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Supporting Information for

Synthesis, Structural Characterization and Solution Chemistry of Ruthenium(III) Triazole-Thiadiazine Complexes

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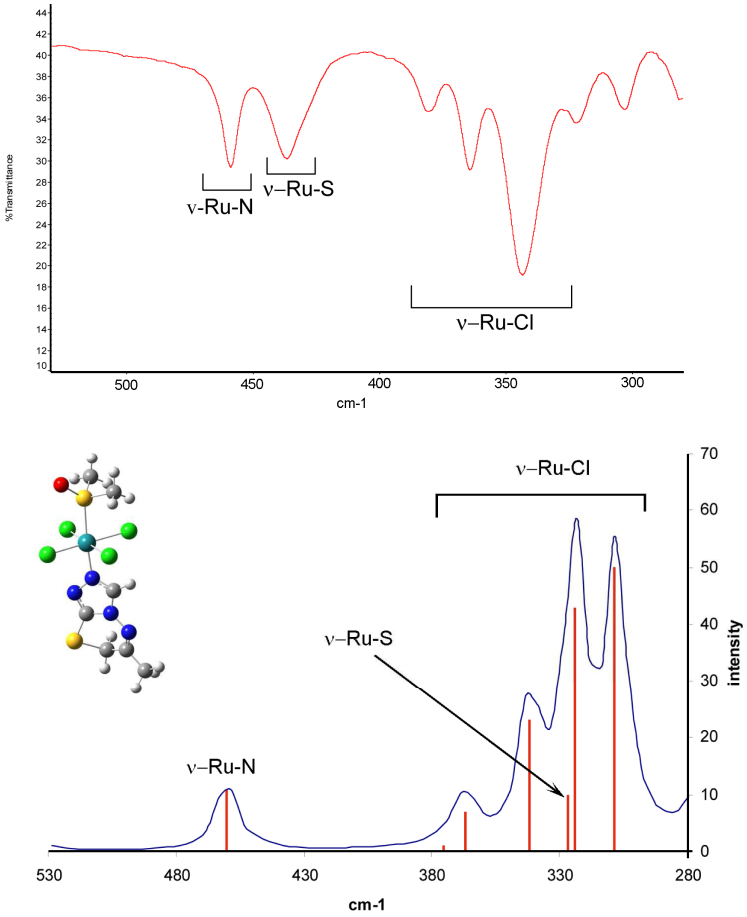

Figure S1. FAR-IR spectrum of Na[$RuCl_4$(L1)(dmso)] (**1**), CsI disk (above); calculated IR spectra b3lyp/lanl2dz(Ru)-6-31G(C H Cl N O S) (below).[S1] The discrepancy between the Ru-S stretching frequency is due to the difference between the experimental geometry (d(Ru-S)=2.310(3)Å) and the optimized geometry (d(Ru-S)=2.531 Å). According to this, in the optimized geometry the Ru-S bond is weakened with respect to the X-ray structure. The discrepancy between the calculated and experimental geometry for the other coordination distances are less than 0.15 Å.

Table S1. Observed frequencies (cm^{-1}) for the Ru-D (D = donor atom) in Ru(III) complexes.

	ν(Ru-N)	ν(Ru-S)	ν(Ru-Cl)
[$(DMSO)_2H$][*trans*-$RuCl_4(DMSO)_2$][a]	-	415	345, 329
Na[$RuCl_4$(DMSO)(L1)] (**1**)	458	436	364, 343
Na[$RuCl_4$(DMSO)(L2)] (**2**)	448	431	356, 332

a): ref.: S2

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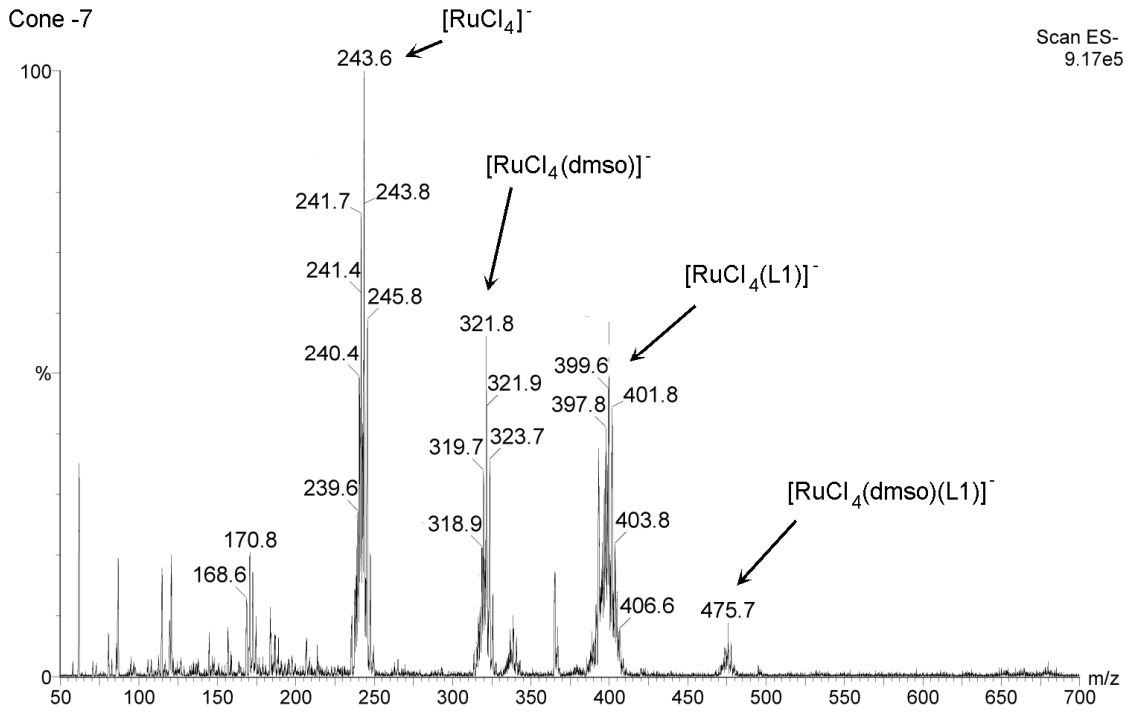

Figure S2. Negative ESI-MS spectrum of Na[*trans*-$RuCl_4$(dmso)(L1)] (**1**) dissolved in acetonitrile.

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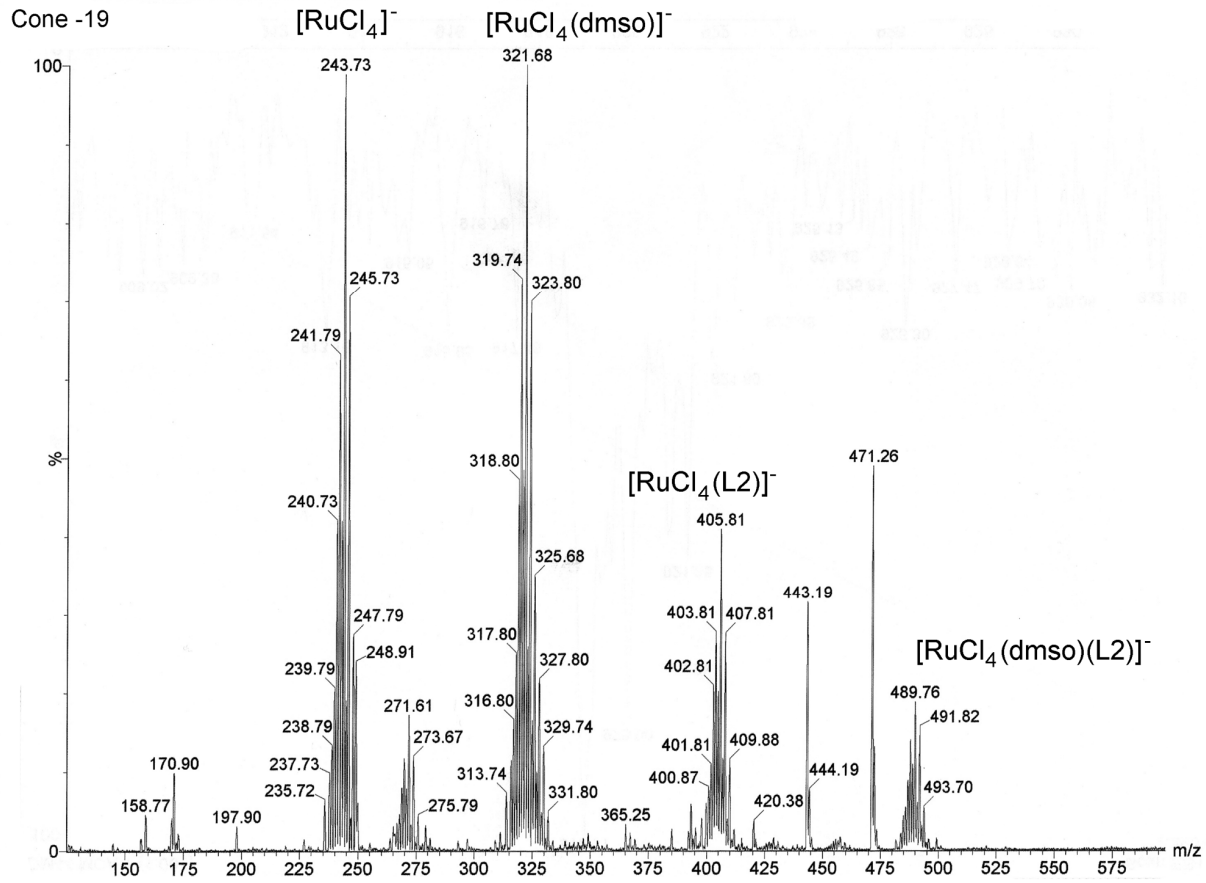

Figure S3. Negative ESI-MS spectrum of Na[*trans*-$RuCl_4$(dmso)(L2)] (**2**) dissolved in acetonitrile.

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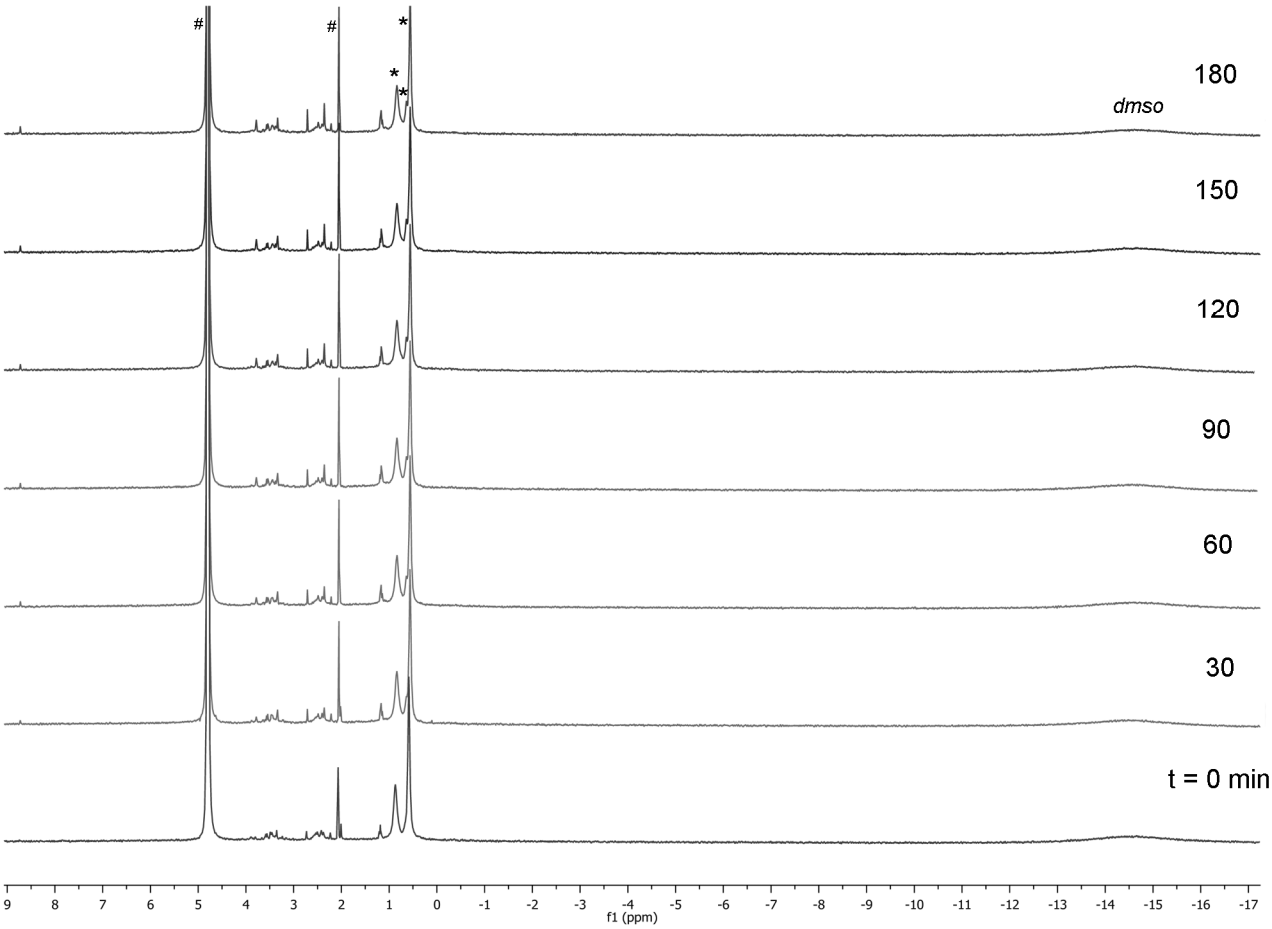

Figure S4. Stack plot of the ^{1}H NMR spectra of **1** in D_2O recorded in the 0-180 min interval. * = coordinated ligand signals. # = water and acetone.

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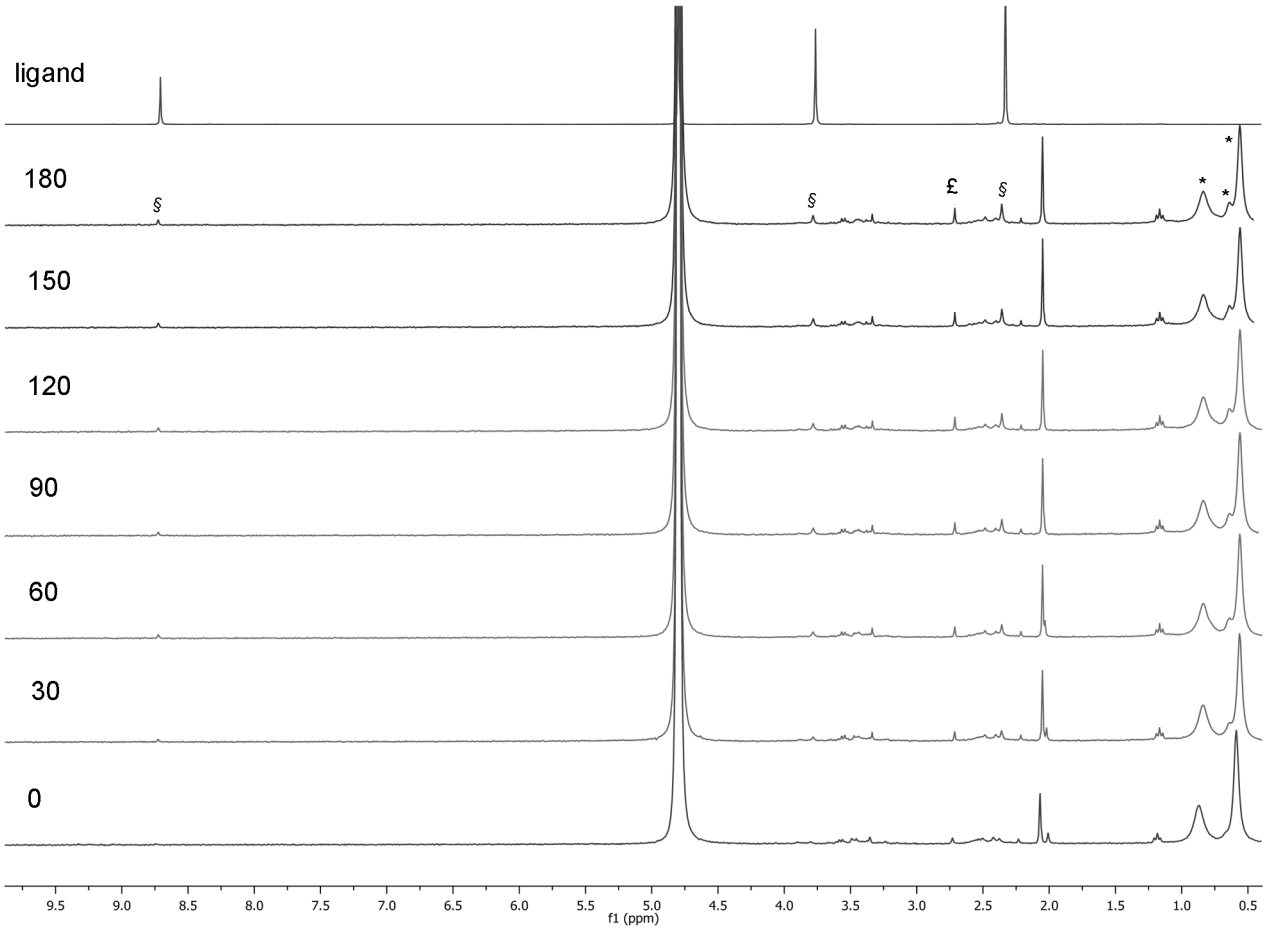

Figure S5. Stack plot of the ^{1}H NMR spectra of **1** in D_2O recorded in the 0-180 min interval, together with the free ligand spectrum in D_2O. * = coordinated ligand signals, § = free ligand signals, £ = free DMSO signal (2.71 ppm, ref. S3).

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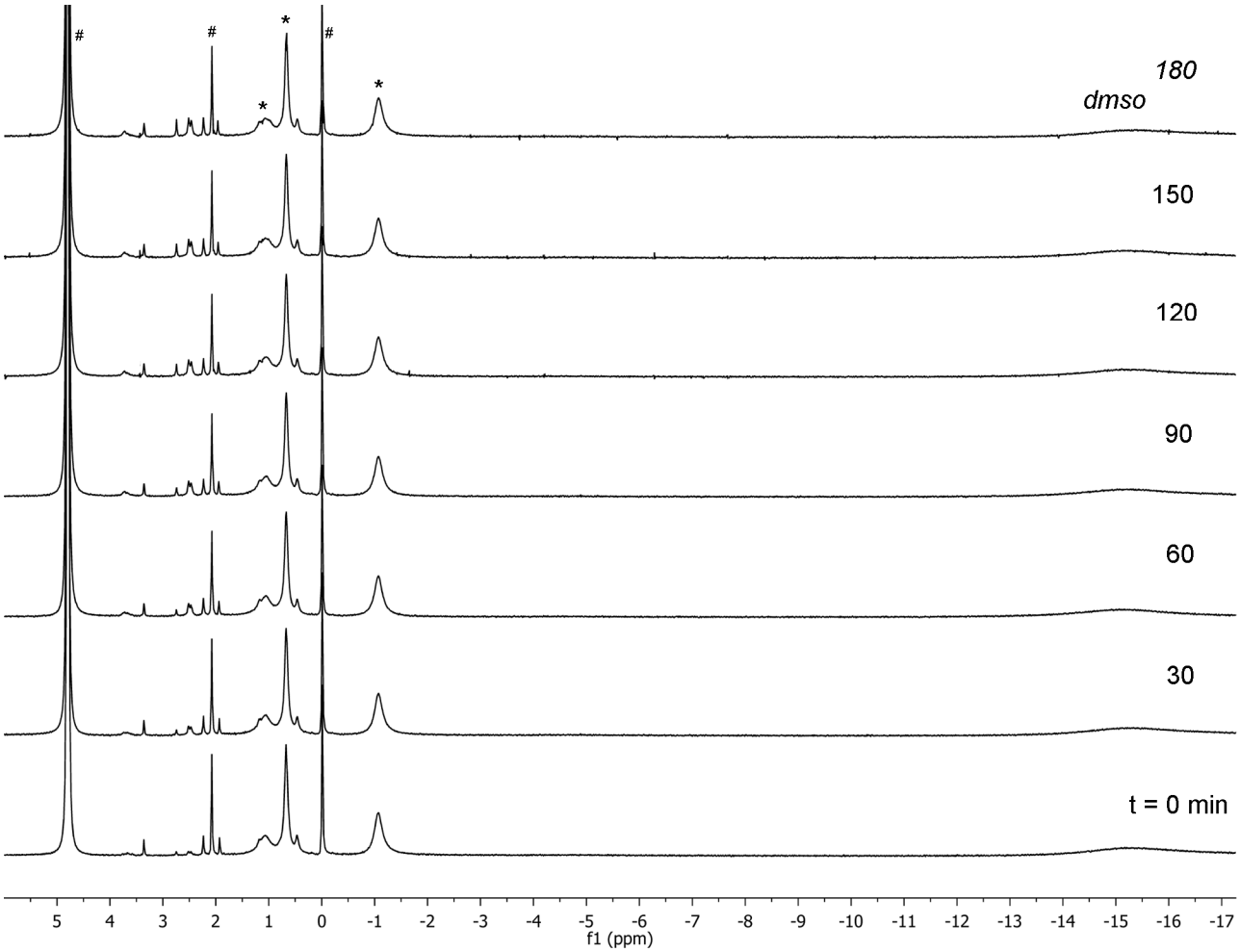

Figure S6. Stack plot of the ^{1}H NMR spectra of **2** in D_2O recorded in the 0-180 min interval. * = coordinated ligand signals. # = water, acetone and 3-(trimethylsilyl)propane sulfonate as reference.

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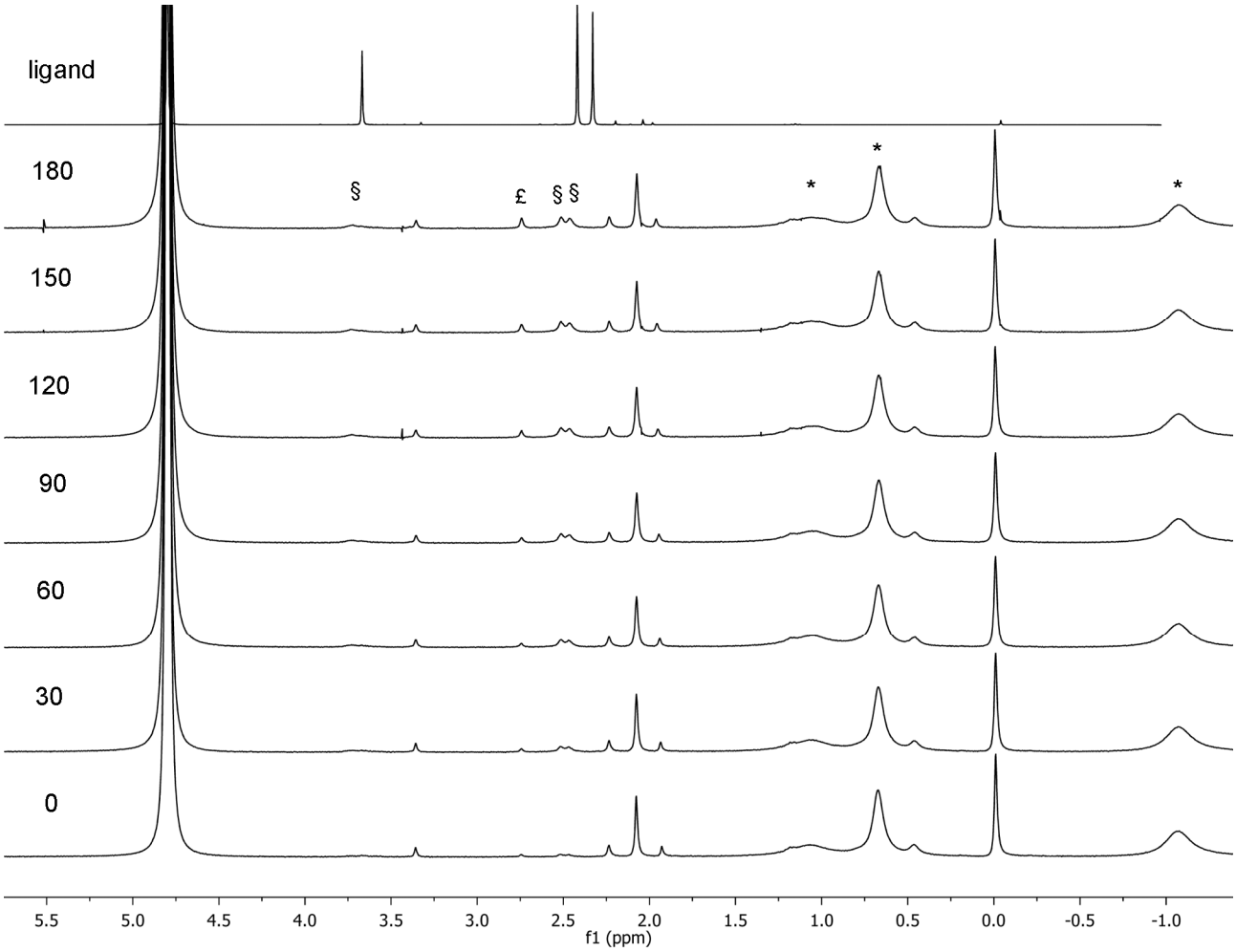

Figure S7. Stack plot of the ^{1}H NMR spectra of **2** in D_2O recorded in the 0-180 min interval, together with the free ligand spectrum in D_2O. * = coordinated ligand signals, § = free ligand signals, £ = free DMSO signal (2.71 ppm, ref. S3).

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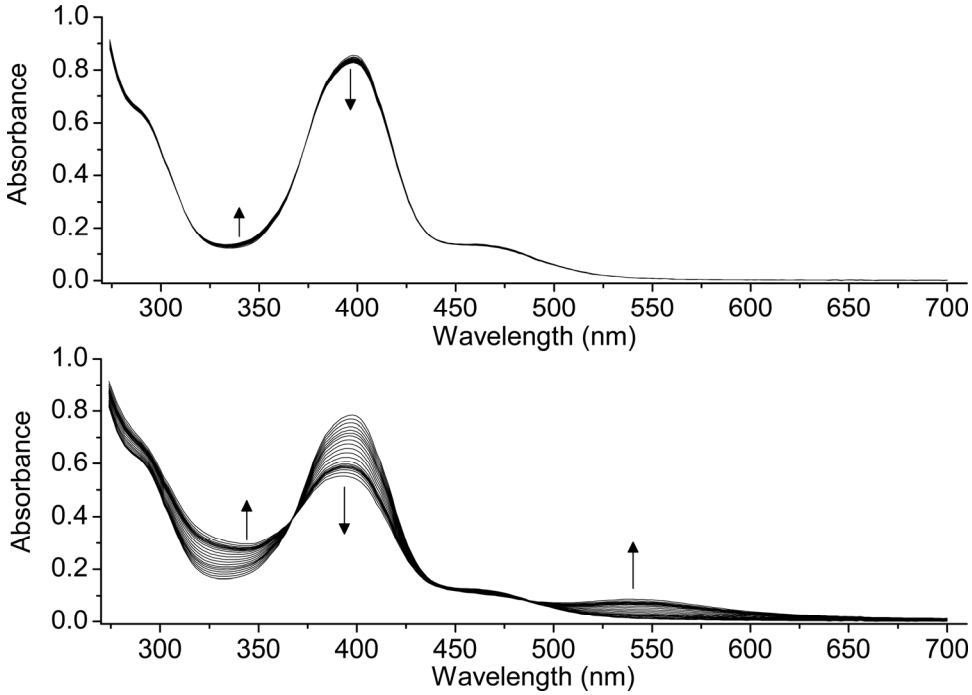

Figure S8. Upper diagram: UV-Vis spectra of Na[$RuCl_4$(dmso)(L2)] (**2**) in water at 7.5 min interval (0-170 min after dissolution). Lower diagram: UV-Vis spectra of **2** in water at 180 min interval (540-3000 min after dissolution).

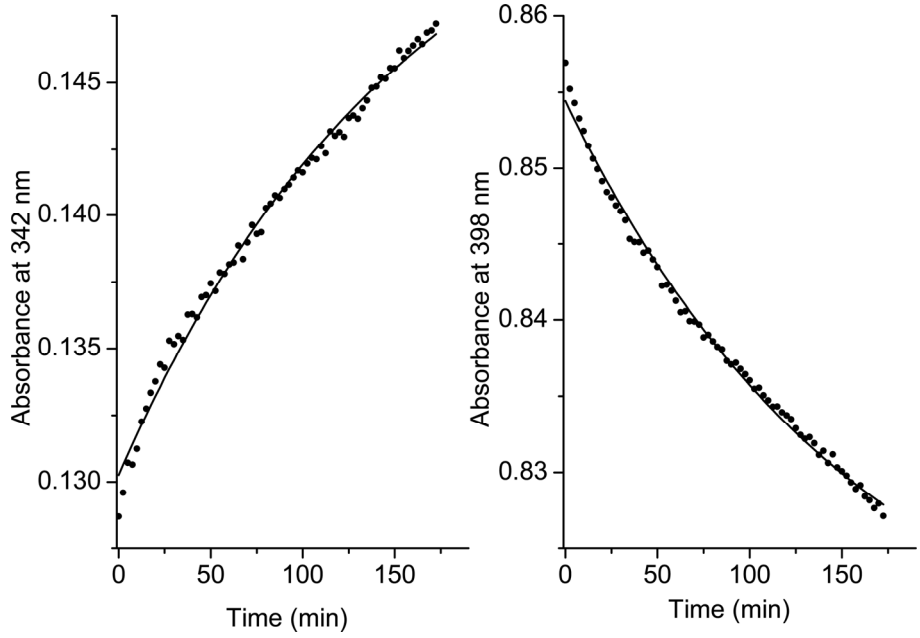

Figure S9. Experimental (dots) and calculated (lines) absorbances for the hydrolytic reaction of Na[$RuCl_4$(dmso)(L2)] (**2**) in water (0-170 min after dissolution) at 342 and 398 nm.

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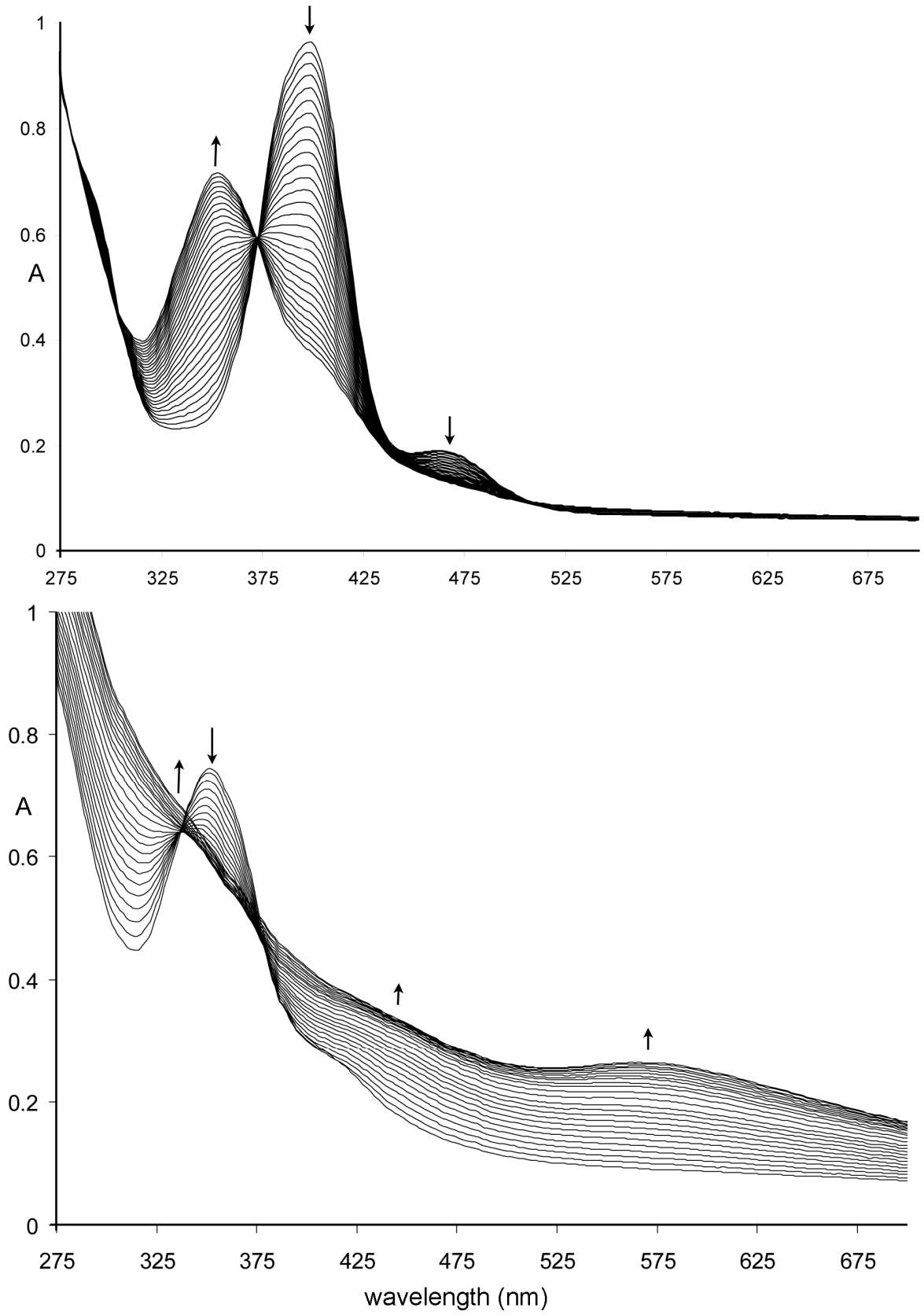

Figure S10. Upper diagram: UV-Vis spectra of Na[$RuCl_4$(dmso)(L1)] (**1**) in buffered water (pH = 7.4) at 60 sec interval (0-30 min after dissolution). Lower diagram: UV-Vis spectra of **1** in buffered water (pH = 7.4) at 120 sec interval (32-180 min after dissolution).

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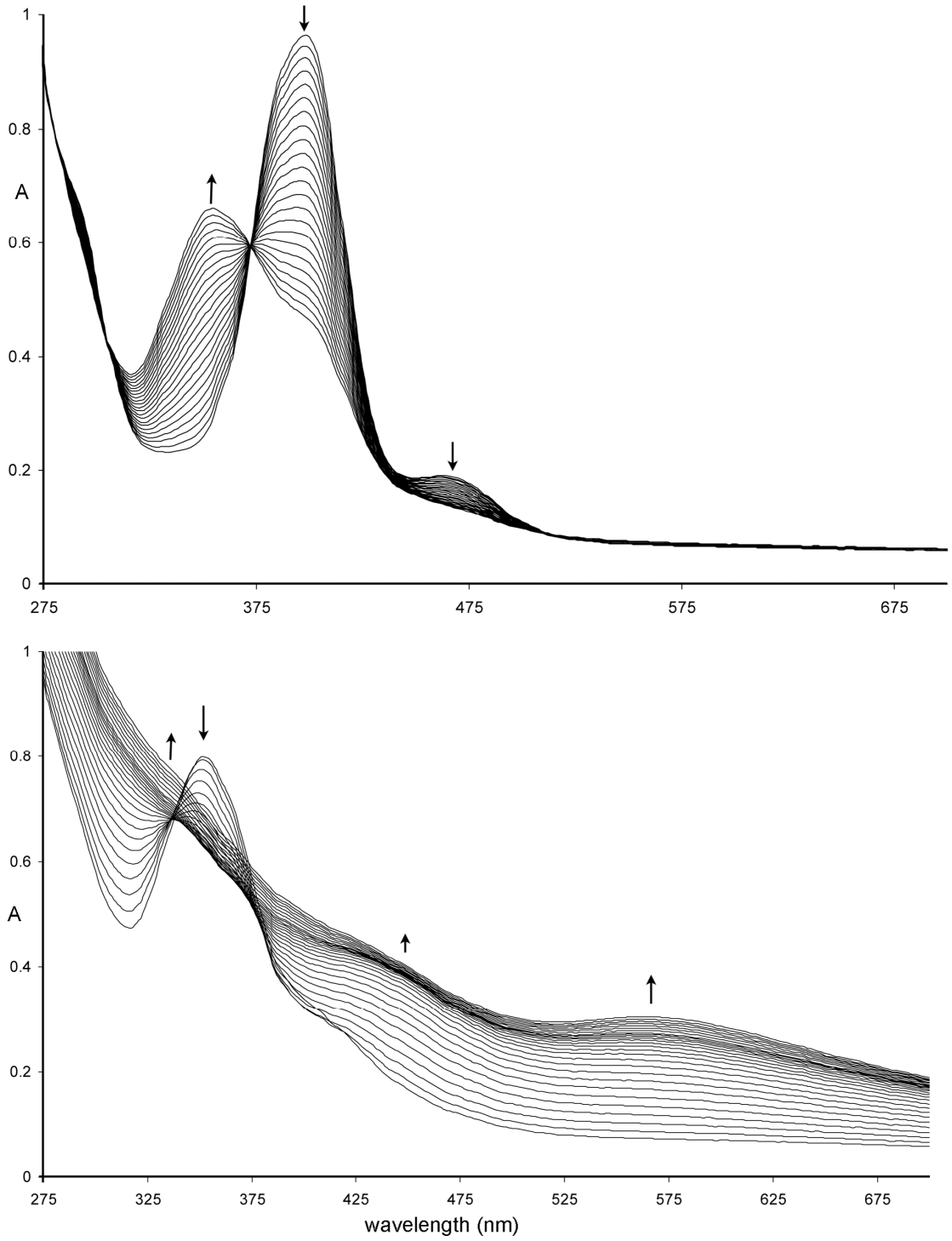

Figure S11. Upper diagram: UV-Vis spectra of Na[$RuCl_4$(dmso)(L2)] (**2**) in buffered water (pH = 7.4) at 60 sec interval (0-26 min after dissolution). Lower diagram: UV-Vis spectra of **2** in buffered water (pH = 7.4) at 120 sec interval (28-180 min after dissolution).

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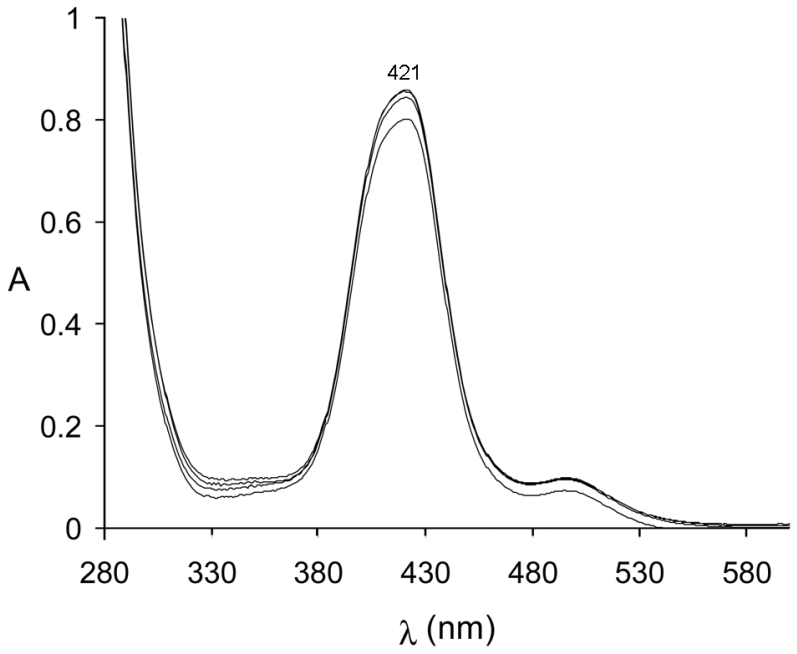

Figure S12. Solvolysis of $Na[RuCl_4(dmso)_2]$ in dmso; t = 0, 1, 3, 6, 24 h. Conc. = 2 x 10^{-4} M.

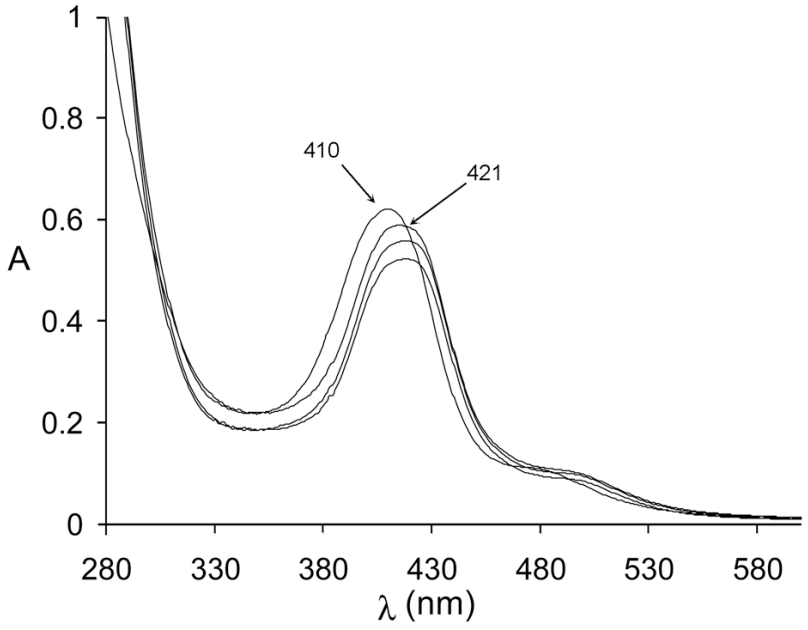

Figure S13. Solvolysis of Na[*trans*-$RuCl_4$(dmso)(L1)] **(1)** in dmso; t = 0, 1, 3, 6, 24 h. Conc. = 2 x 10^{-4} M. At t = 0, λ_{max} = 410 nm.

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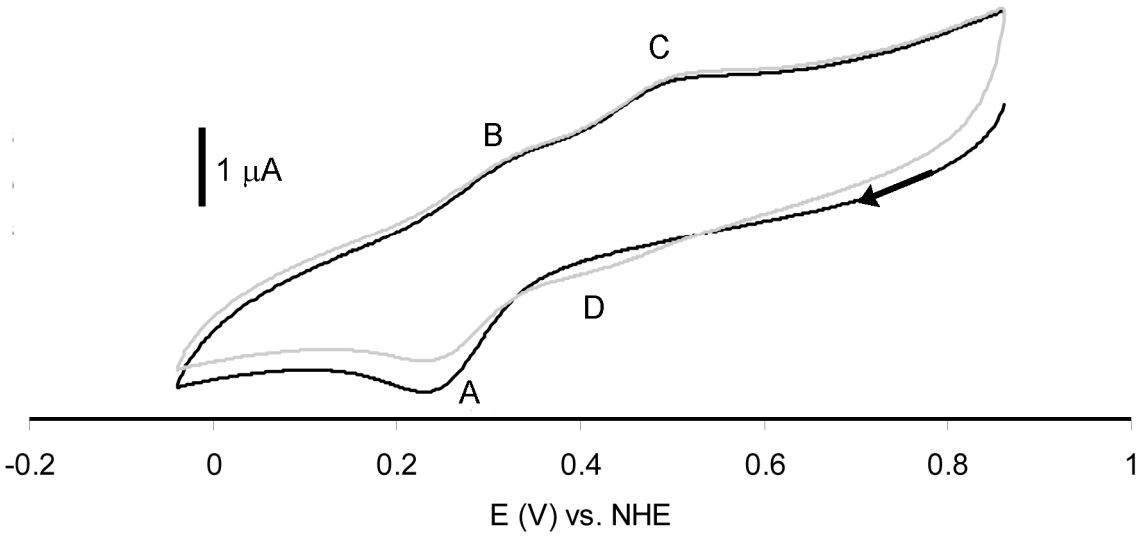

Figure S14. Cyclic voltammograms of a 5 x 10^{-4} M solutions of **2** dissolved in water. Supporting electrolyte: KNO_3 0.1 M. Scan rate: 25 mV/s. First scan (black line), second scan (gray line).

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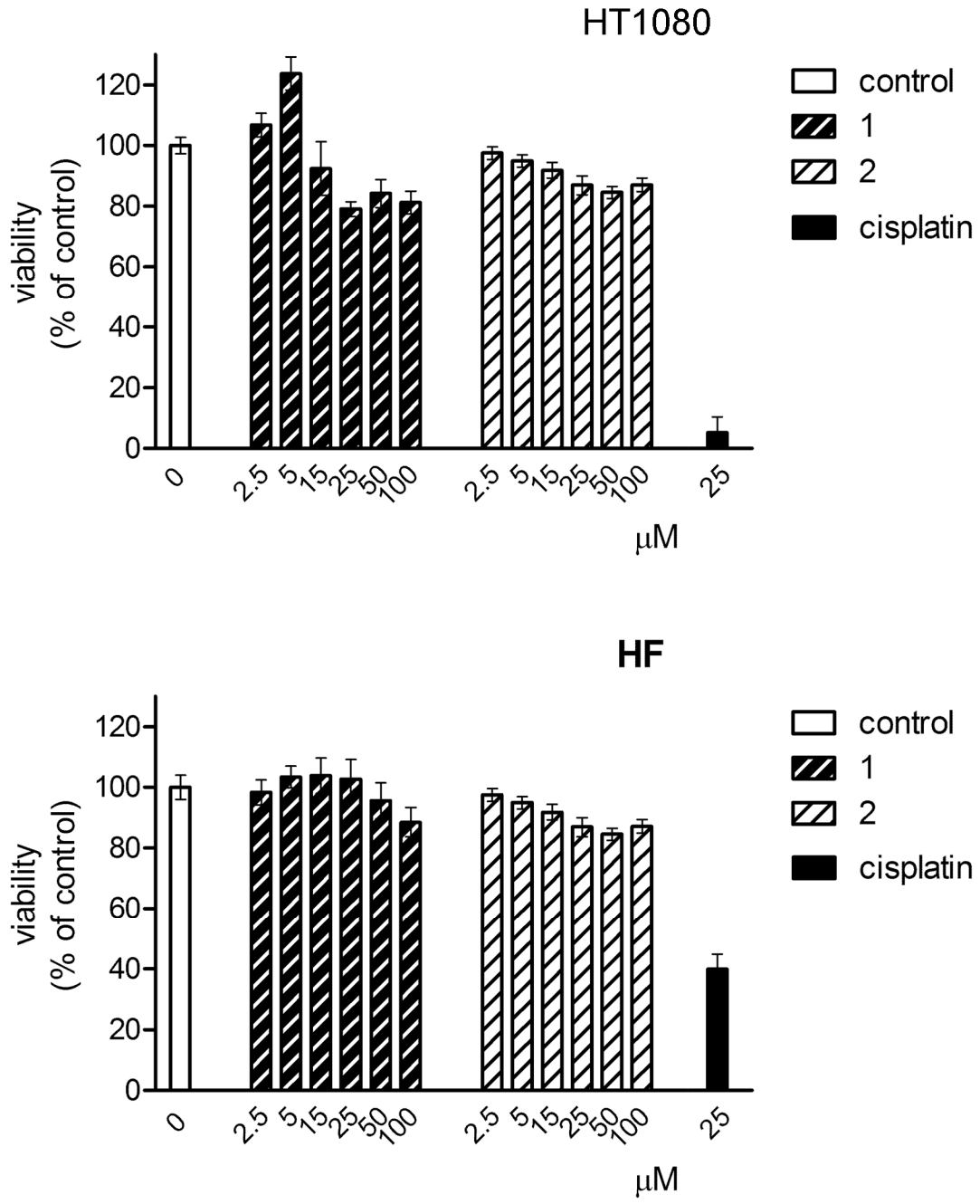

Figure S15. Dose-response plot obtained after a 48 h incubation of HT1080 and HF cells with the indicated concentrations of **1** and **2**. The effect of *cis*-platin on both cell lines is reported for comparison.

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