Substrate-Directed Reactivity Alteration of High-Valent Iron Oxo in Biphenyl Dioxygenase of *Pseudomonas pseudoalcaligenes*

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Biphenyl, flavone and flavanone were used as mechanistic probes to investigate the chemical reactivity of the high-valent iron-oxo species generated during the substrate oxidation by prokaryotic biphenyl dioxygenase from *Pseudomonas pseudoalcaligenes* KF707. While the expected *cis*-diol products were isolated from biphenyl and flavone, biphenyl dioxygenase showed a novel eukaryotic monooxygenase activity for flavanone and produced the epoxide. Extensive NMR characterizations determined the epoxide group located at the same place of the diol formation when flavone was reacted. Flavanone epoxide formation by biphenyl dioxygenase of *P. pseudoalcaligenes* KF707 suggested that the high-valent iron-oxo species could show different chemical reactivity depending on the substrate orientation.