Ru(II)-naphthoquinone complexes with high selectivity for triple-negative breast cancer

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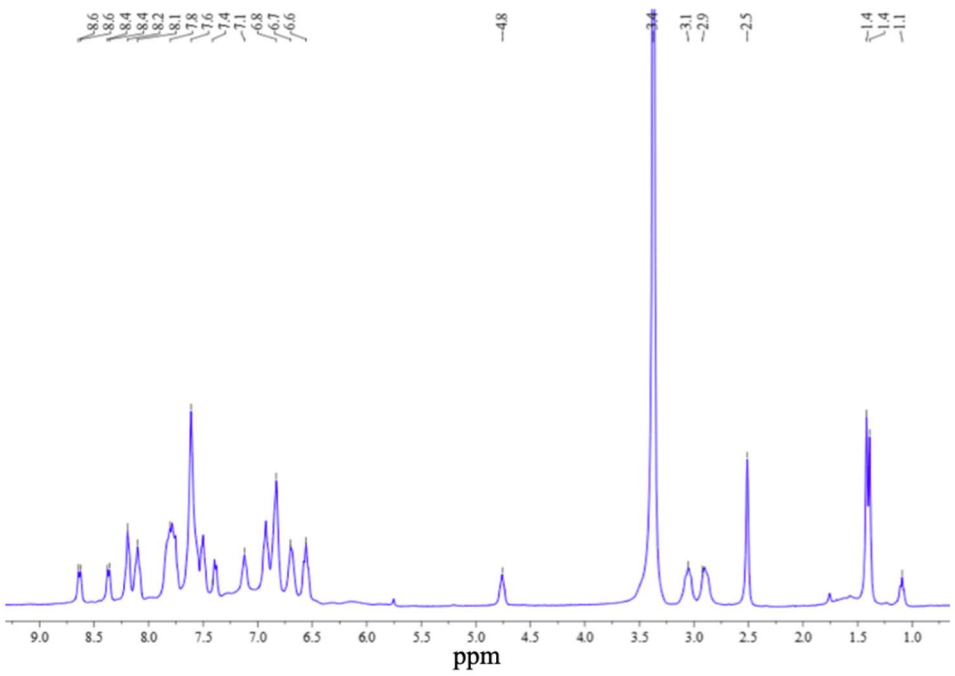

Figure S1. ^{1}H NMR spectra of complex (**1a**) in DMSO-d_6 at room temperature.

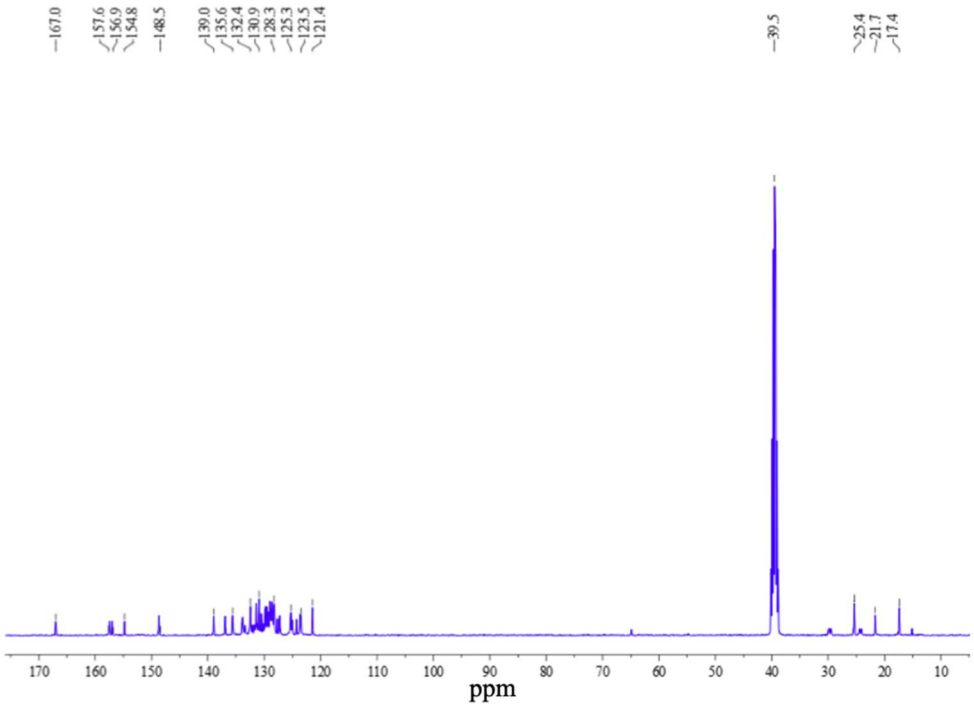

Figure S2. $^{13}C\{^{1}H\}$ NMR spectra of complex (**1a**) in DMSO-d_6 at room temperature.

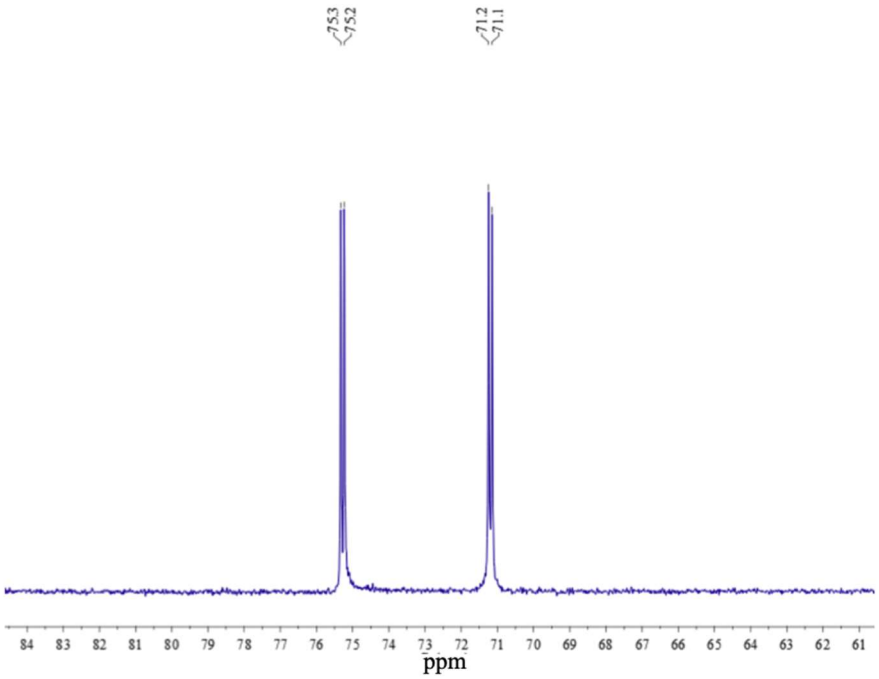

Figure S3. $^{31}P\{^{1}H\}$ NMR spectra of complex (**1a**) in CH_2Cl_2, at room temperature.

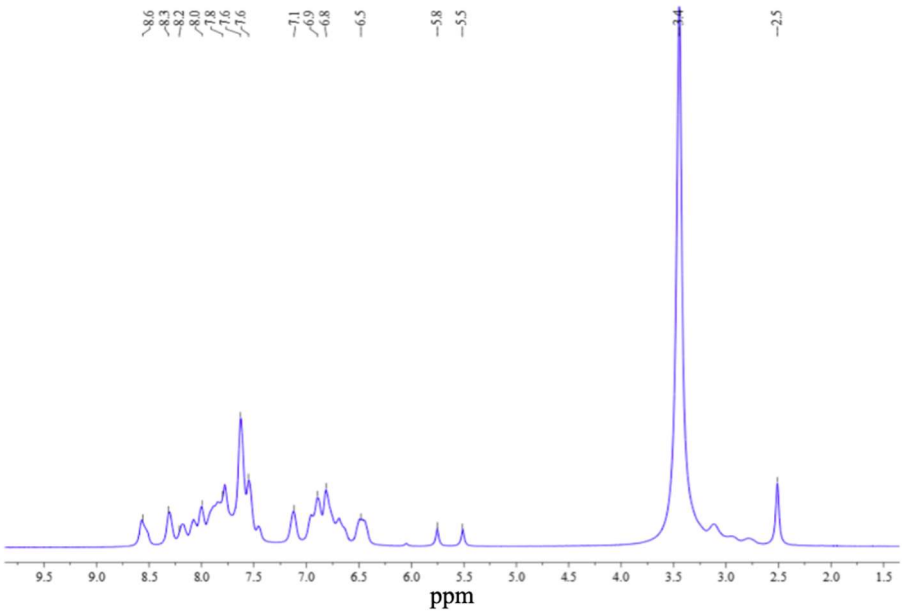

Figure S4. ^{1}H NMR spectra of complex (**1b**) in DMSO-d_6, at room temperature.

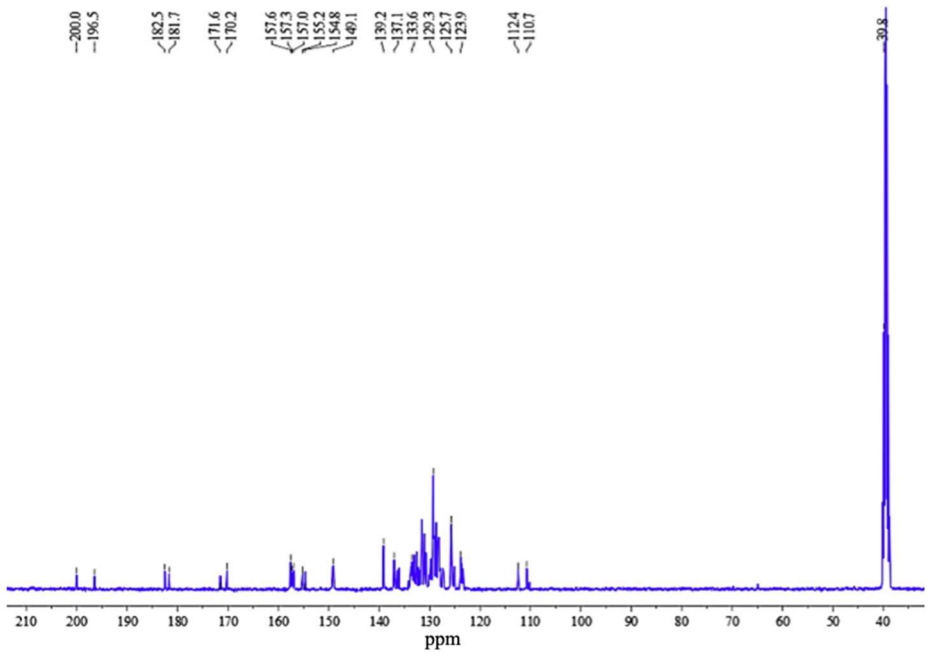

Figure S5. $^{13}C\{^{1}H\}$ NMR spectra of complex (**1b**) in DMSO-d_6, at room temperature.

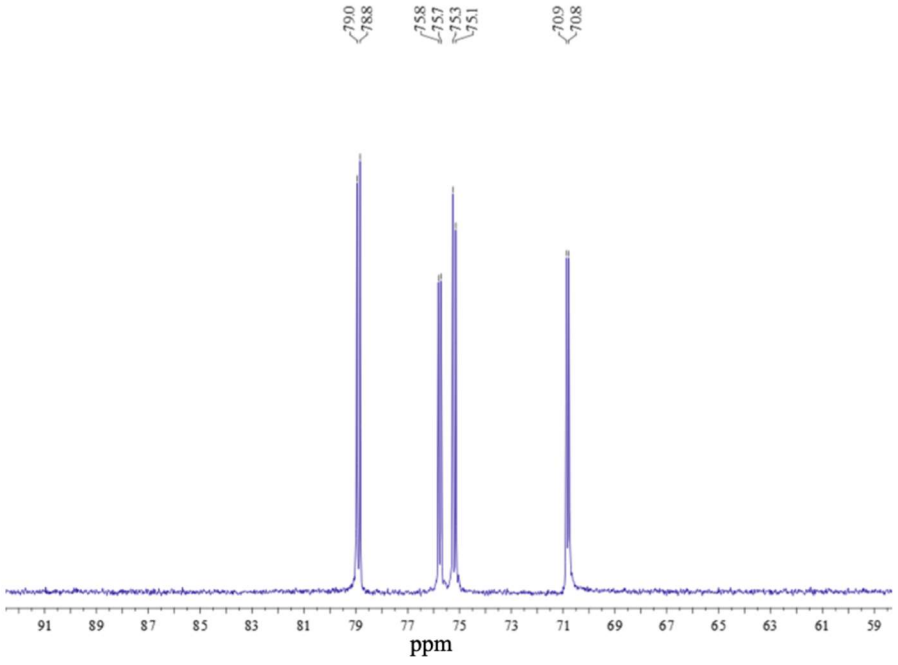

Figure S6. $^{31}P\{^{1}H\}$ NMR spectra of complex (**1b**) in CH_2Cl_2, at room temperature.

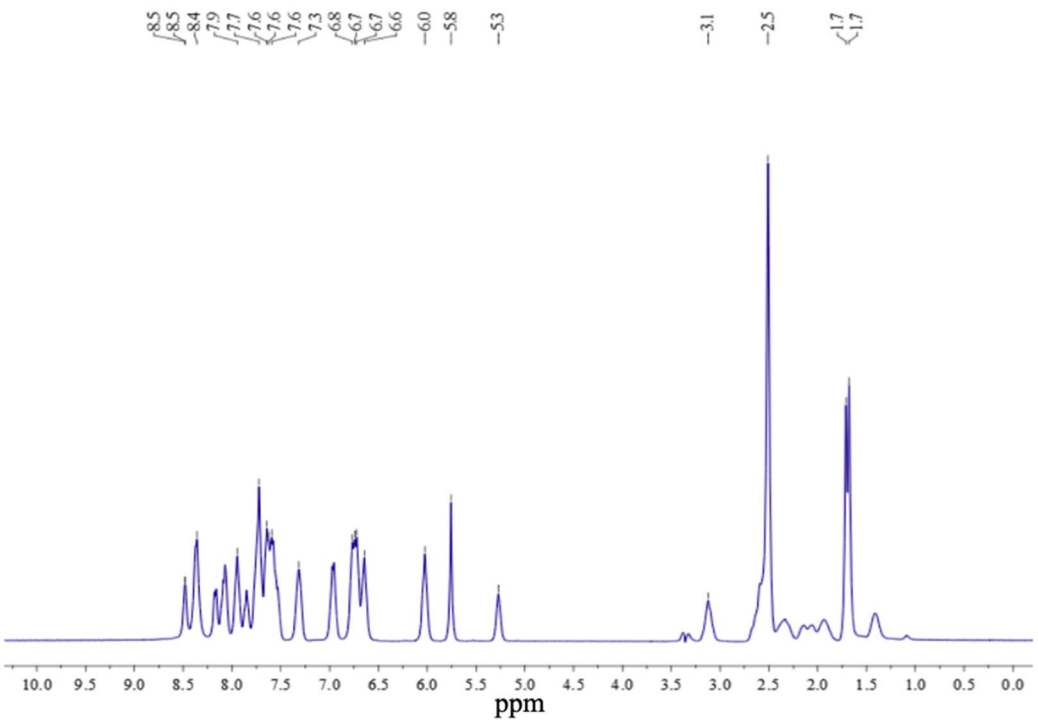

Figure S7. ^{1}H NMR spectra of complex (**2a**) in DMSO-d_6, at room temperature.

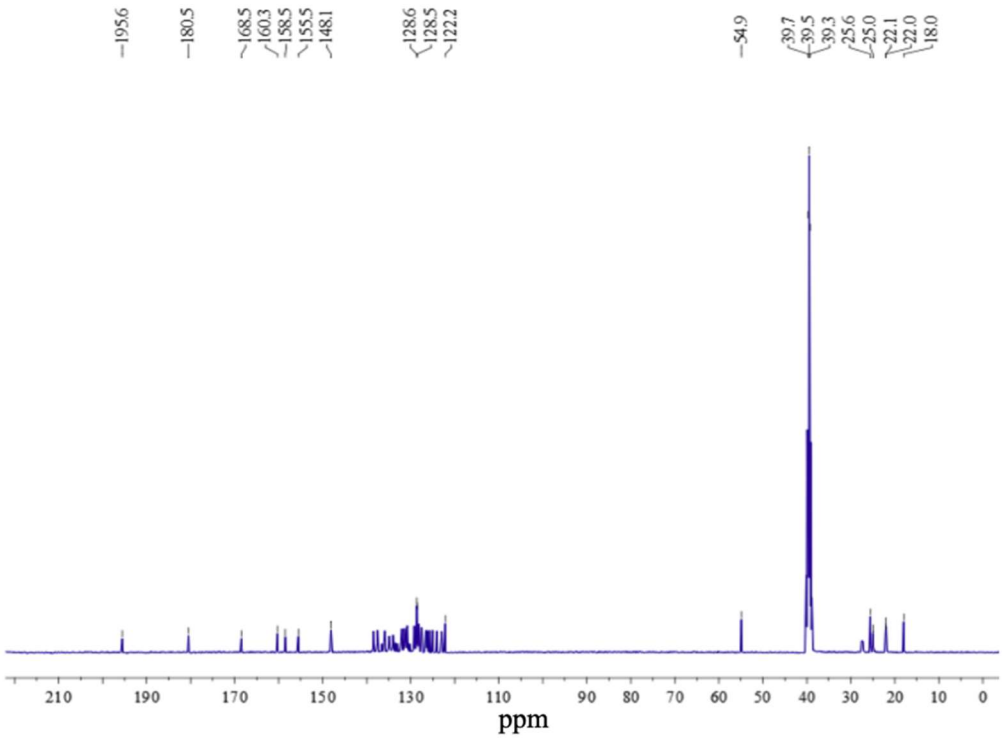

Figure S8. $^{13}C\{^{1}H\}$ NMR spectra of complex (**2a**) in DMSO-d_6, at room temperature.

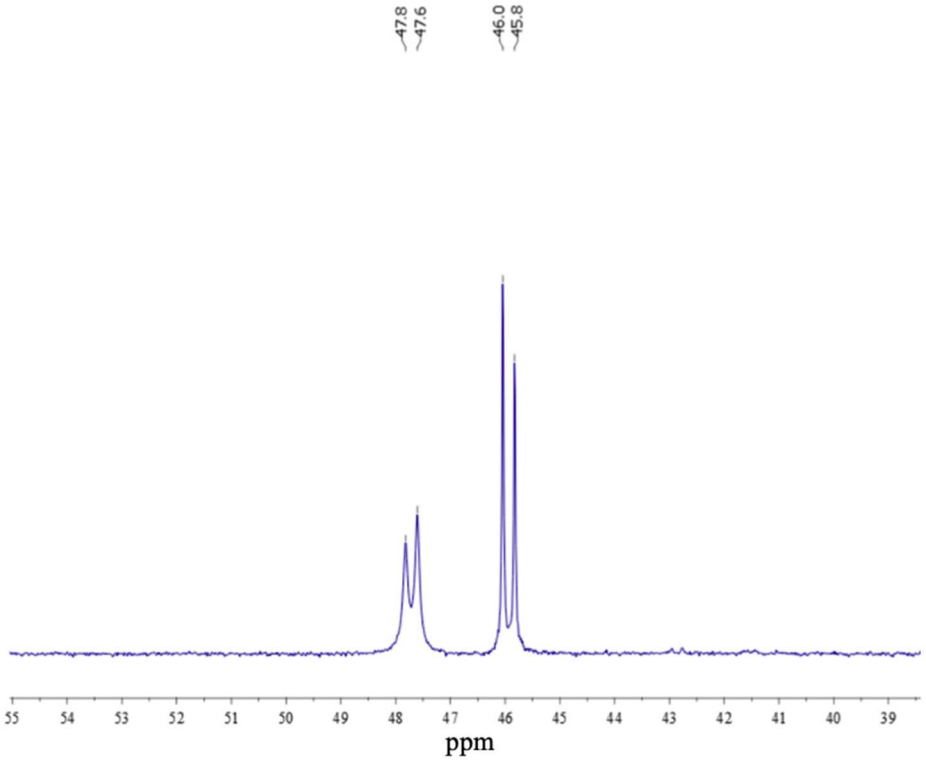

Figure S9. $^{31}P\{^{1}H\}$ NMR spectra of complex (**2a**) in CH_2Cl_2, at room temperature.

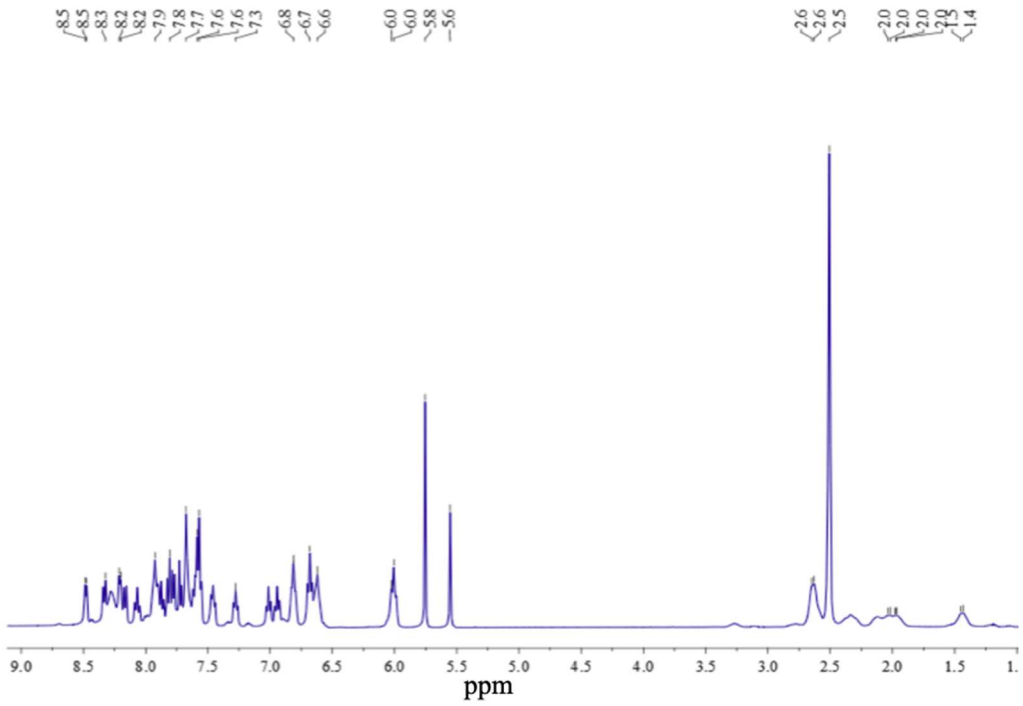

Figure S10. ^{1}H NMR spectra of complex (**2b**) in DMSO-d_6, at room temperature.

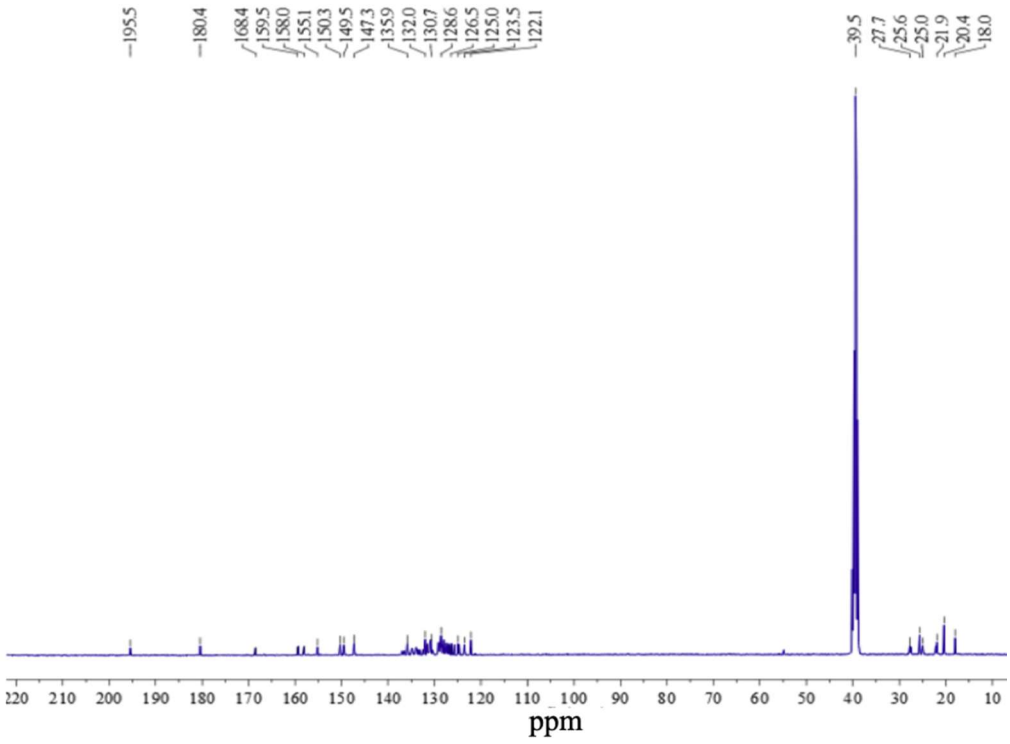

Figure S11. $^{13}C\{^{1}H\}$ NMR spectra of complex (**2b**) in DMSO-d_6, at room temperature.

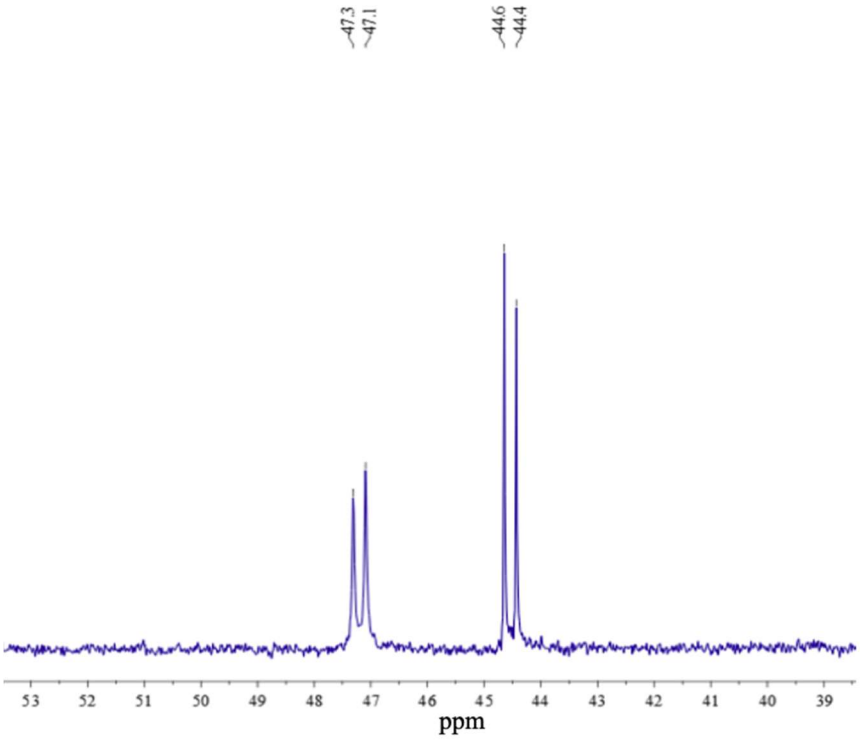

Figure S12. $^{31}P\{^{1}H\}$ NMR spectra of complex (**2b**) in CH_2Cl_2, at room temperature.

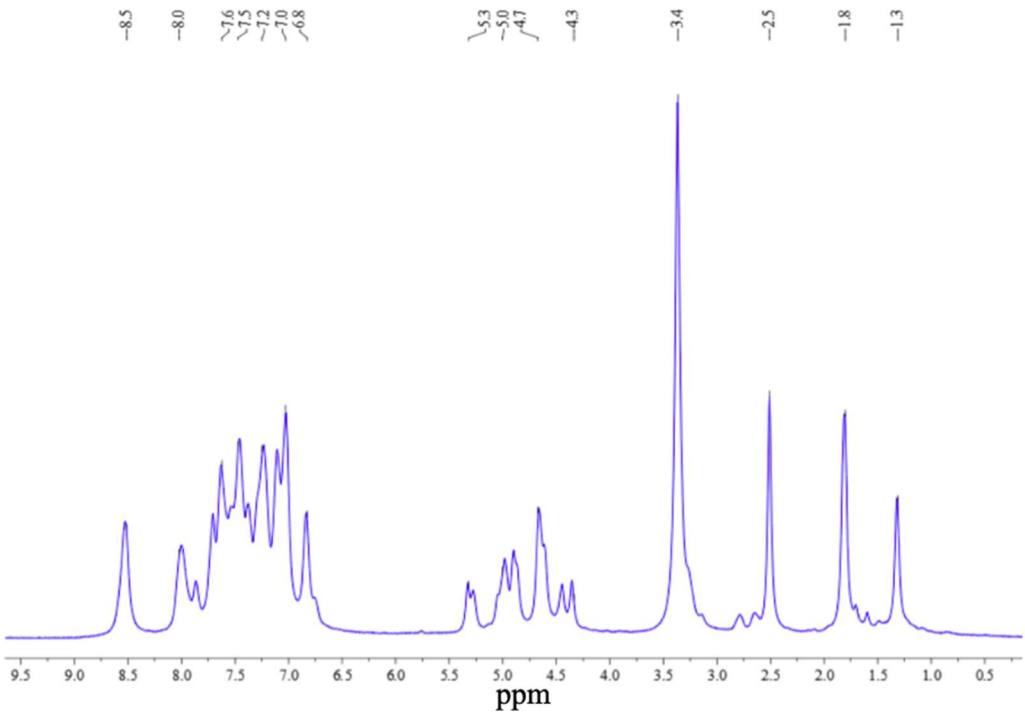

Figure S13. ^{1}H NMR spectra of complex (**3a**) in DMSO-d_6, at room temperature.

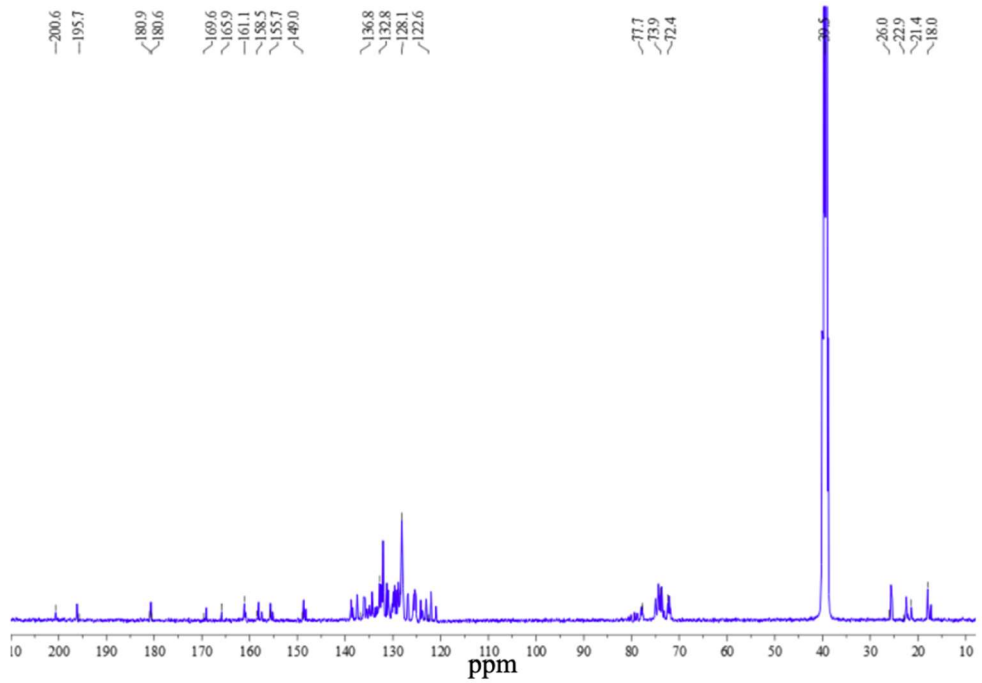

Figure S14. $^{13}C\{^{1}H\}$ NMR spectra of complex (**3a**) in DMSO-d_6, at room temperature.

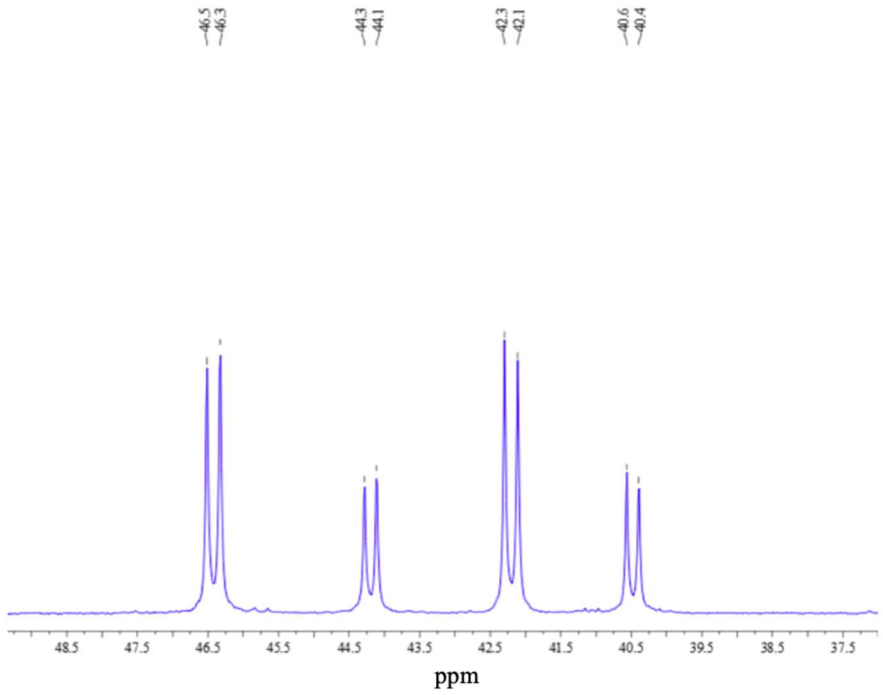

Figure S15. $^{31}P\{^{1}H\}$ NMR spectra of complex (**3a**) in CH_2Cl_2, at room temperature.

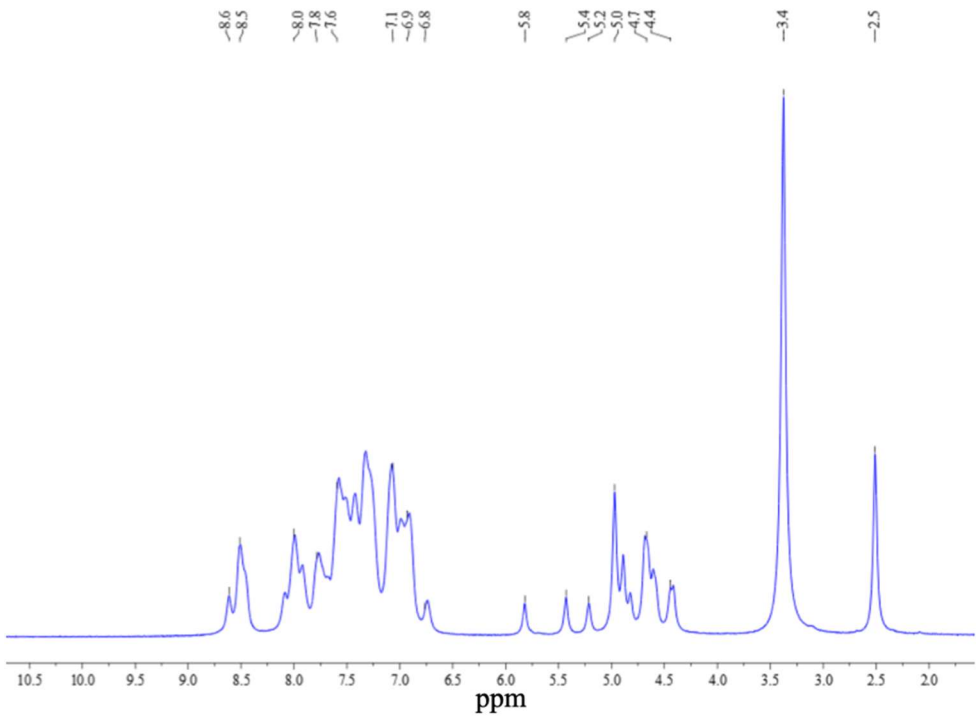

Figure S16. ^{1}H NMR of complex (**3b**) spectra in DMSO-d_6, at room temperature.

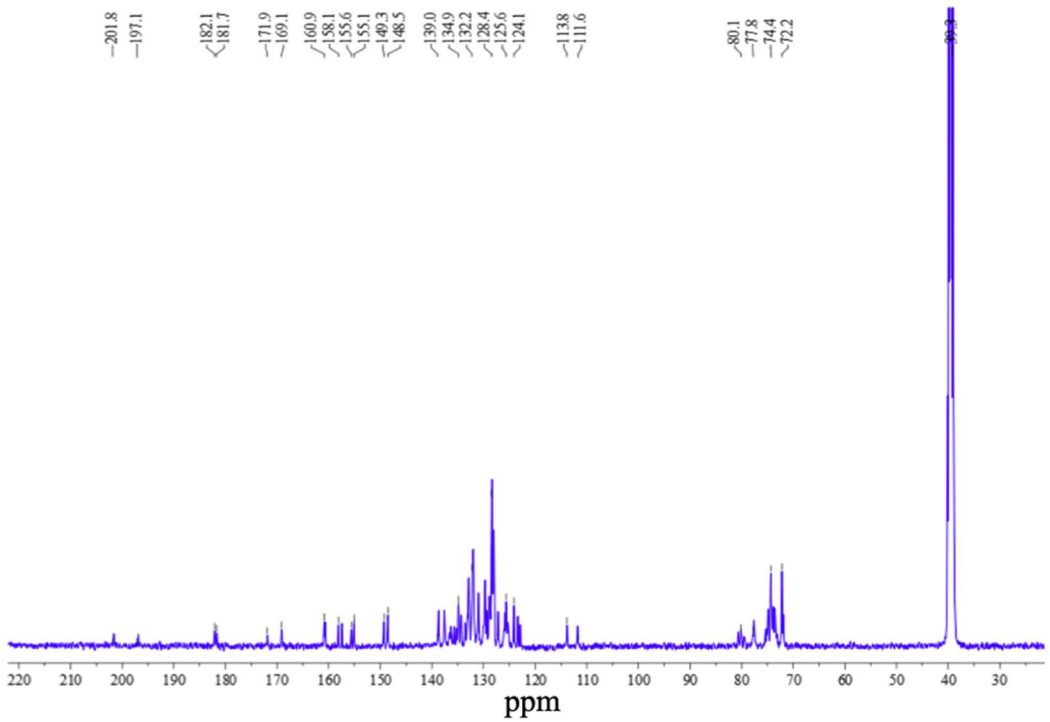

Figure S17. $^{13}C\{^{1}H\}$ NMR spectra of complex (**3b**) in DMSO-d_6, at room temperature.

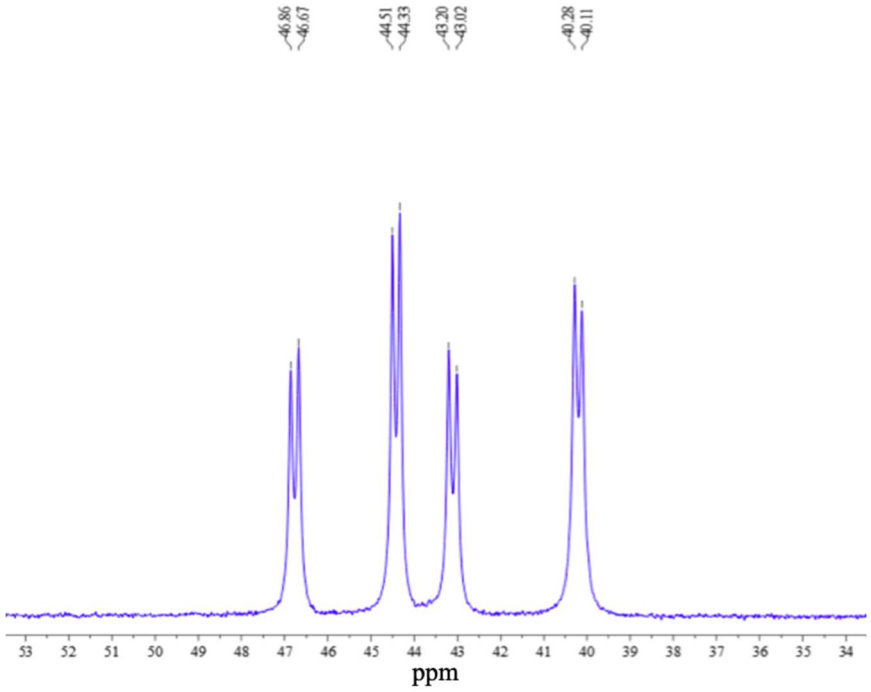

Figure S18. $^{31}P\{^{1}H\}$ NMR spectra of complex (**3b**) in CH_2Cl_2, at room temperature.

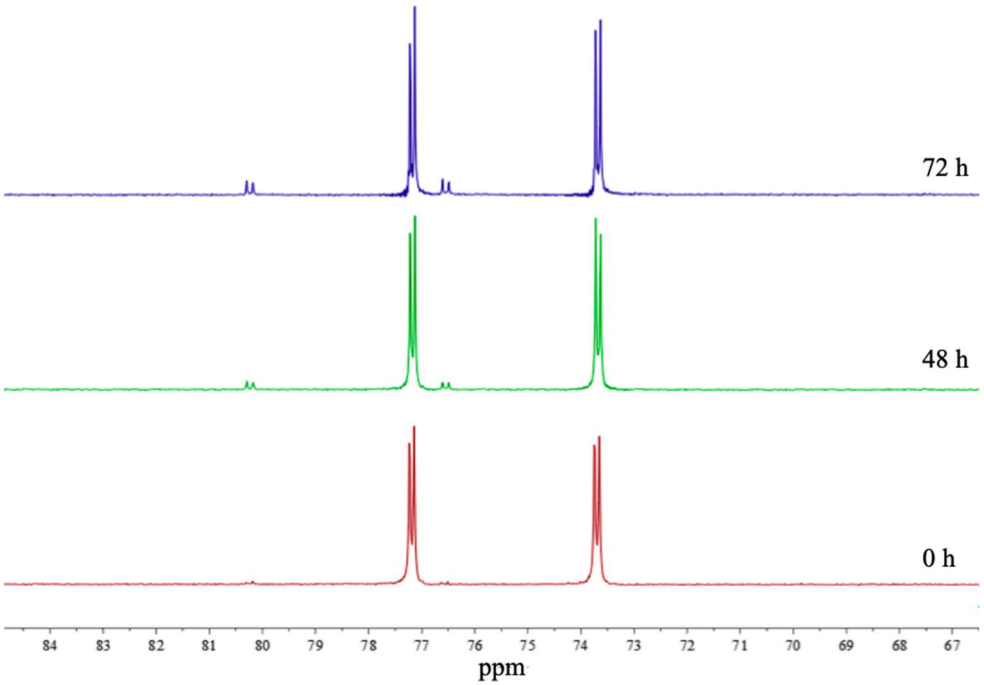

Figure S19. $^{31}P\{^{1}H\}$ NMR spectra of complex (**1a**) in DMSO at different times and room temperature.

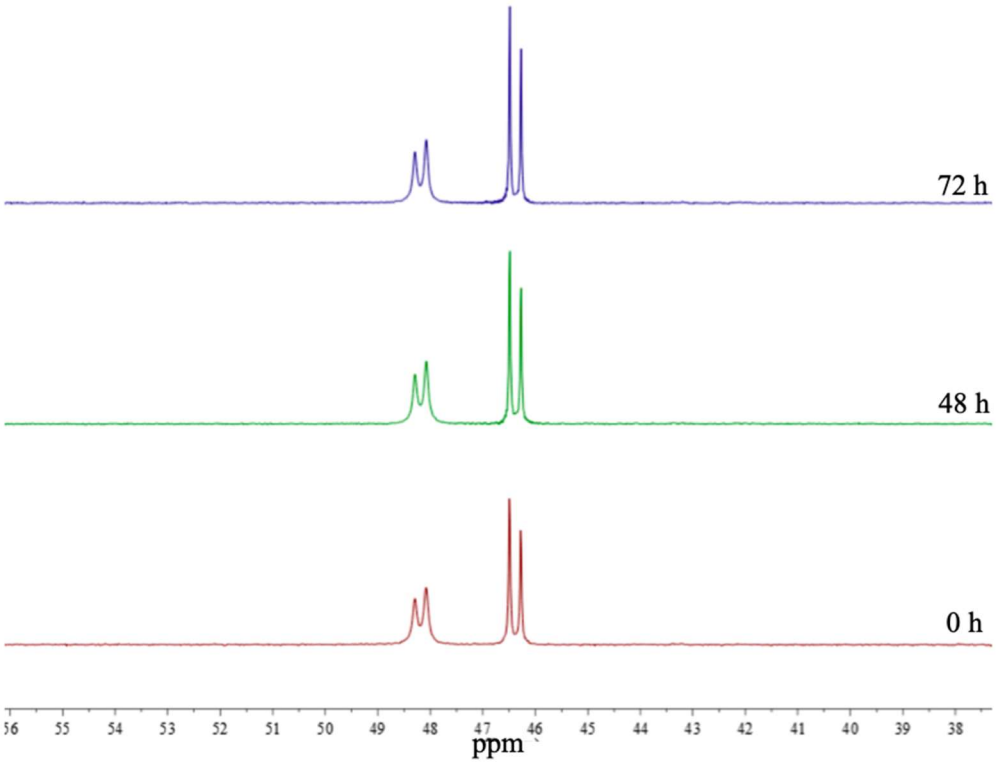

Figure S20. $^{31}P\{^{1}H\}$ NMR spectra of complex (**2a**) in DMSO at different times and room temperature.

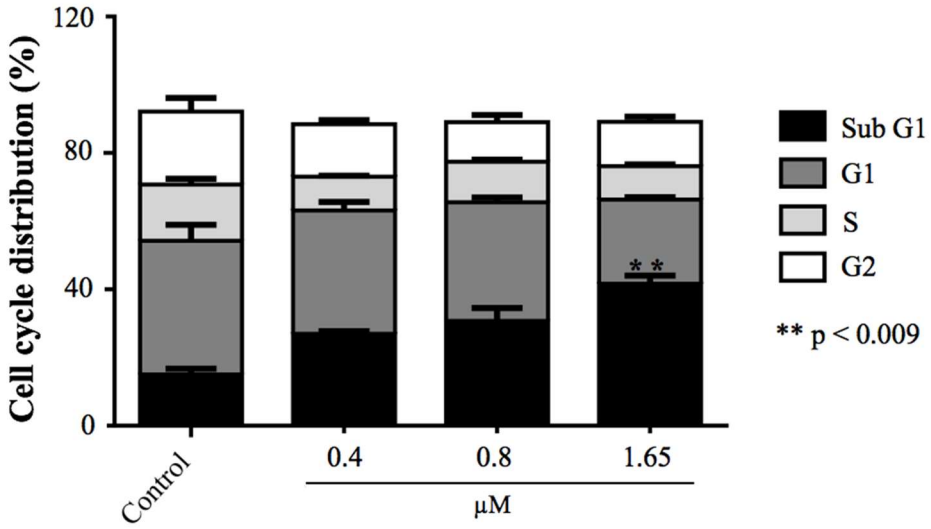

Figure S21. Effect of the complex (**1a**) on the MDA-MB-231 cell cycle distribution analyzed by flow cytometry. The statistical analysis was by using of one-way ANOVA and Tukey's comparison test.

Table S1. X-Ray crystallographic data collection and refinement parameters for complex (**1a**)

Empirical formula	$[RuC_{51}H_{45}N_2O_3P_2]PF_6$. ½ $(CH_3CH_2)_2O$
Formula weight	1078.93
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	I-4
Unit cell dimensions (Å, °)	a = 28.638(1); α = 90°
	b = 28.638(1); β = 90°
	c = 13.096(1); γ = 90°
Volume ($Å^3$)	10740.5(3)
Z	8
Density (calculated) (Mg/m^3)	1.334
Absorption coefficient (mm^{-1})	0.445
F(000)	4424
Crystal size (mm^3)	0.22 x 0.22 x 0.50
Theta range for data collection (°)	3.11 to 26.37
Index ranges	$-35 \leq h \leq 35$, $-33 \leq k \leq 35$, $-16 \leq l \leq 15$
Reflections collected	20830
Independent reflections	9874 [R(int) = 0.0589]
Completeness to θ (%)	99.5
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	9874/402/642
Goodness-of-fit on F^2	0.935
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1071
R indices (all data)	R1 = 0.0701, wR2 = 0.1142
Largest diff. peak and hole ($e.Å^{-3}$)	0.472/-0.437

Table S2. X-Ray crystallographic data collection and refinement parameters for complex (**2a**)

Empirical formula	$[RuC_{53}H_{49}N_2O_3P_2]PF_6\ CH_2Cl_2$
Formula weight	1154.84
Temperature (K)	296.15
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions (Å, º)	a = 11.7860(2); α = 94.5210(10) b = 12.8648(2); β = 100.4210(10) c = 17.3677(2); γ = 92.8070(10)
Volume ($Å^3$)	2576.50(7)
Z	2
Density (calculated) (g/cm^3)	1.489
Absorption coefficient (μmm^{-1})	0.569
F(000)	1180.0
Crystal size (mm^3)	0.30 x 0.12 x 0.07
Theta range for data collection (º)	3.182 to 25.44
Index ranges	$-14 \leq h \leq 14$, $-15 \leq k \leq 15$, $-20 \leq l \leq 20$
Reflections collected	30352
Independent reflections	9463 [R_{int} = 0.0211, R_{sigma} = 0.0265]
Completeness to θ (%)	99.0
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	9463/0/683
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0835
R indices (all data)	R1 = 0.0417, wR2 = 0.0887
Largest diff. peak and hole ($e.Å^{-3}$)	0.78/-0.84

Table S3. X-Ray crystallographic data collection and refinement parameters for complex (**2b**)

Empirical formula	$[RuC_{48}H_{41}N_2O_3P_2]PF_6\ CH_2Cl_2$
Formula weight	1086.73
Temperature (K)	296.15
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_{1/c}$
Unit cell dimensions (Å, º)	a = 13.7656(3); $\alpha = 90$ b = 14.7135(3); $\beta = 91.8920(10)$ c = 23.3155(3); $\gamma = 90$
Volume ($Å^3$)	4719.75(17)
Z	4
Density (calculated) (g/cm^3)	1.529
Absorption coefficient (μmm^{-1})	0.615
F(000)	2208.0
Crystal size (mm^3)	0.34 x 0.71 x 0.1
Theta range for data collection (º)	3.274 to 25.39
Index ranges	$-15 \leq h \leq 16$, $-17 \leq k \leq 16$, $-27 \leq l \leq 28$
Reflections collected	31214
Independent reflections	8631 [$R_{int} = 0.0260$, $R_{sigma} = 0.0264$]
Completeness to θ (%)	99.0
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameters	8631/0/632
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1330
R indices (all data)	R1 = 0.0571, wR2 = 0.1417
Largest diff. peak and hole ($e.Å^{-3}$)	1.24/-0.82