Spotlights ...

Allylations

J. T. Mohr, B. M. Stoltz*

Enantioselective Tsuji Allylations

OTMS
R²

R³

chiral ligand

R²

up to 99% yield up to 99% yield up to 99% yield up to 95% ee

OTMS
R³

R⁴

OR

R³

Pd⁰

chiral ligand

R²

R³

up to 99% yield up to 95% ee

OR

R¹

R³

up to 99% yield up to 99% yield up to 95% ee

up to 99% ee

A fresh take: Several variants of the Tsuji allylation reactions have been rendered enantioselective in recent years. These important developments have provided valuable methods for the synthesis of enantioenriched cycloalkanone building blocks. The use of these asymmetric reactions in total synthesis has also been reported. TMS = trimethylsilyl.

Chem. Asian J.

DOI: 10.1002/asia.200700183

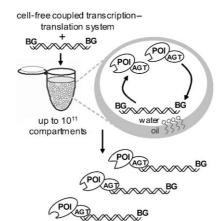
Protein Evolution

V. Stein, I. Sielaff, K. Johnsson, F. Hollfelder*

A Covalent Chemical Genotype–Phenotype Linkage for in vitro Protein Evolution

ChemBioChem

DOI: 10.1002/cbic.200700459



Display model. Proteins fused to O^6 -alkylguanine alkyltransferase (AGT) were expressed in vitro and conjugated to their coding DNA via O^6 -benzylguanine, a suicide inhibitor of AGT. The potential of this display system is demonstrated for several proteins in model selection experiments. Enrichments of up to 100-fold and DNA recovery rates of up to 2.4% are achieved per round of selection.

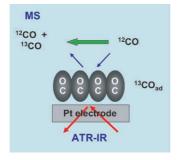
CO Adsorption

M. Heinen, Y.-X. Chen, Z. Jusys, R. J. Behm*

Room Temperature CO_{ad}
Desorption/Exchange Kinetics on Pt
Electrodes—A Combined In Situ IR and
Mass Spectrometry Study

Chem Phys Chem

DOI: 10.1002/cphc.200700425



Desorption and exchange of CO: The exchange of a saturated ¹³CO adlayer by gas-phase ¹²CO is monitored by in situ attenuated total reflection infrared spectroscopy (ATR–IR) spectroscopy and online mass spectrometry (see figure). First-order exchange and the dependence of the exchange rate on the partial pressure of ¹²CO indicate CO_{ad} desorption at room temperature and a desorption-controlled exchange mechanism.

Structure-Activity Relationships

B. R. Hearn,* K. Sundermann, J. Cannoy, D. V. Santi

Semisynthesis and Cytotoxicity of Hypothemycin Analogues

ChemMedChem

DOI: 10.1002/cmdc.200700128

Evaluation of the hypothemycin cytotoxicity SAR identifies the C4'-C8' region of the macrocyclic lactone as relatively intolerant of structural modifications. Manipulation of the 4-position of the resorcylic acid, however, provides new opportunities to improve solubility and pharmacokinetic properties as this site may be modified without negatively impacting cytotoxicity.

4-O-Demethylhypothemycin **5**, IC₅₀ = 43 nM (COLO829)

25, IC₅₀ = 42 nM (COLO829)

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 $\mathbf{M} = \mathbf{C}\mathbf{u}^{II}, \mathbf{C}\mathbf{r}^{III}, \mathbf{M}\mathbf{n}^{II}, \mathbf{F}\mathbf{e}^{III}, \mathbf{C}\mathbf{o}^{II}, \mathbf{N}\mathbf{i}^{II}, \mathbf{Z}\mathbf{n}^{II}, \mathbf{C}\mathbf{d}^{II}, \mathbf{or} \mathbf{M}\mathbf{g}^{II}$

Amorphous coordination polymers, formed by the linkage of [bis-(catechol)salen]Mn^{III} units, function as

recyclable heterogeneous asymmetric epoxidation catalysts.

Heterogeneous Asymmetric Catalysts

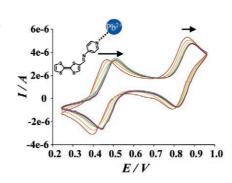
S.-H. Cho, T. Gadzikwa, M. Afshari, S. T. Nguyen,* J. T. Hupp*

[Bis(catechol)salen]Mn^{III} Coordination Polymers as Support-Free Heterogeneous Asymmetric Catalysts for Epoxidation

Eur. J. Inorg. Chem.

DOI: **10.1002/ejic.200700302**

Tetrathiafulvalene-imine-pyridine assemblies have been synthesized and shown to generate both electrochemical and colorimetric responses upon lead binding.



Responsive Ligands

J.-Y. Balandier, A. Belyasmine, M. Sallé*

Tetrathiafulvalene-Imine-Pyridine Assemblies for Pb²⁺ Recognition

Eur. J. Org. Chem.

DOI: **10.1002/ejoc.200700705**

$$[M]^* - NC Me + NC Me + NC Me NC M$$

Performance enhancement: By taking advantage of the knowledge of the relative abundance and stereochemistry of the active metallic intermediates present in the catalytic system (see scheme), a moderate enantioselectivity can be improved to achieve an excellent level of

selection. In addition, such studies provide explanations for unexpected trends, the relationship between the configuration at the metal to the stereochemical outcome, and the efficient reutilization of the catalyst.

Asymmetric Catalysis

D. Carmona,* M. P. Lamata, F. Viguri, R. Rodríguez, F. J. Lahoz, L. A. Oro

Half-Sandwich Rhodium (and Iridium) Complexes as Enantioselective Catalysts for the 1,3-Dipolar Cycloaddition of 3,4-Dihydroisoquinoline *N*-Oxide to Methacrylonitrile

Chem. Eur. J.

DOI: 10.1002/chem.200701140



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