Supporting Information

Dual Action Ru(II) Complexes With Bulky π-Expansive Ligands: Phototoxicity Without DNA Intercalation

Nicholas P. Toupin,[1†] Sandeep Nadella,[1†] Sean J. Steinke,[2] Claudia Turro,[2*] Jeremy J. Kodanko[1,3*]

[1]Department of Chemistry, Wayne State University, 5101 Cass Ave, Detroit, MI 48202

[2]Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH 43210

[3]Barbara Ann Karmanos Cancer Institute, Detroit, MI 48201

[†]These authors contributed equally to this work

*jkodanko@chem.wayne.edu

*turro@chemistry.ohio-state.edu

Table of Contents

General Considerations

MDA-MB-231 and DU-145 cells were obtained from American Type Culture Collection (Manassas, VA). Cells were cultured in Dulbecco's modified eagle's medium containing 10% FBS and 1000 units/ml penicillin/streptomycin and were grown at 37 °C and 5% CO_2. Fluorescence assisted cell sorting (FACS) was performed using a Sysmex Cyflow Space fluorescence assisted cell sorter. Data obtained from FACS was processed using Flomax Fcs processing software. Blue light irradiation (λ_{irr} = 460–470 nm) was performed using an LED panel, made in house, consisting of a project board fitted with 96, 60 mW 5mm blue LED diode bulbs from Chanzon (Shanzhen, China) that irradiate each well of a 96-well plate.

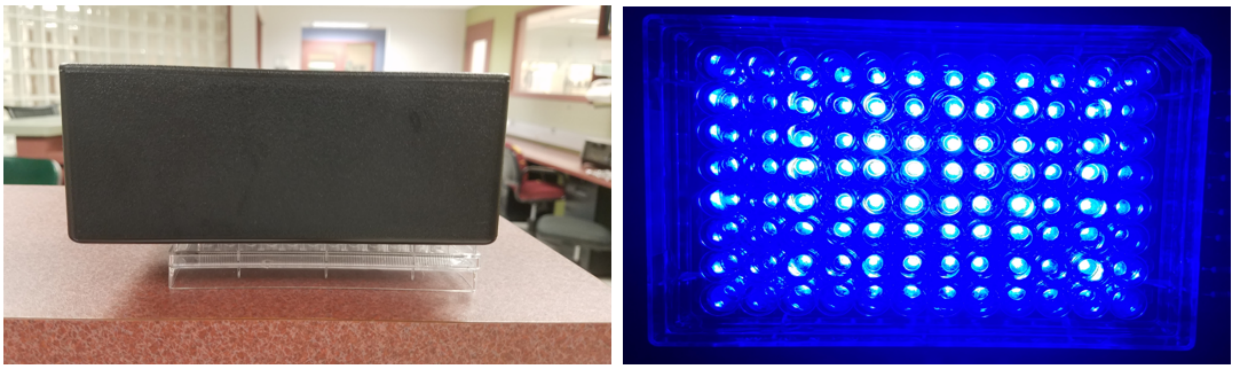


Figure S1: LED panel constructed in house. **Left**: Sideview of blue LED panel while turned off. **Right:** Bottom view of LED panel displaying fit onto 96-well plate while activated.

Atrope Isomerism Figure

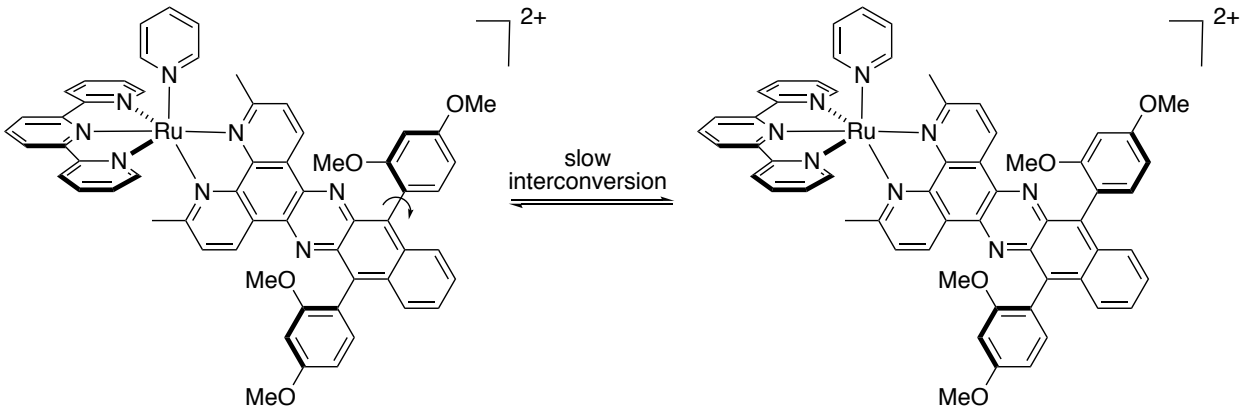


Figure S2: Proposed slow interconversion of atropisomers from **10** on the NMR timescale

Biological Assays

1. **DNA Binding Studies**

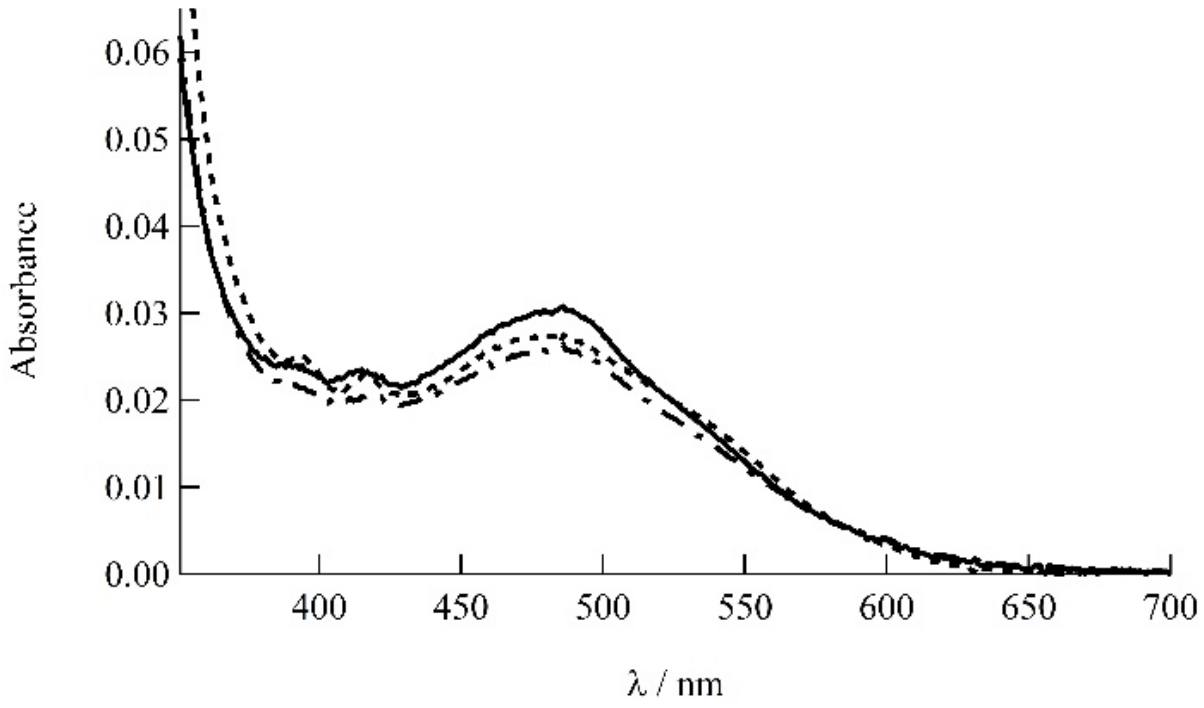


Figure S3. Electronic absorption spectrum of 5 μM **8** (5 mM Tris, 50 mM NaCl, pH 7.0) alone (–) and in the presence of PSS (100 μM) (---) and DNA (100 μM bases) (-•-).

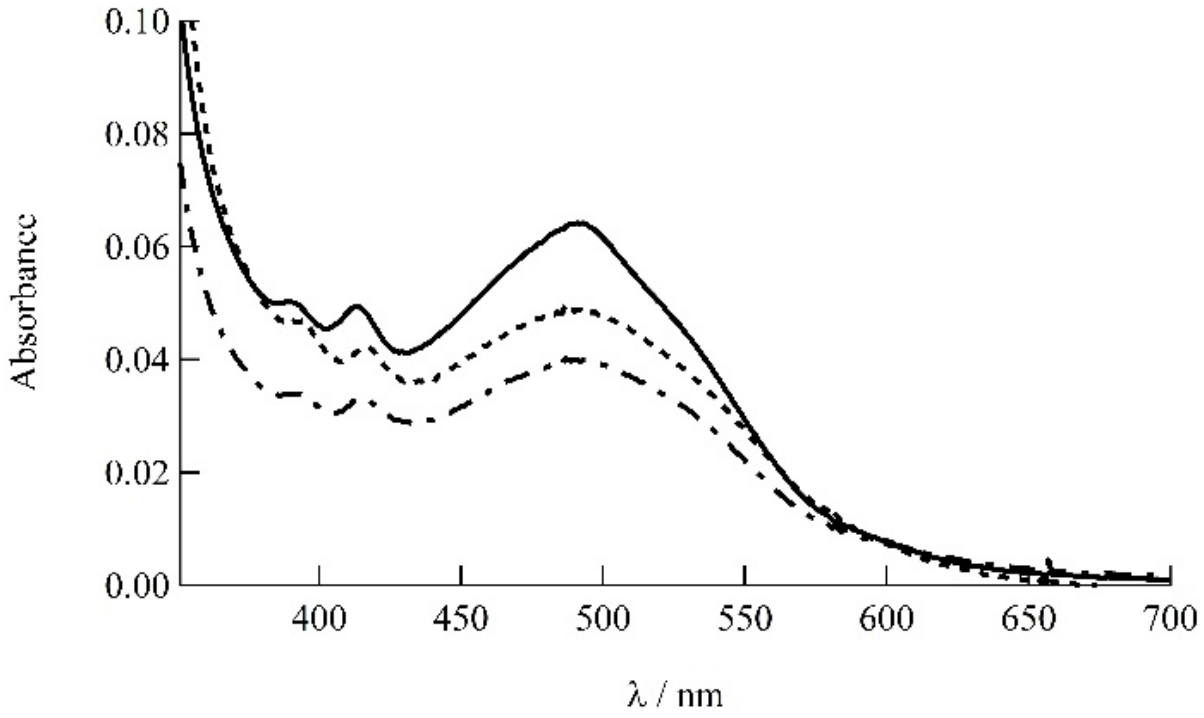


Figure S4. Electronic absorption spectrum of 5 μM **9** (5 mM Tris, 50 mM NaCl, pH 7.0) alone (–) and in the presence of PSS (100 μM) (---) and DNA (100 μM bases) (-•-).

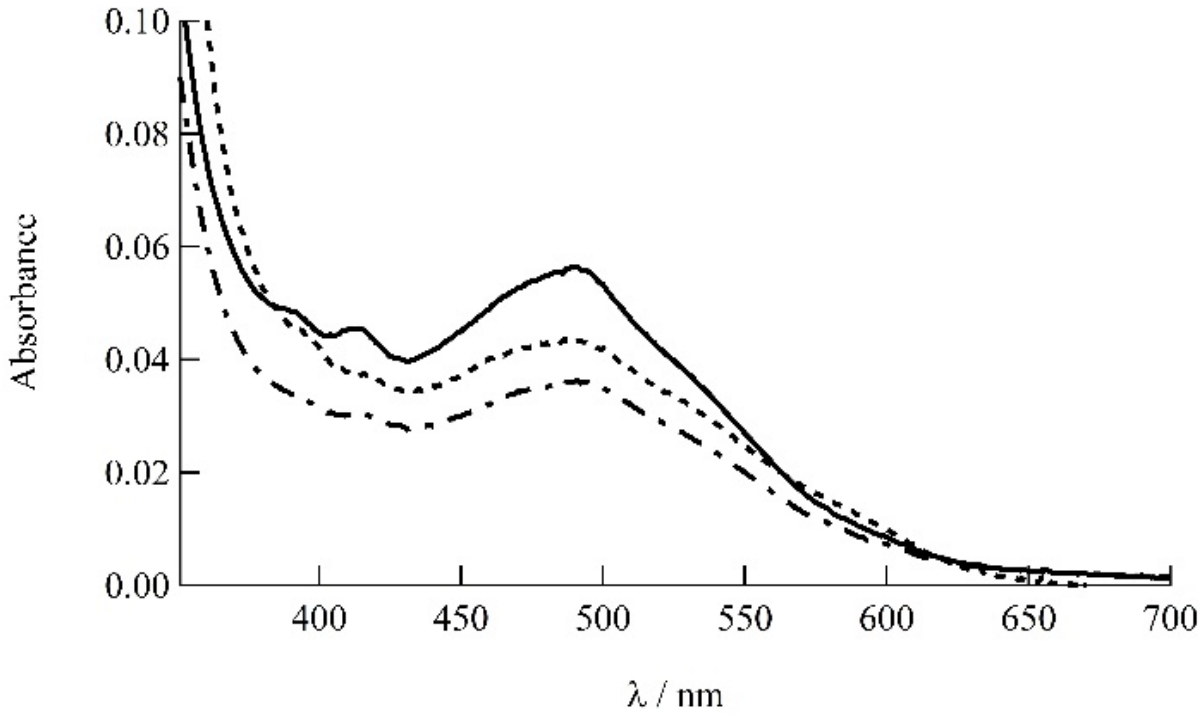


Figure S5. Electronic absorption spectrum of 5 μM **10** (5 mM Tris, 50 mM NaCl, pH 7.0) alone (–) and in the presence of PSS (100 μM) (---) and DNA (100 μM bases) (-•-).

Spectral Data

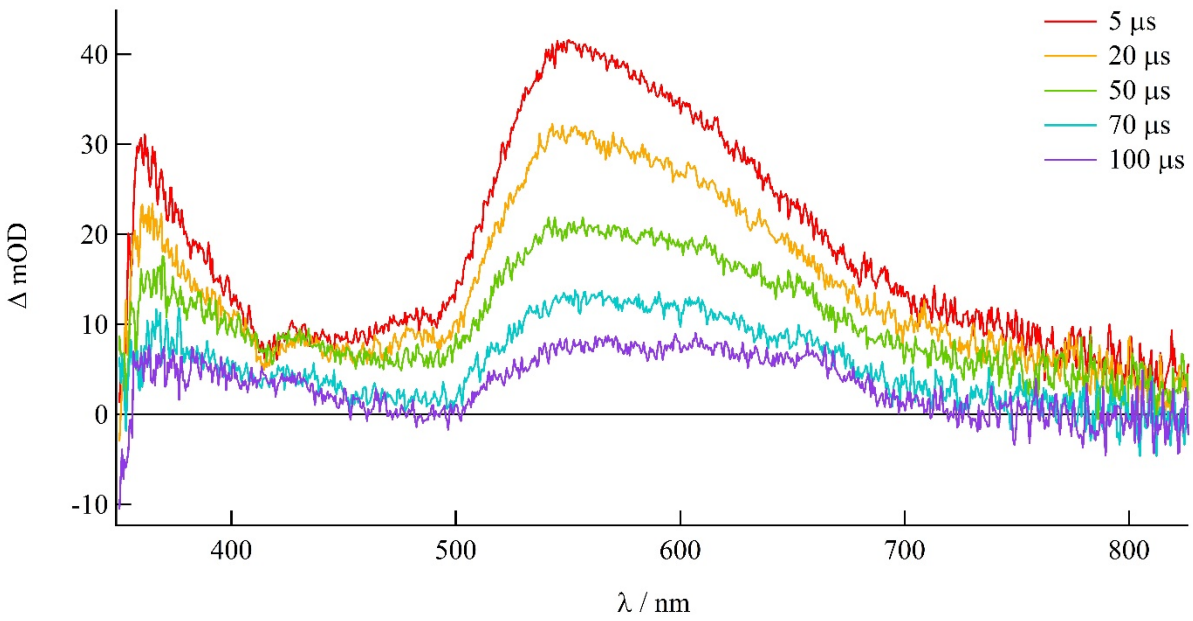


Figure S6: Transient absorption spectrum of **9** in deaerated pyridine

(λ_{irr} = 500 nm, 5.9 mJ/pulse, fwhm = 8 ns).

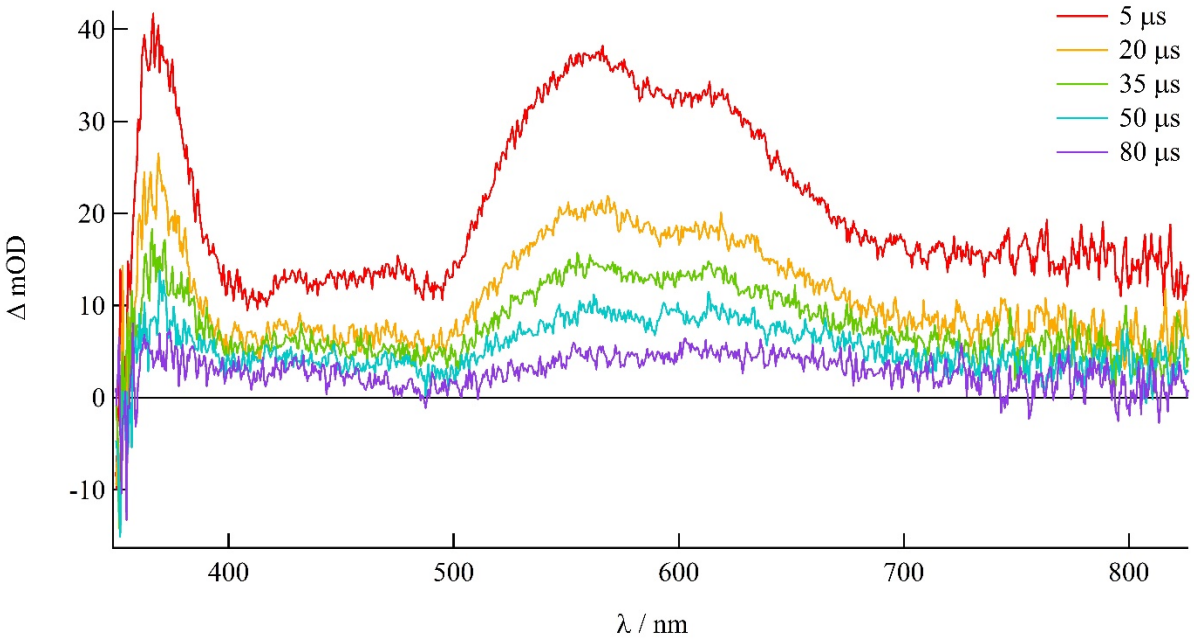


Figure S7: Transient absorption spectrum of **10** in deaerated pyridine

(λ_{irr} = 500 nm, 5.9 mJ/pulse, fwhm = 8 ns).

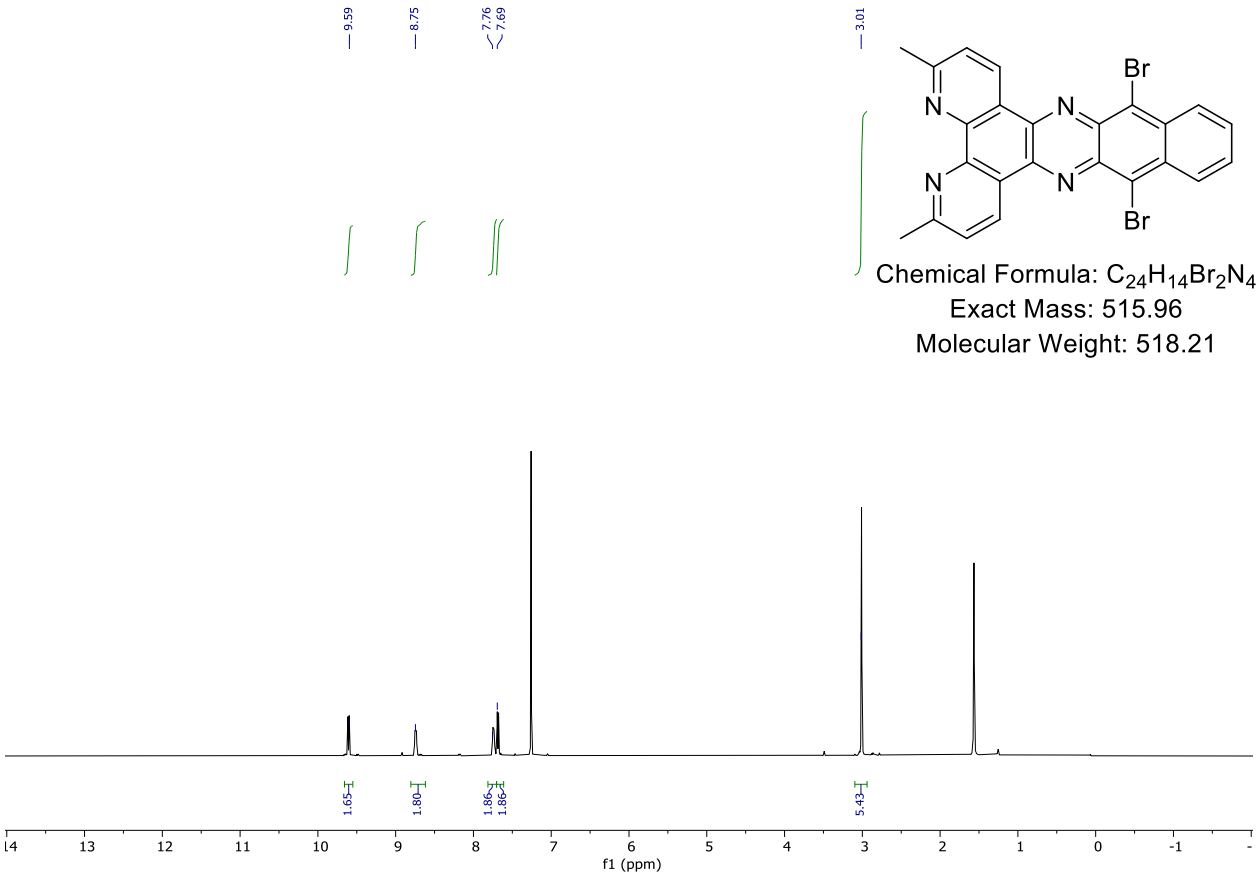


Figure S8: ^{1}H NMR of compound **4** in $CDCl_3$

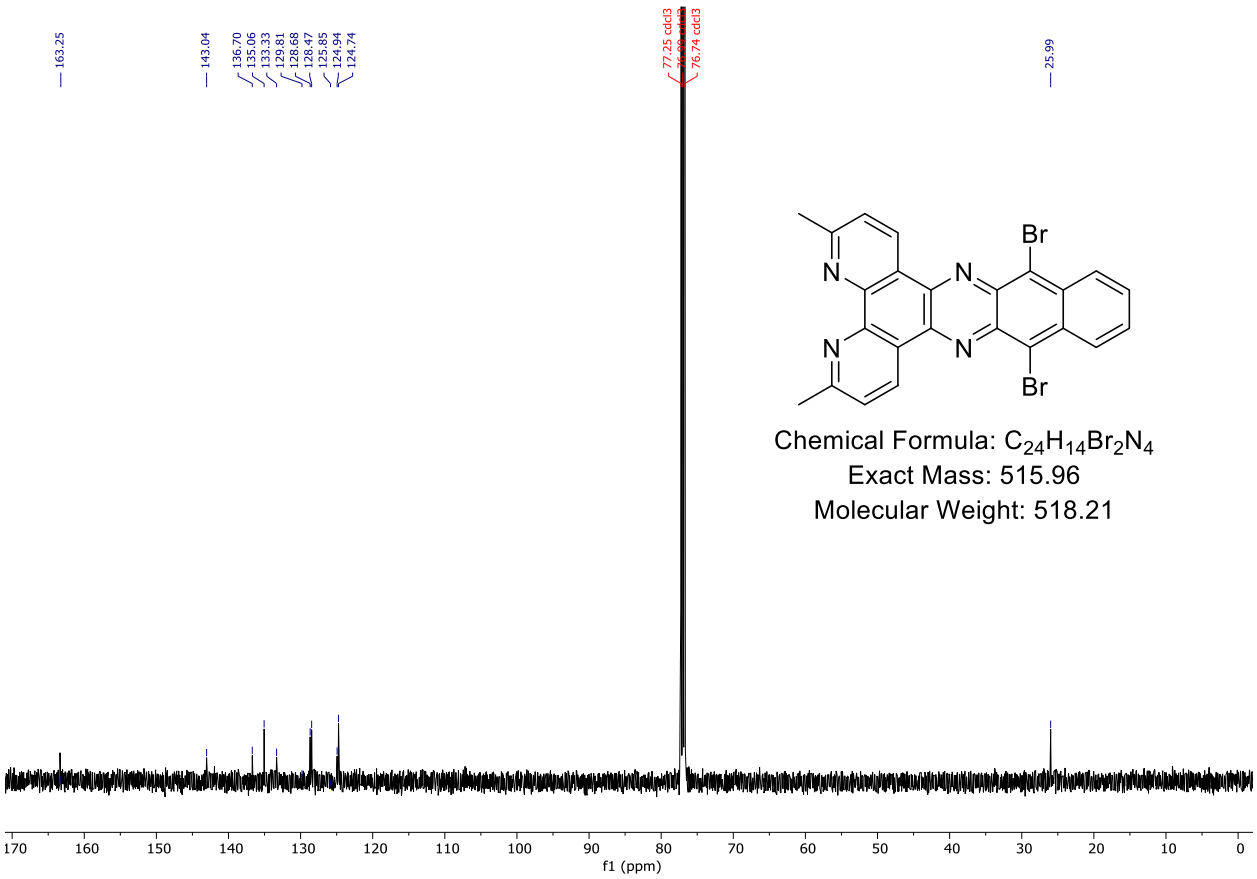


Figure S9: ^{13}C NMR of compound **4** in $CDCl_3$

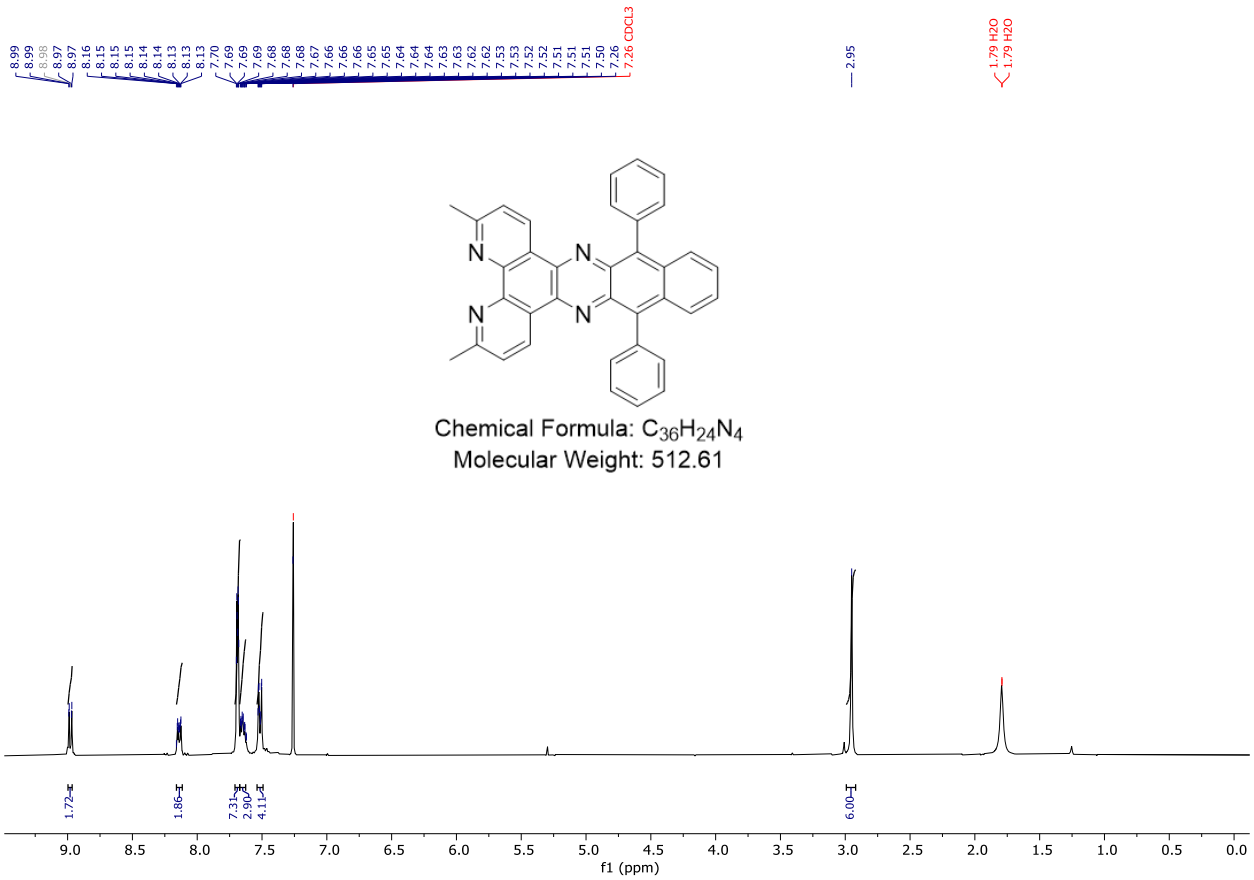


Figure S10: ^{1}H NMR of compound **5** in $CDCl_3$

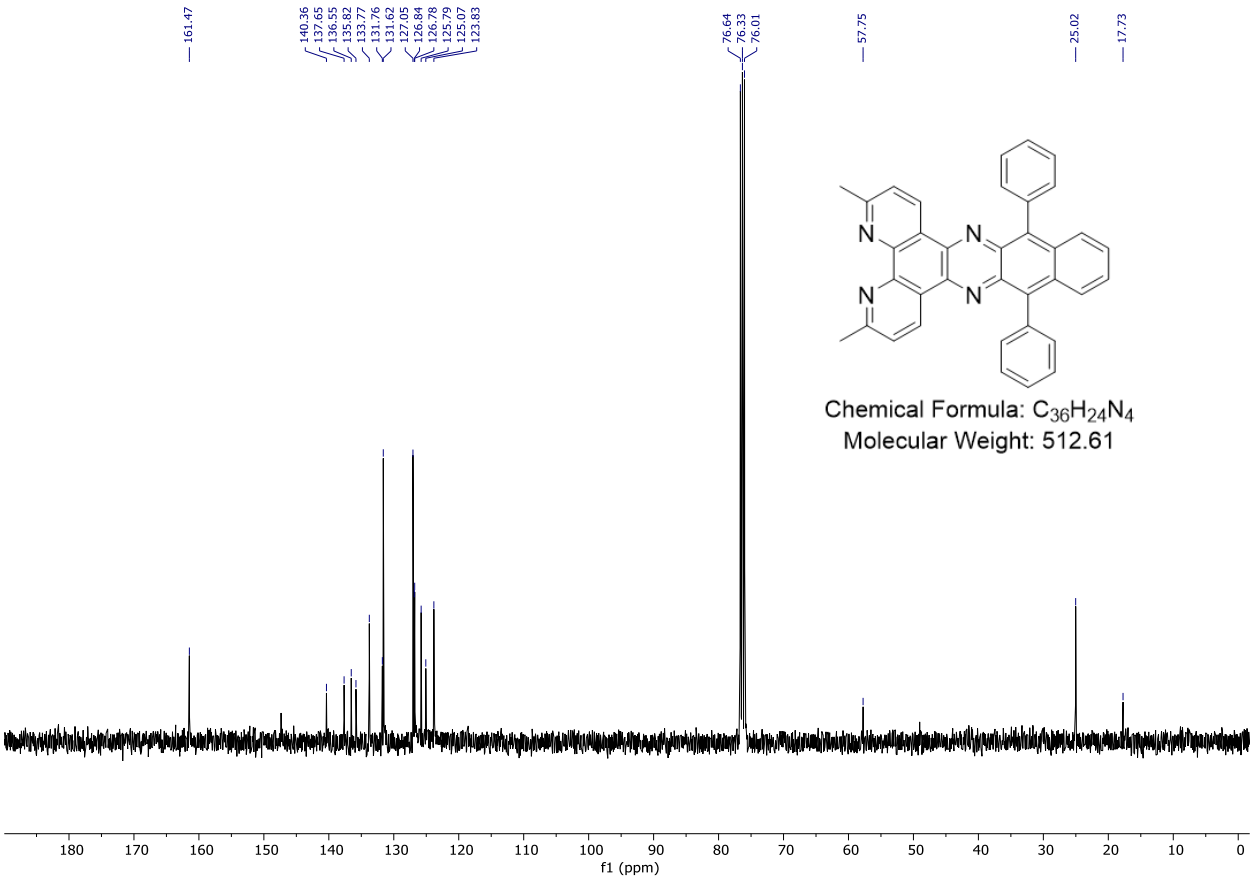


Figure S11: ^{13}C NMR of compound **5** in $CDCl_3$

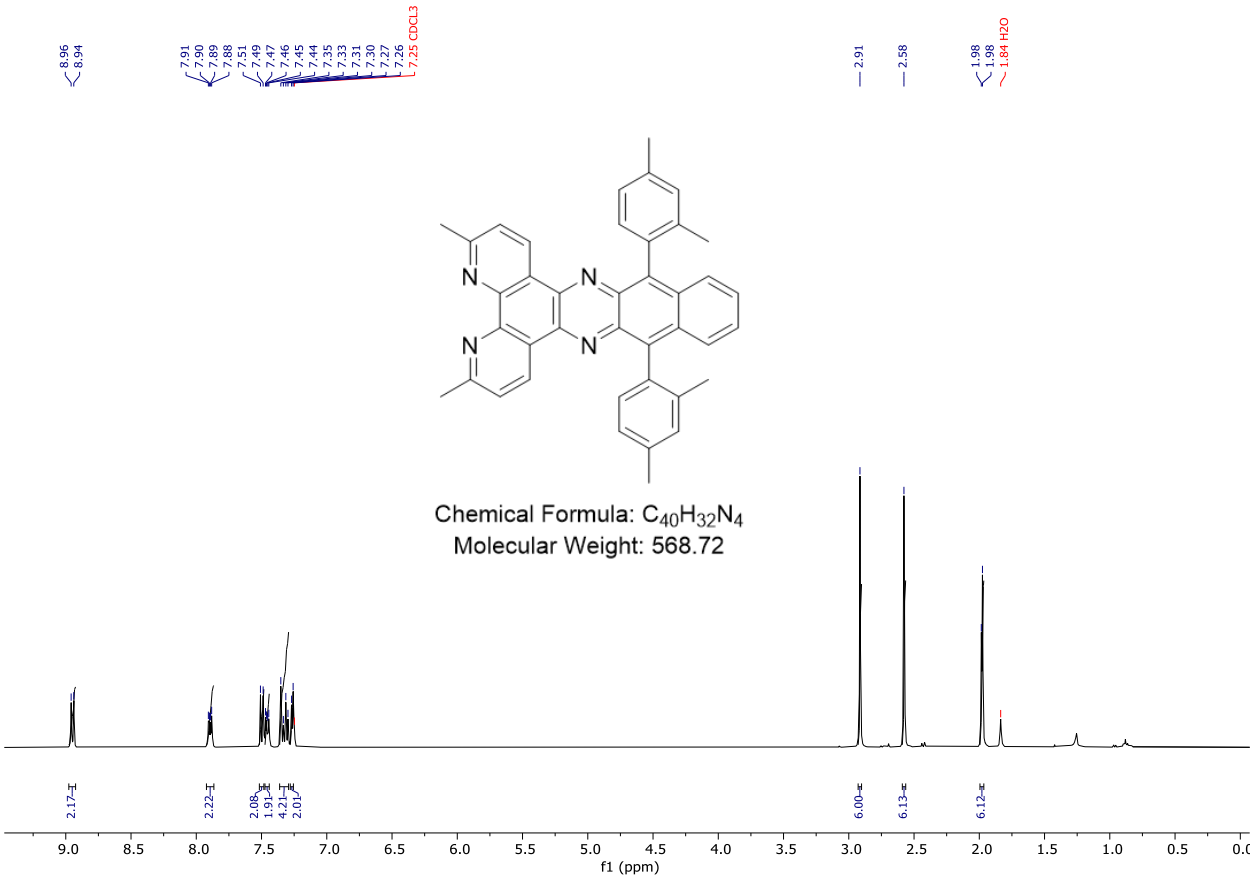


Figure S12: ^{1}H NMR of compound **6** in $CDCl_3$

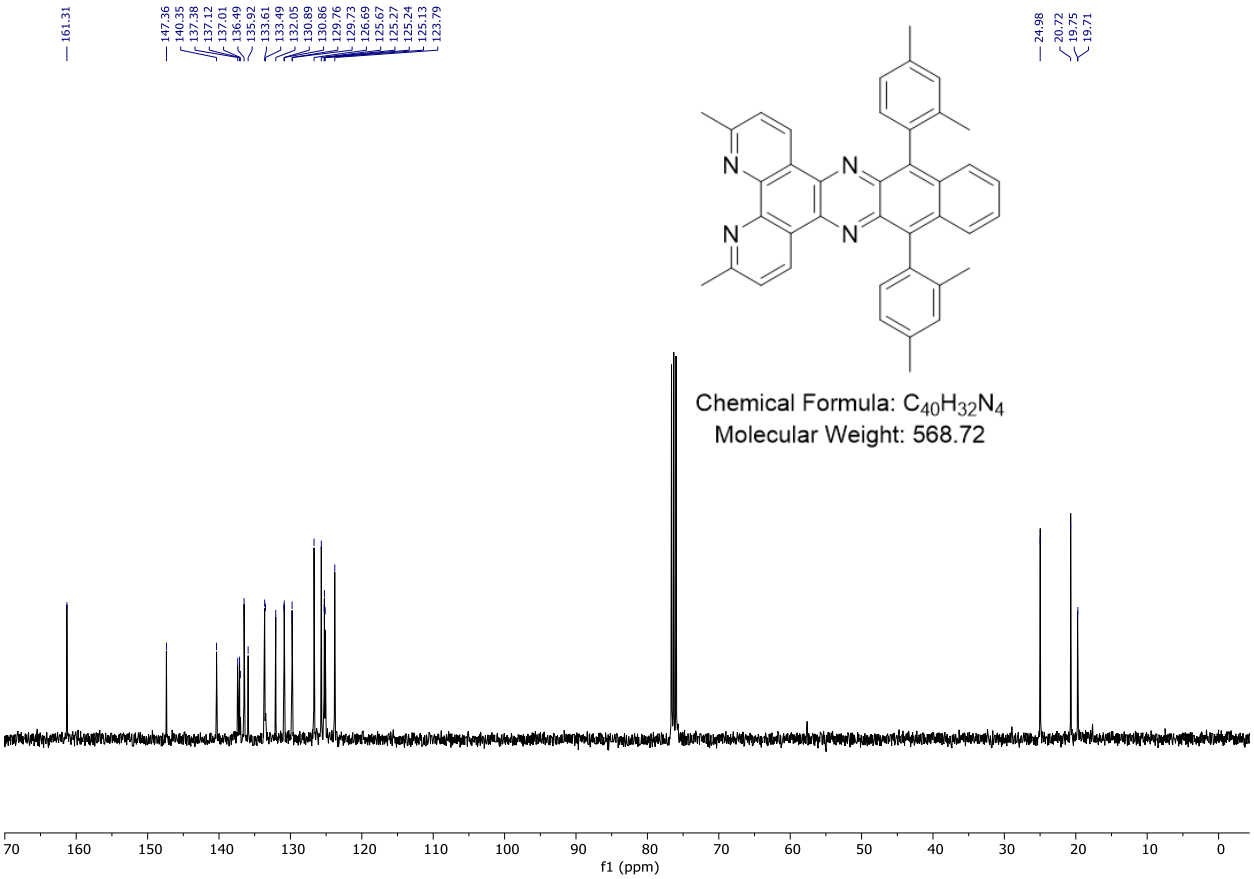


Figure S13: ^{13}C NMR of compound **6** in $CDCl_3$

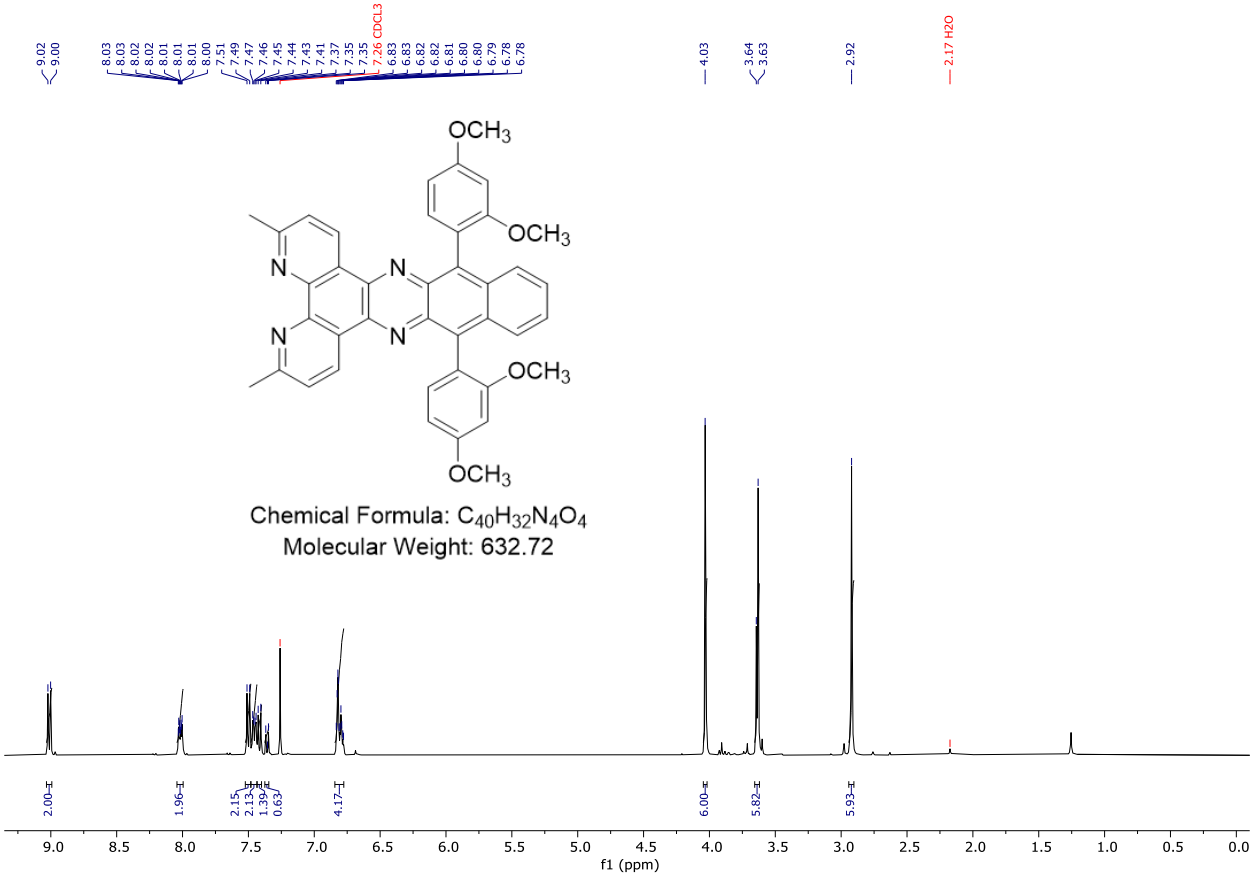


Figure S14: ^{1}H NMR of compound **7** in $CDCl_3$

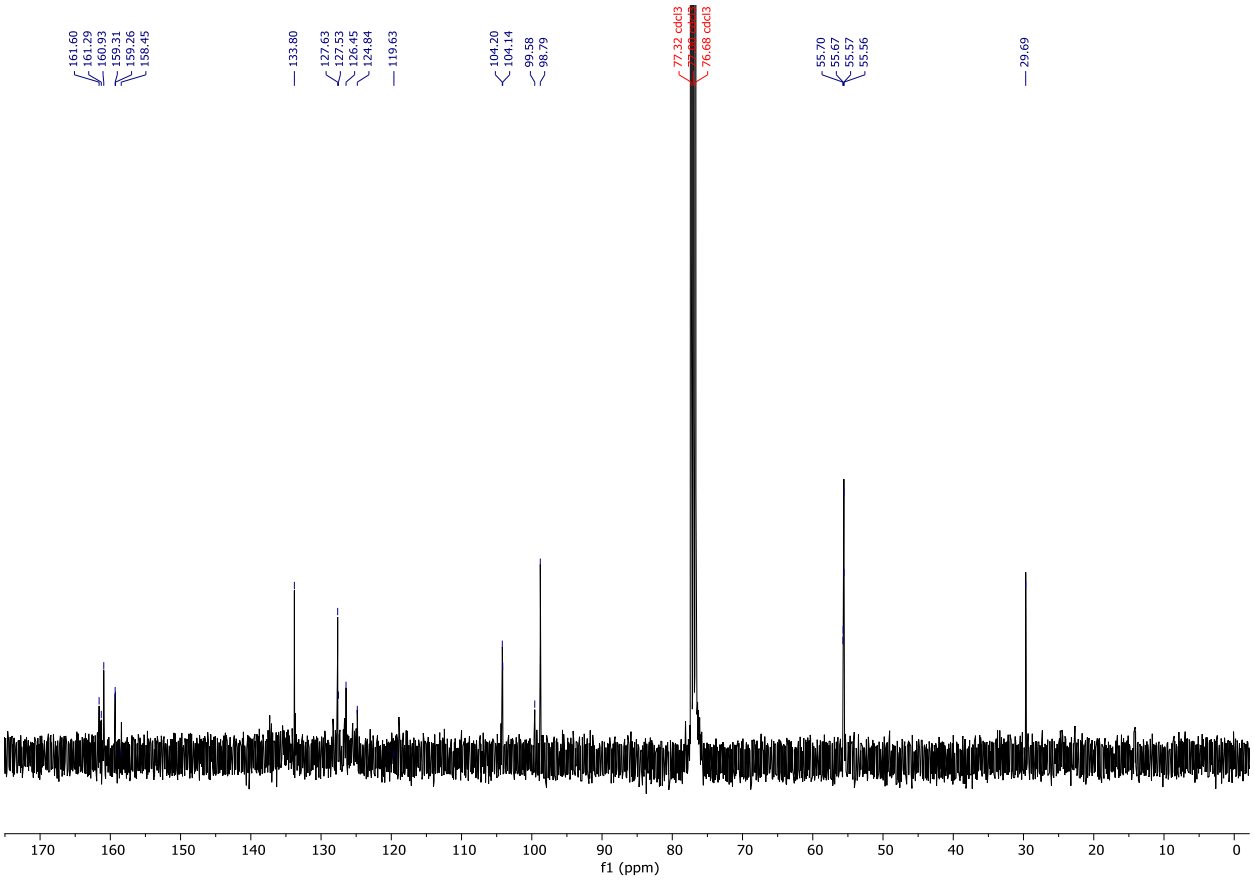


Figure S15: ^{13}C NMR of compound **7** in $CDCl_3$

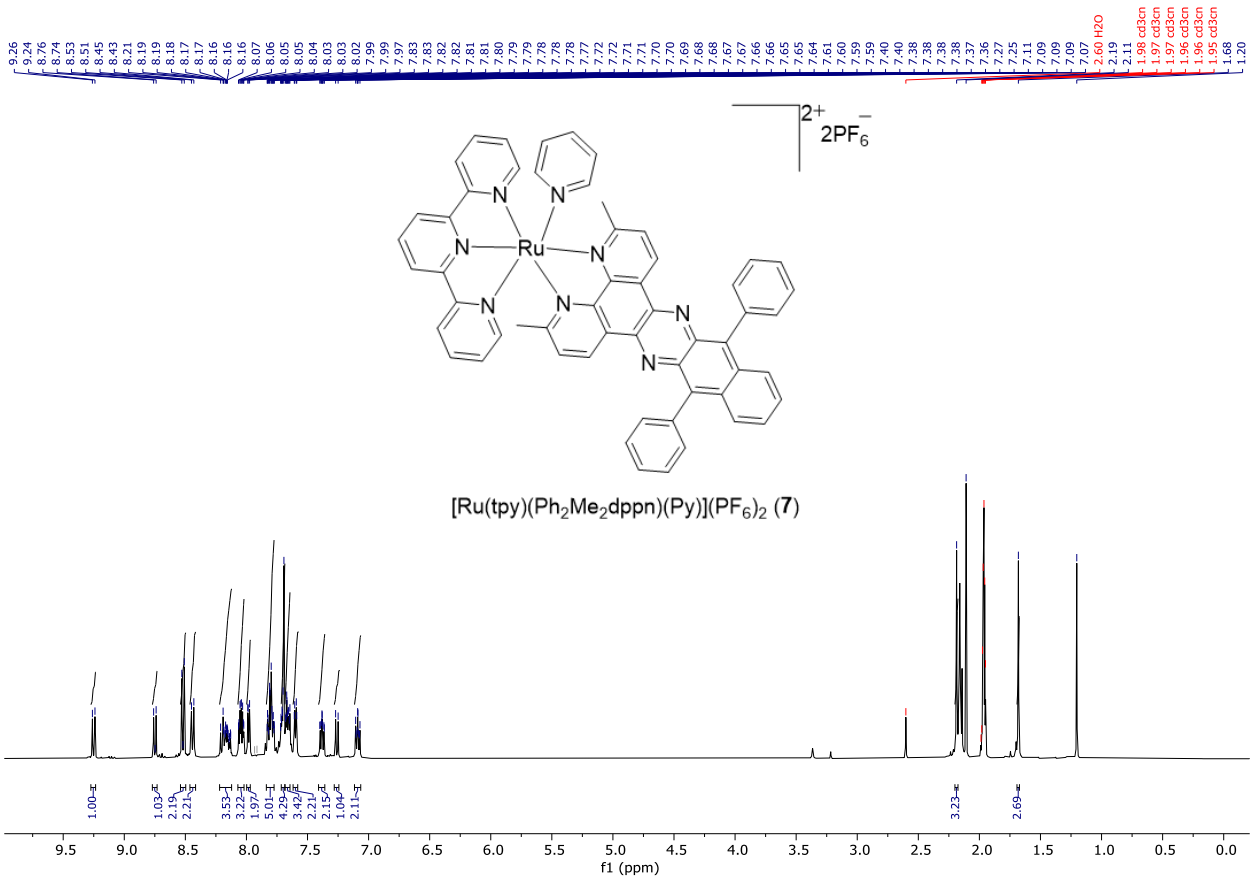


Figure S16: ^{1}H NMR of compound **8** in CD_3CN

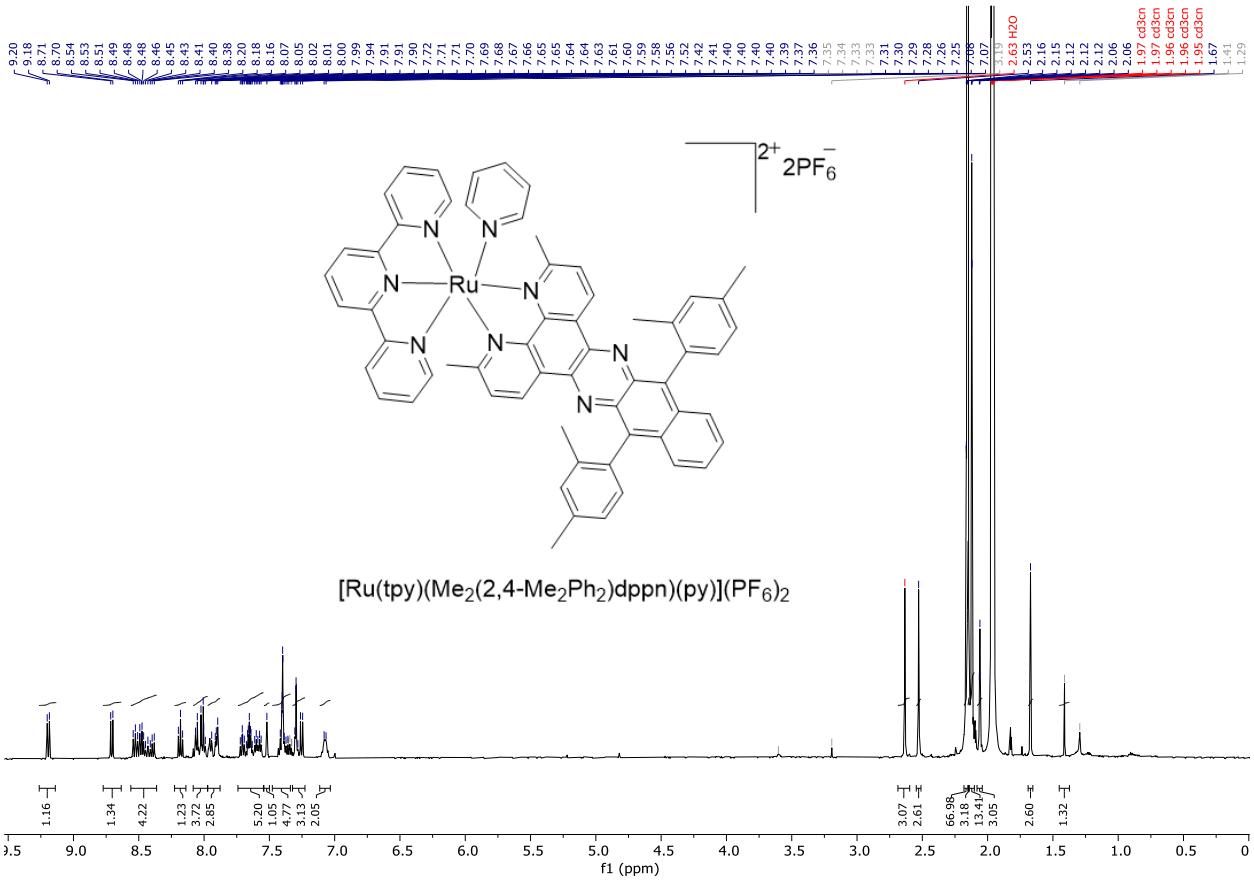


Figure S17: ^{1}H NMR of compound **9** in CD_3CN

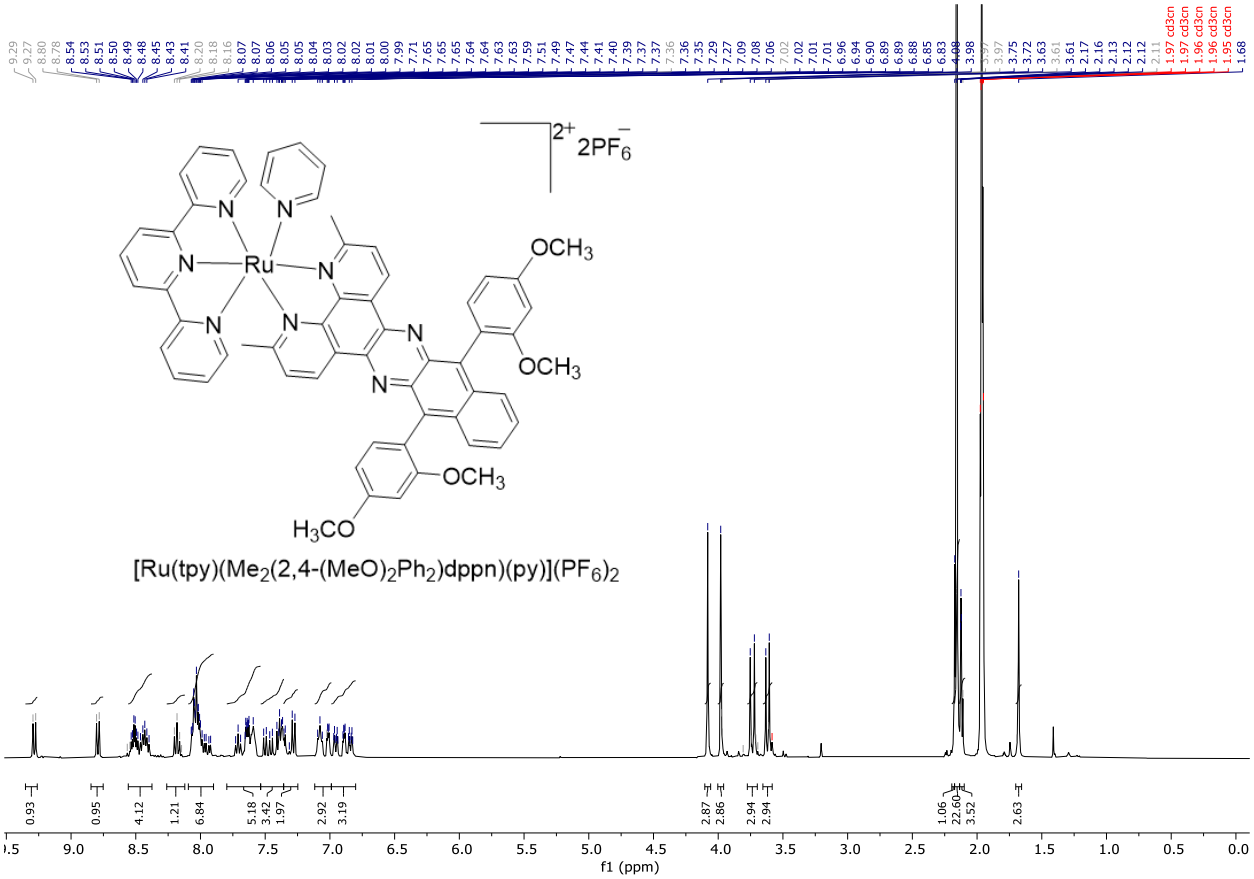


Figure S18: ^{1}H NMR of compound **10** in CD_3CN

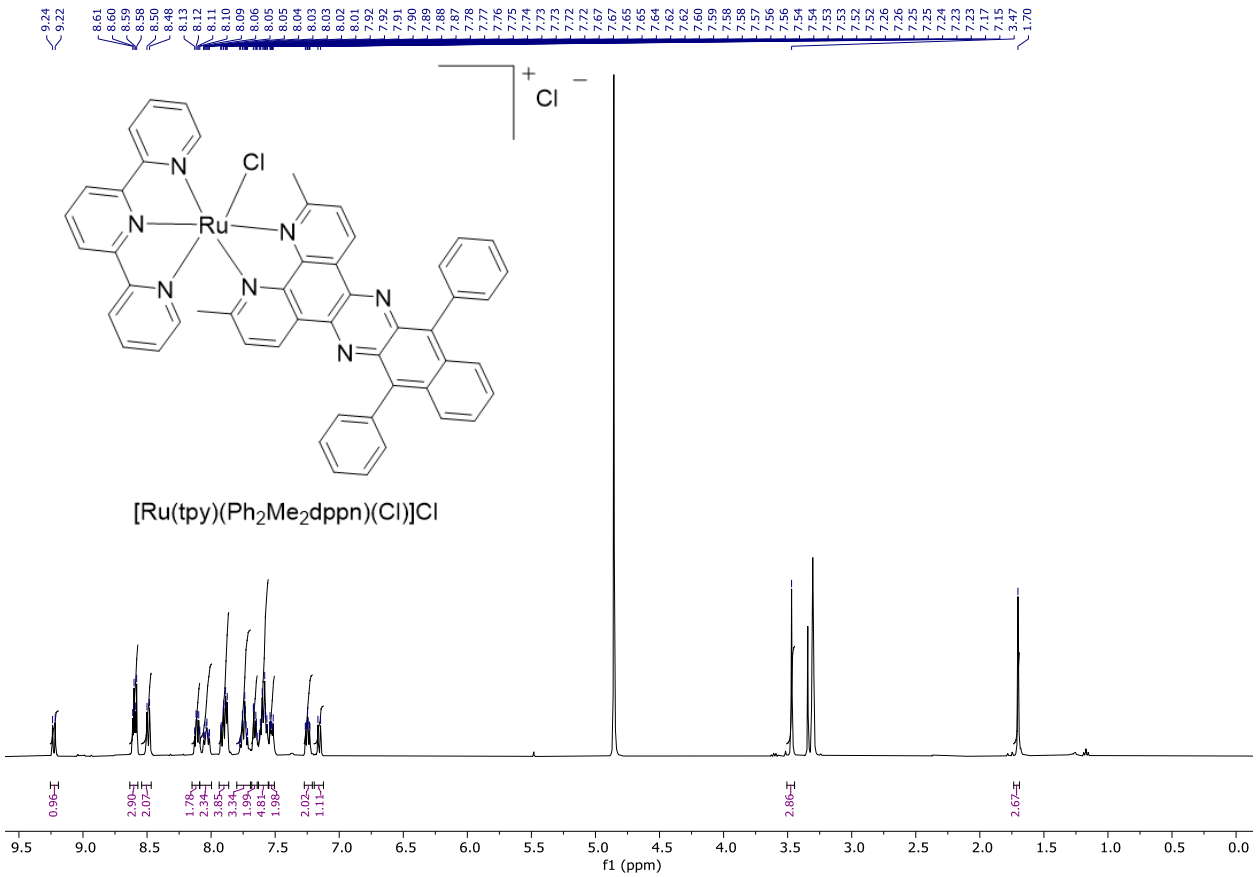


Figure S19: ^{1}H NMR of [Ru(tpy)(Ph$_2$Me$_2$dppn)(Cl)]Cl in CD$_3$OD

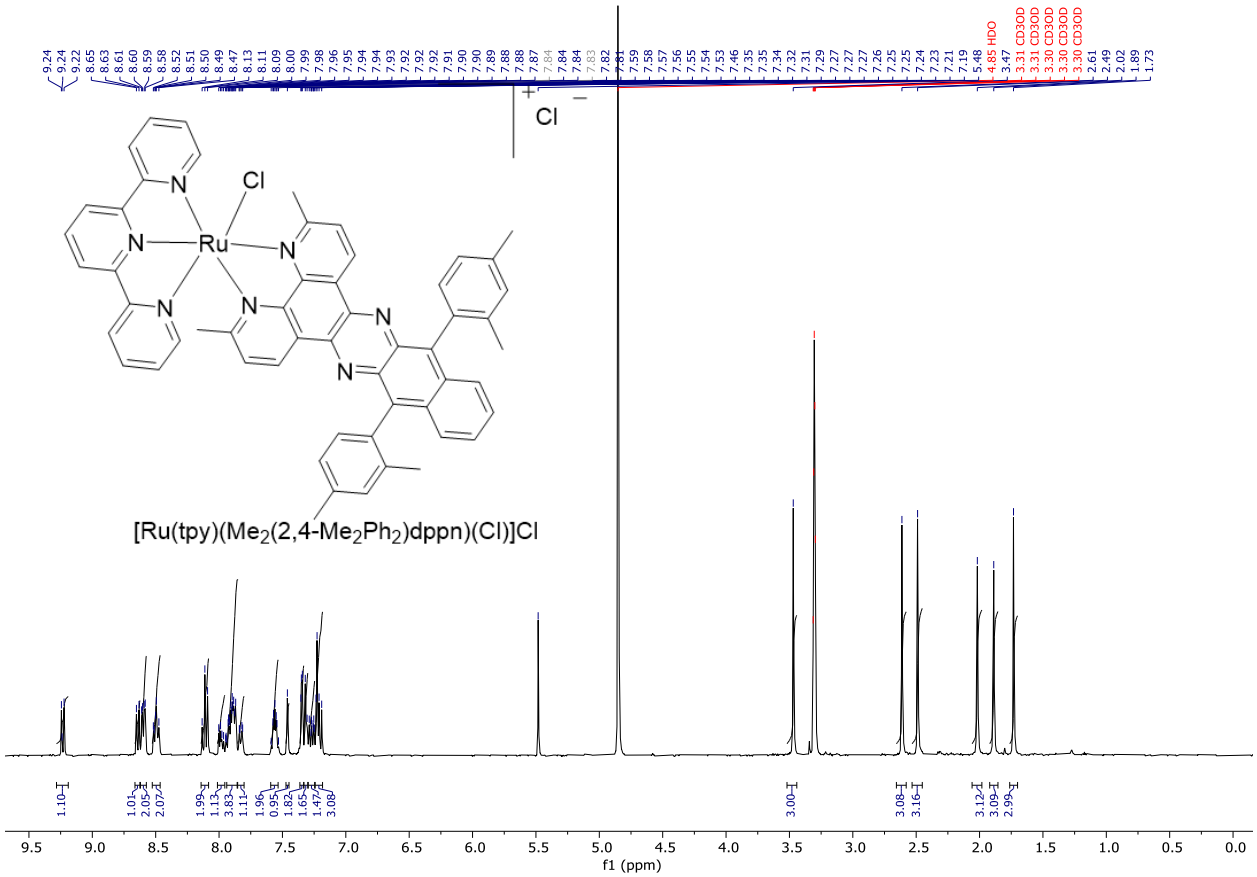


Figure S20: ^{1}H NMR of [Ru(tpy)(2,4-$Me_2Ph_2Me_2$dppn)(Cl)]Cl in CD_3OD

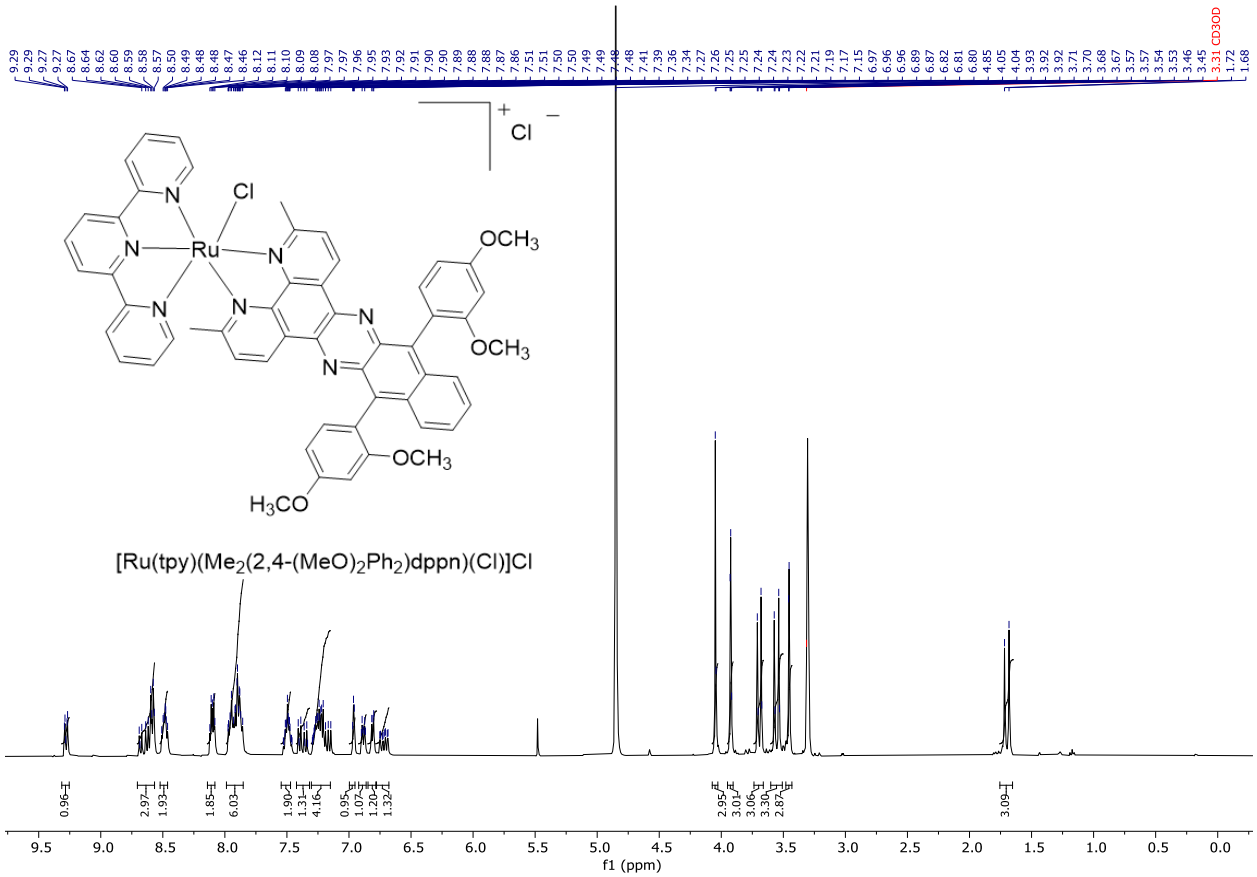
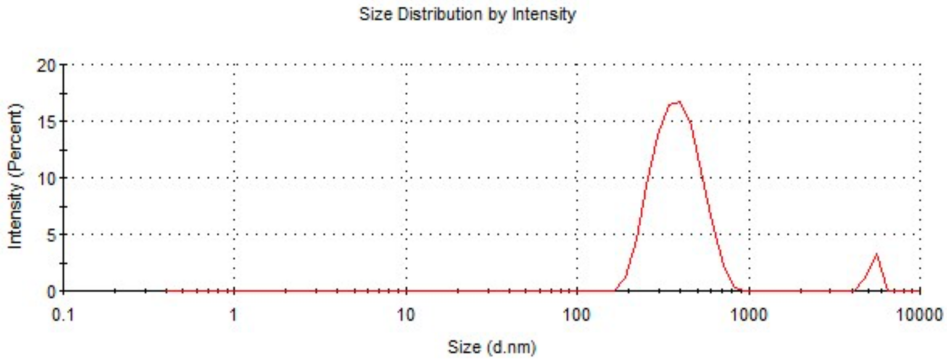
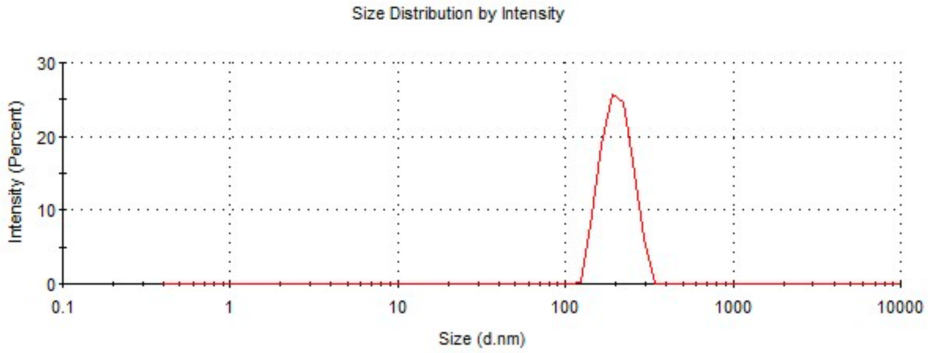


Figure S21: ^{1}H NMR [Ru(tpy)(Me2(2,4-(MeO)$_2$Ph)dppn)(Cl)]Cl in CD_3OD

Compound 1



Compound 8



Compound 9

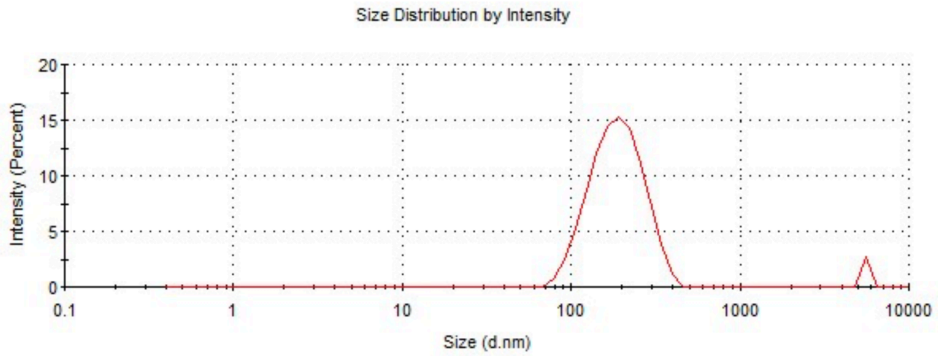


Figure S22. Dynamic light scattering data for compounds **1**, **8** and **9** (5 μM) collected in PBS buffer (0.1 M, pH 7.4) at 298 ±3 K.

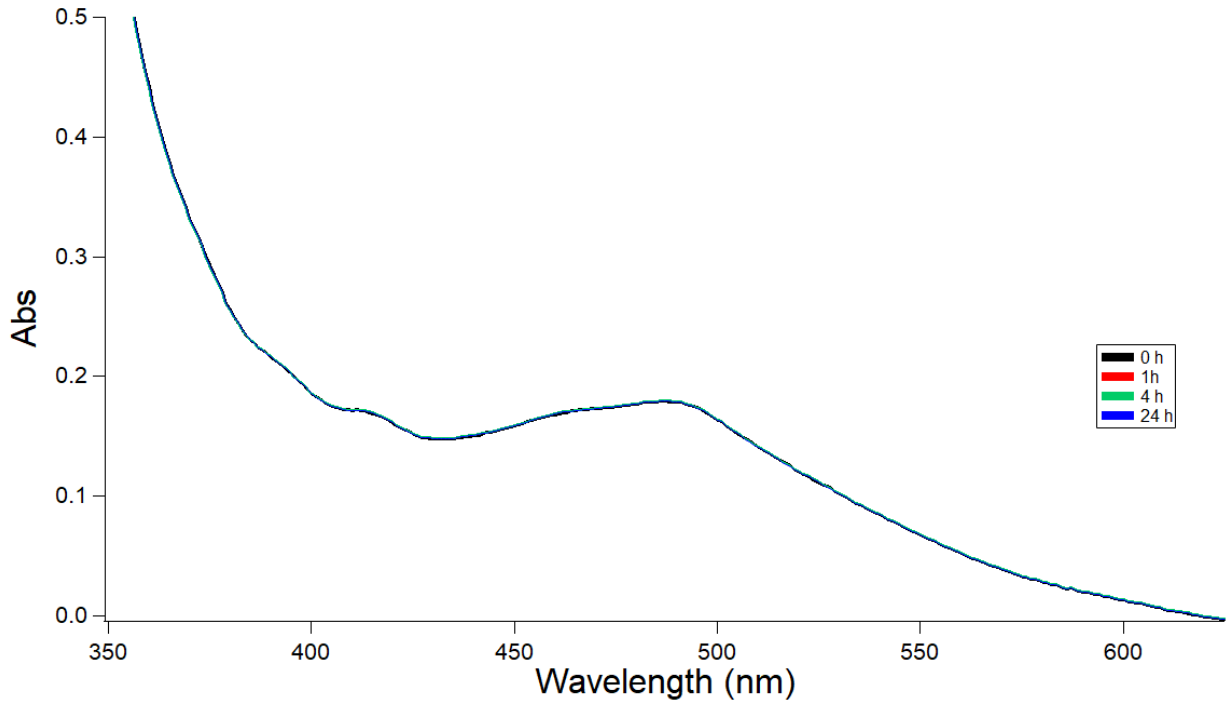


Figure S23: UV-vis spectrum of **8** in PBS after heating at 37 °C for 0 h (black), 1 h (red), 4 h (green), or 24 h (blue)

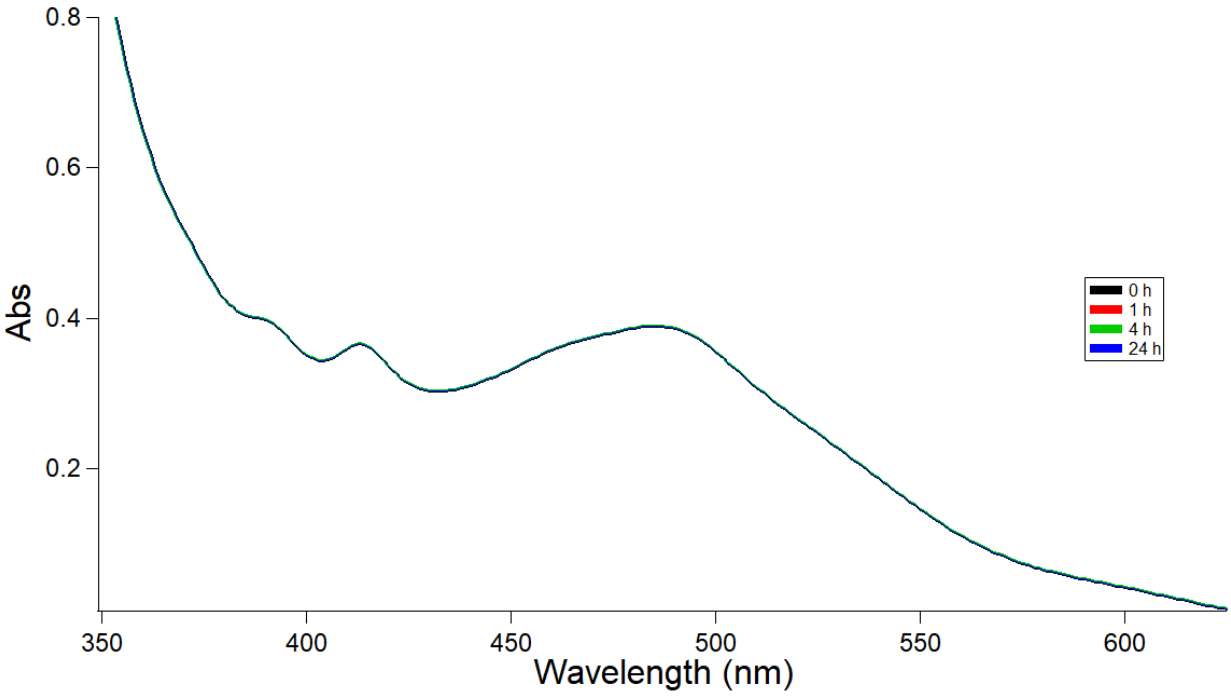


Figure S24: UV-vis spectrum of **9** in PBS after heating at 37 °C for 0 h (black), 1 h (red), 4 h (green), or 24 h (blue)

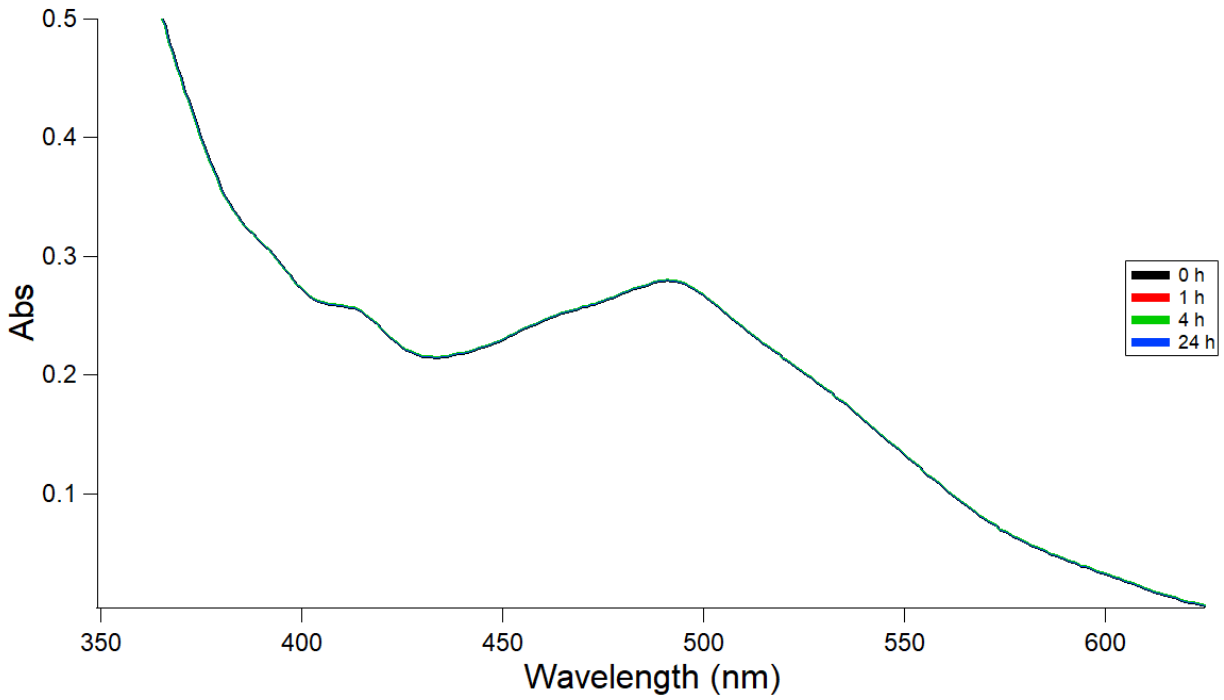


Figure S25: UV-vis spectrum of **10** in PBS after heating at 37 °C for 0 h (black), 1 h (red), 4 h (green), or 24 h (blue)

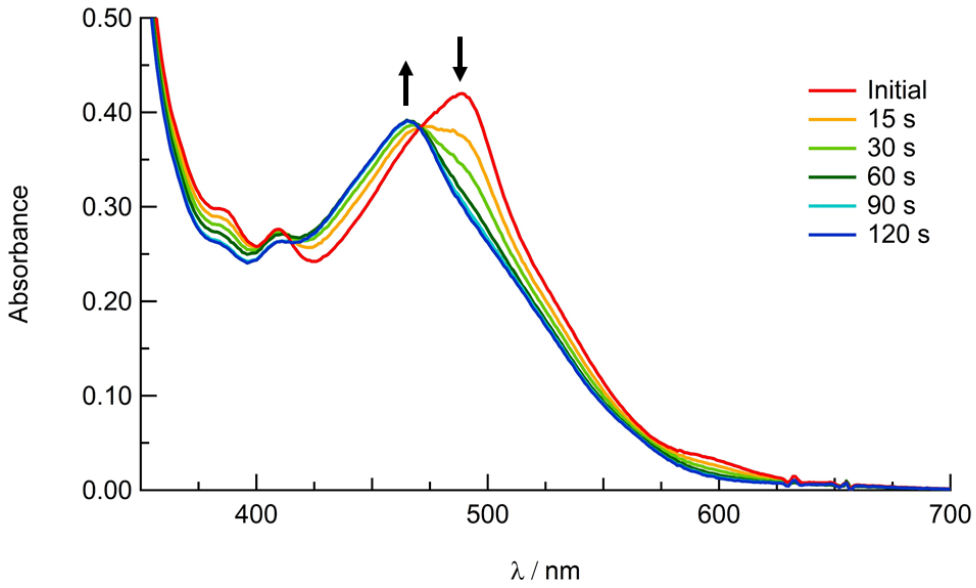


Figure S26: Changes in the electronic absorption spectra of **8** upon irradiation ($\lambda_{irr} \geq 395$ nm) in CH_3CN under a N_2 atmosphere, t_{irr} = 15, 30, 60, 90, and 120 seconds.

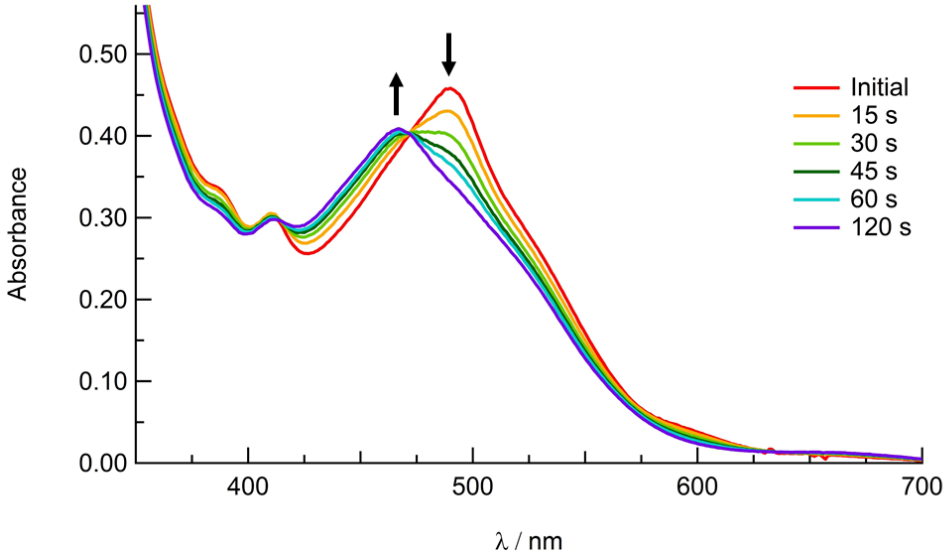


Figure S27: Changes in the electronic absorption spectra of **9** upon irradiation ($\lambda_{irr} \geq 395$ nm) in CH_3CN under a N_2 atmosphere, t_{irr} = 15, 30, 60, and 120 seconds.

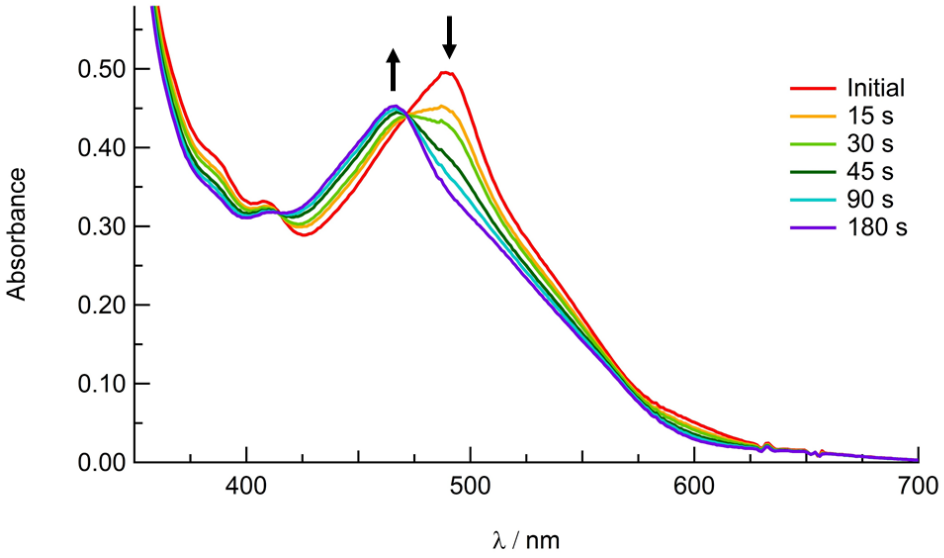


Figure S28: Changes in the electronic absorption spectra of **10** upon irradiation ($\lambda_{irr} \geq 395$ nm) in CH_3CN under a N_2 atmosphere, t_{irr} = 15, 30, 60, and 120 seconds.