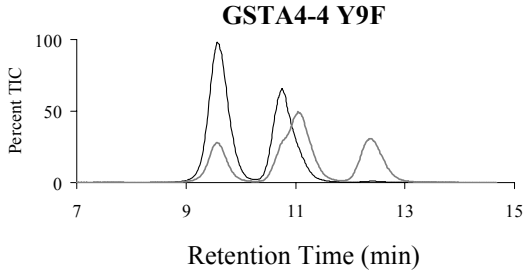
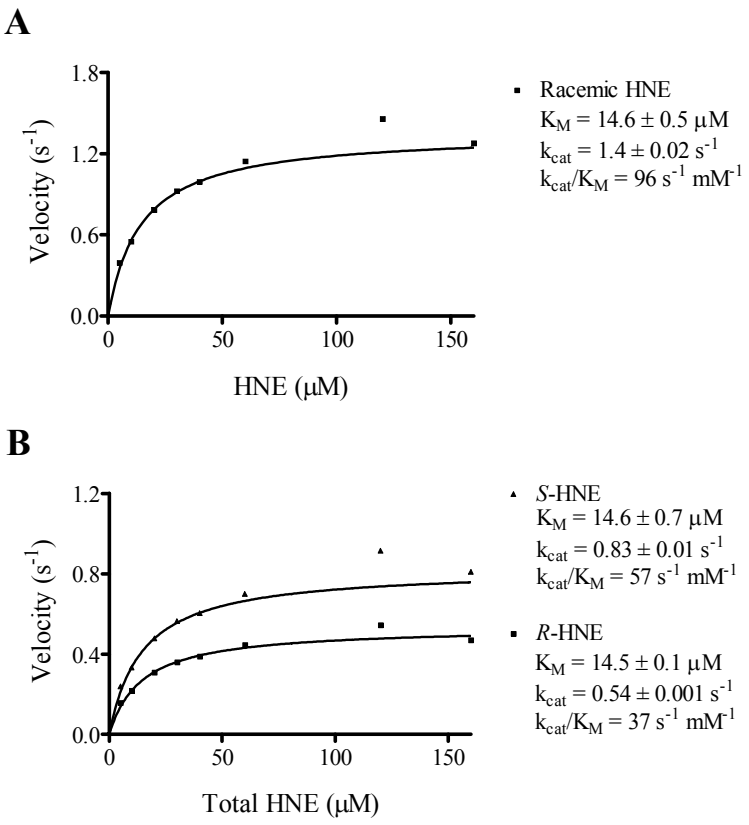
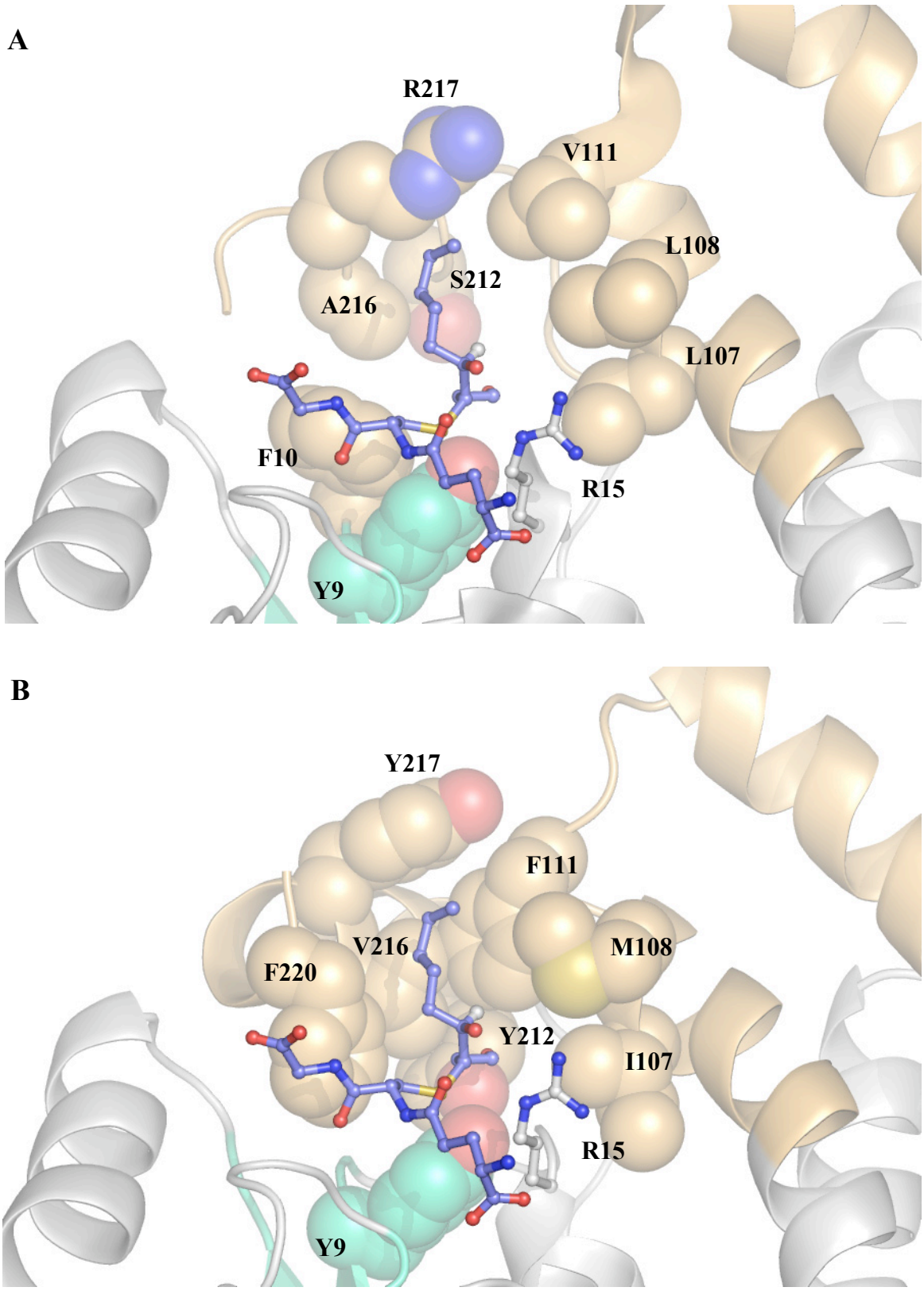



**Supporting Figure 1.** Stereoselectivity of product formation. The GSHNE diastereomers were prepared by incubating GSH and the GSTA4-4 Y9F mutant with racemic HNE and analyzed by LC/MS (ESI+, SIM 464). The corresponding spontaneous reaction (gray line) is also shown for comparison.




**Supporting Figure 2.** Kinetic characterization of the GSTA4-4 Y9F enzyme-catalyzed conjugation of GSH with HNE. (A) Kinetic curve and parameters for racemic HNE. (B) Kinetic curve and apparent parameters for the individual enantiomeric contributions obtained by monitoring the GSHNE diastereomers produced stereoselectively from 4*R*- and 4*S*-HNE. Data points represent the average of duplicate assays and have been corrected for the corresponding spontaneous reaction.




**Supporting Figure 3.** (A) Structural superpostion of the 3*S*,4*R*-GSDHN ligand (blue) within the context of the apo wild-type GSTA1-1 structure (1PKZ, which does not have residues beyond 219 modeled in the structure). GSDHN-bound GSTA4-4 (3IK7) is provided for comparison in (B). The conserved G-site is towards the lower half of each figure with Y9 shown in cyan. Other important active site residues are shown as orange spheres to contrast the hydrophobic cavities.