Strategies for Asymmetric Allylic C-H Oxidation

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Recent advances in our lab have contributed to the growing toolbox of reactions allowing for direct functionalization of C-H bonds in a mild, general way. This class of reactions is of particular immediate value due to its applicability in complex molecule synthesis. To date, our methodologies for oxidizing the allylic position of α-olefins have achieved stereocontrol through tethering of the nucleophile to the substrate. This intramolecular process affords useful quantities of valuable intermediates with good diastereoselectivities. Development of a reagent based method for stereoselection would extend our methodologies to a new level of utility. However, the acidic, oxidative conditions optimal for maintaining the highly electrophilic Pd(II) vital to this chemistry presents problems for typical solutions to asymmetric catalysis. Beginning with the serial ligand catalysis mechanism believed to be operative for this chemistry, strategies for inducing stereoselection in C-H activation/functionalization will be discussed along with current progress toward this problem.