

Figure S1: (a) Simulation of the basic frequency correlation ridges for a spin system with $S=1/2$ and $I=1/2$, assuming HFC tensors $^A\text{H}_{\beta_3}(\text{T1})$ (green), $^B\text{H}_{\beta_3}(\text{T1})$ (red), and $\text{H}_{\beta_2}(\text{T1})$, $\text{H}_{\beta_2}(\text{T2})$, $\text{H}_{\beta_3}(\text{T2})$, $\text{H}_{\beta_2}(\text{T3})$ and $\text{H}_{\beta_3}(\text{T3})$ (blue). (b) For reference purposes, only HFC tensors $^A\text{H}_{\beta_3}(\text{T1})$ (green) and $^B\text{H}_{\beta_3}(\text{T1})$ (red) are simulated here.

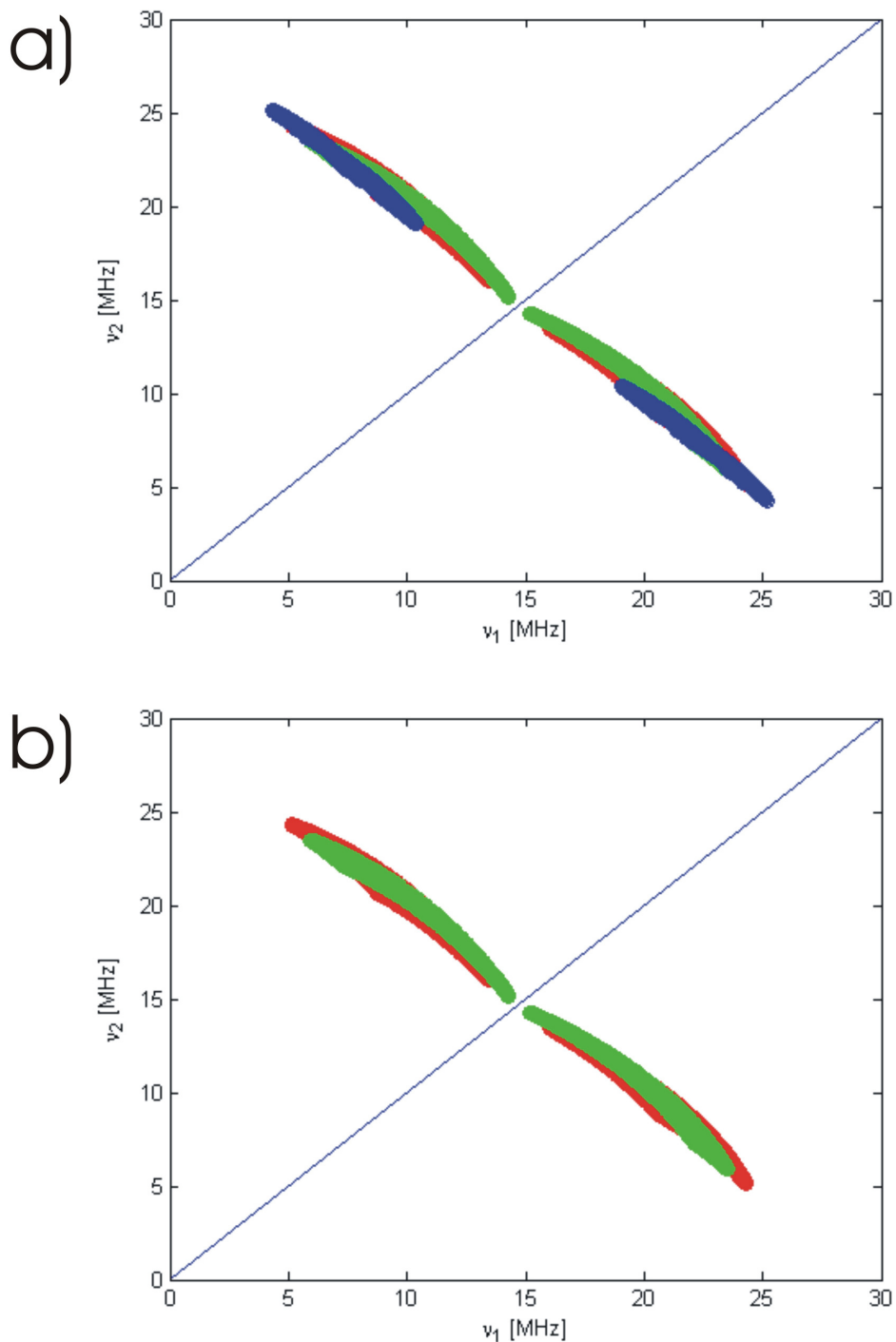


Figure S2: Simulation of the sum correlation ridges expected for a three-spin system $S=1/2$, $I_{\beta 2}=1/2$ and $I_{\beta 3}=1/2$ assuming the HFC tensors of (a) $H_{\beta 2}(T2)$ and $H_{\beta 3}(T2)$ and (b) $H_{\beta 2}(T3)$ and $H_{\beta 3}(T3)$.

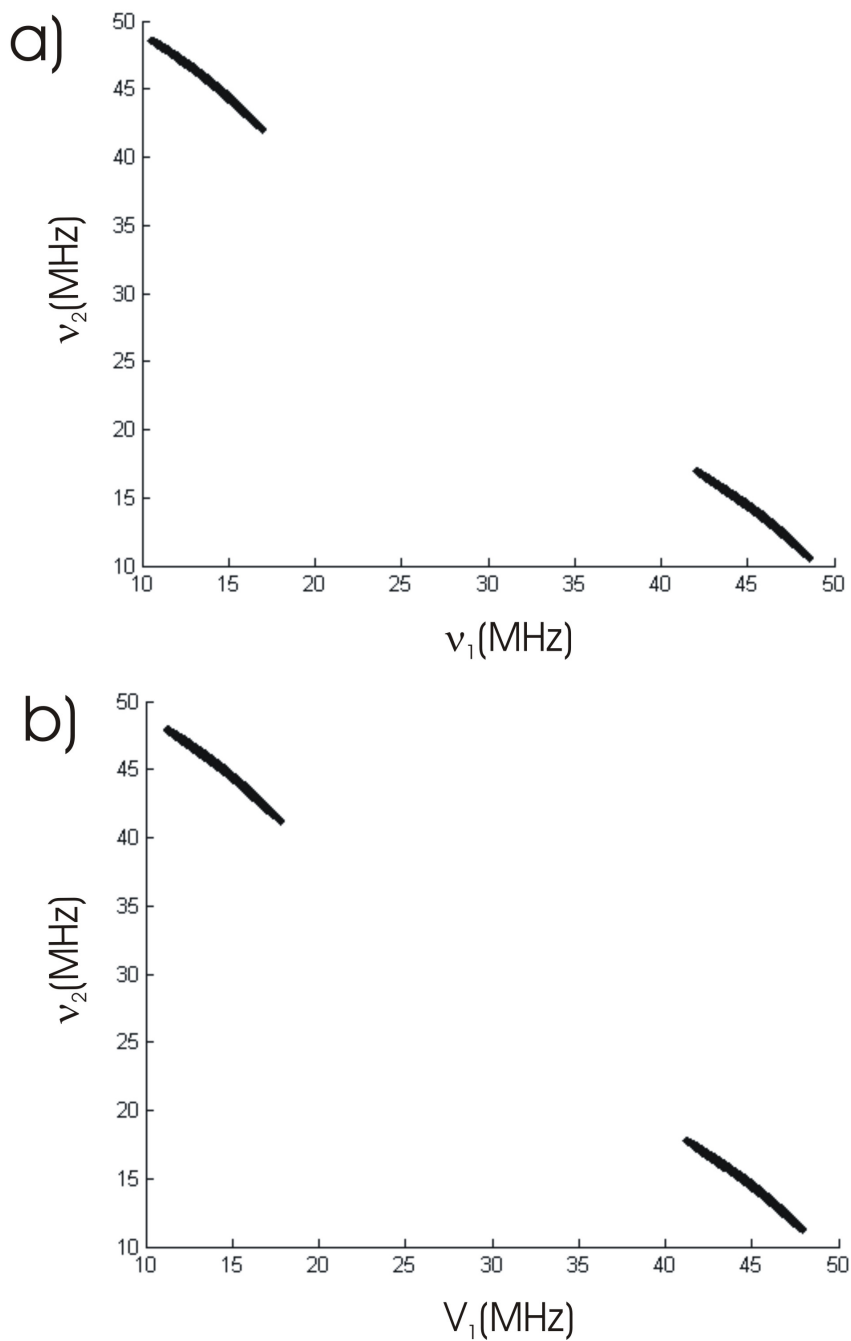


Figure S3: Energy profile for the rotation of the O1-HO1 hydroxy group about the O1-C1 bond in model M5 (see Figure 6 and Figure 9). A methodology identical to that used in ref. 8 was adopted: the proper dihedral angle HO1-O1-C1-C2 (D) was varied in 15° steps over 360° and for each value, a geometry optimisation (in an <ab2c> supercell) was performed for which the dihedral angle was constrained. Full circles indicate the results of constrained optimizations. The red triangle at $D \approx 315^\circ$, obtained by a non-constrained optimization, corresponds to the conformation of model M5 on which EMR calculations were performed (Figure 7 and Table 5). It has the lowest energy ($E = -2.708886.10^6$ kJ/mol) and was taken as reference for the energy scale. There is another, shallower local minimum at $D = 75^\circ$, but the geometry of the radical centre in this conformation is virtually identical to that in the global minimum, and this was therefore not further explored.

