Modern organic synthesis depends heavily on the use of catalysts for selective transformations. We have discovered several classes of synthetic peptides that catalyze a number of enantioselective and regioselective reactions. This presentation will describe the discovery and use of peptides containing proteinogenic and non-natural amino acids for a variety of asymmetric bond formations. Many of the catalysts rely on catalytically active organic functional groups that are localized within a complex molecular architecture. The connections between peptide sequence and stereoselectivity will be explored in a range of mechanistically distinct reactions. Prospects for generalizations and eventual design of catalysts from first principles will be evaluated. Likewise, applications to the synthesis and selective modification of complex molecules, including biologically active natural products, will be described.