Supporting Information for

Anion Dependence in Spin-Crossover Properties of a Fe(II) Podand Complex

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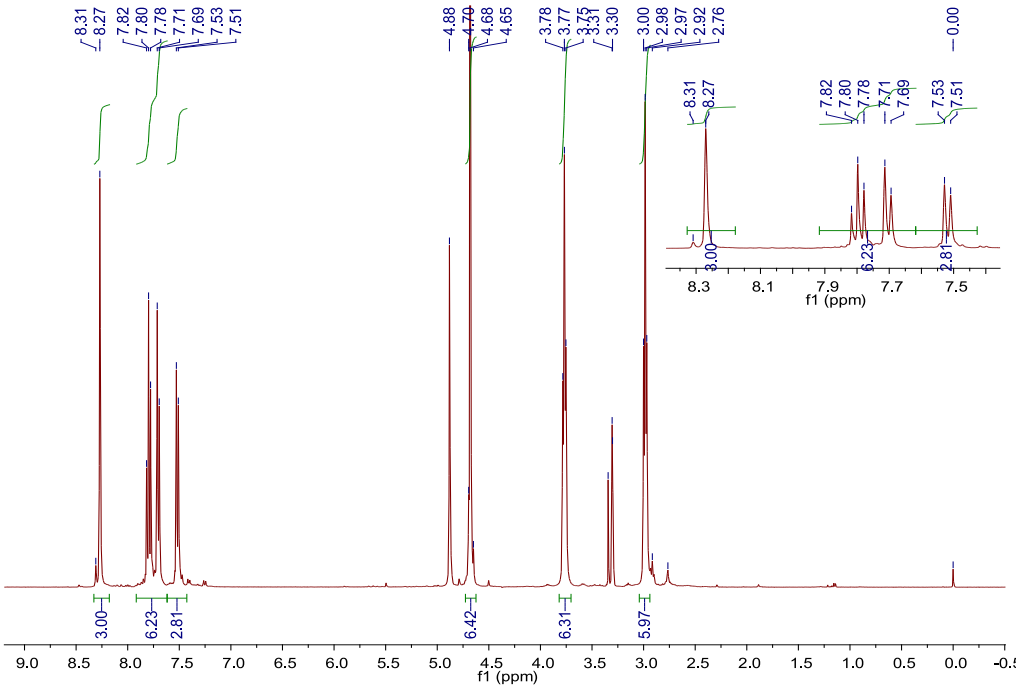

Figure S1. ^{1}H NMR spectrum of $L^{6\text{-OH}}$ in CD_3OD at 400 MHz using TMS as the reference.

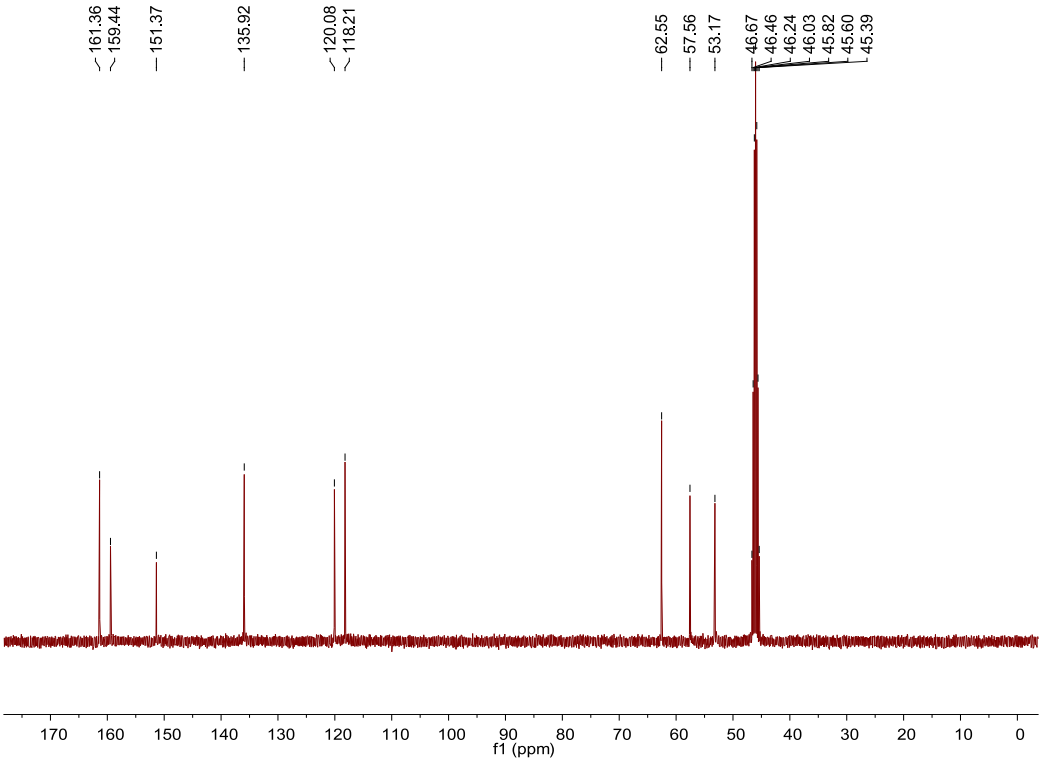

Figure S2. ^{13}C NMR spectrum of $L^{6\text{-OH}}$ in CD_3OD, obtained on a 400 MHz NMR. Multiplet at 46 ppm is CD_3OD.

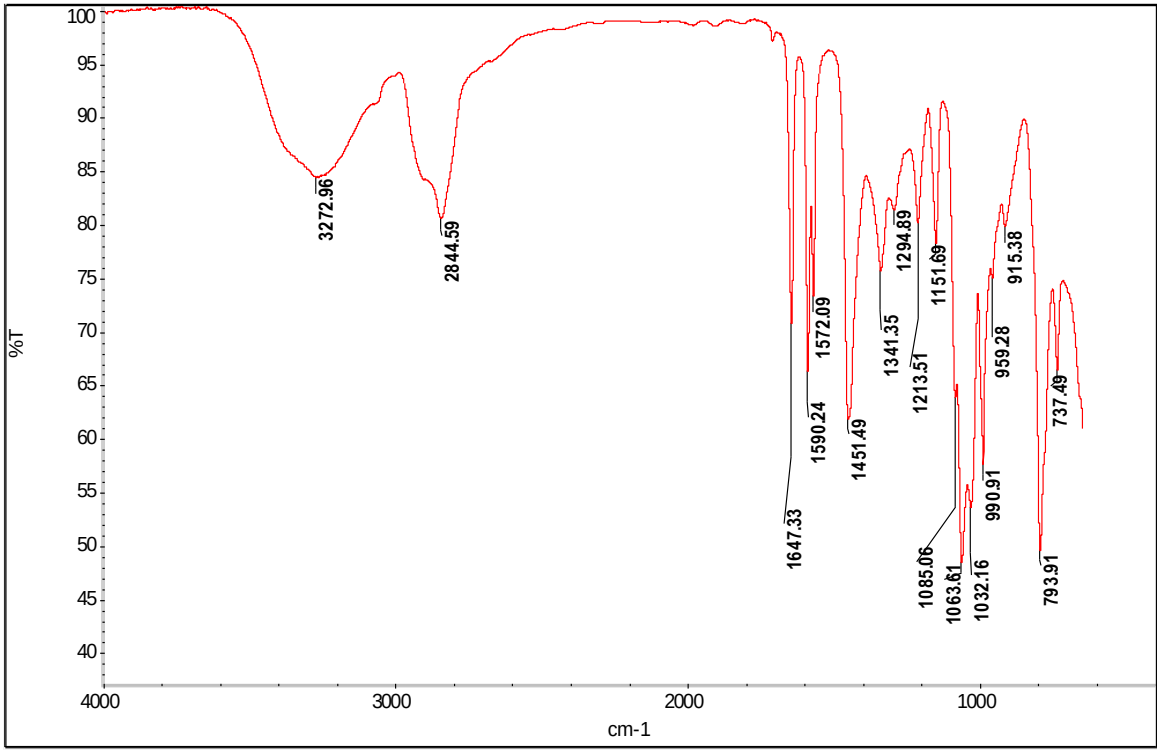

Figure S3. FT-IR spectrum of $L^{6\text{-OH}}$ obtained by pressing a solid sample on a ZnSe ATR crystal.

Synthesis of $[FeL^{6-OH}](BPh_4)_{1.75}Br_{0.25}$·MeCN (4a)

Carried out in a manner similar to the preparation of **3**, anion exchange of **2** (0.073 g, 0.102 mmol) into 6 mL of methanol with $NaBPh_4$ (0.140 g, 0.409 mmol) produced a light pink precipitate. The mixture was stirred for an additional 30 minutes, and then the solid was isolated by filtration. The resulting residue was triturated with methanol (2 × 6 mL) and 6 mL of Et_2O to produce a brick red, free flowing powder. Crystals were obtained by Et_2O diffusion into a concentrated acetonitrile solution (0.069 g, 58 % yield); X–ray quality crystals were not obtained by this method. IR (ATR) ν_{OH} 3509 cm^{-1}. λ_{max} (MeCN)/nm 489 (1340 $M^{-1}\cdot cm^{-1}$). ^1H NMR (CD_3CN) δ 75.3, 56.9, 47.9, 40.7 32.3, 10.4, 8.9 ppm. $\chi_M T$ (SQUID, 296 K) = 3.62 cm^3 K mol^{-1} (μ_{eff} = 5.38 μ_B). Anal. Calcd for $C_{71}H_{71}N_8O_3FeB_{1.75}Br_{0.25}$: C, 72.3; H, 6.1 N, 9.5. Found: C, 72.3; H, 6.0; N, 9.1.

The magnetic behaviour of the mixed anion salt **4a** is distinct from what one might expect from a mixture of **2** and "$[FeL^{6-OH}](BPh_4)_2$" in that no distinct SCO is observed at ca. 100 K. Instead $\chi_M T$ for **4** is 3.62 cm^3 K mol^{-1} at 295 K, and slowly decreases to 2.21 cm^3 K mol^{-1} by 15 K. The sharp downturn in $\chi_M T$ to 1.66 cm^3 K mol^{-1} at 5 K is ascribed to zero–field splitting in the residual HS fraction. The microscopic origins of the unique spin–state behaviour for this compound are unknown, as structural analysis has not been performed on this compound.

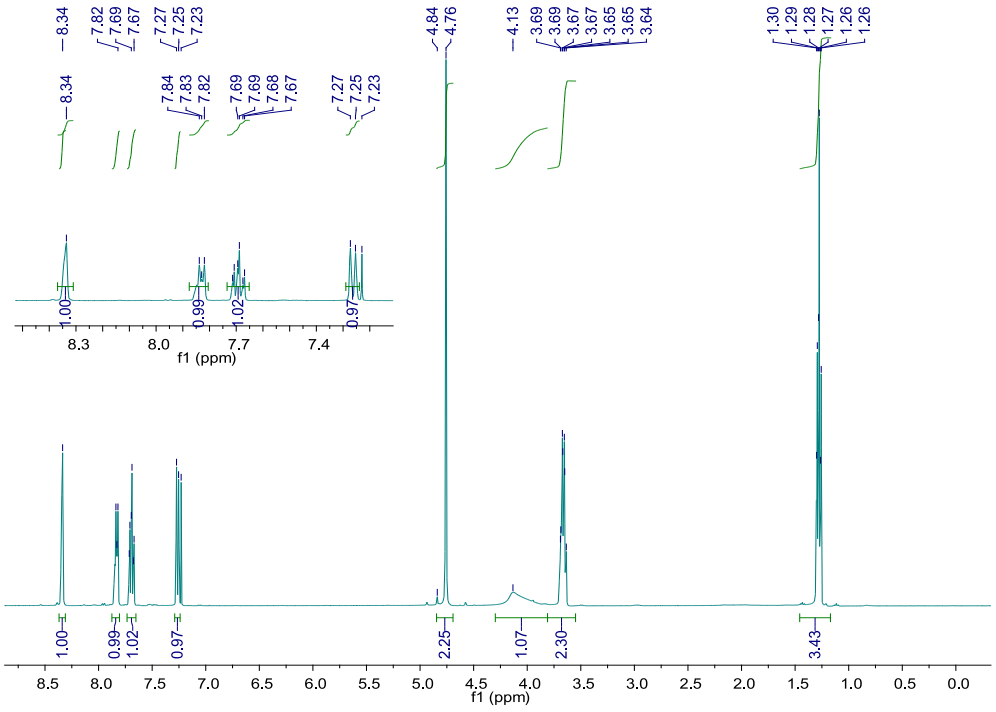

Figure S4. ^1H NMR spectrum of L^2 in $CDCl_3$ at 400 MHz using $CDCl_3$ as the reference.

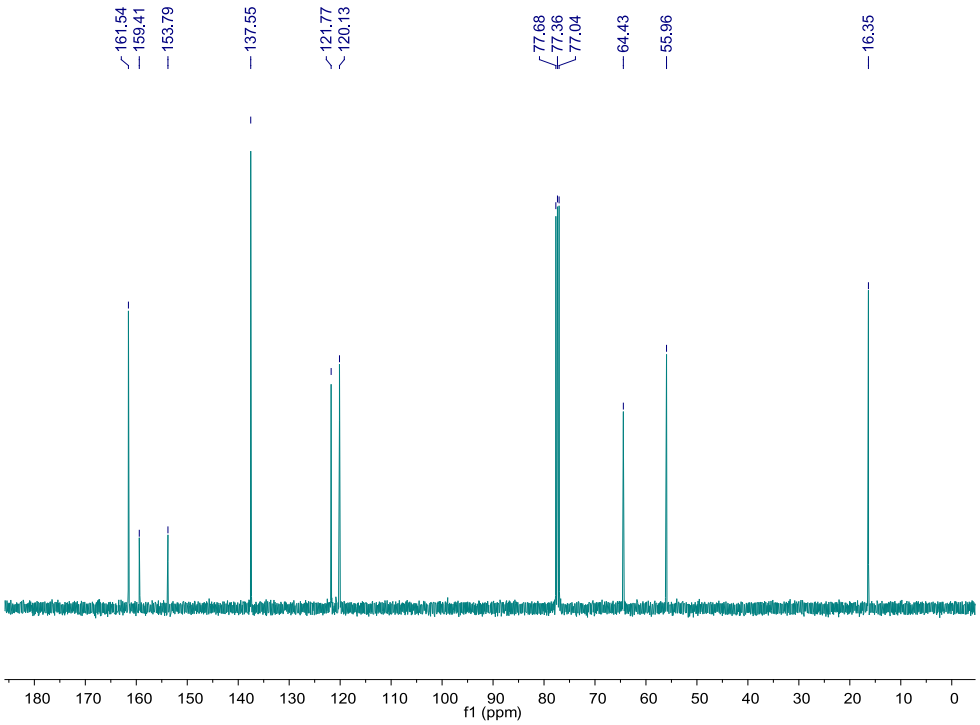

Figure S5. ^{13}C NMR spectrum of L^2 in $CDCl_3$, obtained on a 400 MHz NMR. Multiplet at 77 ppm is $CDCl_3$.

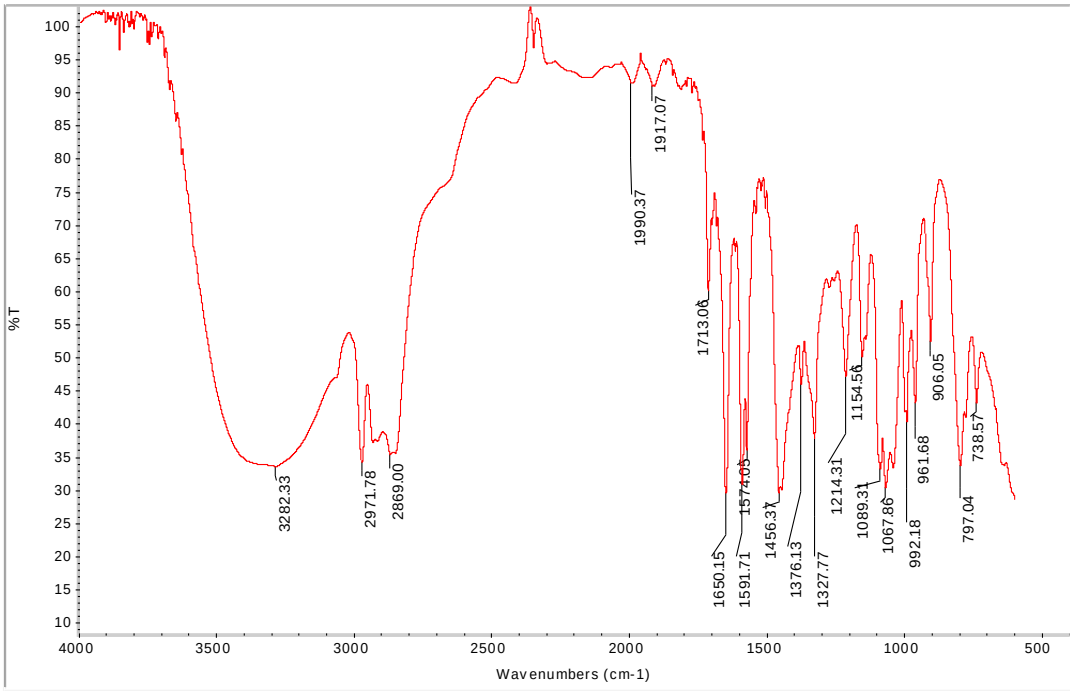

Figure S6. FT-IR spectrum of L^2 obtained by pressing a solid sample using KBr salt plates.

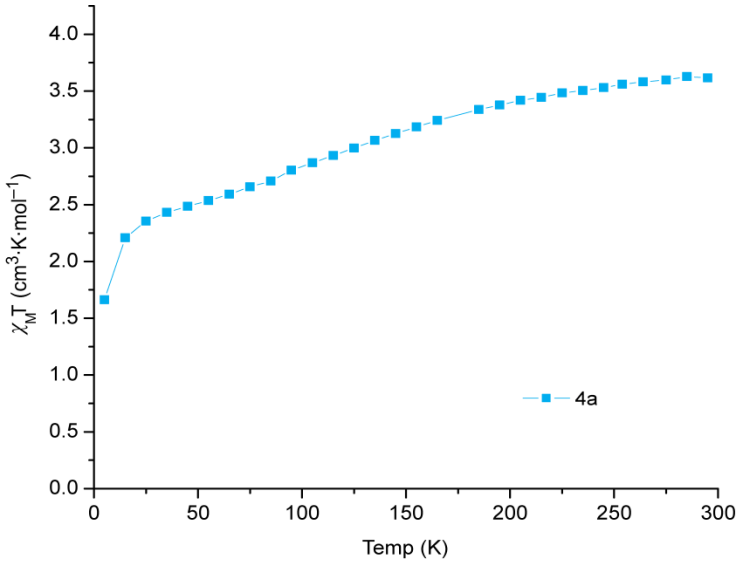

Figure S7. Variable temperature SQUID data for **4a**.

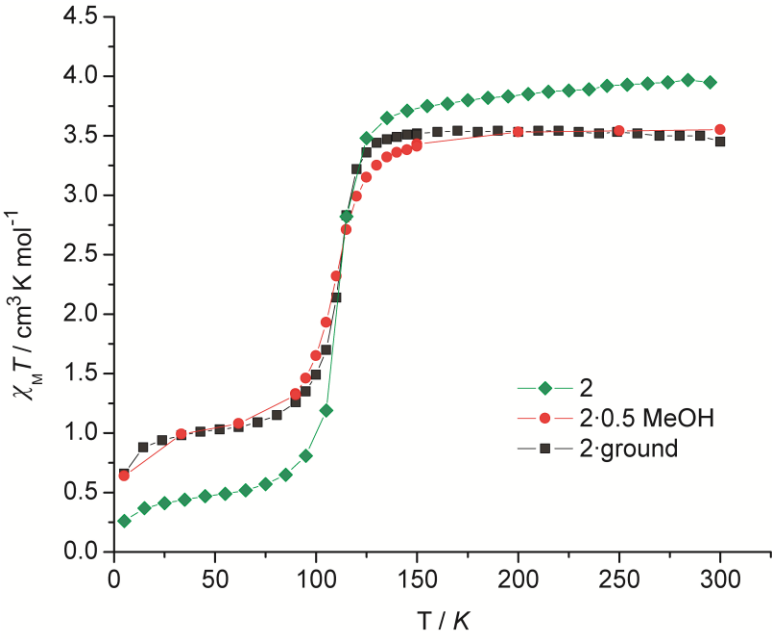

Figure S8. Variable temperature SQUID data for **2** and **2·0.5 MeOH**. Samples **2** and **2·ground** differ only in the amount of grinding applied to the crystals (**2·ground** was ground more vigorously than **2**).

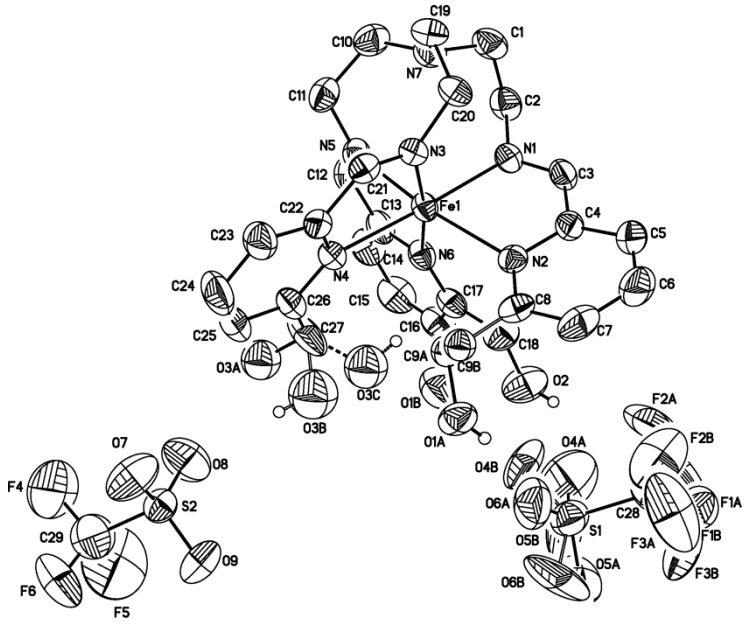

Figure S9. Crystal structure of **1·RT** at 296 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

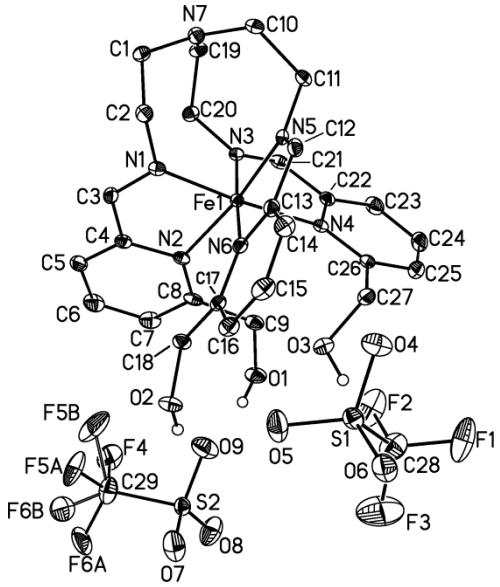

Figure S10. Crystal structure of **1·LT** at 120 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

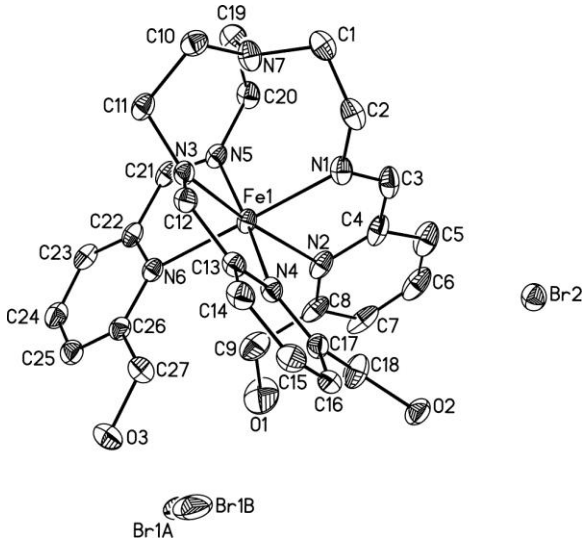

Figure S11. Crystal structure of **2** at 120 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

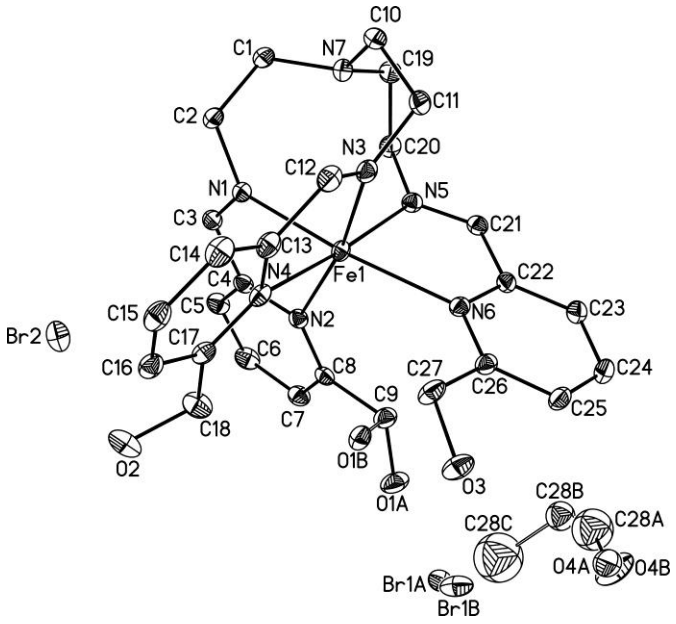

Figure S12. Crystal structure of **2·0.5 MeOH** at 120 K. Hydrogen atoms have been removed for clarity. Atoms rendered with 40% thermal ellipsoids. Solvent molecules (C28a, C28b, C28c, O4a and O4b) were refined isotropically due to high level of disorder.

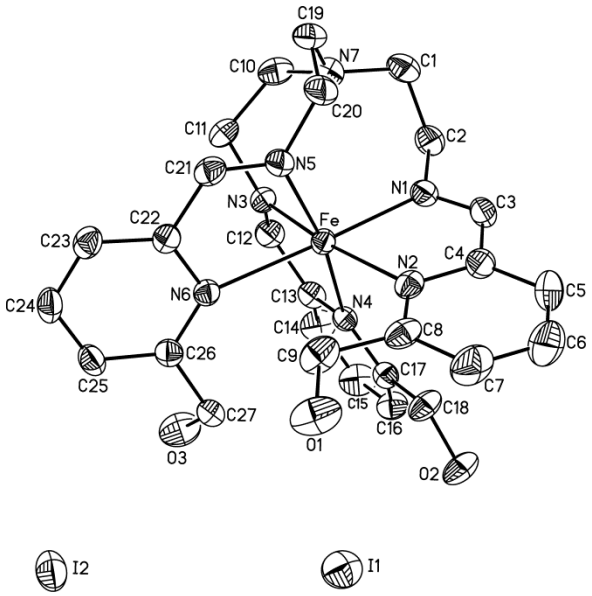

Figure S13. Crystal structure of **3·RT** at 296 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

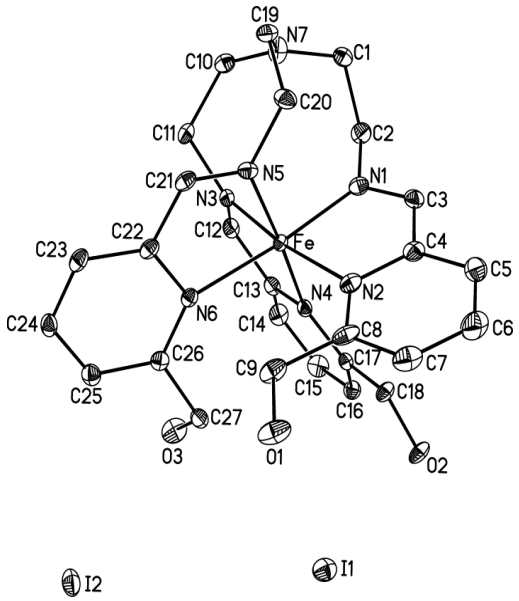

Figure S14. Crystal structure of **3·LT** at 120 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

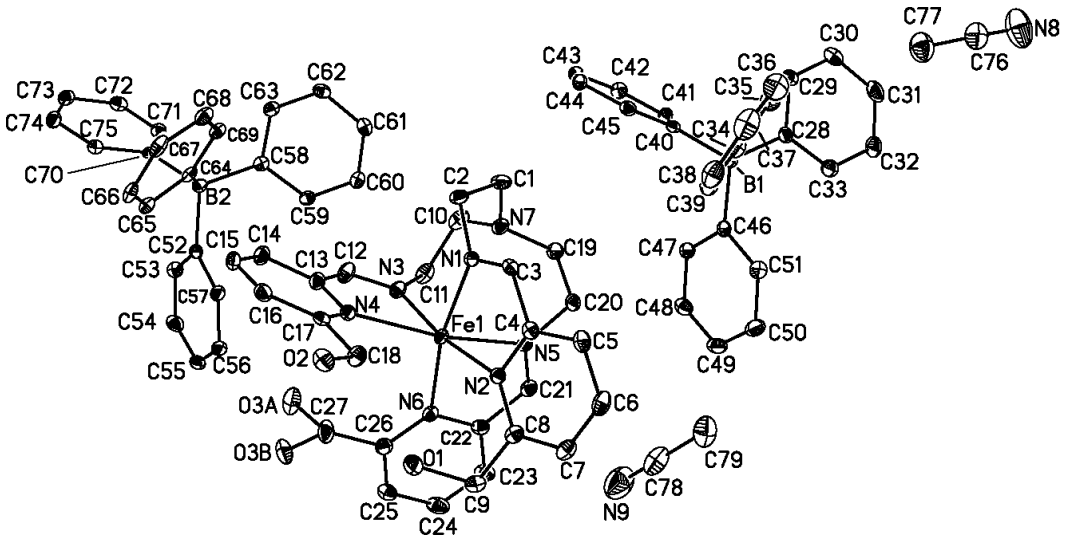

Figure S15. Crystal structure of **4** at 120 K. Atoms rendered with 40% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

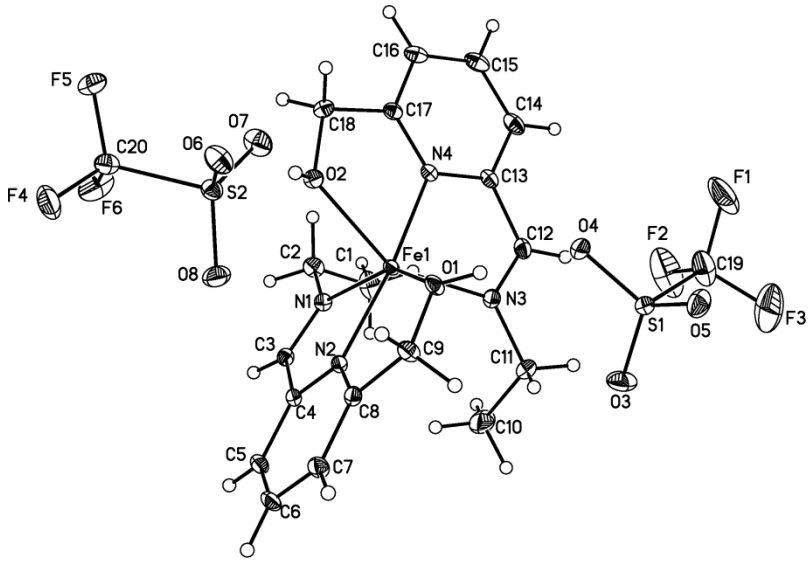

Figure S16. Crystal structure of **5** at 120 K. Atoms rendered with 40% thermal ellipsoids.

Table S1. Shortest intermolecular hydrogen-bond interactions.[a]

	1·RT	**1·LT**	**2**	**2·0.5 MeOH**	**3·RT**	**3·LT**	**4**	**5**
O1···X1 [b]	2.58(1)[c]	2.813(3)[d]	3.354(8)	3.22(4)	3.410(2)	3.360(2)	–	2.636(1)
O2···X1	2.68(1)[c]	2.964(3)[d]	3.203(7)	3.277(6)	4.037(2)	3.888(2)	3.154(7)[e]	2.610(1)
O3···X2	2.83(2)	–	3.224(3)	3.213(2)	3.599(2)	3.596(2)	3.326(13)[e]	–
O3···N7	4.40(9)	2.827(3)	–	–	–	–	–	–
O1···O2a	–	–	–	–	2.743(3)	2.705(3)	2.742(2)	–

[a] Interaction defined as distance less than the sum of the van der Waals radii: (O···O = 3.04 Å, O···Br = 3.37 Å, O···I = 3.50 Å, O···N = 3.02 Å; taken from "Atomic Radii of the Elements," in CRC Handbook of Chemistry and Physics, 92nd Edition (Internet Version 2012), W. M. Haynes, ed., CRC Press/Taylor and Francis, Boca Raton, FL.)

[b] X1 is defined as 'anion 1' (lies closest to the trigonal pocket), X2 is defined as 'anion 2' (See renderings/packing plots).

[c] Interact with two different oxygen atoms of triflate

[d] Interact with same oxygen atom of triflate

[e] Defined as the distance between the centroid of the phenyl and the oxygen

Variations on the anion chelation are seen between **1·RT** and **1·LT**: at room temperature, the two chelating arms bind with two oxygen atoms of the triflate; while at 120 K, the two arms interact with only one oxygen atom (Figure 5 in the manuscript).

In the structures of **3**, we note that the two arms of the iodide-containing structures do not interact with the anion equally, as denoted by significantly different O···I distances.

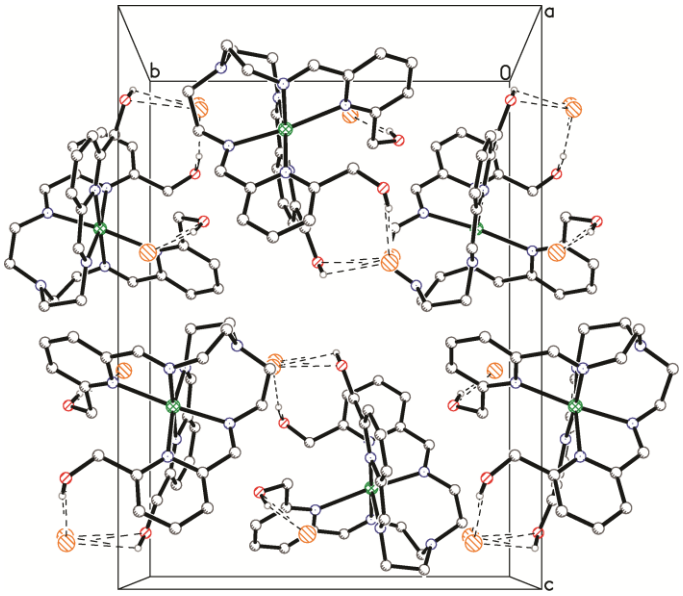

Figure S17. Packing plot of **2** down the *a* axis. Fe, C, N, O, H and Br atoms are colored green, dark gray, blue, red, light gray and orange respectively. Dashed bonds are to emphasize hydrogen bonding interactions.

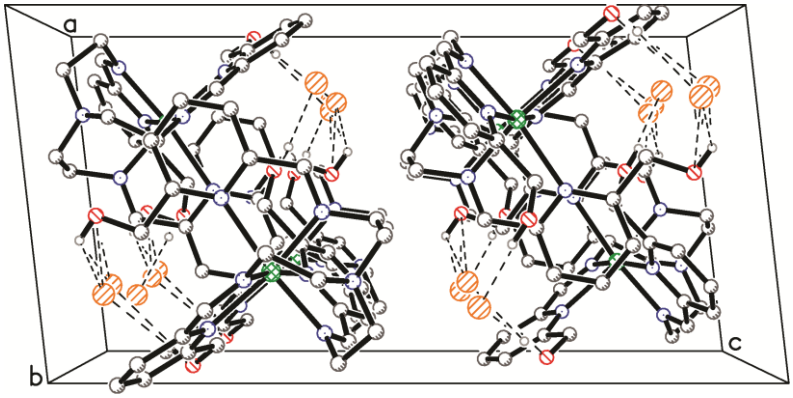

Figure S18. Packing plot of **2** down the *b* axis. Fe, C, N, O, H and Br atoms are colored green, dark gray, blue, red, light gray and orange respectively. Dashed bonds are to emphasize hydrogen bonding interactions.

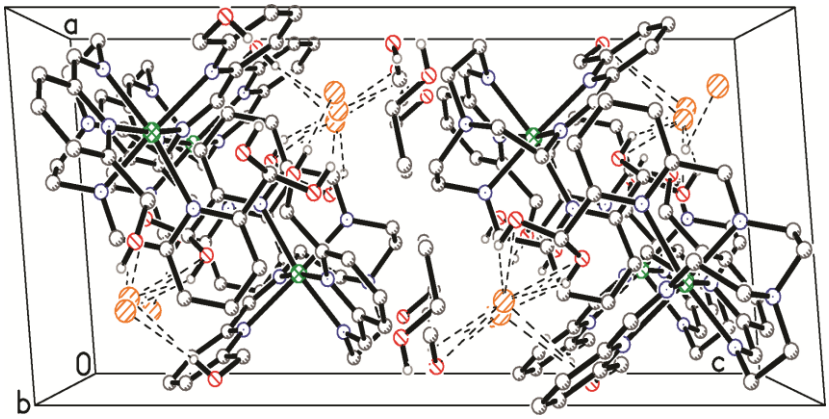

Figure S19. Packing plot of **2·0.5 MeOH** down the *b* axis. Fe, C, N, O, H and Br atoms are colored green, dark gray, blue, red, light gray and orange respectively. Dashed bonds are to emphasize hydrogen bonding interactions.

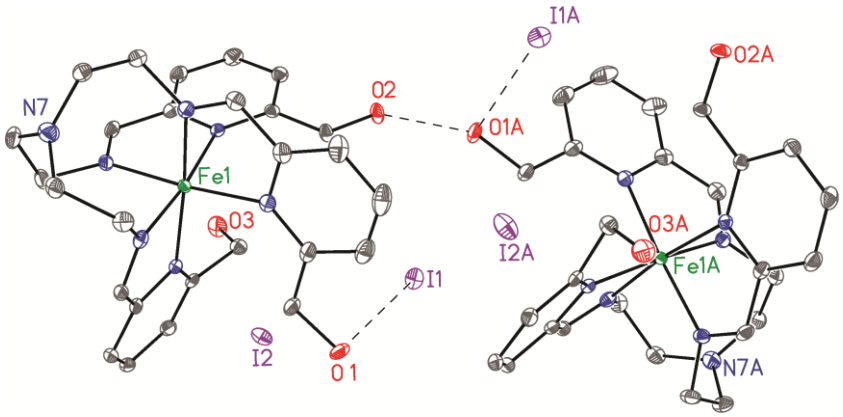

Figure S20. Intermolecular interactions for the structures of compound **3·LT**. Analogous interactions are seen at 296 and 120 K. Atoms rendered with 40% thermal ellipsoids. Fe, C, N, O and I atoms are colored green, dark gray, blue, red and purple respectively. Hydrogen atoms have been omitted for clarity.

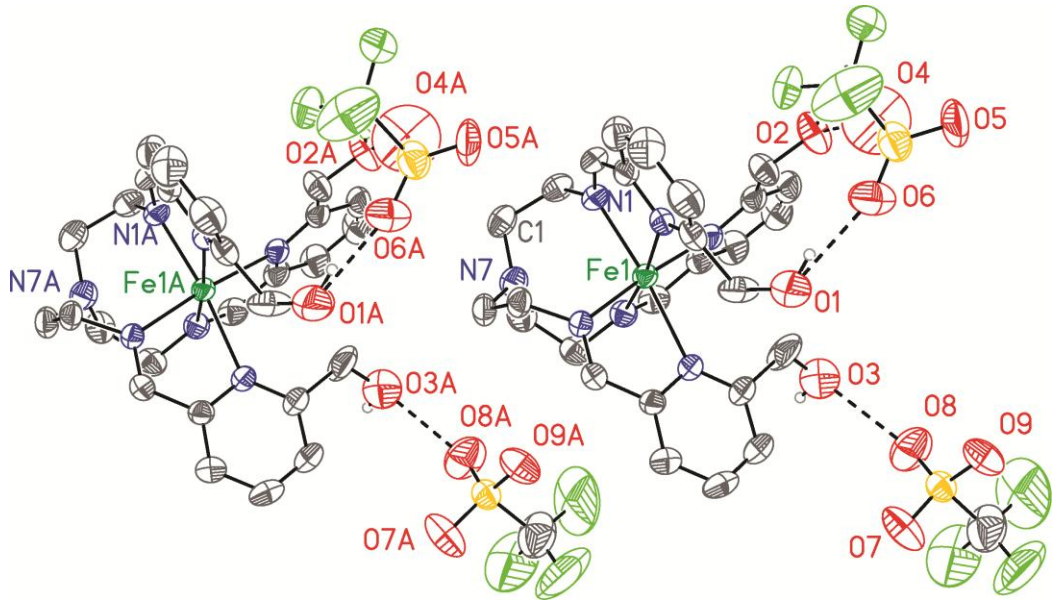

Figure S21. Anion-cation interactions of **1·RT**. Atoms rendered with 40% thermal ellipsoids. Fe, C, N, O, S and F atoms are colored dark green, dark gray, blue, red, yellow and light green respectively. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

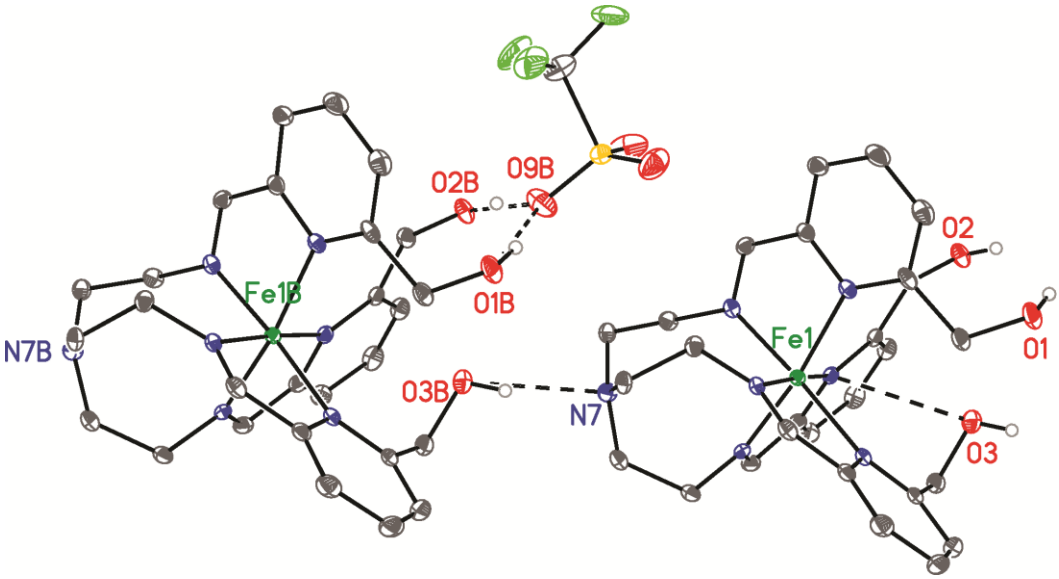

Figure S22. Anion-cation and cation-cation interactions of **1·LT.** Fe, C, N, O, S and F atoms are colored dark green, dark gray, blue, red, yellow and light green respectively. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

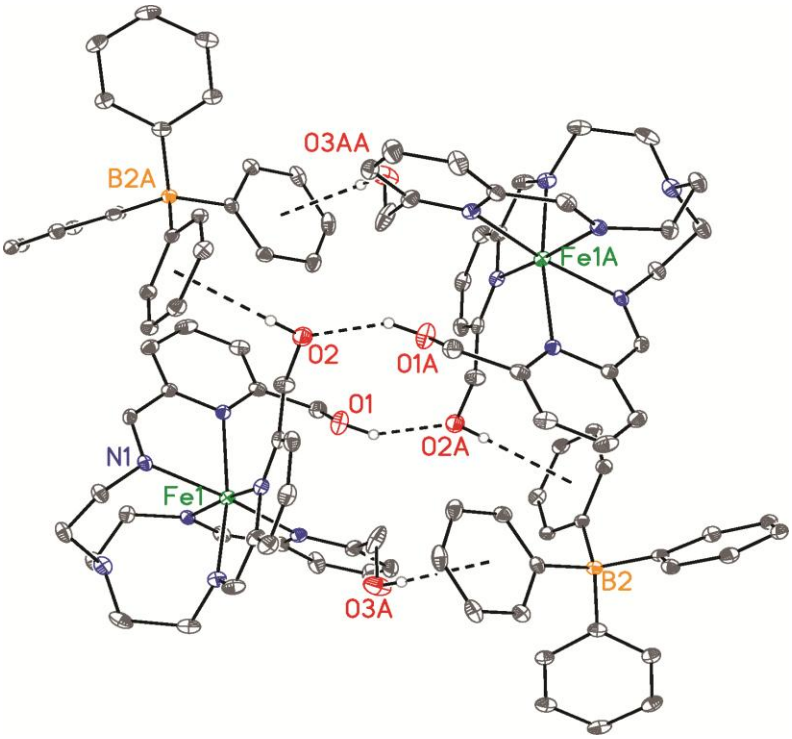

Figure S23. Intermolecular interactions of **4**. Fe, C, N, O, and B atoms are colored dark green, dark gray, blue, red, and yellow respectively. Hydrogen atoms except those of the hydroxyls and disorder of O3 have been omitted for clarity.

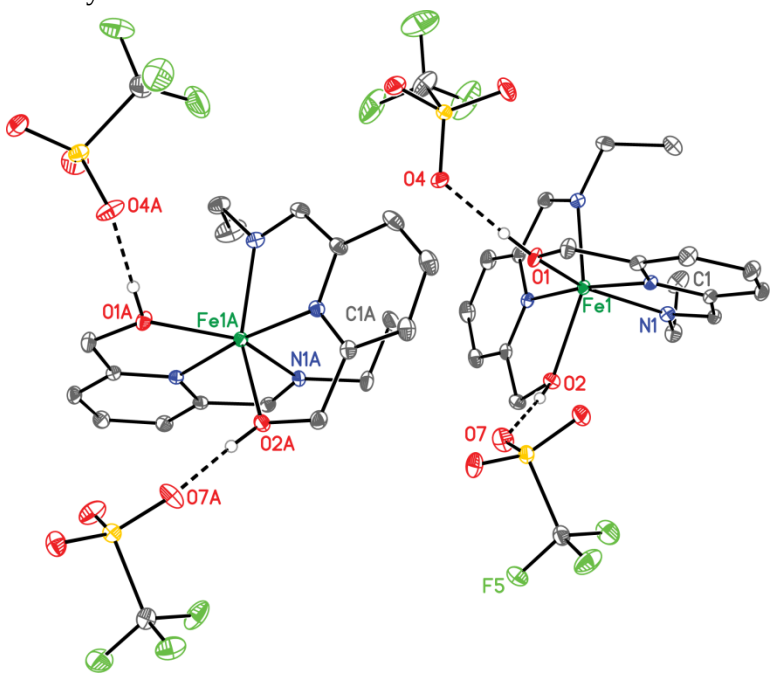

Figure S24. Cation-anion interactions for **5**. Fe, C, N, O, S and F atoms are colored dark green, dark gray, blue, red, yellow and light green respectively. Hydrogen atoms except those of the hydroxyls have been omitted for clarity.

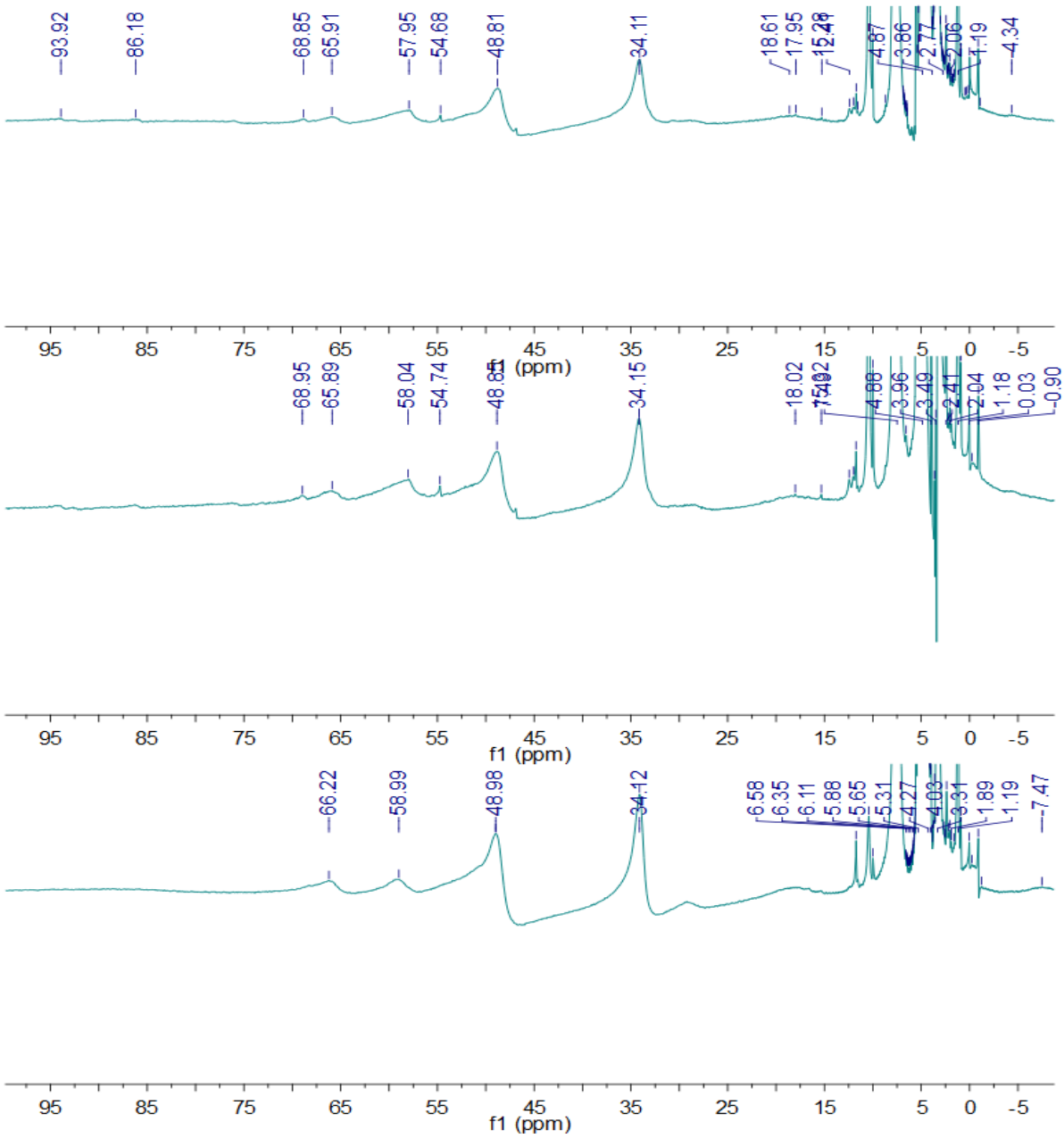

Figure S25. ^{1}H NMR spectra obtained at 295 K at 300 MHz with TMS as the reference of **2** at t=10 min. (bottom), t=24 hr (middle) and t=3 days (top). After 24 hours, additional peaks begin to appear at 54.7, 68.9, 86.2 and 93.9 ppm indicative of complex degradation.

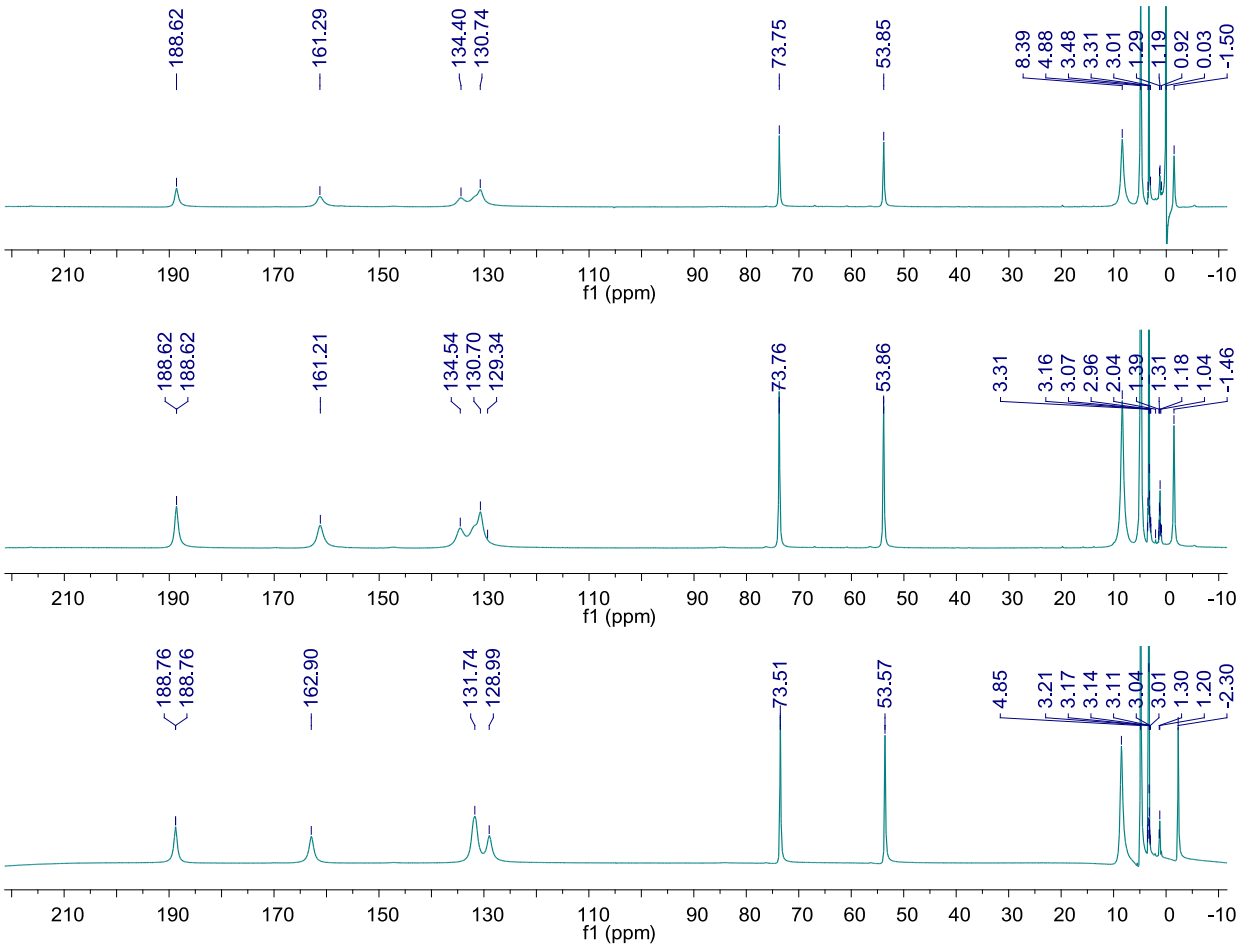

Figure S26. ^{1}H NMR spectra obtained at 295 K at 300 MHz with CD_3OD as the reference of **5** at t=10 min. (bottom), t=1 day (middle) and t=3 days (top). Shifts in some peaks and the growth of small resonances are seen over time.

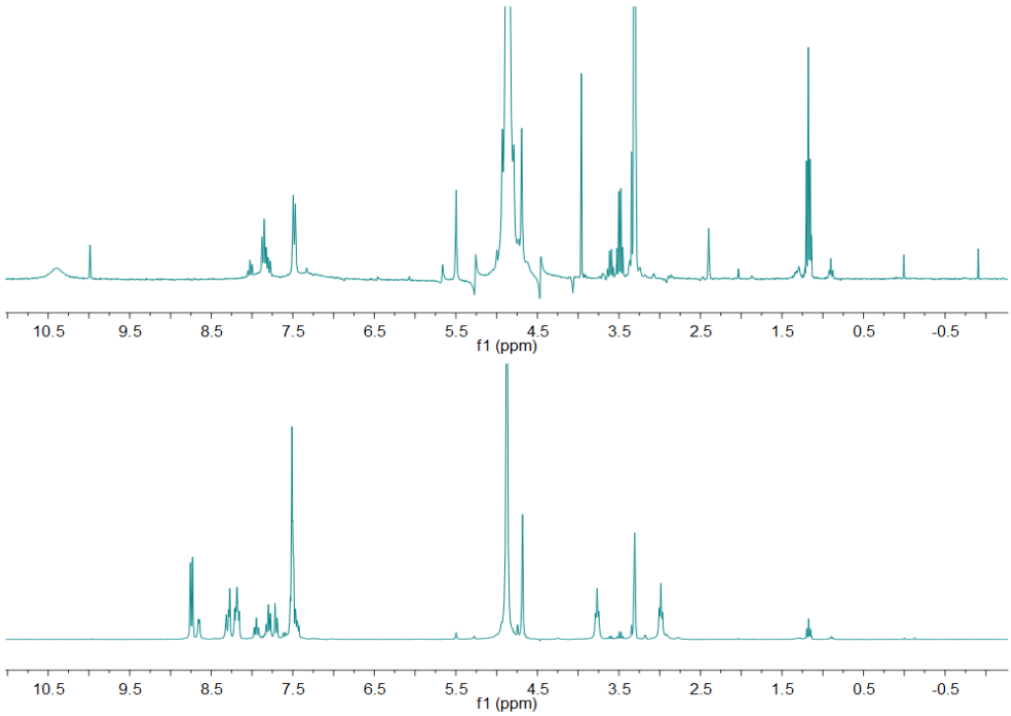

Figure S27. ^{1}H NMR spectra of **2** (normal/diamagnetic window) before (top) and after (bottom) addition of 3 equivalents of 2,2′-bipyridine. NMR spectra obtained at 295 K at 300 MHz with TMS reference.

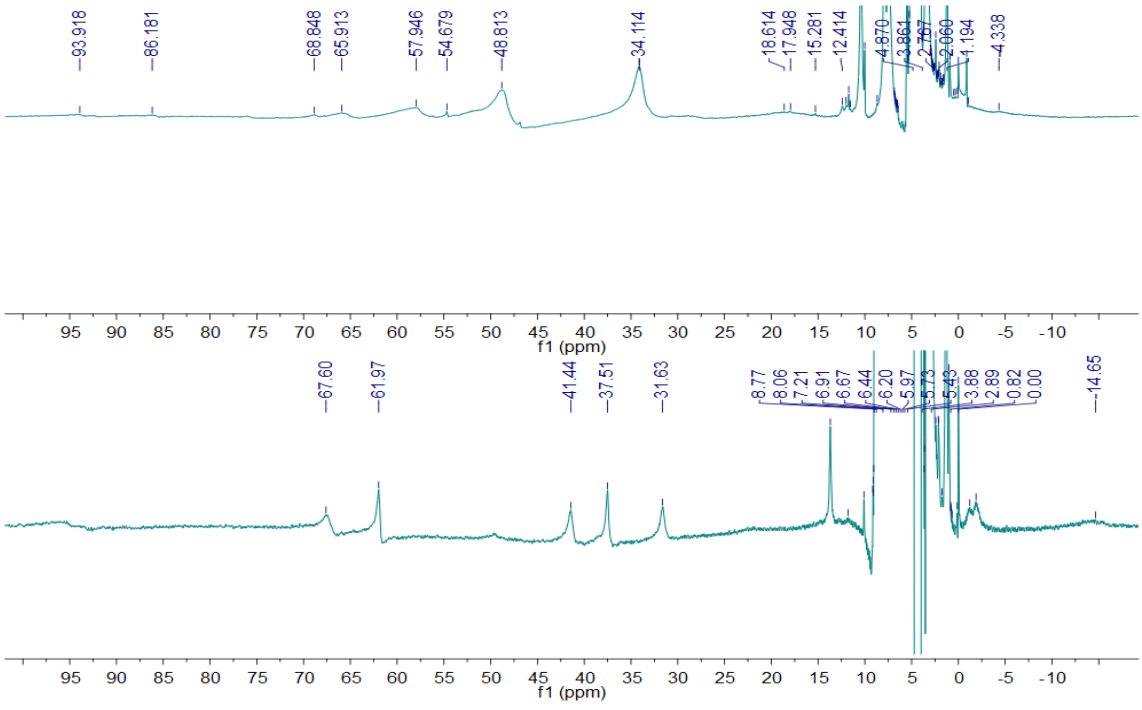

Figure S28. ^{1}H NMR spectra of **2** (wider window) before (top) and after (bottom) addition of 3 equivalents of 2,2′-bipyridine. NMR spectra obtained at 295 K at 300 MHz with TMS as the reference.

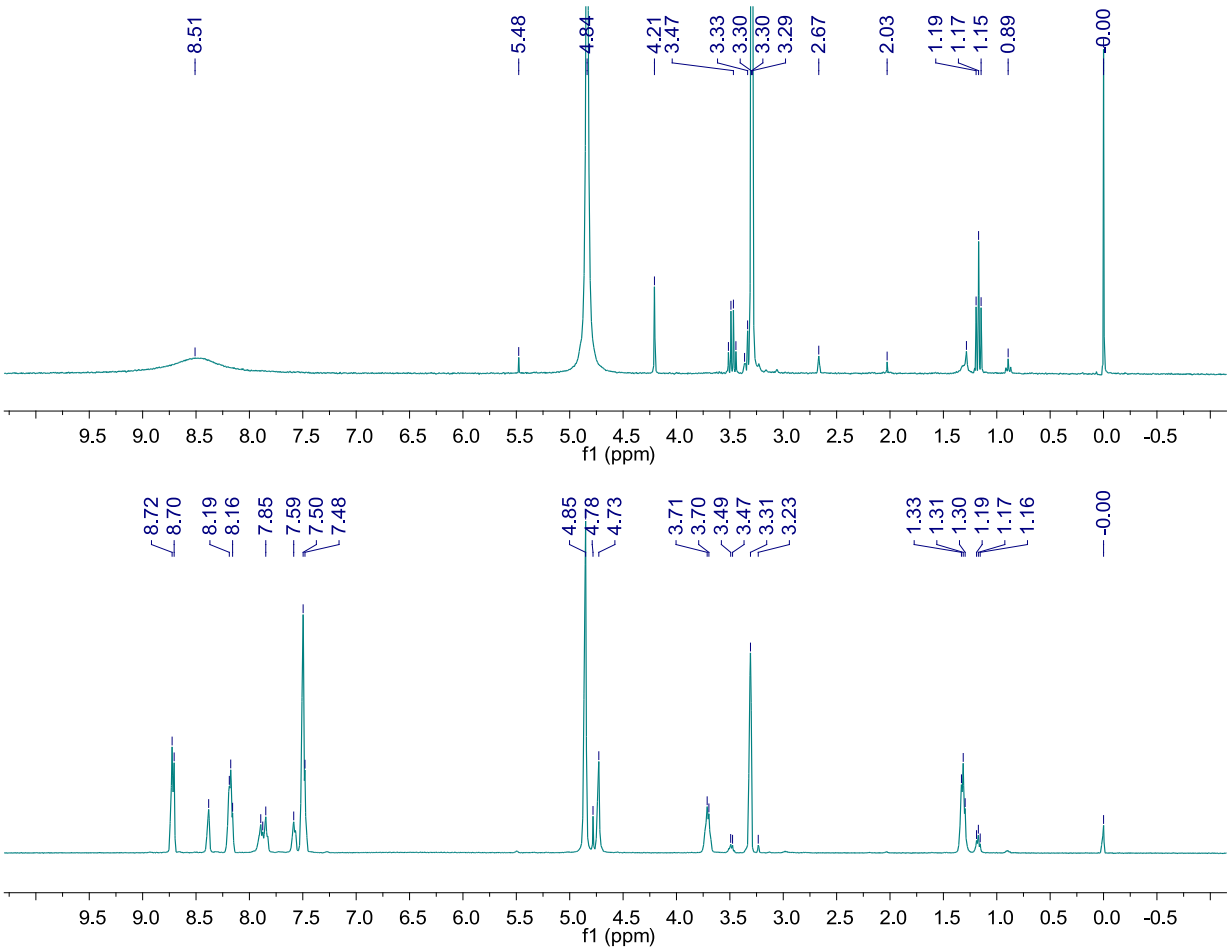

Figure S29. ^{1}H NMR spectra of **5** (normal/diamagnetic window) before (top) and after (bottom) addition of 3 equivalents of 2,2′-bipyridine. NMR spectra obtained at 295 K at 300 MHz with TMS reference**.**

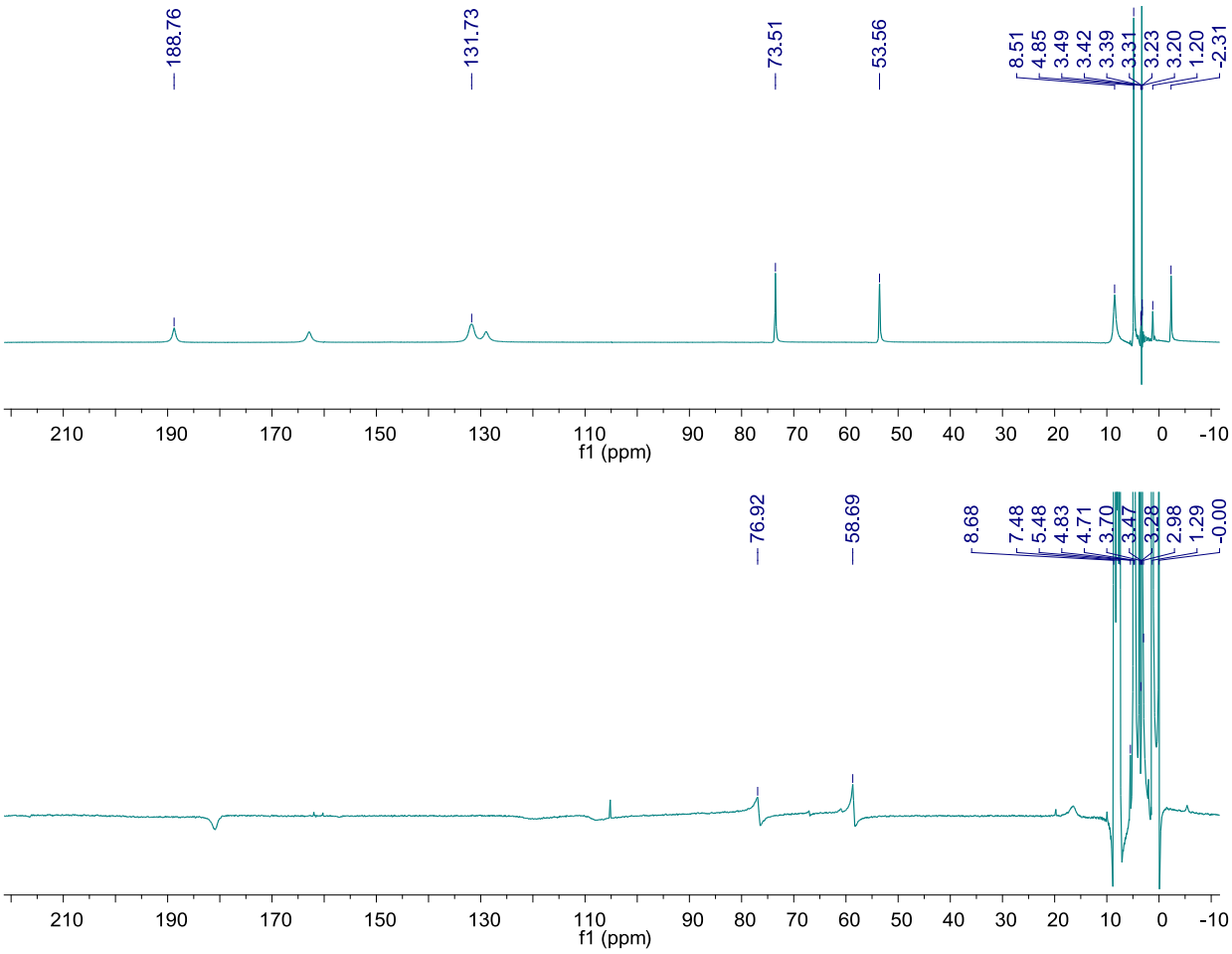

Figure S30. ^{1}H NMR spectra of **5** (wider window) before (top) and after (bottom) addition of 3 equivalents of 2,2′-bipyridine. NMR spectra obtained at 295 K at 300 MHz with TMS reference.

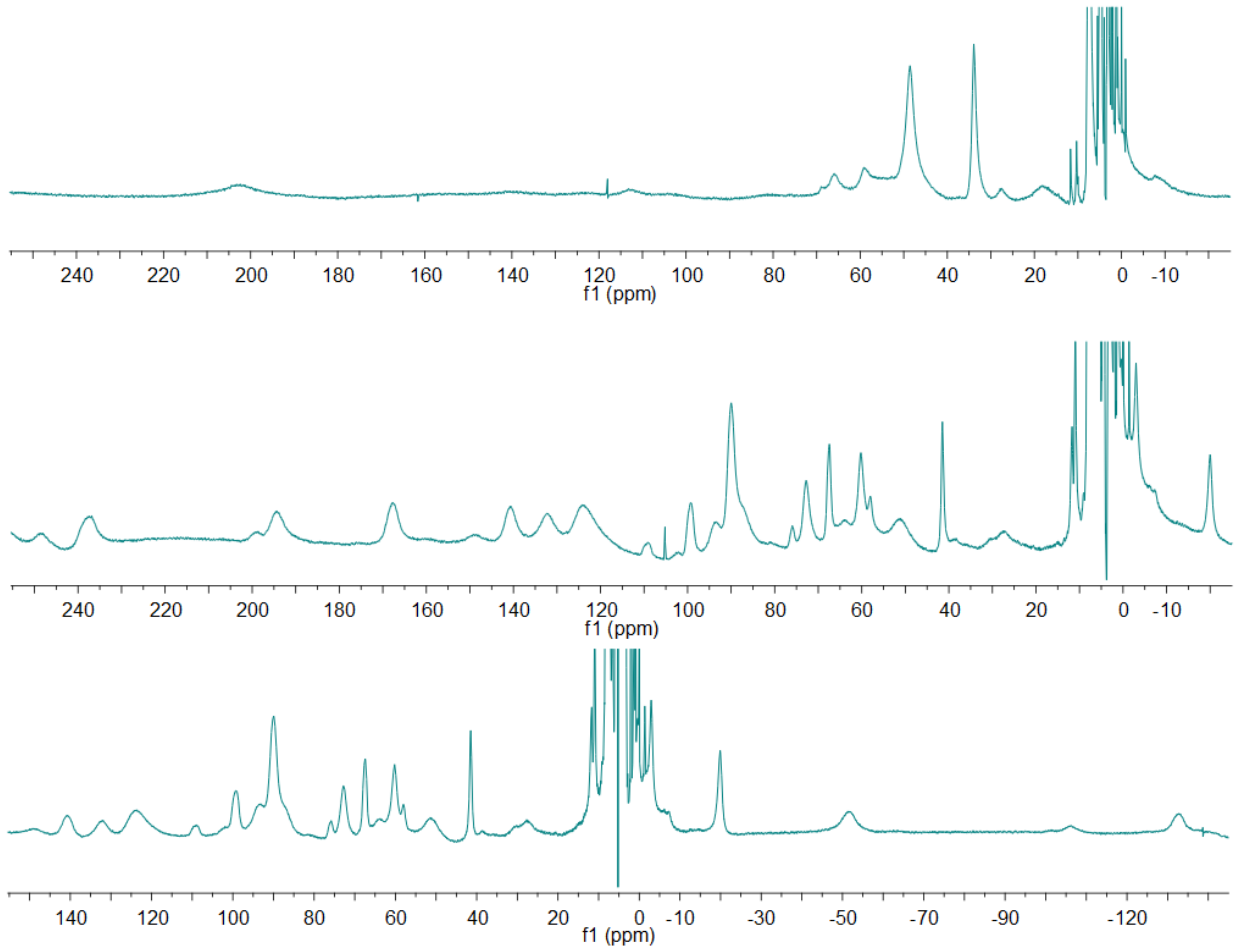

Figure S31. ^{1}H NMR spectra of **1** at 295 K (top) and 213 K (middle and bottom) obtained at 300 MHz with TMS as the reference. At room temperature, no peaks are observed below -20 ppm.

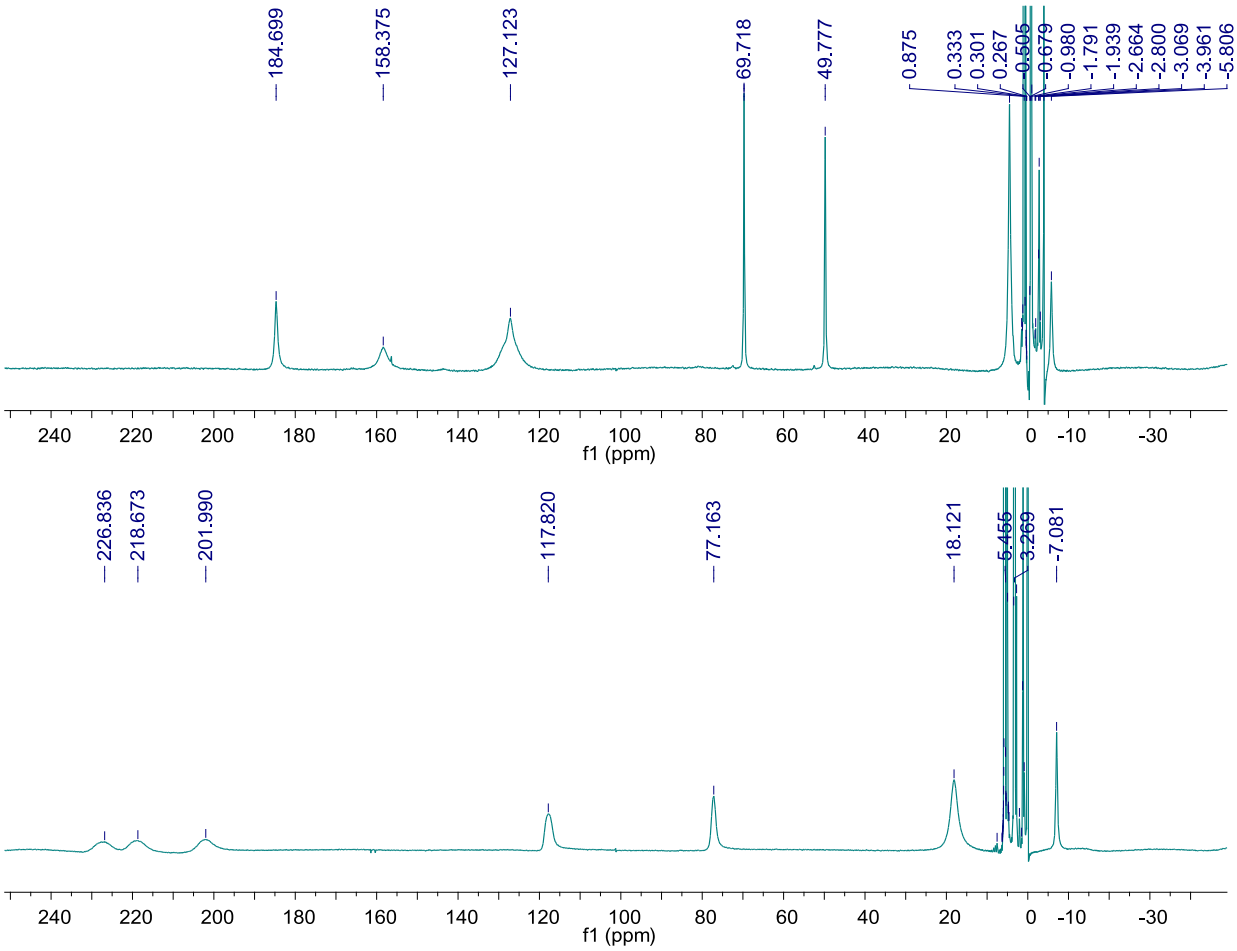

Figure S32. ^{1}H NMR spectra of **1** at 298 K (top) and 193 K (bottom) obtained at 300 MHz with TMS as the reference. The peak at 127.123 ppm has a small shoulder due to peak coalescence at 298 K.

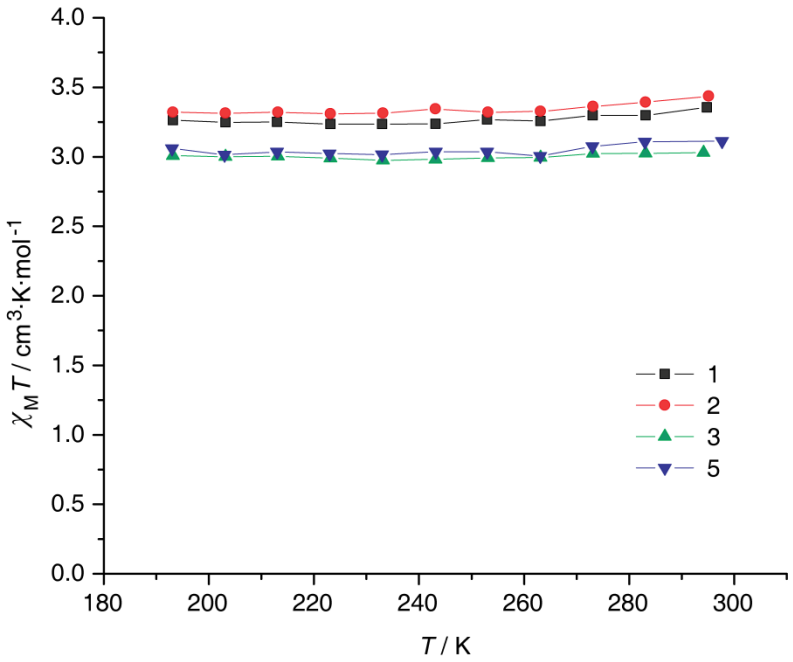

Figure S33. Variable temperature solution magnetic susceptibility of **1**, **2**, **3** and **5** in CD_3OD using Evans' method.

Note: At low temperatures, decreased solubility of compounds may manifest as lower-than-expected magnetic susceptibility values. The samples whose data are shown in figures S17-S20 were prepared so that they maintained complete solubility at 185 K.