

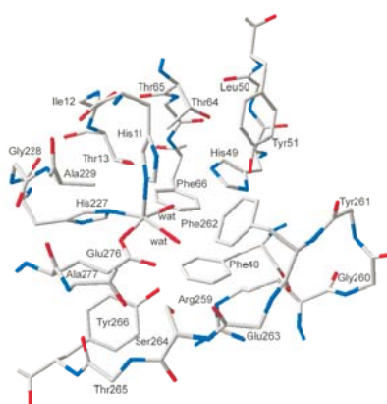
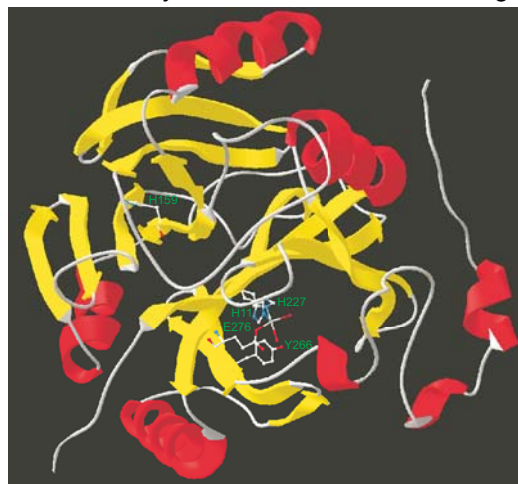
Understanding the Origin of Suicide Inactivation in the Extradiol Dioxygenases

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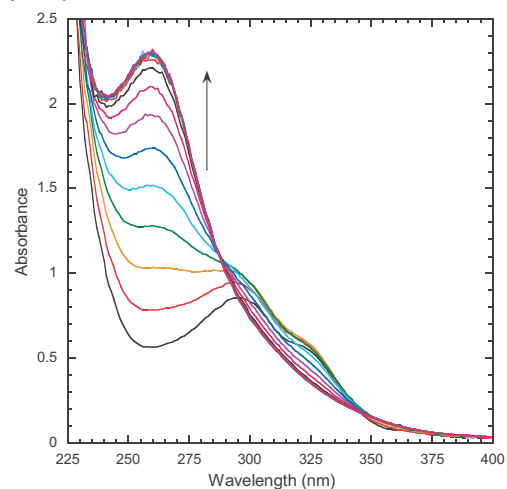
We have re-focused our efforts to study poorly characterized non-catechol ring-cleaving dioxygenases, especially the hydroquinone dioxygenases that actually *prefer* chlorinated (and even brominated) substrates, PcpA and LinE. We are using a two-pronged approach of studying both the actual enzymes and synthesis of novel model complexes:

1. Biochemical studies of unusual Fe(II)-containing ring-cleaving dioxygenases that cleave chlorinated substrates.

Structural model of 2,6-dichlorohydroquinone dioxygenase (PcpA). The overall tertiary structure is shown to the right, the active site to the left



Ring-cleavage of 2,6-dibromohydroquinone by PcpA:

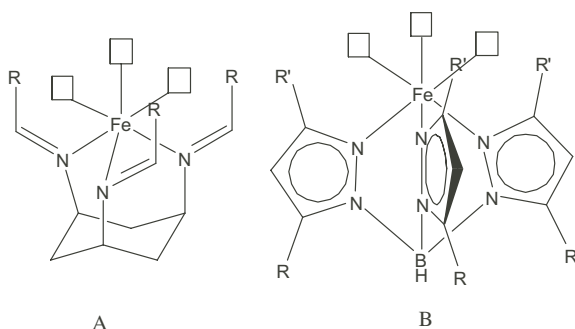


PCR amplification of the gene of another hydroquinone dioxygenase:



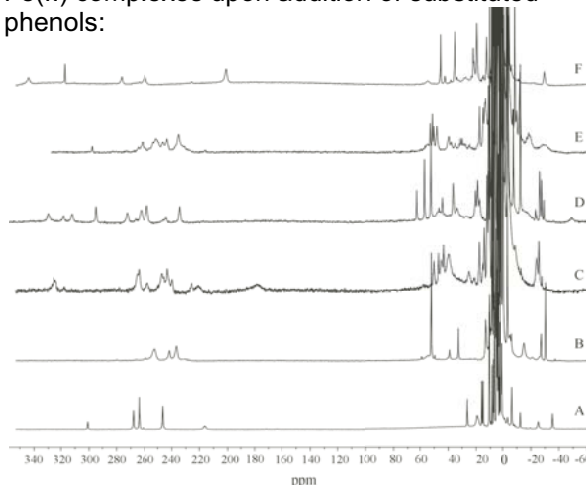
2. Fe(II)-containing model complexes that can coordinate phenols that mimic enzyme substrates.

Design of ligands to mimic the facial capping triad of ring-cleaving dioxygenases:



□ = vacant site for substrate, O₂ mimic coordination

Paramagnetic NMR spectra of (TACH-o-tol)Fe(II) complexes upon addition of substituted phenols:



Crystal structure of [(TACH-o-tol)Fe^{II}(2,6-dichlorophenolate)]OTf:

