























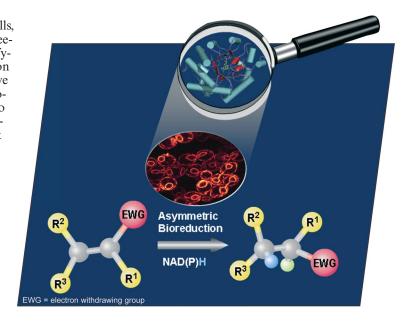




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria.** Czech Republic and Sweden) are Associates of the two journals.

# **COVER PICTURE**

The cover picture shows a culture of yeast cells, whose flavin-dependent reductases - their threedimensional structure is depicted in the magnifying glass – catalyse the asymmetric bioreduction of C=C bonds. Although these enzymes have been identified already in 1932, their true physiological role remains largely a mystery. Thanks to advances in genetic engineering, these biocatalysts are now becoming available in sufficient amounts to allow their application for preparative-scale biotransformations: Although their "natural" substrates are still unknown, the study of K. Faber et al. on p. 1511ff. shows that they accept an astonishing variety of alkenes bearing an electron-withdrawing group — such as enals, enones,  $\alpha,\beta$ -unsaturated imides, or nitroalkenes - to furnish the corresponding alkanes with excellent stereoselectivities. S. Kohlwein and G. Oberdorfer are thanked for their contribution in the design of the graphic.



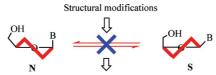
# **MICROREVIEW**

#### **Nucleoside Conformations**

C. Mathé,\* C. Périgaud ....... 1489-1505

Recent Approaches in the Synthesis of Conformationally Restricted Nucleoside Analogues

**Keywords:** Synthesis / Nucleoside analogues / Nucleoside conformation / Conformational analysis



Conformationally restricted nucleosides

This review describes some recent approaches in the preparation of nucleosides modified only on the pentofurano sugar moiety with an additional linkage capable of modulating the dynamic conformational equilibrium of the natural nucleoside. The results of the different structural modifications in terms of pseudorotational analysis, as well as the potential use of such conformationally restricted nucleoside analogues, as monomers, are also briefly presented.

# SHORT COMMUNICATION

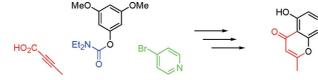
### **Alkaloid Synthesis**

T. K. Macklin, M. A. Reed, V. Snieckus\* ...... 1507–1509



Combined Metalation—Cross Coupling Strategies: A Synthesis of Schumanniophytine by a Key Biaryl *O*-Carbamate Remote Anionic Fries Rearrangement

**Keywords:** Total synthesis / Metalation / Directed remote metalation / C-C coupling



A short synthesis of the alkaloid schumanniophytine starting from simple building blocks and involving directed *ortho* metalation (DoM), Suzuki-Miyaura cross coupling, and a key *ortho*-silicon-directed remote anionic Fries rearrangement is described.

schumanniophytine

10 steps, 24%

# **FULL PAPERS**

## Asymmetric C=C Bond Reduction

M. Hall, C. Stueckler, B. Hauer, R. Stuermer, T. Friedrich, M. Breuer, W. Kroutil, K. Faber\* ............ 1511–1516

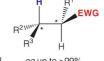


Asymmetric Bioreduction of Activated C=C Bonds Using *Zymomonas mobilis* NCR Enoate Reductase and Old Yellow Enzymes OYE 1-3 from Yeasts

**Keywords:** Reduction / Enzymes / Old Yellow Enzymes / Nitroalkenes / Alkenes / Stereocontrol



Asymmetric bioreduction of  $\alpha,\beta$ -unsaturated aldehydes, ketones, cyclic imides, esters, and nitro compounds by flavin-

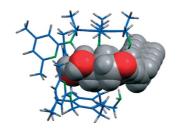


dependent enoate reductases furnished the corresponding saturated products in excellent enantiomeric excess.



### **Artificial Carbohydrate Receptors**

Acyclic receptors incorporating primary amide, hydroxy or amino groups as recognition units used in nature, as well as 2-aminopyridine units as heterocyclic analogues of the asparagine/glutamine primary amide side chains, have been established as highly effective and selective carbohydrate receptors. The design of these receptors was inspired by the binding motifs observed in the crystal structures of protein—carbohydrate complexes.



M. Mazik,\* M. Kuschel ...... 1517-1526

Amide, Amino, Hydroxy and Aminopyridine Groups as Building Blocks for Carbohydrate Receptors

**Keywords:** Molecular recognition / Receptors / Carbohydrates / Supramolecular chemistry / Hydrogen bonds

#### 

Hydroboration and hydroalumination of [1-(trifluoromethyl)propargyl]amines lead stereoselectively to the corresponding [(*Z*)-and (*E*)-1-(trifluoromethyl)allyl]amines.

(*Z*)- and (*E*)-Allylamines with a free amino group can be obtained in good yields and excellent enantioselectivity from the [1-(tri-fluoromethyl)propargyl]amines.

### **Stereoselective Hydrometallation**

G. Magueur, B. Crousse,\*
D. Bonnet-Delpon ...... 1527–1534

Stereoselective Access to Substituted [(E)-or (Z)-1-(Trifluoromethyl)allyl]amines

**Keywords:** Propargylamines / Allylamines / Fluorine / Hydroboration / Hydroalumination

### **Angularly Fused Carbocycles**

A tandem radical cyclization approach to the synthesis of angular tri- and tetracylic carbocycles is reported. On reduction with tributyltin hydride, bromo ketones yield  $\alpha$ -carbonyl radicals which on successive 5exo-dig/trig cyclizations afforded fused carbocycles. C. Prakash, A. K. Mohanakrishnan\* ...... 1535–1543

Synthesis of Angularly Fused Carbocycles via Tandem Radical Cyclization of  $\alpha\text{-Carbonyl}$  Radicals

**Keywords:** Radicals / Cyclization / Polycycles

#### **Z-DNA** Stabilization

The synthesis of an 8-bromo-2'-ethynylarabino-deoxyguanosine phosphoramidite building block was accomplished starting from guanosine. The title compound was incorporated in suitable oligonucleotides and its potential to induce the Z-DNA conformation was studied by CD spectroscopy.

A. Nadler, U. Diederichsen\* ...... 1544–1549

Guanosine Analog with Respect to Z-DNA Stabilization: Nucleotide with Combined C8-Bromo and C2'-Ethynyl Modifications

**Keywords:** Circular dichroism / Conformation / Nucleotide modification / Oligonucleotides / Z-DNA

# **CONTENTS**

#### **Polymethine Dyes**

K. Zyabrev,\* A. Doroshenko,

E. Mikitenko, Yu. Slominskii,

A. Tolmachev ...... 1550-1558

Design, Synthesis, and Spectral Luminescent Properties of a Novel Polycarbocyanine Series Based on the 2,2-Difluoro-1,3,2-dioxaborine Nucleus

**Keywords:** Ab initio calculations / Absorption / Dioxaborine / Fluorescence / Polymethine dye

The basic options for controlling the spectral properties of symmetric cyanine dyes

derived from 2,2-difluoro-1,3,2-dioxaborine have been evaluated.

### **Preorganisation versus Electronics**

A. J. Lowe, G. A. Dyson, F. M. Pfeffer\* ...... 1559–1567

Factors Influencing Anion Binding Stoichiometry: The Subtle Influence of Electronic Effects

**Keywords:** Anion recognition / Hydrogen bonding / Norbornene / Preorganisation / Supramolecular chemistry

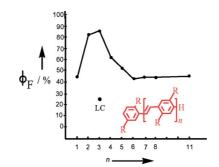
Based on <sup>1</sup>H NMR and UV/Vis studies, subtle electronic factors rather than preorganisation dictate the binding stoichiometry of the new, norbornene-based anion hosts **3a** and **3b** with acetate.

#### **OPV Fluorescence**

H. Meier,\* T. Lifka, U. Stalmach, A. Oehlhof, S. Prehl ...... 1568–1574

(*E,E,E*)-4,4'-Distyrylstilbenes – Synthesis, Photophysics, Photochemistry and Phase Behavior

**Keywords:** Condensation reaction / Fluorescence quantum yields / Liquid crystals / Oligo(phenylenevinylene)s / Photoreaction



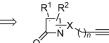
The maximum fluorescence quantum yield in the 2,5-bis(propyloxy)-OPV series is reached in solution for the trimer (n=3), but only a very special substitution pattern provides fluorescent trimers, which form LC systems.

### **C-C Coupling**



Synthesis of Novel Bis(β-lactam)-1,3-diynes by Copper-Promoted Homo- or Cross-Coupling of Alkynyl-2-azetidinones

**Keywords:** Alkynes / Copper / C-C coupling / Lactams / Synthetic methods



 $X, Y = O, CH_2; R^1, R^2, R^3, R^4 = Ar, alkyl; n, m = 0, 1$ 

Copper-mediated homo- and heterocoupling of alkynyl-2-azetidinones allows excellent access to novel racemic and

enantiopure  $C_2$ -symmetrical, as well as unsymmetrical, bis( $\beta$ -lactam)-1,3-diynes.



### Tripodal Scaffold

A convergent synthesis for the preparation of a new orthogonally protected tripodal scaffold has been developed. The scaffold was successfully coupled to a Tentagel solid support and further derivatised at the three attachment points demonstrating its possible use for combinatorial chemistry.

Synthesis of a Tripodal Scaffold for Solid Phase Synthesis of Artificial Receptors

**Keywords:** Receptor / Solid-phase synthesis / Combinatorial chemistry / Peptides / Protecting groups

#### **Organocatalysis**

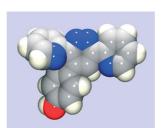
Does the mechanistic pathway of the title reaction pass through an enaminolactone intermediate? Both the experimental and theoretical data have allowed us to suggest a plausible bifunctional catalytic role for proline in the Baylis—Hillman reaction between MVK or EVK and aryl aldehydes using hydrogen carbonate as a co-catalyst. First Evidence of Proline Acting as a Bifunctional Catalyst in the Baylis—Hillman Reaction Between Alkyl Vinyl Ketones and Aryl Aldehydes

**Keywords:** Aldehydes / Baylis—Hillman reactions / Organocatalysis / Proline / Reaction mechanisms / Semi-empirical

calculations

### **Modified Pyridazine Ligands**

The syntheses and characterization of a large family of 3,6-di(2-pyridyl)pyridazines, functionalized in the 4- or 4,5-positions are described, along with representative structural data.



4-Substituted and 4,5-Disubstituted 3,6-Di(2-pyridyl)pyridazines: Ligands for Supramolecular Assemblies

**Keywords:** Cycloadditions / Diazines / Heterocycles / Pyridazine / Tetrazine

#### Heck Reaction

The Heck reaction proves its worth by attaching aromatic side-chains to the scaffold of vinylglycine. A pyrene-modified tripeptide prepared in this way binds to the TAR

RNA of HIV-1 with nanomolar affinity and also shows considerable antibiotic effects.

M. Suhartono, M. Weidlich, T. Stein, M. Karas, G. Dürner, M. W. Göbel\* ....... 1608–1614

Synthesis of Non-Natural Aromatic  $\alpha$ -Amino Acids by a Heck Reaction

**Keywords:** Amino acids / Antibiotics / Cross coupling / Heck reaction / Peptides

# **CONTENTS**

#### **Asymmetric Silylcyanation**

Z. Zeng, G. Zhao, Z. Zhou,\*
C. Tang ....... 1615–1618

A Novel Chiral (salen)Al<sup>III</sup> Complex Catalyzed Asymmetric Cyanosilylation of Aldehydes

**Keywords:** Aluminum / Asymmetric synthesis / Cyanides / Enantioselectivity / Aldehydes

The chiral (salen)Al<sup>III</sup> complex was found to be an efficient catalyst for the asymmetric trimethylsilylcyanation of aldehydes in the presence of tributylphosphane oxide as

an additive. The use of 1 mol-% of the complex led to the corresponding cyanohydrins in high yields with good-to-excellent enantioselectivities.

#### **One-Pot Synthesis of Benzoannulenes**

J. Bornhöft, J. Siegwarth, C. Näther, R. Herges\* ...... 1619–1624

Synthesis of Annulenes via Multiple Wittig
Reactions; In-Situ Dimerization of 1,2;5,6Dibenzocyclooctatetraene

**Keywords:** Wittig reaction / Dimerization / Annulenes / Hydrogenation / Macrocycles

A one-pot multiple Wittig reaction gives E,Z mixtures of dibenzo[8]-, tetrabenzo-[16]- and hexabenzo[24]annulene. The E,Z-

and the Z,Z-dibenzo[8]annulene dimerize in a formal [2+2] cycloaddition.

### **Oxidative Cyclization**

H. Vander Mierde, P. Van Der Voort,D. De Vos, F. Verpoort\* ....... 1625–1631

A Ruthenium-Catalyzed Approach to the Friedländer Quinoline Synthesis

**Keywords:** Nitrogen heterocycles / Ruthenium / Oxidative cyclization / Friedländer reaction

$$OH + R^2 \longrightarrow R^1 \longrightarrow R^R$$

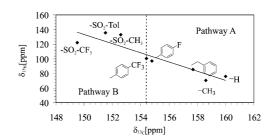
A ruthenium-catalyzed synthesis of substituted quinolines is achieved via an oxidative cyclization reaction of 2-aminobenzyl alcohol with a variety of ketones. Several reaction parameters, such as the choice of the ruthenium catalyst, base and hydrogen acceptor, are studied and optimized. Also the reaction mechanism is discussed.

#### Methanol from Oxazolidin-2-ones

J. Fröhlich, S. Berger\* ...... 1632-1634

The Use of NMR Chemical Shifts to Predict Reaction Pathways: Methanol Formation from Oxazolidinones

**Keywords:** Oxazolidinones /  $^{13}$ C NMR shift /  $^{15}$ N NMR shift / Reduction / Hammett parameter  $\sigma_p$ 



<sup>13</sup>C and <sup>15</sup>N NMR chemical shift analysis of the amide bond in oxazolidin-2-ones

leads to the prediction of the chemical pathway during reduction with LiAlH<sub>4</sub>.

If not otherwise indicated in the article, papers in issue 8 were published online on February 25, 2008