Electronic Supplementary Material (ESI) for Dalton Transactions.

On the reaction mechanism of an endoperoxide ring formation by fumitremorgin B endoperoxidase. The right arrangement makes a difference

Supplementary Information

List of figures:

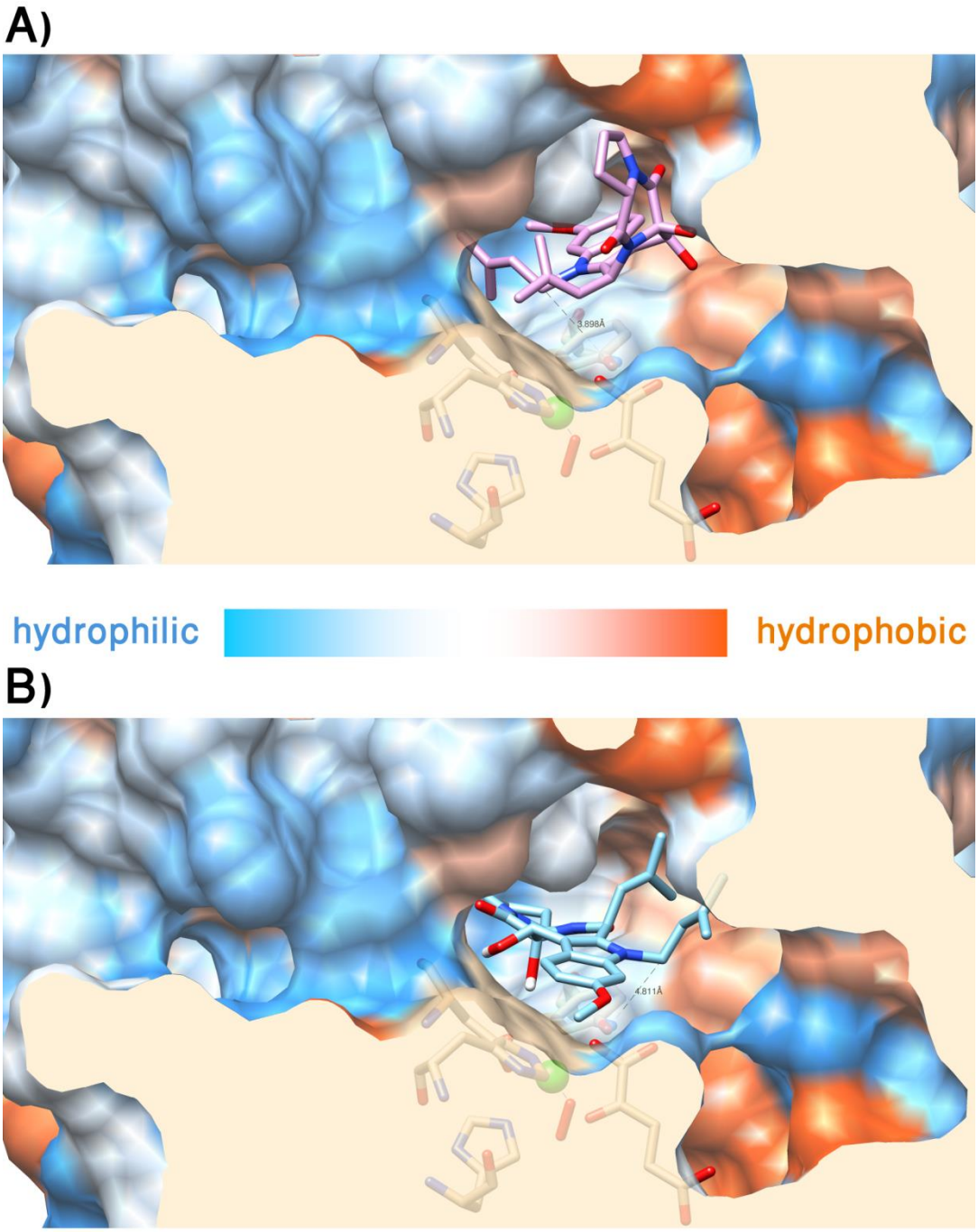

Fig. S1. FtmF cavity with the substrate in geometry **A**) taken from PDB (4ZON) **B**) obtained by docking (AutoDock 4.2.6)

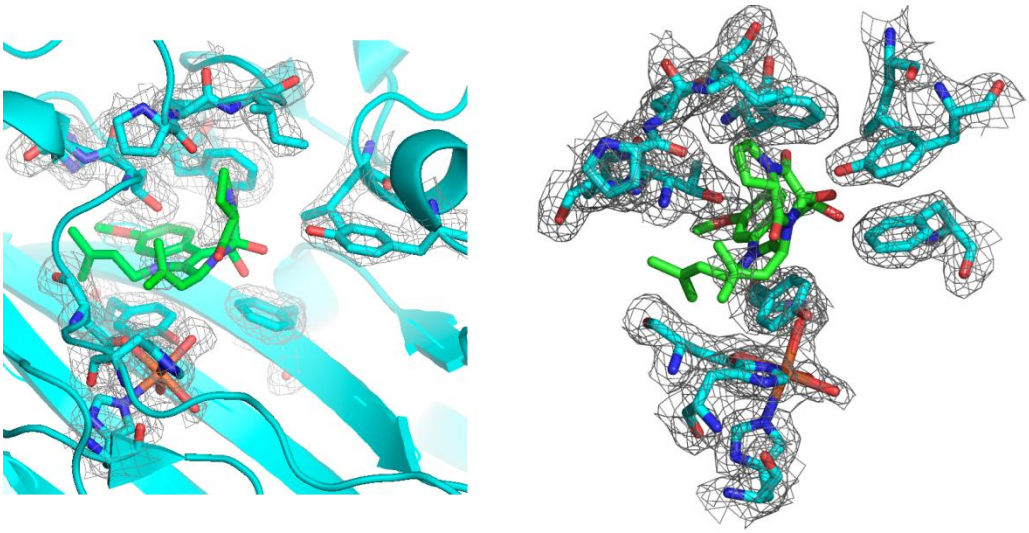

Fig. S2. Active site region of the 4ZON structure with an electron density map displayed.

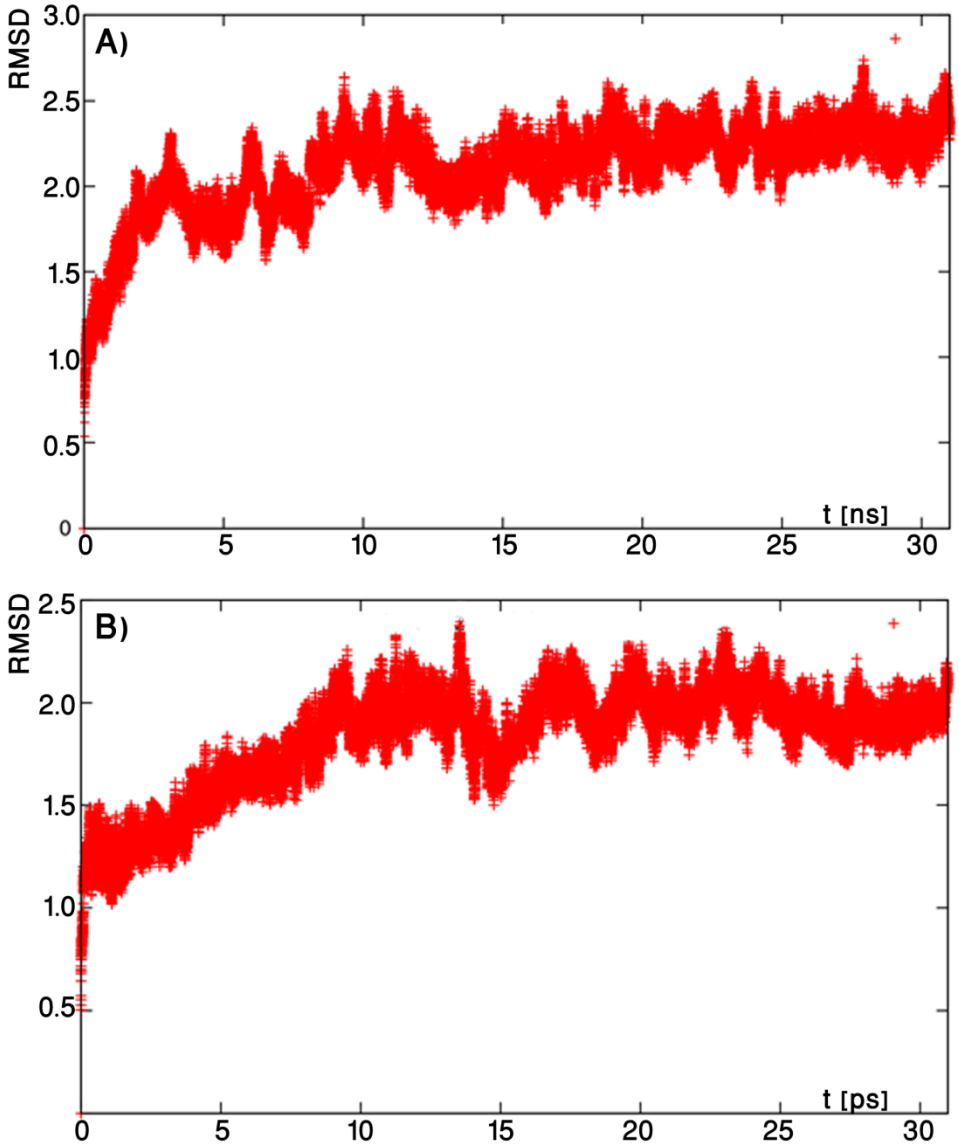

Fig. S3. RMSD plot for 31 ns of MD production run for FtmF with fumitremorgin B bound in orientation as: **A**) in the 4ZON structure, **B**) obtained by docking

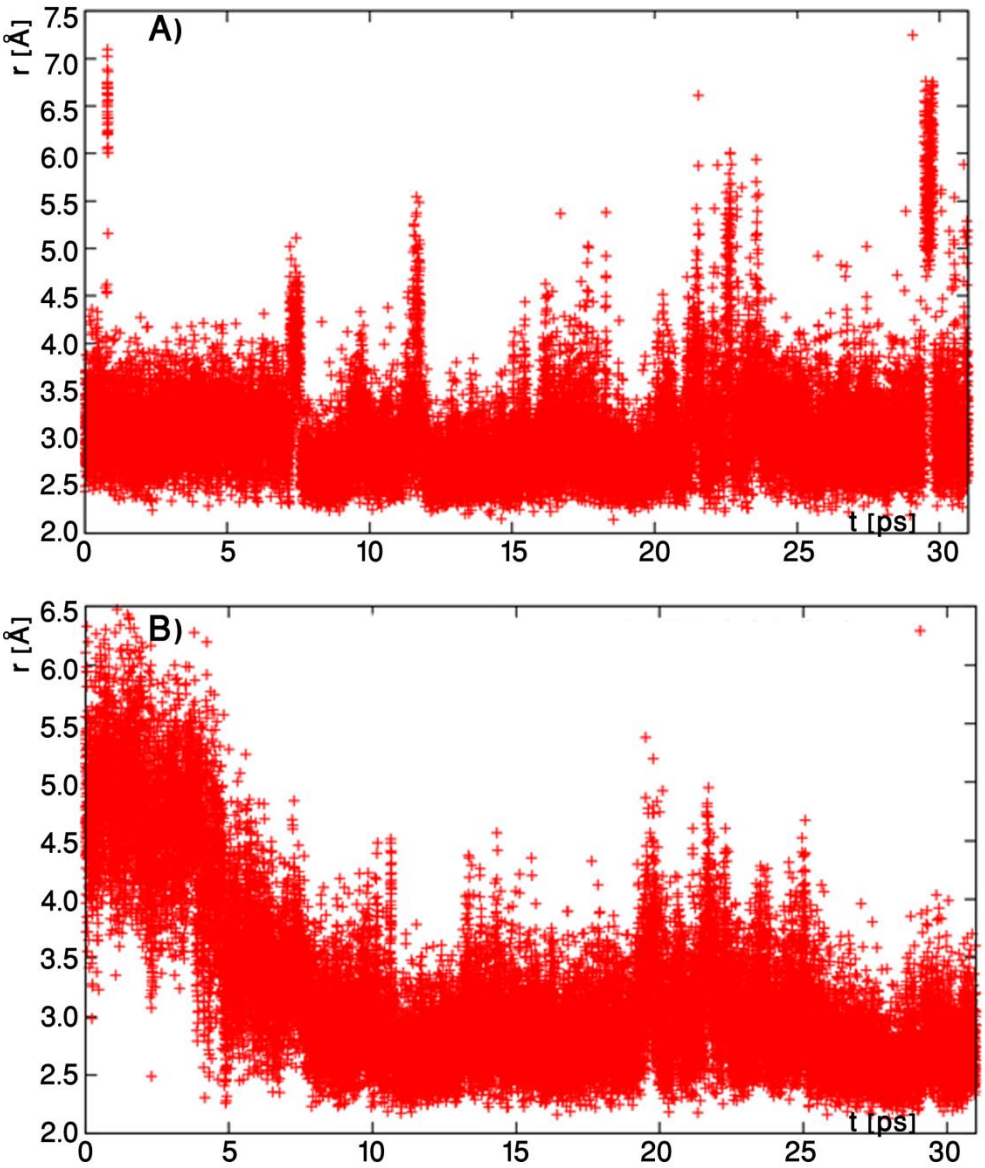

Fig. S4. Distance between the H_R atom of fumitremorgin B and the phenolic oxygen atom of Y224 in MD runs for FtmF with fumitremorgin B bound in orientation as: **A**) in the 4ZON structure, **B**) obtained by docking

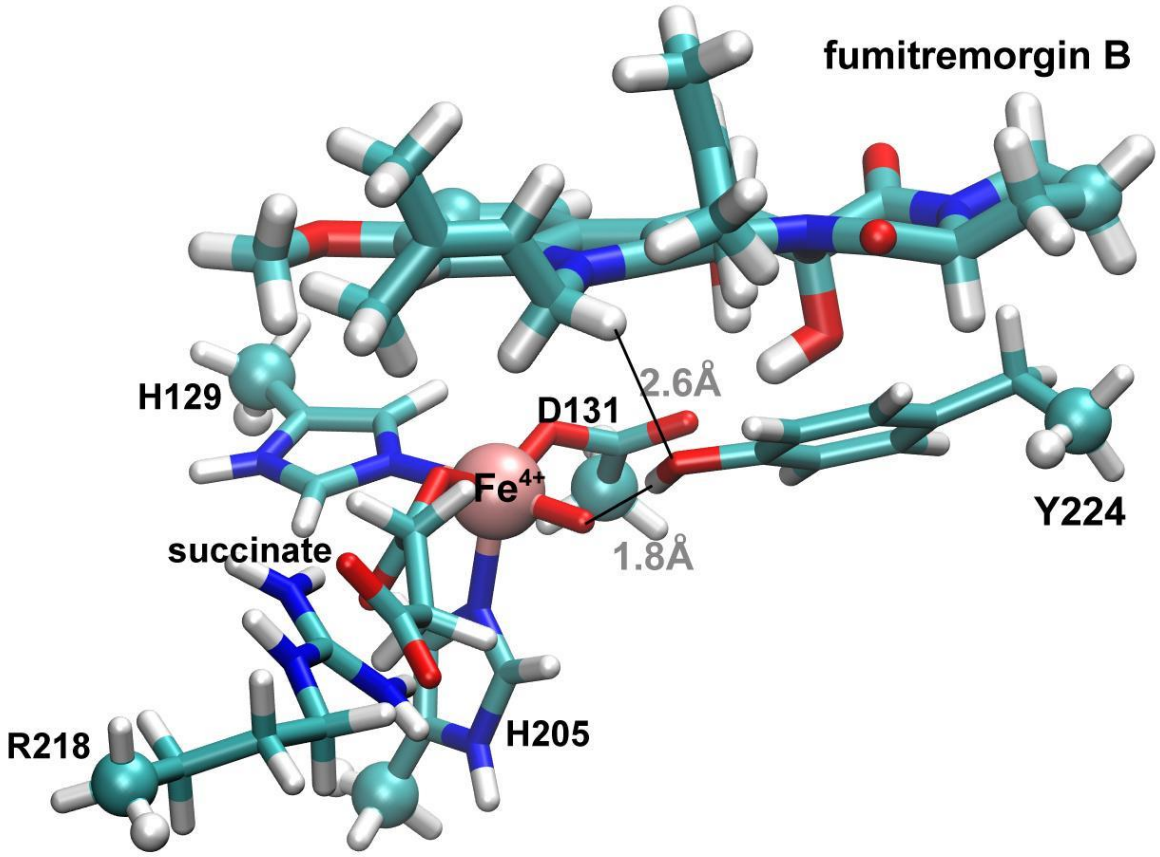

Fig S5. A cluster model used in DFT calculation to study catalytic reaction mechanism of FtmF. Carbons and hydrogens frozen during geometry optimisation are shown as balls. Crucial distances are depicted in gray.

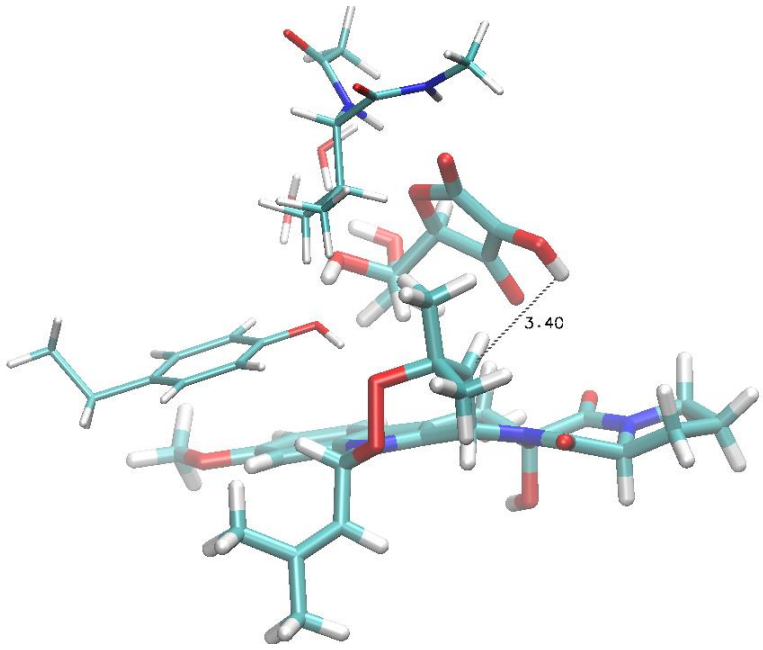

Fig S6. QM model used to study the reaction with ascorbate.

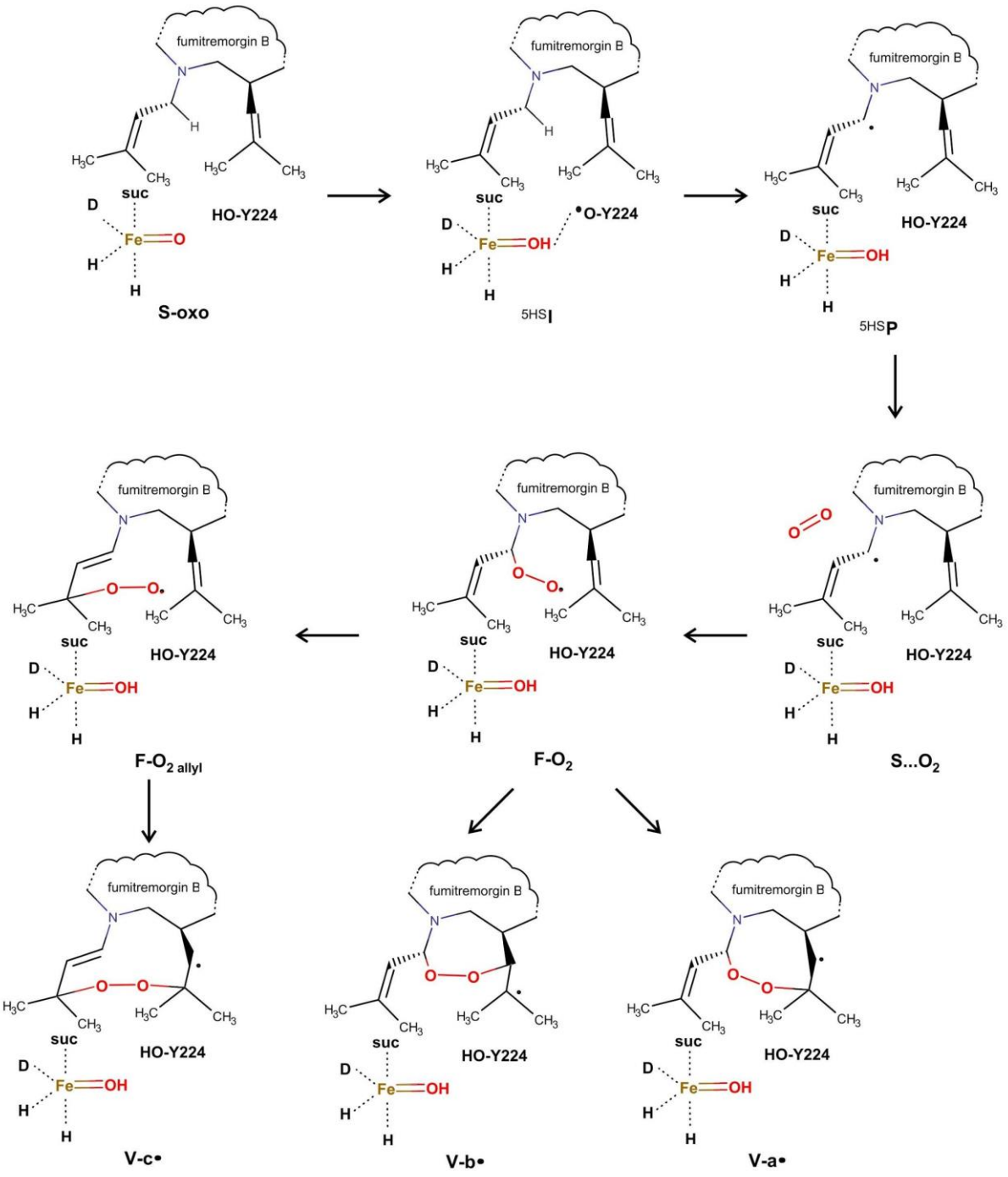

Fig S7. A scheme of reaction pathways considered in this study.