

SPOTLIGHTS ...

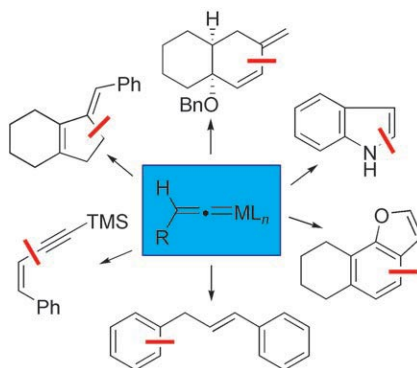
Vinylidenes

B. M. Trost,* A. McClory

Metal Vinylidenes as Catalytic Species in Organic Reactions

Chem. Asian J.

DOI: 10.1002/asia.200700247



It's a very useful thing: Metal vinylidenes may be accessed through transition-metal activation of terminal alkynes. This Focus Review addresses the reactions that these electrophilic species undergo as well as their application in organic synthesis.

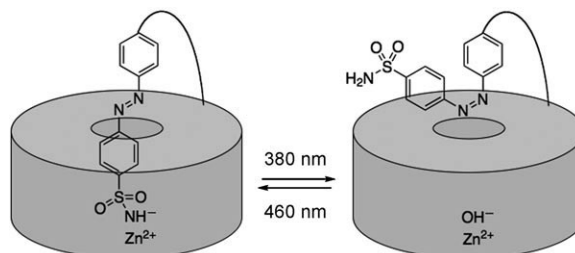
Photoaffinity Labeling

J. H. Harvey, D. Trauner*

Regulating Enzymatic Activity with a Photoswitchable Affinity Label

ChemBioChem

DOI: 10.1002/cbic.200700570



Best PALs: We have applied a photo-switchable affinity label (PAL) to the optical control of protein function. The enzymatic activity of native carbonic anhydrase was controlled with cova-

lently tethered, photoswitchable inhibitors (see scheme). This system allows the photoregulation of native proteins without site-specific introduction of highly reactive residues.

Internal Rotations

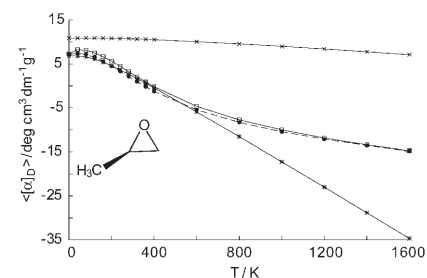
B. C. Mort, J. Autschbach*

A Pragmatic Recipe for the Treatment of Hindered Rotations in the Vibrational Averaging of Molecular Properties

ChemPhysChem

DOI: 10.1002/cphc.200700628

Effects of internal rotations: A computational procedure to treat hindered rotations in the vibrational averaging of molecular properties and their temperature dependence is undertaken. The figure shows the impact of the hindered rotation of the methyl group in (*R*)-methyloxirane on the optical rotation as a function of temperature.



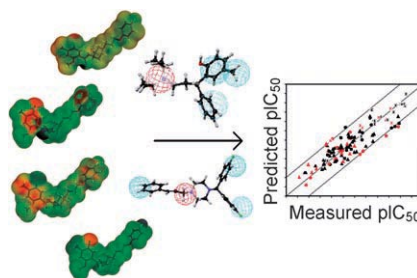
QSAR Models

C. Kramer, B. Beck,* J. M. Kriegl, T. Clark*

A Composite Model for hERG Blockade

ChemMedChem

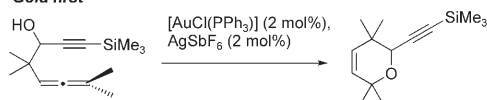
DOI: 10.1002/cmdc.200700221



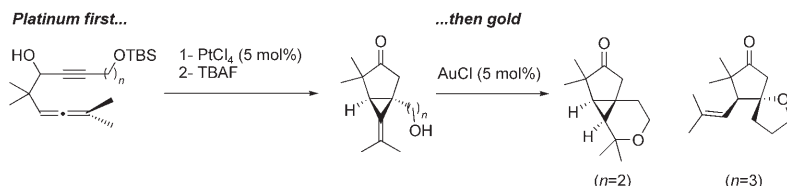
hERG blockade is one of the major toxicological problems in lead structure optimization. We present a predictive QSAR model for hERG blockade that differentiates between specific and nonspecific binding by preliminary pharmacophore scanning. While PLS and SVR models reach competitive R^2 values, the mixture of interpretable quantum mechanically derived descriptors and pharmacophore-based splits of the datasets offers a novel approach toward the understanding of hERG blockade.

... ON OUR SISTER JOURNALS

Gold first



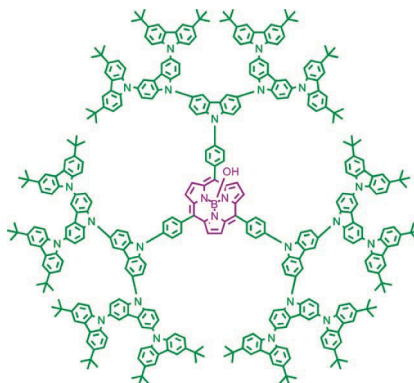
Platinum first...



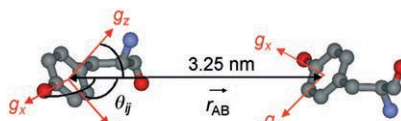
Gamble on gold or platinum? Hydroxylated 1,5-allenynes can be cycloisomerized to dihydropyrans by an allenophilic Au^I catalyst. On the other hand, 6-methylenebicyclo[3.1.0]hexan-3-ones were formed after selective alkynophilic Pt-catalyzed cycloisomerization. The

methylenecyclopropane moiety can in turn be activated by Au^I , with formation of tricyclic compounds resulting from the nucleophilic attack of the double bond or spiro derivatives resulting from the nucleophilic attack of the cyclopropyl ring (see scheme).

Novel dendritic carbazole-functionalized subporphyrins have been synthesized from pyridine-tri(pyrrol-1-yl)borane and the corresponding aldehydes. In these molecules, efficient photoinduced intramolecular energy transfer occurs from the carbazole dendron to the subporphyrin core. The carbazole dendron can significantly influence the absorption and emission spectra of the subporphyrin core, which are blueshifted with increasing dendron generation.



Paramagnetic centers rigidly embedded in proteins serve as a probe in structural studies of macromolecular complexes. Pulse EPR at high frequencies allows the determination of not only the distance but also the relative orientation of these centers (see tyrosyl radicals; C gray, O red, N blue). The method has considerable potential for studying the assembly of protein complexes.



Homogeneous Catalysis

R. Zriba, V. Gandon, C. Aubert, L. Fensterbank,* M. Malacria*

Alkyne versus Allene Activation in Platinum- and Gold-Catalyzed Cycloisomerization of Hydroxylated 1,5-Allenynes

Chem. Eur. J.

DOI: 10.1002/chem.200701522

Dendritic Subporphyrins

T. Xu, R. Lu,* X. Liu, P. Chen, X. Qiu, Y. Zhao

Synthesis and Characterization of Subporphyrins with Dendritic Carbazole Arms

Eur. J. Org. Chem.

DOI: 10.1002/ejoc.200700981

High-Field Pulsed EPR Spectroscopy

V. P. Denysenkov, D. Biglino, W. Lubitz, T. F. Prisner, M. Bennati*

Structure of the Tyrosyl Biradical in Mouse R2 Ribonucleotide Reductase from High-Field PELDOR

Angew. Chem. Int. Ed.

DOI: 10.1002/anie.703753

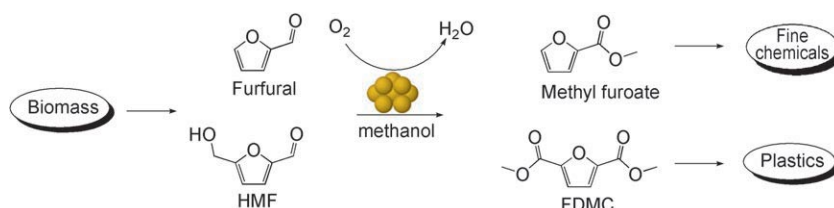
Heterogeneous Catalysis

E. Taarning, I. S. Nielsen, K. Egeblad, R. Madsen, C. H. Christensen*

Chemicals from Renewables: Aerobic Oxidation of Furfural and Hydroxymethylfurfural over Gold Catalysts

ChemSusChem

DOI: 10.1002/cssc.200700033



Aerobic exercise: The biomass-derived platform chemicals furfural and hydroxymethylfurfural (HMF) are readily oxidized in methanol in the presence of oxygen and a supported gold nanoparticle catalyst to afford the corresponding methyl esters (see

scheme). Thus, furfural was oxidized to methyl furoate under very mild conditions, and HMF was converted into furan-2,5-dimethylcarboxylate (FDMC), a potential polymer building block, with high yields.