

Supporting Information:

Chemically Reversible Binding of Hydrogen Sulfide to Metal Phthalocyanines

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Experimental Details

Materials and Methods. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or an Innovative Atmospheres N₂-filled glove box. Metal phthalocyanines (ZnPc, CoPc) were purchased from Strem Chemicals and used as received. Anhydrous sodium hydrogen sulfide (NaSH) was purchased from Strem Chemicals and handled under nitrogen. Hydrogen sulfide gas was purchased from Sigma Aldrich and transferred through a custom-built stainless steel transfer line to a glass storage bulb prior to use. *Note:* Hydrogen sulfide and its salts are highly toxic and should be handled carefully to avoid exposure. Spectroscopic grade THF was degassed by sparging with argon followed by passage through a Pure Process Technologies solvent purification system to remove water and stored over 4Å molecular sieves. THF-*d*₈ was purchased from Cambridge Isotope Laboratories and vacuum transferred from sodium/benzophenone ketyl, subjected to three freeze-pump-thaw cycles, and stored in an inert atmosphere glove box over 4Å molecular sieves. [NBu₄][BH₄] was purchased from TCI and used as received. Glacial acetic acid was purchased from EMD Chemicals and used as received. Anhydrous DMSO was purchased from EMD Chemicals, degassed using four freeze-pump-thaw cycles, and stored in an inert atmosphere glove box over 4Å molecular sieves. Phthalocyanine stock solutions were prepared in dry THF and stored in amber vials at -20 °C in an inert atmosphere glove box until immediately prior to use.

Spectroscopic Methods. UV-vis measurements were acquired on an Agilent Cary 100 UV-Vis spectrophotometer equipped with a QNW dual cuvette temperature controller at 25.00 ± 0.05 °C. All spectroscopic samples were prepared under an inert atmosphere in septum-sealed cuvettes obtained from Starna Scientific. NMR spectra were acquired on a Bruker Avance-III-HD 600 spectrometer with a Prodigy multinuclear broadband CryoProbe at 25.0 °C. Chemical shifts are reported in parts per million (δ) and are referenced to residual protic solvent resonances.

General procedure for UV-vis spectroscopic studies. In a glove box, the phthalocyanine stock solutions were diluted to the desired concentration and 3.0 mL of the resultant solution was transferred to a septum-sealed cuvette and removed from the glove box. Non-phthalocyanine reagents were prepared approximately 10⁵ times more concentrated than the phthalocyanine to provide minimal dilution during the study. NaSH, H₂S, and other reagents were added to the septum-sealed cuvettes by gas-tight syringe. Titration studies were performed using 0.25 equiv. increments unless otherwise noted.

General procedure for NMR studies. In a glove box, 3.0 mL of a ZnPc stock solution (0.60 mM in THF-*d*₈) was prepared and 1.0 mL added to three septum-capped NMR tubes. Stock solutions of NaSH and KOH (35.6 mM in DMSO-*d*₆) were prepared, and 17 μ L of each stock solution was added to two of the NMR tubes using a gas-tight syringe. A control experiment using 17 μ L DMSO-*d*₆ was also performed.

General Procedure for Job Plot Experiments

A 183 μ M stock solution of ZnPc in 1:1 THF:DMSO was prepared in a glove box. Aliquots of various volumes were added to septum-capped air-tight cuvettes in the glove box. A 183 μ M stock solution of NaSH in 1:1 THF:DMSO was prepared outside of the glove box using standard Schlenk technique. Each of the ZnPc cuvettes was diluted to 3 mL total volume with NaSH solution maintaining a total cuvette concentration of 183 μ M, and the UV-vis spectra was immediately taken for all fractions. The job plot was constructed by following 427 nm across all concentrations.

A 38 μM stock solution of CoPc in 1:1 THF:DMSO was prepared in a glove box. Aliquots of various volumes were added to septum-capped air-tight cuvettes in the glovebox. A 39 μM stock solution of NaSH in 1:1 THF:DMSO was prepared outside of the glovebox using standard Schlenk technique. Each of the CoPc cuvettes was diluted to 3 mL total volume with NaSH solution maintaining a total cuvette concentration of 38 μM , and the UV-vis spectra was immediately taken for all fractions. The job plot was constructed by following 467 nm across all concentrations.

Titration of CoPc with [NBu₄][BH₄].

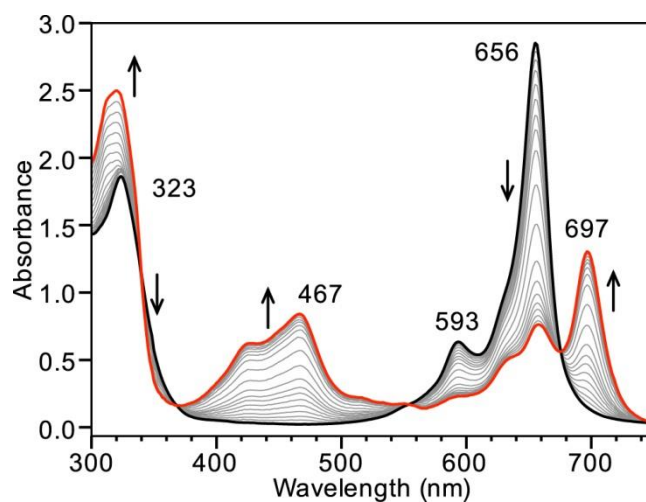


Figure S1. UV-vis titration data of 3.0 mL of 10 μ M CoPc with 2.8 mM [NBu₄][BH₄] in 5.9 μ L aliquots in THF showing reduction of CoPc to [CoPc]⁻. The band at 320 nm observed in the [NBu₄][BH₄] titration is consistent with formation of borane-THF complex.

Job Plots

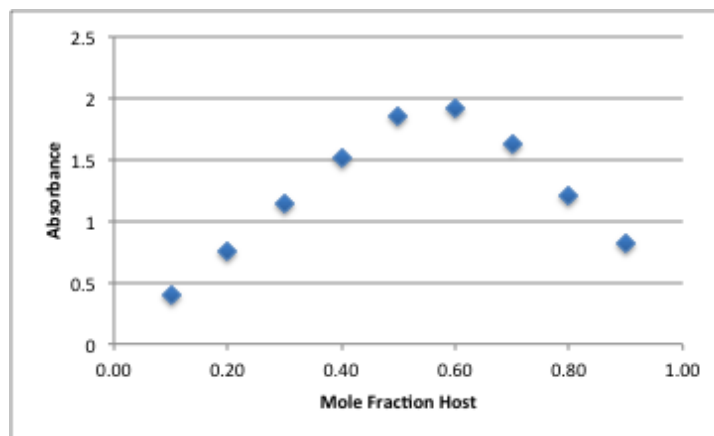


Figure S2. Job plot of ZnPc and NaSH in 1:1 THF:DMSO following the absorbance at 426 nm.

Table S1. Parameters for ZnPc Job Plot in 1:1 THF:DMSO.

Host (μL)	2700	2400	2100	1800	1500	1200	900	600	300
Host Concentration (M)	1.65E-04	1.47E-04	1.28E-04	1.10E-04	9.17E-05	7.34E-05	5.50E-05	3.67E-05	1.83E-05
Guest (μL)	300	600	900	1200	1500	1800	2100	2400	2700
Guest Concentration (M)	1.83E-05	3.66E-05	5.49E-05	7.32E-05	9.16E-05	1.10E-04	1.28E-04	1.46E-04	1.65E-04
Mol frac H	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
Total Concentration	1.83E-04	1.83E-04	1.83E-04	1.83E-04	1.83E-04	1.83E-04	1.83E-04	1.83E-04	1.83E-04

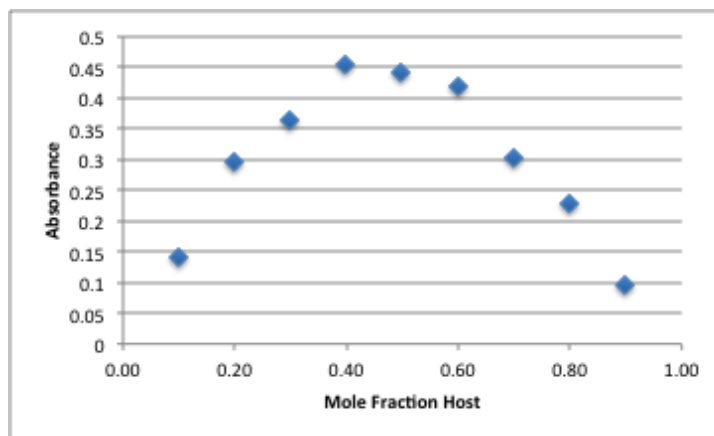


Figure S3. Job plot of CoPc and NaSH in 1:1 THF:DMSO following the absorbance at 467 nm.

Table S2. Parameters for CoPc Job Plot in 1:1 THF:DMSO.

Host (μL)	2700	2400	2100	1800	1500	1200	900	600	300
Host Concentration (M)	3.46E-05	3.08E-05	2.69E-05	2.31E-05	1.92E-05	1.54E-05	1.15E-05	7.70E-06	3.85E-06
Guest (μL)	300	600	900	1200	1500	1800	2100	2400	2700
Guest Concentration (M)	3.88E-06	7.76E-06	1.16E-05	1.55E-05	1.94E-05	2.33E-05	2.72E-05	3.10E-05	3.49E-05
Mol frac H	0.90	0.80	0.70	0.60	0.50	0.40	0.30	0.20	0.10
Total Concentration	3.85E-05	3.86E-05	3.86E-05	3.86E-05	3.86E-05	3.87E-05	3.87E-05	3.87E-05	3.88E-05

^1H NMR spectra for ZnPc

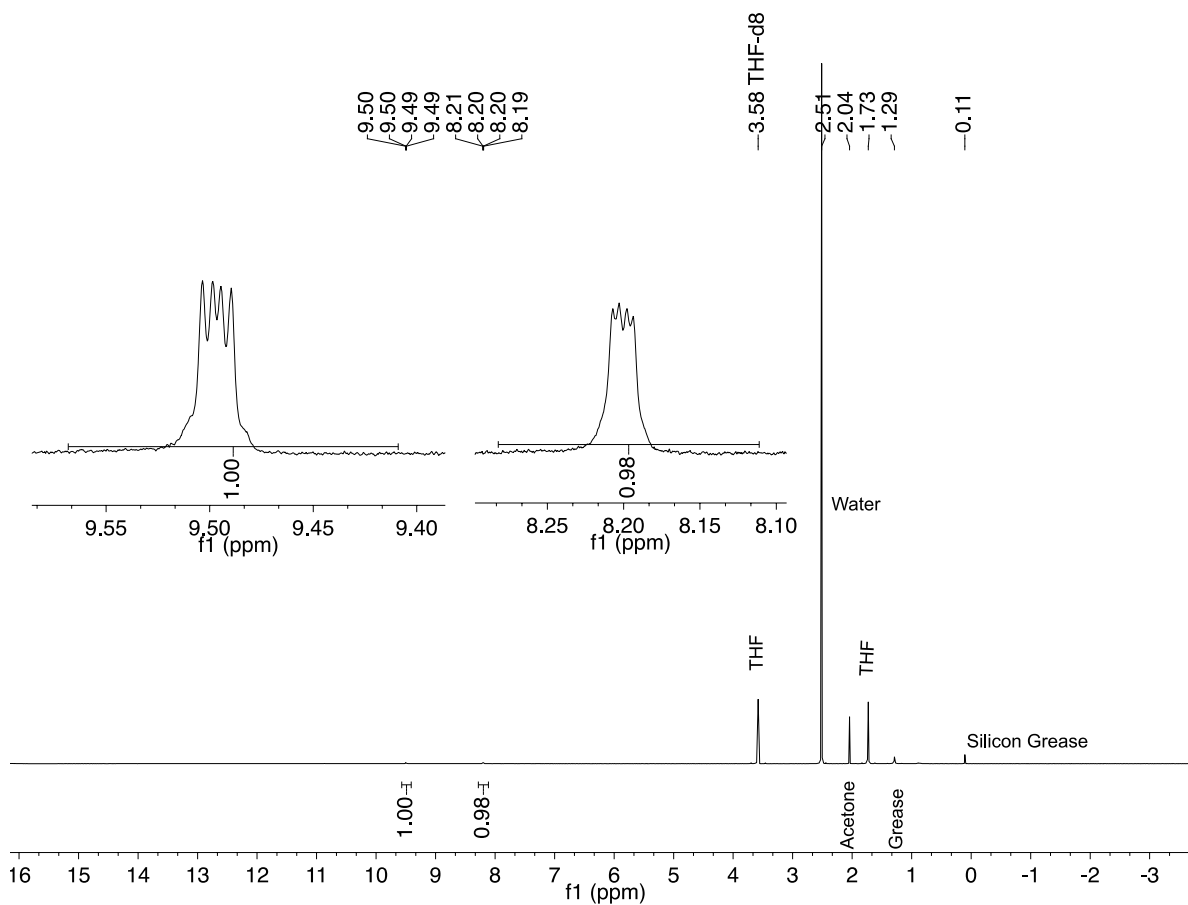


Figure S4. ^1H NMR spectrum of ZnPc in $\text{THF-}d_8$.

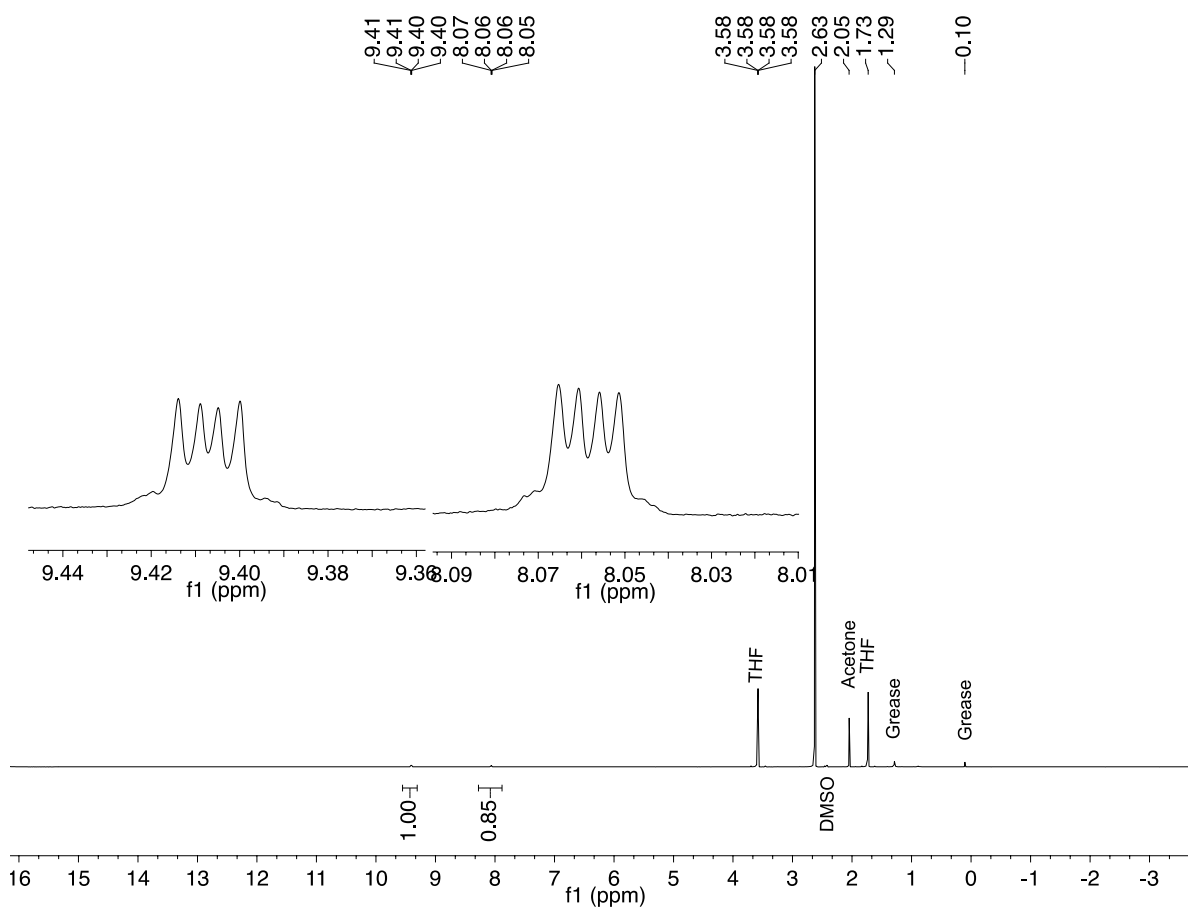


Figure S5. ^1H NMR spectrum of ZnPc in $\text{THF-}d_8$ with 2 equiv. of NaSH in $\text{DMSO-}d_6$.

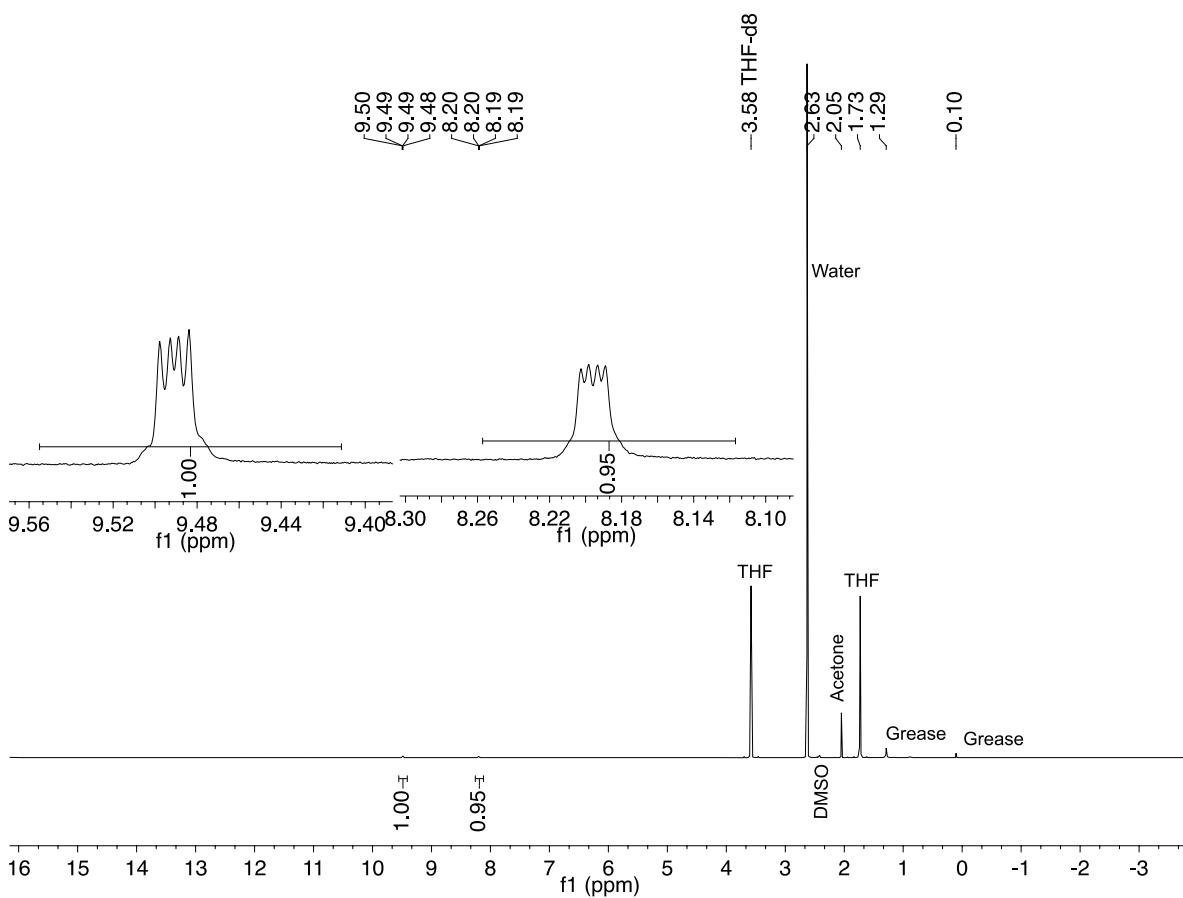


Figure S6. ^1H NMR spectrum of ZnPc in THF- d_8 with 2 equiv. of KOH in DMSO- d_6 .

^1H NMR spectra for CoPc

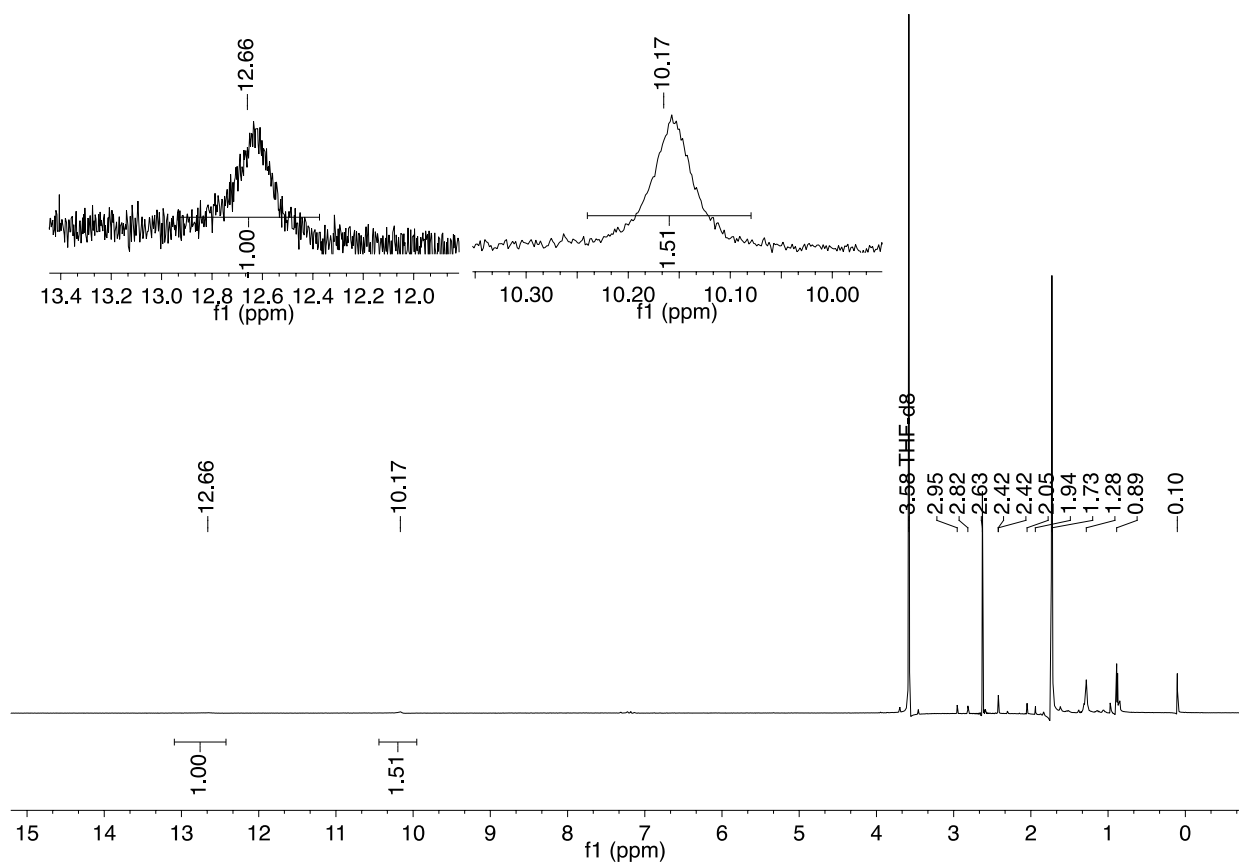


Figure S7. ^1H NMR spectrum of 0.136 mM CoPc in 750 μL of THF- d_8 with 40 μL of added DMSO- d_6 .

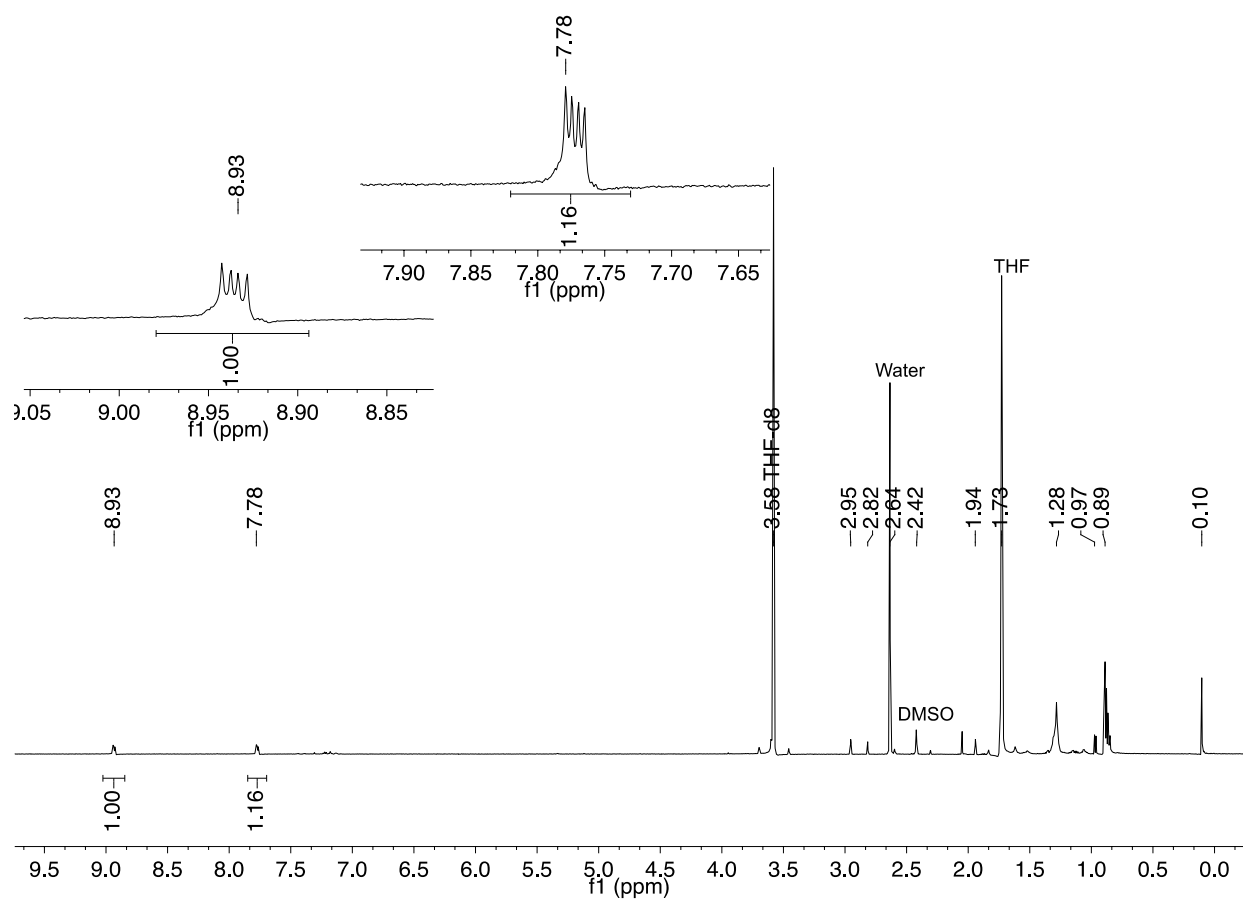


Figure S8. ¹H NMR spectrum of 0.136 mM [Co(I)Pc][−] in 750 μL of THF-*d*₈ with 40 μL of 22.6 mM NaSH (8.8 equiv.) in DMSO-*d*₆ added. The change in the Pc resonances from a broad singlet to well defined peaks is consistent with a change from paramagnetic Co(II) to diamagnetic Co(I).