

# Photophysical Properties and Photobiological Activities of Ruthenium(II) Complexes Bearing $\pi$ -Expansive Cyclometalating Ligands with Thienyl Groups

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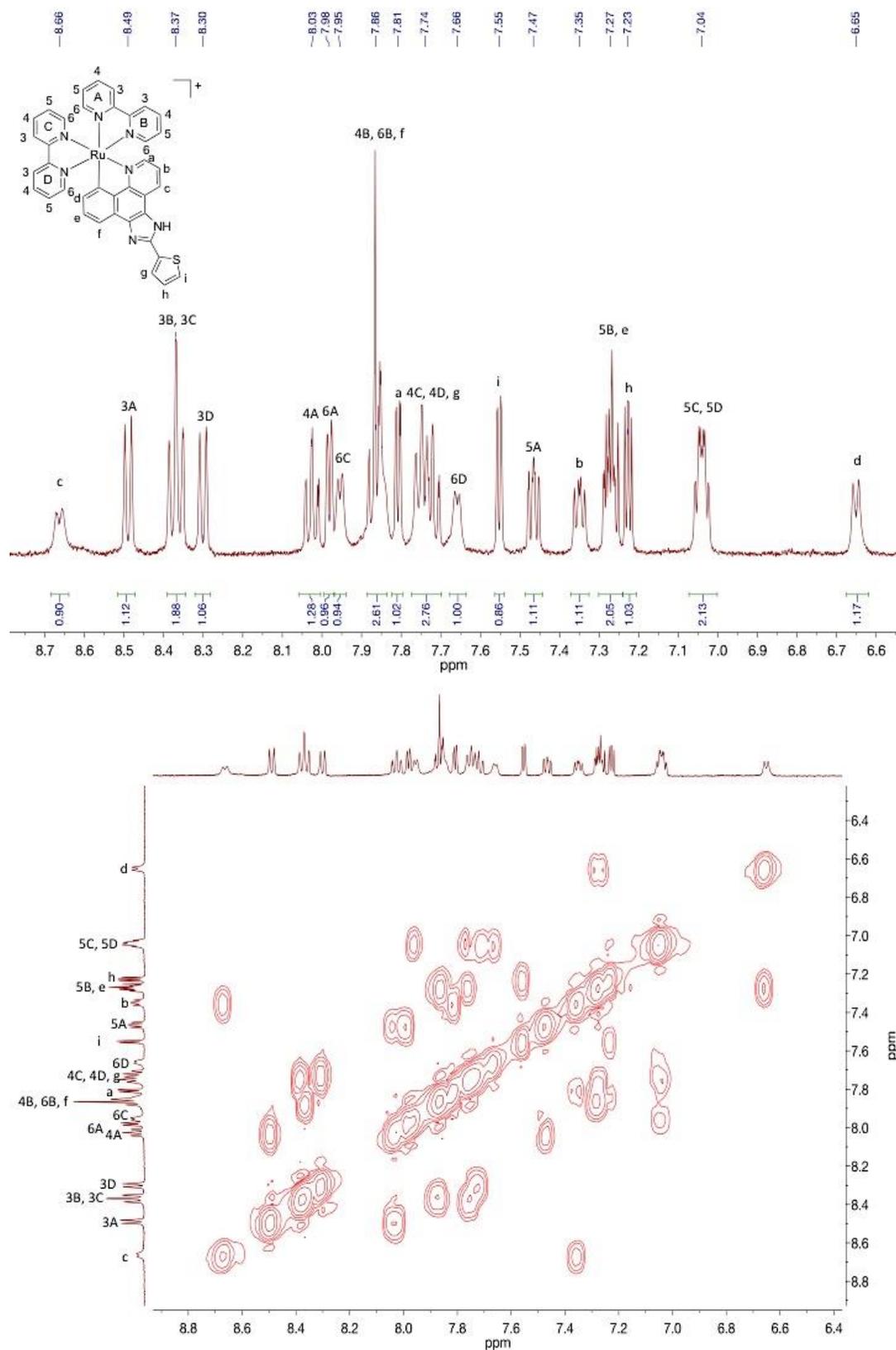


Figure S1.  $^1\text{H}$  (upper) and  $^1\text{H}$ - $^1\text{H}$  COSY (lower) NMR spectra of **1** in  $\text{MeCN-d}_3$ .

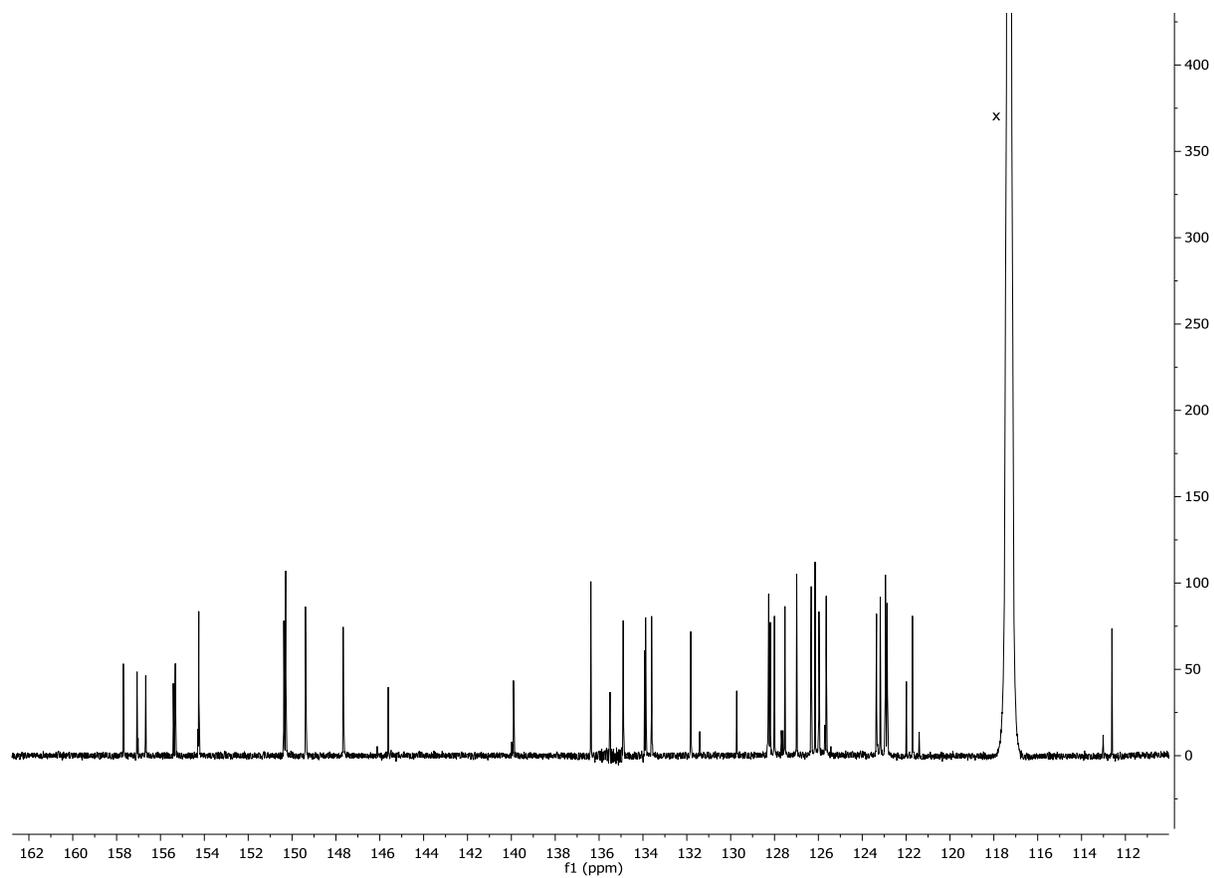


Figure S2.  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{MeCN-d}_3$ , 176 MHz. X =  $\text{MeCN}$ .

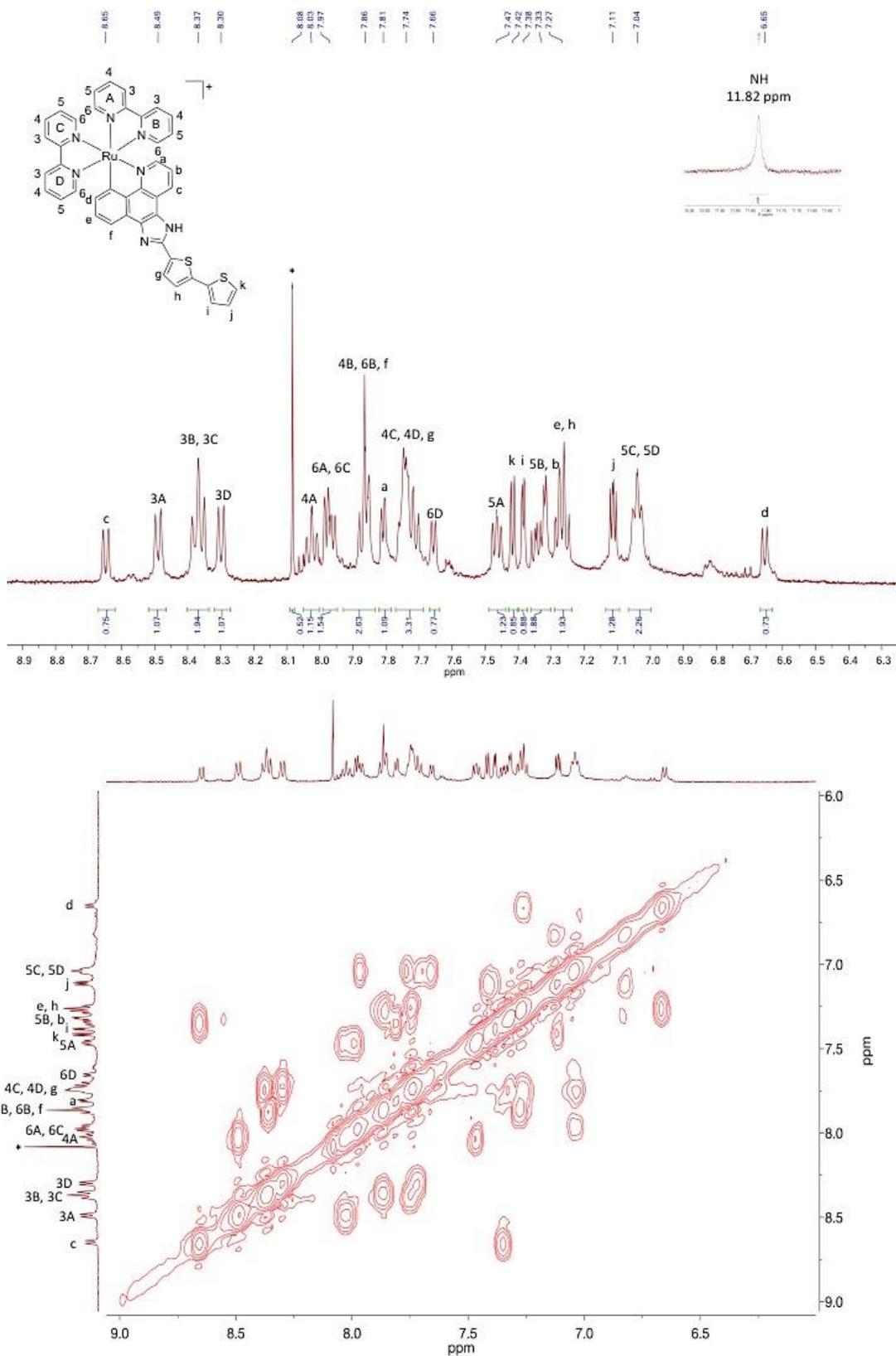


Figure S3.  $^1\text{H}$  (upper) and  $^1\text{H}$ - $^1\text{H}$  COSY (lower) NMR spectra of **2** in  $\text{MeCN-d}_3$ .

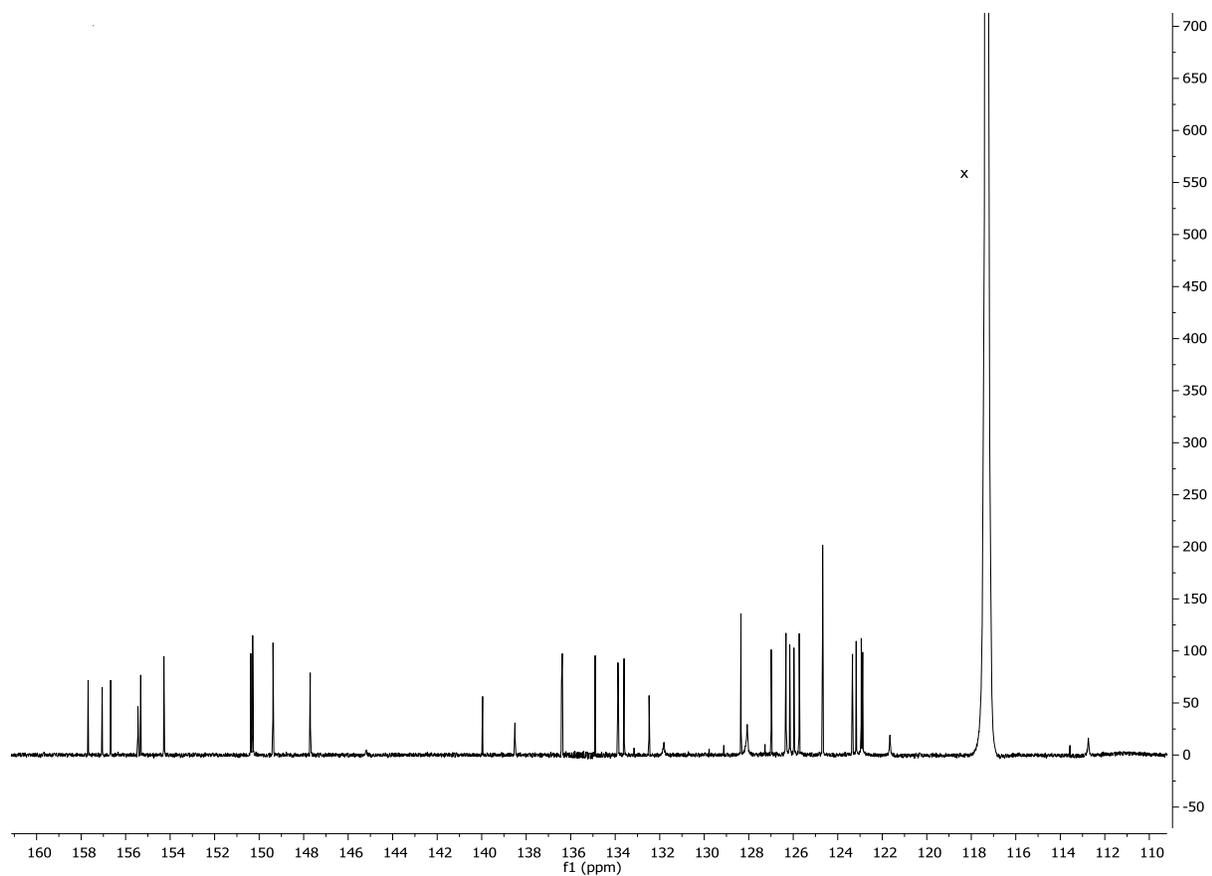


Figure S4.  $^{13}\text{C}$  NMR spectrum of **2** in  $\text{MeCN-d}_3$ , 176 MHz. X = MeCN.

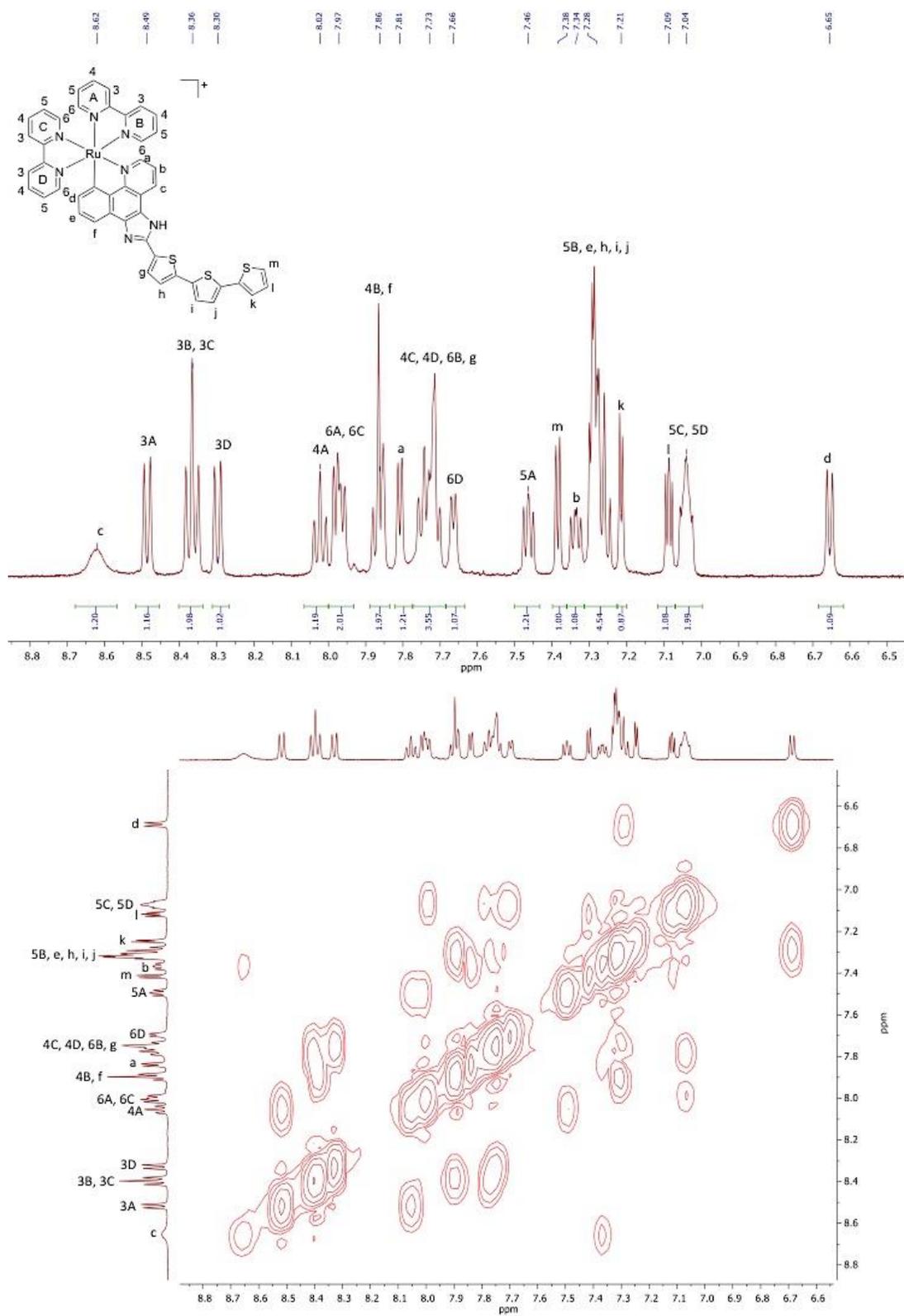


Figure S5.  $^1\text{H}$  (upper) and  $^1\text{H}$ - $^1\text{H}$  COSY (lower) NMR spectra of **3** in  $\text{MeCN-d}_3$ .

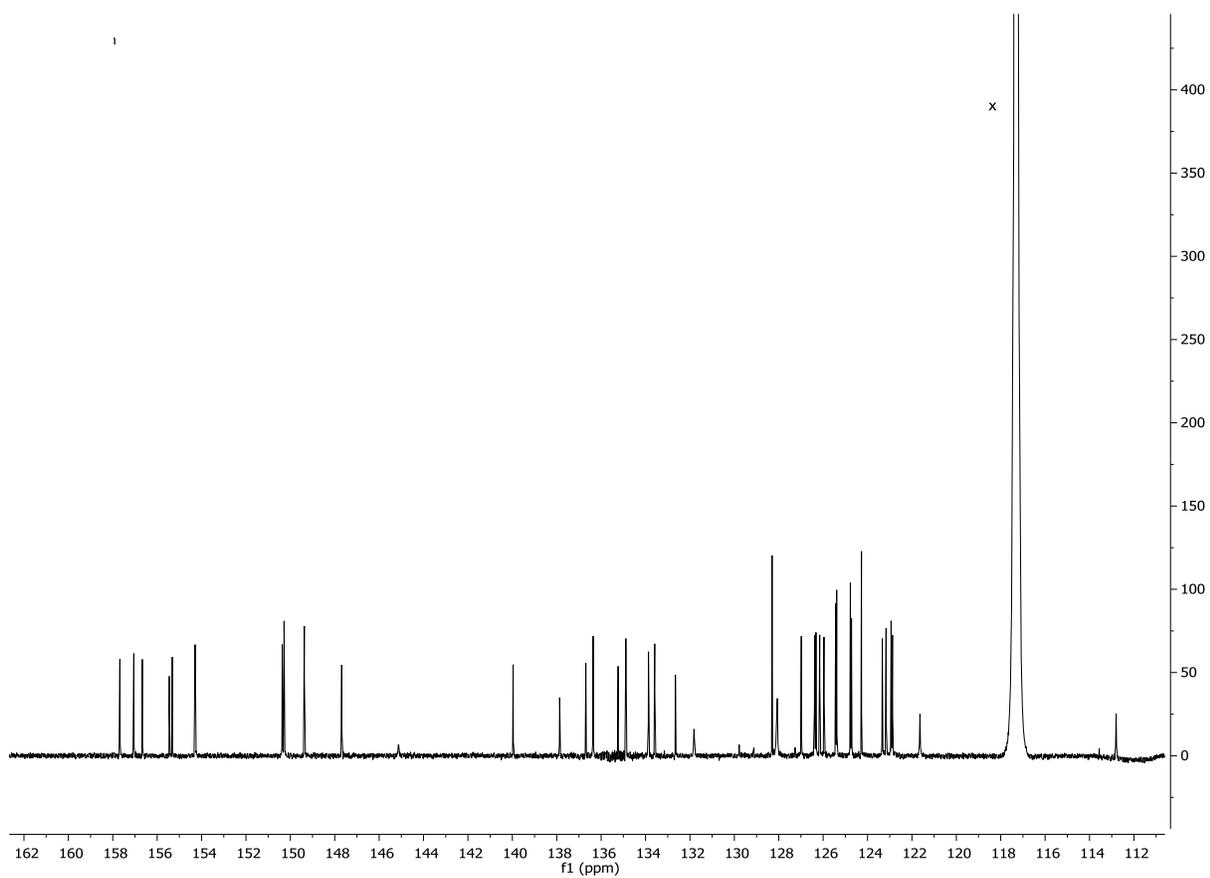


Figure S6.  $^{13}\text{C}$  NMR spectrum of **3** in  $\text{MeCN-d}_3$ , 176 MHz. X =  $\text{MeCN}$ .

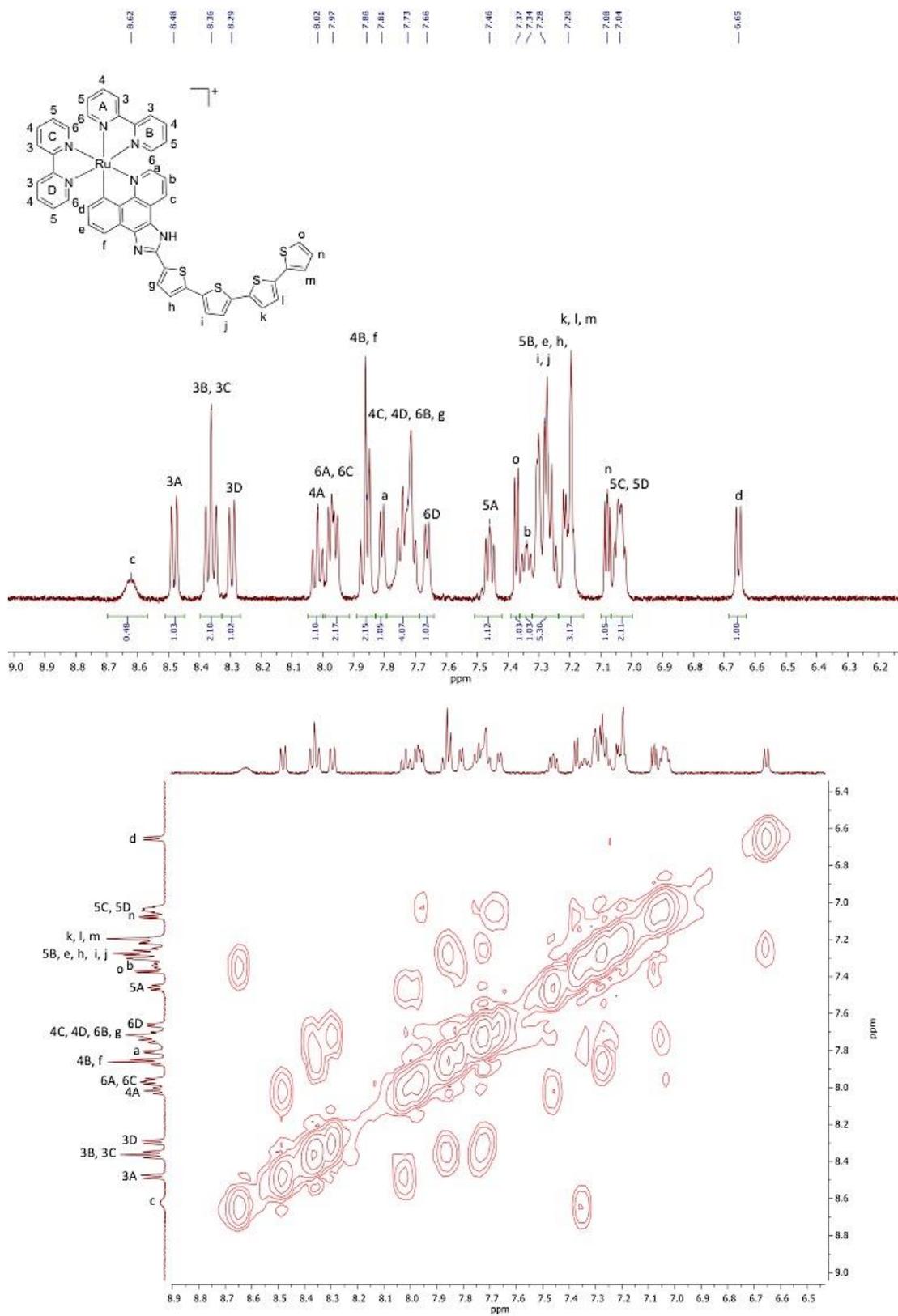


Figure S7. <sup>1</sup>H (upper) and <sup>1</sup>H-<sup>1</sup>H COSY (lower) NMR spectra of **4** in MeCN-d<sub>3</sub>.

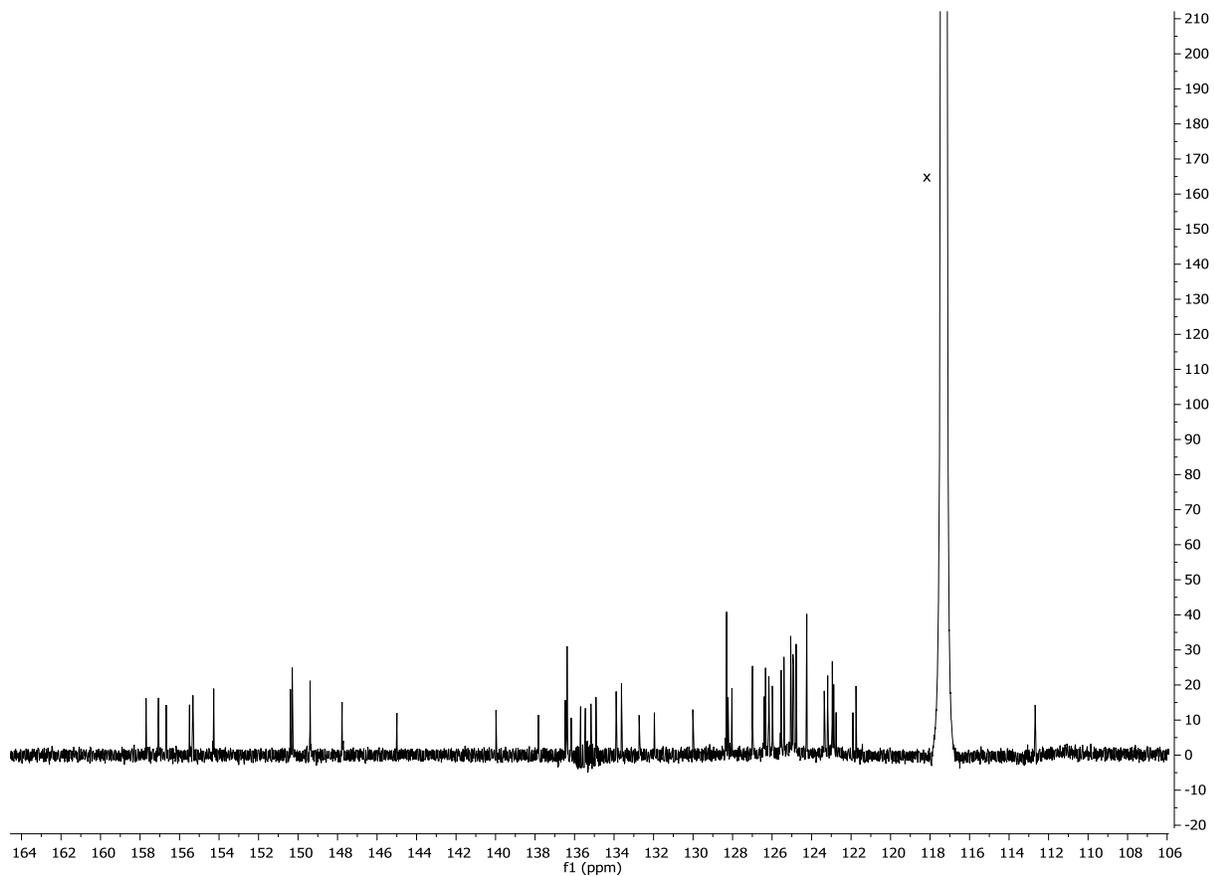


Figure S8.  $^{13}\text{C}$  NMR spectrum of **4** in  $\text{MeCN-d}_3$ , 176 MHz. X = MeCN.

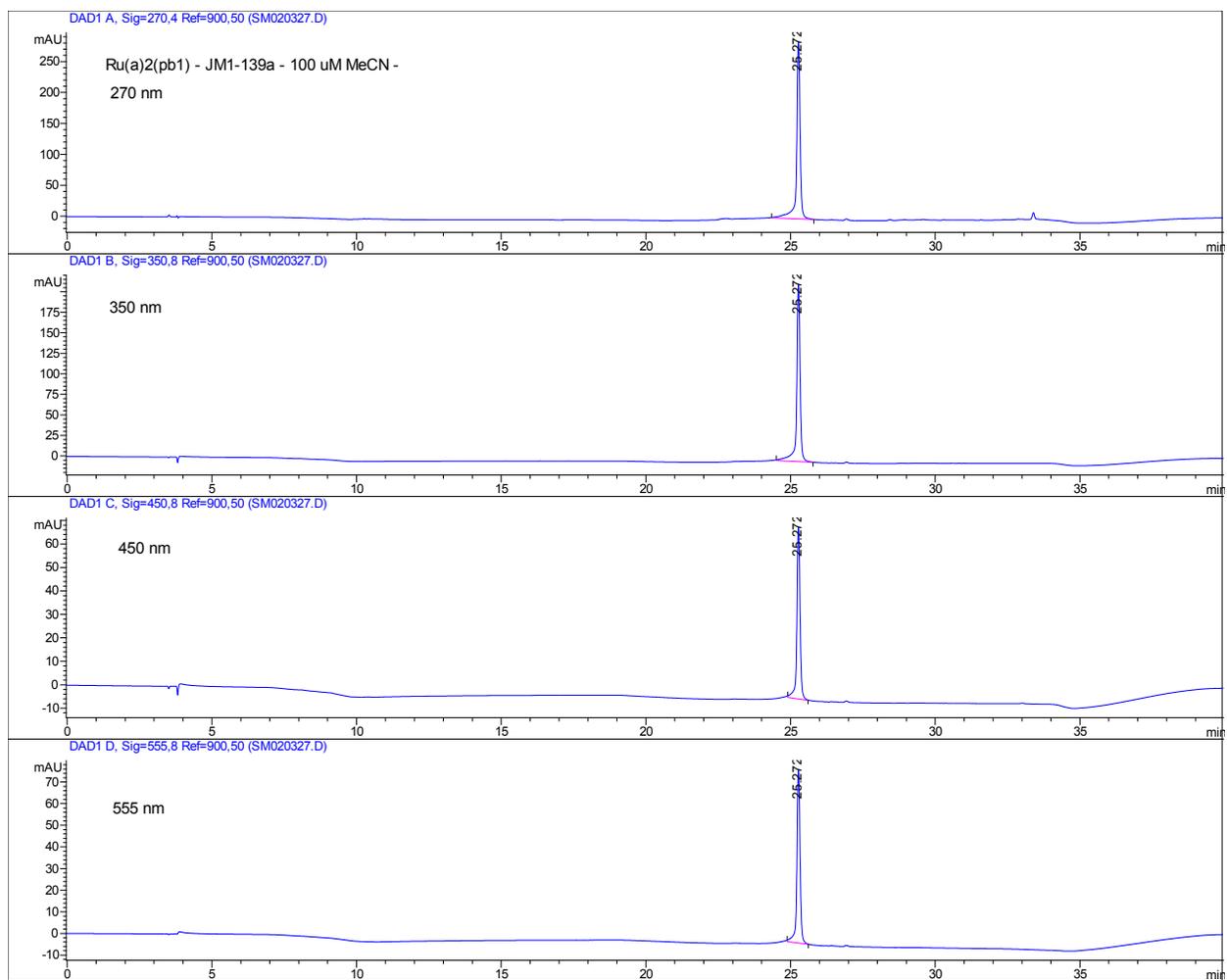


Figure S9. HPLC chromatogram of **1** collected at the following wavelengths: 270, 350, 450, 555 nm (97% purity by peak area).

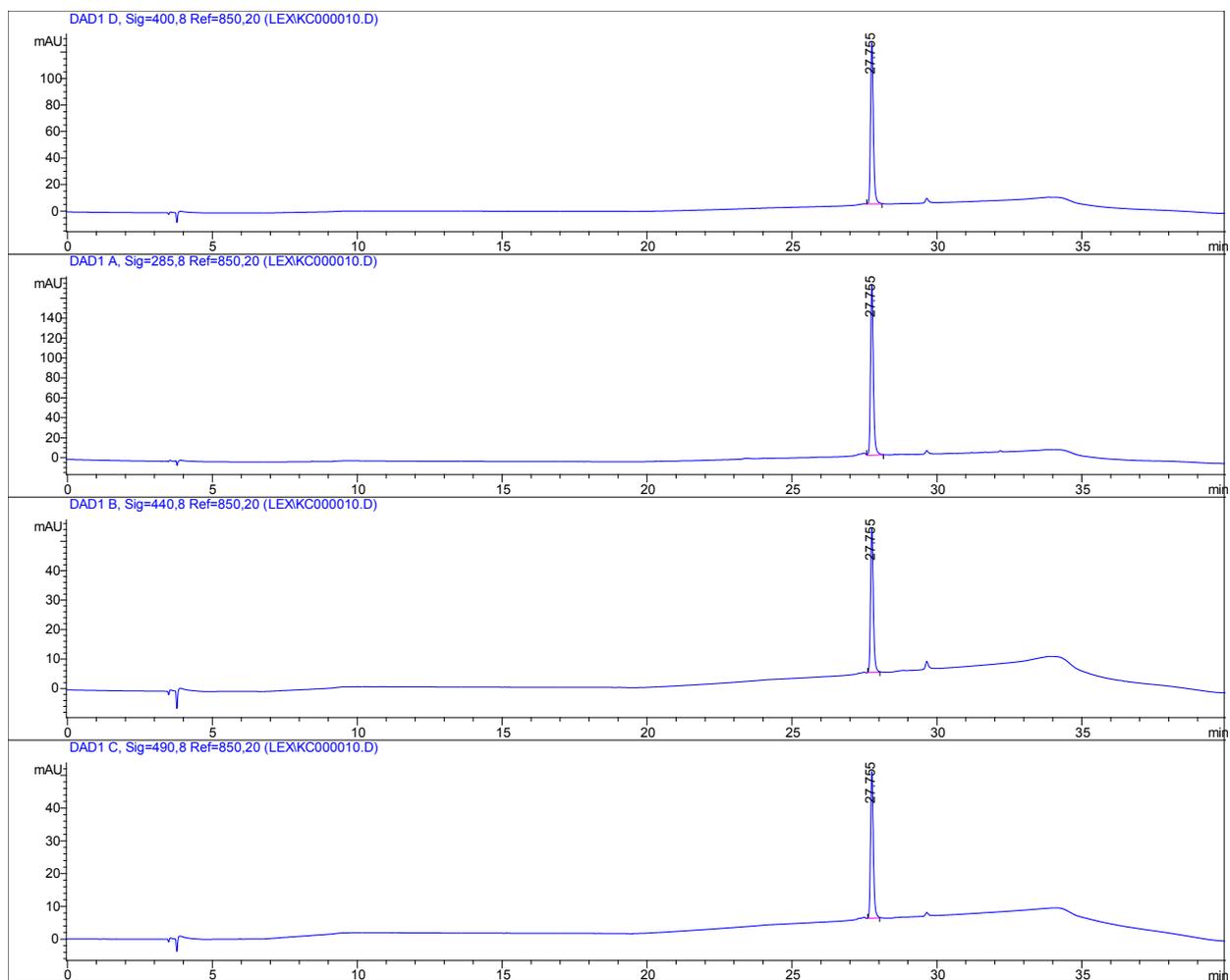


Figure S10. HPLC chromatogram of **2** collected at the following wavelengths: 400, 285, 440, 490 nm (99% purity by peak area).

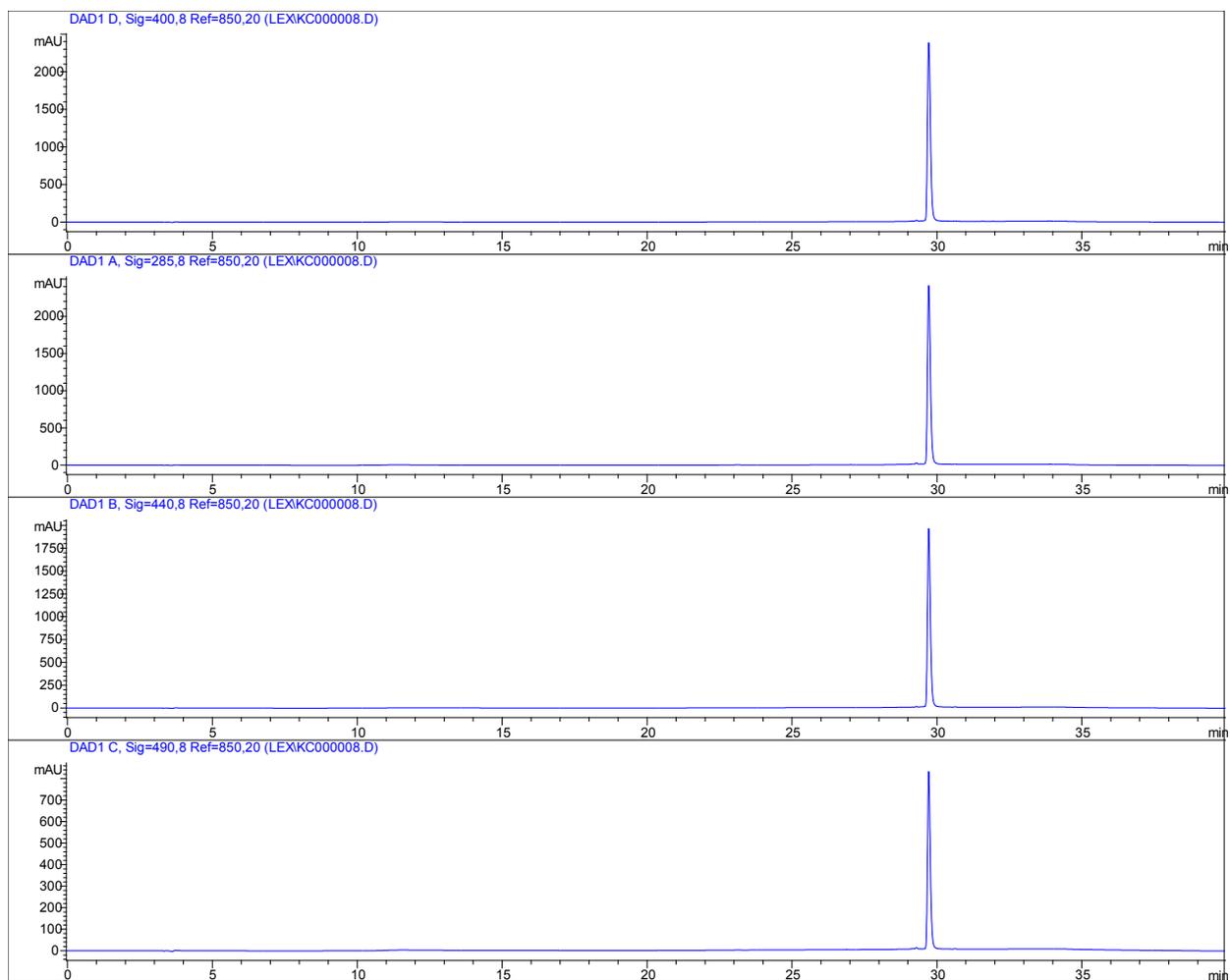


Figure S11. HPLC chromatogram of **3** collected at the following wavelengths: 400, 285, 440, 490 nm (98% purity by peak area).

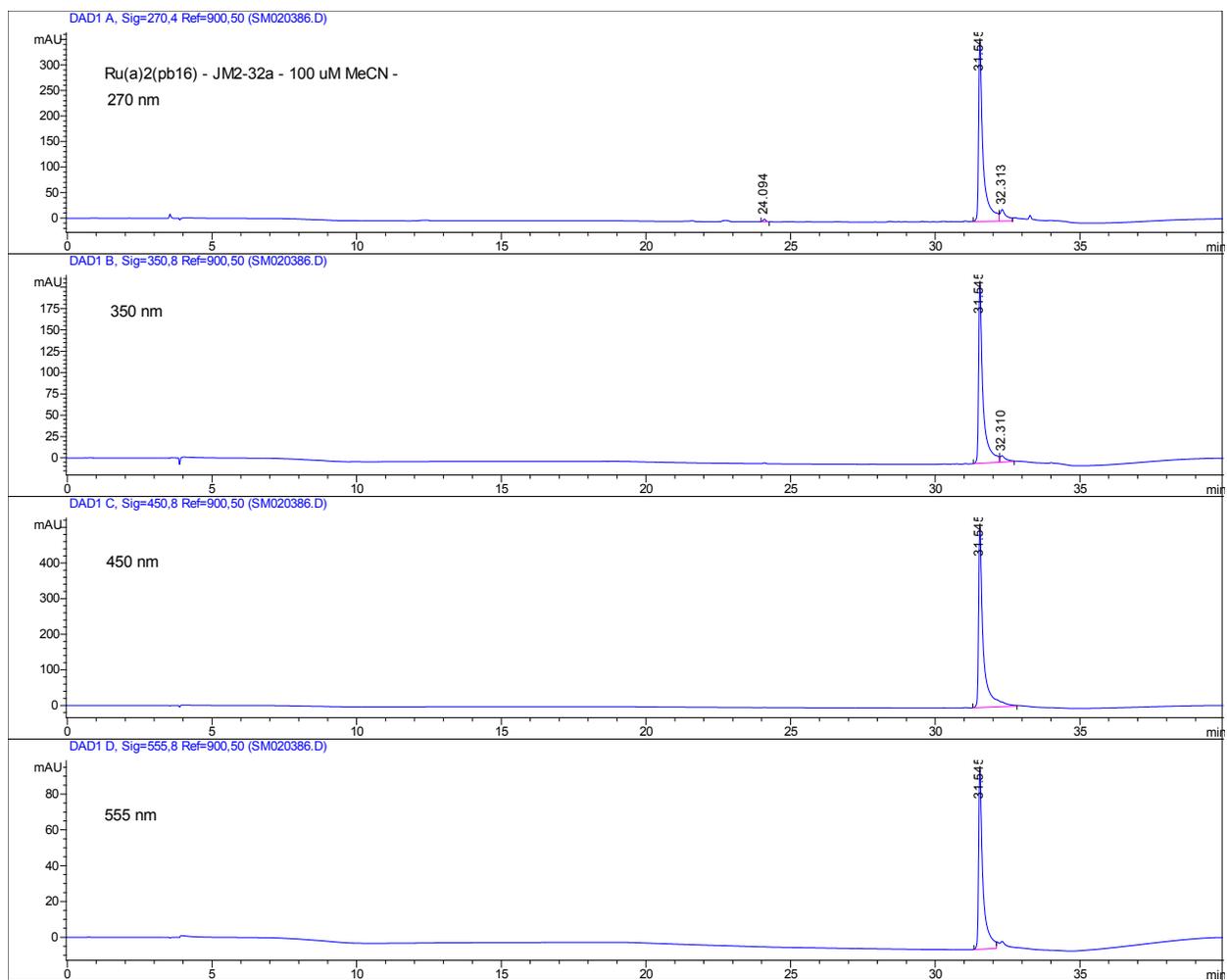


Figure S12. HPLC chromatogram of **4** collected at the following wavelengths: 270, 350, 450, 555 nm (95% purity by peak area).

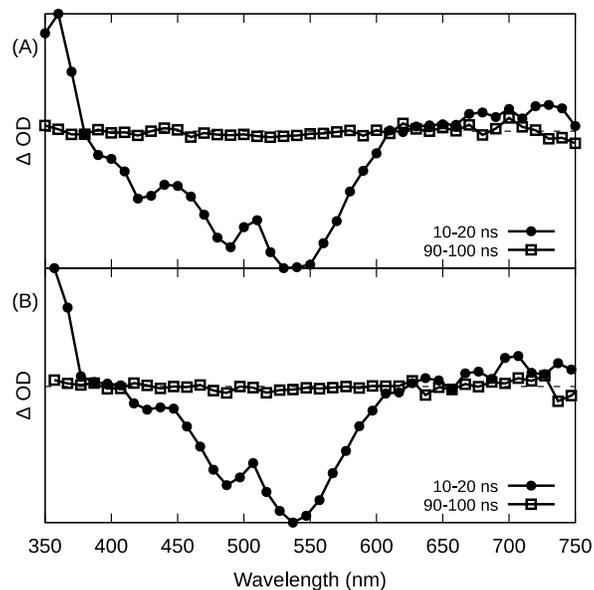


Figure S13. Comparison of the transient absorption decays for Ru(II) C<sup>N</sup> complex **1** collected with  $\lambda_{\text{pump}} = 355 \text{ nm}$  (A) or  $532 \text{ nm}$  (B) integrated over 10 ns starting at 10 or 90 ns after the excitation pulse.

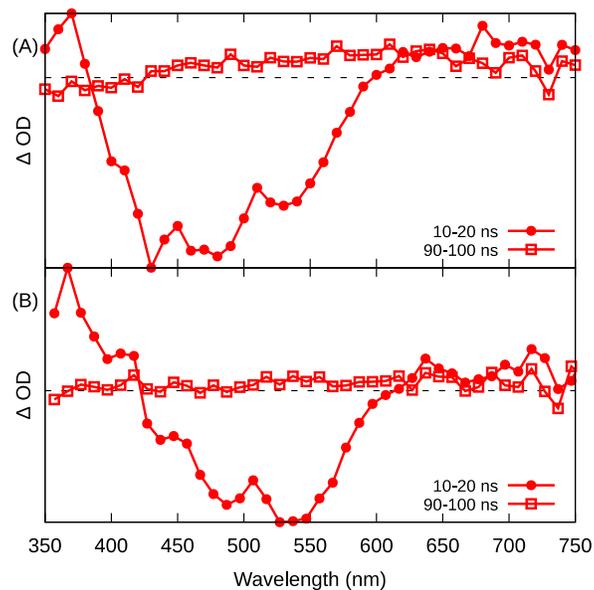


Figure S14. Comparison of the transient absorption decays for Ru(II) C<sup>N</sup> complex **2** collected with  $\lambda_{\text{pump}} = 355 \text{ nm}$  (A) or  $532 \text{ nm}$  (B) integrated over 10 ns starting at 10 or 90 ns after the excitation pulse.

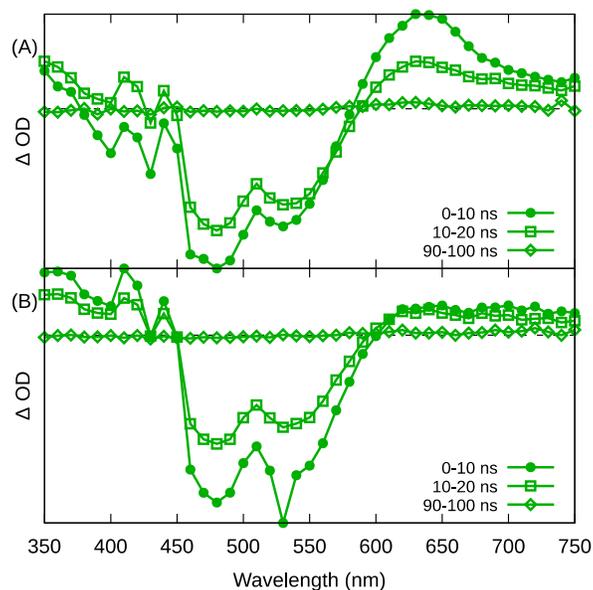


Figure S15. Comparison of the transient absorption decays for Ru(II) C<sup>N</sup> complex **3** collected with  $\lambda_{\text{pump}} = 355 \text{ nm}$  (A) or  $532 \text{ nm}$  (B) integrated over 10 ns starting at zero delay time or 10 or 90 ns after the excitation pulse.

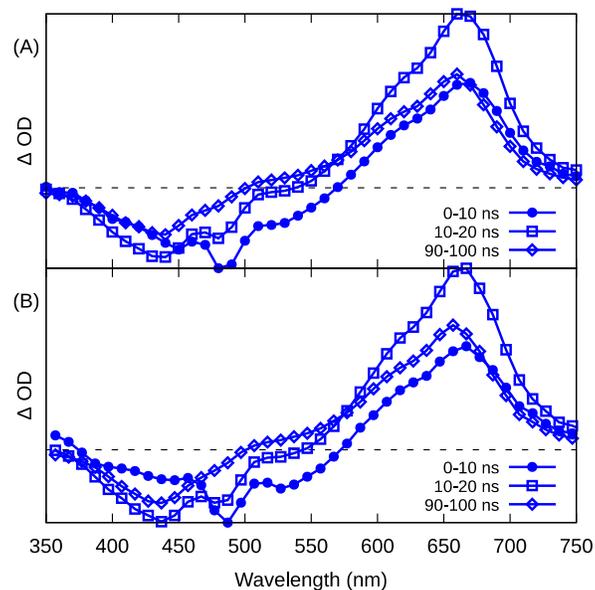


Figure S16. Comparison of the transient absorption decays for Ru(II) C<sup>N</sup> complex **4** collected with  $\lambda_{\text{pump}} = 355 \text{ nm}$  (A) or  $532 \text{ nm}$  (B) integrated over 10 ns starting at zero delay time or 10 or 90 ns after the excitation pulse

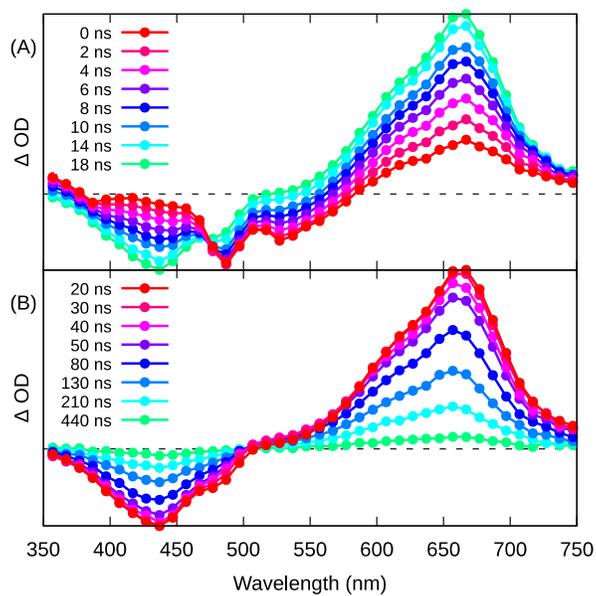


Figure S17. The TA spectrum of **4** excited at 532 nm.

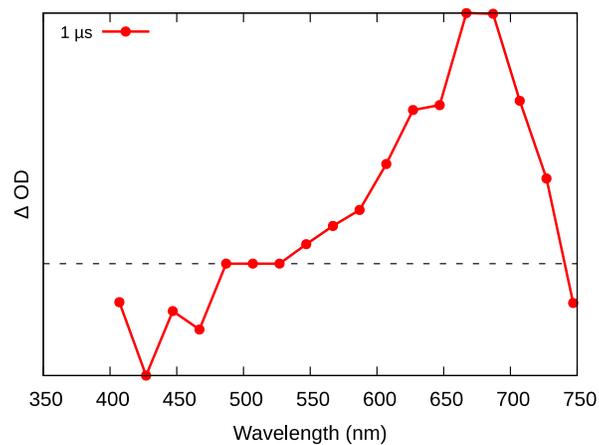


Figure S18. Transient absorption of the IBQ<sub>4</sub>T ligand only, in DMSO containing 1M KI. The 0-1 μs slice is shown.

**Table S1: Emission Data for Complexes 1–4 in 4:1 EtOH:MeOH at 77 K<sup>a</sup>**

Cmpd	$\lambda_{em}$ , nm <sup>1</sup> IL (77 K)	$\lambda_{em}$ , nm <sup>3</sup> MLCT (77 K)	$\Phi_p$ <sup>3</sup> MLCT (77 K)	$\Delta E_s$ , cm <sup>-1</sup>
1	423 (360)	726 (420)	$5.9 \times 10^{-3}$ (530)	1382
2	456 (377)	727 (420)	$5.4 \times 10^{-3}$ (530)	1378
3	503 (405)	730 (433)	$3.3 \times 10^{-3}$ (530)	1276
4	494 (418)	732 (440)	$3.8 \times 10^{-4}$ (530)	1238

<sup>a</sup>Excitation wavelengths (nm) are indicated in parentheses.