



BELGIUM























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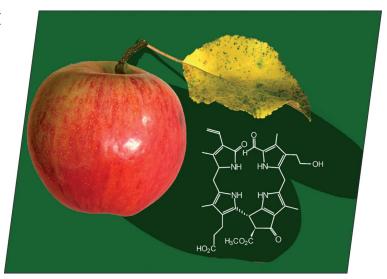




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members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

# **COVER PICTURE**

The cover picture shows a ripe apple and a yellow leaf from an apple tree. In ripening fruit and in leaf senescence, the green plant pigment chlorophyll is degraded to tetrapyrrolic, colourless catabolites (socalled NCCs), such as the one described by the structural formula given. The present knowledge on the occurrence and structural properties of chlorophyll catabolites in higher plants is outlined in the Microreview by B. Kräutler et al. on p. 21ff. Picture courtesy of Dr. Thomas Müller, University of Innsbruck, Austria.



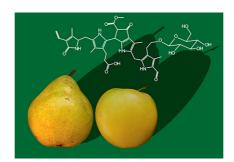
## **MICROREVIEW**

#### **Chlorophyll Catabolites**

S. Moser, T. Müller, M. Oberhuber, B. Kräutler\* ...... 21–31

Chlorophyll Catabolites – Chemical and Structural Footprints of a Fascinating Biological Phenomenon

**Keywords:** Natural products / Chlorophyll / Catabolism / Biomimetic synthesis / Structure elucidation / Tetrapyrroles



The elucidation of the chemical nature of chlorophyll catabolites has allowed the first structural insights into chlorophyll breakdown, assisting in developing understanding of the molecular basis and possible roles of this biological phenomenon. Current knowledge on chlorophyll catabolites in higher plants is outlined, as are their properties. Their antioxidant activity may give added value to fresh fruit.

# SHORT COMMUNICATIONS

#### **Sugars from Dioxanones**

I. Niewczas, M. Majewski\*..... 33-37



Building Higher Carbohydrates via Dioxanone Aldol Chemistry: The  $\alpha,\alpha'$ -Bisaldol Approach

**Keywords:** Aldol reactions / Organocatalysis / Dioxanone / Carbohydrates

A sequence of two aldol reactions on the dioxanone scaffold – the first one organocatalytic and the second proceeding via the lithium enolate – allows access to higher carbohydrates and their derivatives.

#### **Functionalization of Indolylmaleimides**

A. Brennführer, H. Neumann,

A. Pews-Davtyan, M. Beller\* ...... 38-42



Catalytic and Stoichiometric Synthesis of Novel 3-Aminocarbonyl-, 3-Alkoxycarbonyl-, and 3-Amino-4-indolylmaleimides

**Keywords:** Carbonylation / Palladium / Amination / Homogeneous catalysis / Protein kinase C inhibitors / Nitrogen heterocycles

R<sup>2</sup> ON N B Me

 $Nu = OR^3$ ,  $NR^4R^5$ 

Novel 3-substituted 4-indolylmaleimides have been synthesized by means of palladium-catalyzed carbonylation of 3-bromo-1-methyl-4-(2-methyl-3-indolyl)maleimide (1) with alcohols or amines in the

presence of carbon monoxide. In addition, amination of 1 proceeded smoothly in the absence of catalyst and gave the desired 3-amino-4-indolylmaleimides in good yields.



## **FULL PAPERS**

## Poly(vinyl glycoside) Models

Diol and triol derivatives were glycosylated in order to prepare model compounds for the stereo- and regiochemical analysis of poly(vinyl glycoside)s. The  $^{13}$ C NMR chemical shifts of the  $\alpha$ -C atoms of the

aglycon and the anomeric C atoms exhibit a strong dependence on the absolute stereoconfiguration of the  $\alpha$ - and the relative stereoconfiguration of the  $\gamma$ -C atoms, as well as the regiochemistry.

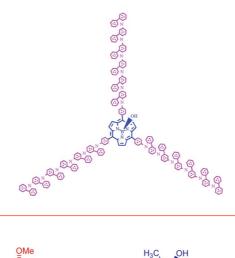
J. Yuan, H. Frauenrath\* ...... 43-52

Synthesis and <sup>13</sup>C NMR Spectroscopy of Model Compounds for theMicrostructure Analysis of Poly(Vinyl Glycoside)s

**Keywords:** Glycosylation / Chiral auxiliaries / Stereochemical effect / Poly(vinyl alcohol) / Microstructure

## **Star-Shaped Subporphyrins**

Novel star-shaped subporphyrins with monodisperse oligocarbazole arms were prepared by using pyridine-tri-*N*-pyrrolylborane as a template. It was found that excitation energy transfer took place from the oligocarbazole arms to the subporphyrin core.

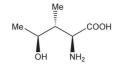


X. Liu, R. Lu,\* T. Xu, D. Xu, Y. Zhan, P. Chen, X. Qiu, Y. Zhao ............... 53-60

Subporphyrins with Monodisperse Oligocarbazole Arms

**Keywords:** Porphyrinoids / Fluorescence / Conjugation / UV/Vis spectroscopy / Energy transfer

#### **Synthetic Insulinotropic Molecules**



(2S,3R,4S)-4-hydroxyisoleucine: a naturally occurring insulinotropic molecule

6 analogues prepared from D-glucose [R = Me, Et, CH(OMe)CH<sub>2</sub>OMe]

racemic molecule prepared from hydroxyacetone

Synthetic analogues of (2S,3R,4S)-4hydroxyisoleucine have been prepared, mainly from D-glucose, by multi-step syntheses and evaluated for their ability to induce insulin secretion in pancreatic  $\beta$ -cells.

Multi-Step Synthesis and Biological Evaluation of Analogues of Insulin Secretagogue (2*S*,3*R*,4*S*)-4-Hydroxyisoleucine

**Keywords:** Carbohydrates / Lactones / Nucleophilic substitution / Amino acids / Biological activity

#### **Diversity in Heterocycle Synthesis**

A common synthetic pathway to convert 7oxanorbornenes into two distinct heterotricycles by selective *N*-allylation and subsequent domino metathesis has been developed. It is proposed that the latter reaction is guided by association of an amide carbonyl group with the Ru metal center of the catalyst. This methodology should be useful for construction of small-molecule libraries. Chemospecific Allylation and Domino Metathesis of 7-Oxanorbornenes for Skeletal and Appendage Diversity

**Keywords:** Alkylation / Combinatorial chemistry / Domino reactions / Metathesis / Multicomponent reactions

## **CONTENTS**

#### **Aminophosphonic Acids**

J. Beck, S. Gharbi, A. Herteg-Fernea,

L. Vercheval, C. Bebrone,

P. Lassaux, A. Zervosen,

J. Marchand-Brynaert\*..... 85-97



Aminophosphonic Acids and Aminobis-(phosphonic acids) as Potential Inhibitors of Penicillin-Binding Proteins

**Keywords:** Phosphonic acids / Amines / Schiff bases / Alkylation / Pudovik reaction / Inhibitors

m = 2

Resistance to penicillins is currently a major health concern. The search for non- $\beta$ -lactam drugs could open new routes in the fight against bacteria. By using aminocitric acid as template, which perfectly fits

n = 1; m = 2

$$\begin{array}{c|cccc} O & H & O \\ H_2N & P & OH \\ OH & P & OH \\ P & OH & P & P & OH \\ HO_2C & O & & O \\ \end{array}$$

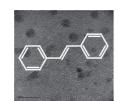
the active site of the BS3 enzyme, we have designed phosphonic analogues and homologues for the inhibition of bacterial  $\beta$ -lactamases and D,D-peptidases.

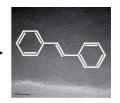
#### Palladium Nanoparticles

D. Tsvelikhovsky, I. Popov, V. Gutkin,

On the Involvement of Palladium Nanoparticles in the Heck and Suzuki Reactions

**Keywords:** C-C coupling / Heterogeneous catalysis / Nanotechnology / Palladium / Sol-gel processes





Whereas sol-gel encaged Pd(OAc)<sub>2</sub> catalyzes Heck and Suzuki reactions in boiling benzene with the formation of metallic colloids, no detectable nanoparticles are

formed when entrapped palladium derivatives of proline, tyrosine, or alanine are used to promote the coupling processes.

#### **Fluorocyclization**

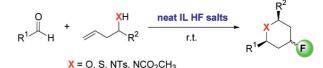
Y. Kishi, S. Inagi,

T. Fuchigami\* ...... 103-109



Prins Cyclization in Ionic Liquid Hydrogen Fluoride Salts: Facile and Highly Efficient Synthesis of 4-Fluorinated Tetrahydropyrans, Thiacyclohexanes, and Piperidines

**Keywords:** Cyclization / Ionic liquids / Fluorine / Heterocycles



Prins cyclization of homoallylic alcohols with various aldehydes was investigated in ionic liquid hydrogen fluoride (HF) salts, which played roles as a reaction medium, a catalyst, and a fluorine source. The reac-

tion afforded the corresponding 4-fluorinated tetrahydropyrans in excellent yields with a high stereoselectivity (*cis* form exclusively). Thia- and aza-Prins cyclization were also studied.

## **Ligand-Free Cross-Coupling**

Very Fast Suzuki-Miyaura Reaction Catalyzed by Pd(OAc)<sub>2</sub> under Aerobic Conditions at Room Temperature in EGME/H<sub>2</sub>O

**Keywords:** C-C coupling / Arenes / Boron / Palladium / Cross-coupling

The ligand-free Pd(OAc)<sub>2</sub>-catalyzed Suzuki—Miyaura C-C coupling performed in ethylene glycol monomethyl ether/H<sub>2</sub>O at room temperature under aerobic conditions is

presented. Very fast and quantitative reactions of aryl bromides with arylboronic acids were observed with TOFs up to  $180000\ h^{-1}$ .



#### Platinum Catalysis

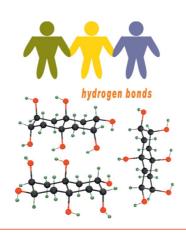
An interesting migration of the rigid structure of benzene was observed in platinumcatalyzed cyclizations of *o*-alkynyl(oxo)benzenes with alkenes. Various 8-oxabicyclo[3.2.1]octane derivatives with many

functional groups could be efficiently synthesized. The high stereo- and regioselectivity involved in this transformation was also attractive.

Platinum-Catalyzed Cyclization of *o*-Alk-ynyl(oxo)benzenes with Alkenes by 1,2-Migration of Benzene: Synthesis of 8-Oxabicyclo[3.2.1]octane Derivatives

**Keywords:** Platinum / 1,2-Migration / Homogeneous catalysis / Alkenes

Self-assembly of three designer perhydro-2,3,4a,6,7,8a-naphthalenehexols, all crafted on a conformationally locked *trans*-decalin framework, exhibit divergent supramolecular architecture, while conforming to core concepts of O–H···O hydrogen bonding identified in the crystal structures of alcohols and sugars.



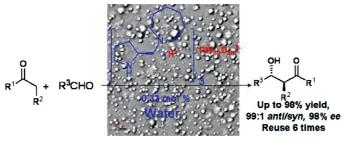
#### **Conformationally Locked Decalins**

G. Mehta,\* S. Sen ..... 123-131

Diverse and Yet Unified: A Comparative Study of the Supramolecular Assemblies of Three Diastereomeric Perhydro-2,3,4a,6,7,8a-naphthalenehexols

**Keywords:** Chirality / Hydrogen bonds / Supramolecular chemistry / Conformational locking

## Chiral Organic-Inorganic Hybrids



Chiral amine—polyoxometalate hybrids were found to be highly efficient and recoverable asymmetric enamine catalysts fora range of transformations with a catalyst loading as low as 0.33 mol-% under both neat and aqueous conditions.

Chiral Amine-Polyoxometalate Hybrids as Recoverable Asymmetric Enamine Catalysts under Neat and Aqueous Conditions

**Keywords:** Polyoxometalates / Amines / Organocatalysis / Immobilization / Biphasic catalysis

The *trans*-epoxide derivative of Combretastatin A-4 was stereoselectively prepared in good yield by sulfur ylide mediated epoxidation of silyl-protected isovanillin. From this key intermediate, a formal synthesis of CA-4, by stereoselective deoxygenation and photoisomerization, was achieved. Alternatively, a *trans*-dioxolane derivative was obtained by stereoselective acetone insertion.

# Combretastatin A-4 1) Nal, ZrCl<sub>4</sub> 2) hv, r.t. Acetone H<sub>3</sub>CO OCH<sub>3</sub> OTBS H<sub>3</sub>CO Acetone Amb. 15, r.t. H<sub>3</sub>CO OCH<sub>3</sub> OTBS

# **Oxygenated Combretastatins**

A Novel Approach to Combretastatins: From *trans*-Epoxide to CA-4 and Its Dioxolane Derivative

**Keywords:** Oxygen heterocycles / Ylides / Isomerization / Epoxidation

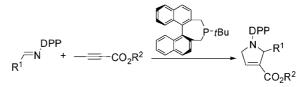
## **CONTENTS**

#### **Asymmetric Organocatalysis**

N. Pinto, N. Fleury-Brégeot, A. Marinetti\* ...... 146-151

Enantioselective Binaphthophosphepine-Promoted [3+2] Annulations of *N*-Ts- and *N*-DPP-Imines with Allenoates and 2-Butynoates

**Keywords:** Phosphanes / Asymmetric catalysis / [3+2] Cyclisations / Allenes / Imines



Comparative studies on the [3+2] cyclisation of *N*-diphenylphospinoyl and *N*-tosylimines with 2,3-butadienoates and 2-butynoates were performed in the presence

of (S)-tBu-binaphthophosphepine as the chiral catalyst. Enantiomerically enriched, (S)-configured N-DPP-pyrrolines were obtained in 73–92% ee.

#### **Nucleoside Modification**

M. K. Lakshman,\* A. Choudhury, S. Bae, E. Rochttis, P. Pradhan,

A. Kumar ...... 152–159



Synthesis of  $N^6$ ,  $N^6$ -Dialkyladenine Nucleosides Using Hexaalkylphosphorus Triamides Produced in Situ

**Keywords:** Inosine / Adenosine / Phosphorus triamide / Iodine / Amines

Tris(dialkylamino)phosphanes, formed in situ by treatment of PCl<sub>3</sub> with secondary amines, in conjunction with I<sub>2</sub> can be used to activate the C-6 amide carbonyl groups of inosine nucleosides. Subsequent dis-

placement of hexaalkylphosphoramide by the secondary amine leads to  $N^6$ , $N^6$ -disubstituted adenosine analogues. <sup>31</sup>P $\{^1H\}$  NMR studies were also conducted to evaluate reaction intermediates.

### D- and L-Fagomines

N. Kumari, B. G. Reddy, Y. D. Vankar\*..... 160–169

Efficient and Stereodivergent Syntheses of D- and L-Fagomines and Their Analogues

**Keywords:** Carbohydrates / Azasugars / Enzymes / Inhibitors / Fagomines / Total synthesis / Hydroazidation

The syntheses of D- and L-fagomines and their isomers from starting D-glycals have been achieved. The syntheses involve elaboration of common amino alcohol precur-

sors obtained from 2-deoxy-1-amino sugar derivatives. The key steps in the syntheses are intramolecular reductive amination and intramolecular N-heterocyclization.

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

If not otherwise indicated in the article, papers in issue 36 were published online on December 8, 2008

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