

Supporting Information

Incorporating Optical Bistability Into a Magnetically Bistable System: A Photochromic Redox Isomeric Complex

Michelle M. Paquette,[†] Roni A. Kopelman,[‡] Elvira Beitler,[†] and Natia L. Frank^{*,†,‡}

[†]*Department of Chemistry, P.O. Box 3065, University of Victoria, Victoria, British Columbia V8W 3V6; Fax: +1 250 721 7147; Tel: +1 250 721 7154* [‡]*Department of Chemistry, P.O. Box 351700, University of Washington, Seattle, Washington 98195-1700*

E-mail: nlfrank@uvic.ca

General synthetic procedures: All reagents were purchased from commercial sources and used without further purification unless otherwise specified. Cyclohexane was dried over and distilled from P₂O₅, and degassed using freeze-pump-thaw cycles. Spectro-grade, dry, and deoxygenated THF and pentane were acquired from an MBraun solvent purification system. Reactions for all organic compounds were run under N₂ and worked up in air. The synthesis and purification procedures for all metal complexes were executed under the strict exclusion of air; manipulations were performed using standard Schlenk line techniques under N₂ or in an inert atmosphere Ar glovebox. ¹H NMR spectra were acquired with Bruker AC300 or AVANCE500 spectrometers. Spectra were calibrated to the solvent residual peaks (CDCl₃ at 7.24 ppm, toluene-*d*₈ at 2.09 ppm). FTIR samples were prepared as KBr pellets, and spectra were acquired with a Perkin Elmer Spectrum One spectrometer. Elemental analyses were performed by Canadian Microanalytical Service Ltd. and Desert Analytics.

Spiro[indoline-phenanthrolineoxazine] (IPSO) (1): 2-methylene-1,3,3-trimethylindoline (2.6 mL, 15 mmol, 1.0 equiv.) was added to a refluxing solution of 5-hydroxy-6-nitroso-1,10-phenanthroline¹ (3.3 g, 15 mmol, 1.0 equiv.) in dry toluene (300

mL). The solution was heated at reflux with a Dean-Stark apparatus in the dark for 16 h before the reaction mixture was filtered and the solvent was removed. The crude product was purified twice using column chromatography on silica gel (1. CH₂Cl₂/CH₃OH 90%:10%; 2. EtOAc/CH₃OH 90%:10%) to give a blue amorphous substance which was recrystallized from EtOAc to afford yellow crystals (1.4 g, 25% yield). Anal. Calcd for C₂₄H₂₀N₄O: C, 75.77; H, 5.30; N, 14.73. Found: C, 75.58; H, 5.13, N, 14.76. ¹H NMR (300 MHz, CDCl₃): δ 9.12 (dd, *J* = 4.5, 1.4 Hz, 1H), 9.07 (dd, *J* = 4.4, 1.5 Hz, 1H), 8.96 (dd, *J* = 8.0, 2.3 Hz, 1H), 8.40 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.83 (s, 1H), 7.67 (dd, *J* = 8.6, 4.4 Hz, 1H), 7.51 (dd, *J* = 8.2, 4.4 Hz, 1H), 7.23 (td, *J* = 7.4, 1.5 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 2.76 (s, 3H), 1.39 (s, 3H), 1.36 (s, 3H). IR (KBr) ν (cm⁻¹): 468 (m), 493 (m), 513 (m), 550 (m), 566 (w), 573 (w), 590 (w), 618 (m), 635 (w), 665 (m), 681 (m), 708 (w), 739 (s), 742 (s), 755 (m), 772 (m), 795 (m), 804 (m), 809 (m), 822 (m), 831 (m), 847 (w), 887 (m), 914 (m), 930 (s), 973 (s), 1002 (s), 1019 (s), 1049 (w), 1068 (m), 1075 (m), 1105 (s), 1109 (s), 1117 (s), 1139 (w), 1156 (sh), 1162 (m), 1173 (m), 1193 (w), 1222 (w), 1238 (m), 1275 (m), 1300 (s), 1319 (s), 1342 (m), 1357 (s), 1383 (m), 1407 (m), 1432 (s), 1447 (s), 1455 (s), 1471 (s), 1484 (s), 1499 (m), 1559 (m), 1583 (s), 1600 (s), 2865 (w), 2904 (w), 2925 (w), 2961 (m), 2976 (w), 2992 (w), 3029 (w), 3050 (w).

Co(DB)₂(IPSO) (2): [Co(DBSQ)₂]₄² (108 mg, 0.0540 mol, 1.00 equiv.) was stirred in dry THF (15 mL) for 1.5 h, whereupon the solution changed from a dark green suspension to a blue-green solution. To this was added a solution of IPSO (81.9 mg, 0.215 mol, 3.98 equiv.) in THF (7 mL) to give a blue solution which was stirred for 3 h before removing the solvent *in vacuo* and redissolving the solid in cyclohexane. After allowing the material to recrystallize over the course of a number of weeks under an inert atmosphere, a dark green solid was recovered and washed with pentane in a yield of 25%. This compound was observed to be quite sensitive to decomposition through exposure to O₂ in solution, as evidenced by ¹H NMR and electronic absorption spectroscopy (*vide infra*), but quite stable in the solid state. Anal. Calcd for CoC₅₂H₆₀O₅N₄: C, 70.97; H, 6.87; N, 6.37. Found: C, 70.85; H, 7.04, N, 5.99. ¹H NMR (500 MHz, toluene-*d*₈) tentative assignment of SO form: δ 99.52 (br s, 1H, phen), 97.73 (br s, 1H, phen), 35.89 (br s, 1H, phen), 33.34 (br s, 1H, phen), 14.19 (br s, 18H, *t*-butyl), 13.02 (br s, 1H, phen),

12.23 (br s, 1H, phen), 7.98 (s, 1H), 6.94 (td, $J = 6.9, 1.5$ Hz, 1H), 6.69 (dd, $J = 7.3, 1.4$ Hz, 1H), 6.66 (br t, $J = 7.1$ Hz, 1H), 6.19 (d, 7.9 Hz, 1H), 2.33 (s, 3H, CH₃), 1.73 (br s, 18H, *t*-butyl), 0.99 (s, 3H, CH₃), 0.96 (s, 3H, CH₃); of PMC form: δ 35.43 (br s, 1H, phen), 32.10 (br s, 1H, phen), 13.30 (br s, 1H, phen), 12.41 (br s, 1H, phen) [or 12.31 (br s, 1H, phen)], 9.33 (s, 1H), 2.83 (s, 3H, CH₃), 1.57 (s, 3H, CH₃). IR (KBr) ν (cm⁻¹): 467 (m), 494 (w), 539 (w), 570 (w), 602 (w), 640 (m), 653 (m), 673 (w), 696 (m), 728 (vs), 744 (w), 775 (m), 786 (m), 801 (w), 825 (m), 846 (vs), 855 (m), 860 (m), 906 (m), 931 (w), 985 (s), 1022 (m), 1028 (m), 1045 (w), 1094 (m), 1143 (w), 1204 (m), 1220 (w), 1245 (s), 1261 (w), 1288 (w), 1332 (w), 1341 (w), 1353 (s), 1359 (w), 1366 (m), 1385 (m), 1413 (m), 1423 (s), 1444 (vs), 1458 (vs), 1468 (vs), 1514 (m), 1559 (w), 1578 (s), 1602 (w), 2865 (s), 2904 (s), 2959 (vs), 3055 (w).

Experimental Details and Discussion

¹H NMR of 2: A powder sample of **2** was dissolved in degassed toluene-*d*₈ and filtered into an NMR sample tube in an inert-atmosphere Ar glovebox. The spectrum of **2** is shown in Figures S1–S5, and a tentative assignment was made by comparison with the spectra of IPSO (Figure S6–S8) and Co(DB)₂(phen) (Figures S9–S11). Peaks at 0.78, 1.14, 5.90, and 6.60 ppm are assigned to free di-*t*-butyl-*o*-benzoquinone (DBBQ) ligand. In the NMR sample prepared carefully in the glovebox as discussed above, free DBBQ was estimated to be less than 1% by weight of the sample. In an NMR sample prepared in deoxygenated solvent under N₂, but exposed briefly to O₂ during transfer to the sample tube, 5–6 % by weight of DBBQ was observed in the ¹H NMR spectrum. This emphasizes the highly sensitive nature of the material towards oxygen exposure in solution.

FTIR of 2: A solution of **2** was prepared in toluene and loaded into a solution cell with quartz windows. The IR spectrum (Figure S12) was acquired with a Perkin Elmer Spectrum One spectrometer. A broad, relatively low intensity peak is observed in the spectrum between 3500 and 5000 cm⁻¹, characteristic of intervalence charge transfer (IVCT) between the SQ and Cat ligands of the Co(III) form of the complex (**2a,2c**). These results are consistent with the presence of at least some Co(III) species in toluene solution at 300 K.

EPR Spectroscopy of 2: EPR data were collected with a Bruker EMX X-Band spectrometer equipped with a standard temperature control accessory. Samples were prepared in a 1:1 mixture of toluene/CH₂Cl₂ and degassed before use. The EPR spectrum of **2** at 250 K is shown in Figure S13.

Electronic Absorption Spectroscopy Studies: Spectra were acquired with an Agilent 8453 Spectrophotometer. The UV-Vis spectra of the two compounds are compared in Figure S14. Because there exists a mixture of SO and PMC isomers in solution in these compounds, it is useful to determine the extinction coefficients of the individual species. To do so, the ϵ values determined for the full solution were corrected for the concentration of the SO or PMC form by using the K_T values extracted from the ¹H NMR spectra of the compounds in toluene-*d*₈ at 300 K while assuming that the differences in solvent deuteration and concentration between UV-Vis and NMR experiments did not affect the equilibrium. The extinction coefficient at 590 nm for the π - π^* transition of the PMC form of **2** (ϵ_{590}) was determined to be 99000 cm⁻¹ M⁻¹. This value is significantly higher than that of the free ligand under the same conditions (ϵ_{582} = 70000 cm⁻¹ M⁻¹). It is possible that there are additional metal-based contributions to the absorption at 590 nm; however, ϵ_{590} for the analogous Co(DB)₂(phen) complex at 295 K is only *ca.* 2500 cm⁻¹ M⁻¹,³ and it is therefore reasonable to conclude that there is still a significant increase in the extinction coefficient upon coordination.

The variable temperature UV-Vis experiment on **2** was performed by preparing a 10⁻⁵ M toluene solution in a long-stemmed quartz cuvette sealed under N₂. This was immersed in a vacuum-sealed quartz dewar filled with spectro-grade acetone. A 300 K spectrum was acquired before cooling the surrounding solution to 196 K with dry ice/acetone and acquiring a low temperature spectrum. A final spectrum was acquired after warming of the solution to 290 K.

For the UV irradiation studies, 10⁻⁵ M toluene solutions of the compounds were prepared and transferred to quartz cuvettes and continuously stirred during irradiation. Because of the air-sensitive nature of **2**, solutions of the complex were prepared under N₂ and purged with N₂ once transferred to the cuvettes, and a stream of N₂ was directed over the cuvettes throughout the kinetic experiments. Irradiation with multiline UV irradiation was carried out using a Spectra-Physics Stabilite 2018 mixed gas Ar-Kr ion laser with a

typical power of 100 mW. The laser beam was focused into the sample at an angle of 90° to the detector array. The rates of thermal reversion, k_T , were determined from the photostationary state (generated by steady state irradiation) by fitting the thermal relaxation kinetic data (at 590 nm) to monoexponential rate functions by linear least-squares methods.

Diffuse Reflectance Spectroscopy: The spectrum of **2** was acquired with a Cary 100 spectrometer equipped with an integrating sphere. The sample was prepared by grinding 1.1% of sample in BaSO₄ and loading this into a quartz sample cell. The spectrum was corrected with a blank BaSO₄ background. (Figure S15).

PXRD Measurements: PXRD data were acquired with a Rigaku Miniflex diffractometer at ambient temperature. Cr radiation was used at 30 kV and 15 mA with a V K β filter, a 4.2° scattering slit, and a 0.3 mm receiving slit. Data were acquired in FT mode, with a step width of 0.01° and a count time of 10.0 s per step between 3 or 4 to 35° (2 θ). (Preliminary scans did not show any significant peaks above this value.) Samples of **2** were prepared in two ways. If only a small amount of material was available, they were prepared by suspending a small amount of powder in a minimal amount of Et₂O and then allowing a few drops of this mixture to evaporate from a glass microscope slide to create a thin film. The remaining samples were prepared by filling an indented silicon zero-background holder with powder. The acquired patterns are shown in Figure S16.

Magnetic Measurements: DC-SQUID measurements were obtained with a Quantum Design MPMS XL-5 system. Magnetization values were measured at a field strength of 10000 Oe and temperature range of 2–350 K. Measurements were performed on two independently synthesized and recrystallized samples of both α and β crystalline phases of **2**, and their magnetic behavior was found to be reproducible. The corrections for diamagnetic susceptibilities of the samples were determined using Pascal's constants (-1.136×10^{-5} emu K mol⁻¹) for Co(DB)₂(IPSO) (unsolvated) and by experimental measurement for the gelule and insertion tube (-2.4×10^{-7} emu K mol⁻¹).

Variable Temperature NMR Measurements and Evan's Method Data Workup: Compound **2** (5.2 mg) was dissolved in CD₂Cl₂ (1.00 mL) in an inert atmosphere glovebox and loaded into a 5 mm NMR tube. This was fitted with a coaxial insert tube which was filled with pure CD₂Cl₂. ¹H NMR spectra were acquired with a

Bruker AVANCE360 NMR spectrometer between 300 K and 200 K at 10 K intervals. The resulting spectra are shown in Figures S17–S23.

Evans method was used to determine the solution-state magnetic susceptibility of the sample over the range of temperatures studied by monitoring the frequency shift of the CDHCl₂ proton resonance. The gram magnetic susceptibility of the sample, χ_g , was calculated with Equation 1,⁴⁻⁶

$$\chi_g = -\frac{3\Delta\nu}{4\pi m\nu} + \chi_{g0} + \chi_{g0} \frac{\rho_0 - \rho_s}{m} \quad (1)$$

where $\Delta\nu$ (Hz) is the shift between the resonances for the solvent containing solute and the reference solvent, ν (Hz) is the operating frequency of the NMR spectrometer, m is the mass (g) of paramagnetic solute in 1.00 mL of solvent, χ_{g0} is the gram magnetic susceptibility of the solvent, ρ_0 is the density of the pure solvent, and ρ_s is the density of the solvent containing solute. The m term was corrected for the change in solvent density at each temperature.⁷ The temperature-dependent density of CD₂Cl₂ was approximated by applying the very nearly linear behavior of the density of CH₂Cl₂ between 200 and 300 K⁸ to the slightly higher density of CD₂Cl₂ at 298 K (1.362 g/mL). The second and third terms in Equation 1 were neglected.⁹ The molar susceptibilities, χ_M , were calculated from the χ_g values and were subsequently corrected for the diamagnetic contribution of the complex, χ_d , to finally obtain the paramagnetic contribution to the magnetic moment, χT .

Variable-temperature ¹H NMR spectra for Co(DB)₂(phen) in CD₂Cl₂, acquired in the same fashion as those for **2**, are shown in Figures S24–28 for comparison purposes. In these spectra, two *t*-butyl resonances are evident at ~ 0.5 and 16.5 ppm, which broaden significantly with decreasing temperature. Four resonances attributed to the phen protons at ~ 11, 18, 30, and 75 ppm decrease in paramagnetic shift with decreasing temperature. There is also evidence of free di-*t*-butyl-*o*-benzoquinone ligand and additional smaller resonance peaks nearby each of the phen proton resonances, which integrate to ~ 5%.

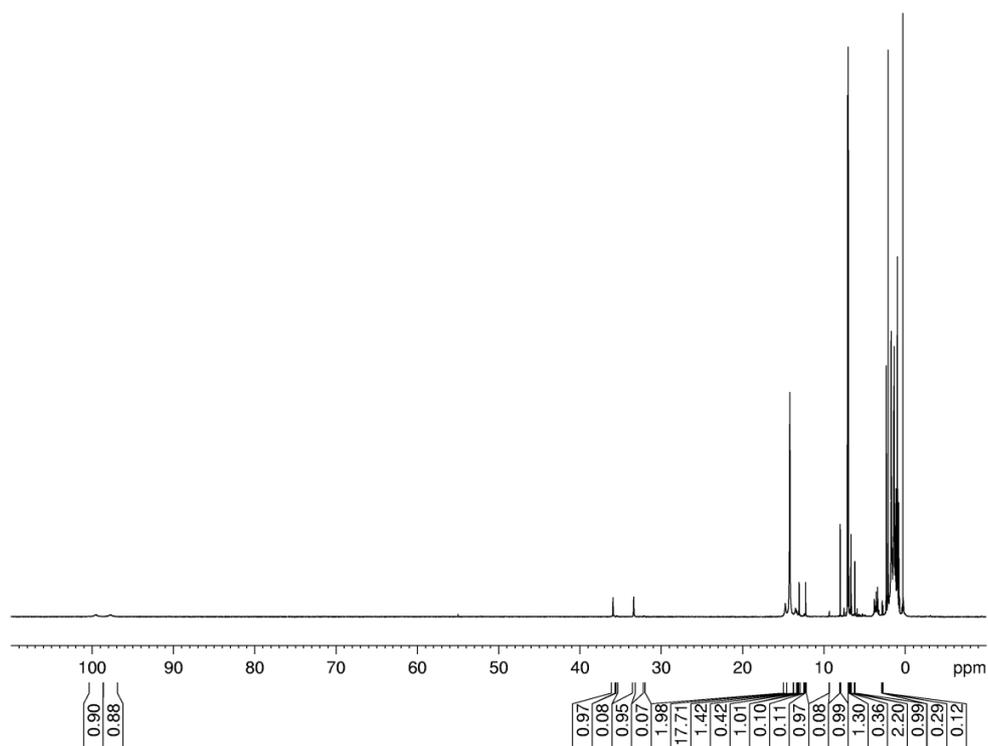


Figure S1: ^1H NMR spectrum of $\text{Co}(\text{DB})_2(\text{IPSO})$ (**2**) in $\text{toluene-}d_8$.

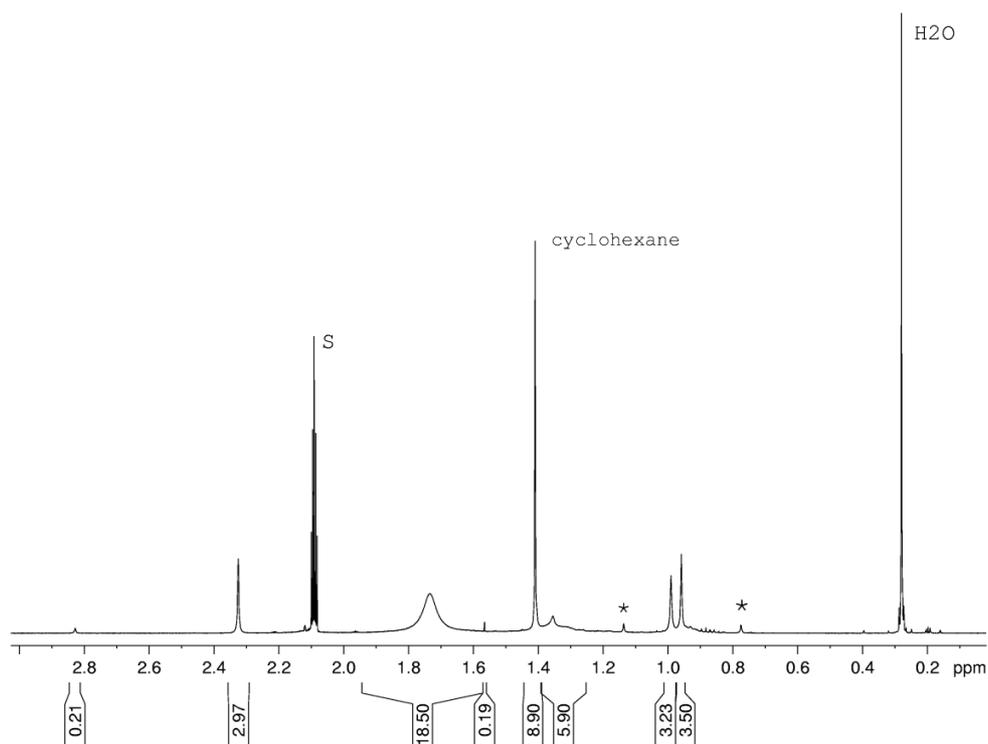


Figure S2: Expansion of the ^1H NMR spectrum of **2** in toluene- d_8 . S = residual solvent, * = free di-*t*-butyl-*o*-benzoquinone. Resonances at 0.96, 0.99, and 2.33 ppm are assigned to the three methyl groups on the IPSO ligand, and the resonance at 1.73 is assigned to a *t*-butyl group.

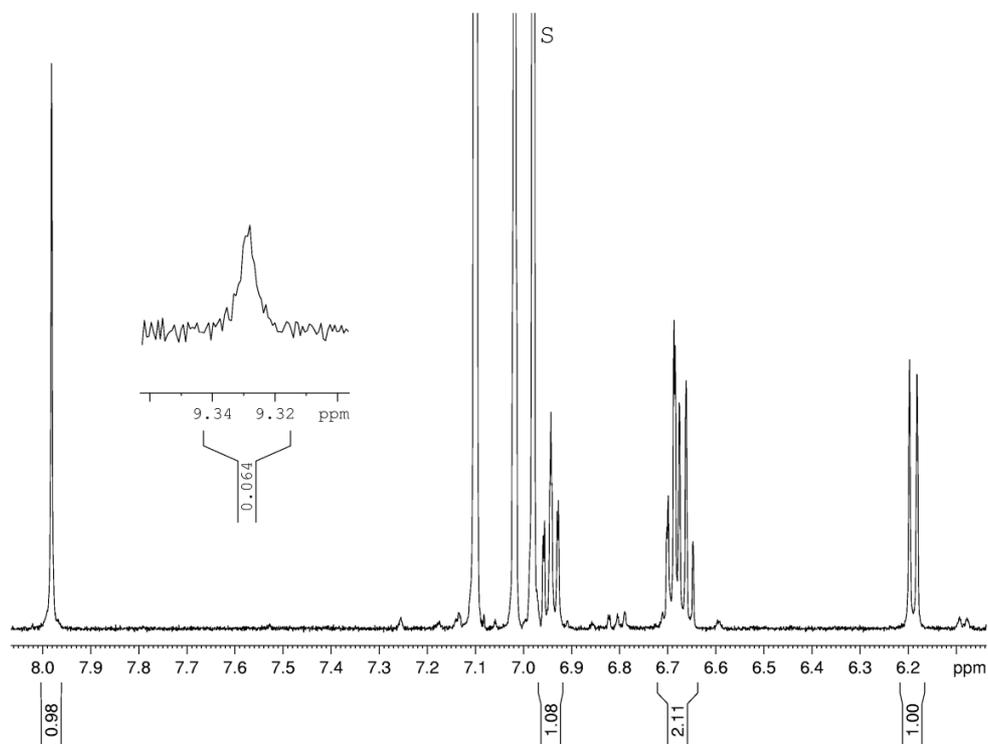


Figure S3: Expansion of the ^1H NMR spectrum of **2** in toluene- d_8 . S = residual solvent. Multiplets at 6.19, 6.66, 6.69, and 6.94 ppm are assigned to the four protons on the indolyl portion of the IPSO ligand, and the resonances at 7.98 and 9.33 are assigned to the azomethine protons of the SO and PMC forms of the IPSO ligand, respectively.

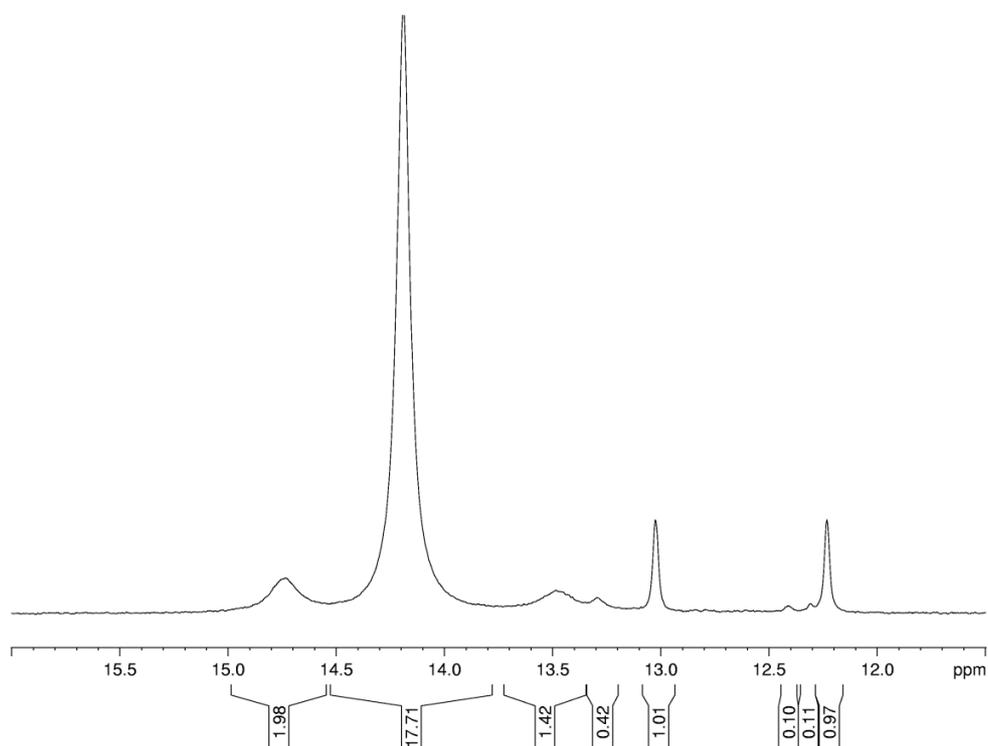


Figure S4: Expansion of the ^1H NMR spectrum of **2** in $\text{toluene-}d_8$. Resonances at 12.23 and 13.02 are assigned to phenanthroline protons, and the resonance at 14.19 is assigned to a *t*-butyl group.

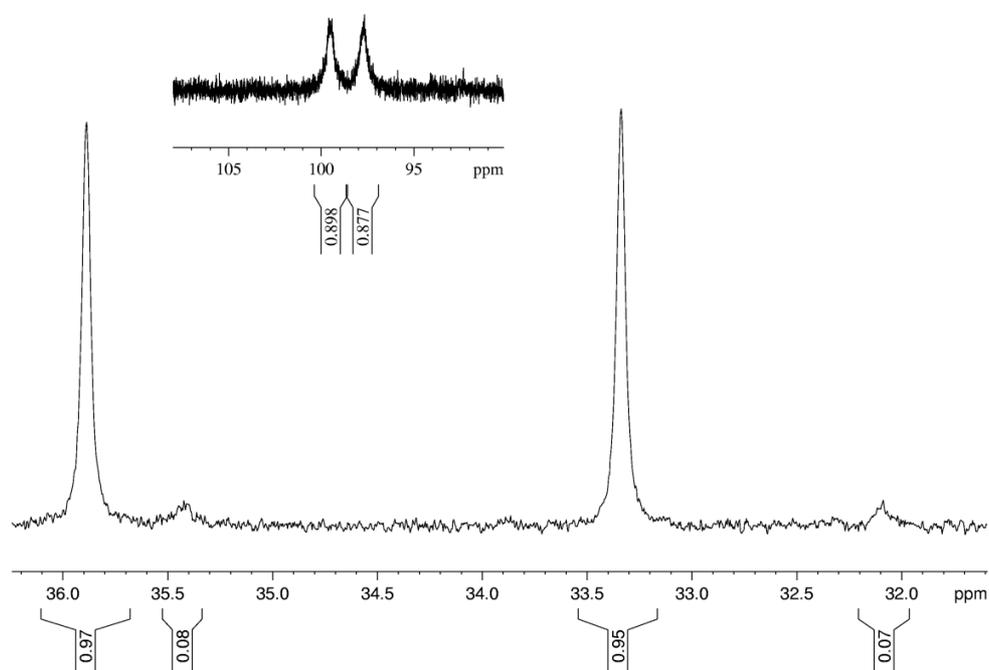


Figure S5: Expansion of the ^1H NMR spectrum of **2** in $\text{toluene-}d_8$. Resonances at 33.34, 35.89, 97.73, and 99.52 ppm are assigned to four phenanthroline protons on the IPSO-SO ligand. Smaller peaks at 32.1 and 35.5 ppm are assigned to the same protons of the PMC form of the ligand.

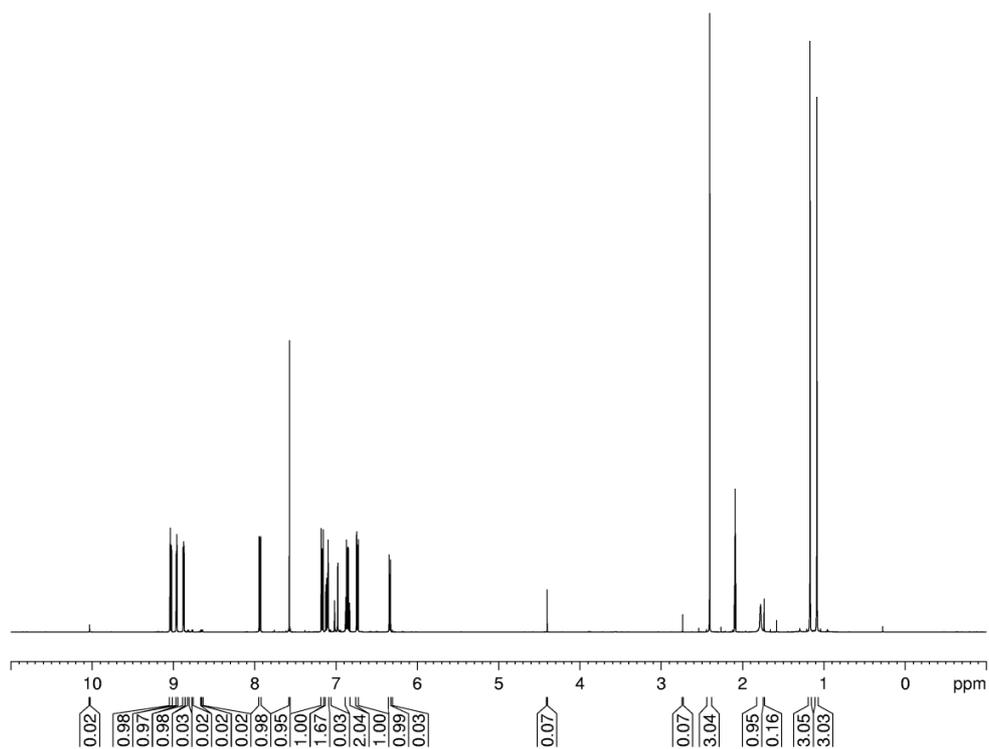


Figure S6: ^1H NMR spectrum of IPSO (**1**) in $\text{toluene-}d_8$.

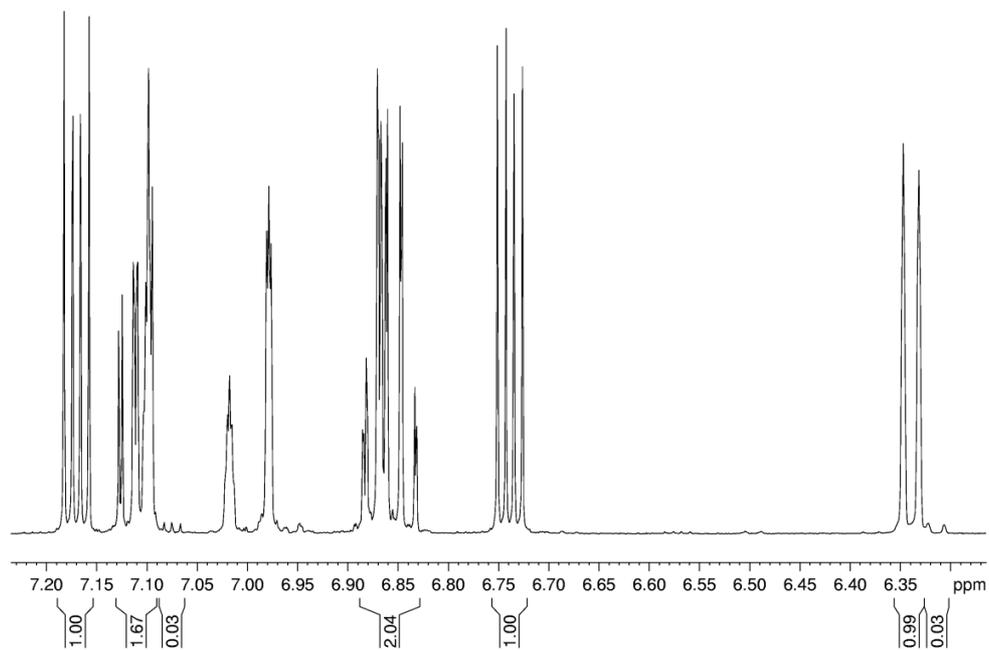


Figure S7: Expansion of the ^1H NMR spectrum of **1** in $\text{toluene-}d_8$.

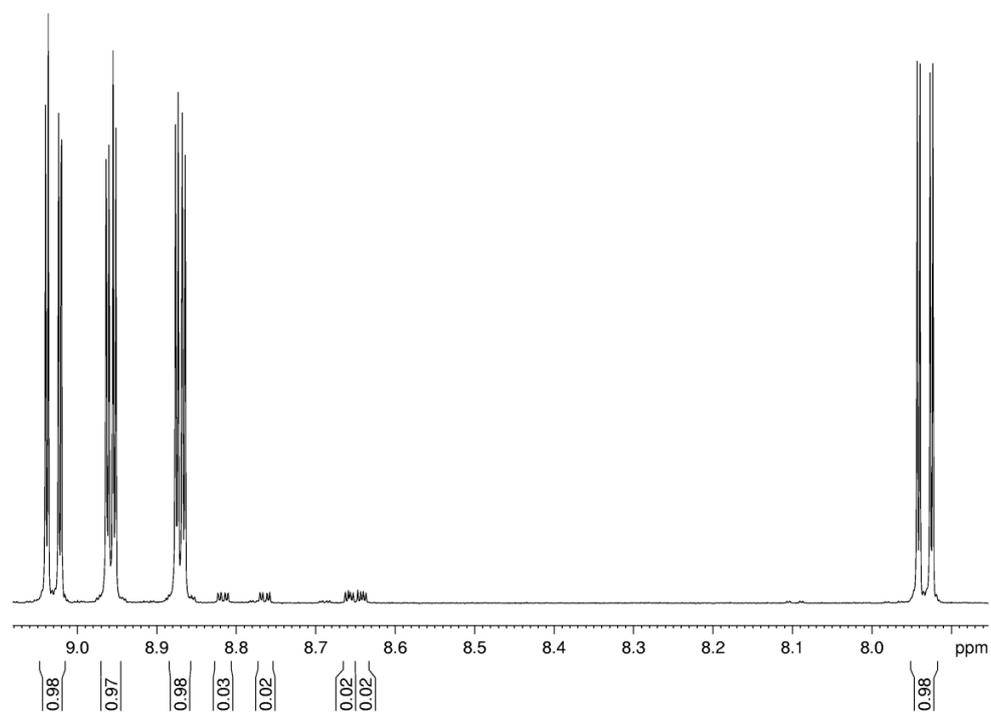


Figure S8: Expansion of the ^1H NMR spectrum of **1** in $\text{toluene-}d_8$.

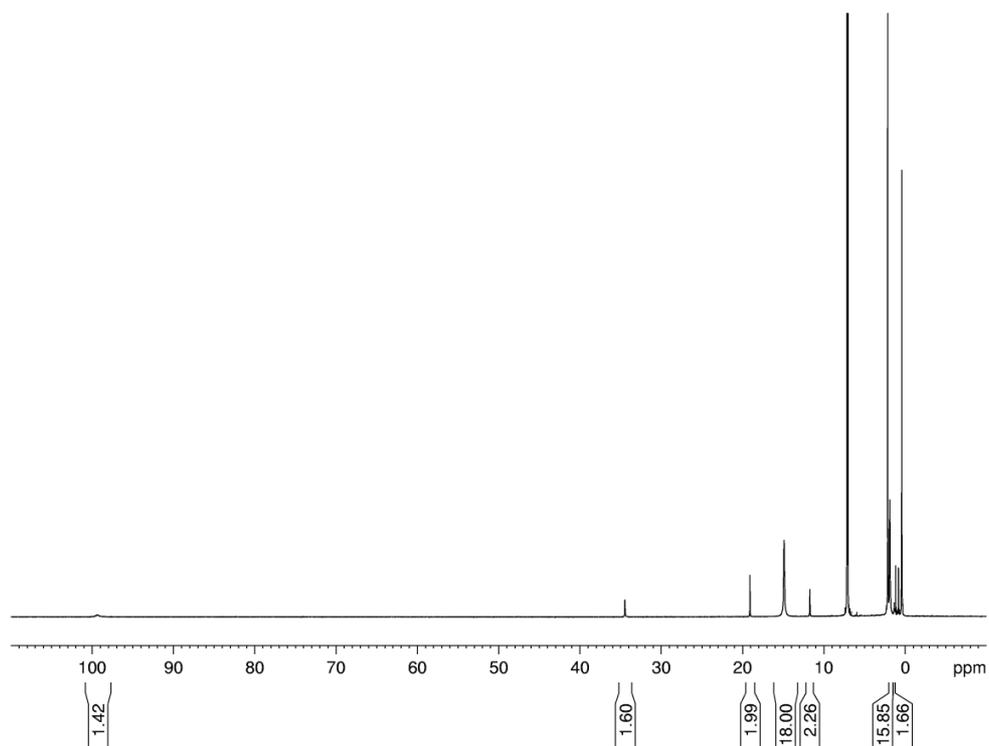


Figure S9: ¹H NMR spectrum of Co(DB)₂(phen)·C₆H₅CH₃ in toluene-*d*₈.

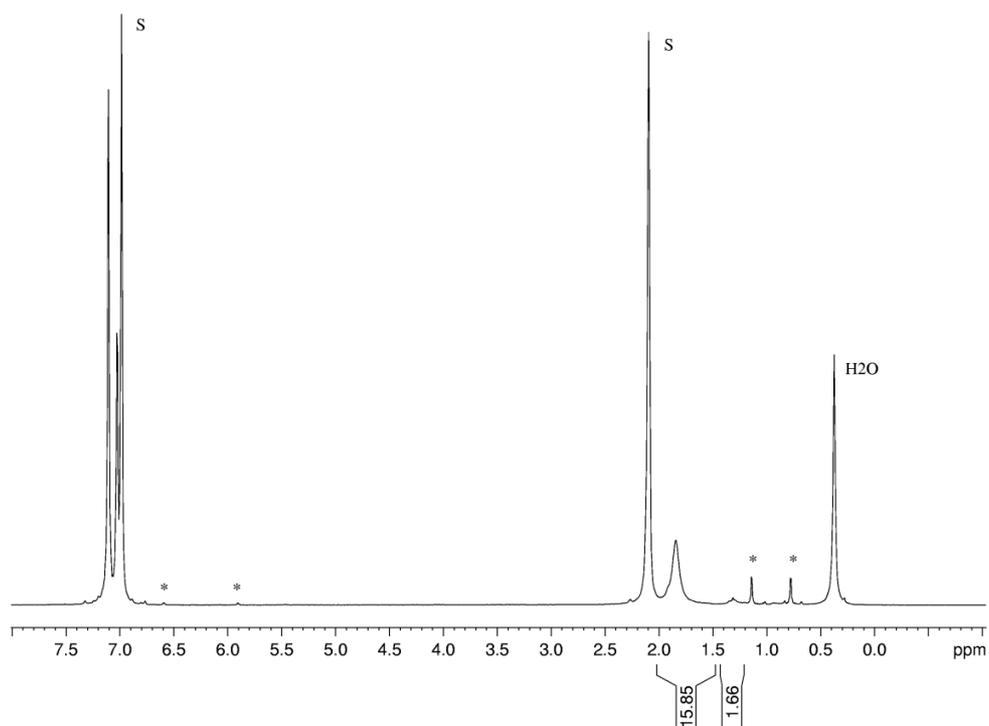


Figure S10: Expansion of the ¹H NMR spectrum of Co(DB)₂(phen)·C₆H₅CH₃ in toluene-*d*₈. S = residual solvent or lattice toluene, * = free di-*t*-butyl-*o*-benzoquinone. The resonance at 1.8 ppm is assigned to a *t*-butyl group.

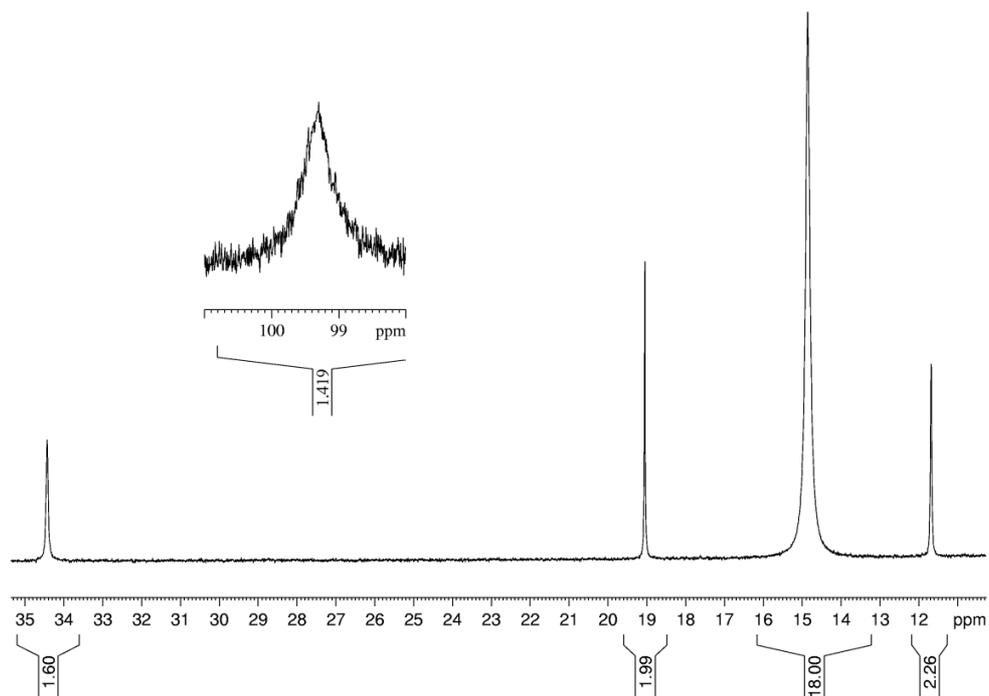


Figure S11: Expansion of the ¹H NMR spectrum of Co(DB)₂(phen)·C₆H₅CH₃ in toluene-*d*₈. The resonance at ca. 15 ppm is assigned to a *t*-butyl group, and the resonances at 11.7, 19.1, 34.5, and 99.4 ppm are assigned to the four different sets of phenanthroline protons.

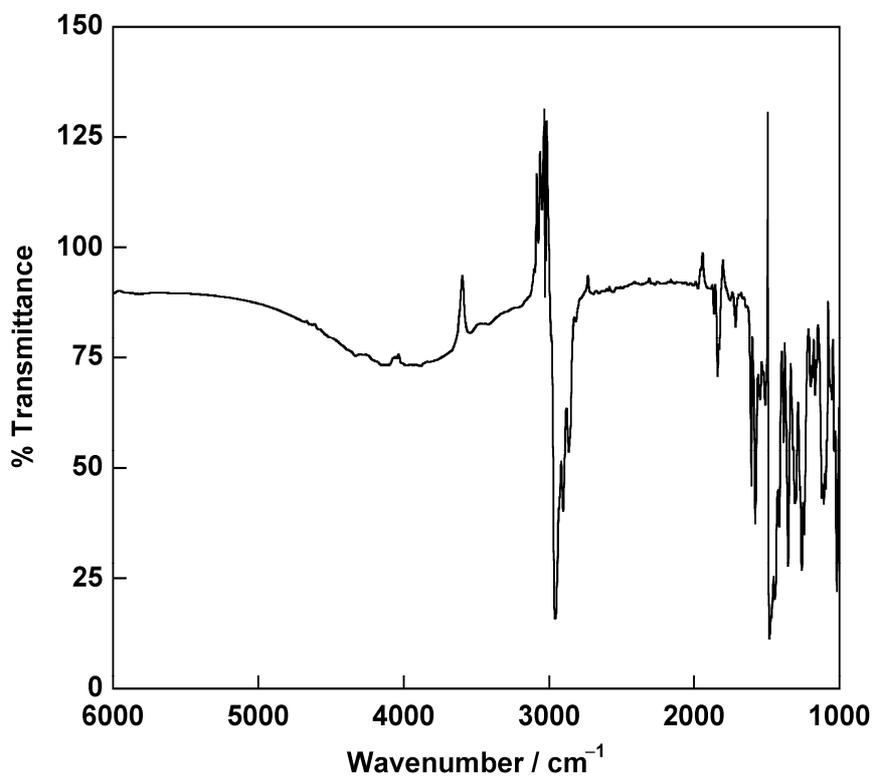


Figure S12: FTIR spectrum of **2** in toluene at r.t.

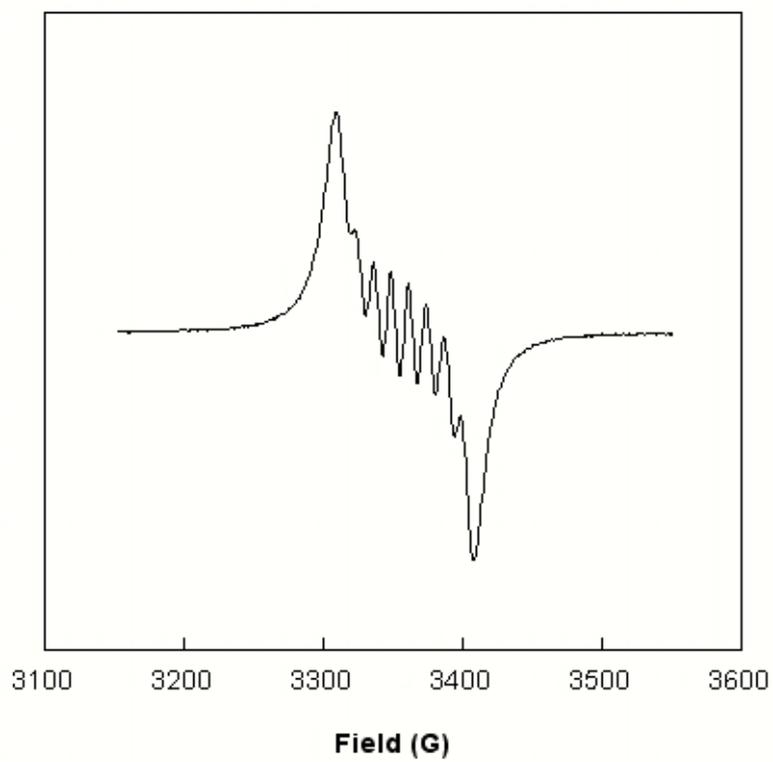


Figure S13: EPR spectrum of **2** in CH₂Cl₂/toluene (1:1) at 250 K.

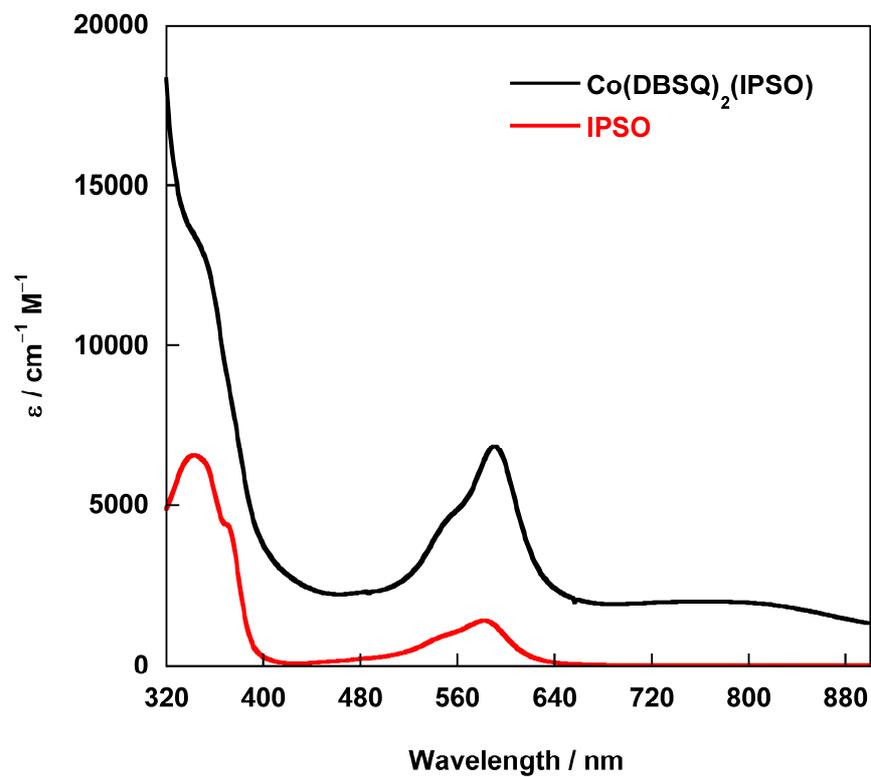


Figure S14: UV-Vis spectra of IPSO (1) and $\text{Co}(\text{DB})_2(\text{IPSO})$ (2) in toluene at r.t.

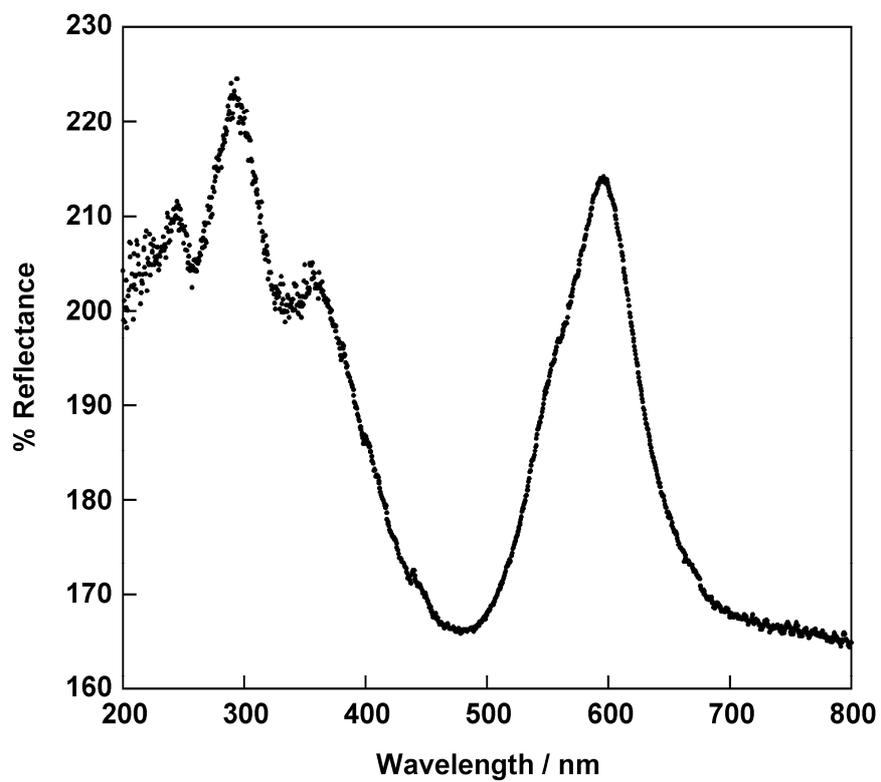


Figure S15: Diffuse reflectance spectrum of **2** in BaSO₄ (1.1 %) at r.t.

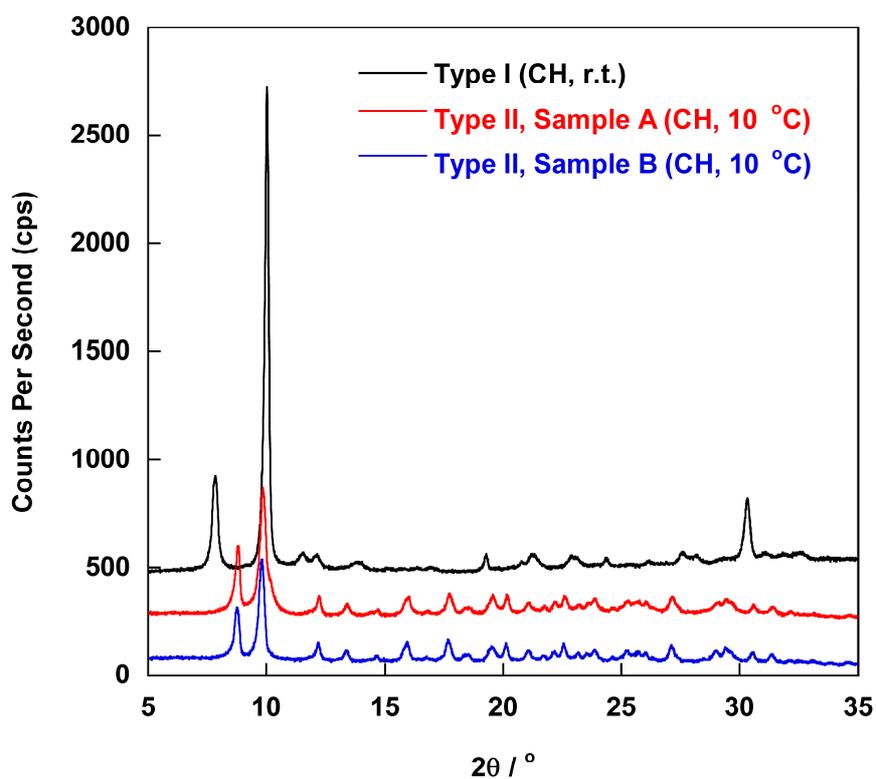


Figure S16: PXRD patterns of individually synthesized samples of **2** recrystallized from cyclohexane at two different temperatures. The sample of type I and sample A of type II were prepared as Et₂O slurries on glass microscope slides, and sample B of type II was prepared as a powder in a silicon zero-background holder.

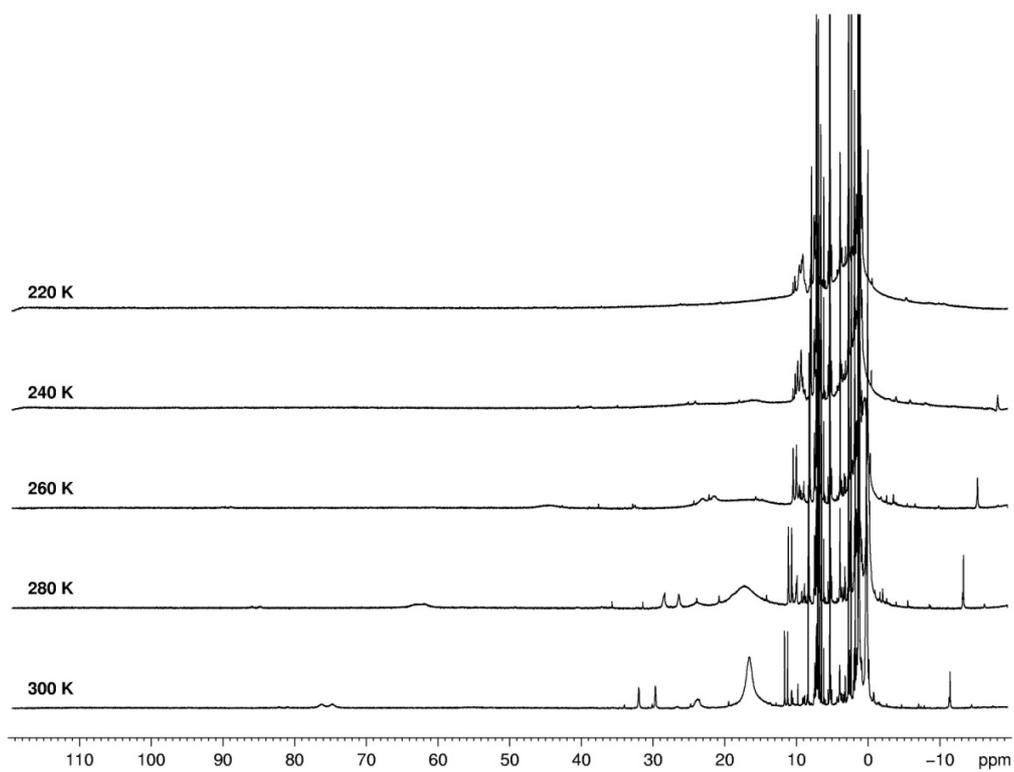


Figure S17: Variable temperature ¹H NMR spectra of Co(DB)₂(IPSO) (**2**) in CD₂Cl₂.

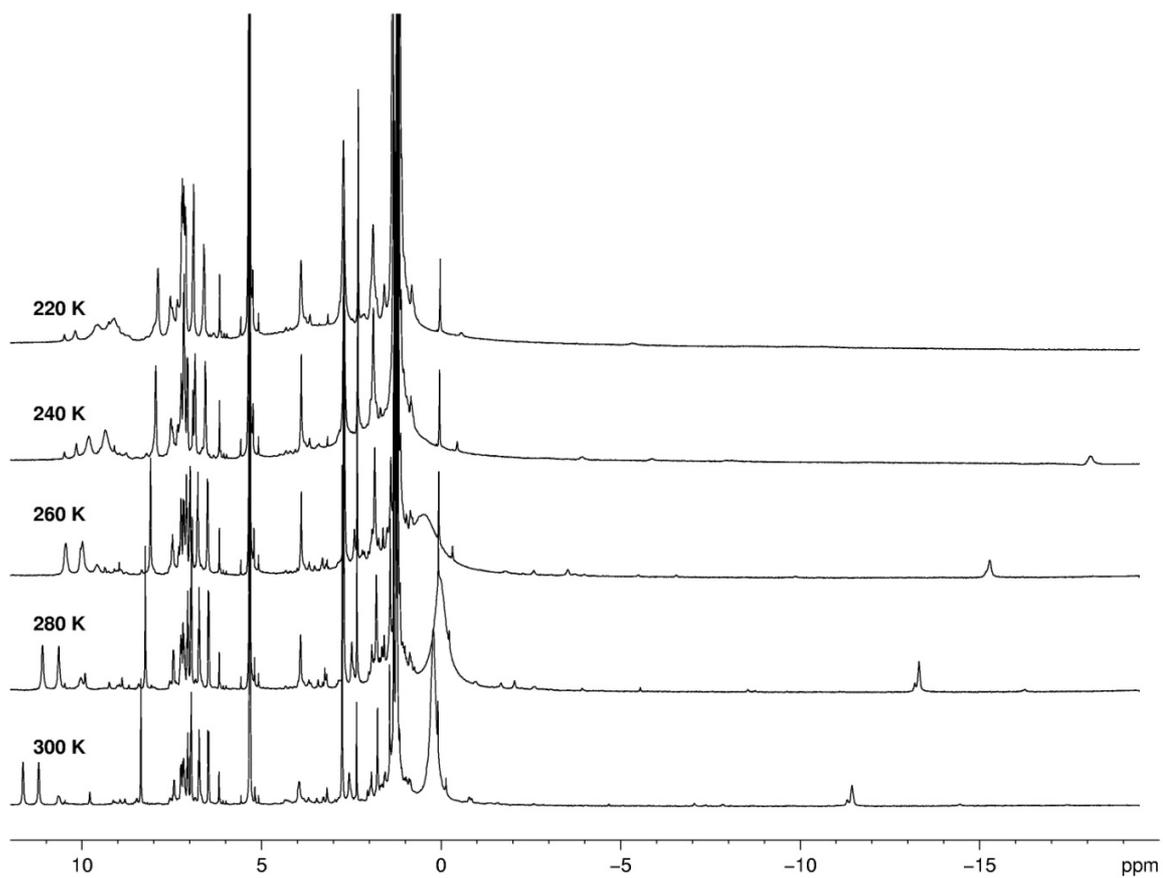


Figure S18: Variable temperature ¹H NMR spectra of **2** in CD₂Cl₂ from -20 to 20 ppm.

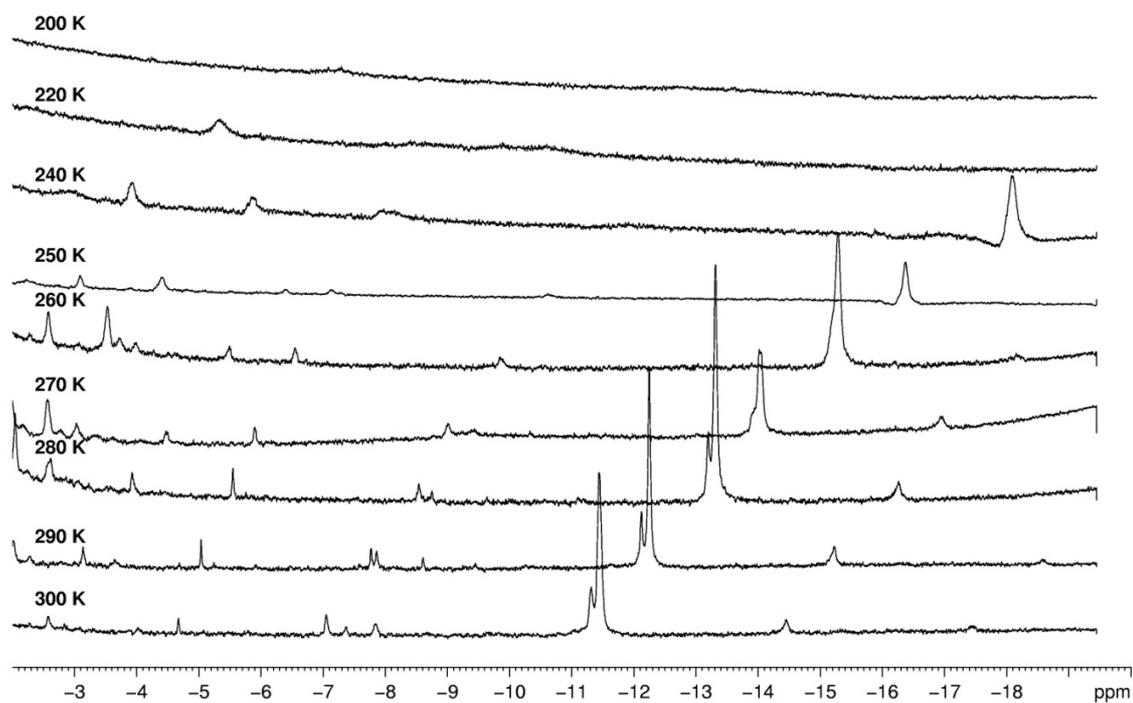


Figure S19: Variable temperature ¹H NMR spectra of **2** in CD₂Cl₂ from -20 to -2 ppm.

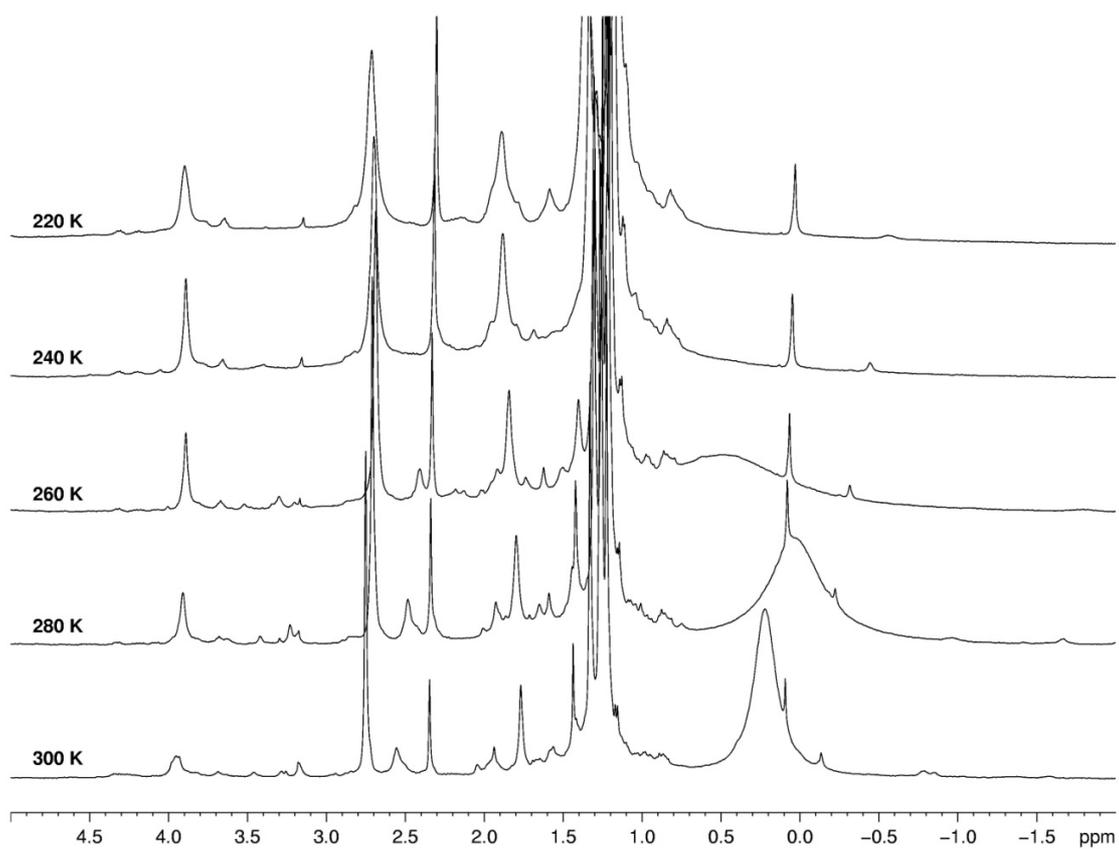


Figure S20: Variable temperature ¹H NMR spectra of **2** in CD₂Cl₂ from -2 to 5 ppm.

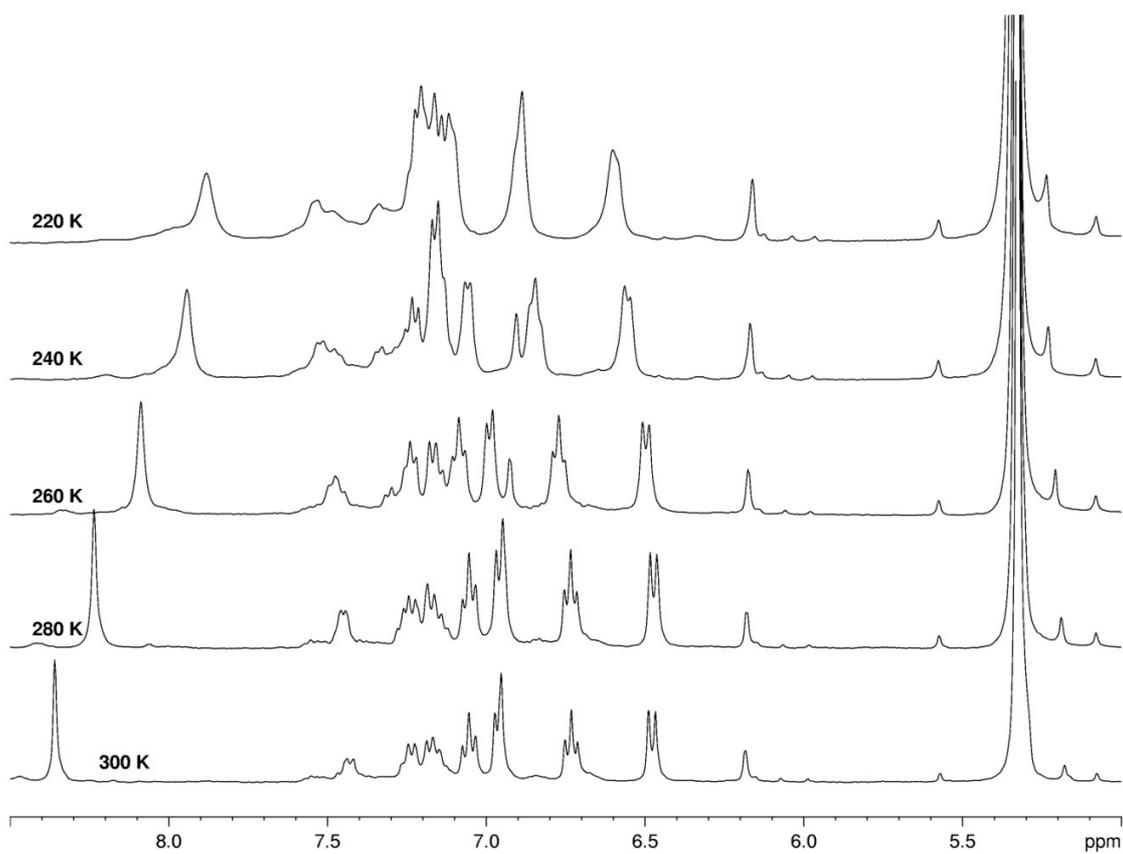


Figure S21: Variable temperature ¹H NMR spectra of **2** in CD₂Cl₂ from 5 to 8.5 ppm.

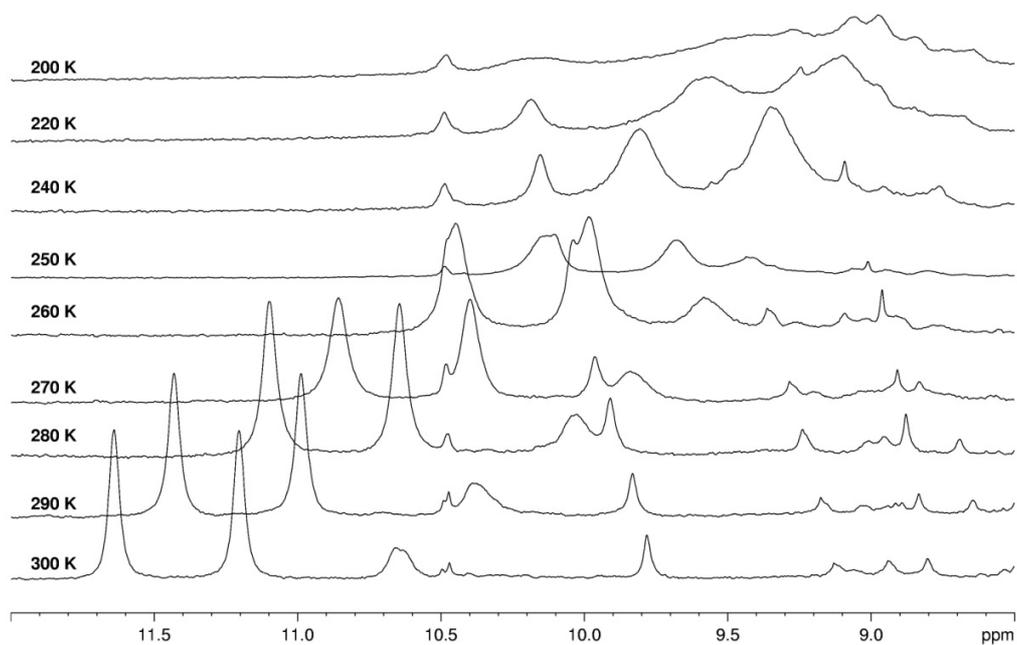


Figure S22: Variable temperature ^1H NMR spectra of **2** in CD_2Cl_2 from 8.5 to 12.5 ppm.

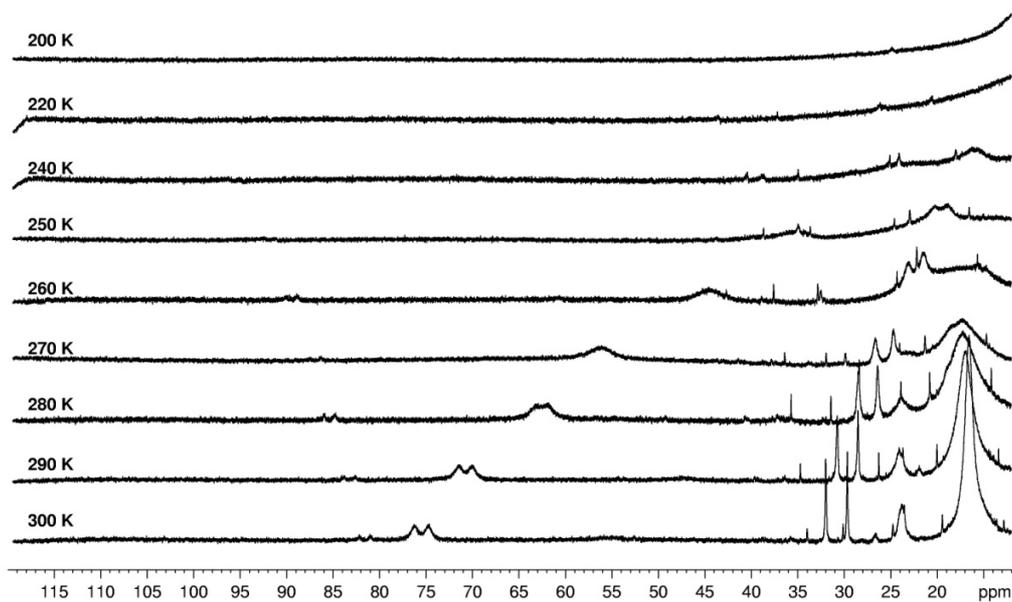


Figure S23: Variable temperature ¹H NMR spectra of **2** in CD₂Cl₂ from 12.5 to 120 ppm.

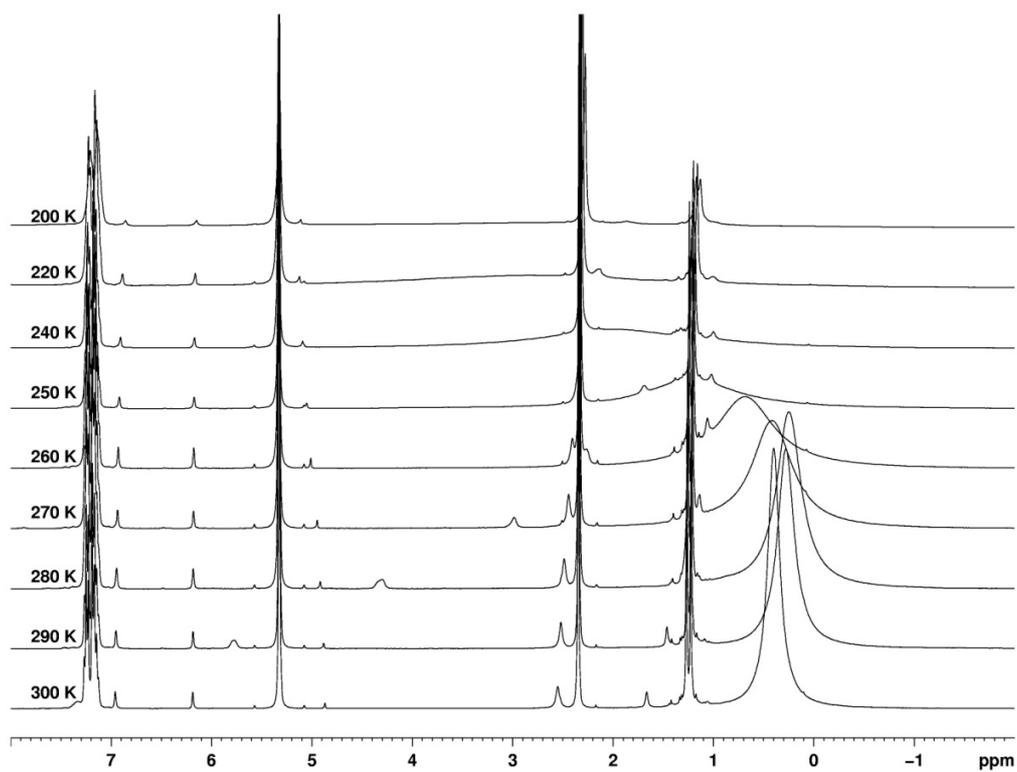


Figure S24: Variable temperature ¹H NMR spectra of $\text{Co}(\text{DB})_2(\text{phen})\cdot\text{C}_6\text{H}_5\text{CH}_3$ in CD_2Cl_2 from -2 to 8 ppm.

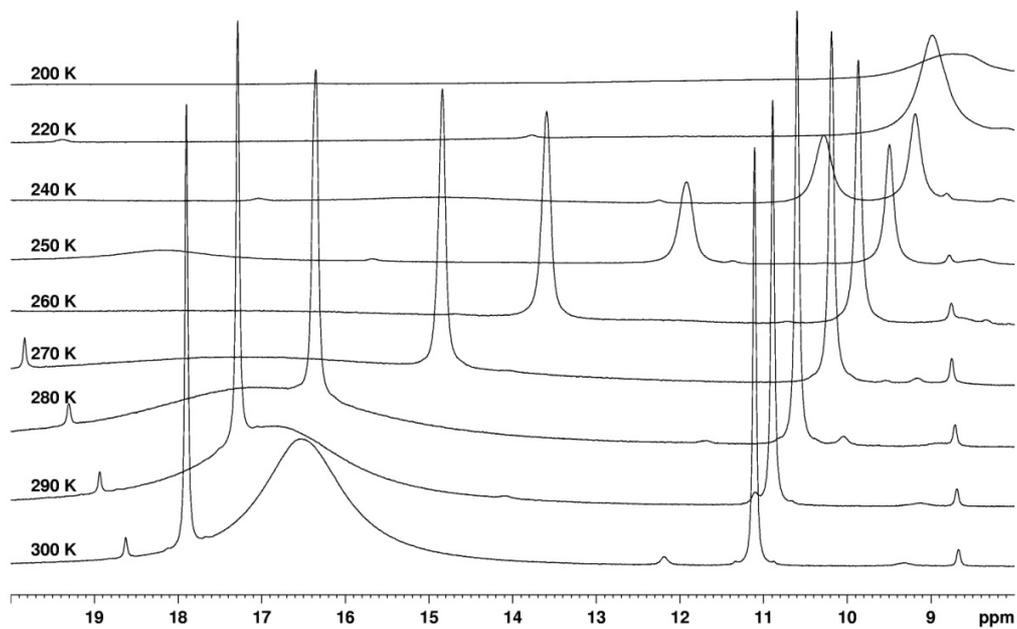


Figure S25: Variable temperature ¹H NMR spectra of $\text{Co}(\text{DB})_2(\text{phen}) \cdot \text{C}_6\text{H}_5\text{CH}_3$ in CD_2Cl_2 from 8 to 20 ppm.

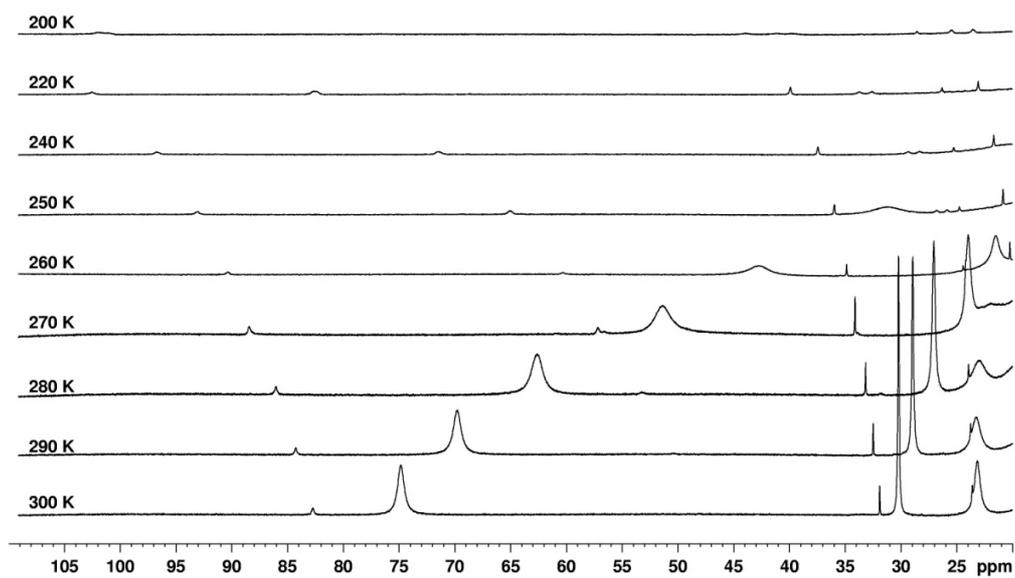


Figure S26: Variable temperature ¹H NMR spectra of $\text{Co}(\text{DB})_2(\text{phen}) \cdot \text{C}_6\text{H}_5\text{CH}_3$ in CD_2Cl_2 from 20 to 110 ppm.

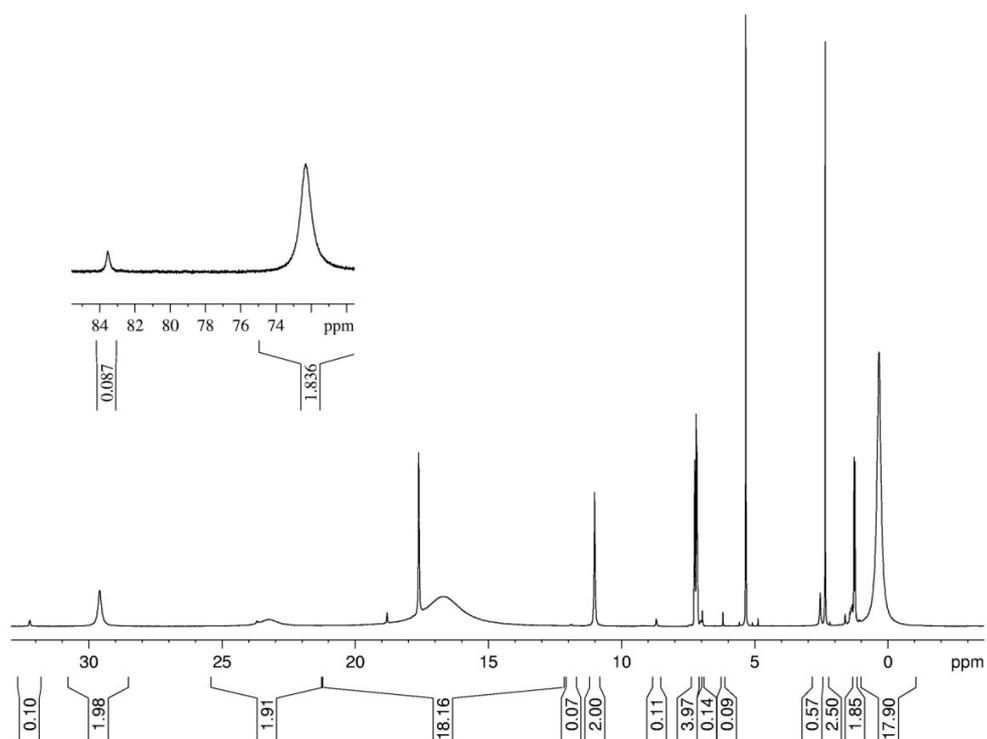


Figure S27: ¹H NMR spectrum of Co(DB)₂(phen)·C₆H₅CH₃ in CD₂Cl₂ at 297 K with integration values.

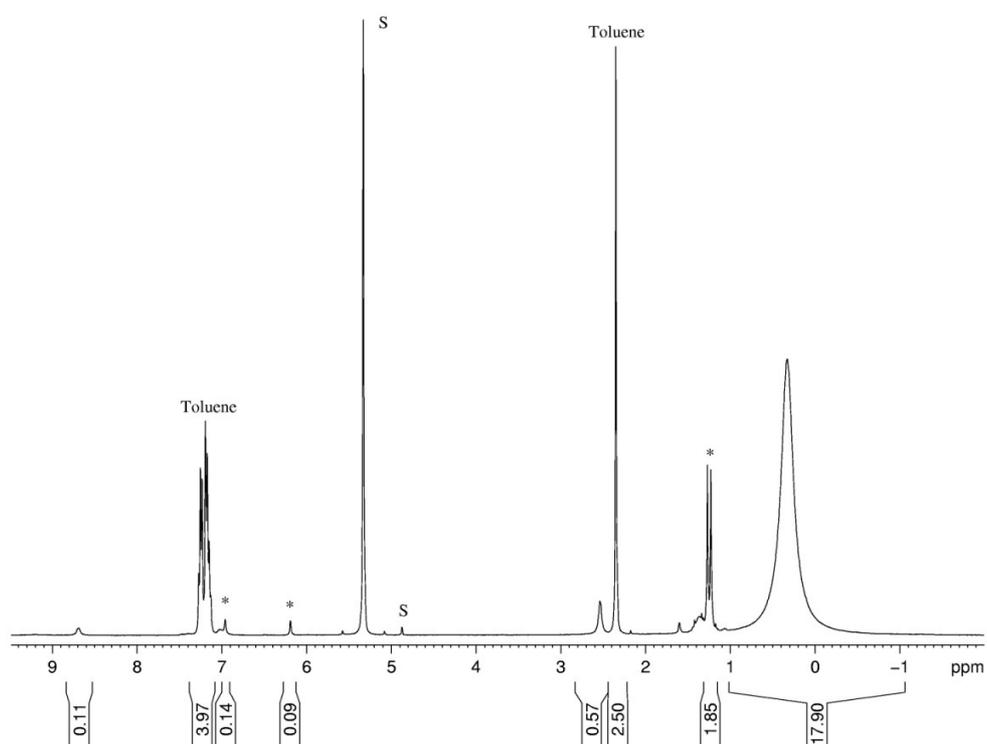


Figure S28: ¹H NMR spectrum of Co(DB)₂(phen)·C₆H₅CH₃ in CD₂Cl₂ at 297 K with integration values. S = residual solvent, * = free di-*t*-butyl-*o*-benzoquinone.

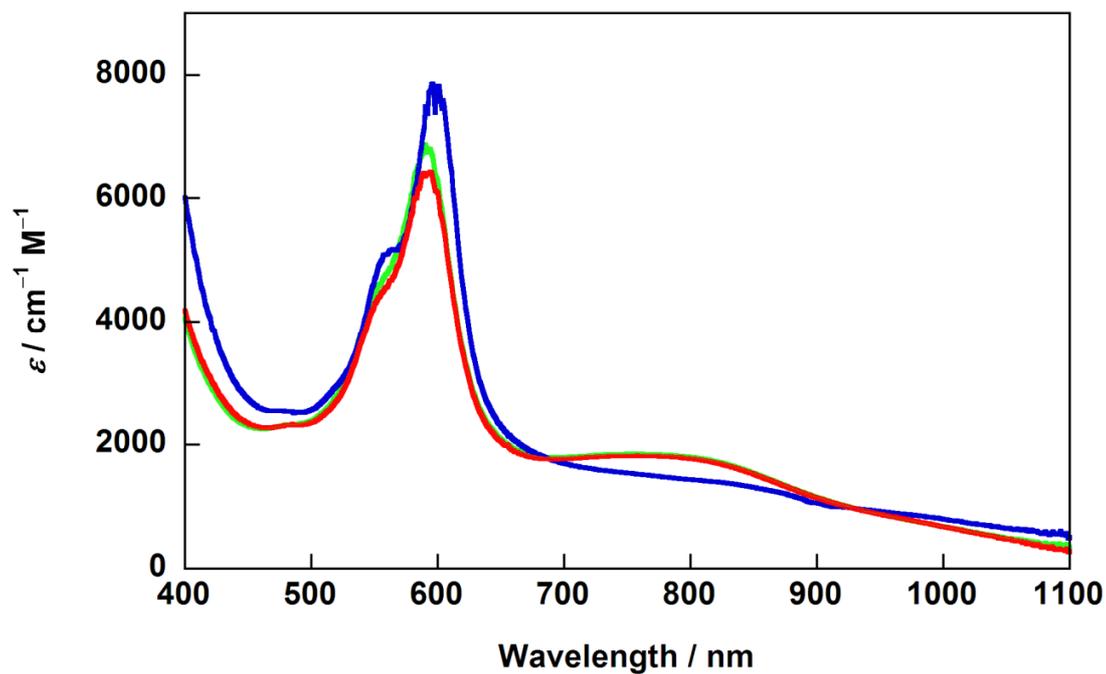


Figure S29: Temperature dependence of the electronic absorption spectrum of **2** in a toluene matrix [— 300 K, — 196 K, — 290 K (after cooling)].

Effect of UV irradiation on Redox Equilibria:

Towards this end, we have found that in solution, irradiation in the UV region leads to photoisomerization and has minor effects on the MLCT band or IR spectrum of the complex. This is reasonable given the lower photoresponsivity of IPSO described in the manuscript.

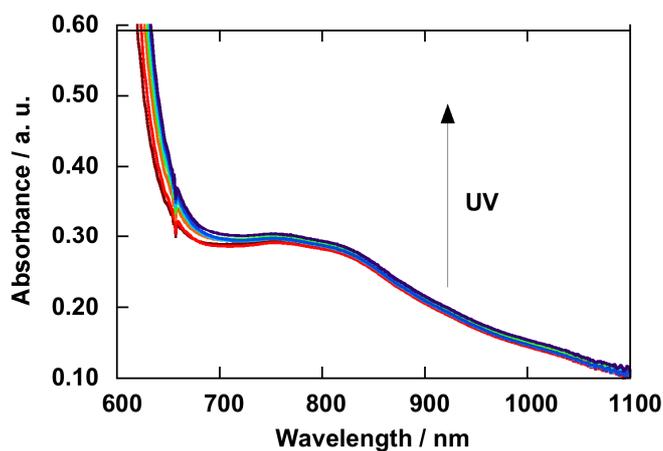


Figure S30: Irradiation (UV) dependence of the electronic absorption spectrum of **2** (the MLCT region) in toluene at 300 K

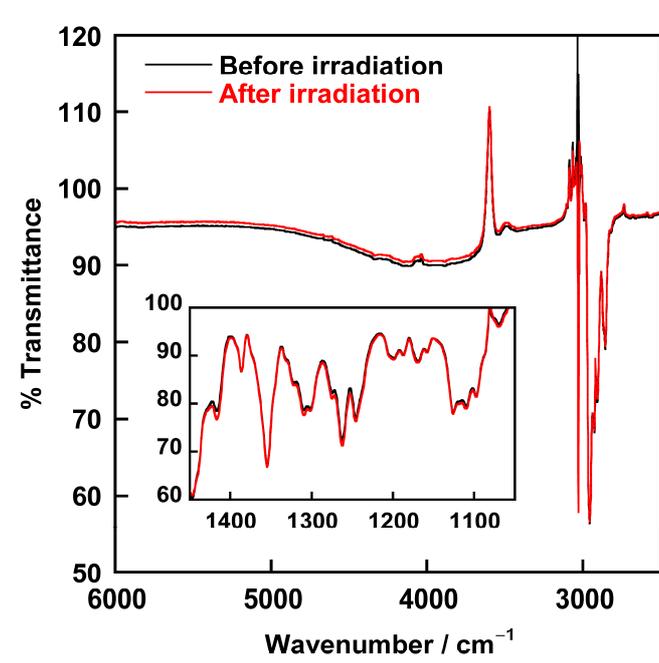


Figure S31: Irradiation (UV) dependence of the infrared spectrum of **2** (left) in toluene at 300 K.

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