Supplementary material for R. J. C. Dixey, F. Orlandi, P. Manuel, P. Mukherjee, S. E. Dutton and P. J. Saines, 2019, Emergent magnetic order and correlated disorder in formate metal-organic frameworks, Phil. Trans. R. Soc. A. doi: 10.1098/rsta.[paper ID in form xxxx.xxxx e.g. 10.1098/rsta.2014.0049]





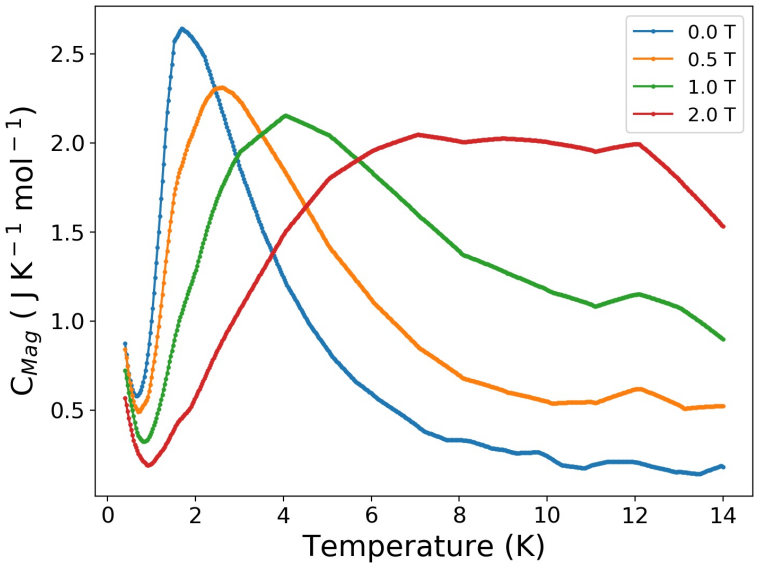
**Neutron diffraction experimental details**

$Tb(DCO_2)_3$ was loaded into an 8 mm copper can and sealed with indium wire, under a helium atmosphere. Measurements were carried out between 0.28 K to 1.95 K, with the sample cooled using a $^3$He Heliox sorption refrigerator. $Ln(DCO_2)_3$ (where *Ln* = Ce, Pr, Nd, Dy, Ho and Er) samples were loaded into 8 mm vanadium cans. Measurements were carried out between 1.6 K to 100 K, with the samples cooled using the standard Oxford Instruments WISH cryostat. Average structure neutron patterns were fitted in FULLPROF [46] using the Rietveld method. The aluminium and copper sample environment peaks were fitted with a Le Bail method. A linear interpolation of points were used to fit the background and using a profile function built from a convolution of back-to-back exponentials with a pseudo-Voight function TOF to fit the peak shapes. To isolate the total magnetic contribution to the neutron-scattering data, data collected at a high temperature $T_{high}$ were subtracted from the low-temperature data of interest, where $T_{high}$ = 20 K. Banks were merged over a Q range of 0.2 to 3.75 $Å^{-1}$ to improve statistics, areas with Bragg peak contamination excised and binned. The data were placed on an absolute intensity scale (barn $sr^{-1}$ $Ln^{-1}$) by normalisation to the calculated nuclear Bragg profile at $T_{high}$. Diffuse neutron patterns were fitted with the reverse monte carlo program - SPINVERT, [40] using a supercell of 52 x 54 x 55 $Å^3$ or 5 x 5 x 13 unit cells.

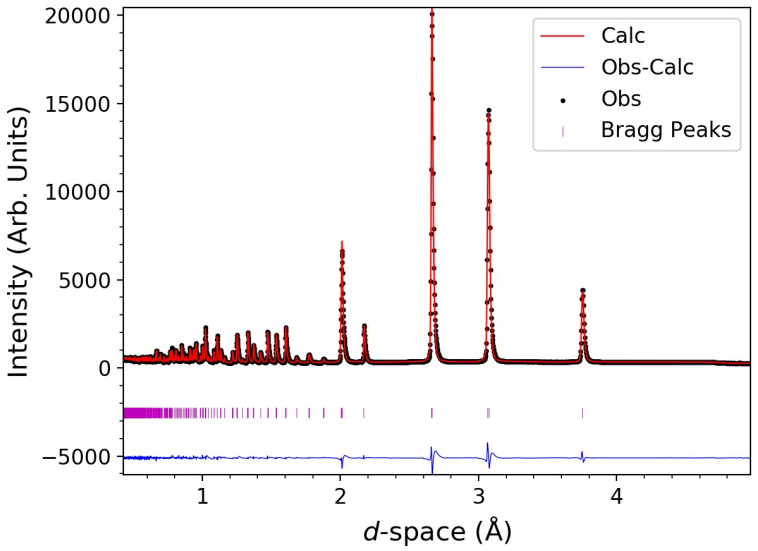
**Physical property measurements experimental details**

Heat capacity measurements were measured on a Quantum Design PPMS DynaCool with 14 T superconducting magnet and $^3$He insert, between 400 mK and 14 K. Samples were ground into a powder, mixed with an equal amount of powdered silver, to improve heat transfer, and pressed into a pellet. Addenda measurements were taken to allow for subtraction after measurement of the sample. To isolate the magnetic contribution to the heat capacity, the addenda, lattice (calculated from the Einstein-Debye equations), and the silver (interpolation of literature data) contributions were subtracted. [53] The 400 mK - 30 K magnetic measurements of the polycrystalline samples were performed using a Quantum Design MPMS SQUID magnetometer, with a $^3$He insert in a 100 Oe DC magnetic field.

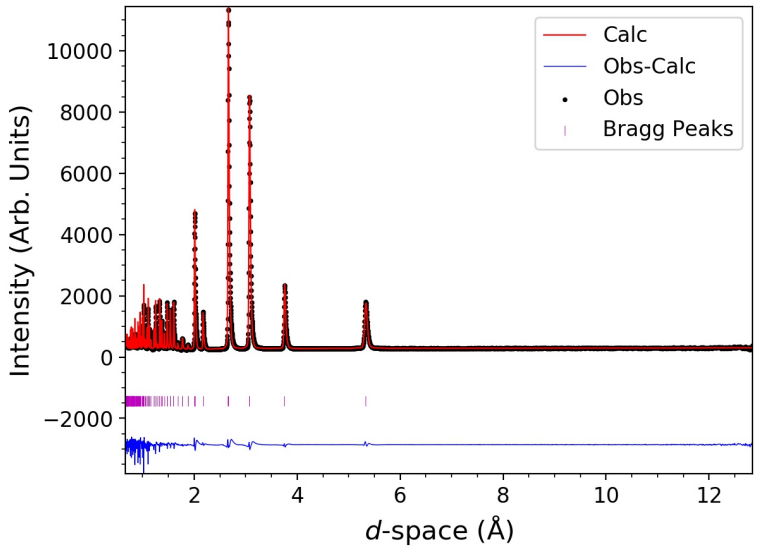
Appendix 1: Experimental Method Appendix



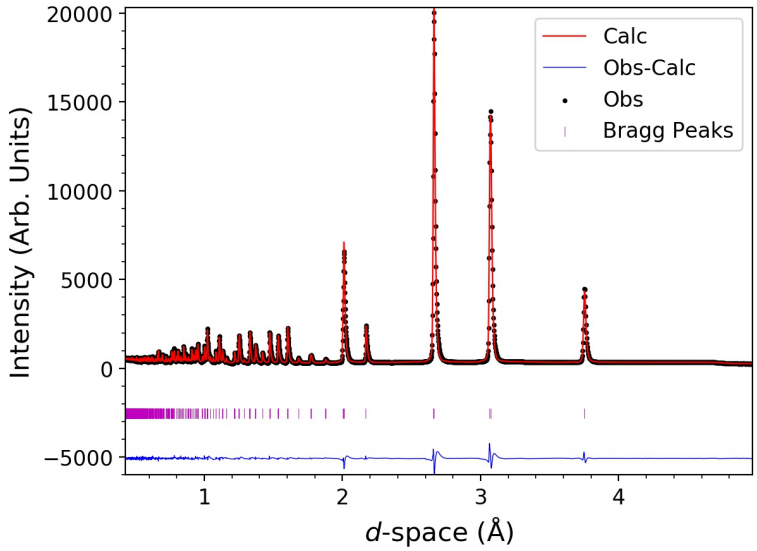

Supplementary Figure 1: $Tb(HCO_2)_3$ magnetic heat capacity - $C_{mag}$ in variable fields



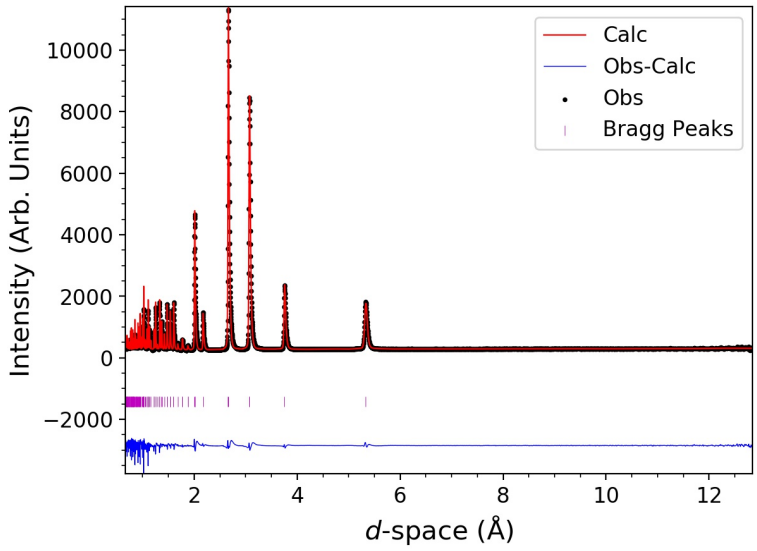

Supplementary Figure 2: Powder neutron diffraction pattern of $Ce(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.71 % and 6.21 % are obtained, respectively from the refinement. Unit cell parameters: $a$ = $b$ = 10.3905(32), $c$ = 4.11018(16) Å and a unit cell volume of 404.218(23) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



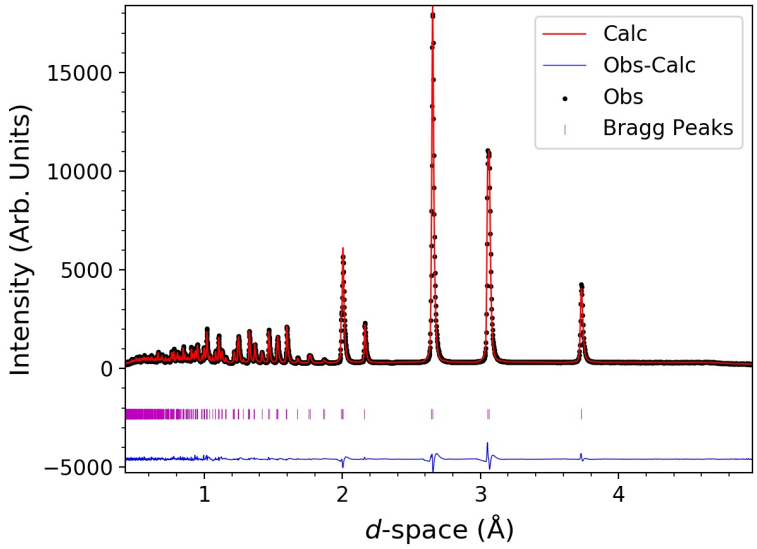

Supplementary Figure 3: Powder neutron diffraction pattern of $Ce(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 7.05% and 5.73 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.3905(32), $c$ = 4.11018(16) Å and a unit cell volume of 404.218(23) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



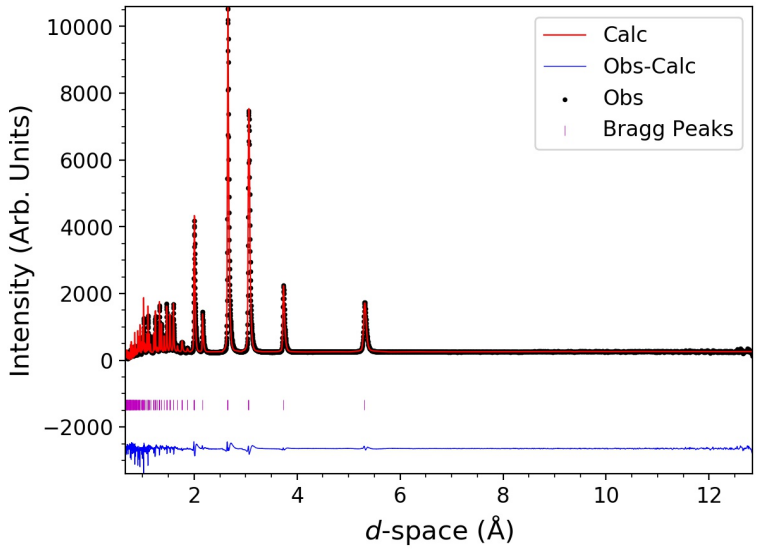

Supplementary Figure 4: Powder neutron diffraction pattern of $Ce(DCO_2)_3$ at 50 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.57% and 6.11 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.65754(13), $c$ = 4.11018(55) Å and a unit cell volume of 404.275(89) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



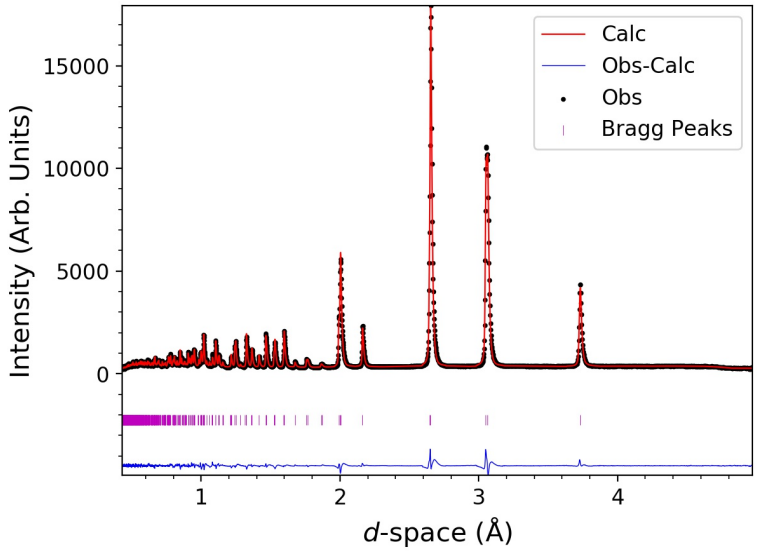

Supplementary Figure 5: Powder neutron diffraction pattern of $Ce(DCO_2)_3$ at 50 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 6.97% and 5.71 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.65754(13)$, $c = 4.11018(55)$ Å and a unit cell volume of 404.275(89) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



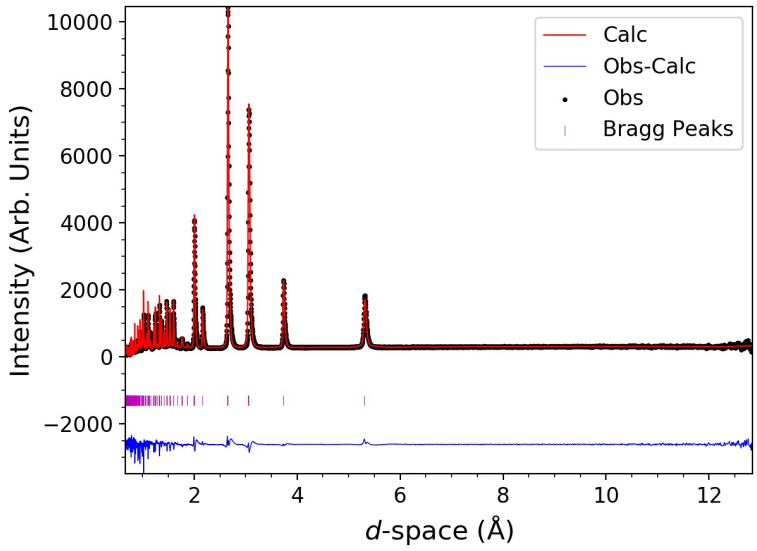

Supplementary Figure 6: Powder neutron diffraction pattern of $Pr(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.60 % and 5.83 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.61446(36)$, $c = 4.08233(18)$ Å and a unit cell volume of 398.322(26) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



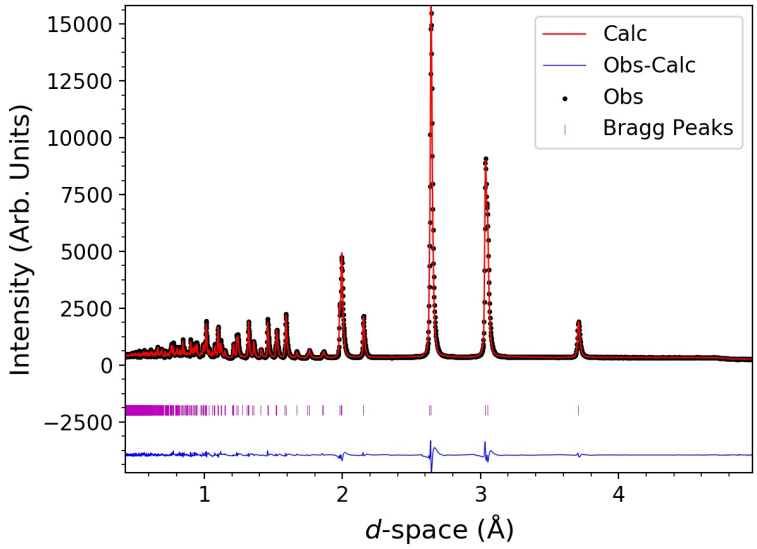

Supplementary Figure 7: Powder neutron diffraction pattern of $Pr(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 8.25 % and 6.67 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.61446(36), $c$ = 4.08233(18) Å and a unit cell volume of 398.322(26) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



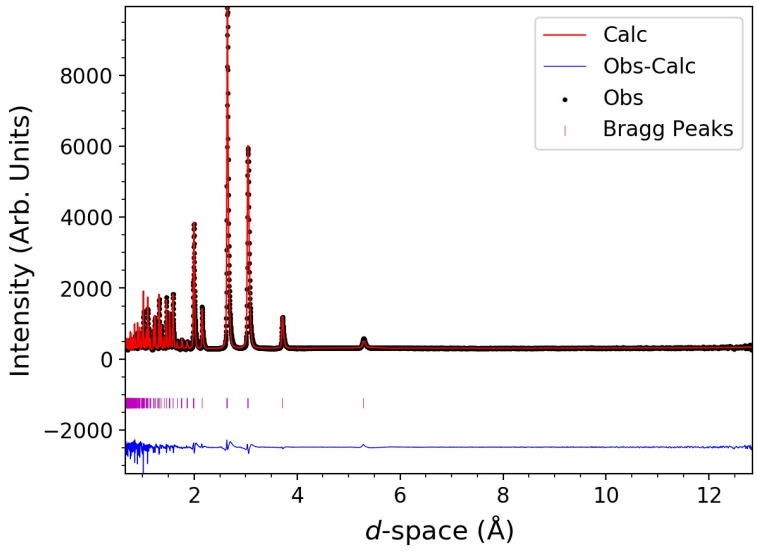

Supplementary Figure 8: Powder neutron diffraction pattern of $Pr(DCO_2)_3$ at 150 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.57 % and 5.91 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.61885(38), $c$ = 4.08246(18) Å and a unit cell volume of 398.322(26) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



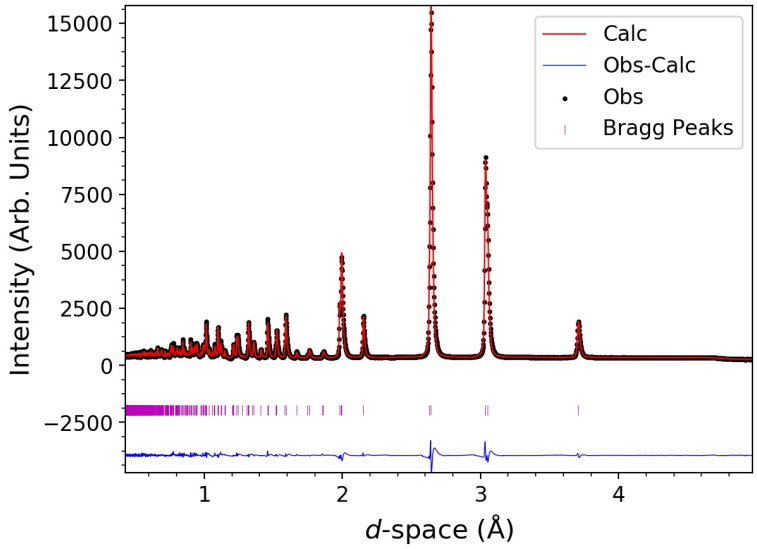

Supplementary Figure 9: Powder neutron diffraction pattern of $Pr(DCO_2)_3$ at 150 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 8.25 % and 5.93 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.61885(38)$, $c = 4.08246(18)$ Å and a unit cell volume of 398.322(26) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



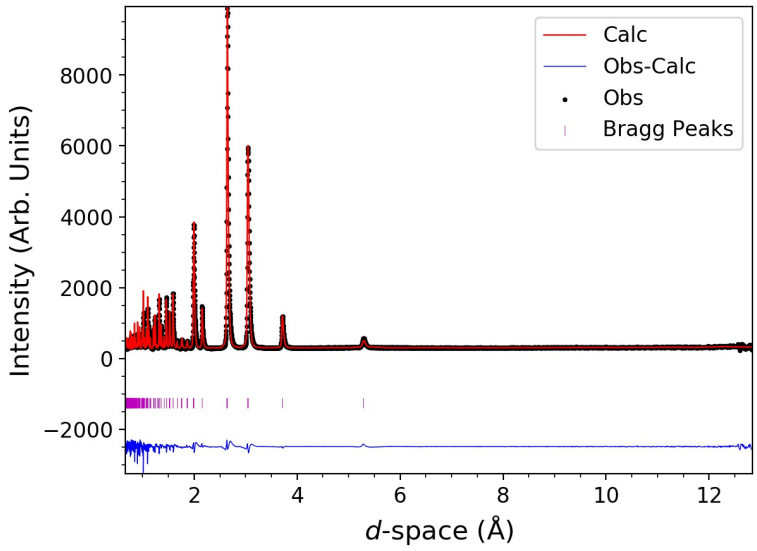

Supplementary Figure 10: Powder neutron diffraction pattern of $Nd(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.12 % and 5.37 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.57028(42)$, $c = 4.05726(19)$ Å and a unit cell volume of 392.587(29) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



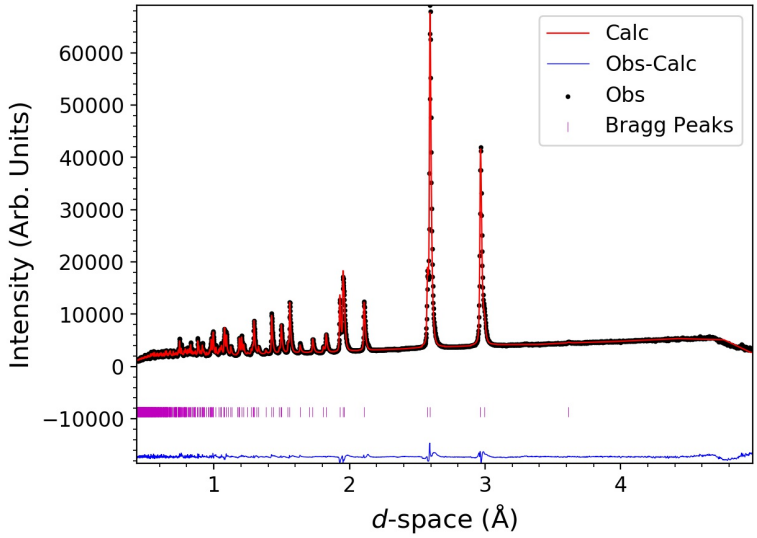

Supplementary Figure 11: Powder neutron diffraction pattern of $Nd(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 5.88 % and 5.16 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.61885(38), $c$ = 4.08246(18) Å and a unit cell volume of 392.587(29) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



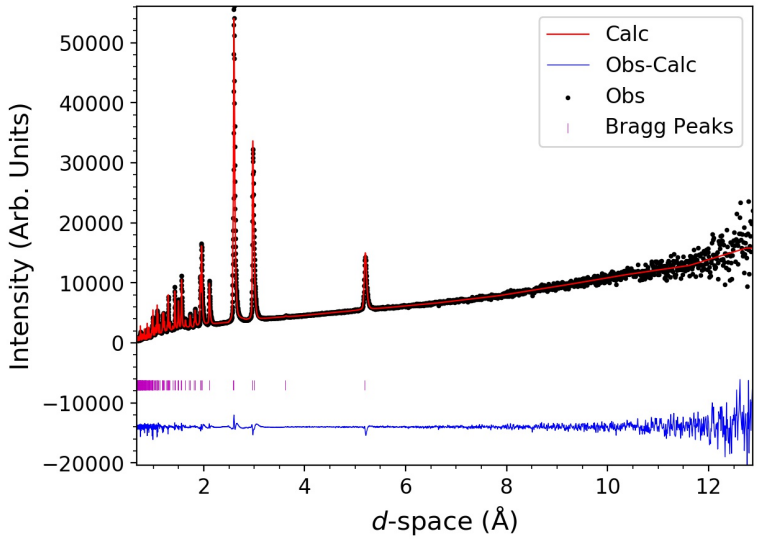

Supplementary Figure 12: Powder neutron diffraction pattern of $Nd(DCO_2)_3$ at 50 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.04 % and 5.33 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.57053(42), $c$ = 4.05726(19) Å and a unit cell volume of 392.606(26) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



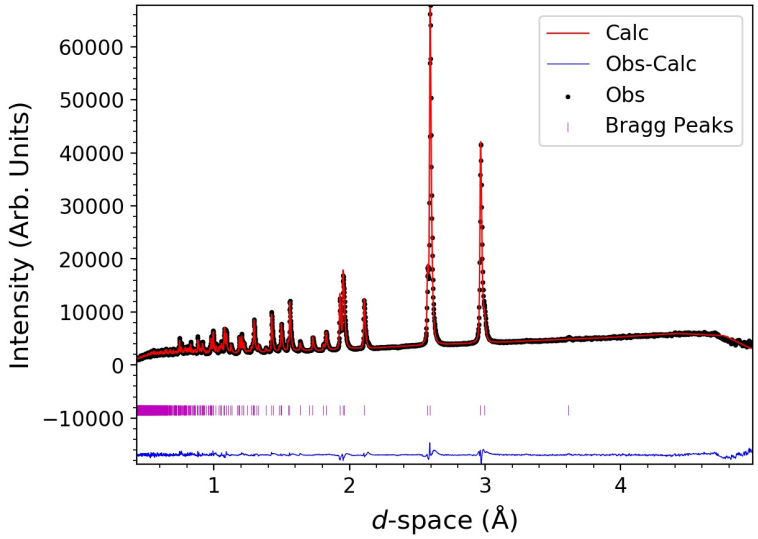

Supplementary Figure 13: Powder neutron diffraction pattern of $Nd(DCO_2)_3$ at 50 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 5.97 % and 5.15 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.57053(42)$, $c = 4.05726(19)$ Å and a unit cell volume of 392.606(26) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



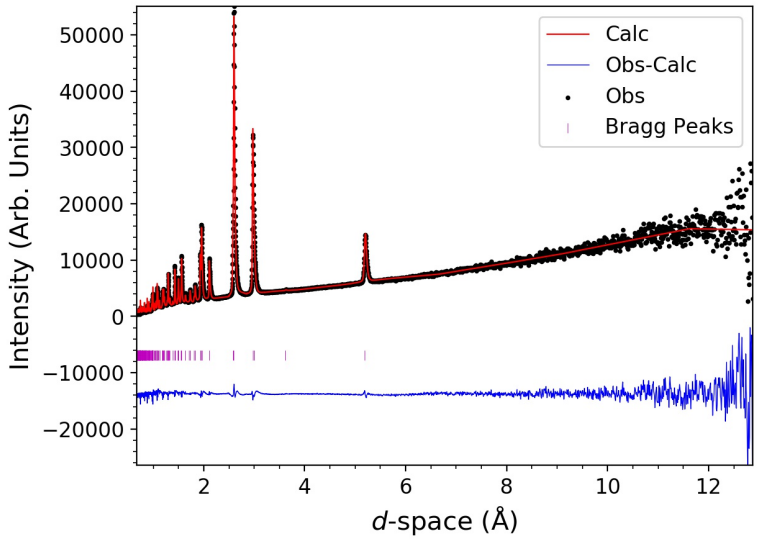

Supplementary Figure 14: Powder neutron diffraction pattern of $Dy(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 3.04 % and 3.56 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.39048(39)$, $c = 3.95540(16)$ Å and a unit cell volume of 369.821(24) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



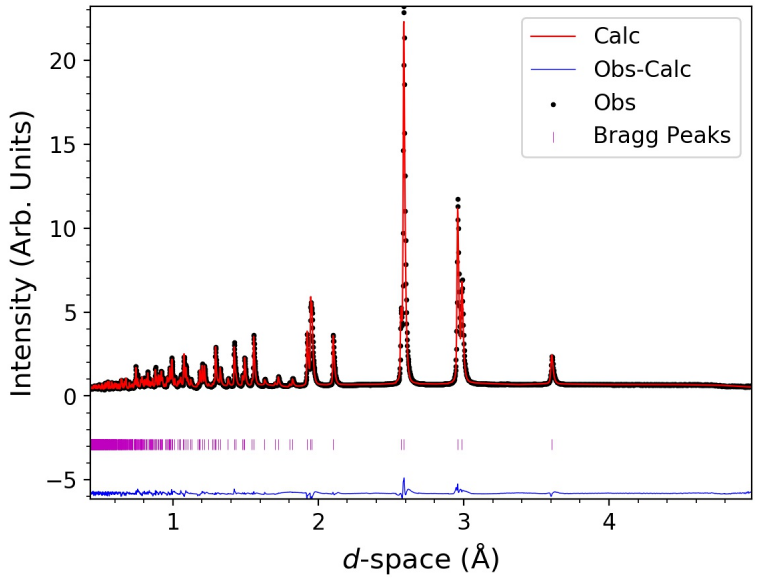

Supplementary Figure 15: Powder neutron diffraction pattern of $Dy(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.86 % and 4.06 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.39048(39)$, $c = 3.95540(16)$ Å and a unit cell volume of 369.821(24) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



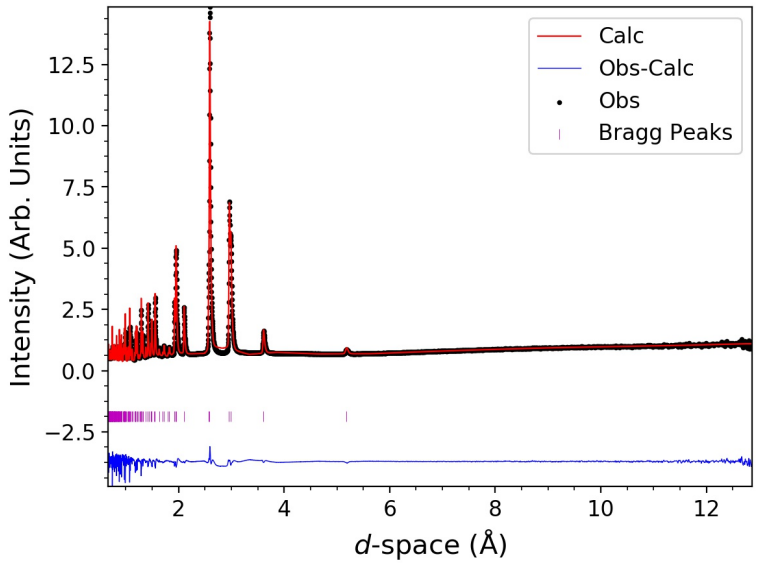

Supplementary Figure 16: Powder neutron diffraction pattern of $Dy(DCO_2)_3$ at 100 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 3.43 % and 3.85 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.39376(42)$, $c = 3.95557(17)$ Å and a unit cell volume of 370.071(26) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



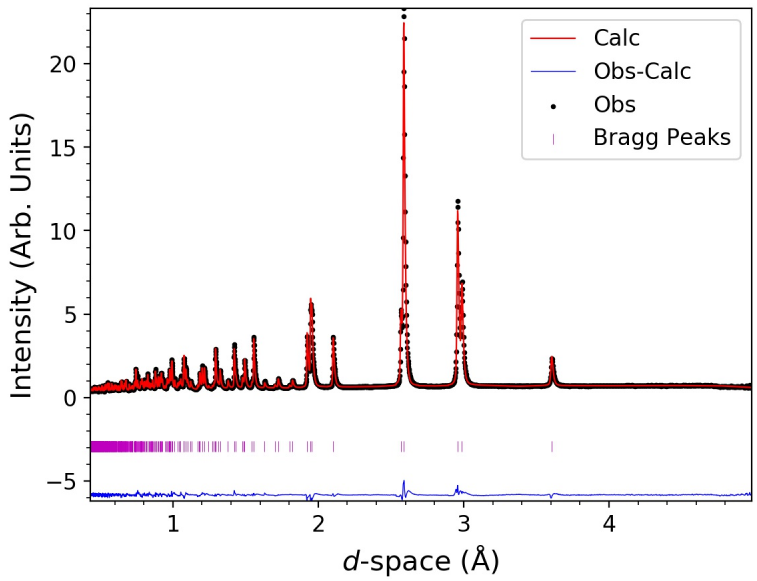

Supplementary Figure 17: Powder neutron diffraction pattern of $Dy(DCO_2)_3$ at 100 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 5.24 % and 8.40 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.39376(42)$, $c = 3.95557(17)$ Å and a unit cell volume of 370.071(26) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



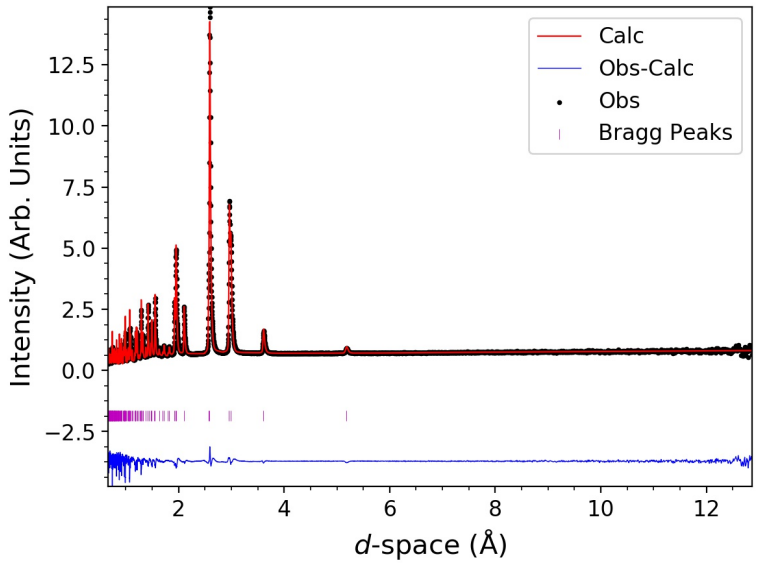

Supplementary Figure 18: Powder neutron diffraction pattern of $Ho(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.22 % and 4.74 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.36026(30)$, $c = 3.94188(12)$ Å and a unit cell volume of 366.416(19) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



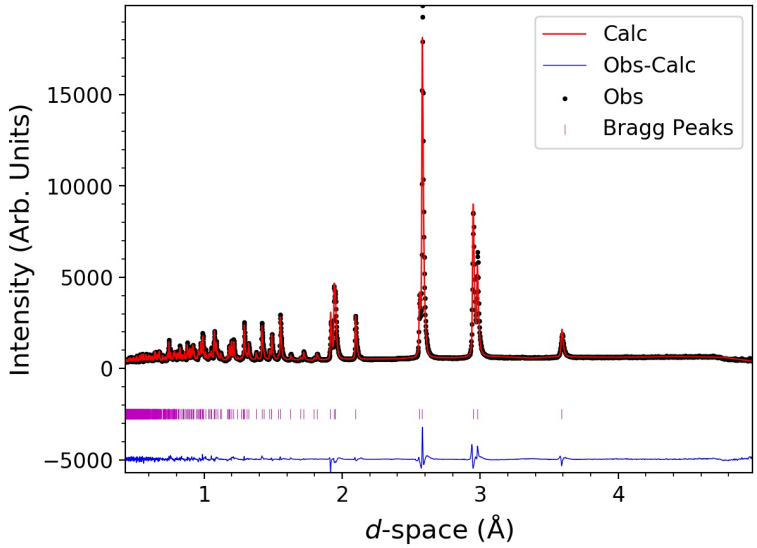

Supplementary Figure 19: Powder neutron diffraction pattern of $Ho(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 6.30 % and 3.32 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.36026(30), $c$ = 3.94188(12) Å and a unit cell volume of 366.416(19) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



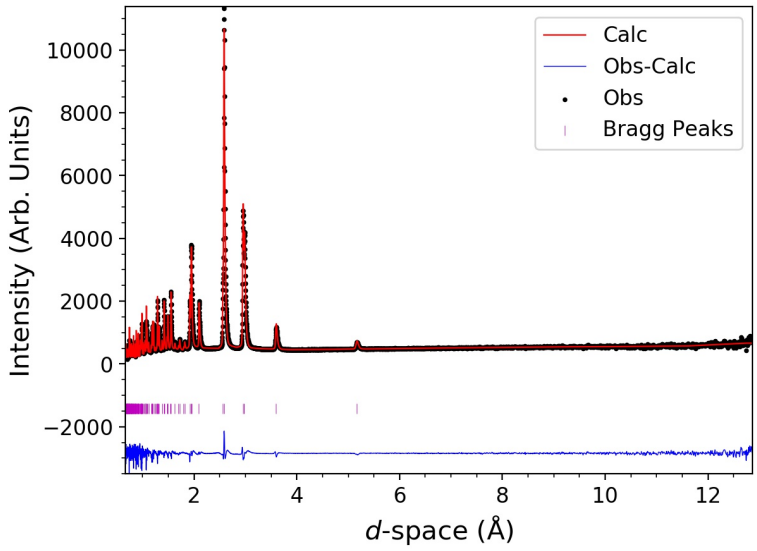

Supplementary Figure 20: Powder neutron diffraction pattern of $Ho(DCO_2)_3$ at 40 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.05 % and 4.51 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.36116(36), $c$ = 3.94220(15) Å and a unit cell volume of 366.510(22) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



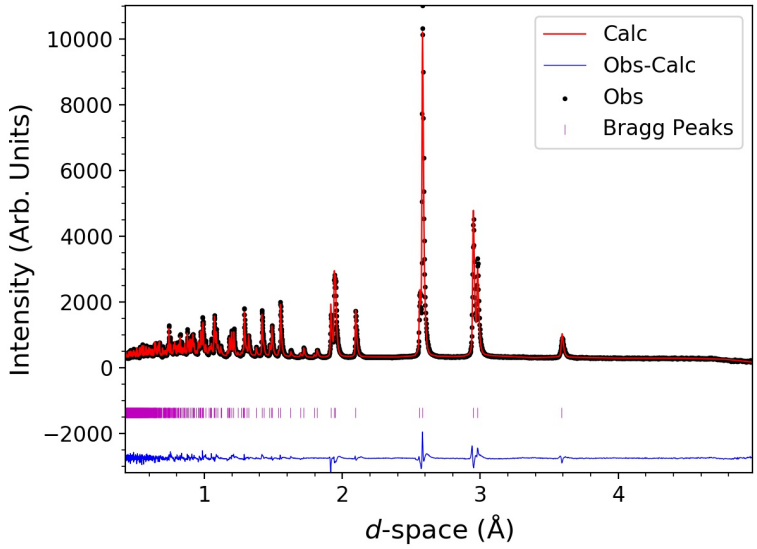

Supplementary Figure 21: Powder neutron diffraction pattern of $Ho(DCO_2)_3$ at 40 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 6.24 % and 3.61 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.36116(36), $c$ = 3.94220(15) Å and a unit cell volume of 366.510(22) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



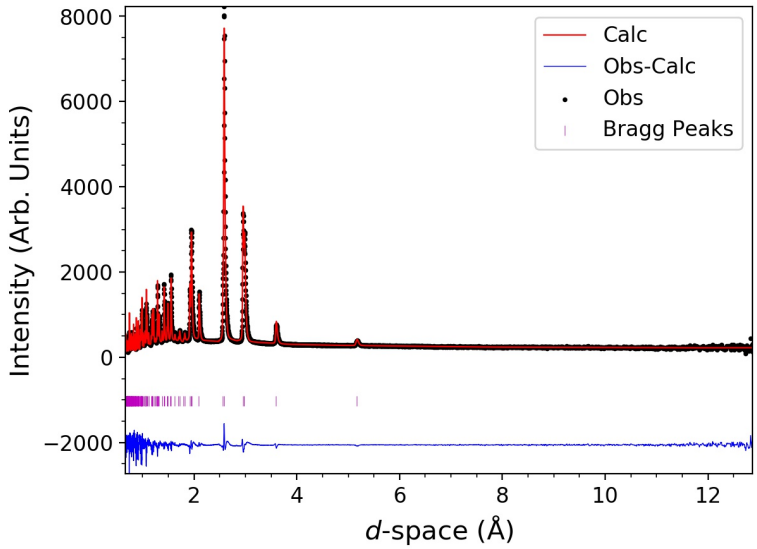

Supplementary Figure 22: Powder neutron diffraction pattern of $Er(DCO_2)_3$ at 1.5 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 4.67 % and 5.50 % are obtained, respectively from the refinement. Unit cell parameters: $a = b$ = 10.33911(44), $c$ = 3.93030(18) Å and a unit cell volume of 363.850(27) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.



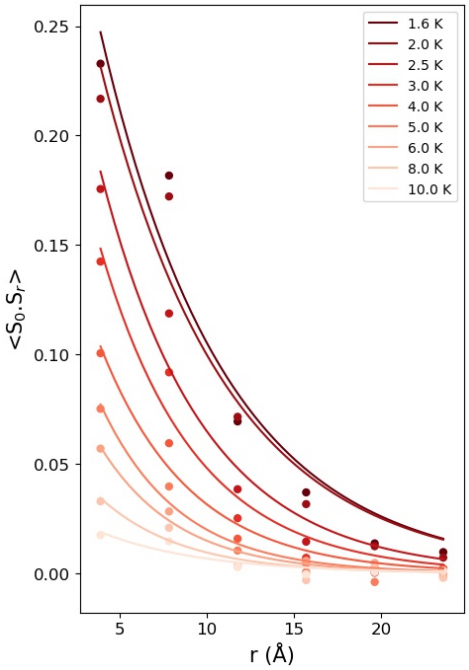

Supplementary Figure 23: Powder neutron diffraction pattern of $Er(DCO_2)_3$ at 1.5 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 6.31 % and 4.21 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.33911(44)$, $c = 3.93030(18)$ Å and a unit cell volume of 363.850(27) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.




Supplementary Figure 24: Powder neutron diffraction pattern of $Er(DCO_2)_3$ at 20 K using bank 5+6 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 5.18 % and 5.64 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.33991(48)$, $c = 3.93033(19)$ Å and a unit cell volume of 363.909(30) Å$^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.




Supplementary Figure 25: Powder neutron diffraction pattern of $Er(DCO_2)_3$ at 20 K using bank 2+9 of the WISH diffractometer, fitted using the Rietveld method with the $R3m$ space group. $R_p$ and $R_{wp}$ of 7.75 % and 4.95 % are obtained, respectively from the refinement. Unit cell parameters: $a = b = 10.33991(48)$, $c = 3.93033(19)$ Å and a unit cell volume of 363.909(30) $Å^3$. Black marks, red line, blue line indicate experimentally observed intensities, calculated intensities and difference respectively.




Supplementary Figure 26: Correlation length fits at various temperatures