Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Unraveling the Origins of Catalyst Degradation in Non-heme Iron-based Alkane Oxidation

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Standard Testing Conditions for the Oxidation of Cyclohexane.

Catalytic oxidations were all run at room temperature. The reaction products were analysed by GC analysis, using GC-MS for product identification. All catalytic data quoted is the average of at least two runs. 2.1 mmol (0.23 mL) of cyclohexane was added to a 75x25 mm sample vial containing 2.1 μmol of complex dissolved in 2.7 mL of acetonitrile and a small egg-shaped stirrer bar, and the mixture stirred until the substrate had fully dissolved. For the addition of 10 equivalents of H_2O_2 (relative to the amount of catalyst), 0.3 mL of 70 mM solution of hydrogen peroxide in acetonitrile was added dropwise over the course of 25 minutes, using a syringe pump (for the addition of 100 equivalents of H_2O_2, 0.3 ml of 700 mM solution was added over the same time). Upon completion of addition, the solution was stirred for a further 15 minutes and subsequently filtered through a pad of silica to remove the catalyst. The silica was then washed with 3.0 mL of acetonitrile and the washings combined with the filtered reaction mixture. The final concentration of the components in the reaction mixture upon the addition of 10 equivalents was: cyclohexane = 700 mM, H_2O_2 = 7mM and catalyst = 0.7 mM. This gave a substrate: oxidant: catalyst molar ratio of 1000: 10: 1. Other ratios between H_2O_2 and catalyst were obtained by adding different amounts of H_2O_2.

The acetonitrile solutions of hydrogen peroxide were prepared from commercially available 35 % aqueous hydrogen peroxide and reagent grade acetonitrile. The resultant acetonitrile solution was used without drying. The silica pads used for catalyst removal were prepared by inserting a glass wool plug into a Pasteur pipette, onto which an approximately 25 mm deep layer of silica was added.

Selected NMR Spectra of ligands and complexes

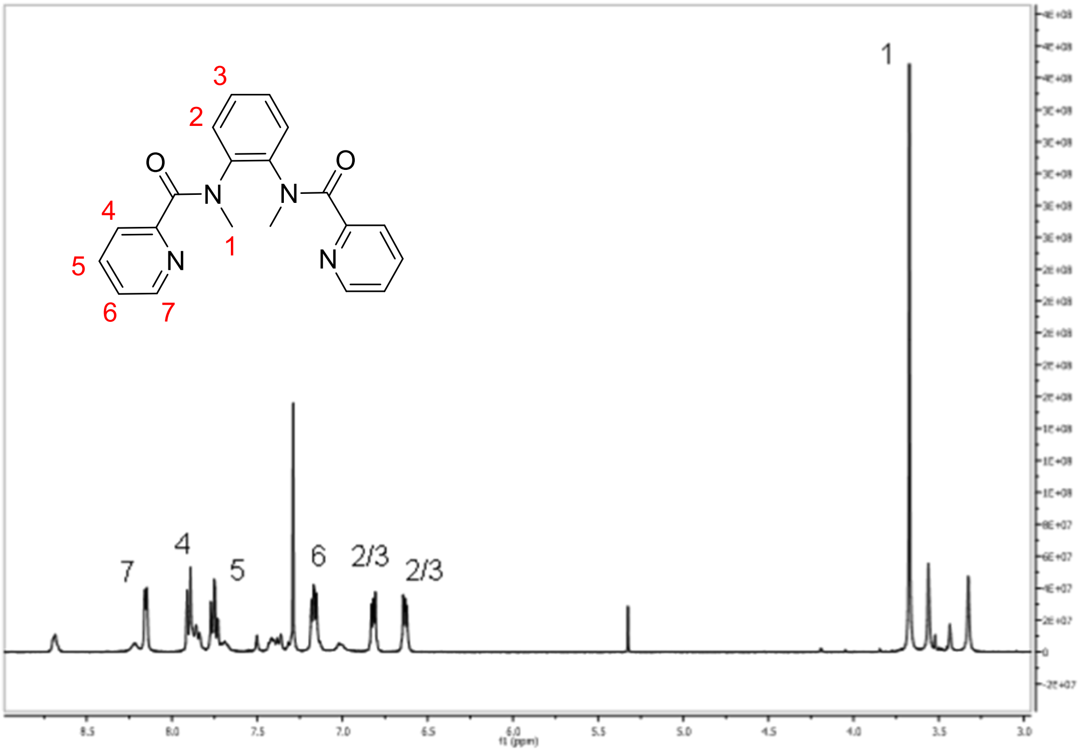

Figure S1. ^{1}H NMR spectrum of ligand **4** in $CDCl_3$ at 298K.

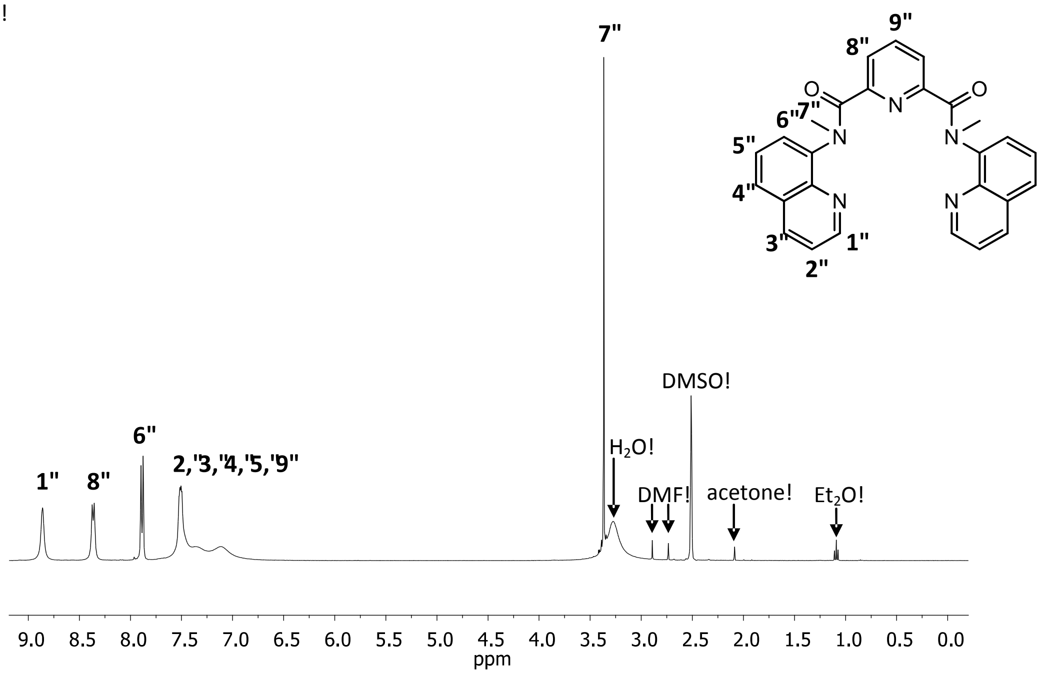

Figure S2. ^{1}H NMR spectrum of ligand **7** in d^6-DMSO at 298 K.

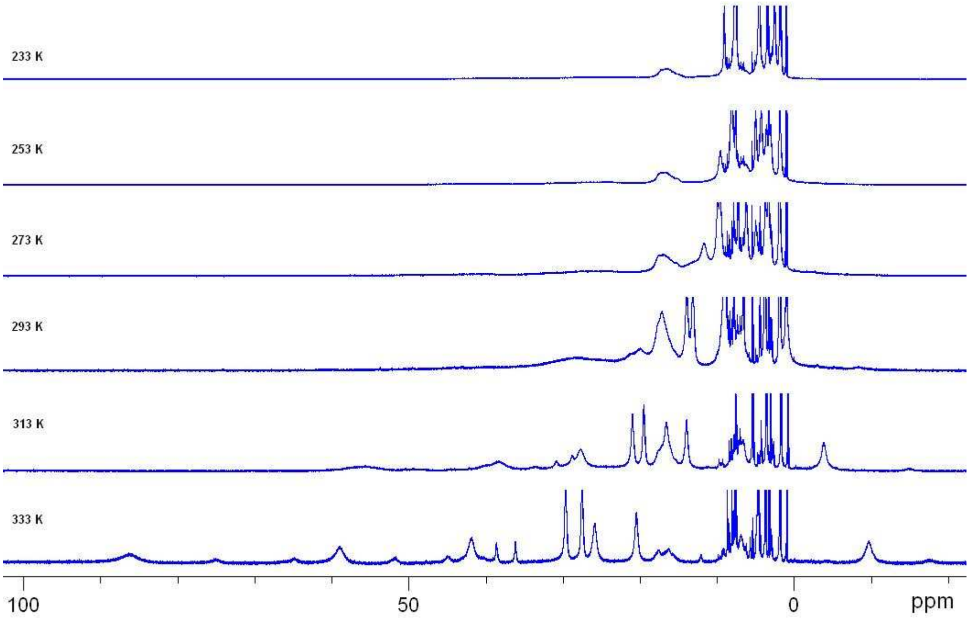

Figure S3. VT- ^{1}H NMR spectra of complex [Fe(**1**)(OTf)$_2$] in CD_3CN between 233 (top) and 333 K (bottom).

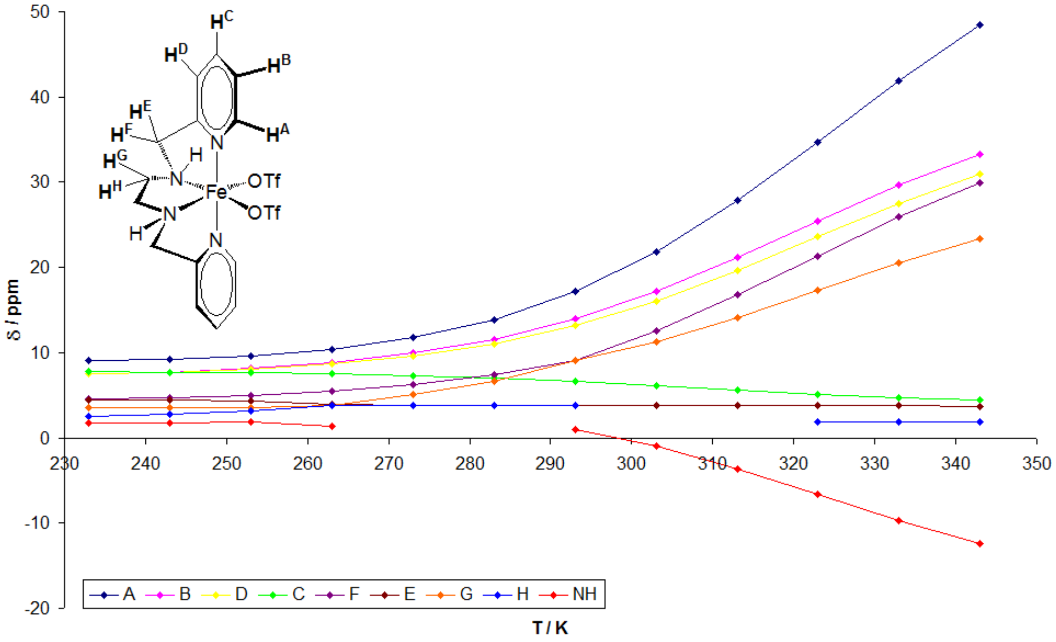

Figure S4. Chemical shift (δ) versus temperature (T) of complex [Fe(**1**)(OTf)$_2$] in CD_3CN between 233 and 343 K. (Some signals were too broad to be assigned).

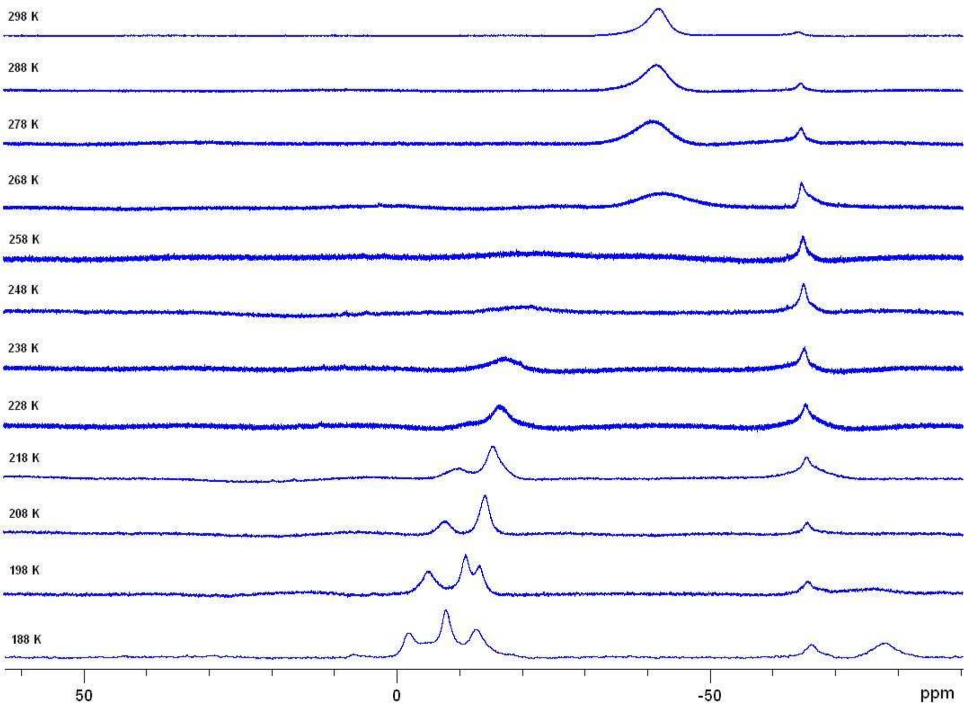

Figure S5. VT- ^{19}F-NMR spectra of complex [Fe(**1**)(OTf)$_2$] in CD_2Cl_2 between 188 K (bottom) and 298 K (top) in steps of 10 K.

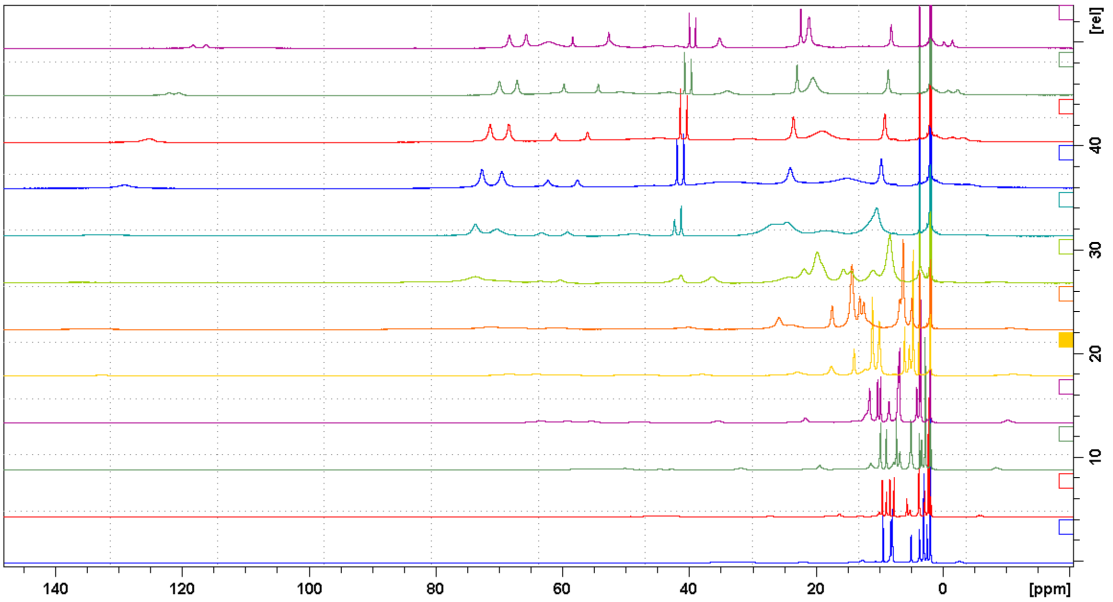

Figure S6. VT- ^{1}H NMR spectra of complex [Fe(**2**)(OTf)$_2$] in CD_3CN between 228 (bottom) and 338 K (top) in steps of 10K.

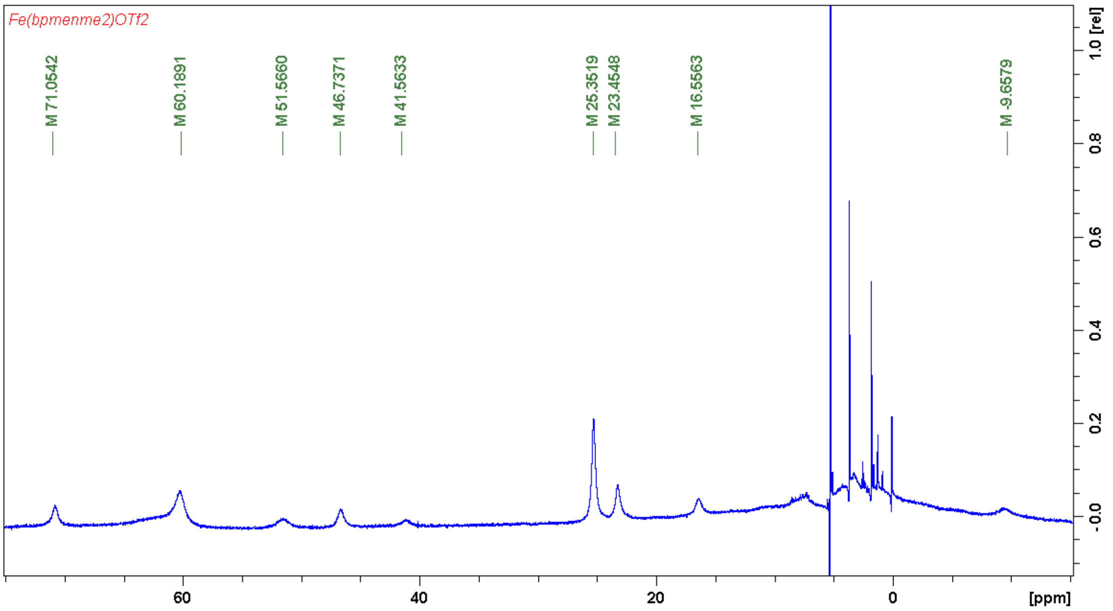

Figure S7. ^{1}H NMR spectrum of complex [Fe(**2**)(OTf)$_2$] in CD_2Cl_2 at 298K.

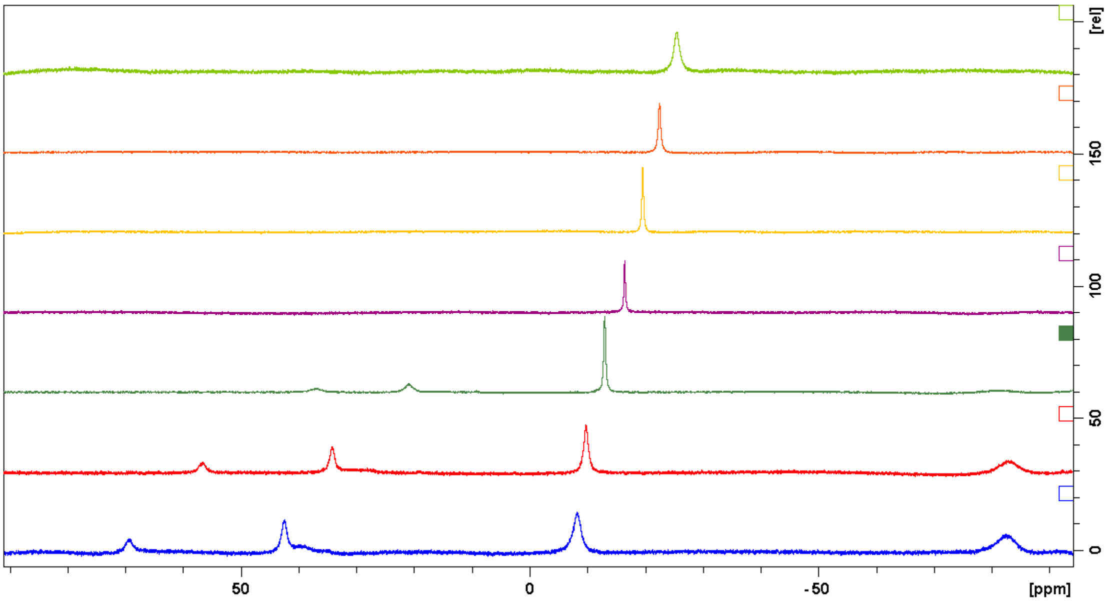

Figure S8. VT- ^{19}F-NMR spectra of complex [Fe(**2**)(OTf)$_2$] in CD_2Cl_2 from 188 K (bottom, blue), 198 K (red) to 298 K (top, green) in steps of 20K.

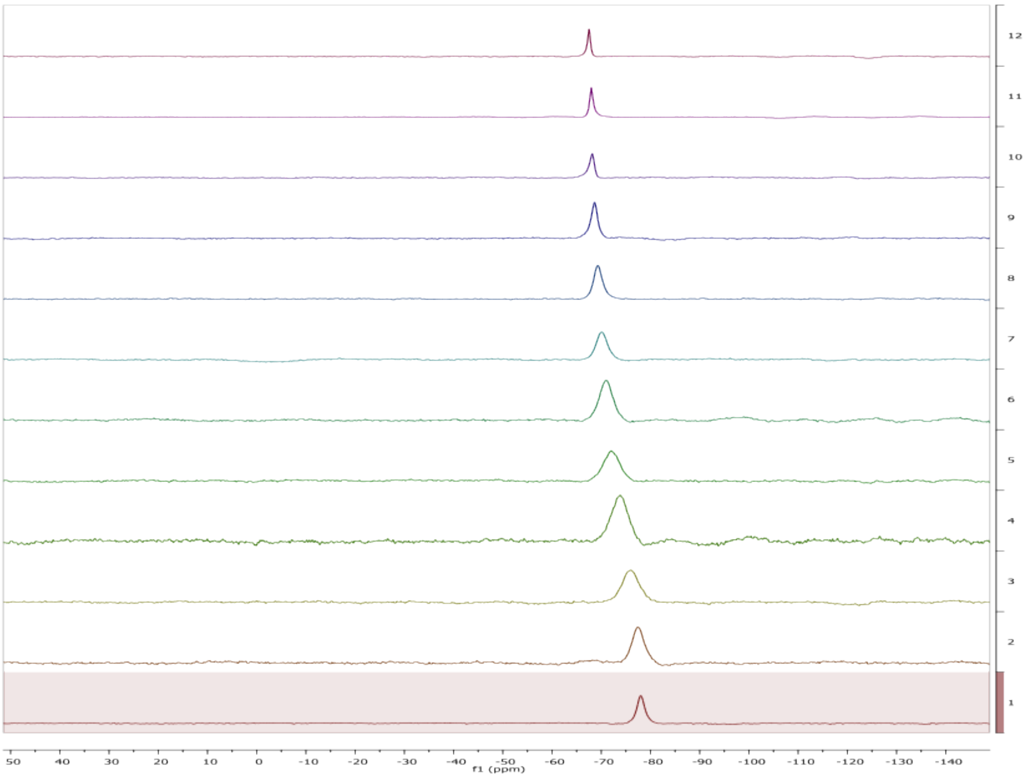

Figure S9. VT ^{19}F NMR spectra of complex [Fe(**3**)(OTf)$_2$] in acetonitrile from 233K (bottom) to 343 K (top) in steps of 10K.

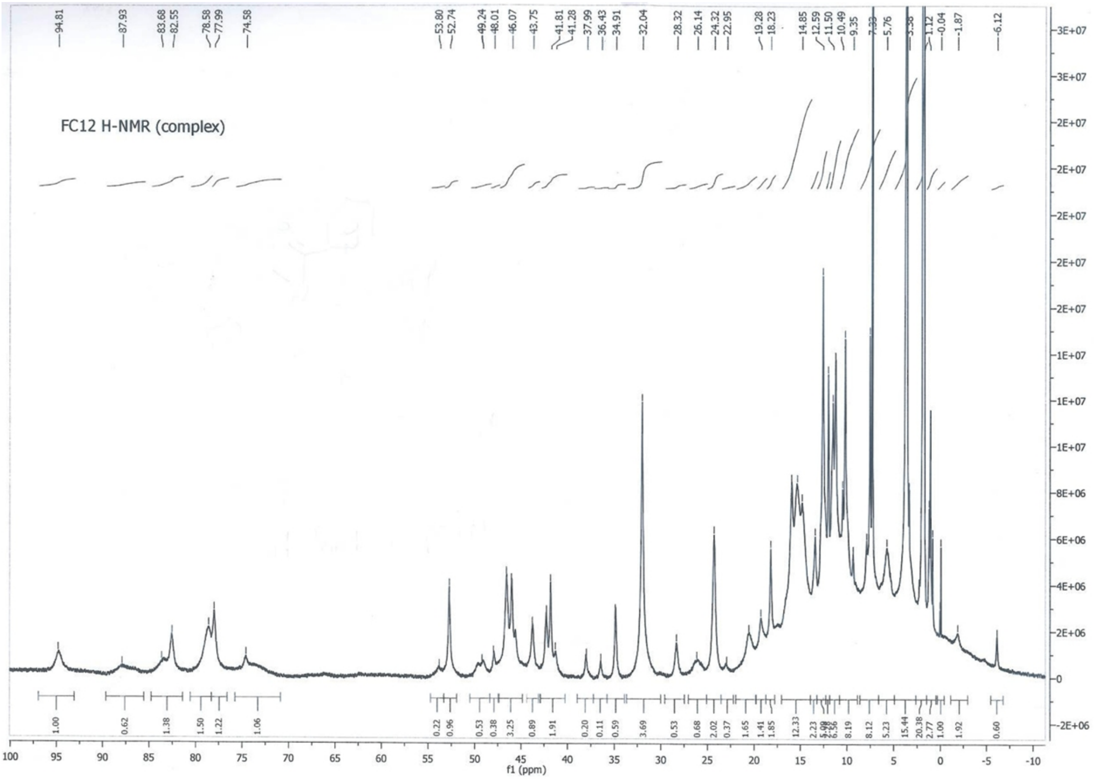

Figure S10. ^{1}H NMR spectrum of complex [Fe(**4**)(OTf)$_2$] in acetonitrile at 298 K.

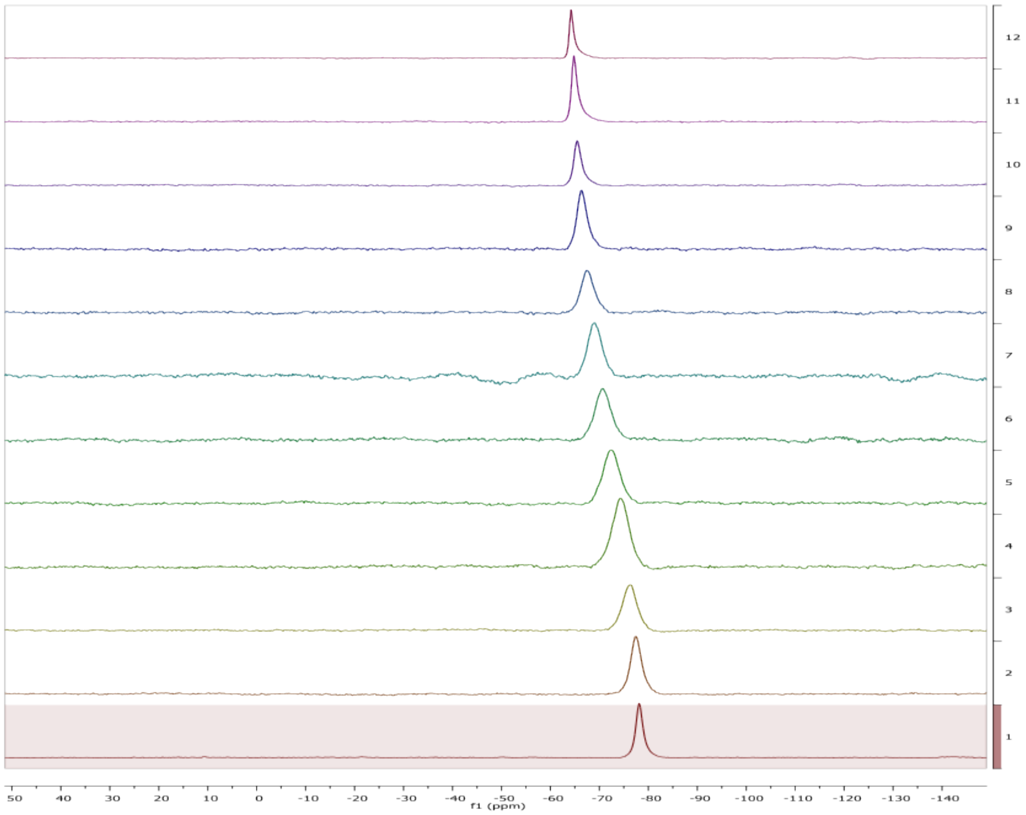

Figure S11. VT ^{19}F NMR spectra of complex [Fe(**4**)(OTf)$_2$] in acetonitrile from 233K (bottom) to 343 K (top) in steps of 10K.

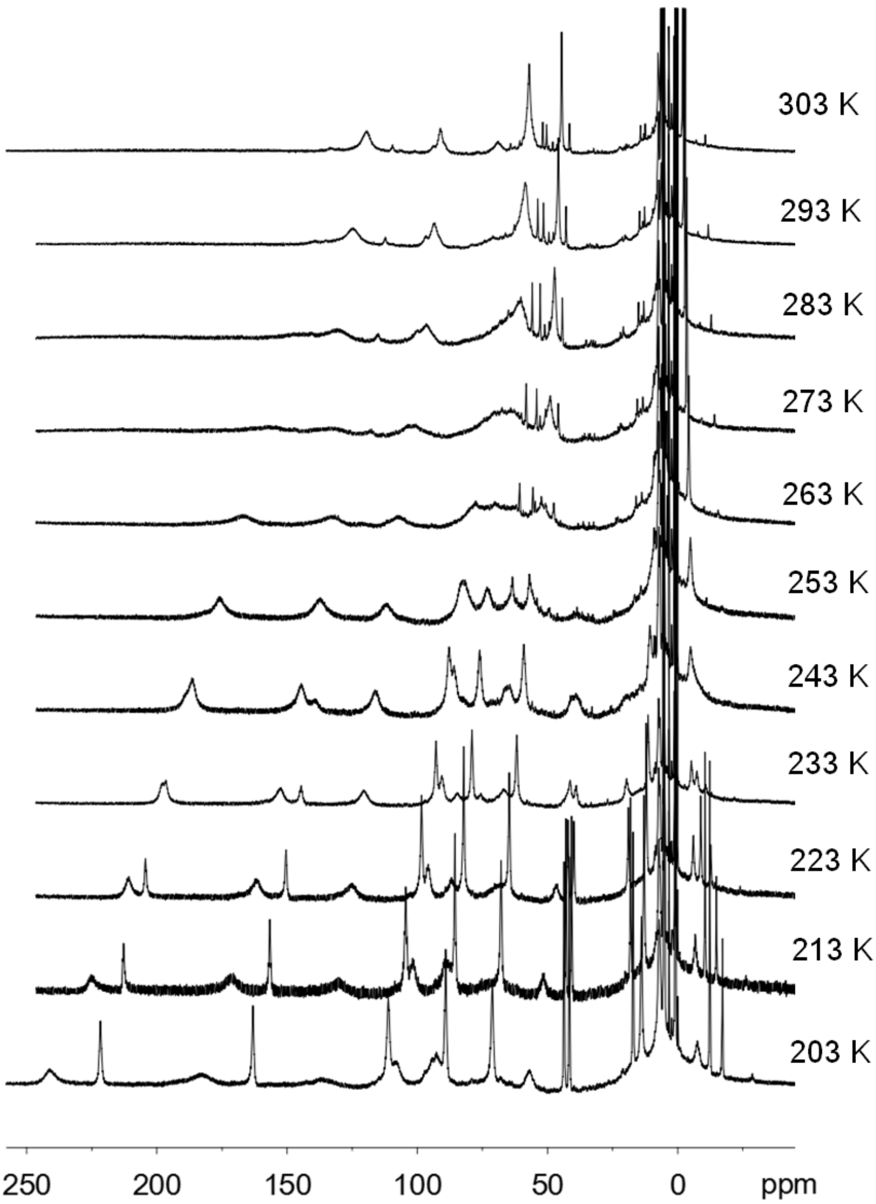

Figure S12. VT-^{1}H NMR spectra of complex [Fe(**5**)(OTf)](OTf) in CD_2Cl_2 from 203 to 303 K.

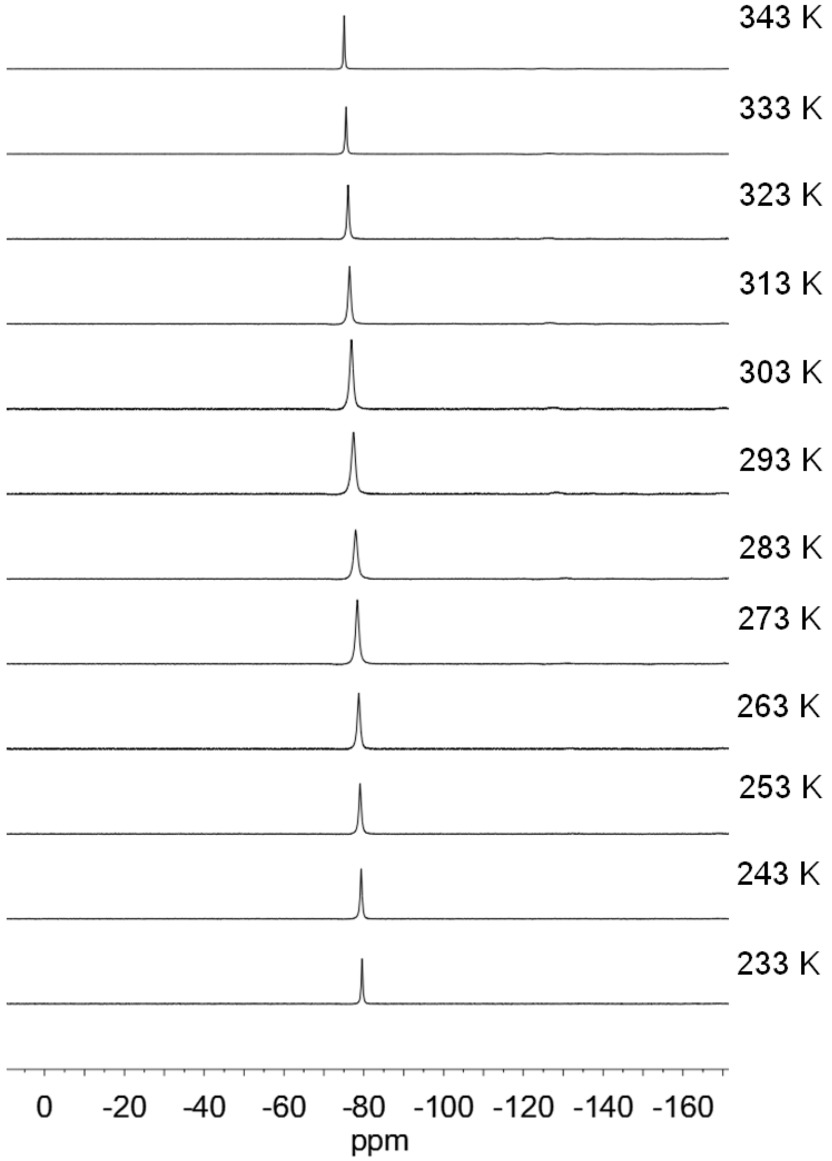

Figure S13. VT-^{19}F NMR spectra of [Fe(**5**)(OTf)](OTf) in CD_3CN from 233 K (bottom) to 343 K (top).

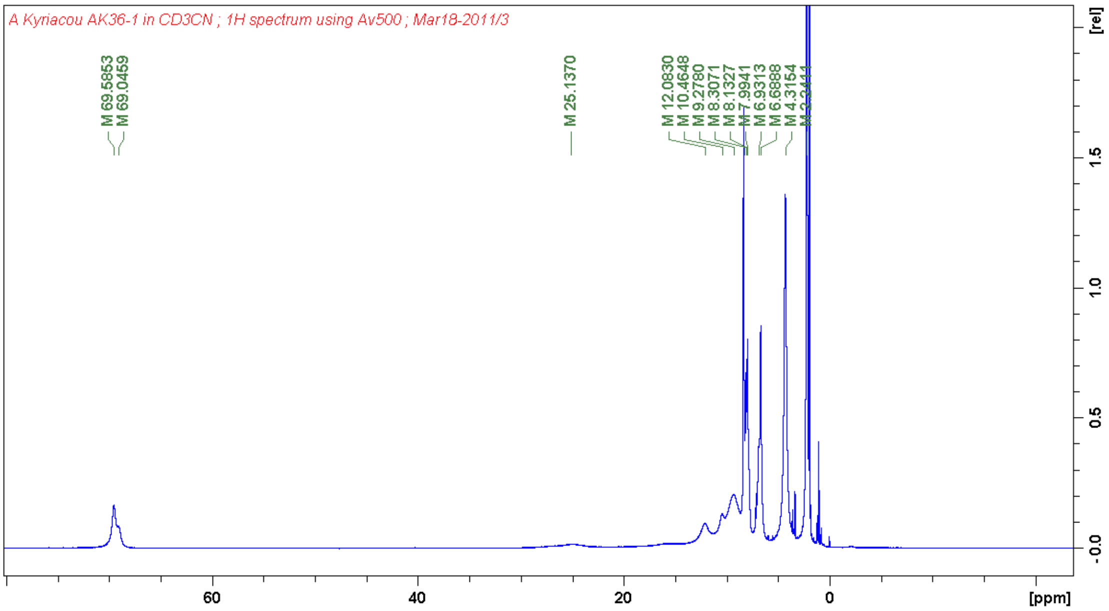

Figure S14. ^{1}H NMR spectrum of complex [Fe(**7**)(OTf)$_2$] in CD_3CN at 298 K.

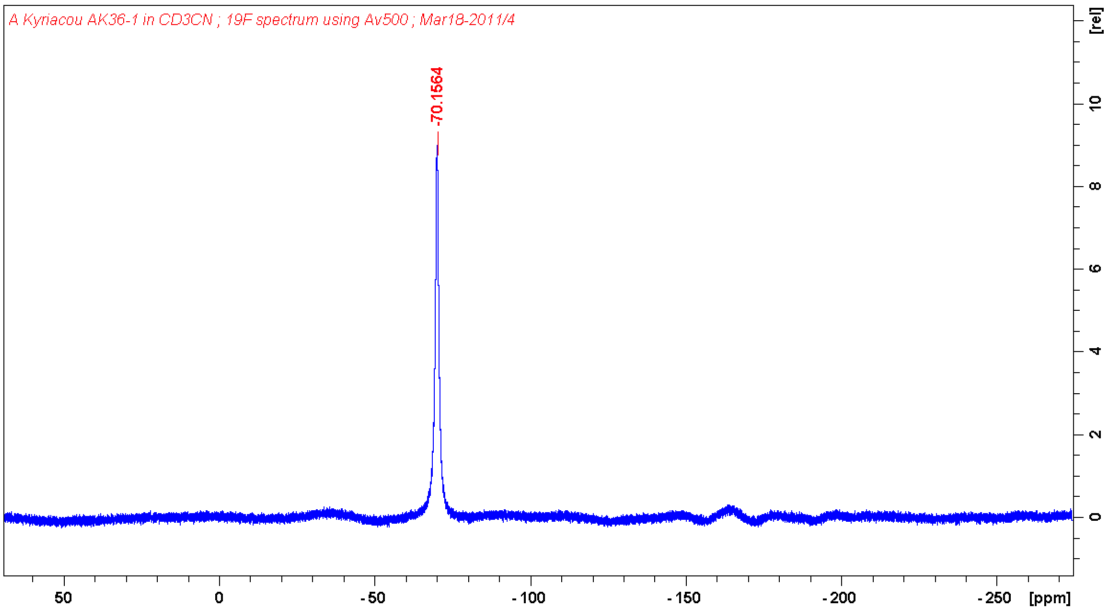

Figure S15. ^{19}F NMR spectrum of [Fe(**7**)(OTf)$_2$] in CD_3CN at 298 K.

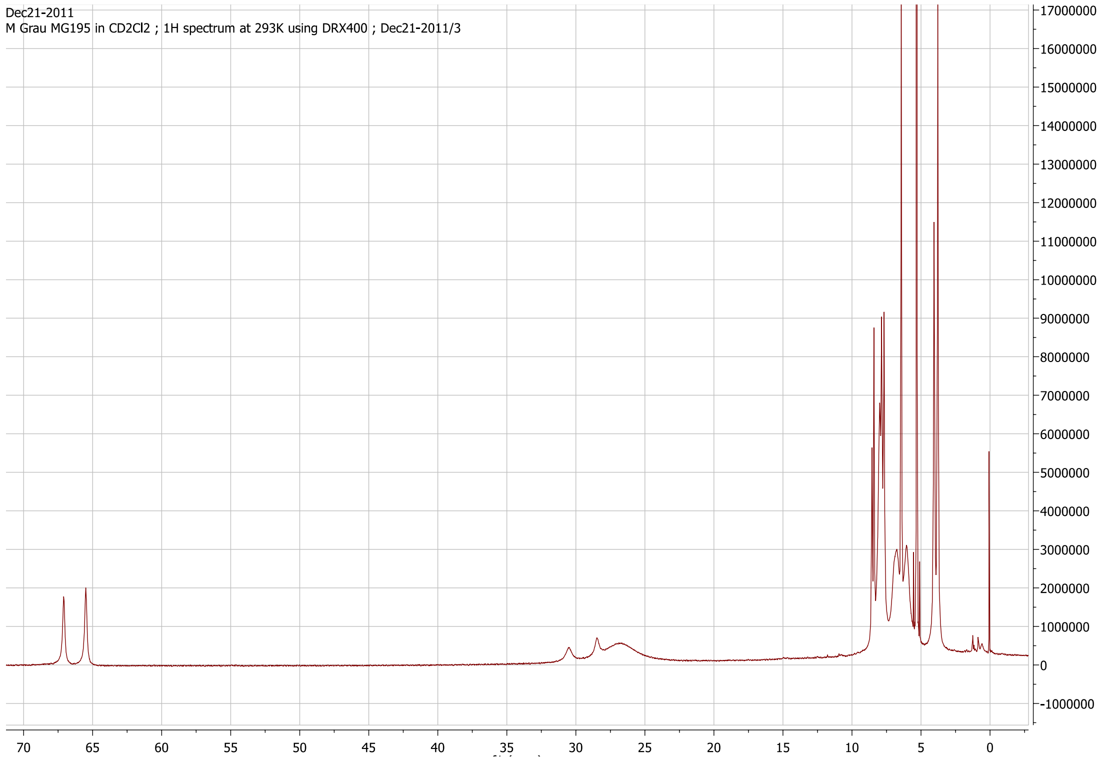

Figure S16. ^{1}H NMR spectrum of complex [Fe(**8**)(OTf)$_2$(thf)] in CD$_2$Cl$_2$ at 298 K.

Supporting Information — X-Ray Crystallography

The X-ray crystal structure of [Fe(**4**)(OTf)$_2$]$_2$

The included solvent molecules in the structure of the C_2-symmetric complex [Fe(**4**)(OTf)$_2$]$_2$ were found to be highly disordered, and the best approach to handling this very diffuse electron density was found to be the SQUEEZE routine of PLATON.[1] This suggested a total of 698 electrons per unit cell, equivalent to approximately 19.4 electrons per asymmetric unit. From an inspection of the electron density maps, combined with a knowledge of the solvents used, the most likely identity for the included solvent was deemed to be acetonitrile, MeCN, C_2H_3N (22 electrons). 1 acetonitrile molecule corresponds to 22 electrons, so this was used as the solvent present (equivalent to 2 per Fe_2 complex).

As a result, the atom list for the asymmetric unit is low by C_2H_3N (and that for the unit cell low by $C_{72}H_{108}N_{36}$) compared to what is actually presumed to be present.

The X-ray crystal structure of [Fe(**8**)(OTf)$_2$(thf)]

The C(15)-based methyl ester unit in the structure of [Fe(**8**)(OTf)$_2$(thf)] was found to be disordered, as was the S(40)-based triflate moiety, and the O(60)-based coordinated thf molecule. In each case two orientations were identified, of *ca.* 81:19, 89:11 and 70:30% occupancy respectively. For each pair of orientations the geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The X-ray crystal structure of [Fe(**6'**)(OH)]$_2$(OTf)$_2$

The unique S(30)-based triflate anion in the structure of the C_i-symmetric complex [Fe(**6'**)(OH)]$_2$(OTf)$_2$ was found to be disordered. Two orientations were identified of *ca.* 85 and 15% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The unique O(20)–H hydrogen atom was located from a ΔF map and refined freely subject to an O–H distance constraint of 0.90 Å.

Figures

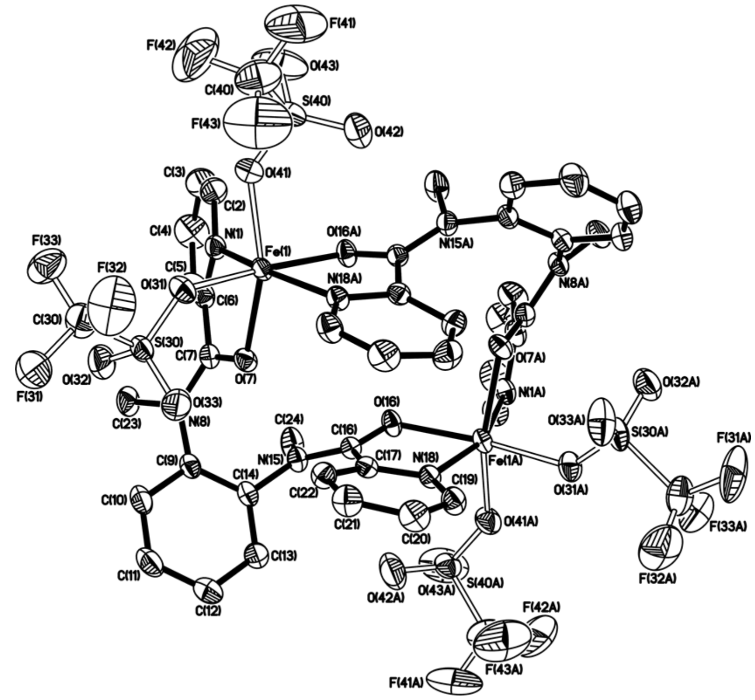

Fig. S19 The crystal structure of the C_2-symmetric complex [Fe(**4**)(OTf)$_2$]$_2$ (50% probability ellipsoids).

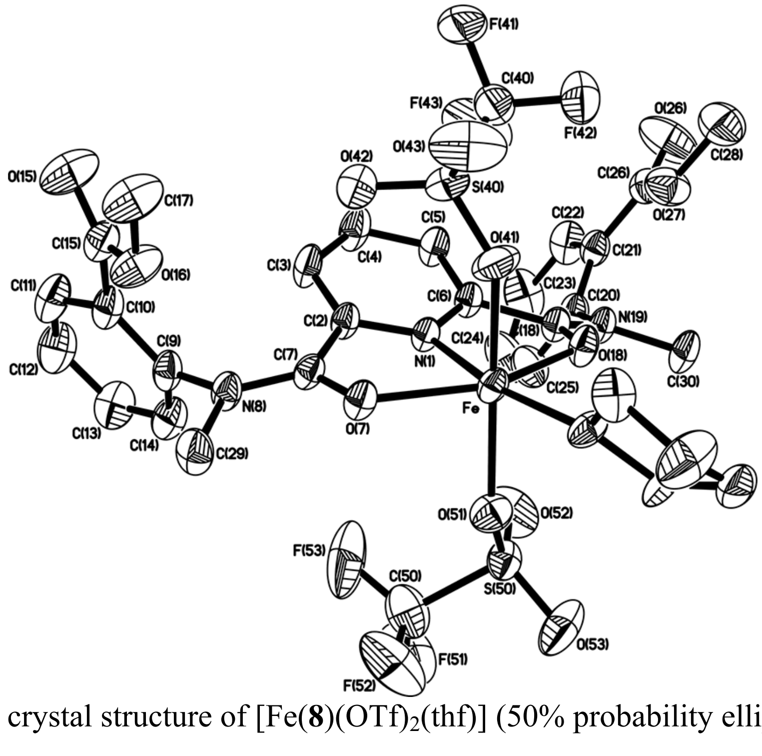

Fig. S20 The crystal structure of [Fe(**8**)(OTf)$_2$(thf)] (50% probability ellipsoids).

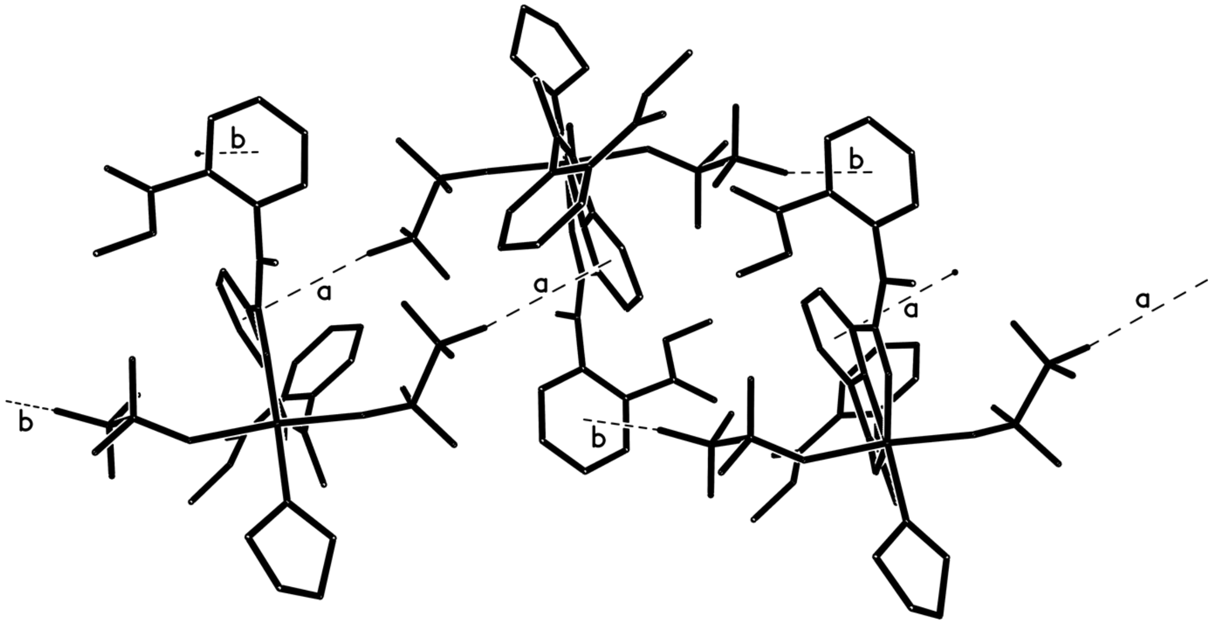

Fig. S21 Part of one of the F···π linked chains of molecules present in the crystal of [Fe(**8**)(OTf)$_2$(thf)].

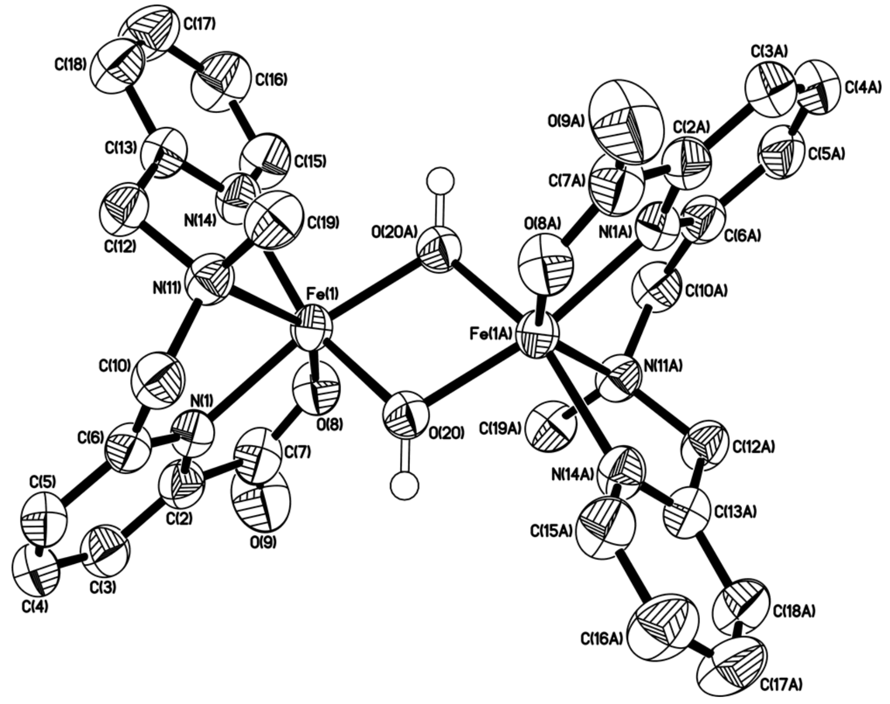

Fig. S22 The structure of the C_i-symmetric di-cation present in the crystal of [Fe(**6'**)(OH)]$_2$(OTf)$_2$ (50% probability ellipsoids).

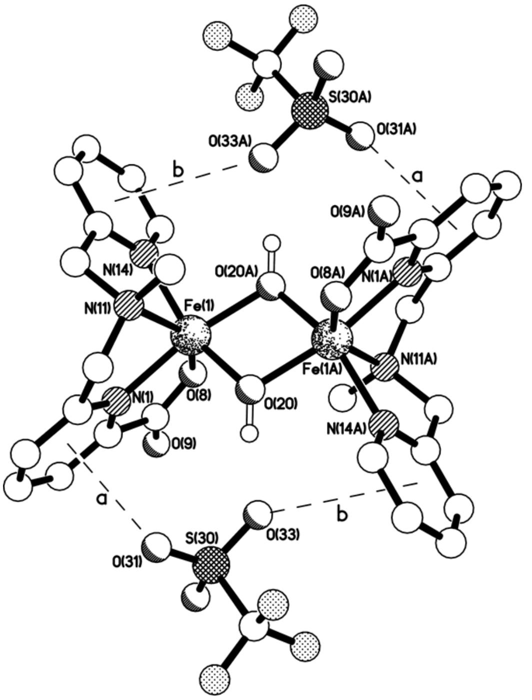

Fig. S23 The crystal structure of [Fe(**6'**)(OH)]$_2$(OTf)$_2$ showing the O···π interactions between the triflate anions and the di-cationic complex.

References

[1] A.L. Spek (2008) PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands. See also A.L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.