM	0	1.0	2.0	3.0	4.0
$k_{obs}/(s^{-1})$	0.0018	0.049	0.080	0.14	0.16

References

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