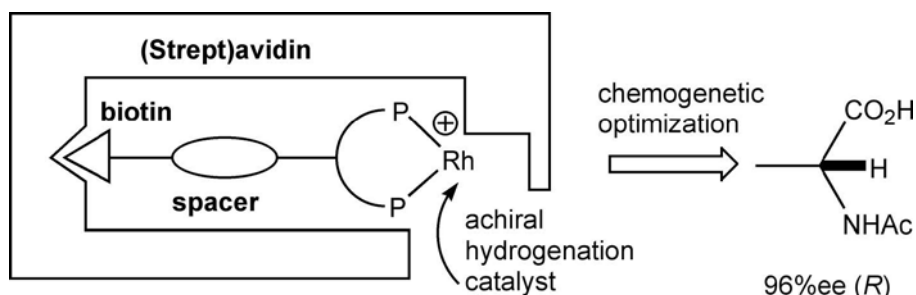


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Artificial Metalloenzymes for Enantioselective Catalysis Based on the Biotin-Avidin Technology

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Homogeneous- and enzymatic catalysis offer complementary means to generate enantiomerically pure compounds. Incorporation of achiral biotinylated rhodiumdiphosphine complexes into (strep)avidin yields artificial metalloenzymes for the hydrogenation of N-protected dehydroaminoacids (Scheme). A chemogenetic optimization procedure allows to produce both enantiomers of acetamidoalanine in good enantioselectivity (up to 96% ee). Analysis of the performance of these hybrid catalysts reveal features reminiscent both of enzymatic and of homogeneous systems.



Scheme. Artificial metalloenzymes for enantioselective hydrogenation reactions. The host protein (either avidin or streptavidin) displays a high affinity for the biotin anchor. Introduction of a spacer and variation of the ligand scaffold allows to chemically optimize the enantioselectivity. Fine tuning of the selectivity can be achieved via site-directed mutagenesis of the (strept)avidin.