Supporting Information

Thiocyanate Anchors for Salt-like Iron(II) Complexes on Au(111): Promises and Caveats

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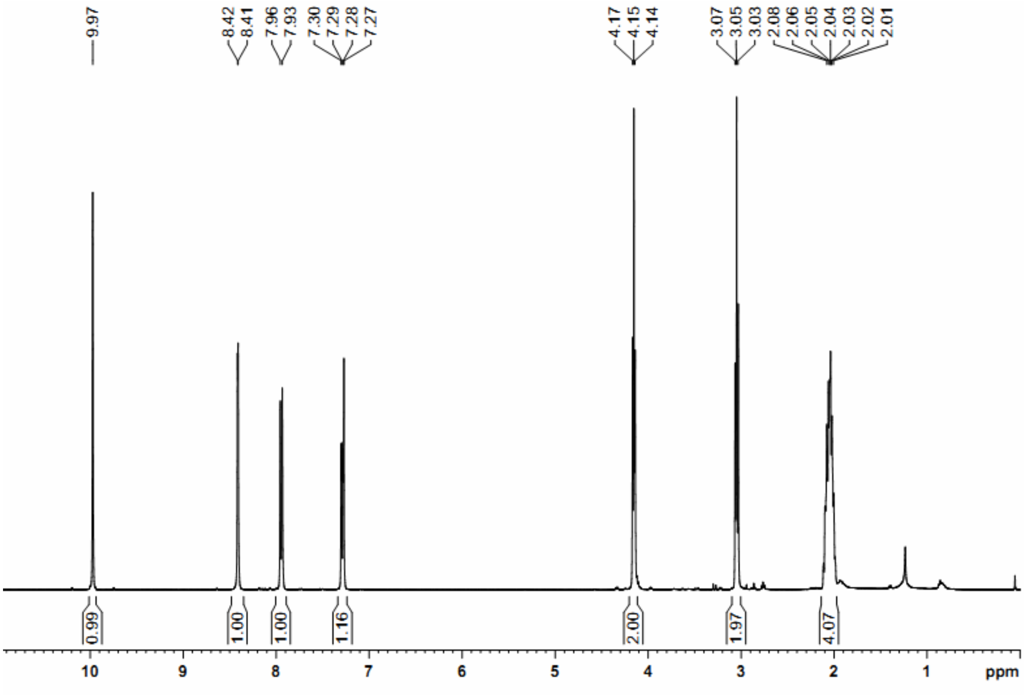

Figure S1. ^{1}H NMR of **3** in CDCl$_3$.

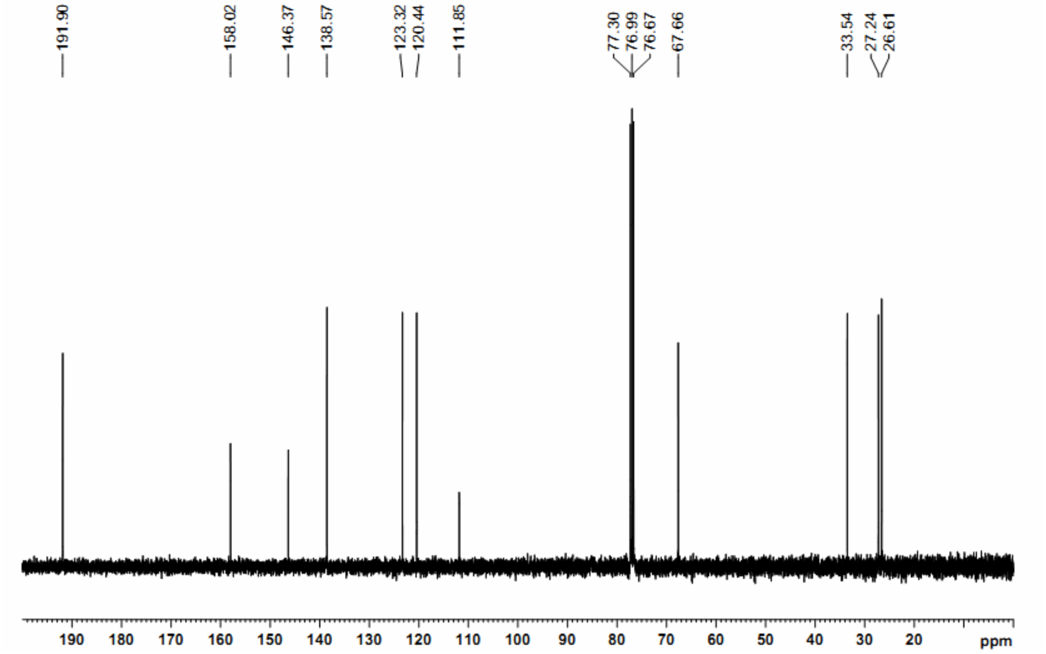

Figure S2. {^{1}H}^{13}C NMR of **3** in CDCl$_3$**.**

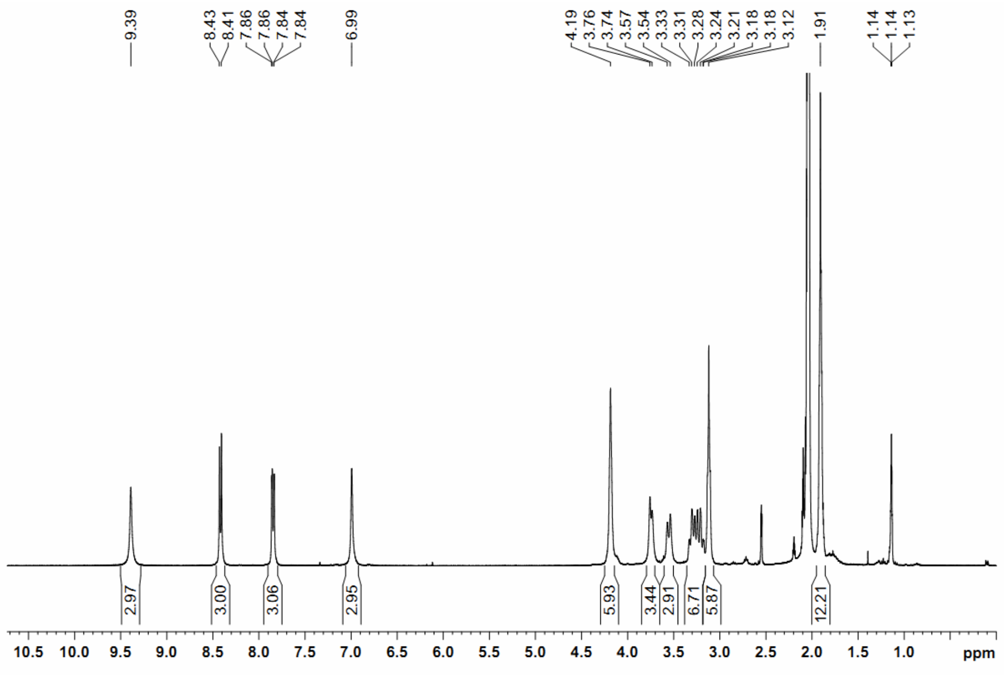

Figure S3. ^{1}H NMR of **6** in [D6]acetone.

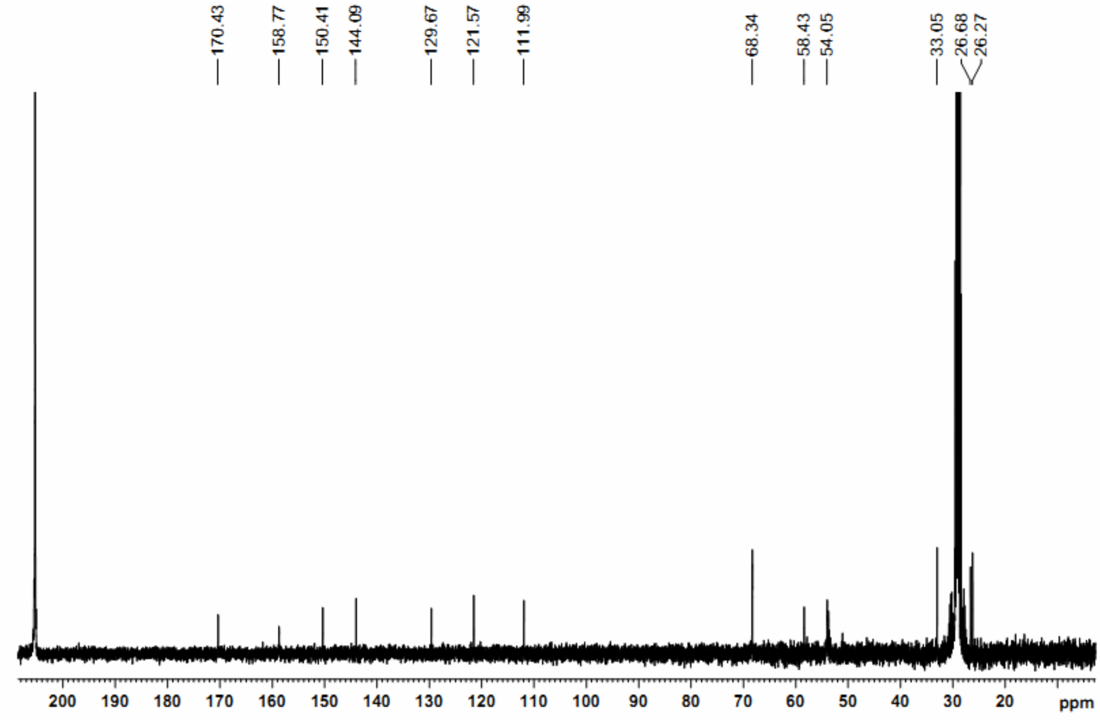

Figure S4. {^{1}H}^{13}C NMR of **6** in [D6]acetone.

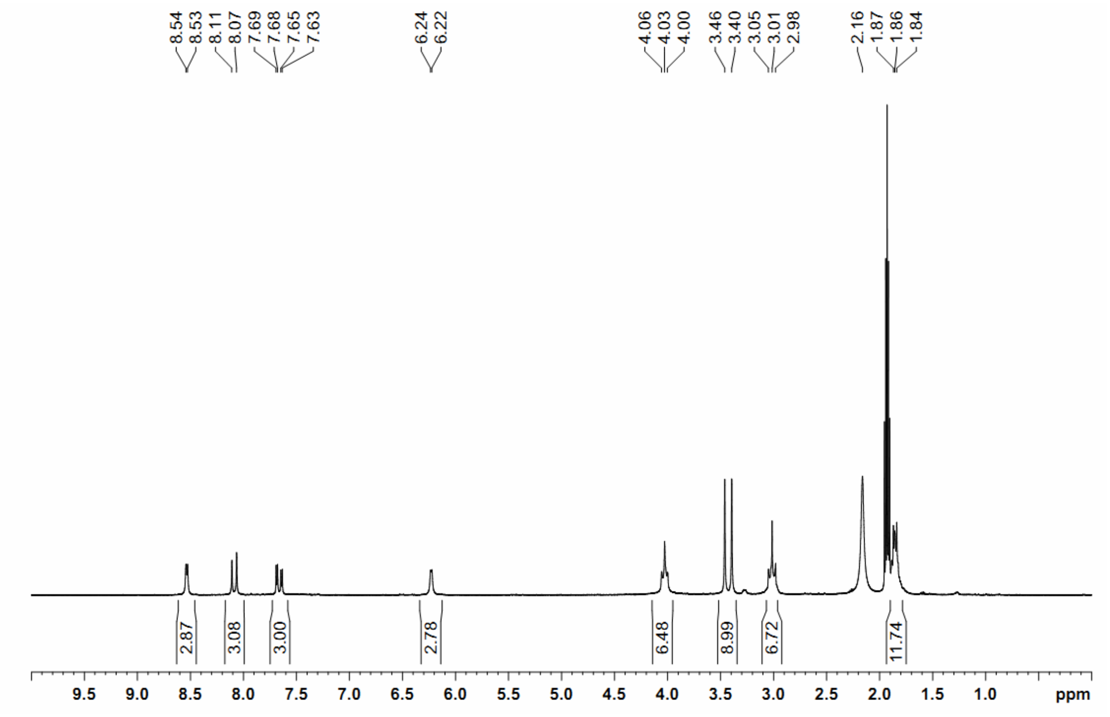

Figure S5. ^{1}H NMR of **7** in [D3]MeCN.

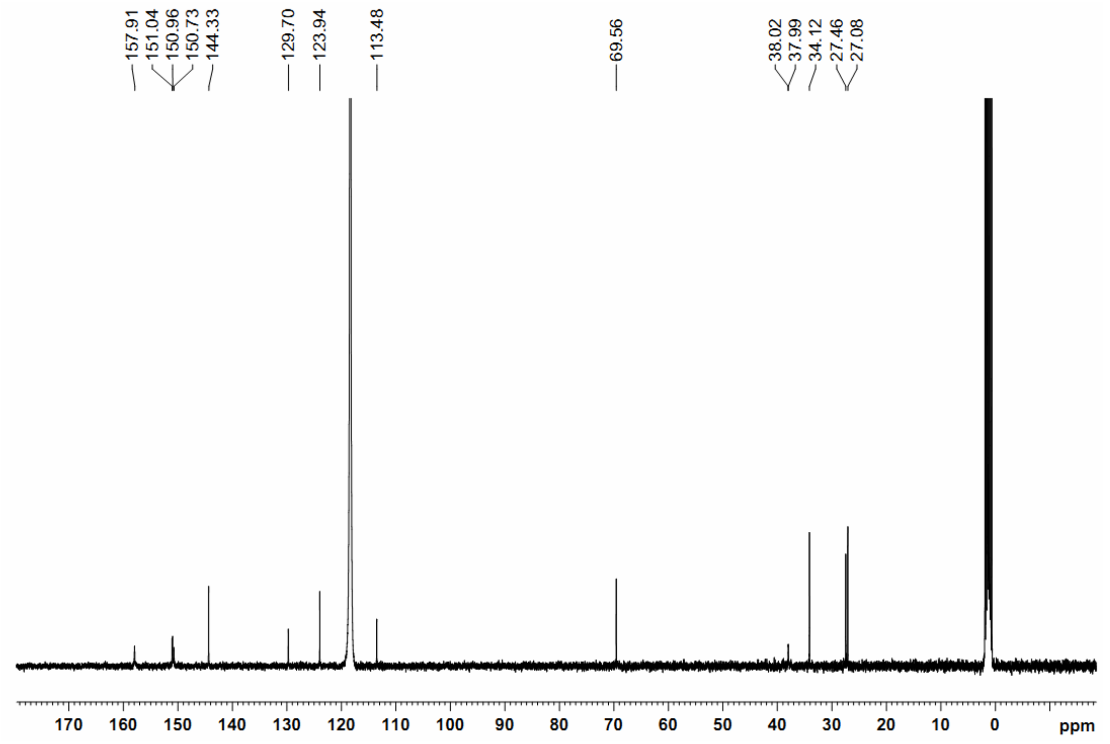

Figure S6. {^{1}H}^{13}C NMR of **7** in [D3]MeCN.

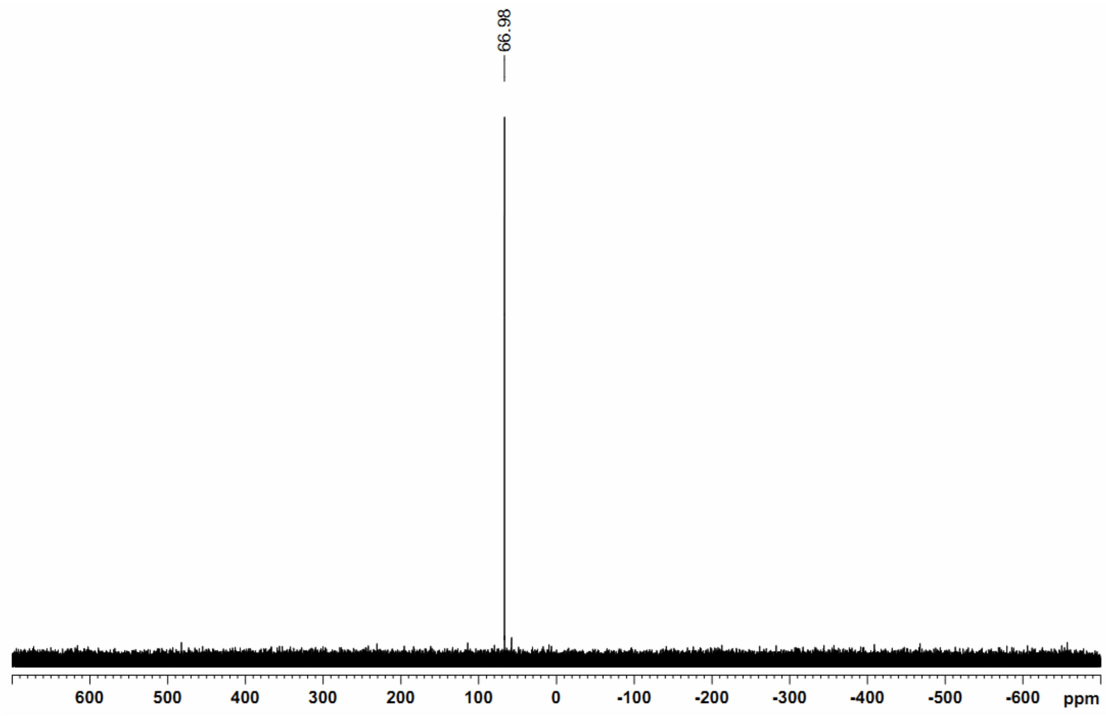

Figure S7. {^{1}H}^{31}P NMR of **7** in [D3]MeCN.

Bulk magnetic behaviour

Solid-state variable-temperature magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL5 SQUID (superconducting quantum-interference device) magnetometer operating at 0.1 T. Diamagnetic corrections for the sample and the sample holder were applied.

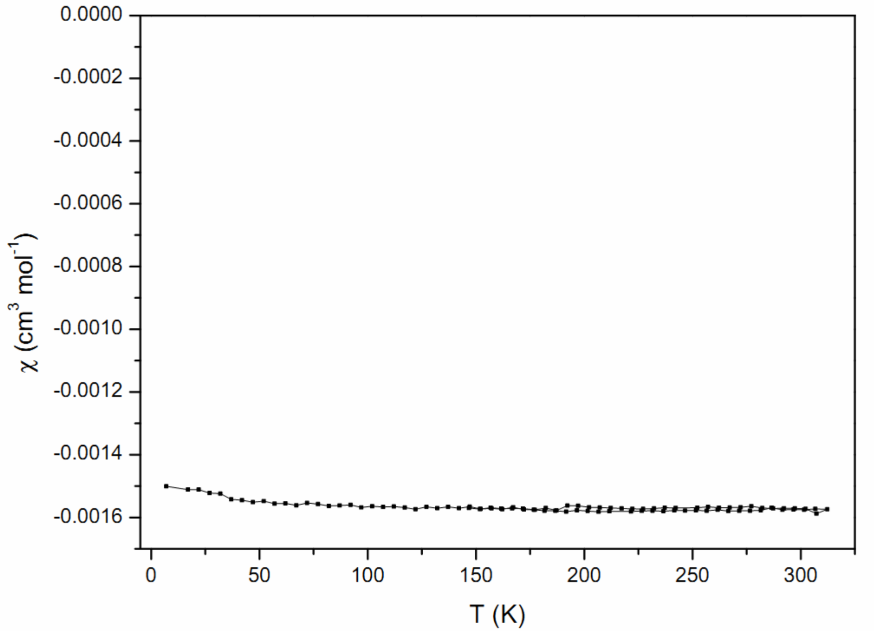

Figure S8. SQUID measurement of compound **6^{Fe}**.

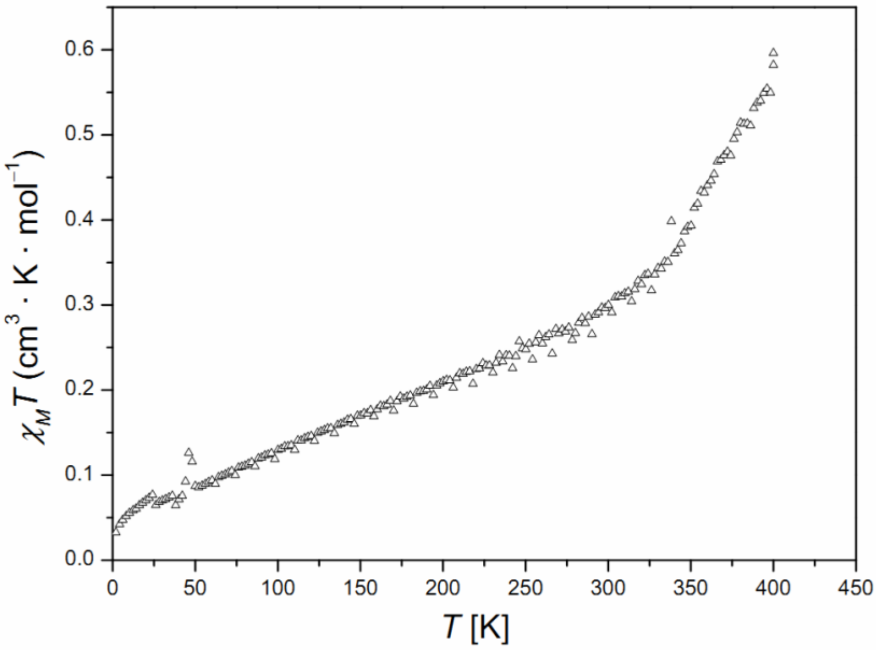

Figure S9. Magnetic susceptibility $\chi_M T$ of compound **7**

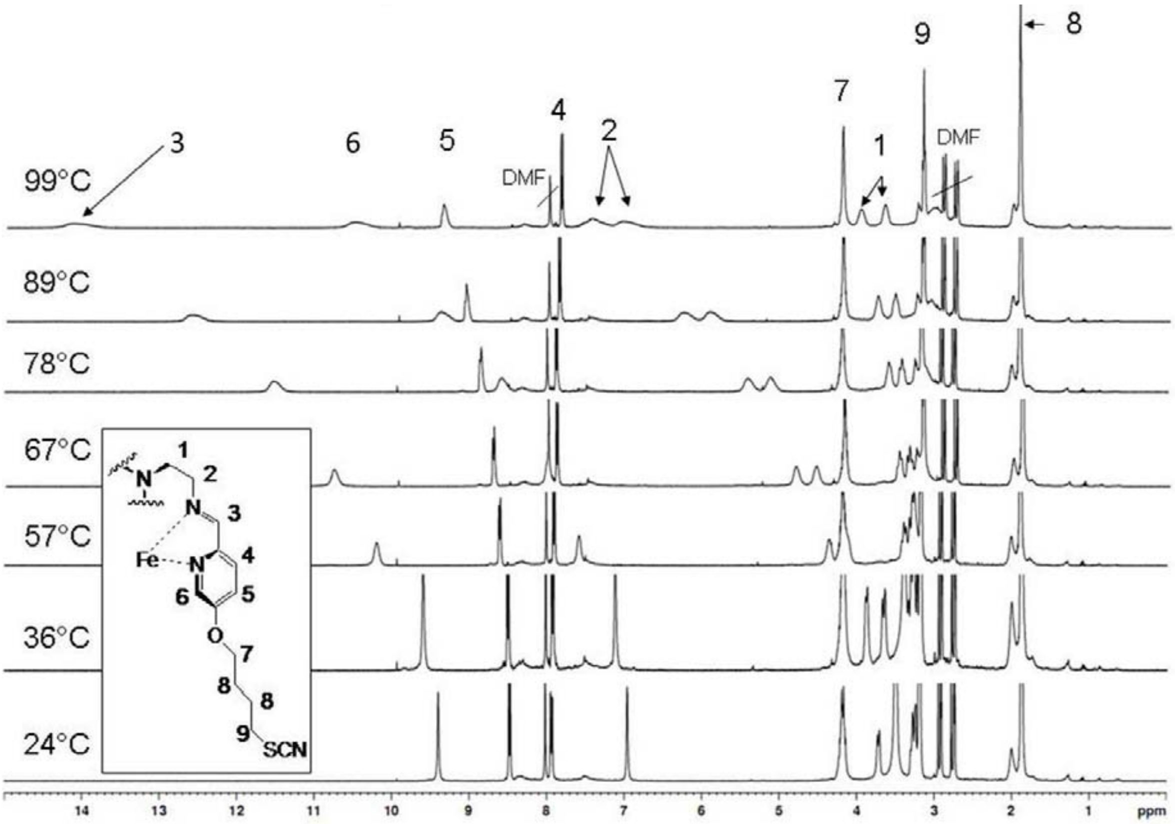

Figure S10. Temperature-dependent ^{1}H NMR spectrum of $\mathbf{6^{Fe}}$ (400 MHz, (D7)DMF).

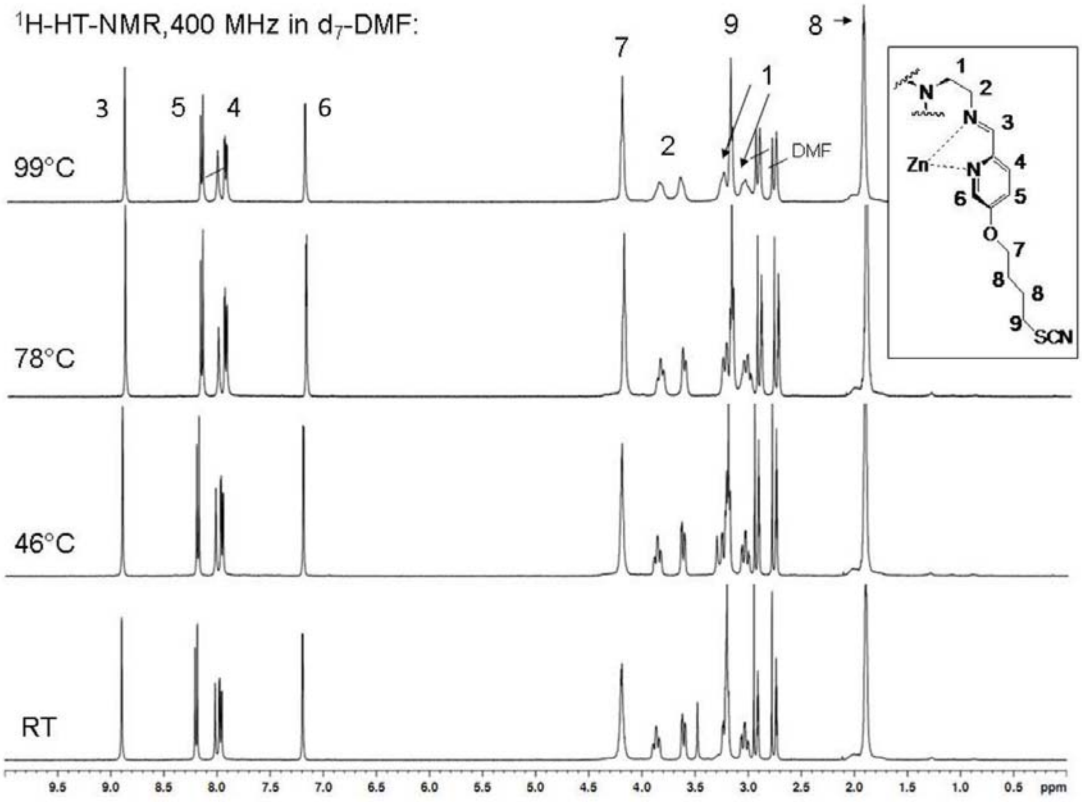

Figure S11. Temperature-dependent ^{1}H NMR spectrum of the zinc complex, $\mathbf{6^{Zn}}$ (400 MHz, (D7)DMF).

UV/Vis Reflectance Spectroscopy: Methods and additional spectra

UV/Vis reflectance spectra at an angle of incidence of 80° in p-polarization were obtained using the following procedure: The retarder was removed from the beam path of the spectroscopic ellipsometer, and both polarizer and analyser were set to p-polarization. The raw intensities I_{mod} of the modified samples were recorded. Using the same setting for the integration time, the detector dark current I_{dark} was measured. In a reference measurement, the reflected intensity I_{ref} from an unmodified, freshly prepared gold surface was recorded. The reflectance absorbance was then computed as $-\log_{10}((I_{\mathrm{mod}}-I_{\mathrm{dark}})/(I_{\mathrm{ref}}-I_{\mathrm{dark}}))$. P-polarization at high incidence angles was used in order to probe transition dipole moment components that are perpendicular to the surface. Only these can be excited on a metallic surface. Spectroscopic ellipsometry at angles of incidence of 50° and 70° was used to determine the thickness d of the adsorbed layers. Briefly, the experiment measures the ratio $r_p/r_s = \tan(\Psi)\ e^{i\Delta}$ (with $i = \sqrt[2]{-1}$) between amplitude reflection coefficients r_{p} for p- and r_{s} for s-polarized light. This ratio is expressed using the two ellipsometric angles Ψ and Δ.[S1, S2] The difference between treated samples and an unmodified gold surface was analysed. For a layer which is thin compared to the wavelength of light, with refractive index n_{s}, the difference in $r_{\mathrm{p}}/r_{\mathrm{s}}$ between covered and uncovered surface is directly related to the first order perturbation parameter, $J_1 = d\ (1-n_s^2)(\ n_s^2-\mathrm{n}_{\mathrm{Au}}^2)/\ n_s^2$.[S3] The wavelength-dependent values of the refractive index n_{Au} of gold were taken from the literature.[S4]

For the surface modification, an isotropic layer of thickness 2.4 nm and a wavelength-independent refractive index of 1.5 were assumed to be adsorbed to gold. These parameters described the obtained ellipsometric data quite well (see section on ellipsometry in the manuscript). For such a system, the dotted line in Figure 2b shows the same slope in the baseline as present in the experimental data, indicating that this feature is not related to absorptions from a layer adsorbed to the surface. In order to understand the effects that a surface layer of finite absorbance has on the shape of the spectra, simulations were carried out in which the dielectric function of the layer was represented by a sum of five harmonic oscillators. Input parameters for oscillator frequency and width were obtained by fitting the UV/VIS spectrum in solution (Figure 3a and Fig. S13a) with a sum of Lorentzian peaks. Absorption features from the molecules deposited on the surface show as additional peaks on top of the baseline.

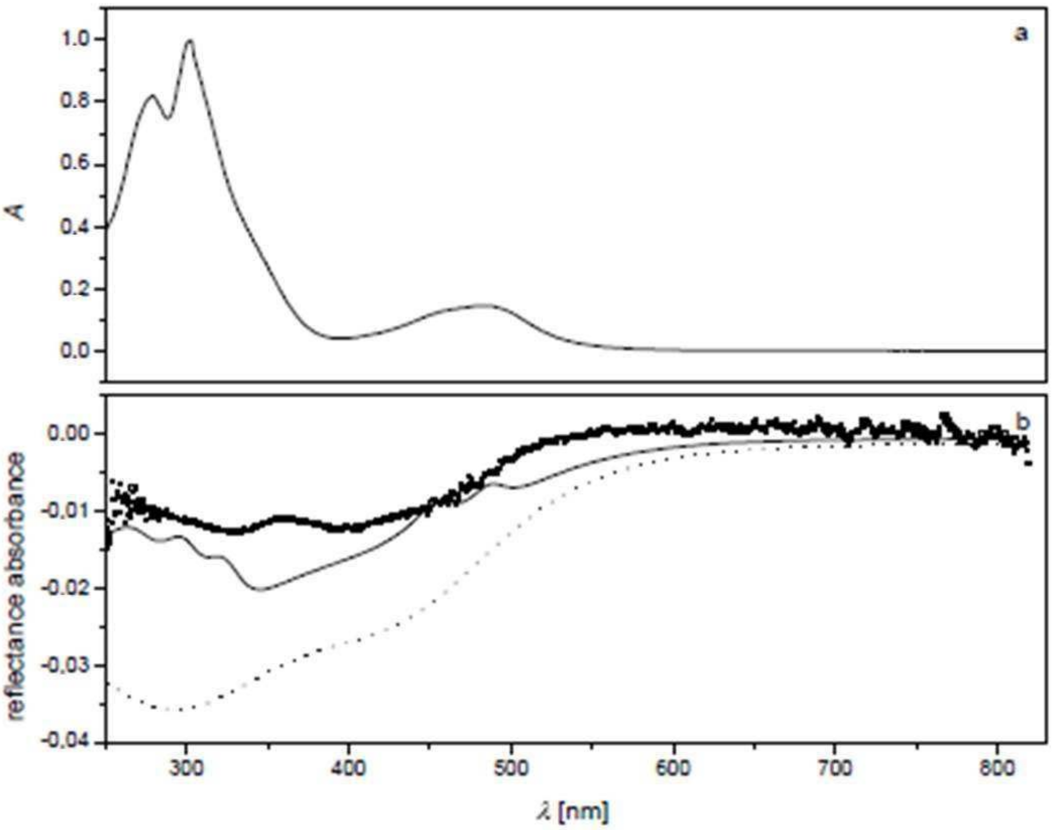

Figure S12. UV/VIS spectra of **7**; (a) measured in transmission in methanol solution; (b) measured in reflection on Au(111); dotted line: simulation of a non-absorbing layer (2.4 nm; refractive index 1.5) on Au; black solid line: simulation of a spectrum with 5 harmonic oscillators with resonance frequencies as obtained from (a).

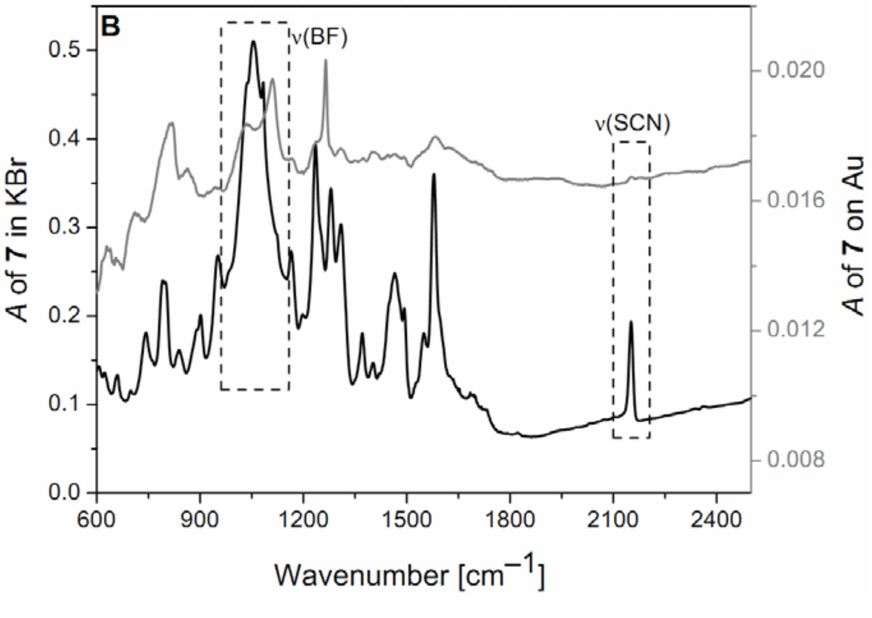

Figure S13. IR spectra of compound **7**. Characteristic absorptions are highlighted by dashed boxes. Grey: sample layer on gold. Black: sample measured as KBr disc.

Reference compound for 7 in control adsorption studies

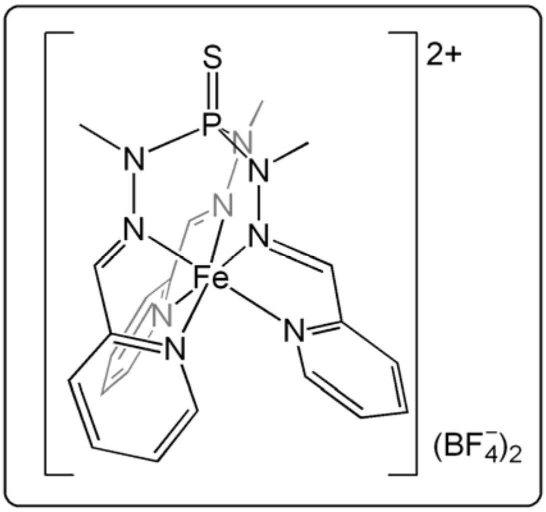

Figure S14. Molecular structure of [Fe{'phos(py)$_3$'}](BF_4)$_2$ (**SI_1**)

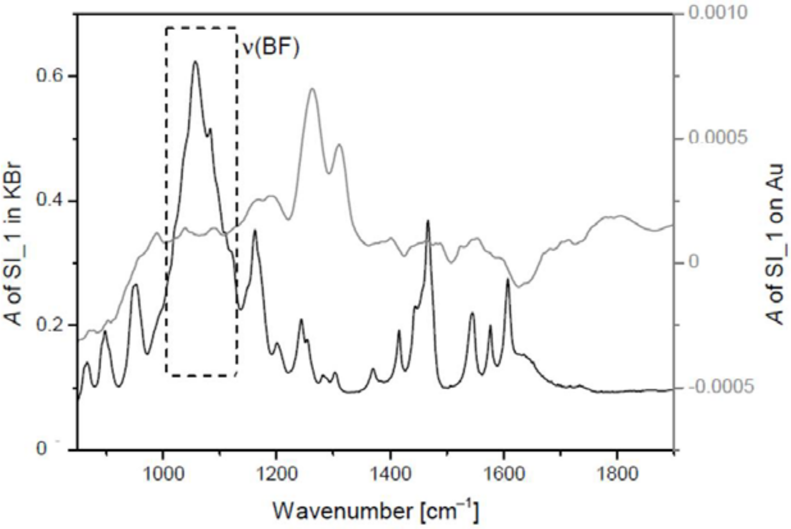

Figure S15. IR spectra of compound **SI_1**. Characteristic absorptions are highlighted by dashed box. Grey: sample layer on gold. Black: sample measured as KBr disc.

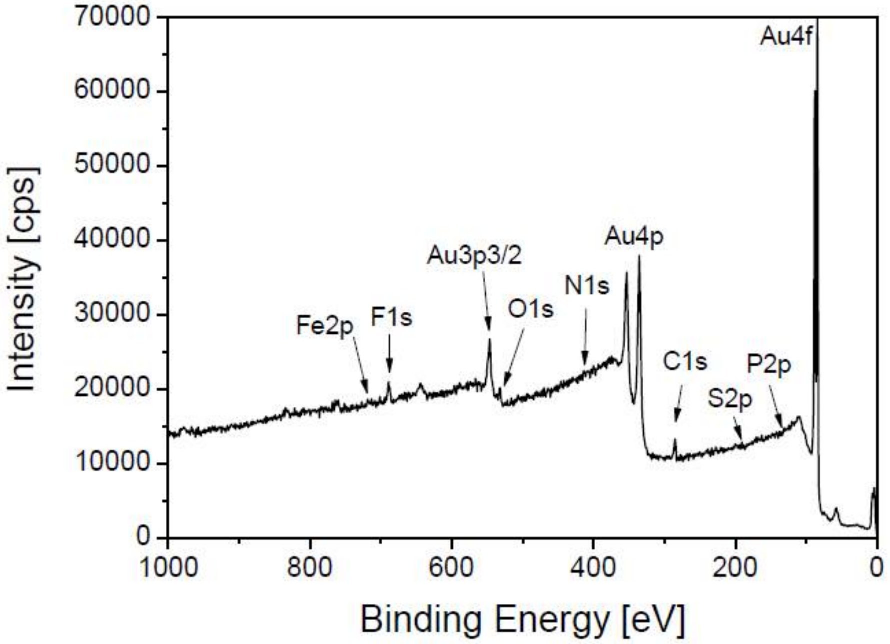

Figure S16. XPS spectrum (survey scan) of **SI_1** on gold**.**

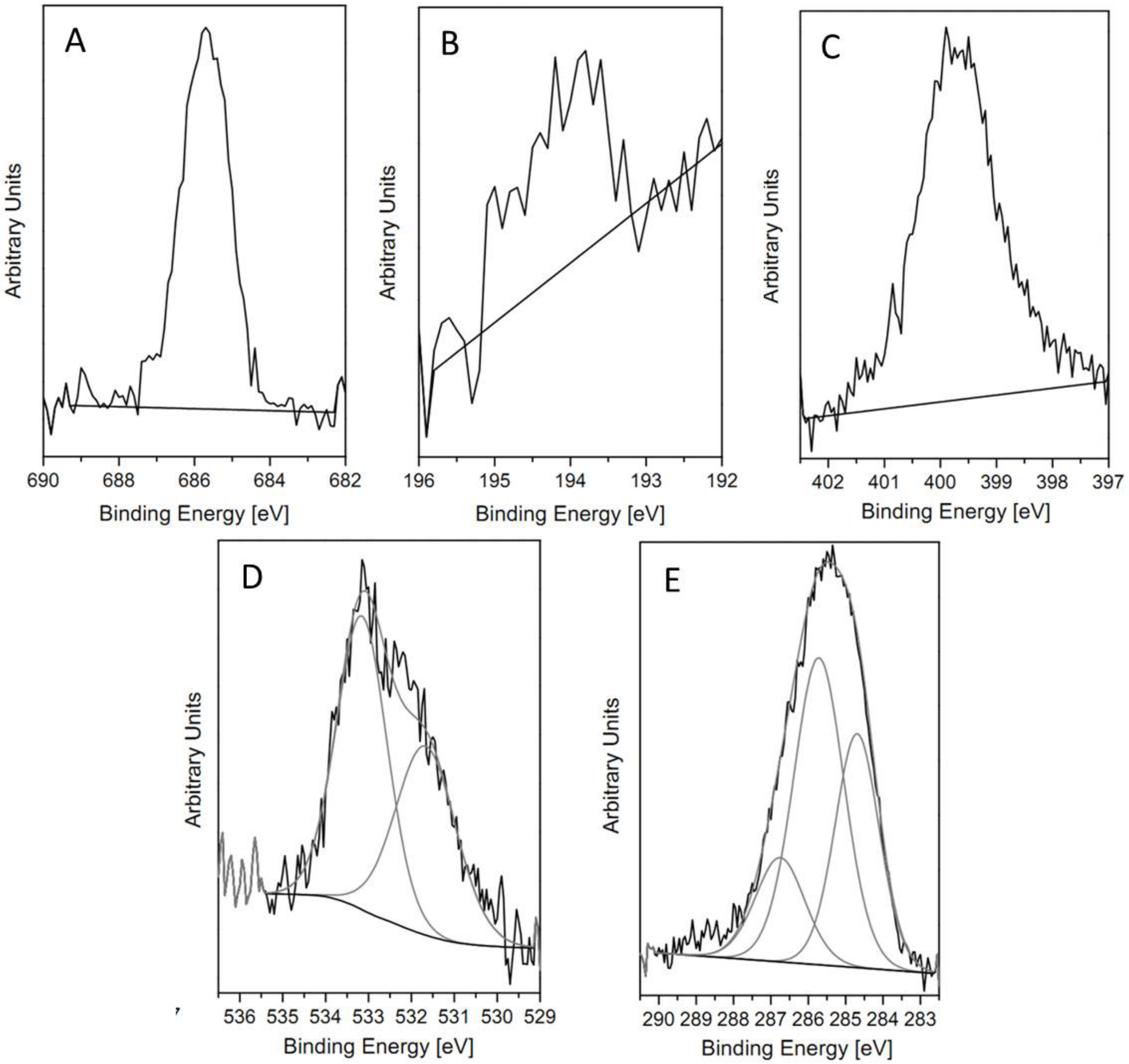

Figure S 17. XPS spectra of a layer of $\mathbf{6^{Fe}}$ adsorbed on Au(111): (A) F 1s, (B) B 1s, (C) N 1s, (D) O 1s, (E) C 1s,. All spectra show the baselines used to calculate the intensity of the signals.

References

(S1) H. Fujiwara, Principles of Spectroscopic Ellipsometry in *Spectroscopic Ellipsometry: Principles and Applications*, John Wiley & Sons, Chichester, **2007**.

(S2) R. M. A. Azzam, N. M. Bashara, *Ellipsometry and Polarized Light*, Elsevier Science, Amsterdam, **1999**.

(S3) J. Lekner, *Theory of Reflection of Electromagnetic and Particle Waves*, M. Nijhoff Publishers, Dordrecht, **1987**.

(S4) P. G. Etchegoin, E. C. Le Ru, M. Meyer, An analytic model for the optical properties of gold, *J. Chem. Phys.* **2006**, *125*, 164705–164708.