

Enantioselective Catalysis (B. Goldfuß)

From basics and principles to applications of drug syntheses and industrial productions

Basics

History and definitions: enantioselective synthesis and catalysis, stereochemistry (isomerism, chirality, stereogenic units, ee, es, er, etc.).

Reductions

homogenous additions of H₂ to alkenes, orbital symmetry, heterogenous Sabatier-hydrogenation, Wilkinson-hydrogenation: catalytic cycle (ox. add., insert, red. el.), neutral and cationic cycles, Horner-Knowles- phosphanes, Monsanto's L-DOPA-synthesis: reaction diagram, Curtin-Hammett-principle, chiral diphosphanes: DIOP, BINAP, dipamp, chiraphos, norphos, prophos, DuPhos, DegPhos, etc.; chelate-ring-rule, Knowles'-quadrant- model, Enichem's (S)-phenylalanine & aspartame synthesis; Noyori-Ru-BINAP-hydrogenations: geraniol → citronellol, β-ketoester-reductions, quadrant model, Takasago's carbapenem synthesis, β-lactam-antibiotics, reductions of non-functionalized ketones: Ru-BINAP, Ru-diamine transfer hydrogenations, Corey-Bakshi-Shibata-reduction.

Oxidations

Katsuki-Sharpless-AE: Prilezhaev- & Henbest- epoxidations, catalysis cycle: chelate effect, peroxide activations, synthetic benefits, prediction of configurations, influence of substituents on enantioselectivity and reactivity, kinetic racemic resolutions; Jacobsen-AE: Mn-Salen- catalysts, Sharpless-AD, cinchona alkaloids; Oxon- epoxidations.

C-C-Couplings (metal- and organo-catalyses)

Additions to prochiral carbonyl compounds: organo lithiums, Grignard compounds, organo zincs, catalytic cycle with DAIB and other. β-amino alcohols, Merck's efavirenz-synthesis; enantioselective cross couplings: catalytic cycle (ox. add., transmetal., red. el.), dynamic kinetic resolution, P-N-ligands: valphos, ferrocenyl amino phosphanes, Negishi-, Suzuki, Stille-couplings, Heck-coupling; allylic substitutions: Pd catalyzed cycle, regio selectivities, allylic substrates: BSA, carbonates, ligands & catalyst concepts: Hayashi's sec. interactions, Trost's chiral pockets (dppba ligand), Helmchen's electronic differentiation (phox ligand); Lewis acid catalysis (aldol, Diels-Alder-additions); Cu-catalyzed 1,4-additions;

organo catalyses: Stetter- and benzoin-type additions, carbenes, phosphonates; sec.-amin-catalyses, prolin- aldol (Mannich)-type additions, Baylis-Hillman couplings; hydrogen-bonding catalysis.

C-heteroatom couplings

enantioselective acylations, kinetic racemic resolutions, allylic aminations.