Supporting information

Oxidation of Phenols by the Excited State of an Osmium(VI) Nitrido Complex

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Table of Contents

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AV400 (400 MHz) FT-NMR spectrometer. Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (Me_4Si). Elemental analysis was performed on an Elementar Vario MICRO Cube elemental analyzer. IR spectra of the solid samples as KBr discs were obtained within the range 4000–400 cm^{-1} on an AVATAR 360 FTIR spectrometer. All of the electronic absorption spectra were recorded on a Hewlett–Packard 8453 or Hewlett–Packard 8452A diode-array spectrophotometer. Electrospray ionization mass spectrometry (ESI-MS) was performed using a PE-SCIEX API 365 triple quadruple mass spectrometer.

X-ray Crystallography. The crystal structures were determined on an Oxford Diffraction Gemini S Ultra X-ray single-crystal diffractometer using graphite-monochromated Mo/K_a radiation (λ = 0.71073 Å) for **1b**, **2a**, **3b**, **4a**, respectively. The structures were solved by using direct methods with the Olex2 for **2a** and SHELX2014 program for **3b, 4a**.[1,2] Crystal data and structure refinement details for compounds **1b**, **2a**, **3b** and **4a** are summarized in Table S1. The positions of the other non-hydrogen atoms were located after refinement by full matrix least-squares by using the SHELXL-2014/7 program.[3] In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by SHELXL-2014/7 program. Crystallographic data (including structure factors) of the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Centre (CCDC) with the depository numbers CCDC **2406139-2406142.**

Reference:

[1] (a)Sheldrick, G. M. SHELX-97: Programs for Crystal Structure Analysis, release 97-2, University of Gottingen, Germany, 1997. (b)Sheldrick, G. SHELXT - Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A* 2015, **71**, 3-8.

[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, **42**, 339-341.

[3] Sheldrick, G. Crystal structure refinement with SHELXL. *Acta Crystallographica Section C* 2015, **71**, 3-8.

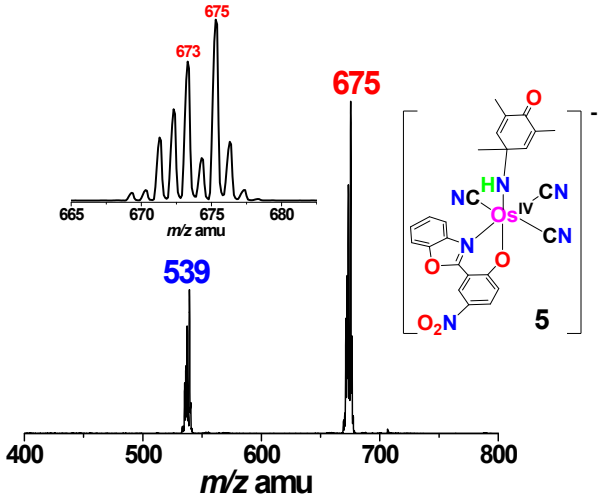

Figure S1. ESI/MS (-ve mode) for the reaction of **OsN** with 10 equiv. 2,4,6-$Me_3C_6H_2OH$.

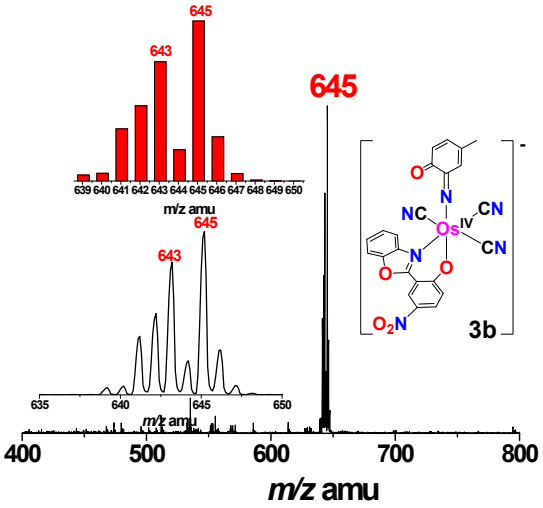

Figure S2. ESI/MS (-ve mode) of **3b** in MeOH.

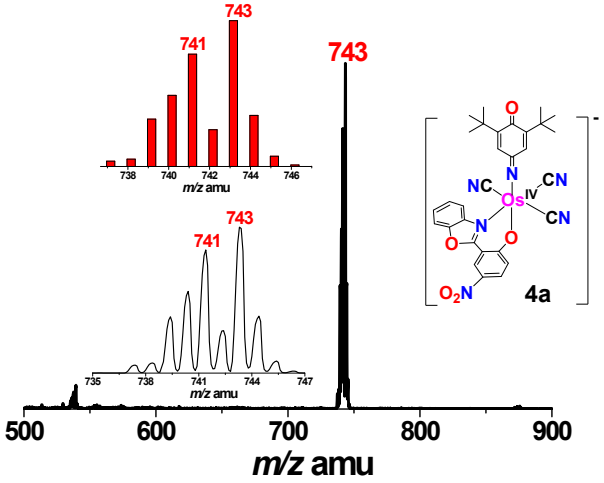

Figure S3. ESI/MS (-ve mode) of **4a** in MeOH.

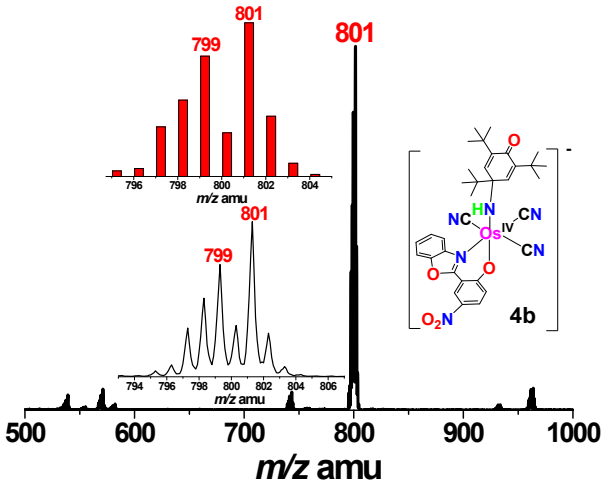

Figure S4. ESI/MS (-ve mode) of **4b** in MeOH.

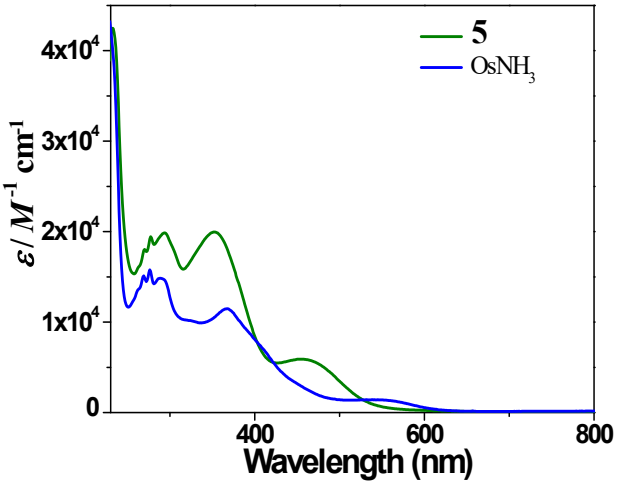

Figure S5. UV/vis spectra of (PPh_4)**5** and **$OsNH_3$**.

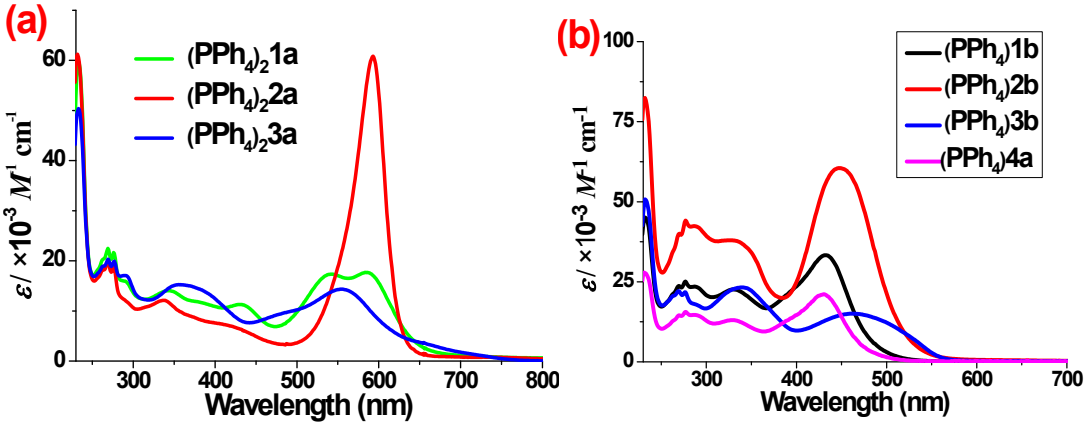

Figure S6. UV/vis spectra of (a) osmium(II) **1a-3a** and (b) osmium(IV) products **1b-3b**, **4a**.

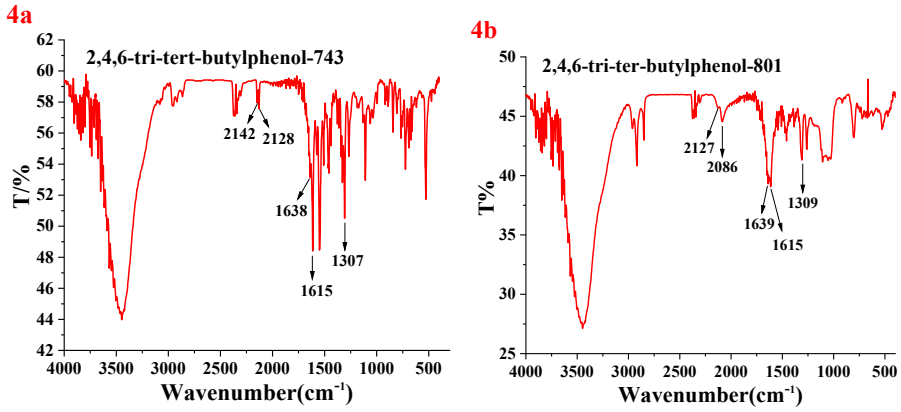

Figure S7. IR spectra of complexes (PPh_4)**4a** and (PPh_4)**4b**.

Table S1. Selected IR data of **1-5.**

	Selected IR (cm^{-1})			
	v(N-H)	*v*(C≡N)	*v*(C=O)	*v*(C=N)
1a	3248	2096,2070	1645	1609
1b	/	2145,2135	1630	1611
2a	3235	2108,2082	1638	1609
2b	/	2153,2141	1639	1614
3a	3253	2125,2086	1645	1612
3b	/	2139,2130	1649	1614
4a	/	2142,2128	1638	1615
5	3247	2135,2127	/	1610

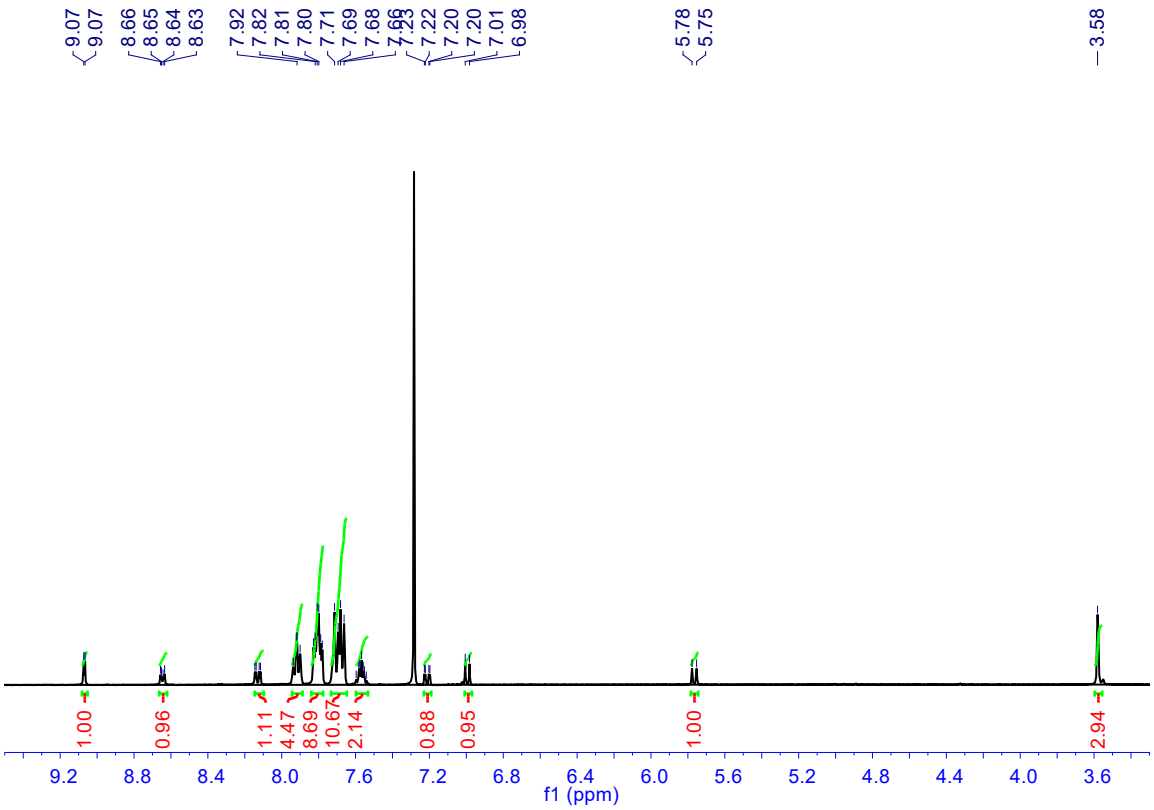

Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (PPh_4)**3b.**

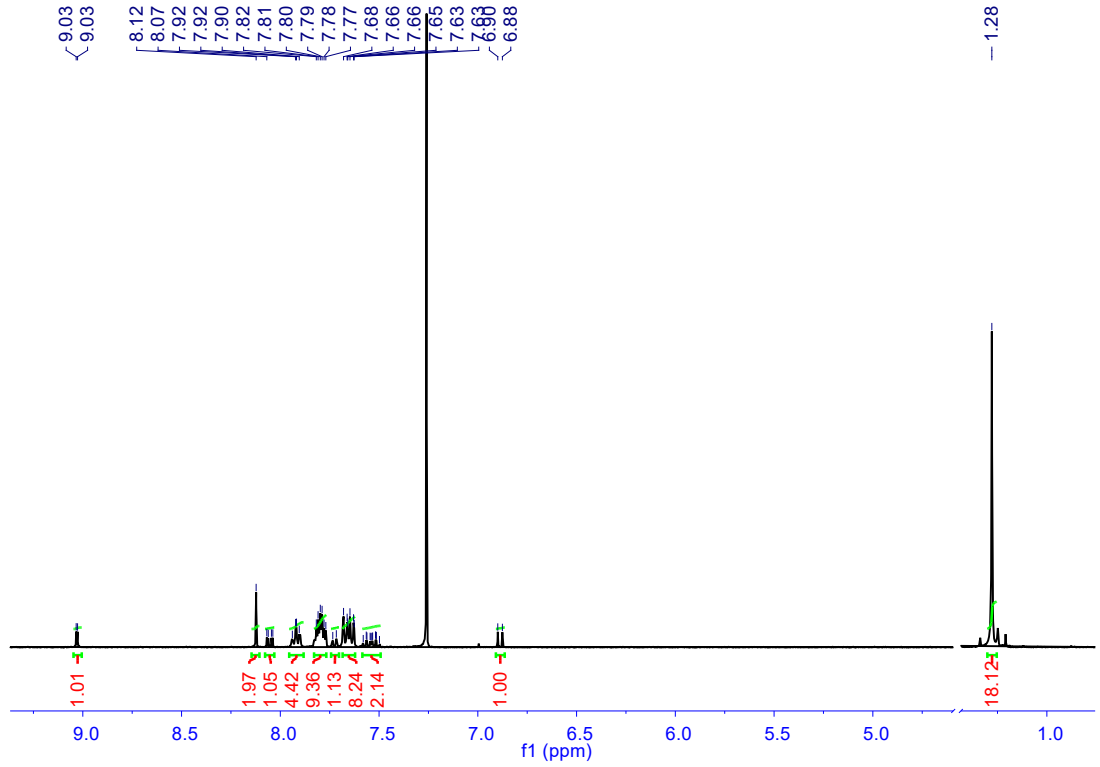

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (PPh_4)**4a.**

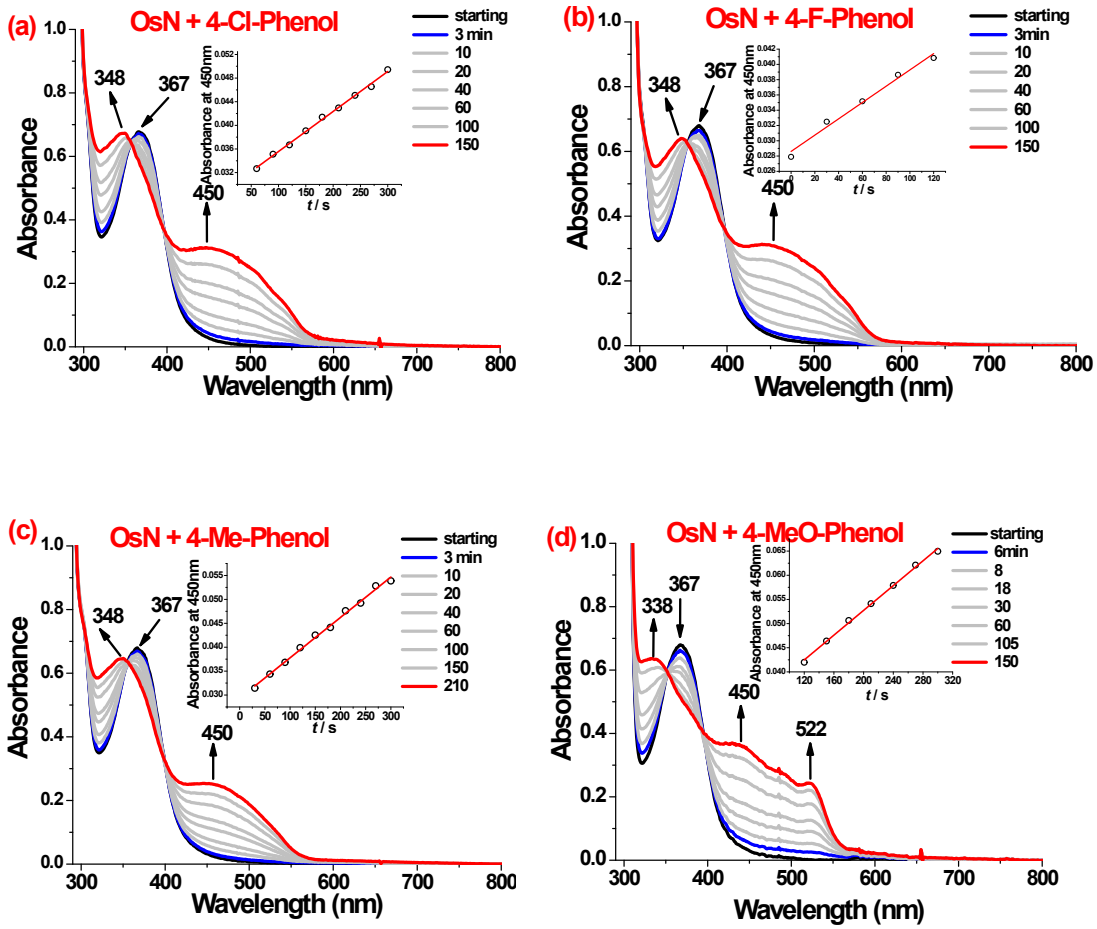

Figure S10. UV/vis spectral changes for the photoreaction of **OsN*** (2.5×10^{-5} M) with 100 equiv. of 4-X-phenols; The inset shows the time-trace of absorbance at 450 nm for the photoreaction of **OsN*** with 4-X-phenols.

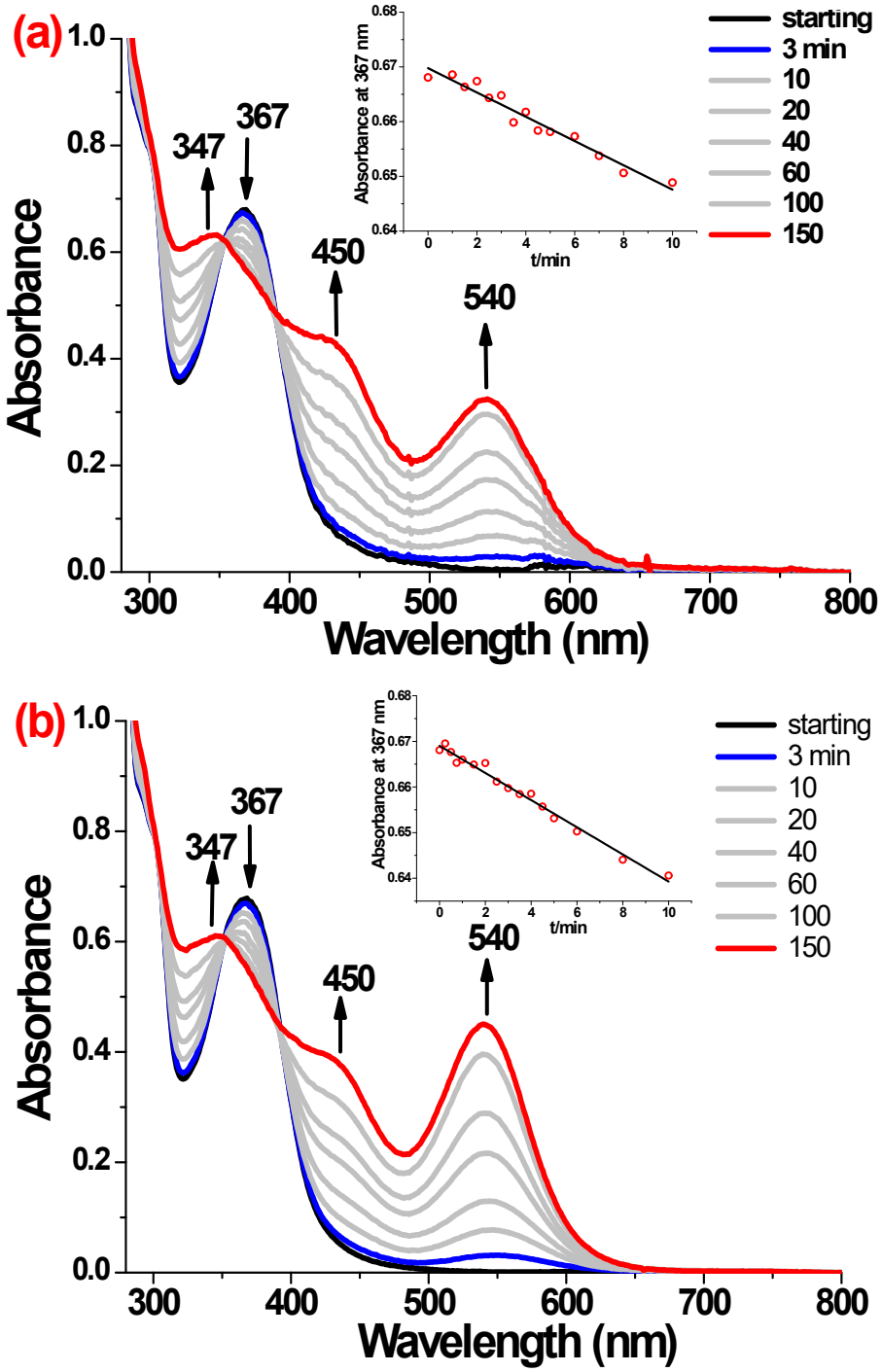

Figure S11. The UV/vis spectral change for the photoreaction of **OsN** (2.5×10^{-5} M) with (a)phenol and (b) d^6-phenol (2.5×10^{-3} M).

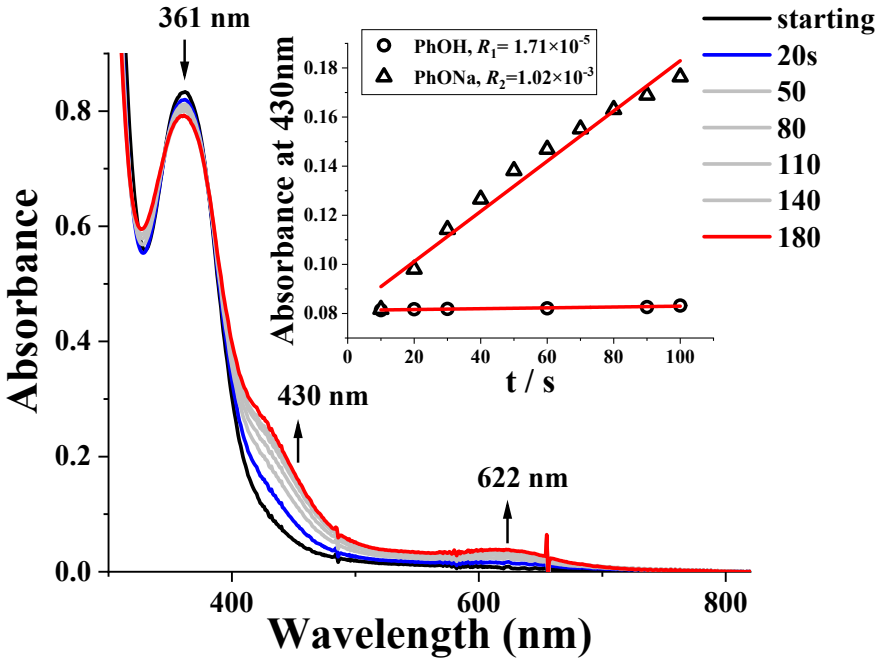

Figure S12. UV/vis spectral changes for the photoreaction of **OsN** (1×10^{-4} M) with phenol (1×10^{-3} M) and sodium phenoxide (1×10^{-3} M) in MeCN. Inset shows the time-trace absorbance at 430 nm. R_1=1.71 × 10^{-5}, R_2=1.02 × 10^{-3}.

Table S2. Crystal data and structure refinement details for (PPh_4)**1b**, $(PPh_4)_2$**2a**, (PPh_4)**3b** and (PPh_4)**4a**.

	(PPh_4)**1b**	$(PPh_4)_2$**2a**	(PPh_4)**3b**	(PPh_4)**4a**
Formula	$C_{48}H_{35}N_6O_5OsP$	$C_{72}H_{60}Cl_2N_6O_8OsP_2$	$C_{47}H_{33}N_6O_5OsP$	$C_{54}H_{47}N_6O_5OsP$
Mr	996.99	1460.30	982.96	1081.14
T /K	100 (1)	100 (1)	296 (2)	193(2)
Crystal syst	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/C$	P-1	P-1	P-1
a/Å	8.1639(2)	11.9163(4)	12.2391 (19)	13.1913(5)
b/Å	15.8744(6)	13.2565 (4)	12.597 (3)	13.8662(5)
c/Å	34.8653(13)	20.5061(4)	14.997 (2)	15.8504(6)
α, (°)	/	85.321(2)	94.686 (4)	70.3260(10)
β, (°)	93.758(3)	85.804(2)	105.948 (3)	87.0720(10)
γ, (°)	/	83.152(3)	92.276 (3)	63.2750(10)
V/ Å^3	4508.7(3)	3198.88(16)	2211.1 (7)	2420.96(16)
Z	4	2	2	2
ρ_{calcd}, Mg m^{-3}	1.469	1.516	1.476	1.483
F(000)	1984	1476	976	1088
Collected refl.	23964	56623	36179	27457
Unique refl.	10738	15815	10020	9889
Final *R* indices, *I* > 2σ(I)	R_1(obs) = 0.053 *w*R(all) = 0.095	R_1(obs) = 0.046 *w*R(all) = 0.104	R_1(obs) = 0.045 *w*R(all) = 0.085	R_1(obs) = 0.039 *w*R(all) = 0.090
GOF	1.06	1.06	1.02	1
No. of par.	552	825	542	610