

Photomodulation of Lewis Basicity in a Pyridine-Functionalized 1,2-Dithienylcyclopentene

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SUPPORTING INFORMATION

General. Solvents for NMR analysis (Cambridge Isotope Laboratories) were used as received. ¹H NMR characterizations were performed on a Bruker AMX 600 instrument. FT-IR measurements were performed on a Nicolet Nexus 670 instrument. The ring-closing reactions were carried out using the light source from a lamp used for visualizing TLC plates at 365 nm (Spectroline E-series, 470 W/cm²). The ring-opening reactions were carried out using the light of a 150-W tungsten source passed through a 490-nm cutoff filter to eliminate higher energy light.

¹H NMR SPECTROSCOPY

A solution of the ring-open isomer **1** (1.14×10^{-3} M, CD₂Cl₂) was irradiated in a quartz NMR tube with 365-nm light until a 1:1 mixture of ring-open and ring-closed isomers was generated (Figure S1) as assessed by measuring the relative integrals of the corresponding pairs of signals for the two isomers. Slightly less than 1 molar equivalent of Ru(TTP)(CO)(EtOH) was added in small increments to the NMR sample whereby a statistical mixture of 'free' (**1** and **2**) and 'bound' (**1(TTP)** and **2(TTP)**) pyridines was generated (Figure S4). The relative ratios of 'bound' to 'free' ligands in the mixture indicated that 0.93 molar equivalents of the metalloporphyrin was added. The sample was treated with 0.75 molar equivalents of 3-bromo-2-methyl-5-pyridylthiophene (**3**) leading to a redistribution of the products (Figure S5). The NMR sample was then irradiated with light greater than 490 nm for 20 minutes leading to the complete ring-opening of **2** and **2(TTP)** (Figure S6). Complete ring-cyclization of **1** and **1(TTP)** was achieved by irradiating the above mixture with 365-nm light for 10 minutes leading to a different distribution of bound **3(TTP)** to free **3** (Figure S7).

FT-IR SPECTROSCOPY

The metalloporphyrin complex (2 mg) and solid KBr (200 mg) were ground together using a mortar and pestle until a fine powder was obtained. A weighed amount of that mixture (100 mg) was then cast in a pellet and the spectrum was recorded. Irradiation of the pellets was performed as described above.

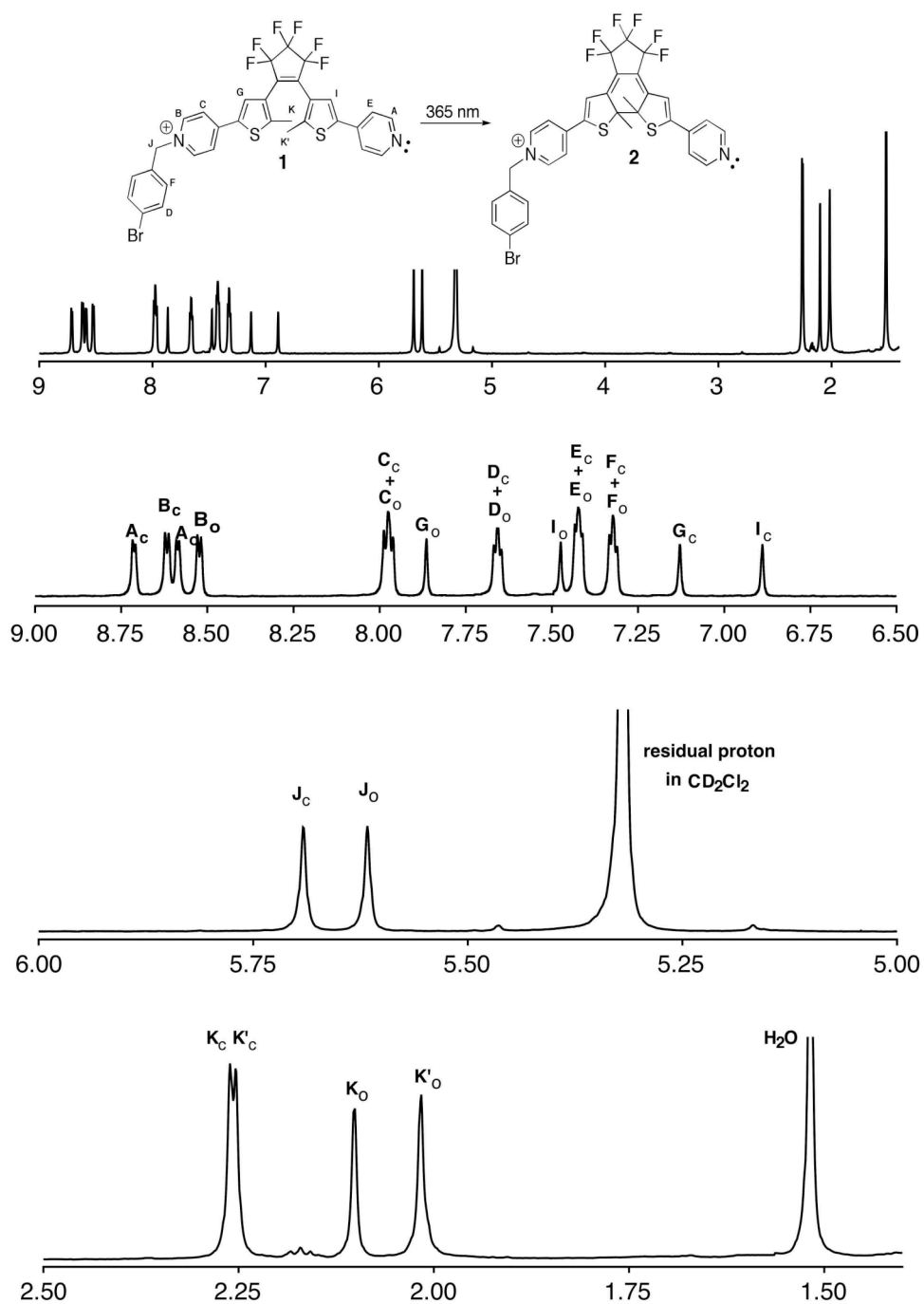


Figure S1. ¹H NMR spectra of a 1:1 mixture of ring-open isomer **1** (labeled with the subscript 'o') and ring-closed isomer **2** (labeled with the subscript 'c'). The 1:1 mixture was obtained by irradiating a solution of **1** with 365-nm light until the appropriate ratio was achieved.

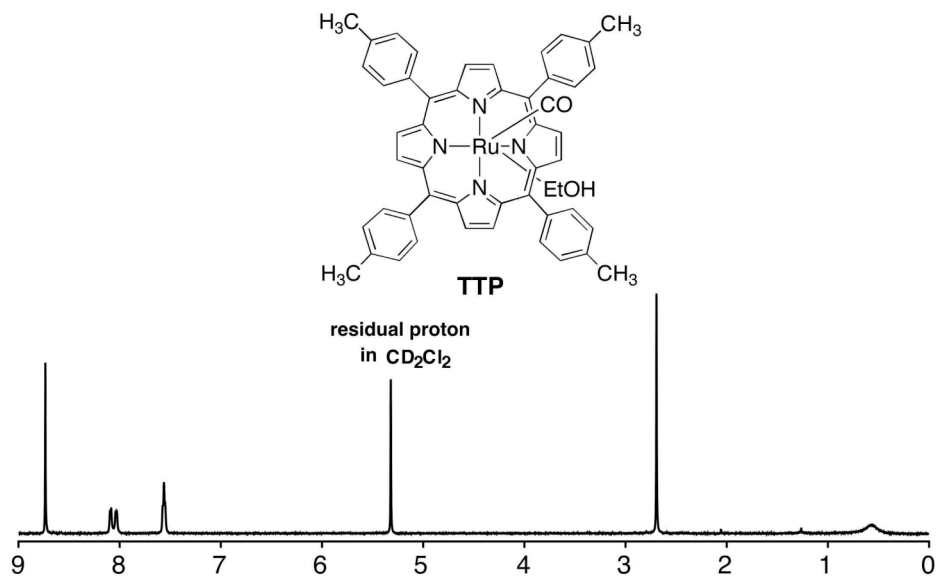


Figure S2. ¹H NMR spectra of metalloporphyrin, Ru(TTP)(CO)(EtOH) (**TTP**).

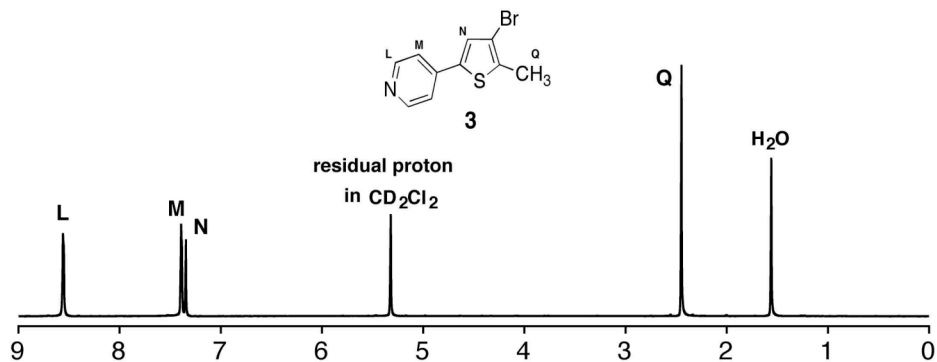


Figure S3. ¹H NMR spectrum of 3-bromo-2-methyl-5-pyridylthiophene (**3**) used as a 'control' in the ¹H NMR experiment.

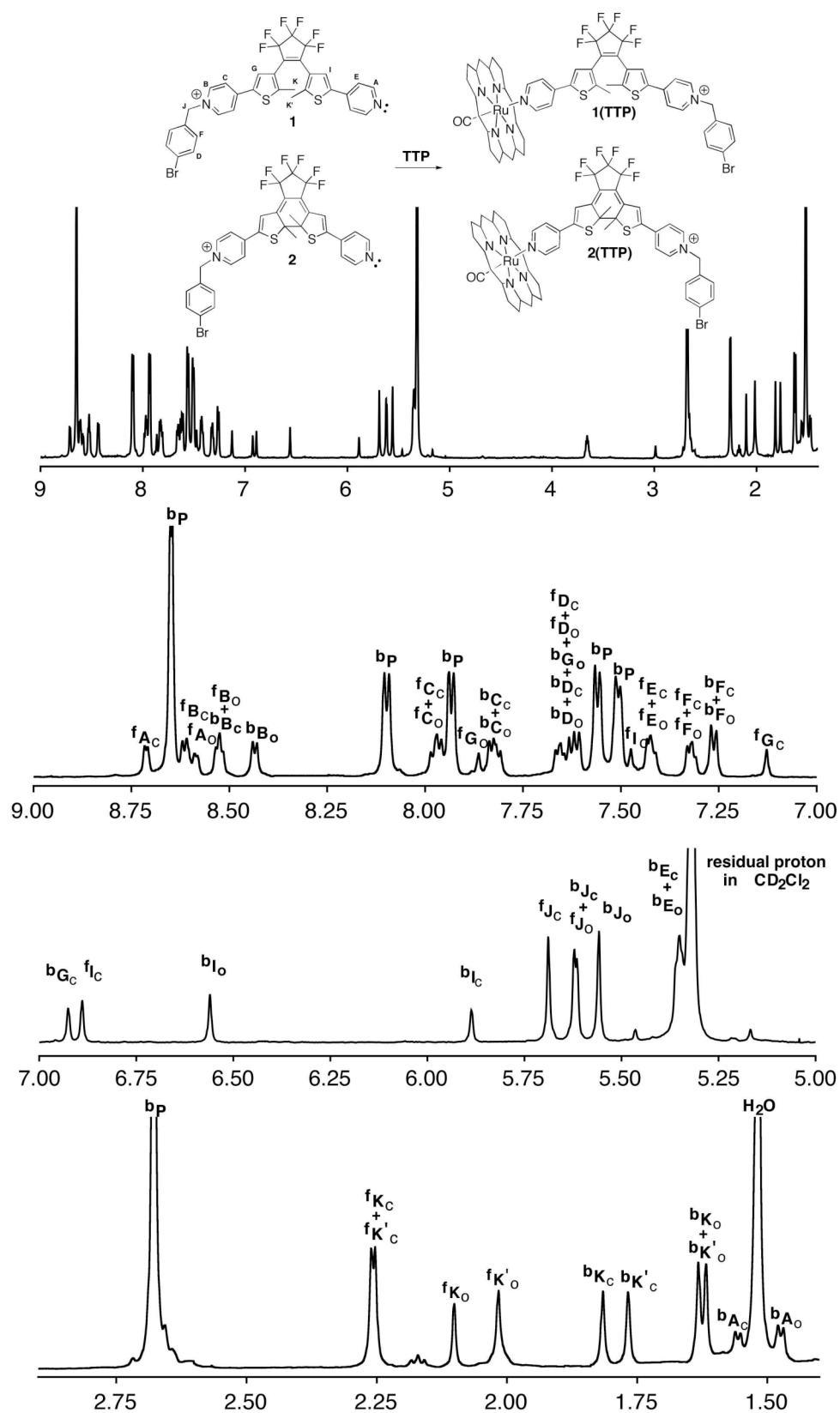


Figure S4. ¹H NMR of the 1:1 mixture of **1** and **2** and 0.93 mol equiv of TTP (labeled 'p'). Protons corresponding to the bound form **1(TTP)** and **2(TTP)** are labeled 'b' while those corresponding to the free forms **1** and **2** are labeled 'f'.

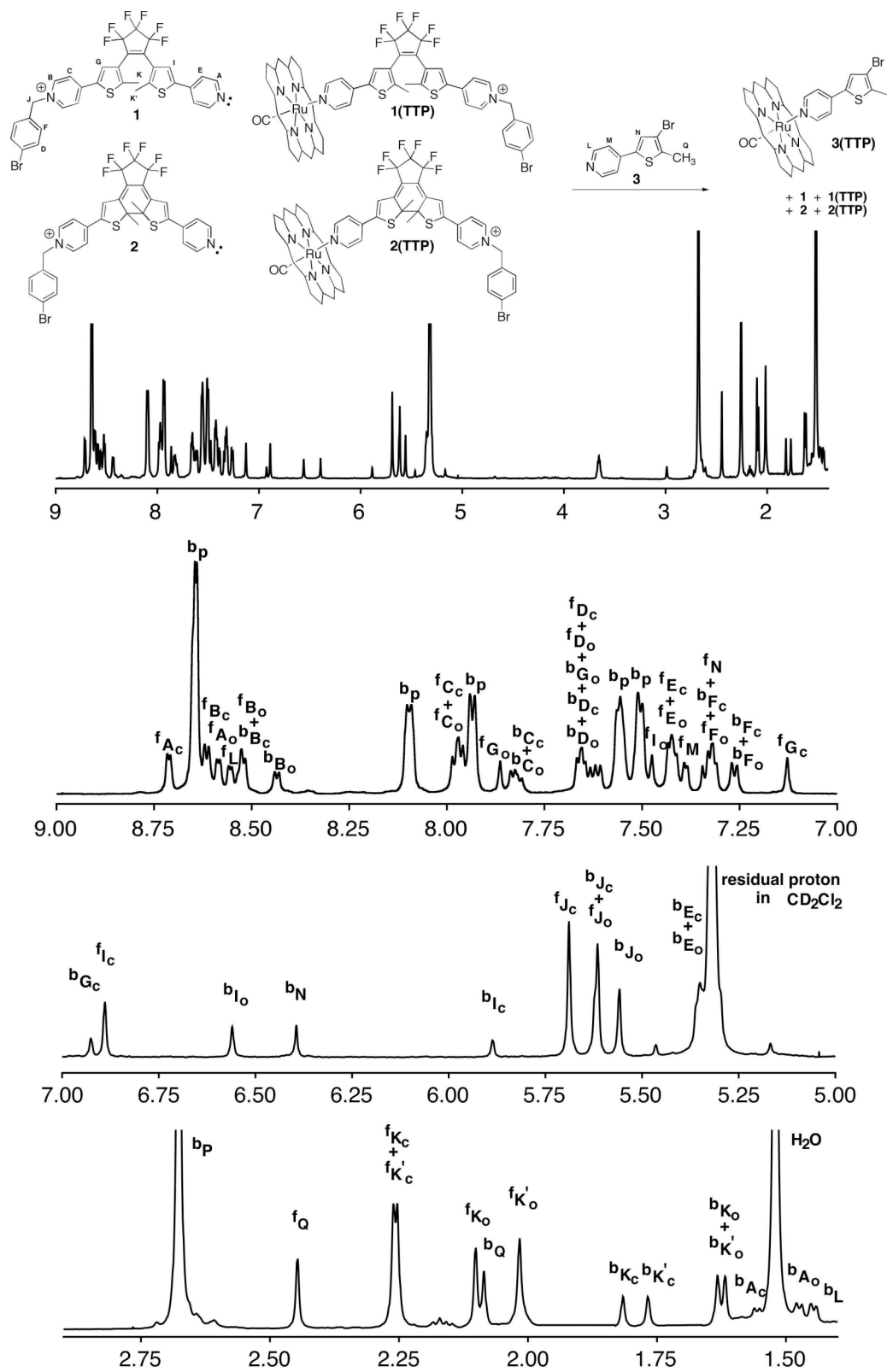


Figure S5. ^1H NMR spectra when 0.75 mol equiv of thienylpyridine **3** is added to the 1:1:0.93 mixture of **1**, **2**, and **TTP**.

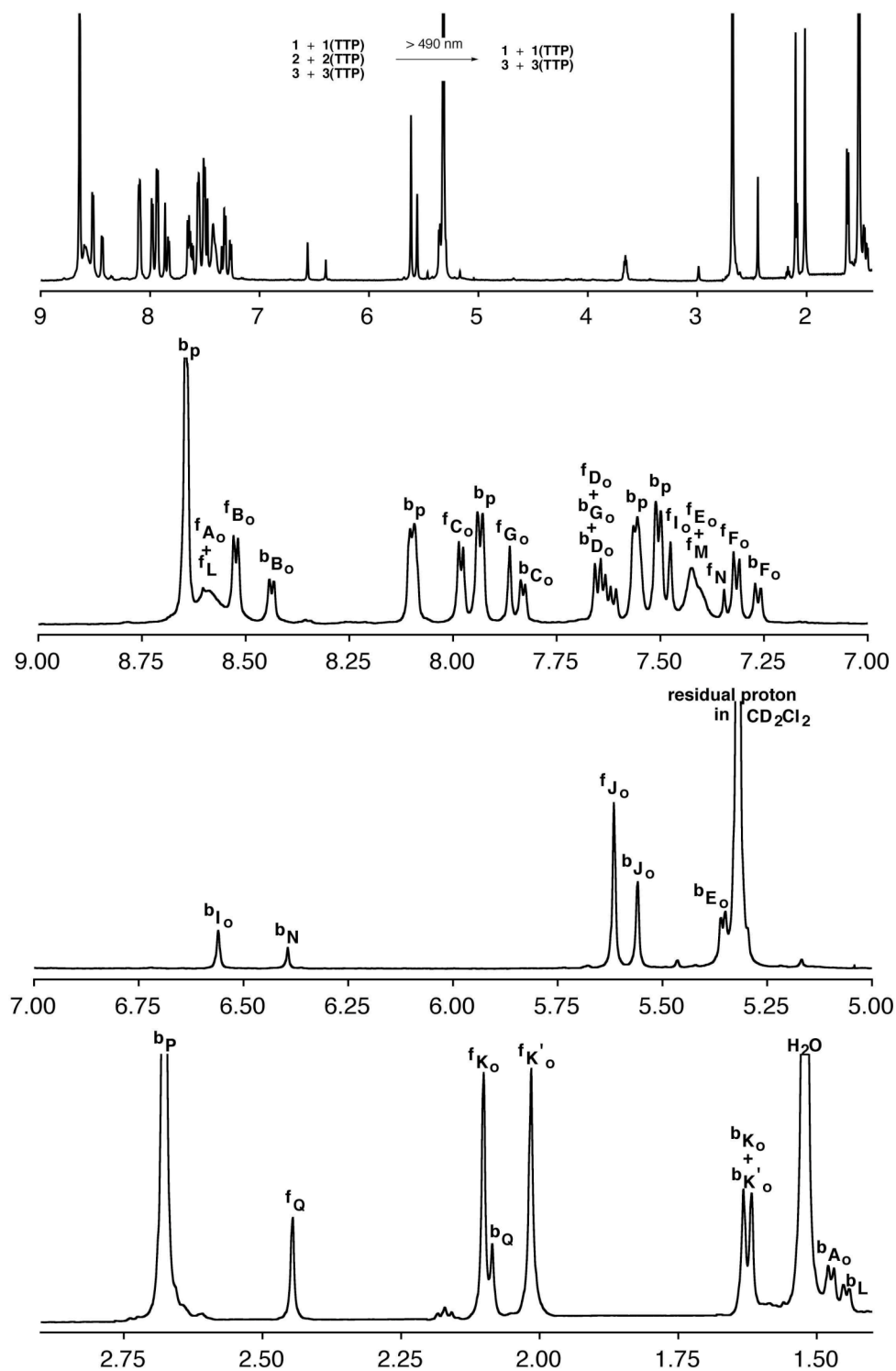


Figure S6. ^1H NMR spectra showing the relative intensities of the peaks for the free pyridylthiophene **3** and bound complex **3(TTP)** when the monocation is in its all-ring-open form. Complete ring-opening was achieved by irradiating the mixture at wavelengths greater than 490 nm for 20 minutes.

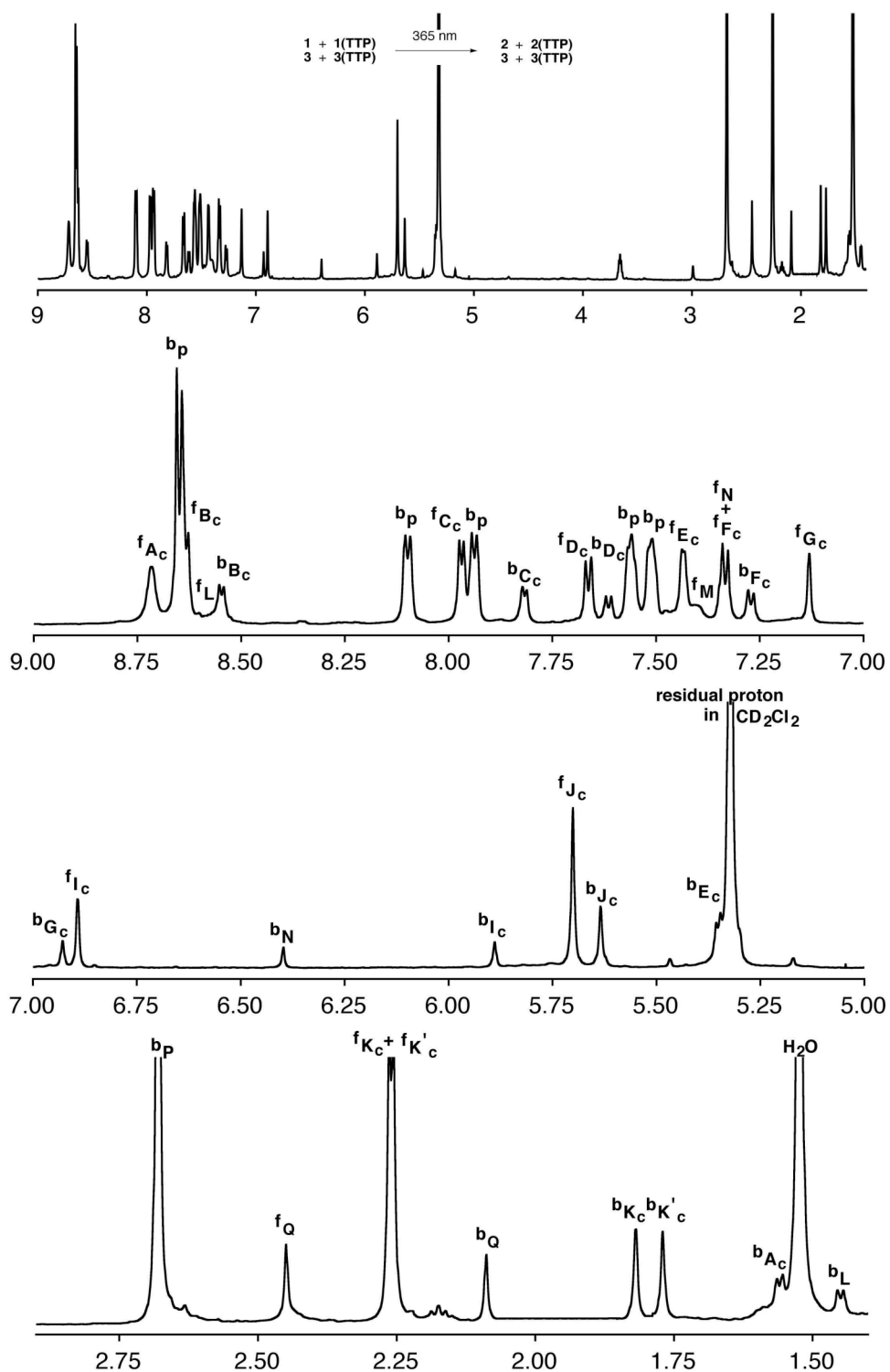


Figure S7. ^1H NMR spectra showing the change in the relative intensities of the peaks for the free control **3** and bound **3(TTP)** when the monocation is in its all-ring-closed form. Complete ring-closing was achieved by irradiating the mixture using 365-nm light for 10 minutes.

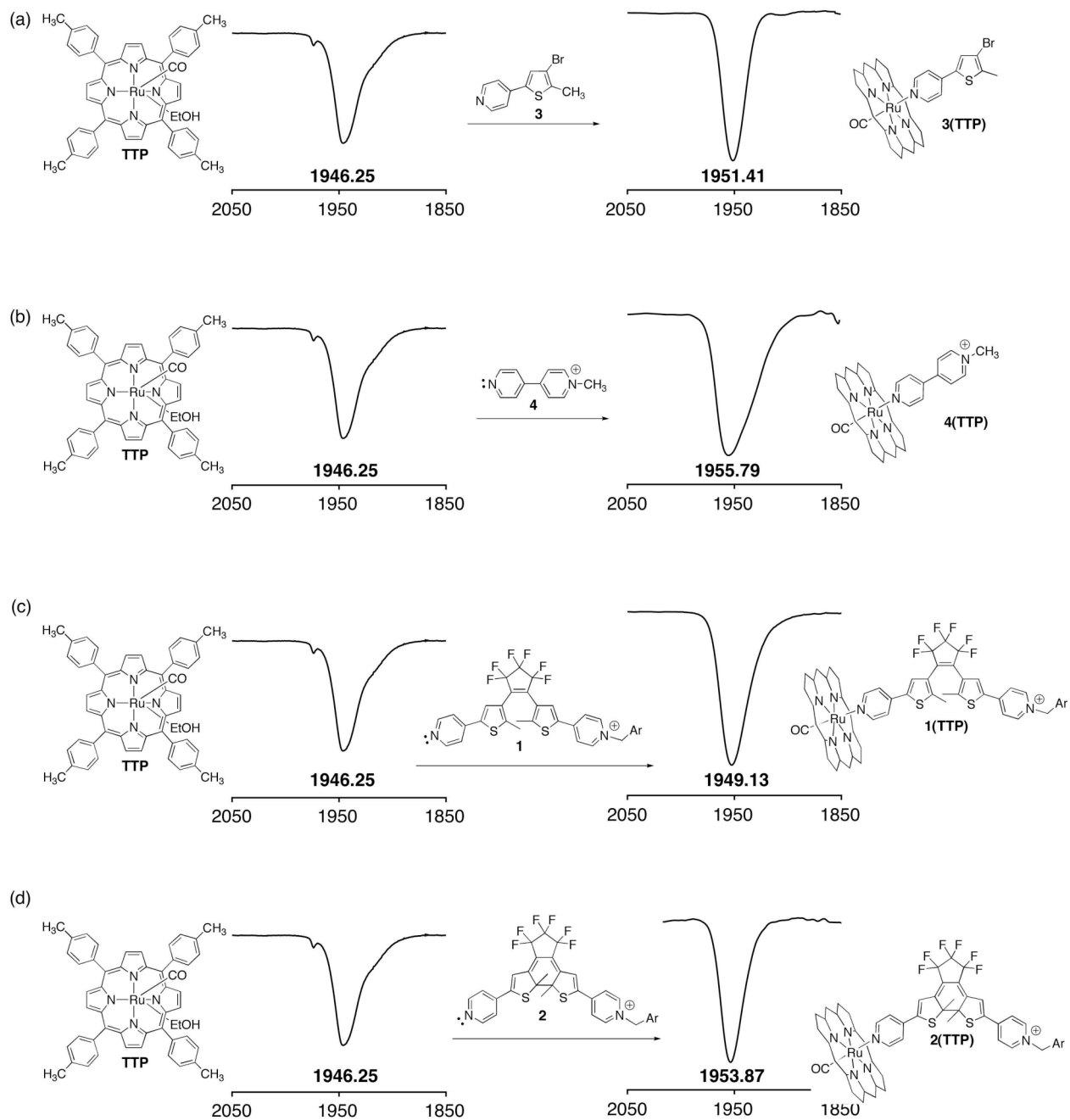


Figure S8. Selected IR spectra showing the C=O stretching frequencies when Ru(TTP)(CO)(EtOH) (**TTP**) is complexed to (a) pyridylthiophene **3**, (b) cationic bipyridine **4**, (c) the ring-open isomer **1**, and (d) the ring-closed form **2**. The C=O stretching frequency for the metalloporphyrin starting material Ru(TTP)(CO)(EtOH) appears at 1946 cm^{-1} in the IR spectrum.

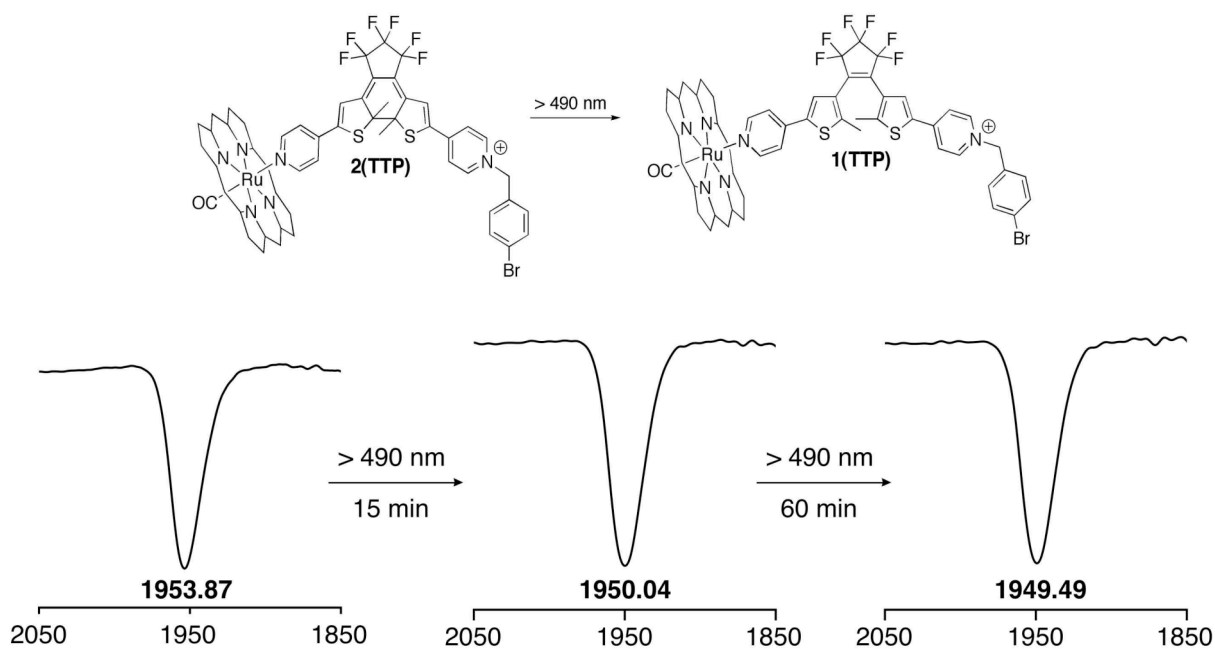


Figure S9. Selected IR spectra (KBr pellet) showing the gradual shift in the band corresponding to the C=O stretching frequency of the ring-closed complex **2(TTP)** upon irradiation of the pellet using > 490 -nm light.

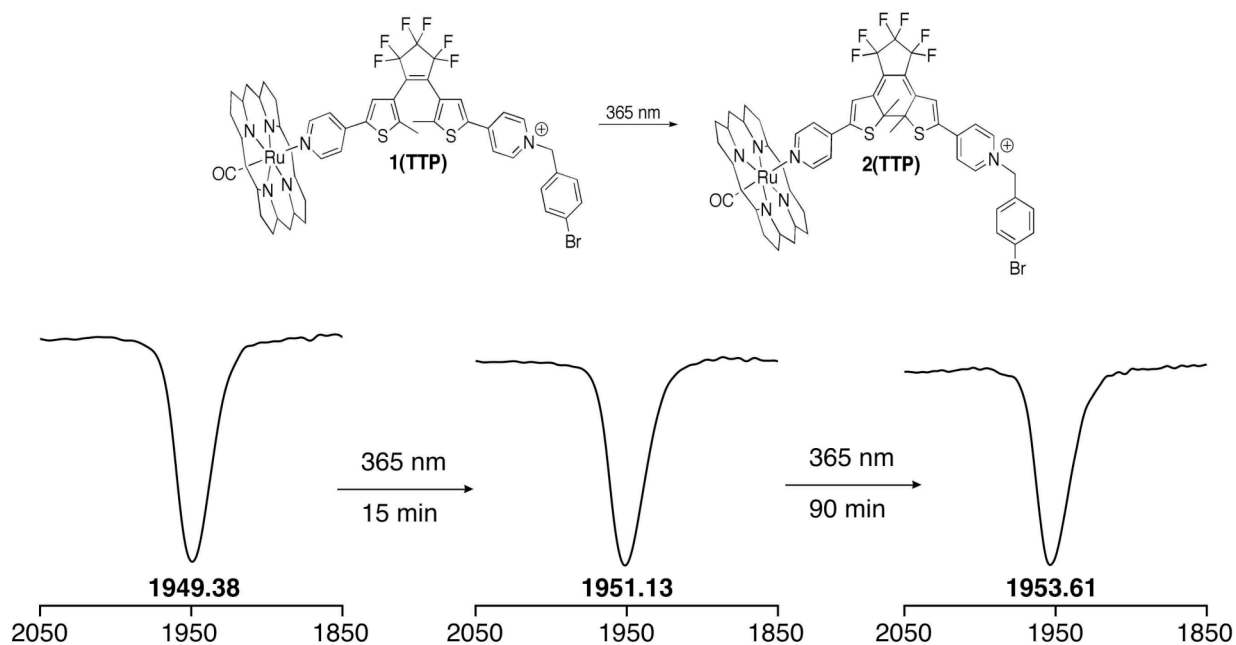


Figure S10. Selected IR spectra (KBr pellet) showing the gradual shift in the band corresponding to the C=O stretching frequency of the ring-open complex **1(TTP)** upon irradiation of the pellet using 365 -nm light.