

Electronic Supplementary Information

A half-sandwich Ru(II)-p-cymene nitrite complex selectively induces cell death in cisplatin-resistant malignant melanoma cells.

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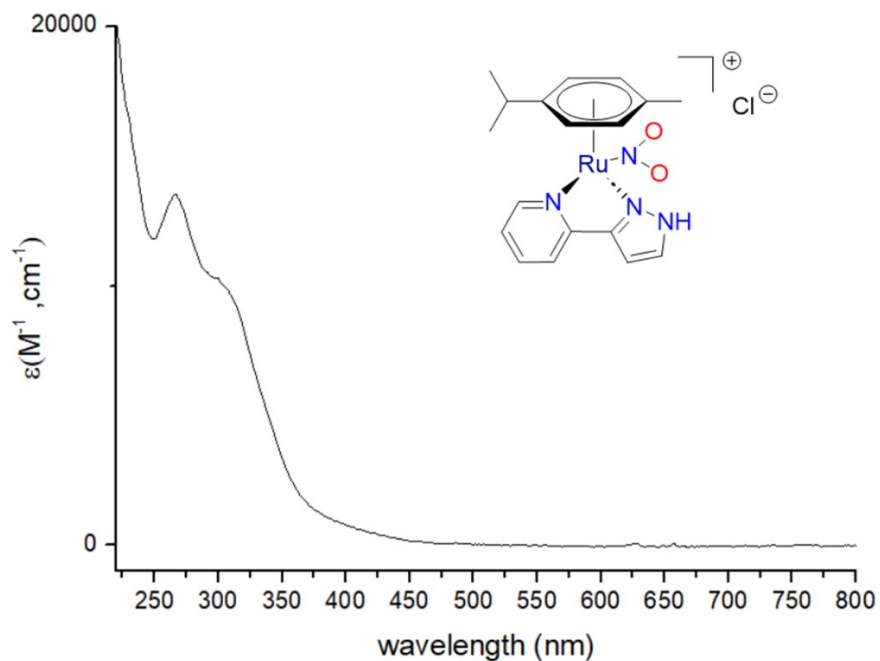


Figure S1. UV-Vis spectrum of **Ru4** (CH₃OH, 10⁻⁴M)

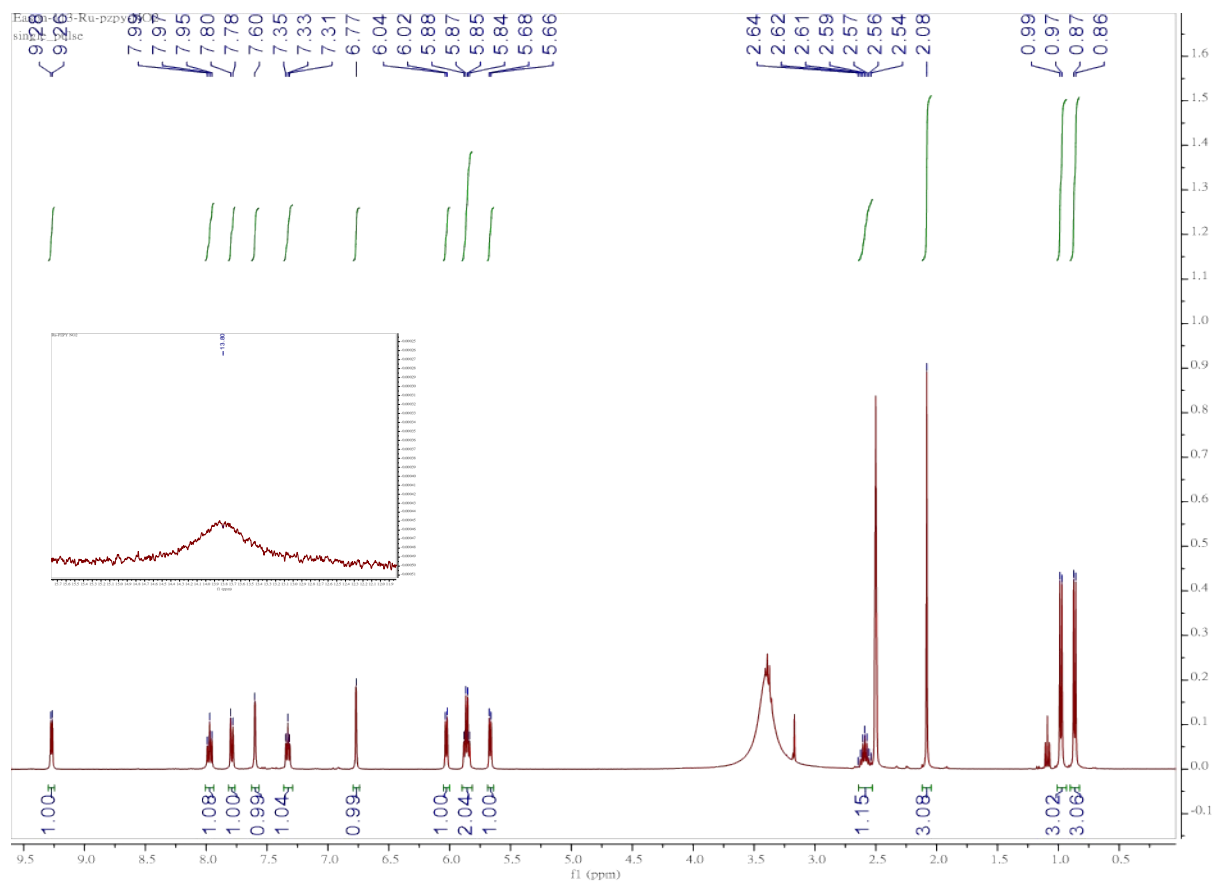


Figure S2. ¹H NMR spectrum for complex **Ru4** in d-DMSO.

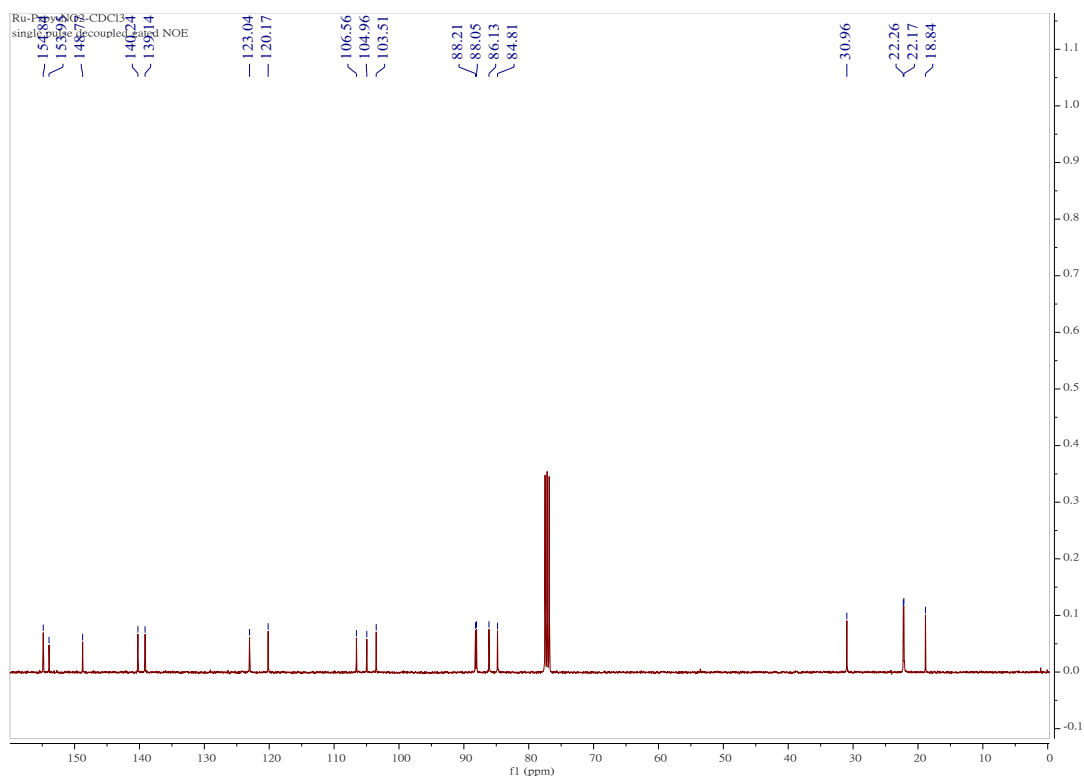


Figure S3. ^{13}C NMR spectrum for complex **Ru4** in CDCl_3 .

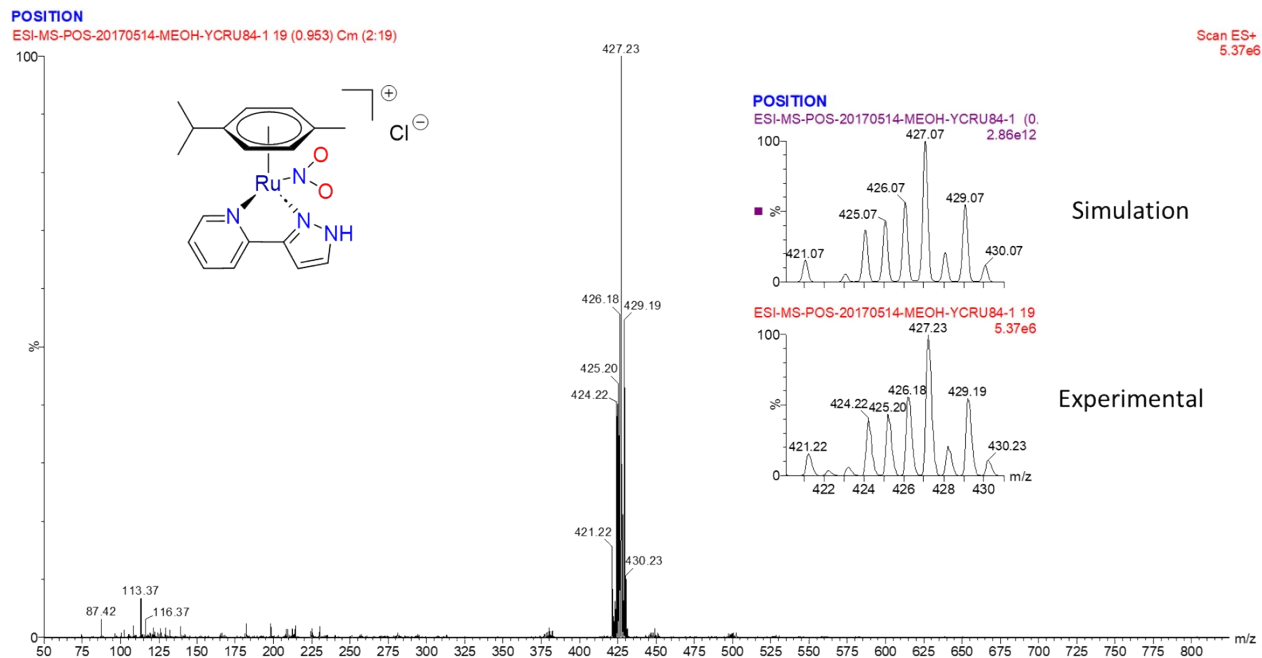


Figure S4A. ESI-Mass spectrum for complex **Ru4** in water [*p*-cymene-Ru-pzpy-NO₂]⁺ (*m/z* = 427.23).

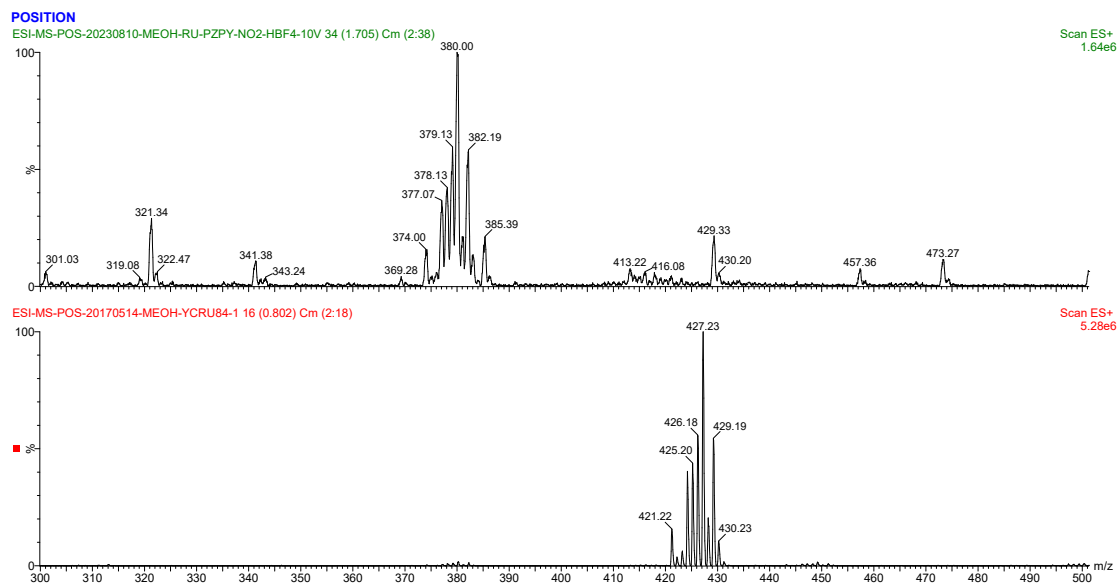


Figure S4B. ESI-Mass monitoring spectra of **Ru4** (down) and after **Ru4** treatment with HBF₄ (top). The signals at 427.23 *m/z* represent species [**Ru4**]⁺, and signals at *m/z* 380.00 represent species [**Ru4**-NO₂-H]⁺.

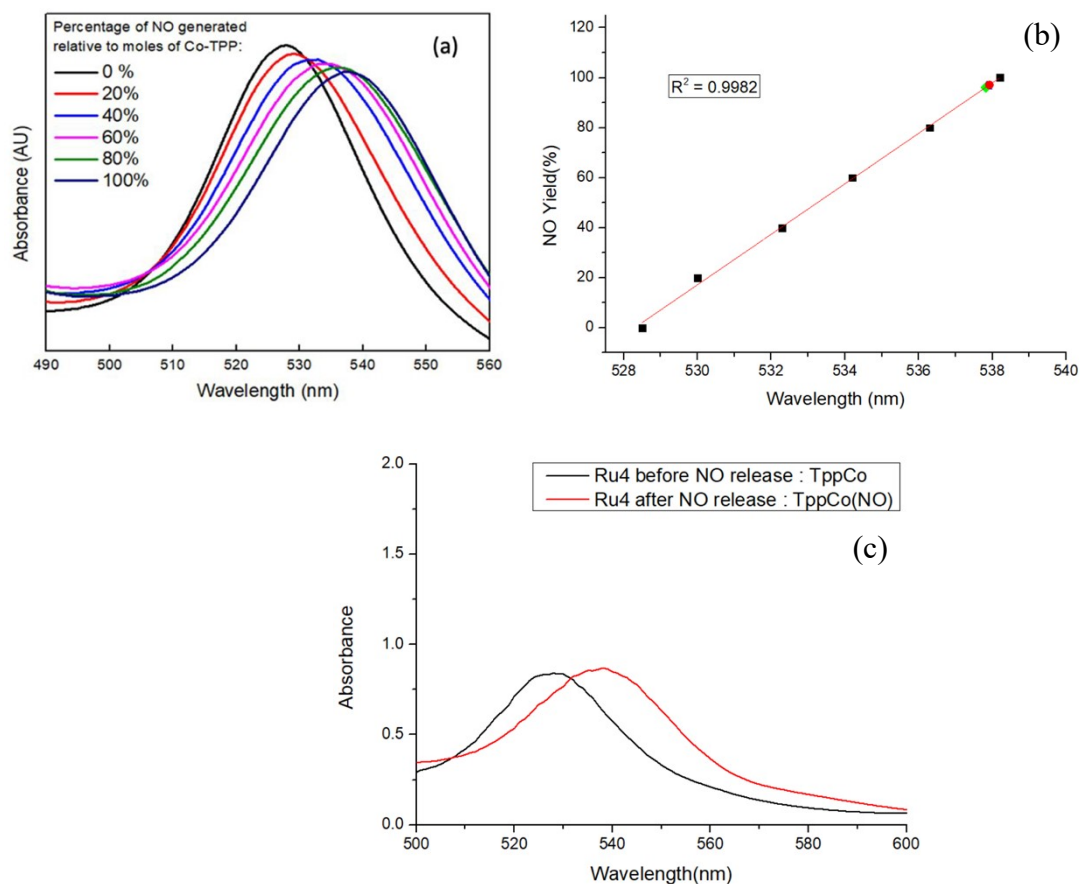


Figure S5. (a) UV-vis spectra showing the shift in the absorbance band of cobalt(II) porphyrin Co(TPP) (TPP = tetraphenylporphyrin) with increasing levels of complexation to NO. (b) Calibration curve extracted from the peak maxima, showing the linear trend in absorption maximum shift with % complexation to NO. The red dot is the NO generation yield in 96% of **Ru4**. (c) NO generation experiments for **Ru4**.

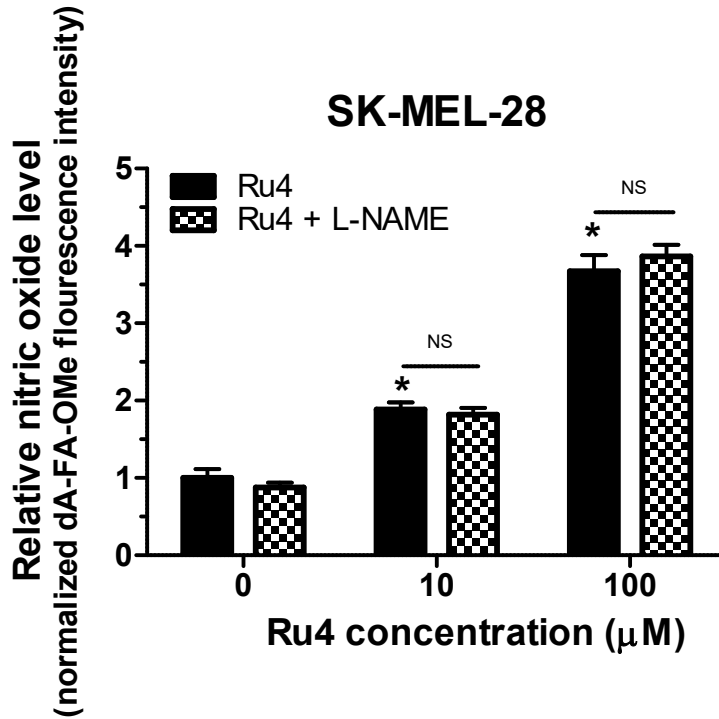
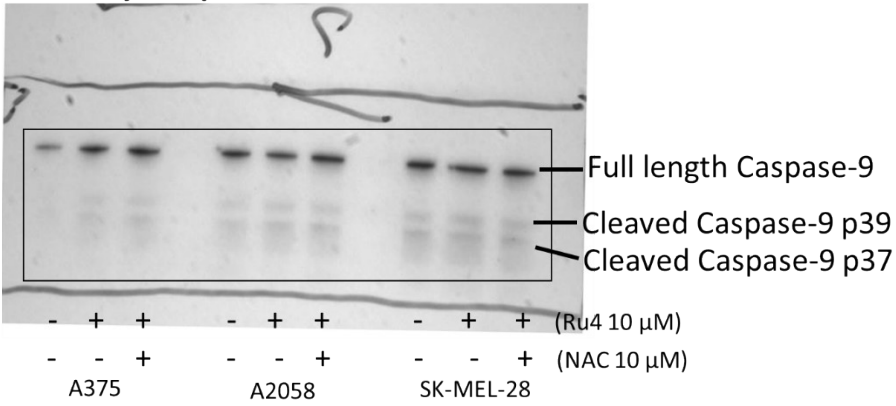
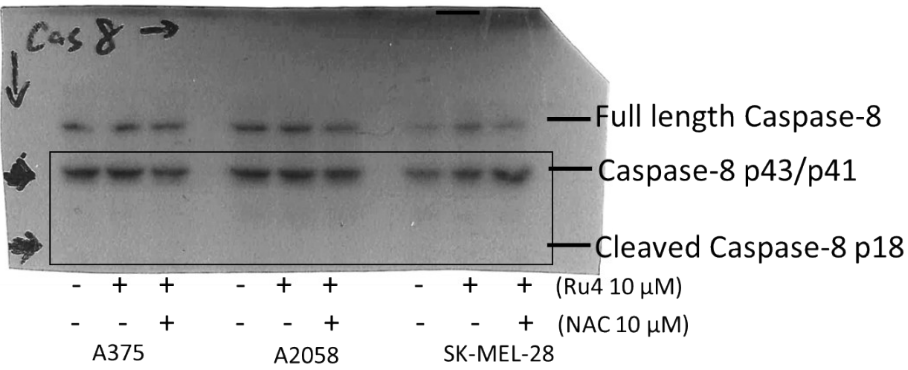


Figure S6. Ru4 treatments increased NO levels in SK-MEL-28 cells. Cultured SK-MEL-28 cells were treated with 10 or 100 μM of Ru4 for 24 h. After treatment, the NO production was detected by dA-FA-OMe probe. Non-fluorescent FA-OMe can specifically interact with NO and form the fluorescent product dA-FA-OMe. The generated fluorescence in SK-MEL-28 cells were detected by flow cytometry with 488 nm excitation laser. * $p < 0.05$, Ru4 treated vs untreated by the Kruskal-Wallis test; N = 3, means \pm SD.

Antibody: Caspase-9



Antibody: Caspase-8



Antibody: GAPDH

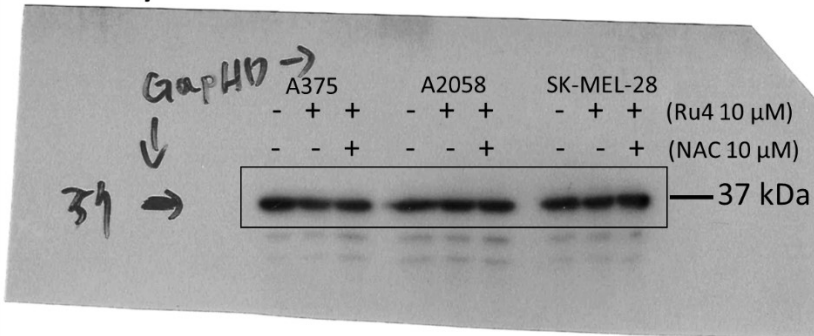


Figure S7. Western blotting images from Ru4/NAC treated A375, A2058 or SK-MEL-28 cells. The cleaved caspase 9/8 were their active forms.

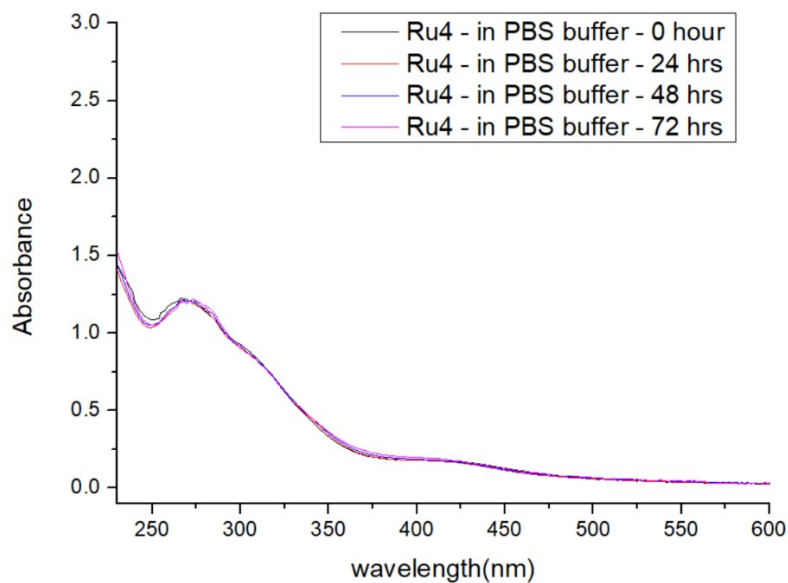


Figure S8. Time dependence of UV-vis spectra of the complex **Ru4** in phosphate-buffered saline (PBS, pH = 7.4) buffer.

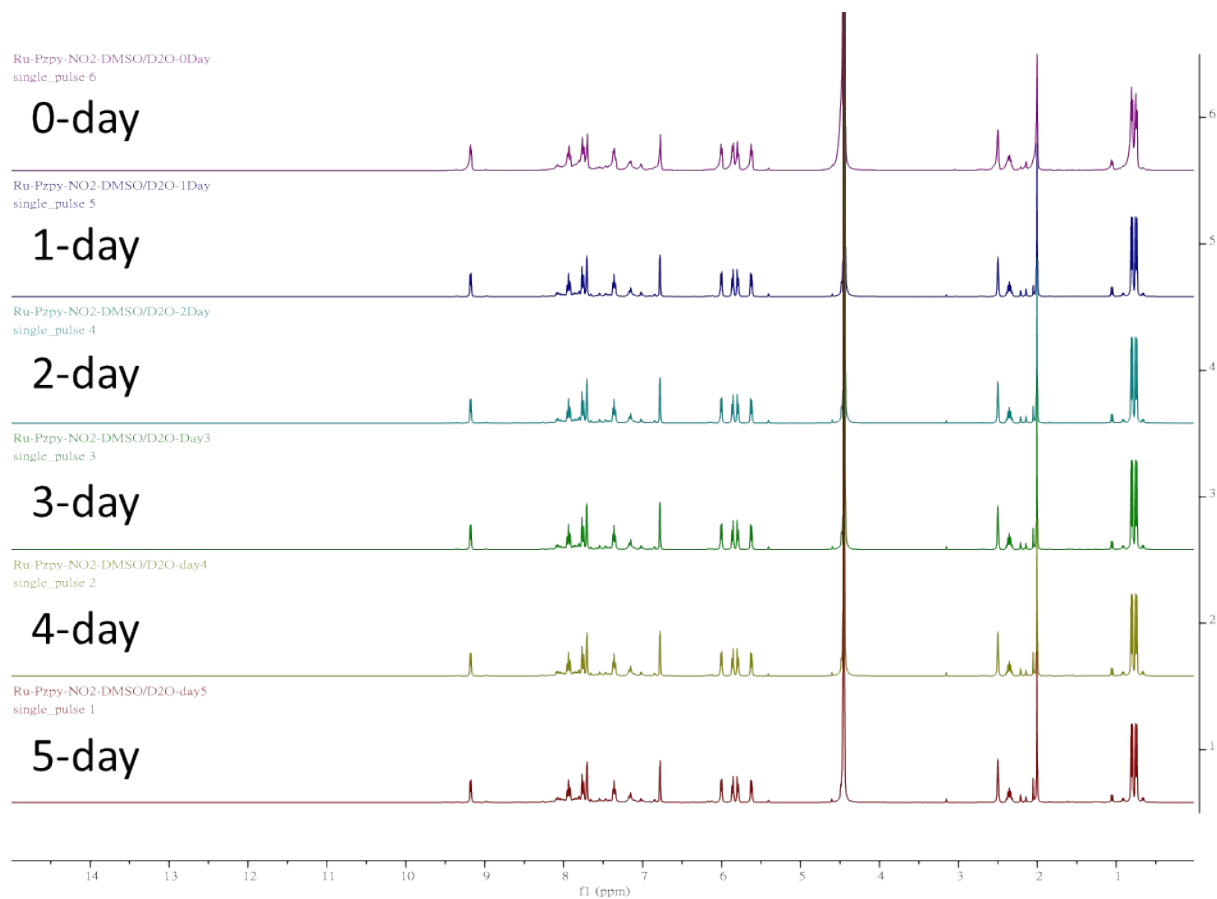


Figure S9. Time dependence of ^1H NMR spectra of the complex **Ru4** in a 1:1 $\text{D}_2\text{O}/\text{DMSO-d}_6$ solution.

Table S1. Crystal data and structure refinement for complex **Ru4-PF₆**

Crystallographic Parameters	Complex Ru4-PF₆
CCDC Number	2256904
Empirical formula	C ₁₈ H ₂₁ F ₆ N ₄ O ₂ P Ru
Formula weight	571.43
Temperature	200(2)K
Crystal system	Monoclinic
Space group	P ₂ 1/c
a Å	13.5961(4)
b Å	14.7808(5)
c Å	10.8245(3)
α deg	90
β deg	96.1970(1)
γ deg	90
Z	4
Density (calc, Mg/m ³)	1.755
Absorption coefficient(mm ⁻¹)	0.873
Crystal color, morphology	Yellow/prism
Crystal size(mm ³)	0.61 x 0.07 x 0.03
Refns meads/indep	23947/3792
Data/restrains/parameter	3792 / 0 / 289
GOF	1.111
R _{int}	0.0370
R ₁ [I>2σ](all data)	0.0299/0.0650
wR2 [I>2σ](all data)	0.0370/0.0689
max peak/hole(e/Å ³)	0.551/-0.561