Supplementary Information (SI) for New Journal of Chemistry.

Supporting Information

Logic gate copolymers of *cinchona* alkaloid-ferrocene derivatives

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Experimental

Chemicals

Acetone (GPR Grade, LEVO Laboratory Services), acetonitrile (HPLC Grade, Fischer Chemicals), acrylamide (99%, Merck), ammonium persulfate (99%, Sigma-Aldrich), 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride (98%, TCI), cinchonine (98%, TCI), cinchonidine (98%, TCI), celite (HPLC Grade, Across Organics), N,N′-dicyclohexylcarbodiimide (DCC), DMSO-d_6 (99.8%, VWR), diethyl ether (HPLC Grade, Carlo Erba), dichloromethane (HPLC Grade, Carlo Erba), ethyl acetate (HPLC Grade, Carlo Erba), ethanol (HPLC Grade, Carlo Erba), EDTA (99%, Pancreac), ferrocenecarboxaldehyde (97%, TCI), hydrochloric acid (37%, Fischer Scientific), methanesulfonic acid (99.5%, TCI), pentane (HPLC Grade, Carlo Erba), potassium bromide (99.8%, Sigma Aldrich), potassium permanganate (99%, Fluka), potassium persulfate (GPR, BDH), potassium iodide (99%, VWR), quinine (98%, TCI), quinidine sulfate dihydrate (98%, TCI), sodium chloride (98%, Scharlau), sodium hydroxide (98%, Fluka), triethylamine (Synthesis grade, Scharlau), tetrahydrofuran (HPLC Grade, Carlo Erba), tetramethylammonium hydroxide (98% in water, Fluka), vinyl ferrocene (97%, TCI). 4 Å molecular sieves (Thermo scientific) activated in a furnace at 350 °C for 24 hours before use. Silica gel 60A (70-230 mesh, Carlo Erba) and silica on TLC aluminium foil (silica gel matrix with fluorescent indicator 254 nm, Sigma Aldrich) were used for column and thin-layer chromatography, respectively.

Instrumentation

Reactions were carried out in either a one-neck or two-neck round bottom flasks (50 mL, 100 mL or 250 mL) partially immersed in mineral oil and heated using an IKA C-MAG HS 7 hotplate with IKA ETS-D5 temperature probe. Melting points were determined by a Stuart 8 SMP40 digital melting point apparatus using the rapid melt mode at a ramp rate of 0.1 °C. All polymers decompose upon heating beyond 200 °C and showed no melting point. This may indicate that polymers are of an amorphous nature. Rotary evaporator connected to a Laboport N 815 mini diaphragm vacuum pump and a Stuart RE300DB digital water bath. An international Clinical Centrifuge Model 40652H was used to separate the product from the solvent for the work-up of the acrylamide copolymers. ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6. A Bruker Avance III HD 500 MHz NMR spectrometer equipped with an Ascend 500 11.75 Tesla Superconducting magnet at a frequency of 500.13 MHz for ^{1}H NMR and 125.76 MHz for ^{13}C NMR with a multinuclear 5 mm PABBO probe. Jasco V-650 spectrophotometer and 1.0 cm pathlength quartz cells were used to obtain UV-Vis absorption spectra. Parameters were set at 1.0 nm bandwidth and scan speed at 400 nm/min. Samples were scanned over the range of 250-500 nm. A blank background run was performed for all spectra to correct for solvent. Fluorescence emission spectra were performed using a Jasco FP-9300 spectrophotometer. Fluorescent switching of solutions was observed using a UVGL-58 handheld lamp with long wavelength (365 nm) and short wavelength (254 nm) functions. The pH of the solutions used for UV and fluorescence titrations were recorded by Hanna instrument 210 microprocessor pH meter after calibrating with buffer solutions at pH 4.00 and 7.00. Prior to obtaining fluorescence spectra, a blank run was performed using air and water to correct for the solvent. A 1.0 cm pathlength (QS) quartz cuvette with clear sides was used. Bandwidth wavelength was set at 2.5 nm, response time of 50 msec, and scanning speed 200 nm/min.

Spectroscopic Experiments

Solutions of **1**-**4** were prepared in 1 M methanesulfonic acid with an absorbance of 0.1. The concentrations were 0.20 g L^{-1} **1**, 0.70 g L^{-1} **2**, 0.11 g L^{-1} **3**, 0.036 g L^{-1} **4**. Each solution contained 5×10^{-9} M EDTA as a buffer and to chelate to trace metal ions. Solutions of 1 M, 100 mM, 10 mM, 1 mM, 0.1 mM $(CH_3)_4NOH$ were used to adjust the pH, measured with a calibrated pH meter using buffer solutions at pH 4 and pH 7. Solutions were stirred after each addition of base aliquot throughout each titration to ensure homogeneity, and then the fluorescence and absorbance spectra were recorded.

The Henderson-Hasselbalch equation, shown by Eq. 1, relates the pK_a and pH to an equilibrium constant of an acid in the dissociated and non-dissociated form in which pK_a represents the acid dissociation constant, $[A^-]$ is the concentration for the conjugate base and $[HA]$ is the concentration for the weak acid. The pK_a is measured as a function of pH from a sigmoidal curve.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[A^-]}{[HA]} \tag{1}$$

By fluorescence spectroscopy, the intensity is plotted against pH resulting in a sigmoidal curve according to Eq. 2,

$$\log\left(\frac{I_{F_{max}} - I}{I - I_{F_{min}}}\right) = \mathrm{pH} - \mathrm{p}K_a \qquad (2)$$

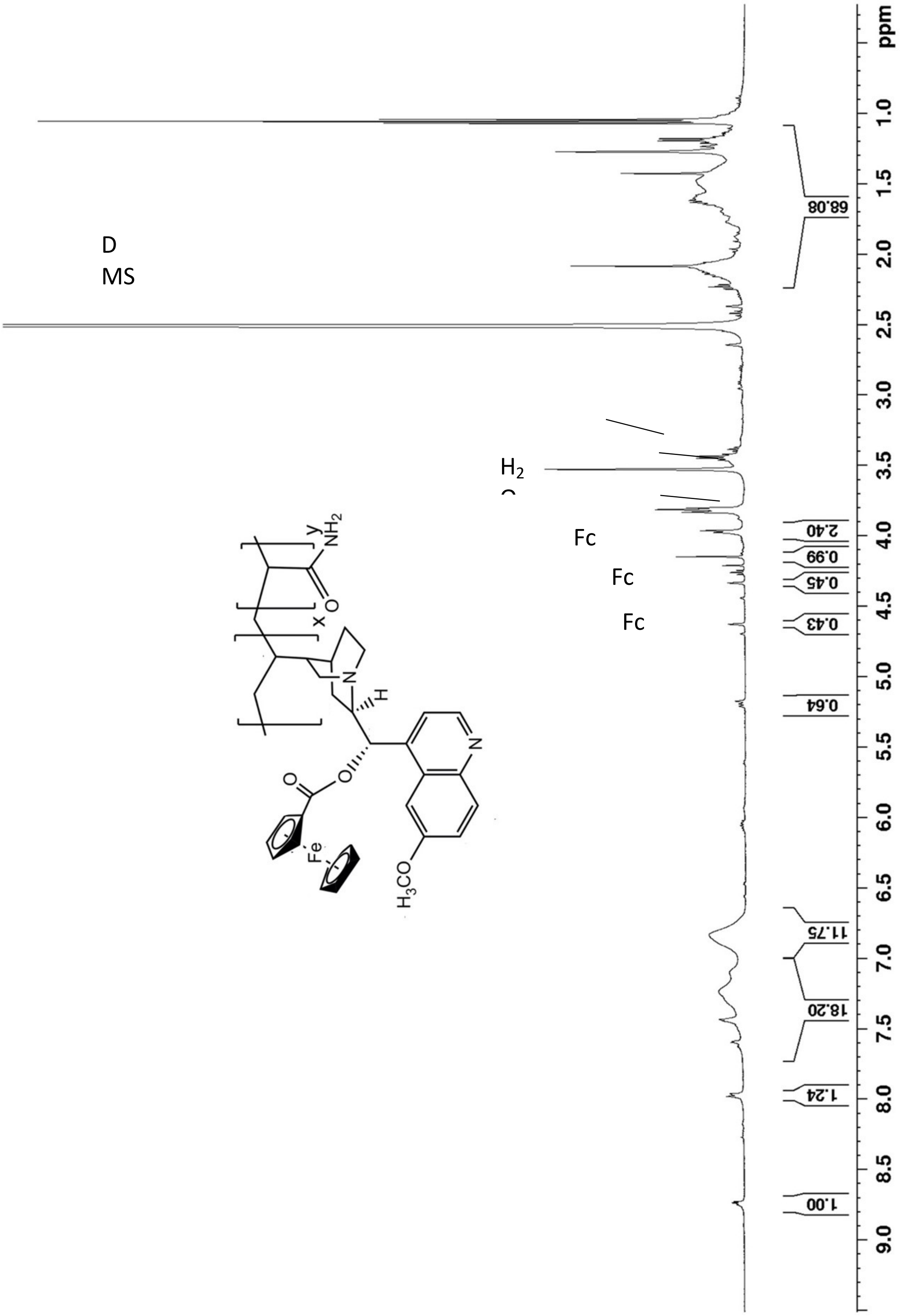

Fig. S1 ^{1}H NMR spectrum of **1** in DMSO-d_6.

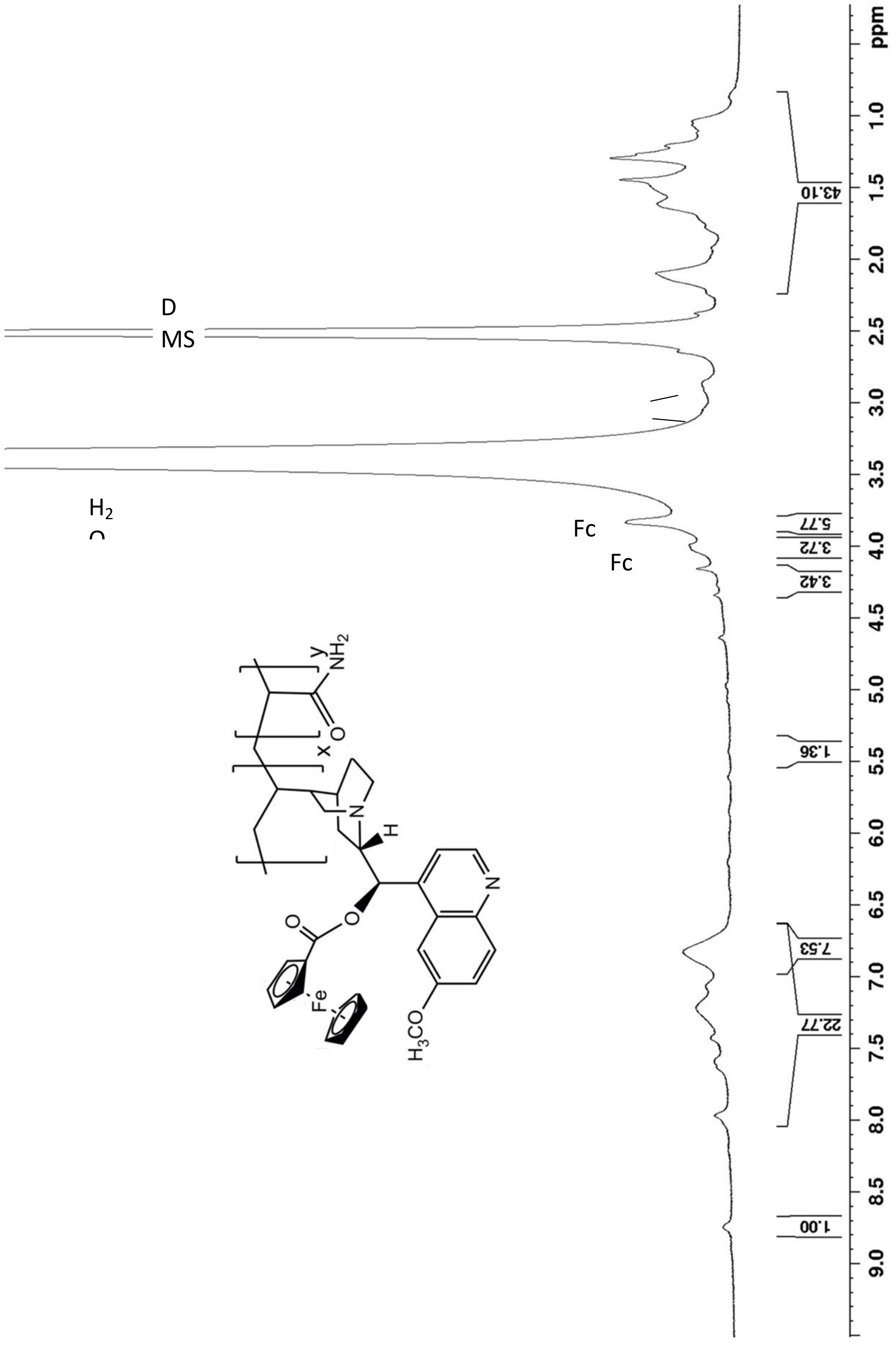

Fig. S2 ^{1}H NMR spectrum of **2** in DMSO-d_6.

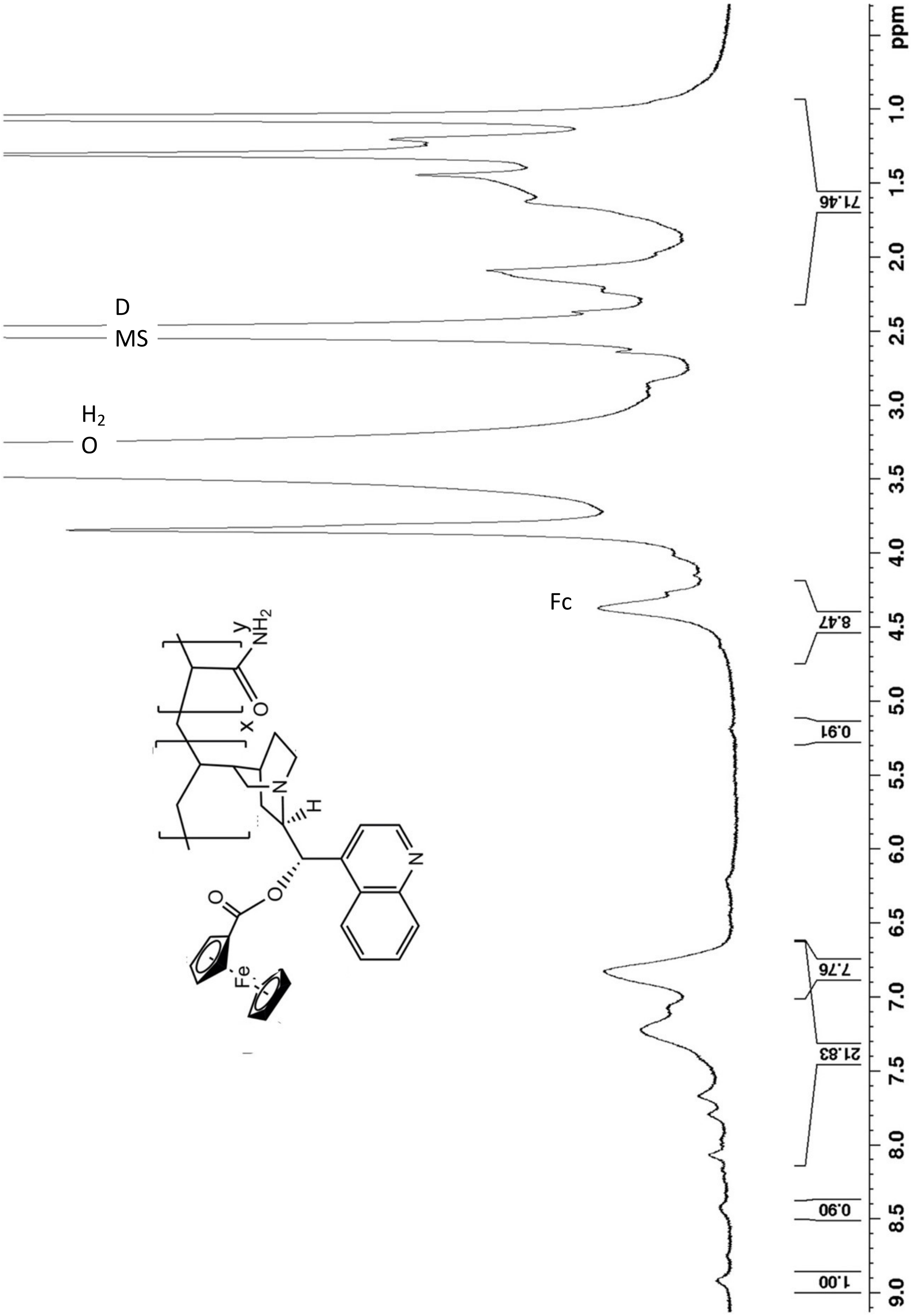

Fig. S3 ^{1}H NMR spectrum of **3** in DMSO-d_6.

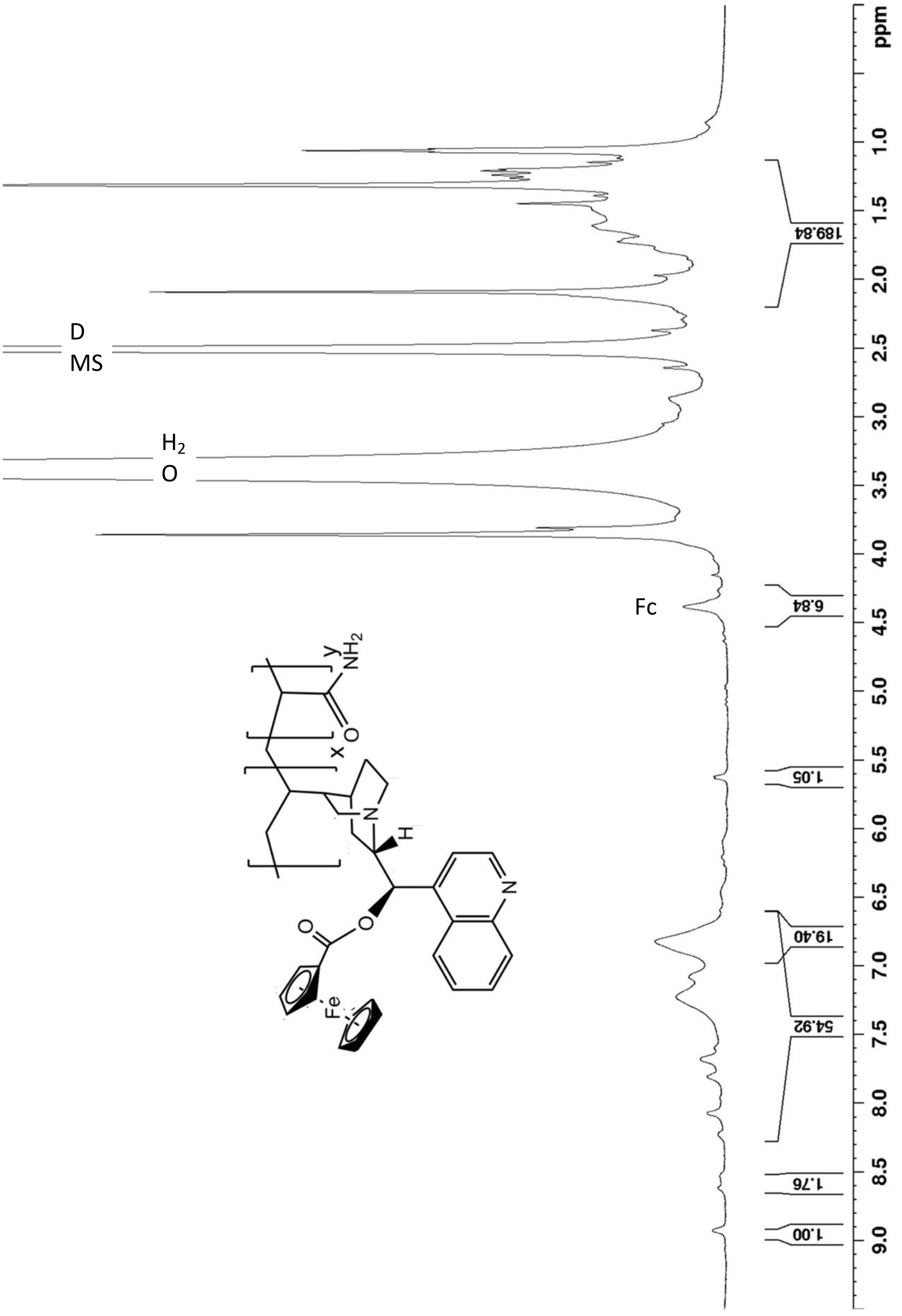

Fig. S4 ^{1}H NMR spectrum of **4** in DMSO-d_6.

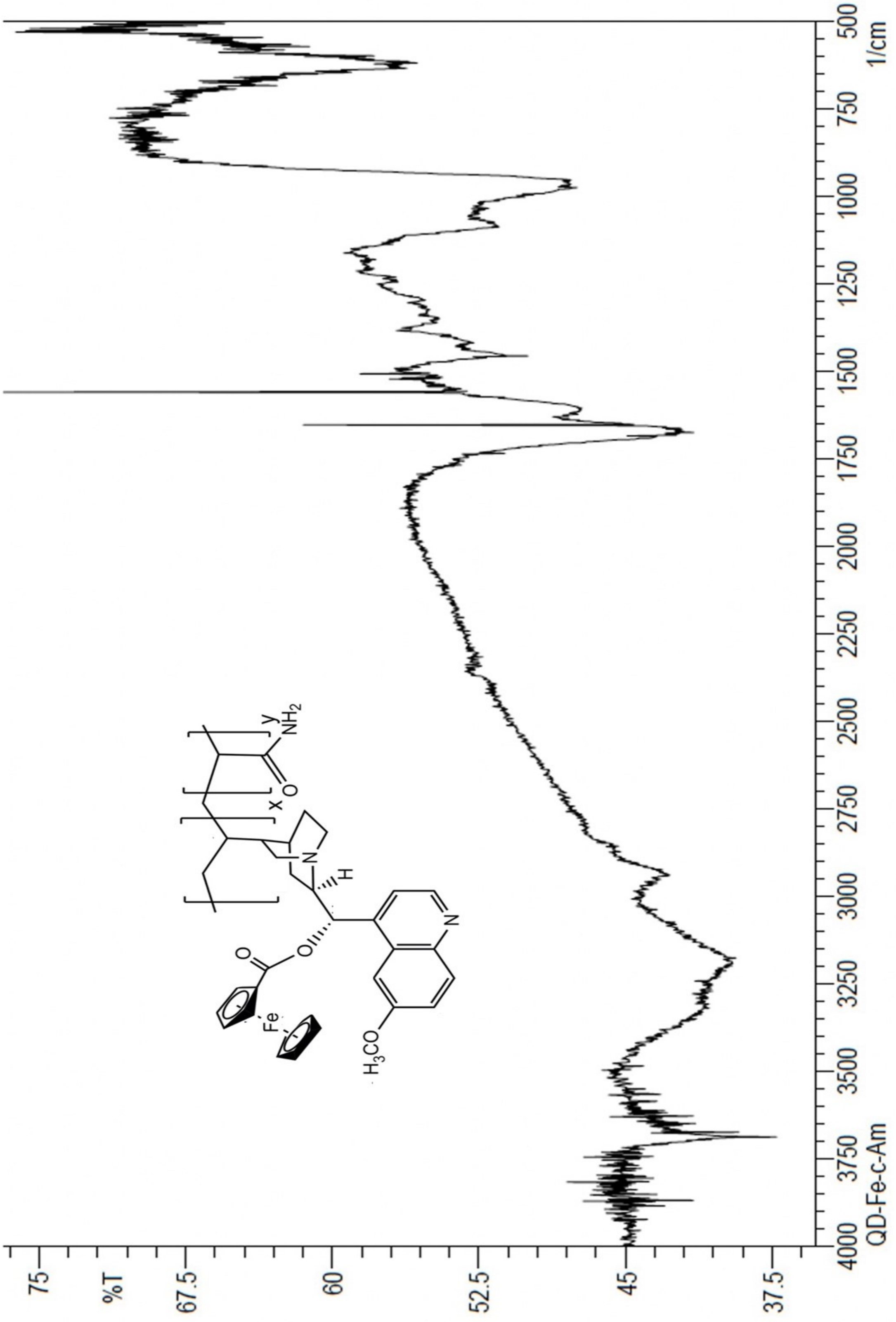

Fig. S5 IR spectrum of **1** (KBr disc).

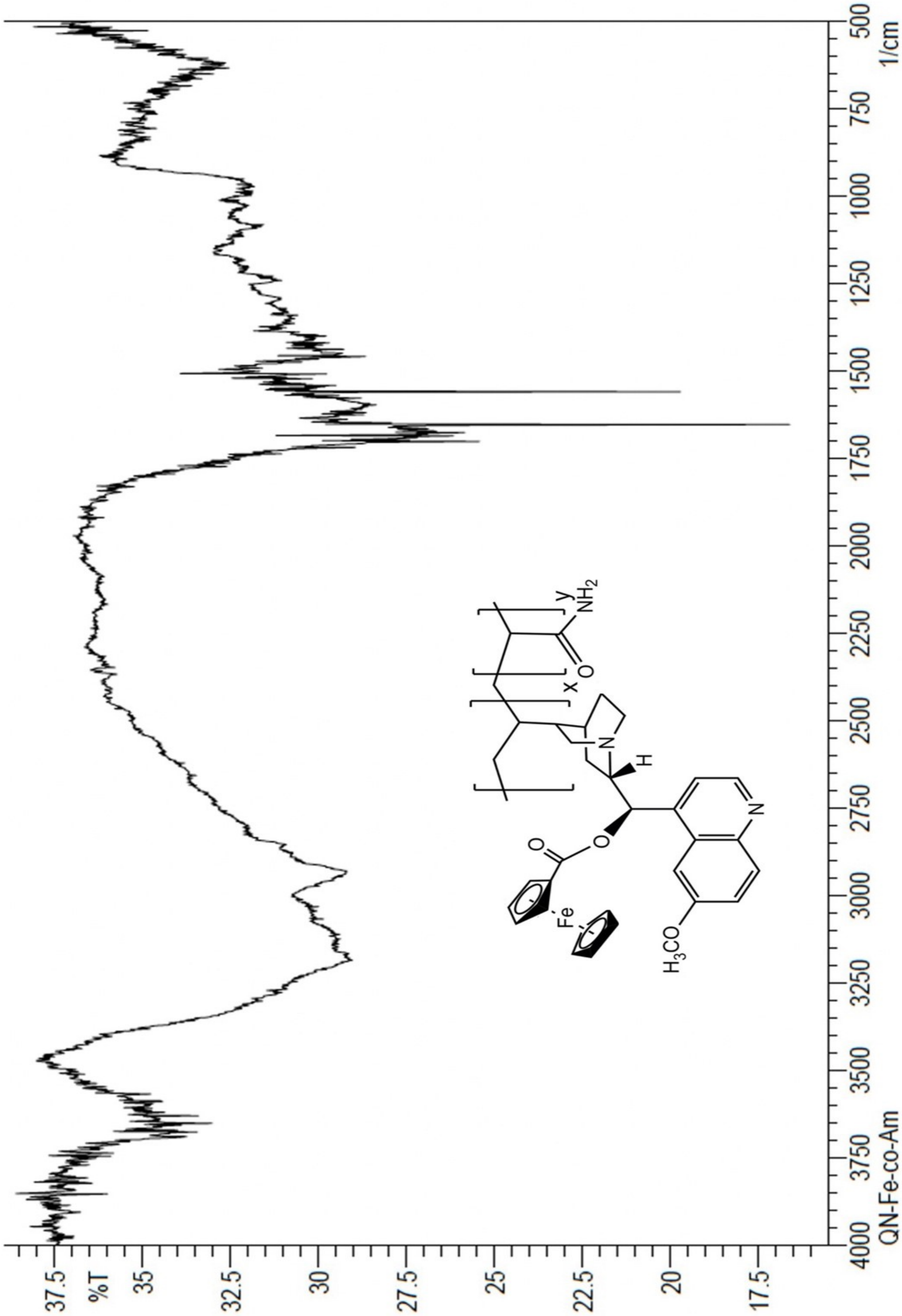

Fig. S6 IR spectrum of **2** (KBr disc).

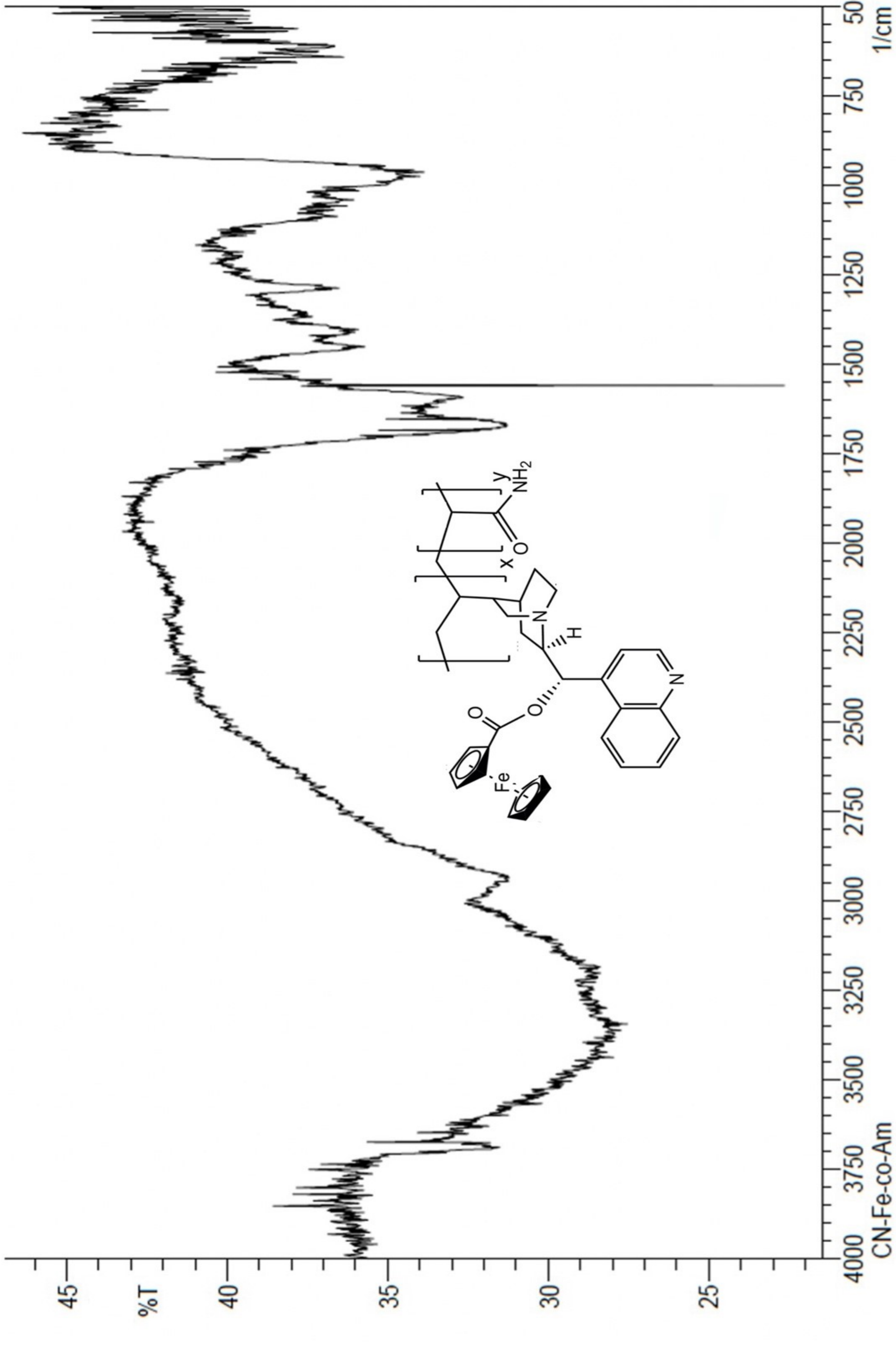

Fig. S7 IR spectrum of **3** (KBr disc).

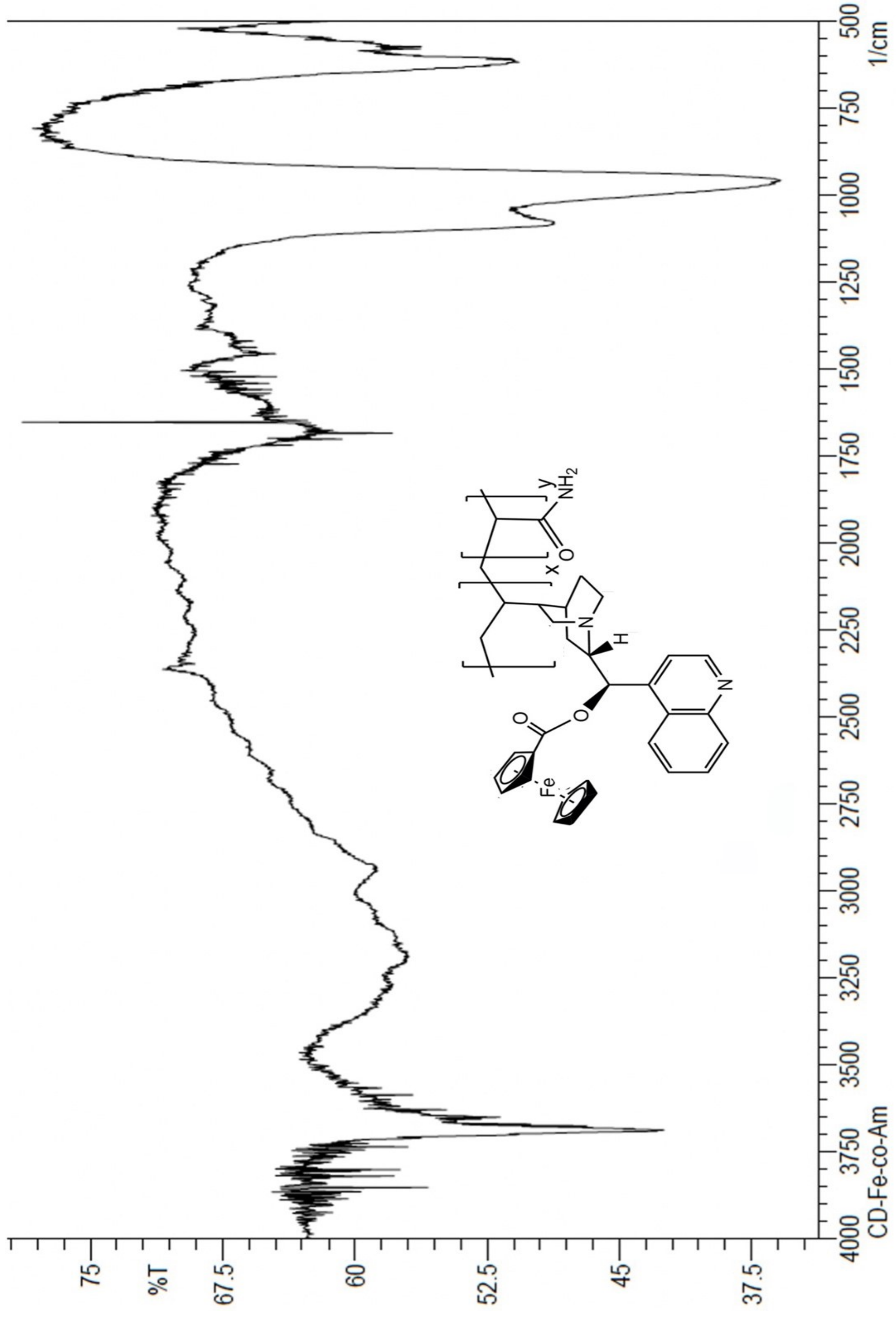

Fig. S8 IR spectrum of **4** (KBr disc).

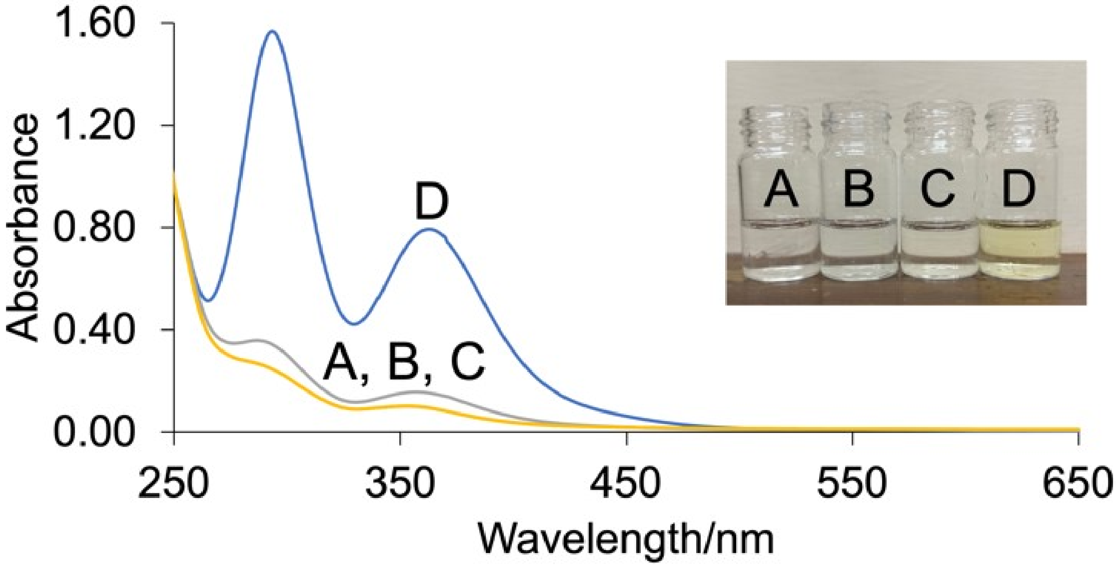

Fig. S9 UV-vis absorbance spectra (solvent subtracted) of 0.20 g/L of poly(QD-Fe-co-Am) **1** in water: (A) 10^{-9} M H^+ (B) 10^{-2} M H^+ (C) 10^{-9} M H^+, 200 mM I^- (D) 10^{-2} M H^+, 200 mM I^- after 48 hours. The copolymer operates as a H^+, I^--driven AND logic gate.

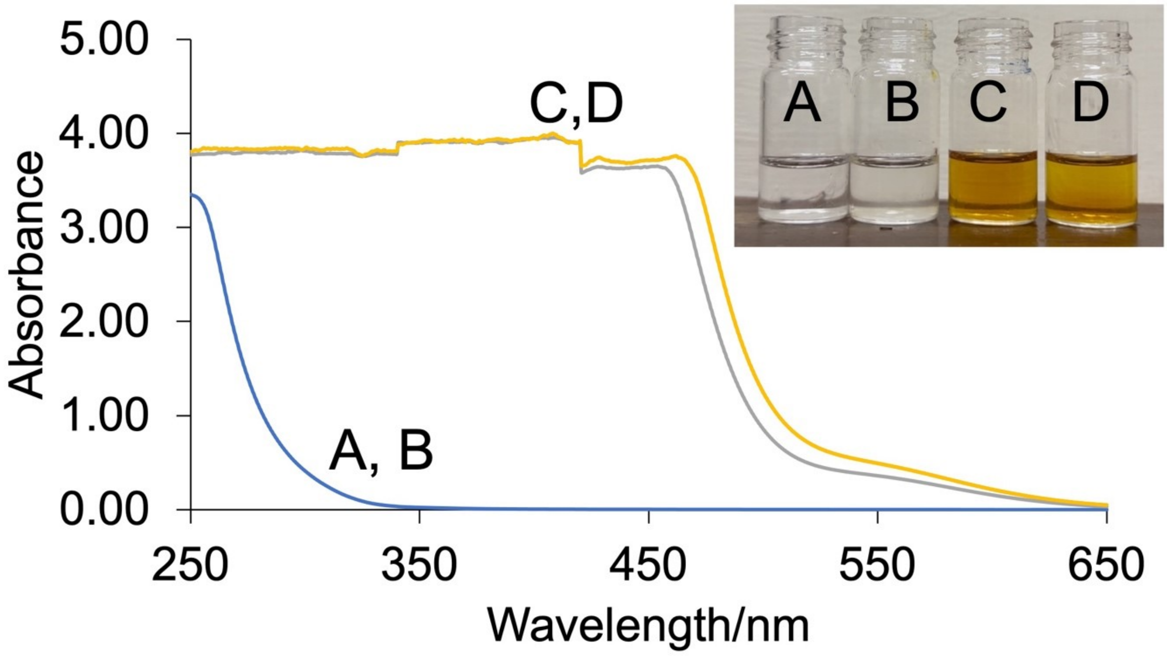

Fig. S10 UV-vis absorbance spectra (solvent subtracted) of 0.20 g/L of poly(QD-Fe-co-Am) **1** in 9:1 (v/v) THF/water: (A) 10^{-9} M H^+ (B) 10^{-2} M H^+ (C) 10^{-9} M H^+, 10 mM I^- (D) 10^{-2} M H^+, 10 mM I^- after 1 minute. The copolymer operates as a H^+, I^--driven AND logic gate.

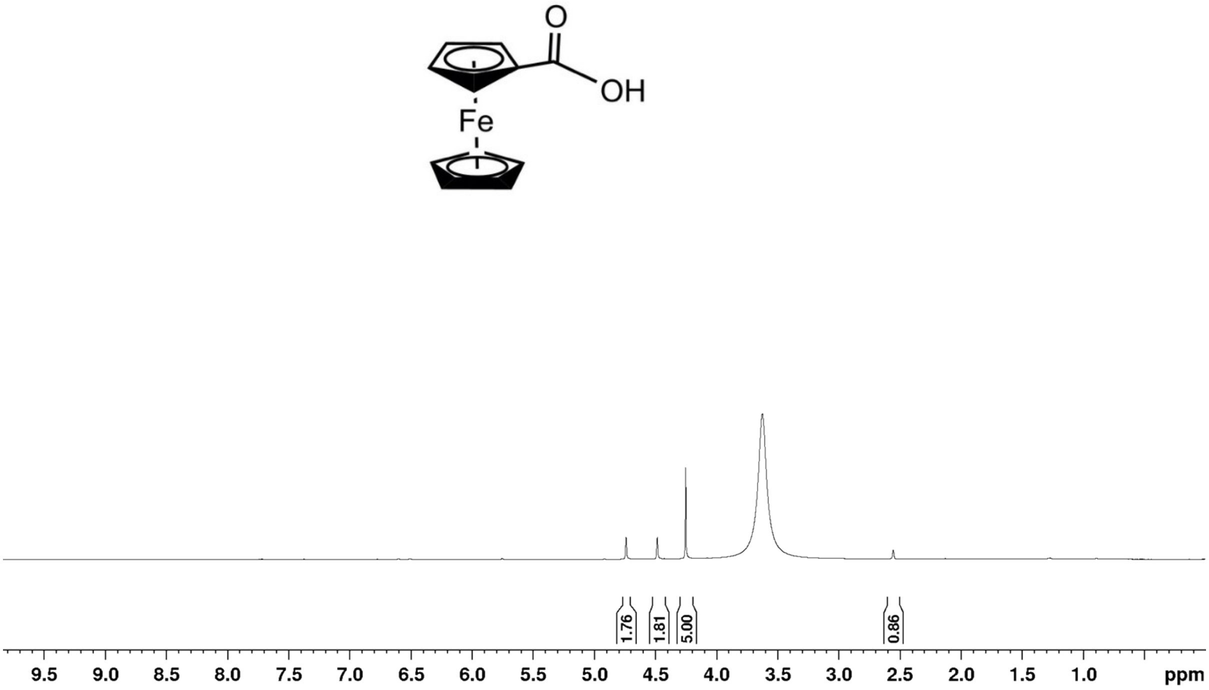

Fig. S11 ^{1}H NMR spectrum of ferrocenecarboxylic acid in DMSO-d_6.

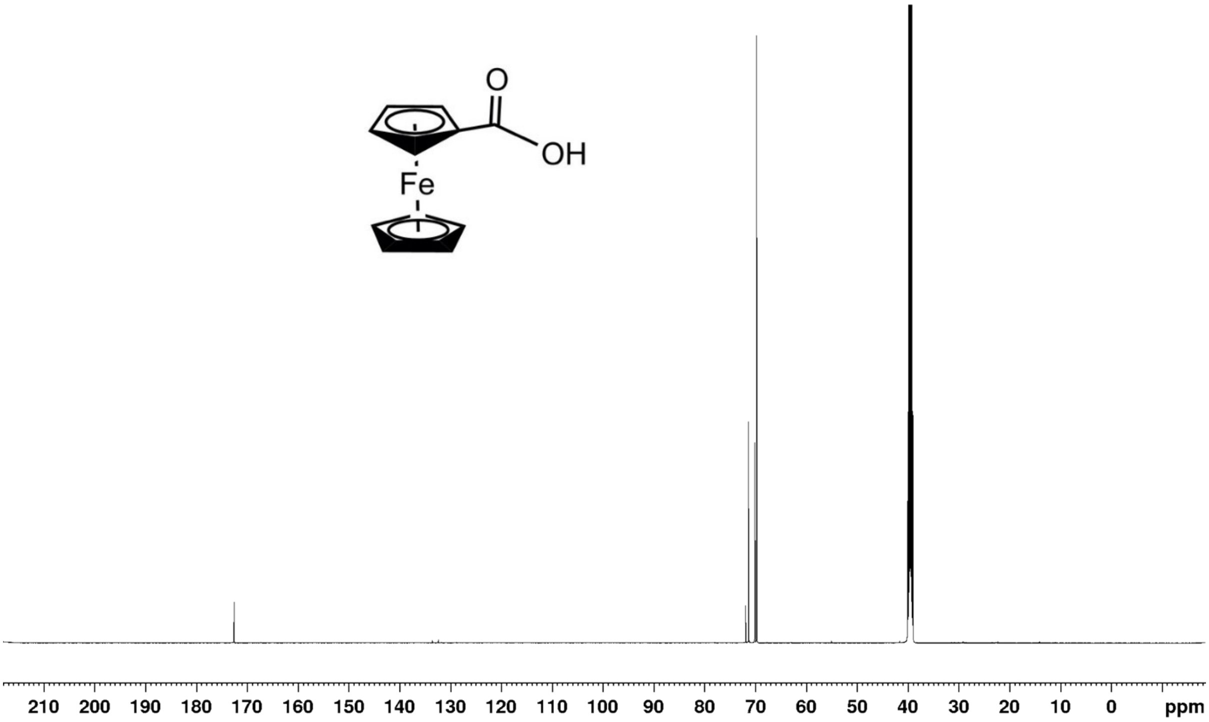

Fig. S12 ^{13}C NMR spectrum of ferrocenecarboxylic acid in DMSO-d_6.

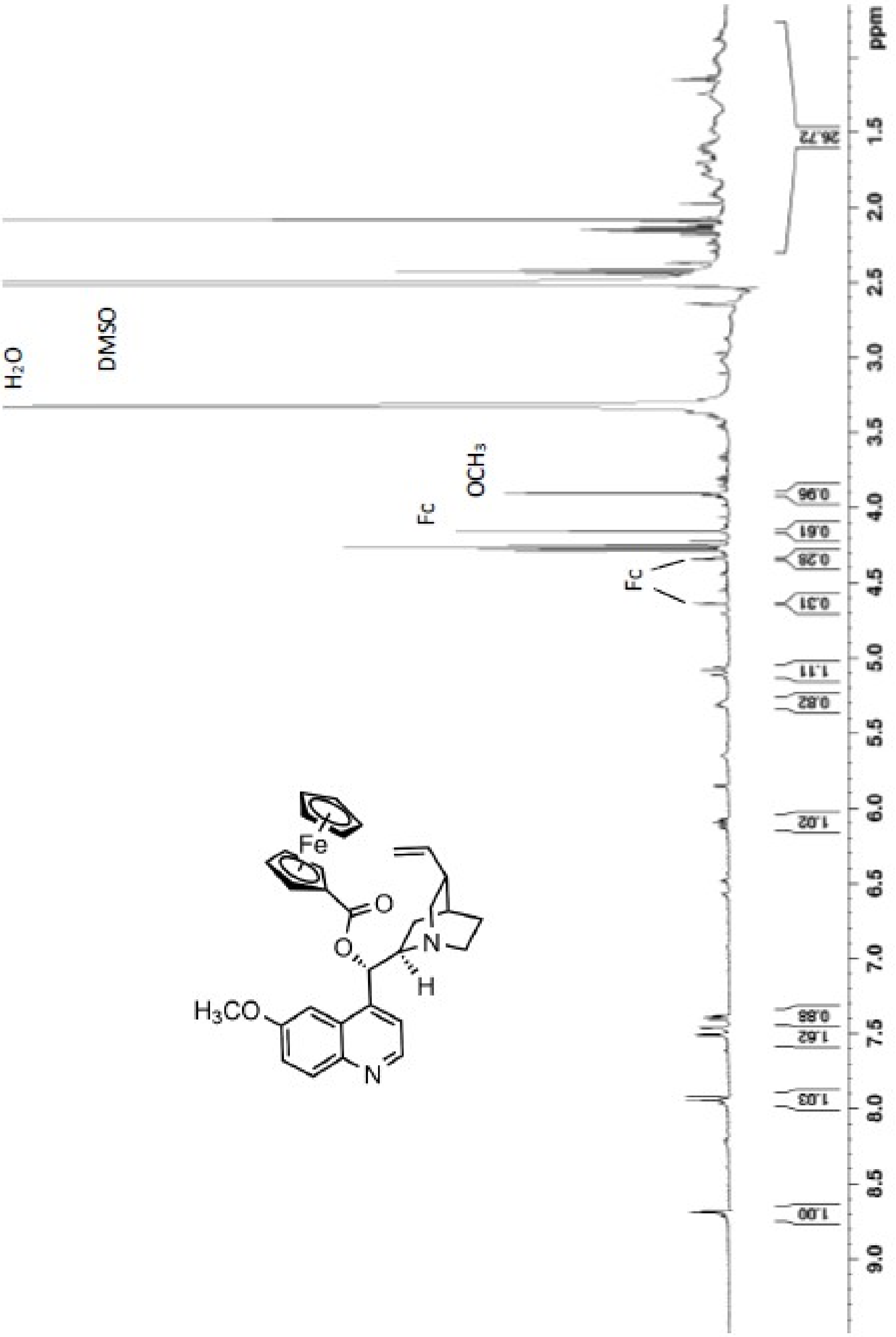

Fig. S13 ^{1}H NMR of **QD-Fe-ester** in DMSO-d_6.

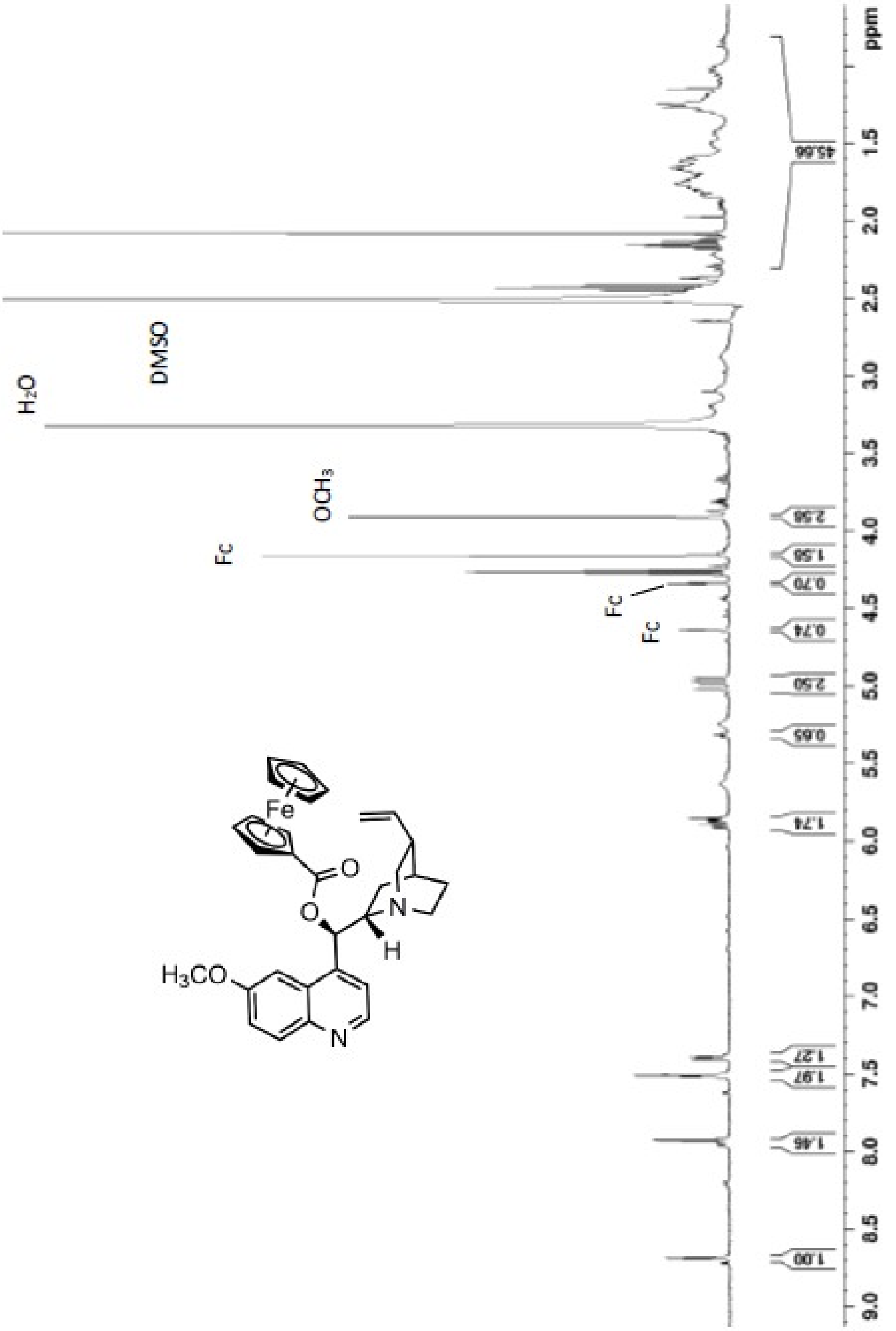

Fig. S14 ^{1}H NMR of **QN-Fe ester** in DMSO-d_6.

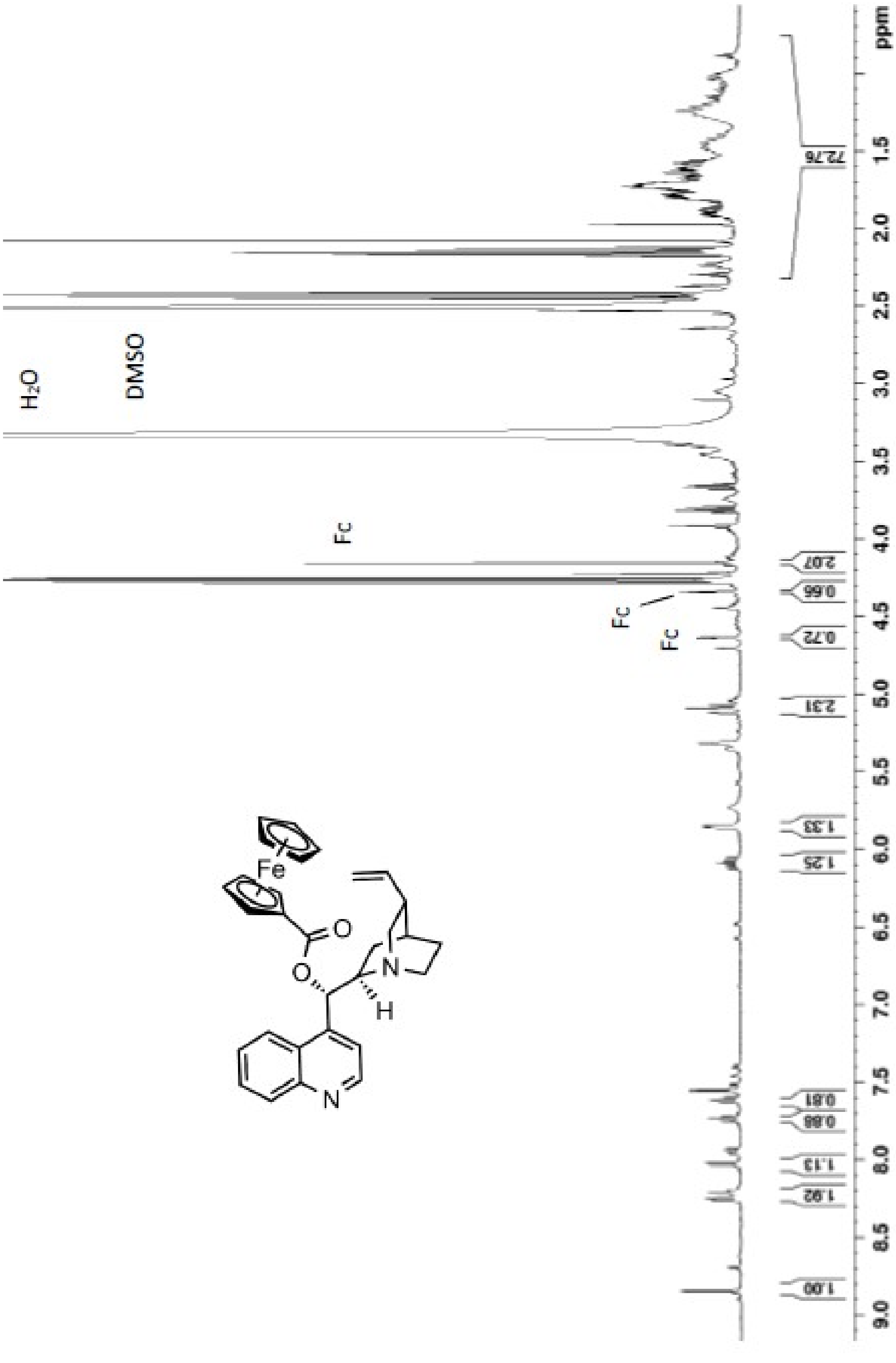

Fig. S15 ^{1}H NMR of **CN-Fe ester** in DMSO-d_6.

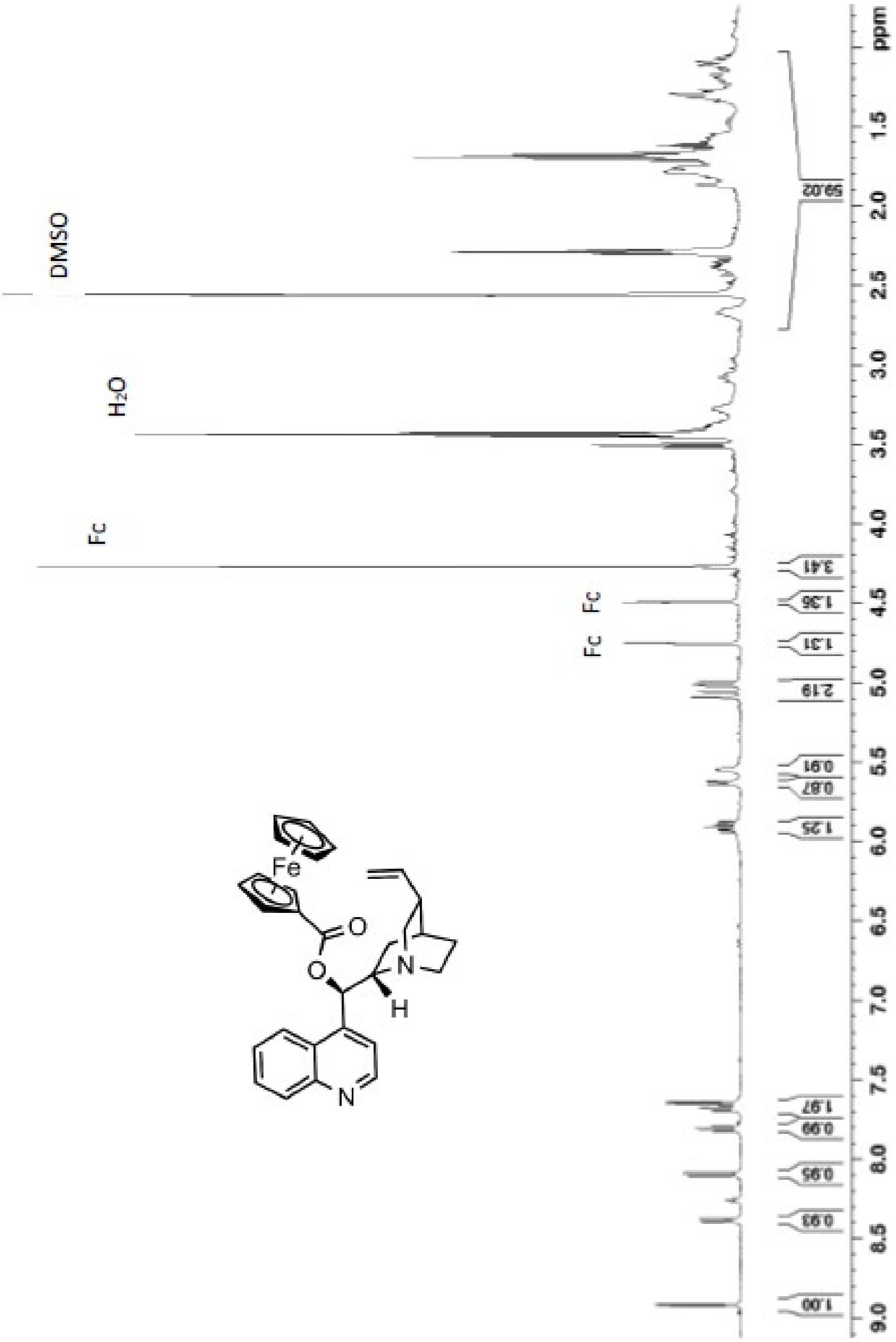

Fig. S16 ^{1}H NMR of **CD-Fe ester** in DMSO-d_6.