SPOTLIGHTS ...

Asymmetric Hydrogenation

C. A. Sandoval,* Y. Li, K. Ding, R. Novori*

The Hydrogenation/Transfer Hydrogenation Network in Asymmetric Reduction of Ketones Catalyzed by [RuCl₂(binap)(pica)] Complexes

Chem. Asian J.

DOI: 10.1002/asia.200800246

AH vs. ATH: Asymmetric reduction of pinacolone is best achieved in ethanol containing the Ru catalyst (S)-1 ($X^1 = X^2 = Cl$; $X^1 = H$, $X^2 = BH_4$) and base under H_2 at ambient temperature to give (S)-3,3-dimethylbutanol in 97–98% *ee.* In contrast, asymmetric reduction of acetophenone with (S)-1 is attained with both H_2 (ambient temperature) and 2-propanol (> 60 °C), forming (R)-1-phenylethanol with lower enantioselectivity.

Protein Structures

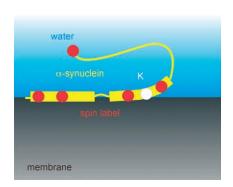
M. Drescher, F. Godschalk, G. Veldhuis, B. D. van Rooijen, V. Subramaniam.* M. Huber*

Spin-Label EPR on α-Synuclein Reveals Differences in the Membrane Binding Affinity of the Two Antiparallel Helices

ChemBioChem

DOI: 10.1002/cbic.200800238

Hidden peel: The interaction of α-synuclein (αS) with membranes is implicated in Parkinson's disease. Through EPR, the mobility of spin labels attached to αS was determined as a function of membrane composition. It revealed that αS peels off gradually from the membrane, an indication that the membrane interaction could be initiated at the N terminus of αS .



Femtochemistry

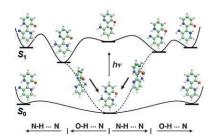
J. M. Ortiz-Sánchez, R. Gelabert, M. Moreno,* J. M. Lluch

Study of the Photochemical Properties and Conical Intersections of [2,2'-Bipyridyl]-3-amine-3'-ol

ChemPhysChem

DOI: 10.1002/cphc.200800322

Photoinduced proton transfer: The photochemical behavior of [2,2'-bipyridyl]-3-amine-3'-ol (see figure) is analyzed theoretically and compared with that of the isoelectronic analogues [2,2'-bipyridyl]-3,3'-diamine and [2,2'-bipyridyl]-3,3'-diol. Conical intersections play a key role in the photochemistry of these systems.



Antiviral Agents

S. Pettersson, V. I. Pérez-Nueno,

L. Ros-Blanco,

R. Puig de La Bellacasa, M. O. Rabal,

X. Batllori, B. Clotet,

I. Clotet-Codina, M. Armand-Ugón,

J. Esté, J. I. Borrell, J. Teixidó*

Discovery of Novel Non-Cyclam Polynitrogenated CXCR4 Coreceptor Inhibitors

ChemMedChem

DOI: 10.1002/cmdc.200800145

NH HN
AMD3100

N
$$\left\{CH_{2}\right\}_{n}$$

Y = -NH-CH₂; Z = -CH₂-NH-
2 Y = -NS-CH- 7 = -CH=N-

8 Y = -N=CH-; Z = -CH₂-NH-

Improving on a good thing: A combinatorial library of non-cyclam polynitrogenated compounds was designed by preserving the main features of AMD3100. A selection of diverse compounds from this library were prepared, and their in vitro activity was tested in cell cultures against HIV strains. This led to the identification of novel potent CXCR4 coreceptor inhibitors without cytotoxicity at the tested concentrations.

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Aldehyde Oxidation

Transition-metal-free organocatalytic oxidations of various aldehydes proceed with the TEMPO radical as a mild organic oxidant; the resulting TEMPO esters are formed in moderate to excellent yields (see scheme).

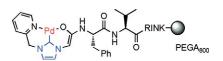
N-Heterocyclic carbenes (NHCs) are efficient catalysts and activate aldehydes for electron-transfer reactions. The TEMPO esters are readily hydrolyzed and the nitroxide can be regenerated by aerobic oxidation.

J. Guin, S. De Sarkar, S. Grimme, A. Studer*

Biomimetic Carbene-Catalyzed Oxidations of Aldehydes Using TEMPO

Angew. Chem. Int. Ed. DOI: 10.1002/anie.200802735

Peptide-based NHC-pyridine ligands and their palladium complexes were synthesized on solid support and characterized by NMR and mass spectrometry. The supported ligands were complexed to palladium by treatment with BEMP and PdCl₂COD. Successful catalytic applications were demonstrated in Sonogashira and Suzuki cross-coupling reactions performed in organic solvent or water.



NHC-Pyridine Complexes

K. Worm-Leonhard, M. Meldal*

Green Catalysts: Solid-Phase Peptide Carbene Ligands in Aqueous Transition-Metal Catalysis

Eur. J. Org. Chem.

DOI: 10.1002/ejoc.200800633

1. Homologation 2. β-gluco selective glycal fluoro-phosphorylation HO OH Heptosyl transferase

Antibacterial agent 007: Heptosides are found in important bacterial glycolipids such as lipopolysaccharide (LPS), the biosynthesis of which is targeted for the development of novel antibacterial agents. This work describes

the synthesis of a fluorinated analogue of ADP-L-glycero- β -D-manno-hepto-pyranose, the donor substrate of the heptosyl transferase WaaC, which catalyzes the incorporation of this carbohydrate into LPS (see scheme).

Fluorophosphorylation

H. Dohi, R. Périon, M. Durka, M. Bosco, Y. Roué, F. Moreau, S. Grizot, A. Ducruix, S. Escaich, S. P. Vincent*

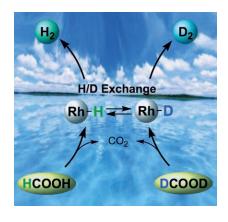
Stereoselective Glycal Fluorophosphorylation: Synthesis of ADP-2-fluoroheptose, an Inhibitor of the LPS Biosynthesis

Chem. Eur. J.

DOI: 10.1002/chem.200801279

Forming formate and generating gas:

The water-soluble rhodium aqua complex $[Rh^{III}(Cp^*)(bpy)(H_2O)]^{2+}$ efficiently and selectively catalyzes the decomposition of formic acid to H_2 and CO_2 in aqueous solution at 298 K. Hydrogen evolution occurs through formation of the formate complex, $[Rh^{III}(Cp^*)\{OC(O)H\}(bpy)]^+$, followed by a rate-determining β -hydrogen elimination to afford the hydride complex, $[Rh^{III}(Cp^*)(H)(bpy)]^+$, the catalytic active species.



Hydrogen Generation

S. Fukuzumi,* T. Kobayashi,

T. Suenobu

Efficient Catalytic Decomposition of Formic Acid for the Selective Generation of H₂ and H/D Exchange with a Water-Soluble Rhodium Complex in Aqueous Solution

ChemSusChem

DOI: 10.1002/cssc.200800147