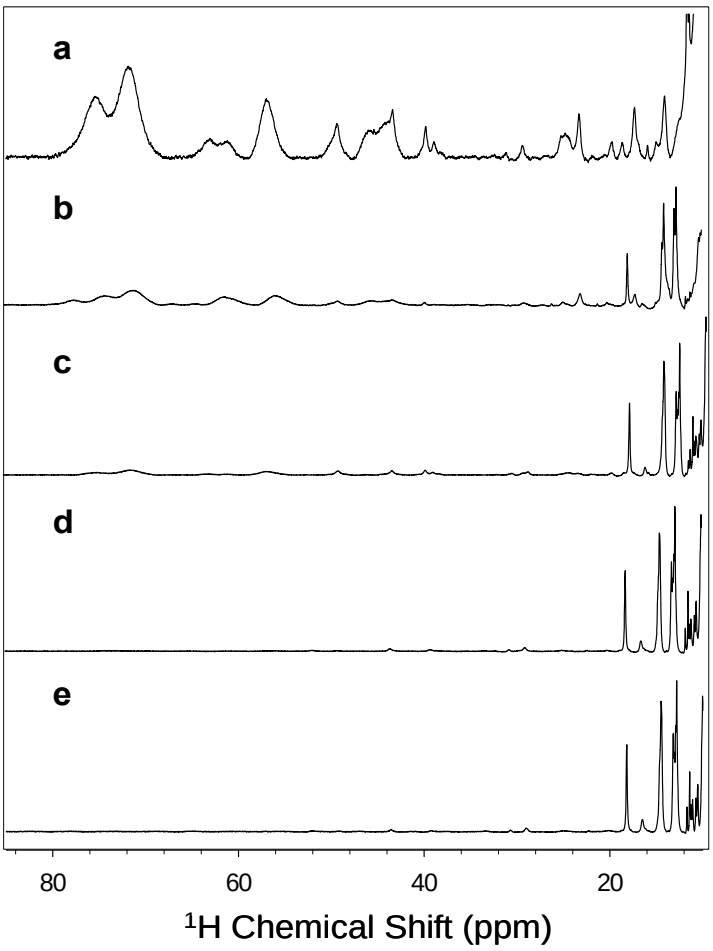
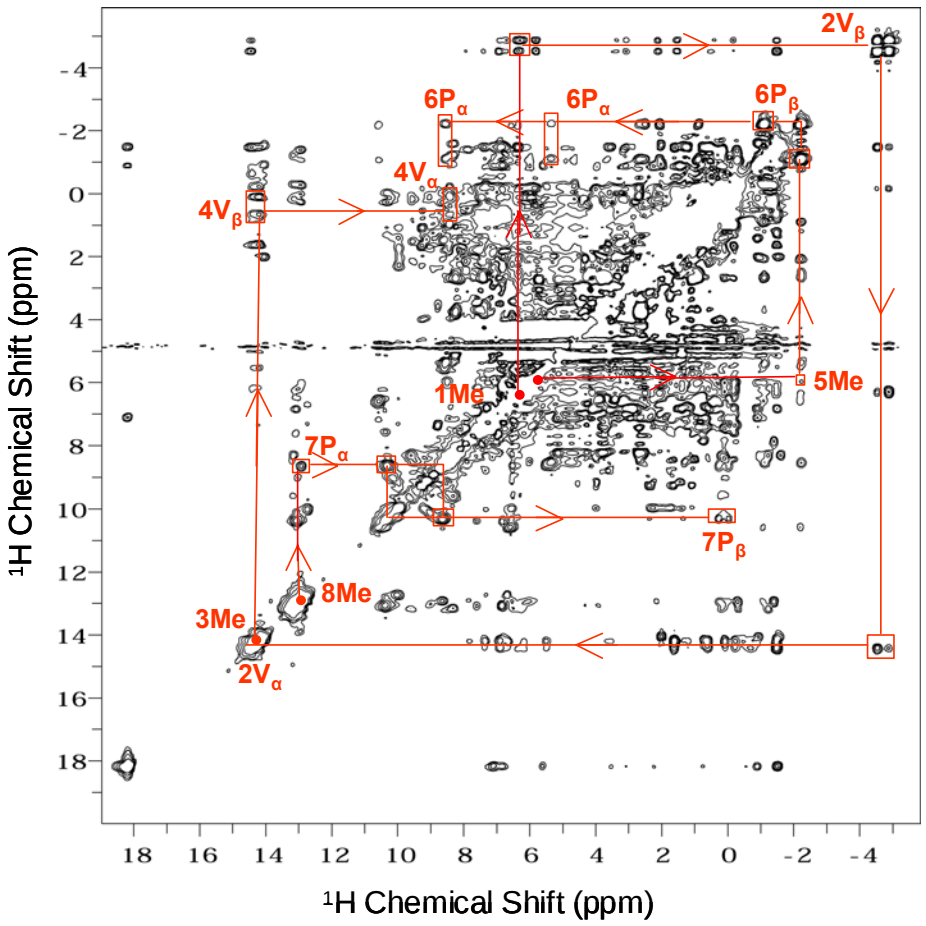
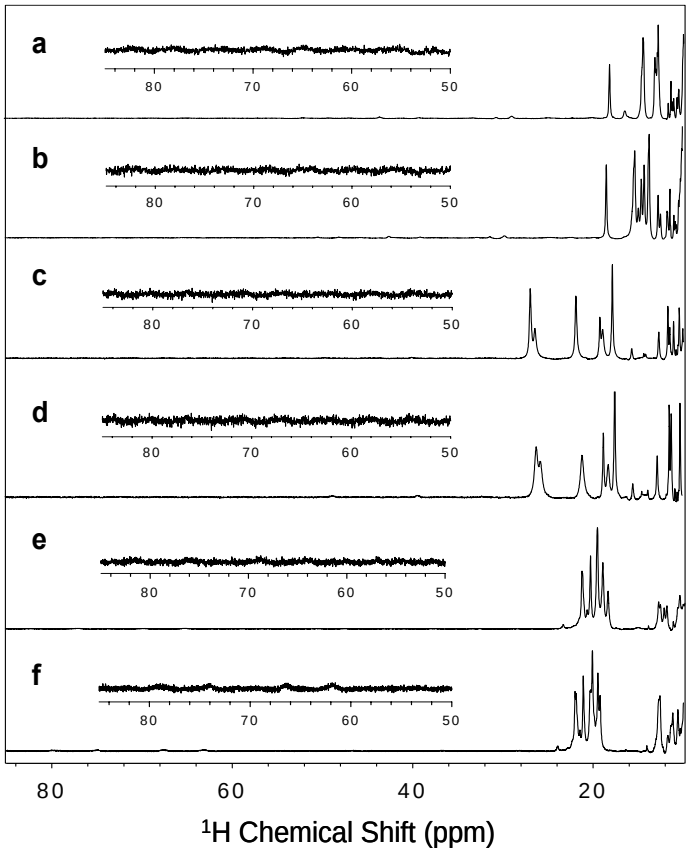


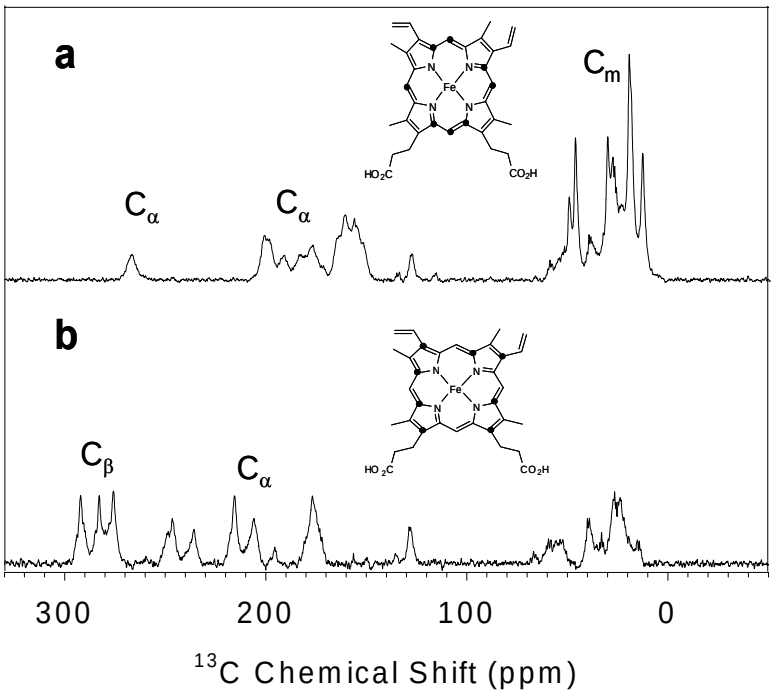
S1. High frequency portion of the ^{1}H NMR spectra (25 °C) of (a) *pa*-HO resting state and after addition of (b) 0.5, (c) 1, (d) 10 and (e) 15 equivalents of sodium azide.



S2. WEFT-NOESY spectrum of the *pa*-HO-N_3 complex obtained at 25 ºC. Resonances are assigned by following the dipolar connectivities indicated by red lines. The chemical shifts of the heme methyl resonances are indicated by red dots in the diagonal and the order of these resonances is 3Me > 8Me > 1Me > 5Me.



S3. High frequency portions of the ^{1}H NMR spectra of *pa*-HO in the presence of 15 equivalents of NaN_3 acquired at (a) 25 °C and (b) 35 °C. (c) and (d) High frequency portions of the ^{1}H NMR spectra of *pa*-HO-OH (pD 10.0) acquired at 25 °C and 35 °C, respectively. (e) and (f) High frequency portion of the ^{1}H NMR spectra of *nm*-HO in the presence of 25 equivalents of NaN_3 obtained at 25 °C and 35 °C, respectively. The inset in each plot shows a 10x magnified spectrum between 50 ppm to 85 ppm. Traces of a high-spin component (less than 3%) were only observed in *nm*-HO-N_3 at 35 °C (f).



S4. Non-decoupled ^{13}C NMR spectra of azide-inhibited *pa*-HO obtained at 35 ºC. (a) *pa*-HO-N_3 complex with heme labeled at C_α and C_m. (b) *pa*-HO-N_3 complex with heme labeled at C_α and C_β.