Electronic Supplementary Information

*Synthesis and characterization of **1** and **2***:

All manipulations were carried out under nitrogen using standard Schlenk techniques, and dried deoxygenated solvents.

Synthesis of 1: 2,9-bis(3-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline (0.18 g, 0.290 mmol, prepared via the method of Sauvage *et al*[1] from the reaction of 4,7-diphenyl-1,10-phenanthroline with 3-trifluoromethylphenyl lithium) and $[Re(CO)_5Cl]$ (0.10 g, 0.277 mmol)were dissolved in toluene (25 mL) and heated to reflux for 6 hours. Upon cooling, an orange solid precipitated which was collected by filtration (Yield: 0.21 g, 81 %) and purified by sublimation at 275°C at $5x10^{-6}$ mbar (there was a small amount (< 10 % by weight) of decomposition on sublimation). Anal. Calcd for $C_{41}H_{22}ClF_6N_2O_3Re$ requires C, 53.16; H, 2.39; N, 3.02 %. Found: C, 53.22; H, 2.38; N, 3.04 %. ^{1}H NMR ($CDCl_3$): δ 8.11 (s, 2H, Ar-*H*), 8.10 – 7.65 (m, 10H, Ar-*H*), 7.58 (bs, 10H, Ar-*H*). ^{19}F NMR ($CDCl_3$): δ -63.1 (s). IR (nujol): *ν*(CO) 2020, 1926, 1892 cm^{-1}. Emission spectra (CH_2Cl_2): λ_{ex} 396, λ_{max} 635 nm; CIE: 0.626, 0.373; thin film (λ_{ex} 396, λ_{max} 610 nm; CIE: 0.569, 0.429.

Synthesis of 2: 2,9-bis(4-trifluoromethylphenyl)-4,7-diphenyl-1,10-phenanthroline (0.18 g, 0.290 mmol, prepared via the method of Sauvage *et al*[1] from the reaction of 4,7-diphenyl-1,10-phenanthroline with 4-trifluoromethylphenyl lithium) and $[Re(CO)_5Cl]$ (0.10 g, 0.277 mmol) were dissolved in toluene (25 mL) and heated to reflux for 6 hours. Upon cooling, an orange solid precipitated which was collected by filtration (yield 0.24 g, 92 %) and purified by sublimation at 265°C at $5x10^{-6}$ mbar (there was a small amount (< 10 % by weight) of decomposition on sublimation). Anal. Calcd for $C_{41}H_{22}ClF_6N_2O_3Re$ requires C, 53.16; H, 2.39; N, 3.02 %. Found: C, 53.38; H, 2.59; N, 2.84 %. ^{1}H NMR ($CDCl_3$): δ 8.11 (s, 2H, Ar-*H*), 8.00–7.80 (m, 10H, Ar-*H*), 7.70–7.50 (bs, 10H, Ar-*H*). ^{19}F NMR ($CDCl_3$): δ -63.4 (s). IR (nujol, cm^{-1}): *ν*(CO) 2028, 1936, 1877. Emission spectra (CH_2Cl_2): λ_{ex} 451, λ_{max} 596 nm; CIE: 0.554, 0.442; thin film (λ_{ex} 468, λ_{max} 585 nm; CIE: 0.535, 0.461.

Reaction of 1 with dmso

Using a the method of Mayer *et al*, [2] **1** (0.25 g, 0.27 mmol) in dichloromethane (20 ml) was treated with a slight excess of dmso (0.02 ml, 0.28 mmol) and stirred for 12 h at ambient temperature. Volatiles were then removed *in-vacuo* to afford a yellow brown oily material. Trituration with hexane (20 ml) afforded a yellow brown glass (0.25 g, 93 %). Anal. Calcd for $C_{43}H_{28}ClF_6N_2O_4SRe$ requires C, 51.4; H, 2.8; N, 2.8 %. Found: C, 51.5; H, 2.6; N, 2.6 %. IR (nujol, cm^{-1}): *ν*(CO) 2019, 1891b; *ν*(SO) 951. Mass Spec (MALDI): 991.7 (M^+ - Cl + Na) (the sodium is picked up from the stainless steel target).

Figure S1. Alternative view of **1.**

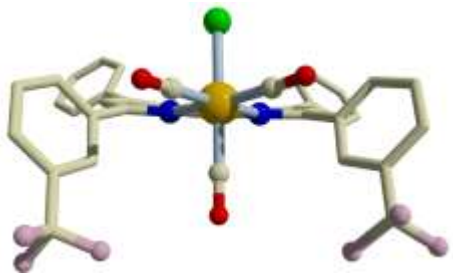


Figure S2. Alternative view of **1**.

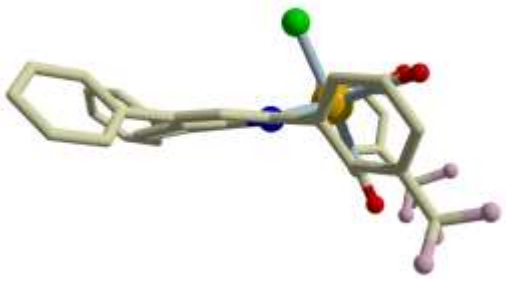


Figure S3. Alternative view of **1**.

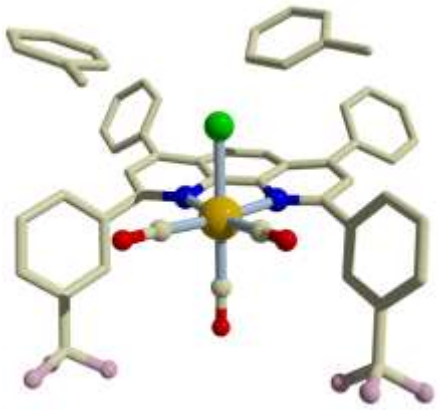
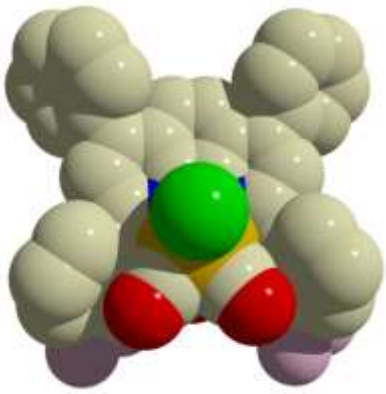


Figure S4. Alternative view of **1**.



Optical studies

Figure S5. Example of PL spectra for **1** excitation wavelength 390 nm (recorded in CH_2Cl_2).

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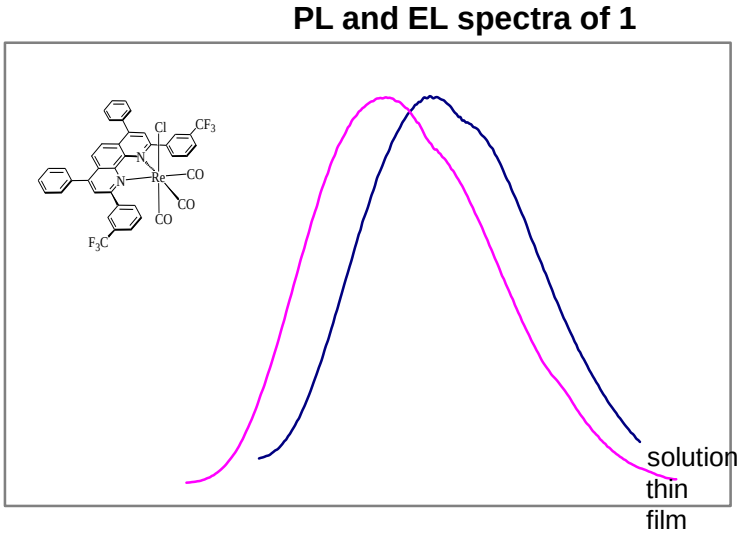


Quantum Yield measurement

The photoluminescence (PL) emission spectra were taken for **1** and **2** dissolved in toluene in a quartz cuvette (10 mm × 10 mm), using a Perkin-Elmer LS55 spectrophotometer with emission bandwidth of 5 nm. The excitation wavelength was set at 390 nm and 410 nm respectively.

The quantum yield (QY) was calculated by preparing five solutions of the sample at varying concentrations in toluene, and measuring the absorbance at 500 nm and the area under the emission peak at each different concentration. The absorbance was plotted against the integrated intensity and compared to a standard of known quantum yield (Rhodamine B). [7] This data was used to obtain a value for the quantum yield.

Figure S6. Plot of integrated intensity against absorbance for **1**

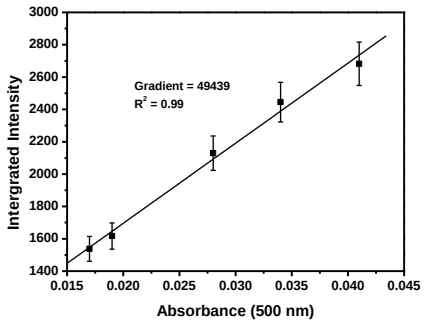


Figure S7. Plot of integrated intensity against absorbance for **2**

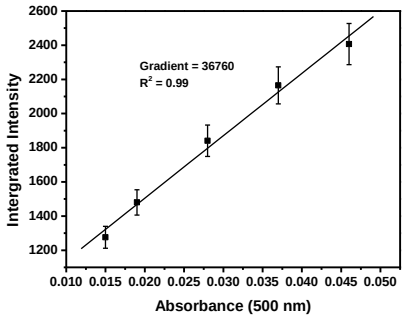
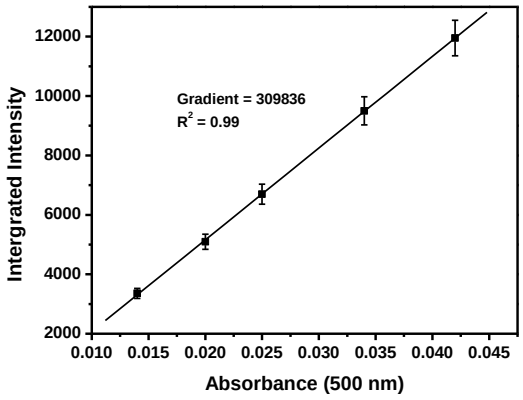


Figure S8. Plot of integrated intensity against absorbance for Rhodamine B



The quantum yield of **1** and **2** in toluene was calculated using the following equation:

$$Q = Q_R(\frac{Grad}{Grad_R})(\frac{\eta^2}{\eta_R^2})$$

Q=Quantum yield

Q_R=Quantum yield of reference

η = refractive index of sample

η_R = refractive index of Reference

Here Rhodamine B was used as reference, which has a quantum yield of 100 % when dissolved in Ethanol. Ethanol had a refractive index of 1.346, while the refractive index of toluene **is** 1.497.

$$Q_1 = 50\,(49439/308936) \times (1.497^2/1.361^2) = 9.7\ \%$$

$$Q_2 = 50\,(36760/308936) \times (1.497^2/1.361^2) = 7.2\ \%$$

UV-VIS spectra for **1** and **2**

Figure S9. UV-Vis absorption spectrum of **1**

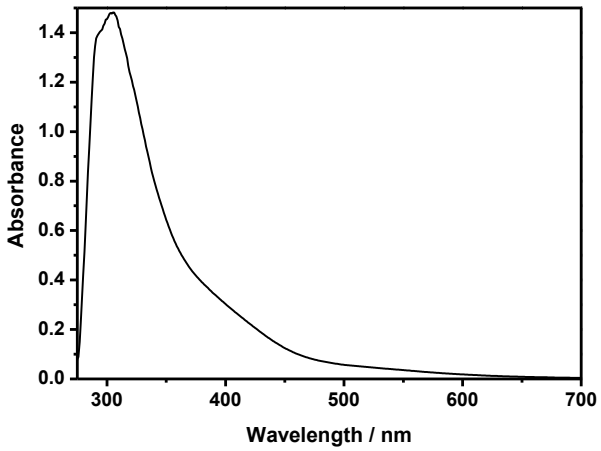
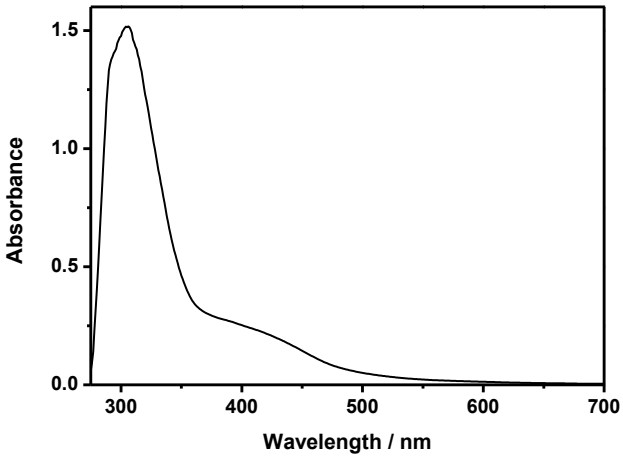


Figure S10. UV-Vis absorption spectrum of **2**



PL aging for **1**′ and **2**′

Figure S11. Photoluminescence emission under excitation wavelength 350 nm, showing the change in luminescence for **1**′ over 21 days (recorded in toluene, post DMSO treatment).

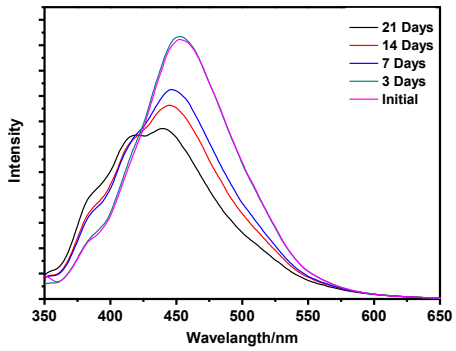
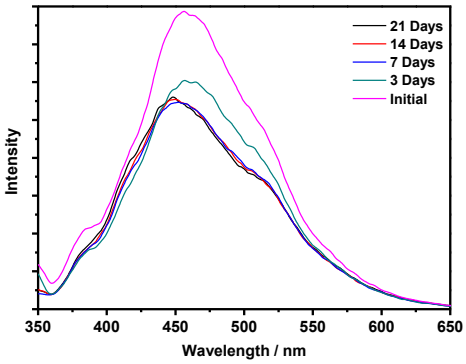


Figure S12. Photoluminescence emission under excitation wavelength 350 nm, showing the change in luminescence for **2**′ over 21 days (recorded in toluene, post DMSO treatment).



Biological Methods. *Cell Viability Studies*. MTS (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) assays were performed using a CellTiter 96® AQ_{ueous} Non-Radioactive Cell Proliferation Assay (Promega). All cell lines used have been described earlier [3-4]. All cells were incubated at 37 ˚C. Freshly harvested CHO or HeLa cells were suspended in DMEM (Dulbecco's modified Eagle's medium) (Invitrogen) with 10 % Foetal Calf serum and 2mM glutamine, THP-1 and HL-60 cells in RPMI 1640 (Roswell Park Memorial Institute 1640) (Invitrogen) with 10 % Foetal Calf serum and 2mM glutamine, at a concentration of $1x10^5$ cells /mL. The cells were incubated in experimental media consisting of DMEM or RPMI supplemented with the test compounds dissolved in DMSO at different concentrations for 72 hrs at 37 °C in a humidified atmosphere and 5% CO_2. After incubation, cell viability was assessed using the CellTiter 96 Aqueous One Solution Cell Proliferation Assay (Promega). The 3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium (MTS) tetrazolium compound is bioreduced by cells into a colored formazan product that is soluble in tissue culture medium [5]. This conversion is presumably accomplished by NADPH or NADH produced by dehydrogenase enzymes in metabolically active cells [6]. Aliquots of 20 µl of the CellTiter 96 Aqueous One Solution Reagent were added directly to the wells and the plates were incubated for 4 h at 37 °C in a humidified atmosphere, 5 % CO_2 and then absorbance at

490 nm was read with a plate reader. The quantity of formazan product as measured by the absorbance at 490 nm is directly proportional to the number of living cells in culture [6].

Live Cell Confocal Imaging. CHO cells were seeded on a sterile coverslip in a 6-well plate and grown at 37°C under a 5 % CO_2 atmosphere for 12 hours, HL60 cells were grown in solution under the same conditions. The growth medium was then removed, and replaced with fresh medium and **1**$^{/}$ or **2**$^{/}$ was added at 100nM. The cells were subsequently incubated for 4 or 24 hours, then the medium was removed, the cells were washed with PBS three times and were then mounted onto glass slide and then imaged using an inverted Leica DMII fluorescence microscope. To visualize the nuclei or the actin cytoskeleton, cells were stained with 4',6-diamidino-2-phenylindole (DAPI, Sigma Aldrich) or Alexa Fluor 488® phalloidin (Invitrogen), respectively, according to manufacturers protocols.

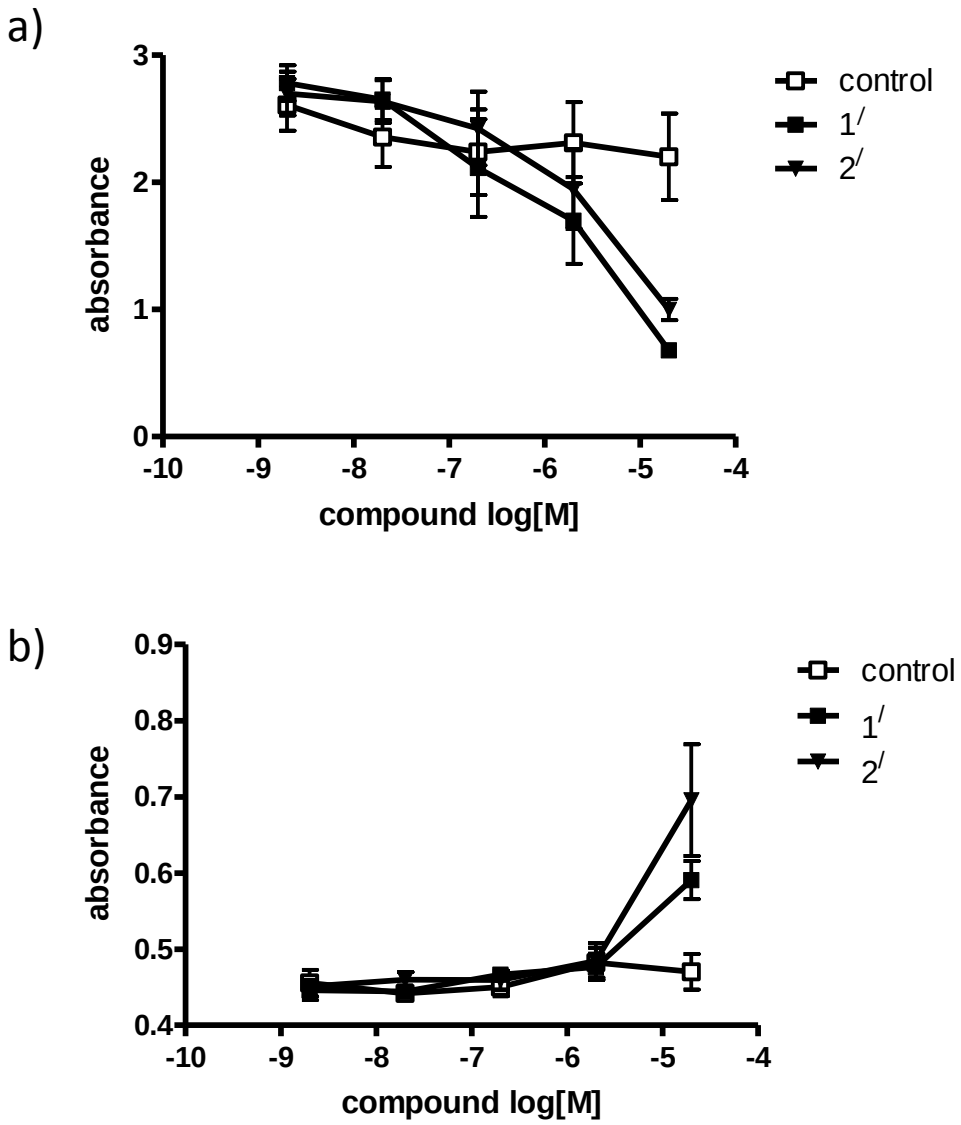


Figure S13: Representative cell viability assays. a) HeLa cells, b) 16HBE cells tested for proliferation after 72 hours using an MTS assay. DMSO was used as a vehicle control in all studies, data represent at least mean ±SEM of at least three independent experiments done in duplicate.

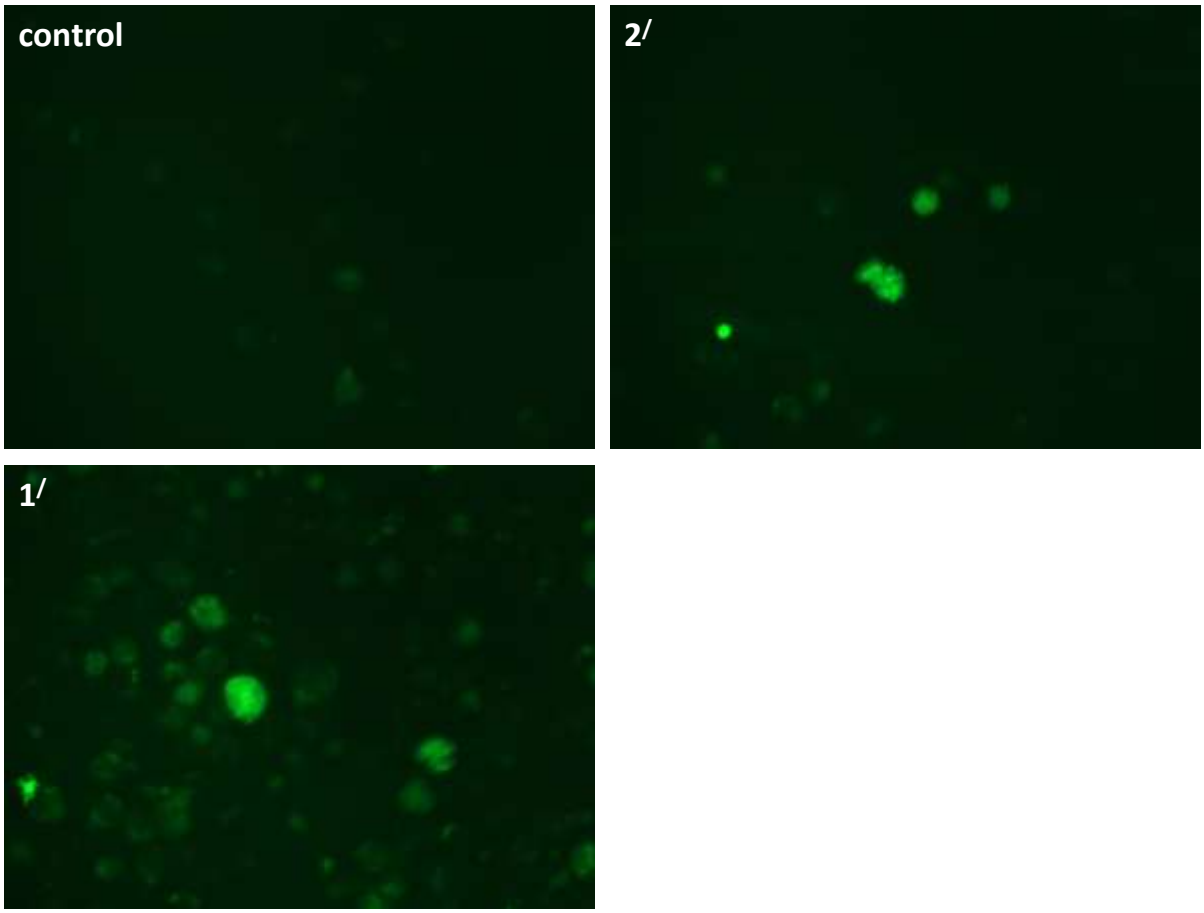


Figure S14: HL60 cells were grown in solution overnight and incubated with **1**$^{/}$, **2**$^{/}$ or vehicle (DMSO) for the control for 4 hours. Cells were washed 3 times with PBS and pictures were taken on live cells using a Leica fluorescence microscope. Pictures show representative cells of several stains.

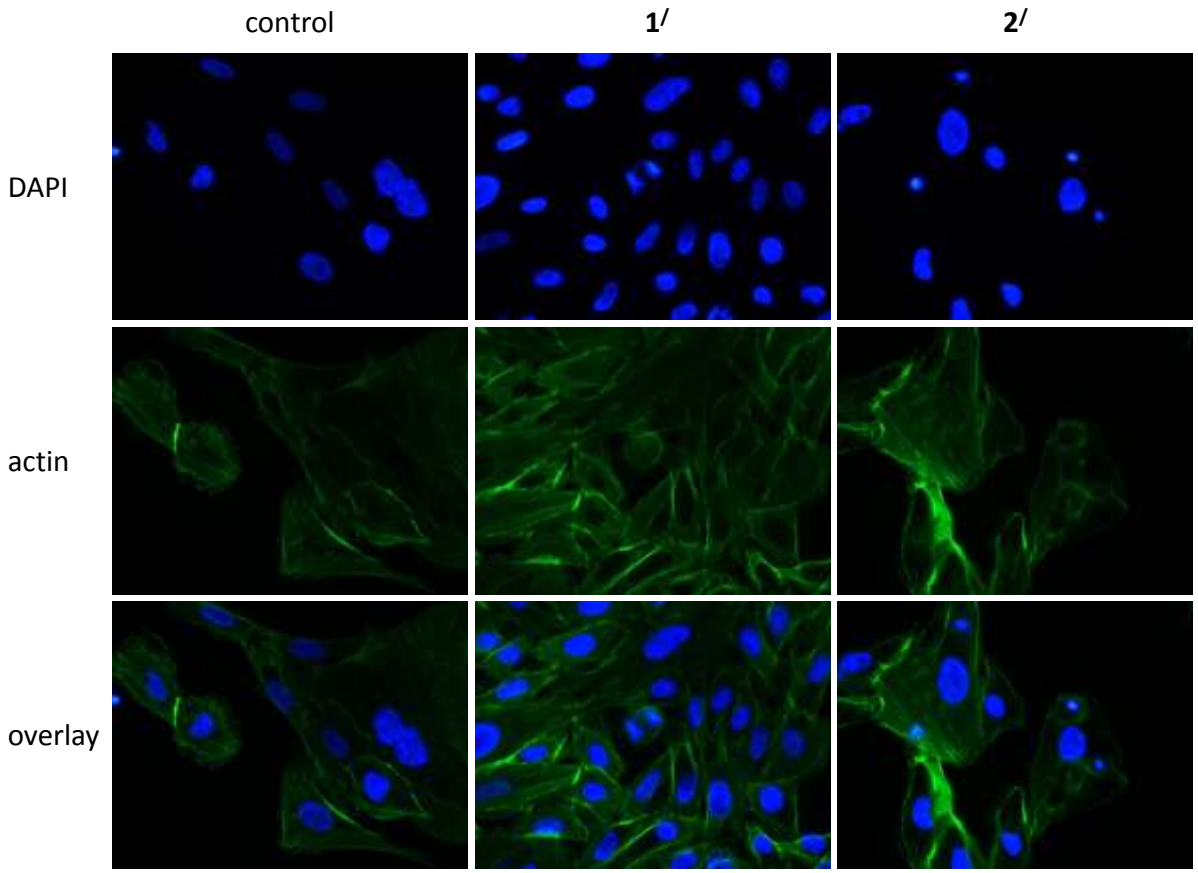


Figure S15: CHO cells were grown on coverslips overnight, incubated with DMSO (control), **1**$^{/}$ and **2**$^{/}$ respectively for 24 hours and then stained with DAPI and Alexa Fluor 488® phalloidin. Pictures were taken on live cells using a Leica fluorescence microscope.

REFERENCES:

[1] C.O. Dietrich-Buchecker, P.A. Marnot and J.P. Sauvage, *Tet. Lett*. **1982**, *23*, 5291.

[2] D.D. DuMez and J.M. Mayer, *Inorg. Chem*. **1995**, *34*, 6396.

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[4] C.M. Cardaba, J.S. Kerr and A. Mueller, *Cell Signalling*, **2008**, *20*, 1687-1694.

[5] A.H. Cory, T.C. Owen, J.A. Barltrop and J.G. Cory, *Cancer Commun*. **1991**, *3*, 207–212.

[6] M.V. Berridge and A.S. Tan, *Arch. Biochem. Biophys***. 1993**, *303*, 474–482.