Supporting Information

Selective Synthesis of 4-Hydroxyisophorone and 4-Ketoisophorone by Fungal Peroxygenases

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Figure S1. Comparison of GC-MS retention times of the products from isophorone (IP) reaction with CglUPO (A) and rHinUPO (C), compared with the corresponding 4KIP and 4HIP (from 4KIP chemical reduction) authentic standards (B and D).
Figure S2. Mass spectra of isophorone (A) and the products from the enzymatic reaction with CglUPO, 4HIP (B) and 4KIP (C).
Figure S3. Mass spectra of isophorone (A) and the products from enzymatic reaction 7HIP (B) and 7FIP (C).
Figure S4. Kinetic curves of enzymatic hydroxylation of isophorone (IP) by CgUPO (A), rHinUPO (B) and AaeUPO (C) from GC-MS estimation of 4HIP/4KIP formation (initial rates), adjusted as described in Experimental.
Figure S5. GC-MS (left) and chiral HPLC (right) analyses of isophorone (IP) hydroxylation by CglUPO (A), rHinUPO (B) and AaeUPO (C) and the chemical reduction of 4KIP (D), showing the R-4HIP, S-4HIP, 4KIP and 7FIP products.
Figure S6. R-4HIP and S-4HIP enantiomers during reaction of 4-hydroxyisophorone (4-HIP) racemate with rhinUPO (A), CgUPO (B) and AaeUPO (C), in percentage (%) of the initial chiral substrate.
Figure S7. Individual PELE plots for isophorone (IP) diffusion in AaeUPO (B), rCciUPO (C), rHinUPO (D), CglUPO (E) and MroUPO (F) showing the C₄-oxo distance vs the binding energy, compared with the overlapping plots shown in Figure 4A (A).
Figure S8. Comparison of C₄- and C₇-oxo distances vs binding energy during isophorone (IP) diffusion on CglUPO (A) and AaeUPO (B) using adaptive PELE. For the same binding energy, the C₇ distances are always shown by black dots, while the C₄ distances for CglUPO and AaeUPO are shown by red and green dots, respectively.