



## Swiss Science Concentrates

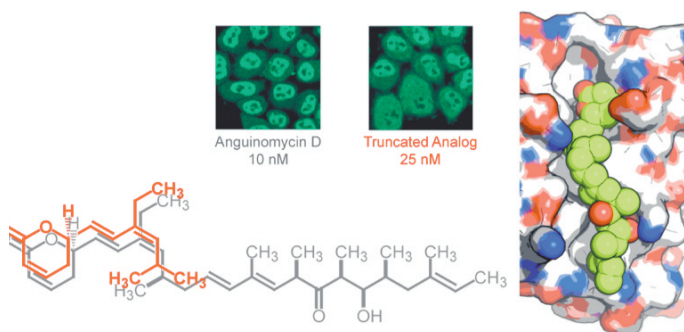
A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

### Anguinomycins and Derivatives: Total Syntheses, Modeling, and Biological Evaluation of the Inhibition of Nucleocytoplasmic Transport

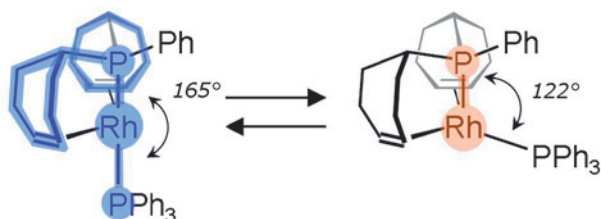
S. Bonazzi, O. Eidam\*, S. Güttinger, J.-Y. Wach, I. Zemp, U. Kutay\*, and K. Gademann\*, *J. Am. Chem. Soc.* **2010**, *132*, 1432  
EPF Lausanne, University of California, San Francisco, ETH Zürich

Synthetic routes to polyketide natural products anguinomycins C and D and simpler (yet very active) analogues are reported. Negishi stereoinversion cross coupling, Jacobsen Cr(III)-catalyzed hetero-Diels-Alder reaction, Evans Boron-mediated *syn*-aldol chemistry, and B-alkyl Suzuki-Miyaura cross coupling are used in the key steps. The structural basis for the inhibition was demonstrated by modeling the transport inhibitors into X-ray crystal structures, thus highlighting key points for successful and strong biological action of anguinomycins.



### Electromeric Rhodium Radical Complexes

F. F. Puschmann, J. Harmer, D. Stein, H. Rügger, B. de Bruin\*, and H. Grützmacher\*, *Angew. Chem., Int. Ed.* **2010**, *49*, 385  
ETH Zürich, Universiteit van Amsterdam, University of Oxford  
Electromers are species with significantly different electronic but only slightly different geometrical structures. In this report, the authors provide compelling evidence for the existence of two rapidly interconverting and energetically almost degenerate organometallic electromers in the paramagnetic complex  $[\text{Rh}(\text{trop}_2\text{PPh})(\text{PPh}_3)]$ . One single P-Rh-P angle determines whether the odd electron is delocalized over the whole molecule (see picture, blue) or is localized on the P-Rh unit (red).

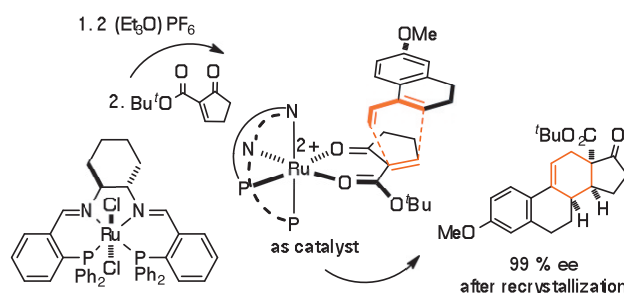


### Asymmetric Diels-Alder Reactions of Unsaturated $\beta$ -Ketoesters Catalyzed by Chiral Ruthenium PNNP Complexes

Christoph Schotes and Antonio Mezzetti\*, *J. Am. Chem. Soc.* **2010**, *132*, 3652

ETH Zürich

Dicationic ruthenium PNNP complexes, which efficiently catalyze asymmetric Michael addition, hydroxylation, and fluorination of saturated  $\beta$ -ketoesters, also promote the enantioselective Diels-Alder reaction of  $\alpha$ -methylene  $\beta$ -ketoesters to give tetrahydro-1-indanones. This approach allows the first enantioselective synthesis of both *nat*- and *ent*-enantiomers of estrone derivatives bearing an ester functionality at the  $\alpha$ -carbonyl bridgehead position.



### P-Chiral Ferrocenephospholanes: Synthesis, Reactivity, Metal Complex Chemistry and Application in the Asymmetric Hydrogenation of Olefins

Björn Gschwend, Benoit Pugin\*, Andreas Bertogg, and Andreas Pfaltz\*, *Chem. Eur. J.* **2009**, *15*, 12993

University of Basel, Solvias AG

Here the authors described the synthesis of P-chiral ferrocenephospholanes *via* a diastereoselective ortho-lithiation of a ferrocene derivative and a stereoconvergent intramolecular hydrophosphination. These mono- or bidentate ligands were converted to the corresponding Rh and Ir complexes which were tested in the asymmetric hydrogenation of functionalized and unfunctionalized olefins (*ee* up to 93%).

