Supplementary Information to the Paper

Kinetics and mechanism of PPh_3 oxygenation with $^3O_2$ catalyzed by a 1,3,2-oxazaphosphole as flavin mimic.

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Kinetics

The method of Hiatt et al.[1] was adopted. The λ_{max} value for PPh_3 is 260 (ε = 14000 Mcm^{-1}) nm. That of $OPPh_3$ is 260 nm with ε = 2200 Mcm^{-1}. Because of the almost identical λ_{max} of PPh_3 and $OPPh_3$ correction have to be made according to the following:

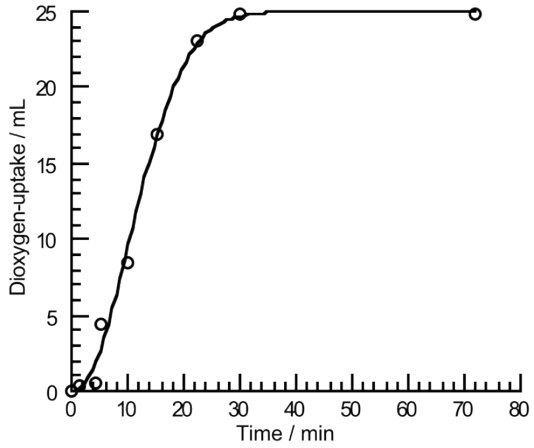
$$A = (\varepsilon_{PPh3} [PPh_3] + \varepsilon_{OPPh3} [OPPh_3]) l$$

$$[PPh_3] = [PPh_3]_0 - [OPPh_3]$$

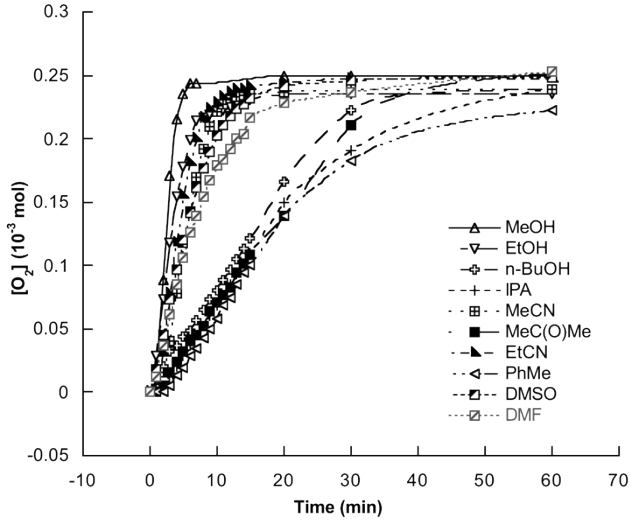
where A is absorbance measured, l the pathway of the cuvette and $[PPh_3]_0$ the starting concentration in mol dm^{-3}.

1 R. Hiatt, R. J. Smythe and C. McColeman, *Can. J. Chem*. 1971, **49**, 1707-1711.

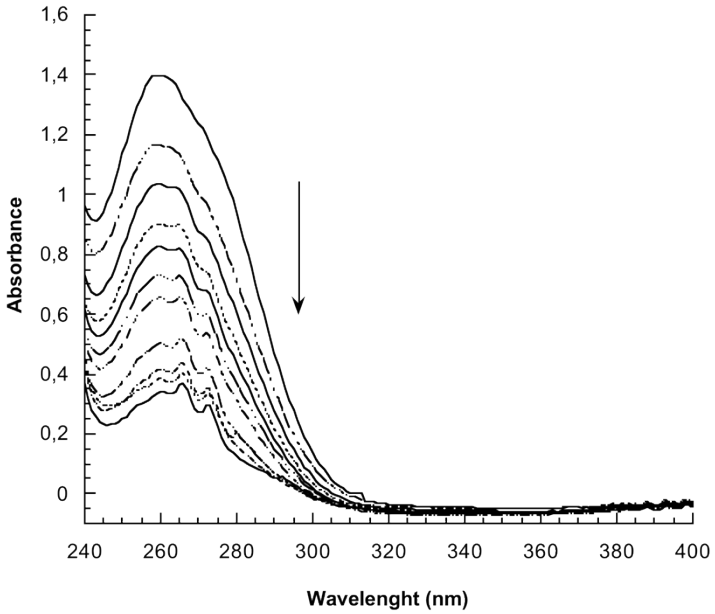
Figure 1. The dioxygen uptake of 2,2-dihydro-2,2,2-triphenylphenanthro [9,10-d]1,3,2λ^5-oxazaphosphole (**3**) 1.06 mmol in 10 ml acetonitrile at 20°C and 1 bar O_2 pressure.



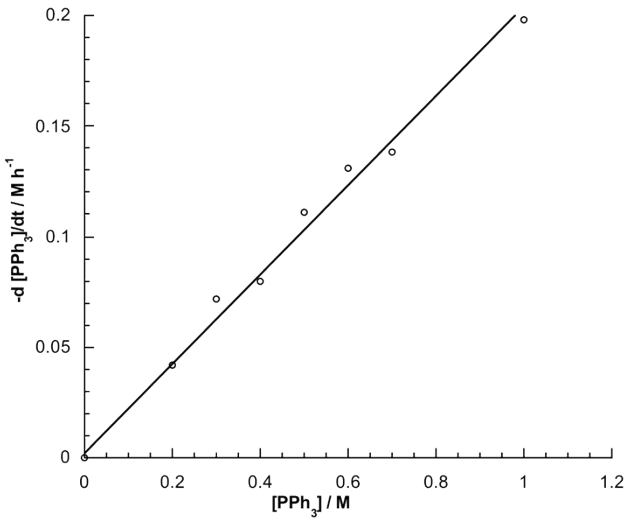
SFigure 2. The dependence of O_2-uptake of **3** on the solvents. Conditions: Solvent 20 mL, 1,3,2-oxazaphosphole (**3**) 0.25 mmol, 25ºC, 1 bar O_2 pressure.



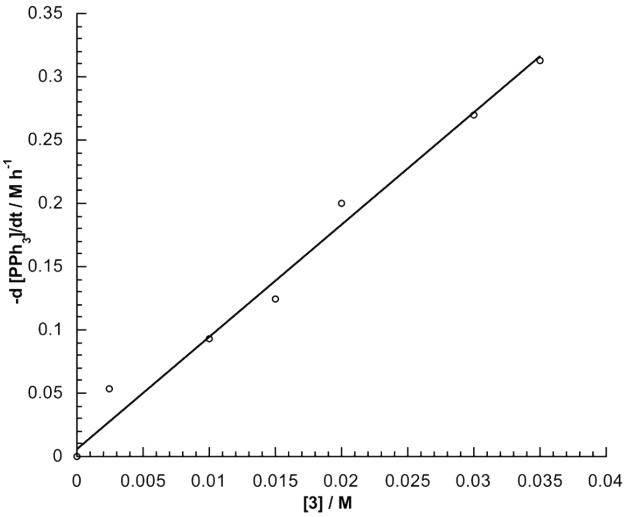
SFigure 3. The time course of the PPh_3 oxygenation followed by UV-Vis spectroscopy at 260 nm, 80ºC, 1 bar O_2 pressure in DMF 20 mL.



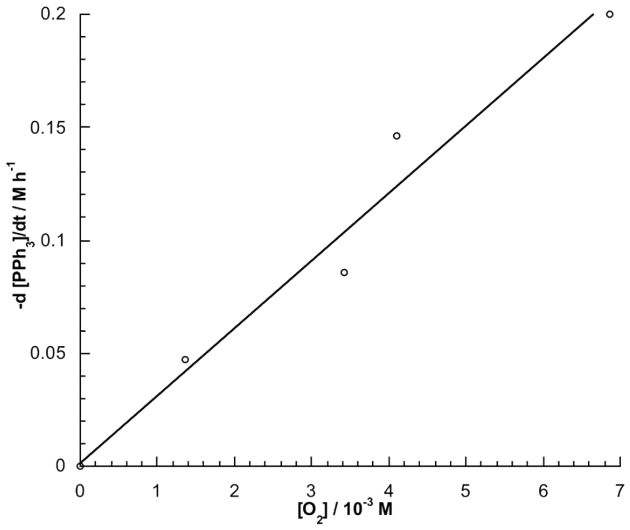
SFigure 4. Plot of reaction rate *vs.* the initial concentration of PPh_3.



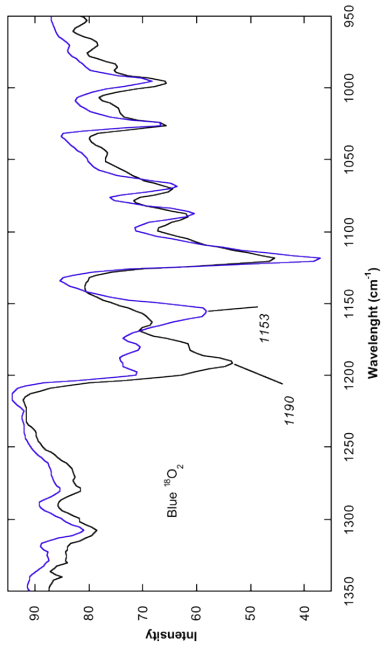
SFigure 5. The dependence of the reaction rate of the catalyst concentration [**3**].



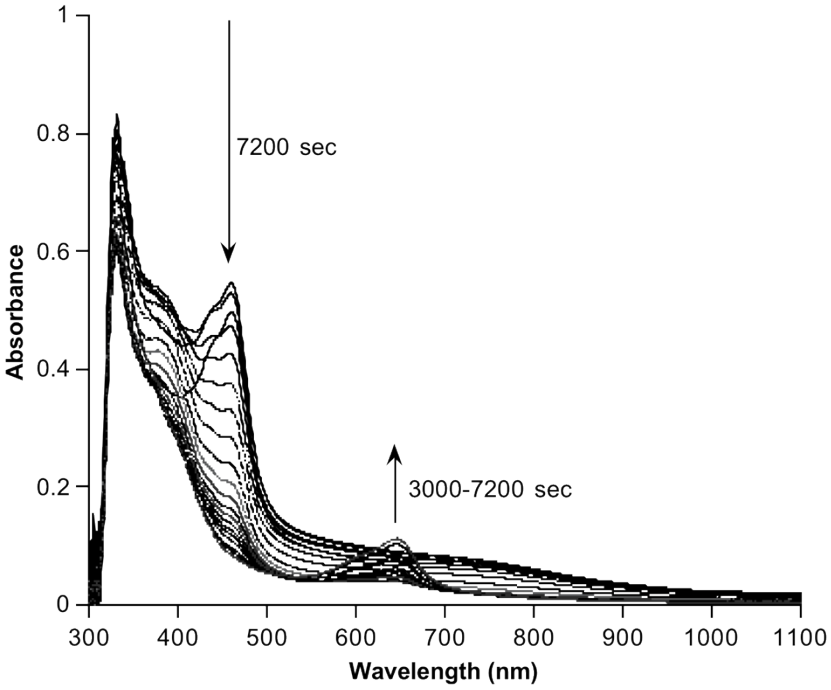
SFigure 6. The dependence of the reaction rate on the dioxygen concentration.



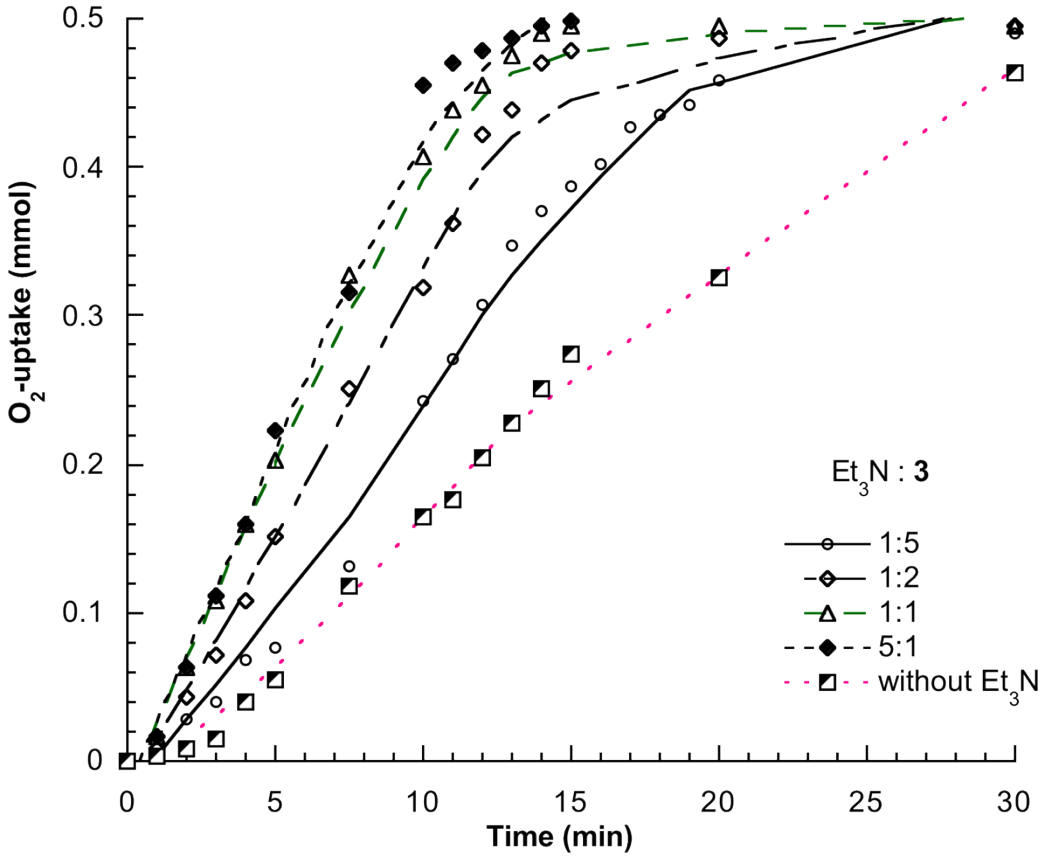
SFigure 7. The IR spectra of the reaction product O=PPh_3 using $^{16}O_2$ or $^{18}O_2$.



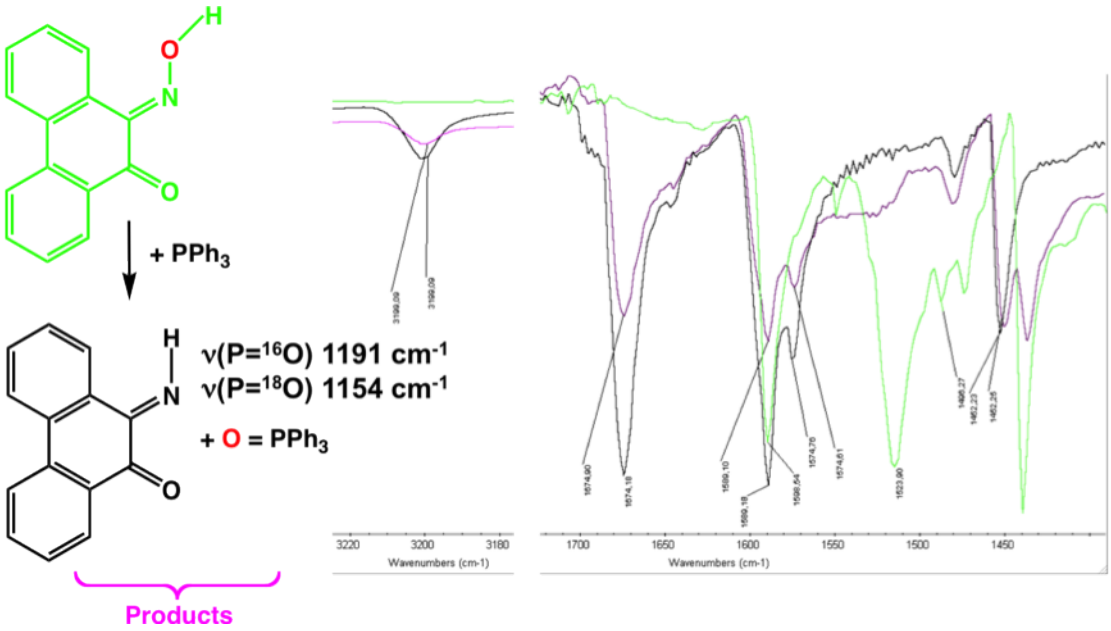
SFigure 8. UV-Vis spectra of the reaction of **7** with KO_2.



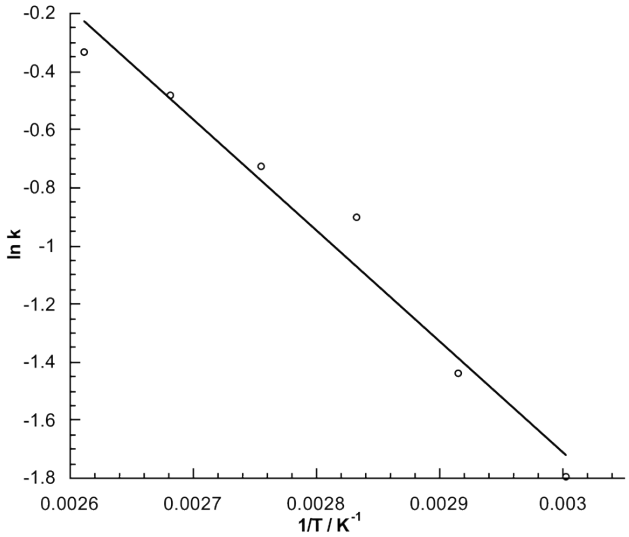
SFigure 9. The effect of added NEt_3 on the reaction rate.



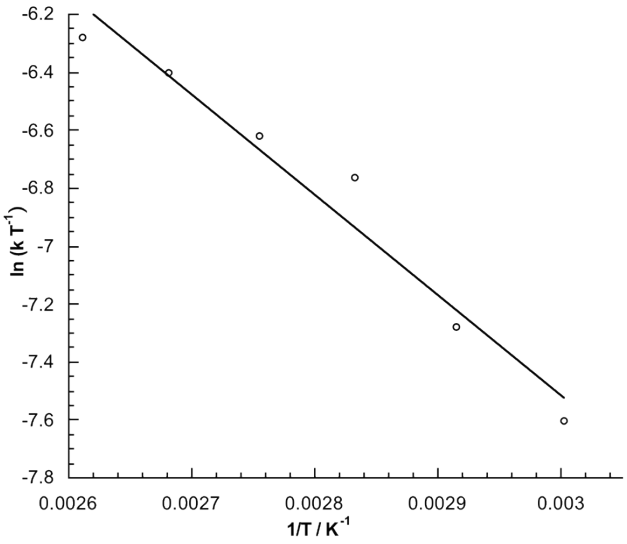
SFigure 10. The IR spectra of the reaction product (red) of 9,10-phenanthrenequinone oxim (green) and PPh_3. The 9,10-phenanthrenequinone imine (black) is also shown. The ν(P=O) vibrations of $OPPh_3$ are not shown.



SFigure 11. The Arrhenius plot.



SFigure 12. The Eyring plot.



STable 1. Summary of the kinetic data.

Entry	T (K)	$[O_2]$ (10^{-3}M)	$[PPh_3]$ (M)	[cat] (10^{-2} M)	$d[PPh_3]/dt$ ($10^{-5}s^{-1}$)	k_{obs} ($10^{-1}M^{-2}s^{-1}$)
1	353	6.86	0.2	2.00	5.44±0.18	3.97±0.13
2	353	6.86	0.3	2.00	5.67±0.56	4.13±0.41
3	353	6.86	0.4	2.00	6.14±0.15	4.47±0.11
4	353	6.86	0.5	2.00	5.56±0.22	4.05±0.16
5	353	6.86	0.6	2.00	6.03±0.12	4.39±0.09
6	353	6.86	0.7	2.00	5.28±0.07	3.85±0.05
7	353	6.86	1.0	2.00	5.50±0.20	4.01±0.14
8	353	6.86	0.5	1.00	2.58±0.07	3.77±0.10
9	353	6.86	0.5	1.50	3.44±0.10	3.35±0.10
10	353	6.86	0.5	3.00	7.47±0.75	3.63±0.37
11	353	6.86	0.5	3.50	8.92±0.22	3.71±0.09
12	353	1.37	0.5	2.00	1.31±0.19	4.77±0.70
13	353	3.42	0.5	2.00	2.39±0.11	3.49±0.16
14	353	4.10	0.5	2.00	3.78±0.19	4.61±0.23
*						**3.91±0.08**
15	333	6.20	0.5	2.00	2.06±0.07	1.66±0.06
16	343	6.56	0.5	2.00	3.11±0.15	2.37±0.11
17	363	7.48	0.5	2.00	7.22±0.53	4.83±0.35
18	373	7.70	0.5	2.00	9.53±0.40	6.19±0.26
19	383	7.45	0.5	2.00	10.67±0.70	7.16±0.47

*Mean value of the kinetic constant k_{obs} and its standard deviations $\sigma(k_{obs})$ were calculated as $k_{obs} = (\sum_i w_i k_i / \sum_i w_i)$ and $\sigma(k_{obs}) = (\sum_i w_i (k_i - k_2)^2/(n-1)\sum_i w_i)^{1/2}$, where $w_i = 1/\sigma^2_i$.

Activation parameters

Ea = 31.61±2.86 kJ mol^{-1}

$\Delta H^{\ddagger}$ = 28.67±2.88 kJ mol^{-1}

$\Delta S^{\ddagger}$ = -174±8 J mol^{-1} K^{-1}