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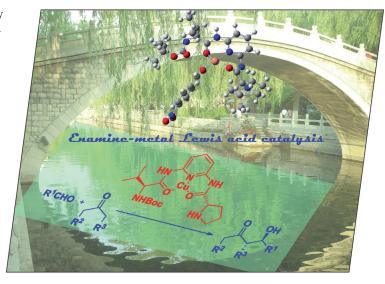




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## **COVER PICTURE**

The cover picture shows aldol reactions catalyzed by an enamine-metal Lewis acid bifunctional catalyst. The proposed transition state is also shown at the top. This bifunctional catalyst was developed by using a tridentate ligand to bring the Lewis acid and Lewis base in close proximity without quenching each other. The catalyst was found to catalyze aldol reactions in high activity and stereoselectivity. Details are discussed in the Short Communication by H. Wong et al. on p. 4581ff. The authors acknowledge Bo Wang for helping with the cover page design and Mike Novak for useful discussions.



# **MICROREVIEW**

#### **Stabilized Electrochromics**

S. Ito,\* N. Morita ...... 4567-4579



Creation of Stabilized Electrochromic Materials by Taking Advantage of Azulene Skeletons

**Keywords:** Cyanines / Cations / Redox chemistry / Electrochemistry / Liquid crystals

$$\left[\begin{array}{c} C & X & C \\ Z & & & \\ Y & \end{array}\right]^{1-l/t} \xrightarrow[+e]{-e} \left[\begin{array}{c} Z & X \\ & & \\ \end{array}\right]^{0} \xrightarrow[+e]{-e} \left[\begin{array}{c} X & X \\ & & \\ \end{array}\right]^{1+l/t}$$

Combinations of cyanine and/or violene substructures enable the design of stabilized electrochromic materials, including polyelectrochromic materials. Novel structural motifs based on utilization of the ability of the azulene skeleton to stabilize ionic states are demonstrated in several examples.

# **SHORT COMMUNICATIONS**

### **Bifunctional Catalysts**

Z. Xu, P. Daka, I. Budik, H. Wang,\* F.-Q. Bai, H.-X. Zhang ........ 4581–4585



Enamine—Metal Lewis Acid Bifunctional Catalysis: Application to Direct Asymmetric Aldol Reaction of Ketones

**Keywords:** Organocatalysis / Aldol reactions / Lewis acids / Lewis bases / Amino acids / Tridendate ligands

R<sup>1</sup>CHO + Cu(SbF<sub>6</sub>)<sub>2</sub> (20 mol-%) Q OH R<sup>2</sup> R<sup>3</sup> R<sup>3</sup> up to 96% yield, 99/1 
$$dr$$
 and 99%  $ee$ 

The direct asymmetric aldol reactions of ketones were catalyzed by metal Lewis acid/Lewis base bifunctional catalysts derived from proline in high yields with good to excellent stereoselectivity.

### **Cobalt Catalysis**

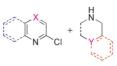
G. Toma,\* K. Fujita,

R. Yamaguchi\* ...... 4586-4588



Cobalt-Catalyzed C-N Bond-Forming Reaction between N-Aromatic 2-Chlorides and Secondary Amines

**Keywords:** Cobalt / Cross-coupling / C-N bond formation / Nitrogen heterocycles / Amines



الري Y=C,N,O

A cobalt-catalyzed C-N bond-forming reaction where a variety of N-aromatic 2-chlorides were employed is reported. Use of potassium carbonate as base and DPPP as ligand gave the best results. The present

X=C,N

reaction is the first Co-catalyzed C-N bond forming reaction involving N-aromatic 2-chlorides and secondary amines having a certain amount of versatility and functional group tolerance.



#### Mild Vinvlation Method

The development of a novel, microwave-assisted, heterogeneous, palladium-catalyzed (Pd/C) vinylation of 2(1H)-pyridones using potassium vinyltrifluoroborate as vinyl donor in water or NMP/water is described. This protocol is applicable to various iodo and bromo 2(1H)-pyridones providing a methodology for the synthesis of various compounds derived from this ring system.

B. K. Singh, C. Cavalluzzo, M. De Maeyer, Z. Debyser, V. S. Parmar,

E. Van der Eycken\* ...... 4589-4592

Microwave-Assisted Palladium-Catalyzed Heterogeneous Vinylation of 2(1H)-Pyridones



Keywords: Microwave chemistry / Heterogeneous catalysis / Nitrogen heterocyles / Natural products

# **FULL PAPERS**

Two novel metal-chelating amino acid building blocks were synthesized and incorporated in peptides with DNA-binding potential. The new amino acids are designed to mimic the imidazole ring of histidine with a triazole moiety while providing a tridentate ligand system for additional metal binding.

### **Metal-Binding Amino Acids**

A. Nadler, C. Hain, U. Diederichsen\* ...... 4593-4599

Histidine Analog Amino Acids Providing Metal-Binding Sites Derived from Bioinorganic Model Systems

Keywords: Amino acids / Metal binding / Coordination modes / Zinc finger / Click chemistry / Bioinorganic chemistry

#### Carene **\beta-Amino** Alcohols

Four recently reported carene β-amino alcohols are subject of careful conformational analysis and specific optical rotation calculations by using the TDDFT/ B3LYP approximation with the aug-ccpVDZ basis set. Despite their conformational flexibility and relatively small experimental specific rotations, we were able to theoretically confirm the absolute configuration of three of the studied systems.

K. Z. Łączkowski, A. Baranowska\* ...... 4600-4605

Conformational Analysis and Optical Rotation of Carene β-Amino Alcohols: A **DFT Study** 

Keywords: Amino alcohols / Density functional calculations / Conformational analysis / Optical rotation

#### **Heterocycles for NSAIDs**

The metathesis of heteroatom-substituted olefins, where the newly formed double bond can undergo versatile chemical transformations, is a valuable process in organic synthesis. In this study, to obtain new insight into enamide/ene metathesis, we established a novel method for the synthesis of 2,3-substituted indoles, which are a key unit of many biologically active molecules such as indomethacins.

Y. Kasaya, K. Hoshi, Y. Terada, A. Nishida, S. Shuto,\* M. Arisawa\* ...... 4606-4613

Aromatic Enamide/Ene Metathesis toward Substituted Indoles and Its Application to the Synthesis of Indomethacins

Keywords: Heterocycles / Metathesis / Iso-



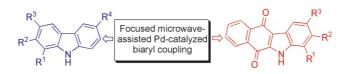
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#### **Carbazole Synthesis**

V. Sridharan, M. A. Martín, J. C. Menéndez\* ...... 4614–4621

Acid-Free Synthesis of Carbazoles and Carbazolequinones by Intramolecular Pd-Catalyzed, Microwave-Assisted Oxidative Biaryl Coupling Reactions — Efficient Syntheses of Murrayafoline A, 2-Methoxy-3-methylcarbazole, and Glycozolidine

**Keywords:** C-H activation / Heterocycles / Natural products / Quinones / Biaryl coupling



Focused microwave irradiation promotes the acid-free mild and efficient transformation of diarylamines into carbazoles through palladium-catalyzed oxidative biaryl coupling processes involving a double

C-H bond activation. The scope of this protocol is demonstrated through the total synthesis of three carbazole natural products, and it is also applied to the synthesis of benzo[b]carbazolequinones.

### **Conjugate Addition Reactions**

X. Pu, P. Li, F. Peng, X. Li, H. Zhang, Z. Shao\* ...... 4622–4626



Asymmetric Conjugate Addition of Acetylacetone to Nitroolefins with Chiral Organocatalysts Derived from Both  $\alpha$ -Amino Acids and Carbohydrates

**Keywords:** Amino acids / Asymmetric catalysis / Carbohydrates / Organocatalysis

Both enantiomers of a product of conjugate addition of acetylacetone to various nitroolefins can be achieved in almost the same enantiomeric excess with the

"matched" and "mismatched" chiral tertiary amine thioureas derived from both  $\alpha$ -amino acids and carbohydrates.

#### **Glycal Transformations**

A. M. Gómez,\* A. Pedregosa, A. Barrio, S. Valverde, J. C. López\* ...... 4627–4636

Synthesis of Furanosyl *C*-1 Glycals through Palladium-Catalyzed Reactions of a Furanosyl 2,3-Anhydro-*exo*-glycal

**Keywords:** Glycals / Carbohydrates / Electrophilic substitution / Nucleophilic substitution / Palladium / Umpolung

Pd(0)
Nucleophile (NuH)
or
Et<sub>2</sub>Zn, Electrophile (E)

$$R \longrightarrow SnR_3$$
 $R^1 = Nu, E_3$ 

Palladium-catalyzed transformations of a furanose-derived epoxy-exo-glycal, available in four steps from D-mannose, led to highly functionalized C-1 glycals through a  $\pi$ -allyl palladium intermediate.

#### **Alkaloid Synthesis**

C. C. Silveira, E. L. Larghi, S. R. Mendes, A. B. J. Bracca, F. Rinaldi,

T. S. Kaufman\* ...... 4637-4645



Electrocyclization-Mediated Approach to 2-Methyltriclisine, an Unnatural Analog of the Azafluoranthene Alkaloid Triclisine

**Keywords:** Synthesis design / Nitrogen heterocycles / Natural products / Alkaloids / Azafluoranthenes / Electrocyclization

The synthesis of an unnatural analog of the azafluoranthene alkaloid triclisine is reported. The synthesis was carried out in 10 steps and 21% overall yield through the in-

termediacy of 3,4-dimethoxyfluoren-9-one and featured a final microwave-assisted electrocyclization reaction.



### Temporary P-H Protection

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} O \\ P \end{array} \\ \begin{array}{c} O \\ H \end{array} \end{array} \begin{array}{c} \begin{array}{c} O \\ P \end{array} \\ \begin{array}{c} O \\ P \end{array} \end{array} \begin{array}{c} O \\ P \end{array} \begin{array}{c} O \end{array} \begin{array}{c} P \end{array} \begin{array}{c} O \\ P \end{array} \begin{array}$$

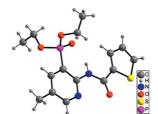
Because numerous organic reactions are not compatible with the presence of a P-H bond, the temporary protection of the P-H bond of H-phosphinates was investigated. Our methods have expanded the scope of available H-phosphinate starting materials. Various applications of the protection strategy are presented.

Temporary Protection of H-Phosphinic Acids as a Synthetic Strategy

Keywords: Phosphorus / Palladium / Metathesis / Cross-coupling / Synthetic methods

#### **Phosphonylation Method**

The synthesis of 2-amino- and 2-acylamidopyridine-3-phosphonates and 2-aminoquinoxaline-3-phosphonates by PdCl2-catalyzed coupling of the bromo precursors with triethyl phosphite is presented. The catalyst is formed in situ from PdCl2 and the phosphonylation reagent itself.



M. S. S. Adam, M. K. Kindermann, M. Köckerling, J. W. Heinicke\* ...... 4655-4665

Phosphonylation of 2-Amino- and 2-Amido-3-bromopyridines and 2-Amino-3chloroquinoxalines with Triethyl Phosphite

Keywords: Cross-coupling / Palladium / Nitrogen heterocycles / Phosphorus / Phosphonylation

#### Natural Products

The antitumour agent pancratistatin is prepared in a total of 25 steps from piperonal and xylose. The key transformation is a zinc-mediated tandem reaction between allylic bromide A and iodofuranoside B. Subsequent ring-closing metathesis furnishes lactone C, which is then converted into the natural product.

Convergent Synthesis of Pancratistatin from Piperonal and Xylose

**Keywords:** Allylation / Antitumour agents / Metathesis / Natural products / Total synthesis

Configuration is crucial: cis-silyloxiranes add a silvlthioacetal anion to give substitution with a Peterson olefination, whereas trans-silvloxiranes add the silvlthioacetal anion to give functionalized tetrahydrofurans.

### Silvloxirane Ring Opening

J. Lange, E. Schaumann\* ..... 4674-4684

Configuration-Dependent Ring Opening of Silvloxiranes: Synthesis of Functionalized Alkenes or Tetrahydrofurans

Keywords: Carbanions / Carbenes / Silanes / Oxygen heterocycles

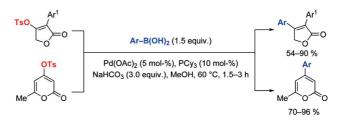
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### **Pd-Catalyzed Arylation**

F. Bellina,\* C. Marchetti, R. Rossi\* ....... 4685–4690

An Economical Access to 3,4-Diaryl-2(5H)-furanones and 4-Aryl-6-methyl-2(2H)-pyranones by Pd-Catalyzed Suzuki-Type Arylation of 3-Aryl-4-tosyloxy-2(5H)-furanones and 6-Methyl-4-tosyloxy-2(2H)-pyranones, Respectively

**Keywords:** Synthetic methods / C-C coupling / Palladium / Cross-coupling / Heterocycles



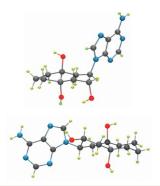
The  $Pd(OAc)_2/PCy_3$ -catalyzed arylation of 3-aryl-4-tosyloxy-2(5*H*)-furanones and 6-methyl-4-tosyloxy-2(2*H*)-pyranones with arylboronic acids in methanol at 60 °C in

the presence of NaHCO<sub>3</sub> as the base provides 3,4-diaryl-2(5*H*)-furanones and 4-aryl-6-methyl-2(2*H*)-pyranones, respectively, in high yields.

#### **Nucleoside Analogues**

Conformationally Restricted Nucleocyclitols: a Study into their Conformational Preferences and Supramolecular Architecture in the Solid State

**Keywords:** Chirality / Structure elucidation / Solid-state structures / Hydrogen bonding / Supramolecular chemistry / Adenine



A general synthetic strategy, directed towards the rapid functionalization of the aromatic nucleus in indane and tetralin into "conformationally constrained" nucleocyclitols, is offered. As the first representatives of this hitherto unexplored class of nucleoside analogues, two adeninederived, annulated nucleocyclitols were synthesized and their crystal structures studied. The self-assembly of the two nucleocyclitols occurs indivualistic.

Supporting information on the WWW (see article for access details).

If not otherwise indicated in the article, papers in issue 26 were published online on August 24, 2009

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