SUPPORTING INFORMATION

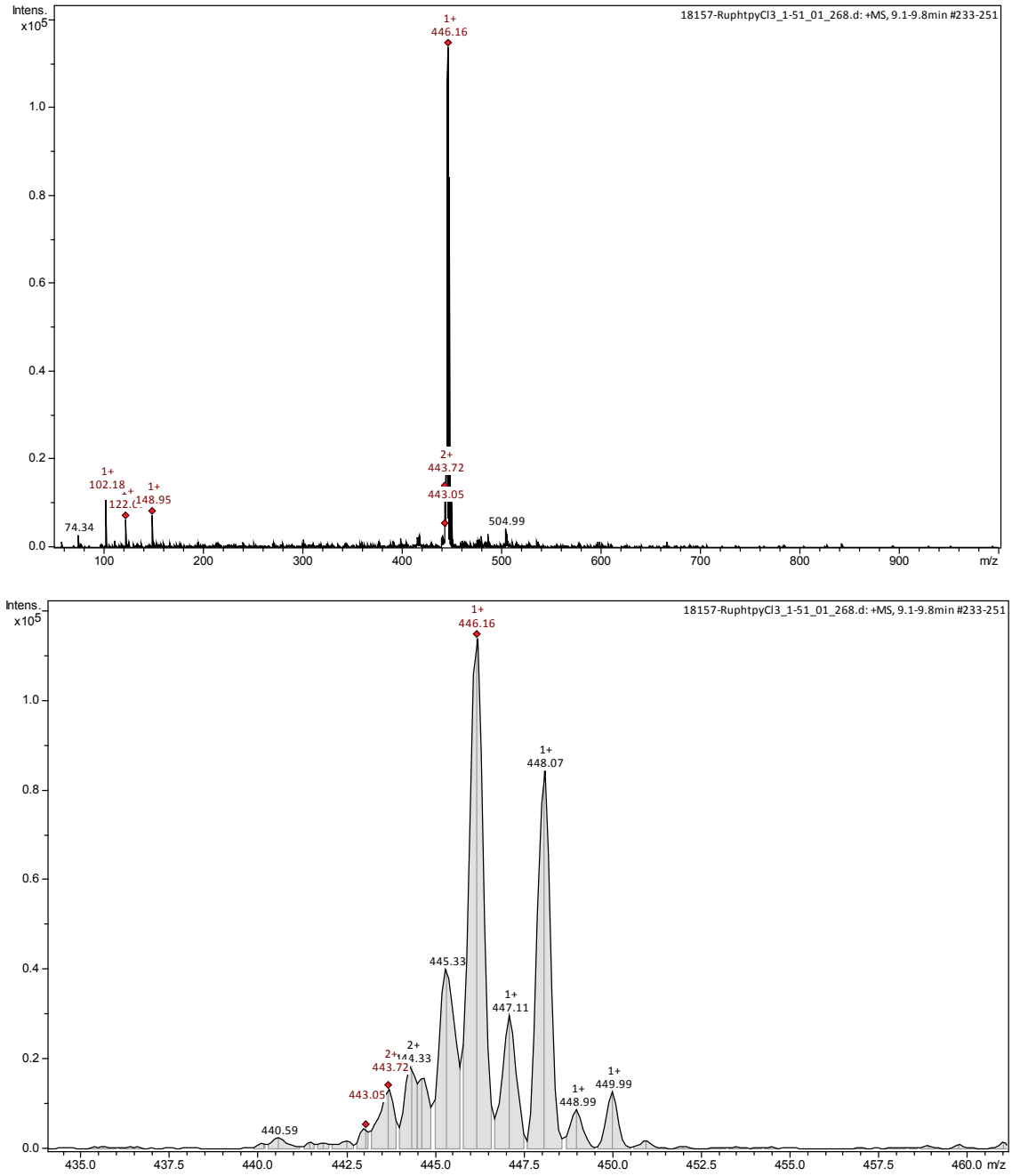

Figure S1. ESI-MS spectrum of the $[Ru(phtpy)Cl_3]$ precursor complex, showing the molecular peak corresponding to the $[Ru^{II}Cl(phtpy)]^+$ species.

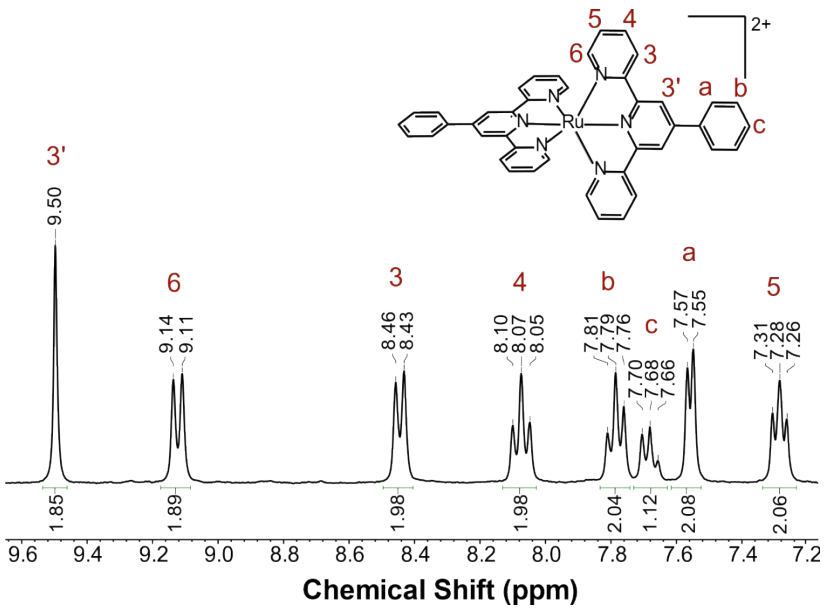

Figure S2. ^{1}H-NMR (DMSO-d_6) spectrum of the main fraction "A" (Figure 1b) of a typical silica gel column chromatography separation process and respective peak assignments. The spectrum is consistent with the $[Ru(phtpy)_2]^{2+}$ complex.

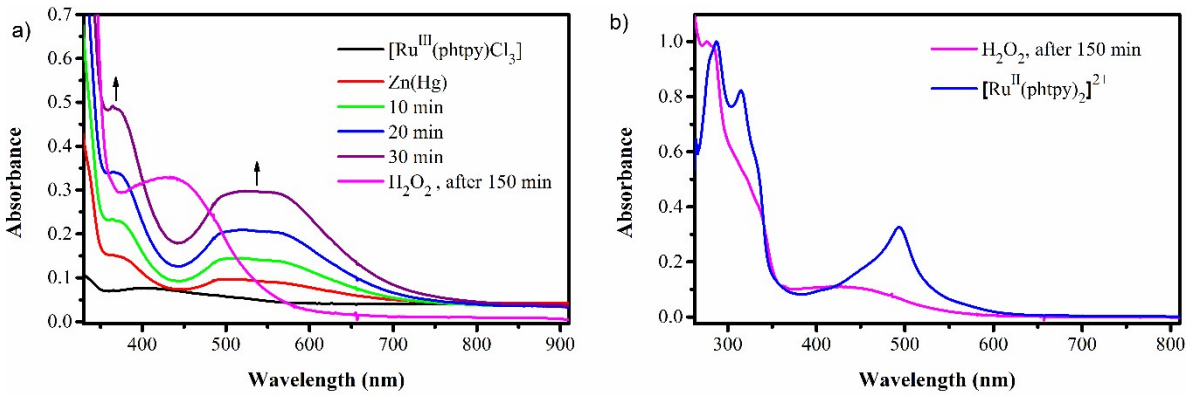

Figure S3: a) Evolution of the UV-Vis spectrum as a function of time after addition of zinc amalgam, Zn(Hg), into a solution of $[Ru^{III}(phtpy)Cl_3]$ in MeOH at 50 °C under N_2 atmosphere, generating a spectral profile similar to that shown in Fig. 2a. b) Spectra of $[Ru^{III}(phtpy)L_1L_2L_3]$ derivatives (where L_n = solvent or Cl^-) generated upon addition of H_2O_2 solution into the solution in (a) after 150 min (magenta line of Figure S3a) compared with that of $[Ru(phtpy)_2]^{2+}$ (blue line) in MeOH.

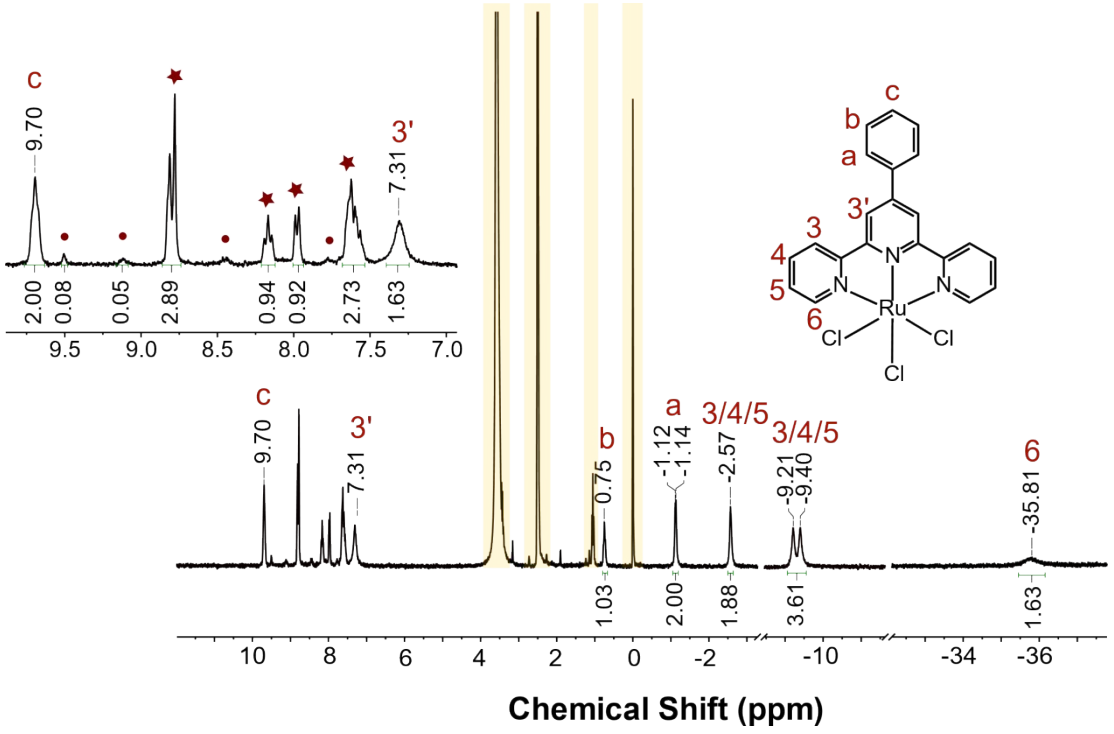

Figure S4. ^{1}H-NMR spectrum (300 MHz) of the [Ru(phtpy)Cl_3] complex in DMSO-d_6, showing signals corresponding to the Ru(III) and Ru(II) species (labeled with stars), and the presence of $[Ru^{II}(phtpy)_2]^{2+}$ complex as impurity (dots). The contrasting spectrum of free phtpy ligand in dmso-d_6 is shown in Figure 4.

Table S1. Representative experiments carried out for preparation of the binuclear $[\{Ru(phtpy)Cl\}_2(dpimH_2)]^{2+}$ complex by reaction of $[Ru^{III}(phtpy)Cl_3]$ precursor and the $dpimbH_2$ ligand in a 2:1 stoichiometric ratio.

Experiment	Solvent	Eq. LiCl	T (°C)	Time (hours)	Reducing Agent	Result
1	DMF/H_2O	10	reflux	4	NEM	mixture
2	DMF/H_2O	3	70	0.5	NEM	mixture
3	DMF*	0	54	2	NEM	mixture
4	EtOH/H_2O	3	R.T.	19	TEA**	mixture
5	EtOH/H_2O	3	40	6	TEA	mixture
6	EtOH	0	37	12	TEA	mixture
7	MeOH/H_2O***	1.5	80	2	TEA	mixture

- Using the aqua complex [$RuCl_2(H_2O)$(phtpy)]

** Triethylamine (TEA)

**Slow addition of [$RuCl_3$(phtpy)] to the reaction mixture.

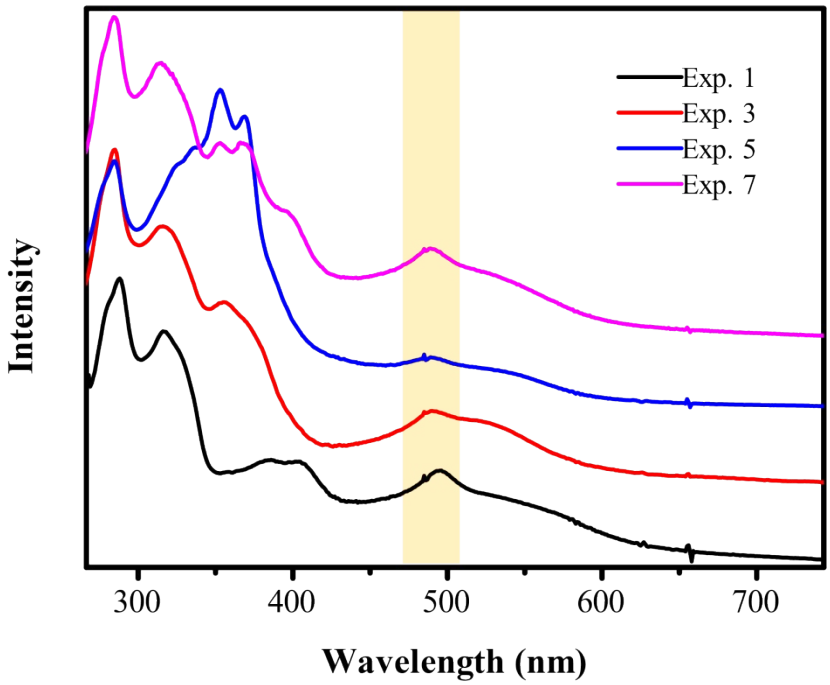

Figure S5. UV-vis spectra of some representative experiments among those listed in table S1 relative to the attempts for preparation of $[\{Ru(phtpy)Cl\}_2(dpimH_2)]^{2+}$ complexes, using a 2:1 stoichiometric ratio of the $[Ru^{III}(phtpy)Cl_3]$ complex and the $dpimbH_2$ ligand.