Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Conversion mechanismof enoylthioesters into acyl thioesterscatalyzed by 2-enoyl-thioester reductases from *Candida Tropicalis*

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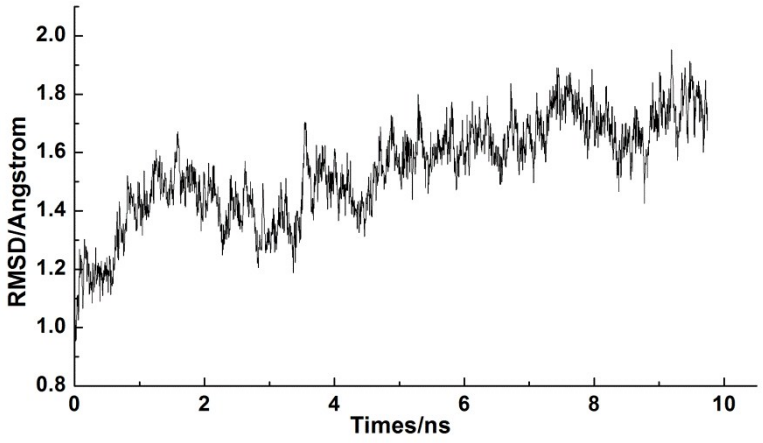

Figure S1 Time dependence of RMSDsfor the backbone atomsof reactant **R'**during 10 ns MD simulations.

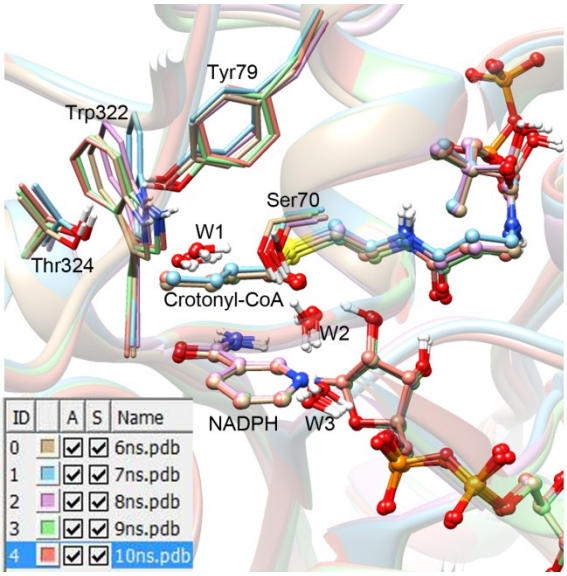

Figure S2 Superimposition offive snapshots for the reactant **R'**extracted from the 10 ns MD trajectories at 6, 7, 8, 9 and 10ns.For clarity, the ribbons of the protein in the front are hidden.For clarity, the ribbons of the protein in the front are hidden.

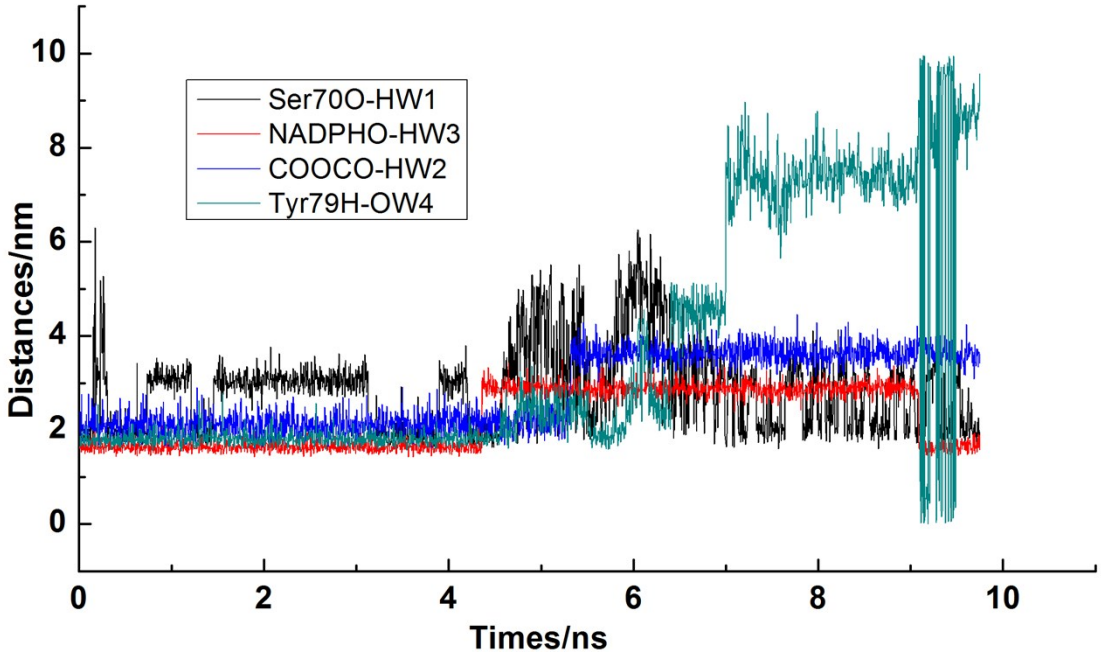

Figure S3 Time dependence of the distances between two atoms of different residues in the active site during the 10 ns MD simulations.

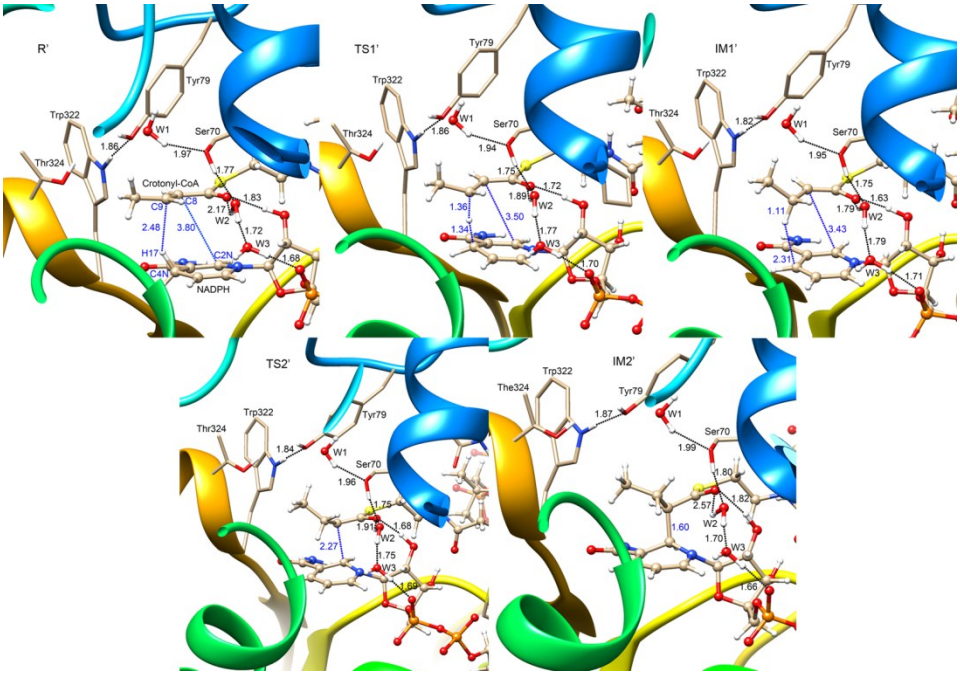

Figure S4 QM/MM-optimized geometries of the reactant **R'**, transition states and the intermediates in path I and Ib(Scheme 2). All the distances are in angstrom.

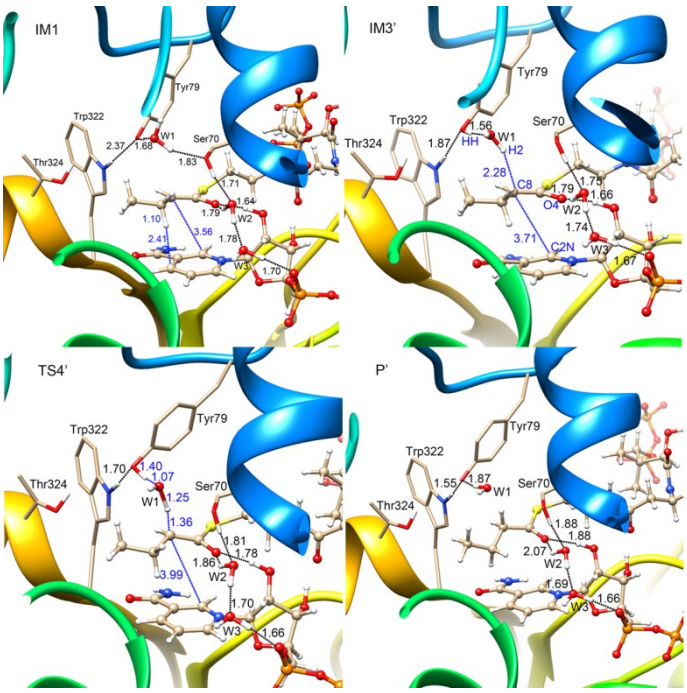

Figure S5 QM/MM-optimized geometries of the intermediates, transition state and the product **P'**（path b in Scheme 4B) for the proton transfer. Hydrogen bonds and the distances between two atoms are represented by black and blue dashed lines, respectively. All distances are given in angstrom. For clarity, the ribbons of the protein in the front are hidden.

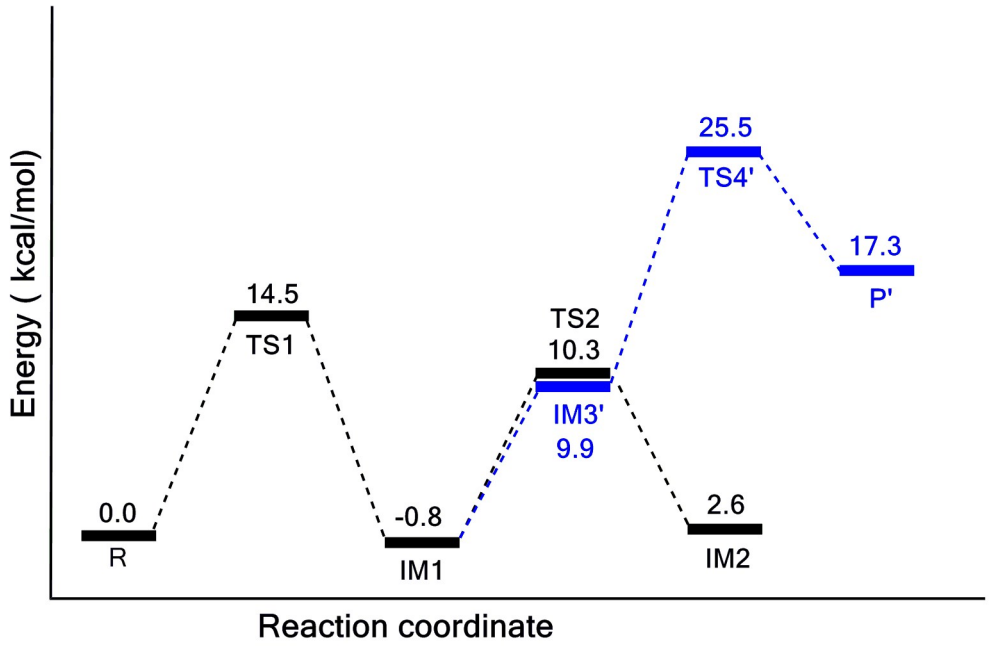

Figure S6 Energy profile for the conversion of crotonyl-CoA into butyryl-CoA catalyzed by Etr1p (path b in Scheme 4B).

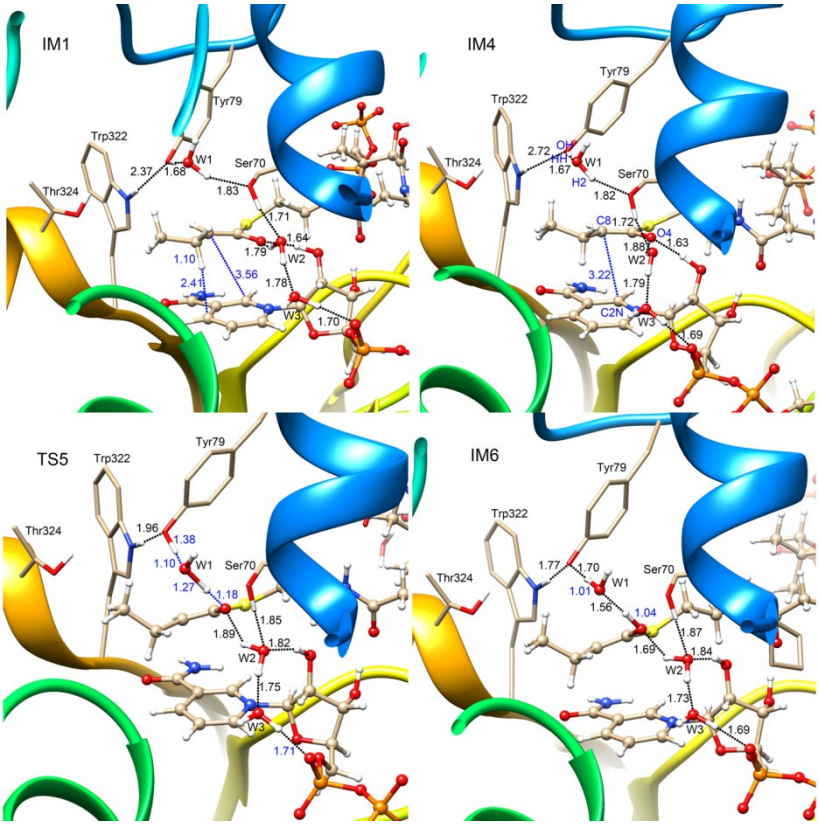

Figure S7 QM/MM-optimized geometries of the intermediates and transition states (path c in Scheme 4B) for theproton transfer reactions catalyzed by Etr1p. Hydrogen bonds and the distances between two atoms are represented by black and blue dashed lines, respectively. All distances are given in angstrom. For clarity, the ribbons of the protein in the front are hidden.

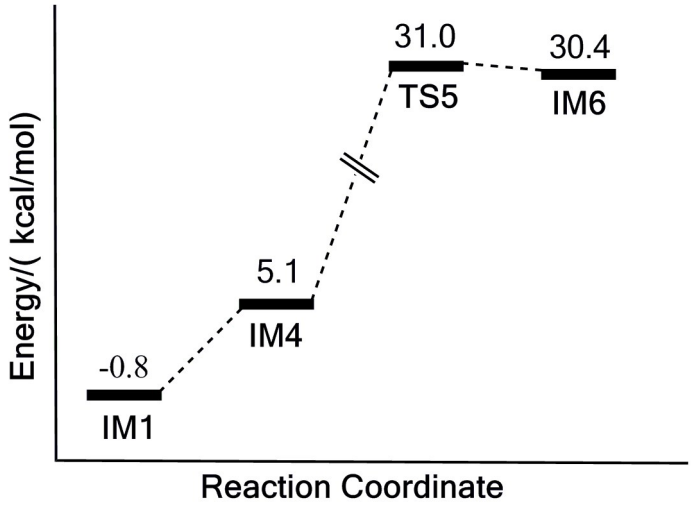

Figure S8 Energy profile for the conversion of crotonyl-CoA into butyryl-CoA catalyzed by Etr1p (path c in Scheme 4B).