Expanding the reaction scope of biological catalysts beyond the realm of enzymatic transformations occurring in nature can create new opportunities for the exploitation of biocatalysis for organic synthesis. In this lecture, we will present recent progress made by our group toward the design, investigation, and application of engineered myoglobins for catalyzing abiological carbene transfer reactions. These efforts have recently led to the development of efficient and stereoselective biocatalysts for the asymmetric construction of carbon-carbon and carbon-heteroatom bonds via carbene insertion into olefins, heteroatom-hydrogen bonds, C—H bonds, and carbonyls. These myoglobin-based catalysts could be successfully applied for the stereoselective synthesis of chiral building blocks and drug molecules at the multigram scale. Presentation of these results will be complemented with a discussion of our current understanding of the mechanism of these reactions and of the structural determinants of reactivity and stereoselectivity in this new class of ‘carbene transferases’.