

## *Supplementary Information*

### **A Cytotoxic Nitrido-osmium(VI) Complex Induces Caspase-mediated Apoptosis in HepG2 Cancer Cells**

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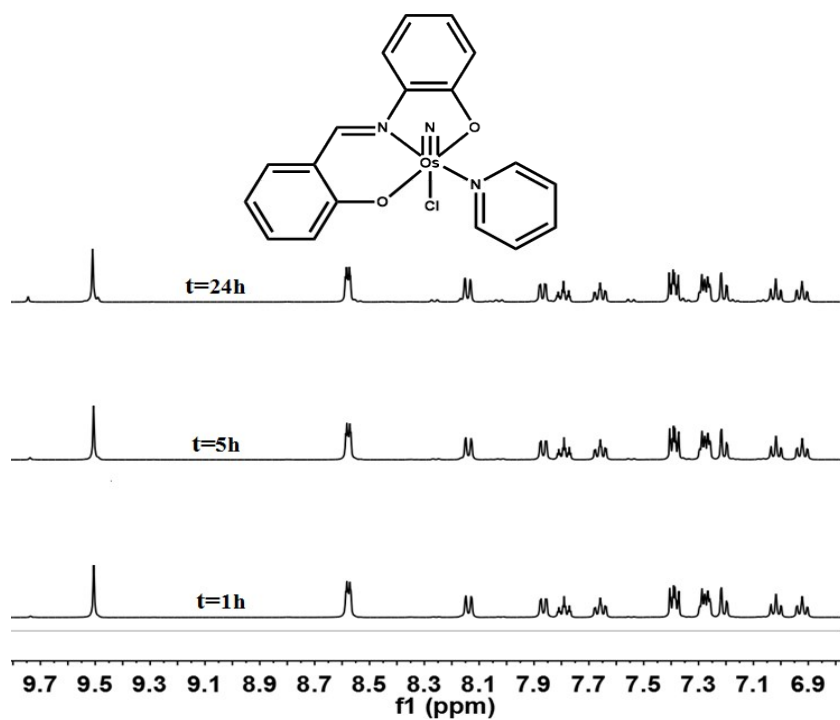
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**Table S1** Crystal data and structure refinement details for **2·1.5CH<sub>2</sub>Cl<sub>2</sub>**

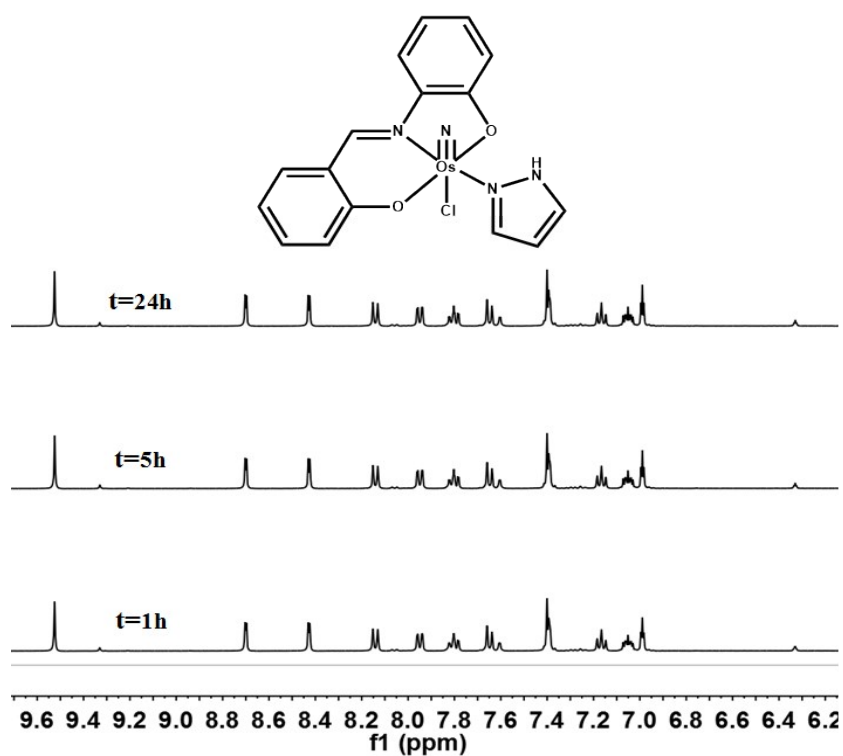
	<b>2·1.5CH<sub>2</sub>Cl<sub>2</sub></b>
Formula	C <sub>39</sub> H <sub>34</sub> Cl <sub>8</sub> N <sub>6</sub> O <sub>4</sub> Os <sub>2</sub>
Mr	1314.72
Crystal system	Triclinic
Space group	<i>P</i> -1
a/Å	7.1575(3)
b/Å	12.0799(5)
c/Å	12.5607(5)
α (°)	78.544(3)
β (°)	87.869(3)
γ (°)	84.639(3)
V/ Å <sup>3</sup>	1059.54(8)
Z	1
ρ <sub>c</sub> /Mg m <sup>-3</sup>	2.060
F(000)	630
N <sub>ref</sub>	6725
Unique refl.	3935
Final R indices, I > 2σ(I) R <sub>a</sub>	R1(obs) = 0.0427, wR(all) = 0.1097
GOF	1.066
No. of parameters	335

**Table S2.** Selected bond lengths (Å) and angles (deg) of complex **2**.

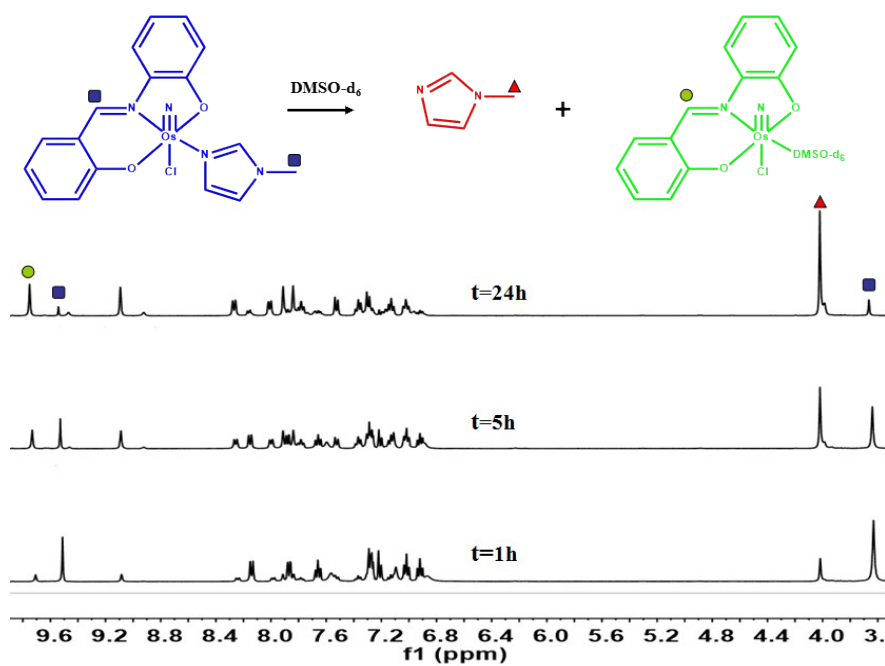
<b>Bond lengths</b>			
Os(1)-Cl(1)	2.6109(14)	Os(1)-O(1)	2.008(4)
Os(1)-O(2)	2.024(4)	Os(1)-N(1)	2.110(12)
Os(1)-N(2)	2.038(5)	Os(1)-N(3)	1.642(5)
<b>Bond angles</b>			
O(1)-Os(1)-Cl(1)	83.33(14)	N(2)-Os(1)-Cl(1)	84.46(16)
O(1)-Os(1)-O(2)	163.5(2)	N(2)-Os(1)-N(1)	165.2(5)
O(1)-Os(1)-N(1)	85.7(4)	N(3)-Os(1)-Cl(1)	175.76(19)
O(1)-Os(1)-N(2)	95.4(2)	N(3)-Os(1)-O(1)	99.2(2)
O(2)-Os(1)-Cl(1)	80.45(14)	N(3)-Os(1)-O(2)	97.2(2)
O(2)-Os(1)-N(1)	94.7(4)	N(3)-Os(1)-N(1)	95.7(6)
O(2)-Os(1)-N(2)	80.10(19)	N(3)-Os(1)-N(2)	98.7(2)
N(1)-Os(1)-Cl(1)	81.0(5)		



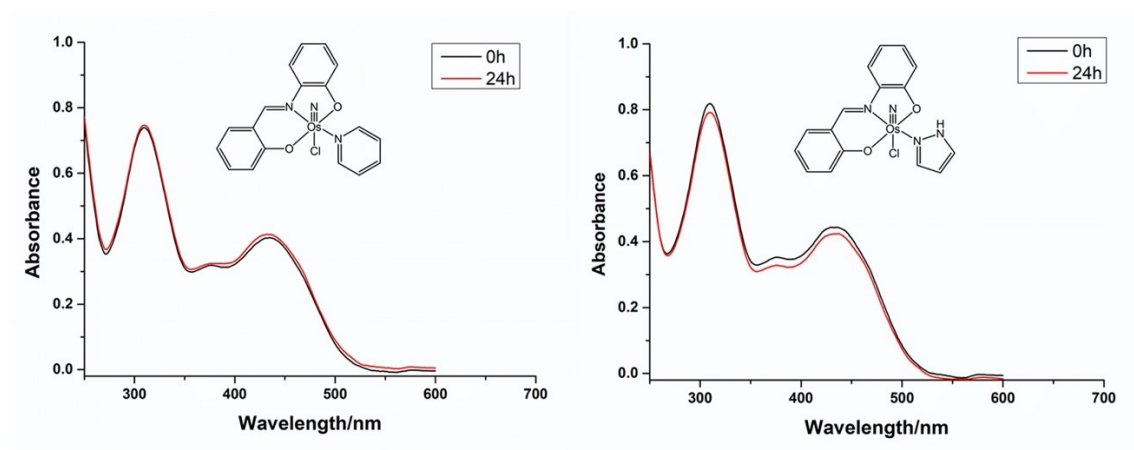
**Figure S1.**  $^1\text{H}$  NMR spectra of **2** ( $d_6$ -DMSO) collected at 1, 5 and 24h.



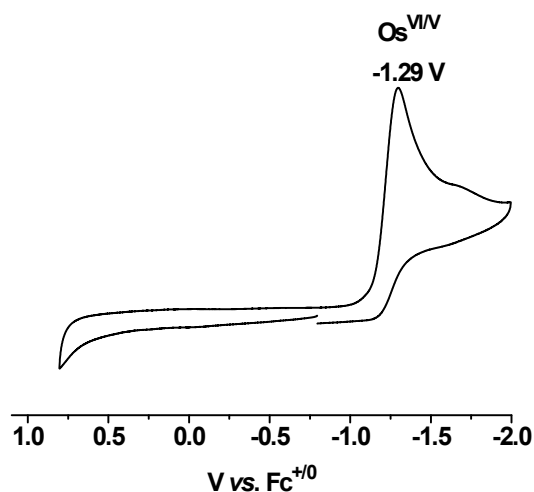
**Figure S2.**  $^1\text{H}$  NMR spectra of **3** ( $d_6$ -DMSO) collected at 1, 5 and 24h.



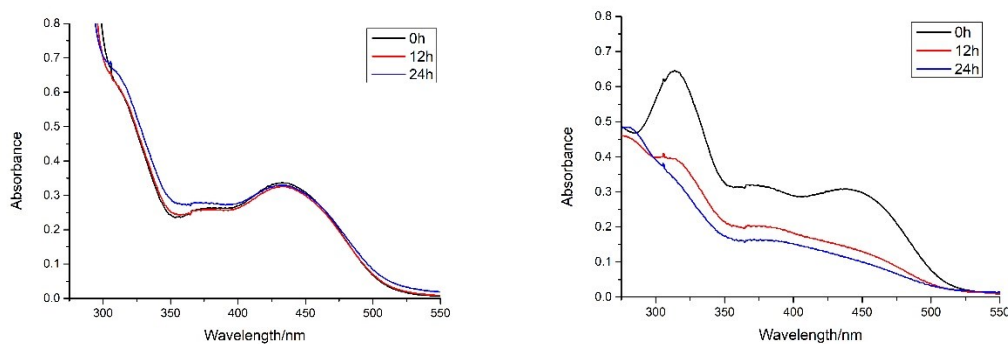
**Figure S3.**  $^1\text{H}$  NMR spectra of **4** ( $\text{d}_6$ -DMSO) collected at 1, 5 and 24h.



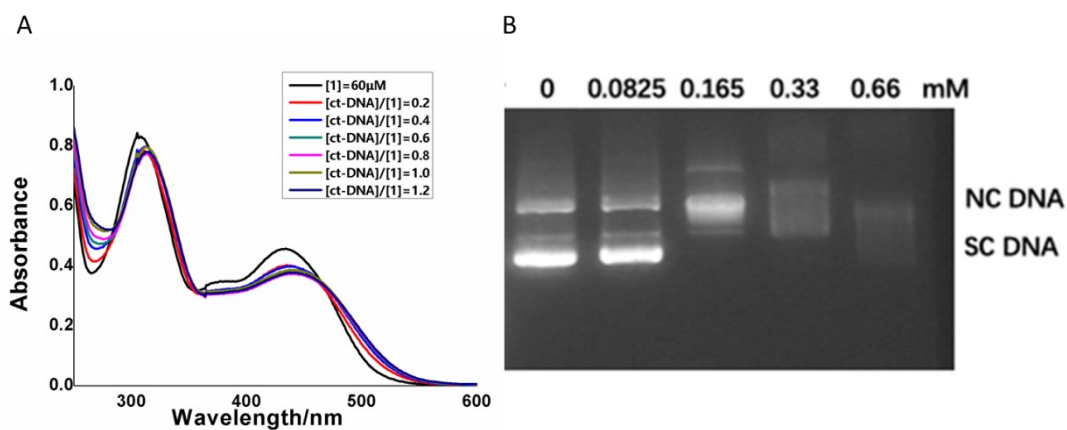
**Figure S4.** UV-Vis spectral changes of 66 $\mu\text{M}$  **2** (left) and **3** (right) in DMSO/PBS (3:1000) taken at 0 and 24h.



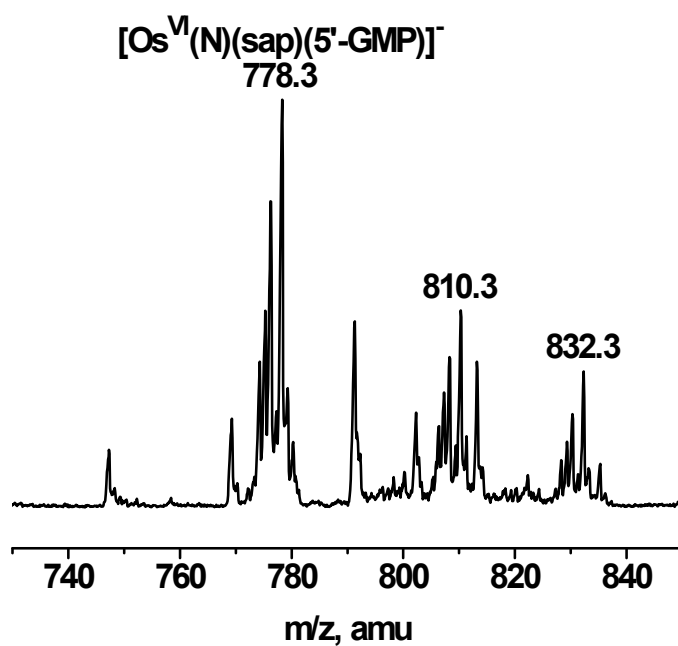
**Figure S5.** Cyclic voltammogram of **2** in CH<sub>3</sub>CN with 0.1M [N<sup>n</sup>Bu<sub>4</sub>](PF<sub>6</sub>) supporting electrolyte.



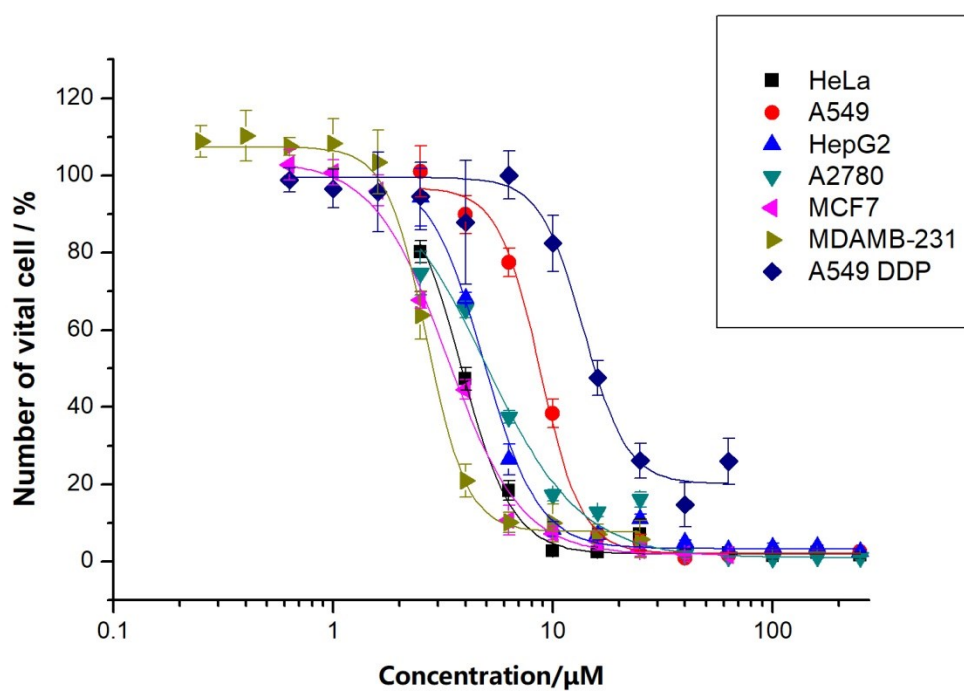
**Figure S6.** UV-vis spectral changes for the reaction of **2** (50 μM) with eight equiv. ascorbic acid (left) and GSH (right) from 0 to 24h.



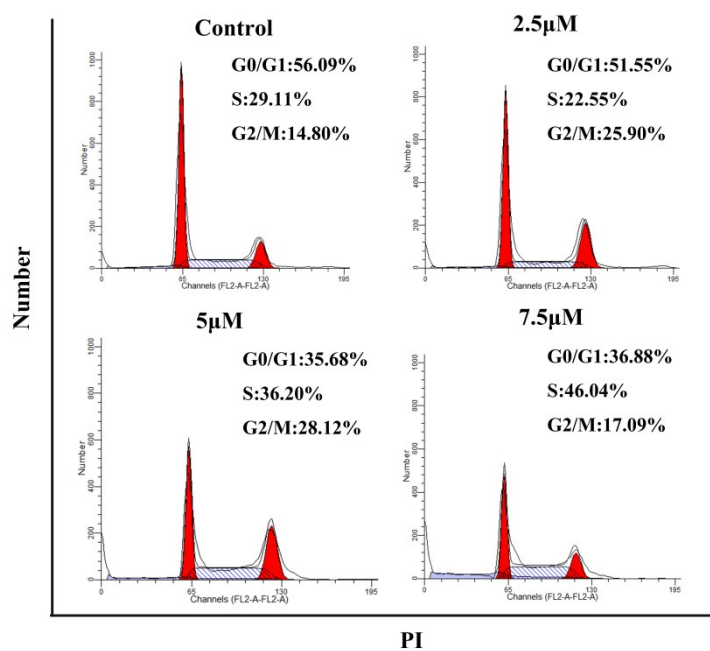
**Figure S7.** (A) UV-Vis spectral change for the reaction of **1** CT-DNA at different [DNA]/[**1**] ratios. (B) Agarose gel electrophoresis study of plasmid DNA pBR322 treated with various concentration of complex **1** for 24 h at 25°C.



**Figure S8.** ESI mass spectrum for the mixture containing **2** and 5'GMP in MeOH/H<sub>2</sub>O. The two peaks at  $m/z$  810 and 832 are assigned to  $\{[\text{Os}^{\text{VI}}(\text{N})(\text{sap})(5'-\text{GMP})]\cdot\text{MeOH}\}^-$  and  $\{\text{Na}[\text{Os}^{\text{VI}}(\text{N})(\text{sap})(5'-\text{GMP}_{-\text{H}})]\cdot\text{MeOH}\}^-$ , respectively

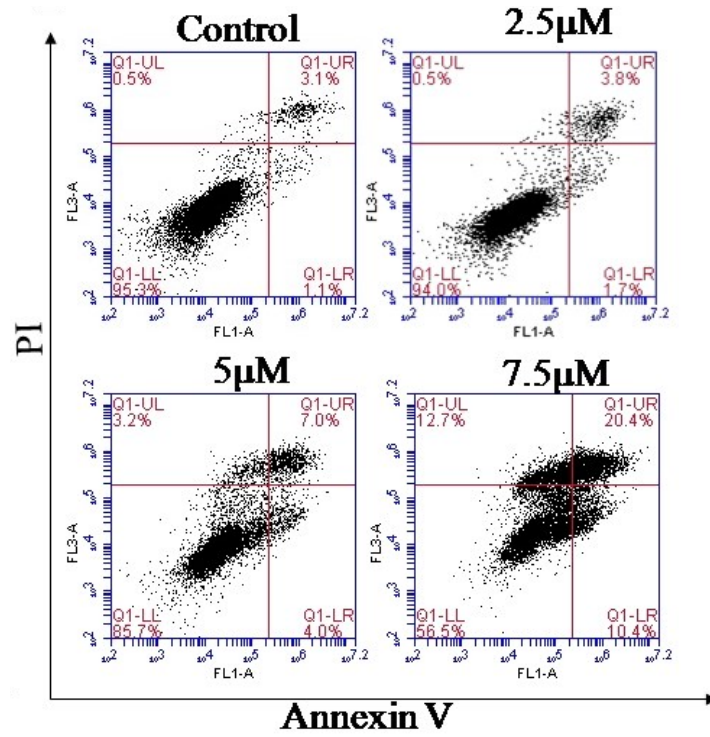


**Figure S9.** The concentration-viability curves of **2** toward seven cell lines for 48h.



**Figure S10.** Cell cycle detection in HepG2 cells using propidium iodide (PI) staining after treated with compound **2** for 24h.





**Figure S11.** Apoptosis detection in HepG2 cells of different [2] after 24 h treatment using annexin V and propidium iodide (PI) double staining.