

















FRANCE







**SWEDEN** 

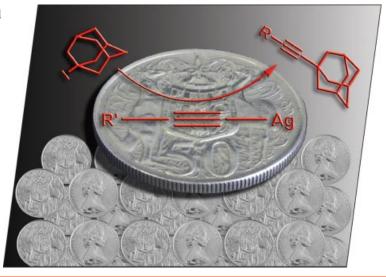




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further **EUChemSoc Societies (Austria,** Czech Republic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

# **COVER PICTURE**

The cover picture shows a rare, 80% silver, round Australian 50-cent piece, which was introduced in 1966 when Australia changed currency from the Australian pound to the Australian dollar. It was later replaced with a copper/nickel dodecagonal (12-sided) version in 1969. The coin underpins the reaction of a silver(I) acetylide with adamantyl iodide affording the bridgehead-substituted adamantylacetylene. This new methodology has nanotechnological ramifications as discussed in the article by C. M. Williams et al. on p. 241 ff. Brett D. Schwartz is acknowledged for preparing the artwork for the cover picture.



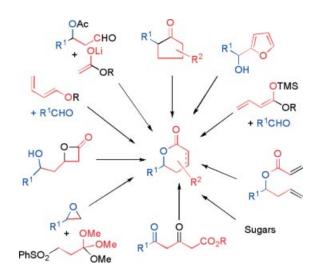
### **MICROREVIEW**

#### **Synthetic Strategies**

V. Boucard, G. Broustal, J. M. Campagne\* ...... 225-236

Synthetic Approaches to  $\alpha,\beta$ -Unsaturated  $\delta$ -Lactones and Lactols

**Keywords:** Lactones / Natural products / Total synthesis



Six-membered unsaturated  $\delta$ -lactones are ubiquitous in a number of natural products possessing potent cytotoxic activities. This

Microreview is focused on recent advances in the asymmetric synthesis of such compounds.

# SHORT COMMUNICATION

#### **Natural Product Synthesis**

A. B. Leduc, M. A. Kerr\* ...... 237-240



Total Synthesis of (±)-Decursivine

**Keywords:** Decursivine / Diels-Alder / Indole / Total synthesis / Boron aldol



A Diels—Alder/Plieninger indolization protocol sets the stage for elaboration of the resulting indole resulting in the first synthesis of the antimalarial natural product decursivine shown here against its source plant *Rhaphidophora decursiva*.

# **FULL PAPERS**

#### Polishing Silver for Bridgehead Substitution

R. H. Pouwer, J. B. Harper,K. Vyakaranam, J. Michl, C. M. Williams,\*C. H. Jessen, P. V. Bernhardt .... 241–248

Investigating Direct Alkynylation at the Bridgehead of Bicyclic Cages Using Silver(I) Acetylides

**Keywords:** Alkynylation / Silver(I) acetylides / Carbon-carbon bond formation / Bridgehead reactions / Bicyclic cages / Adamantanes / Carborate anions

$$X + Ag \xrightarrow{-AgX}$$

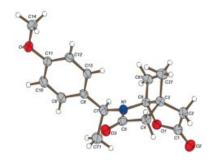
Although silver(I) acetylides have seen little synthetic use to-date, their ability to perform bridgehead substitution on bicyclic cages has been developed. This type of

methodology is of considerable importance due to relevant applications in the rapidly emerging field of nanotechnology.



**Chiral Hydroporphyrins** 

An optically active *N*-alkylated lactam-lactone and its diastereomer were used to prepare entantiomerically pure building blocks for the synthesis of hydroporphyrins.



G. Etornam Adukpo, T. Borrmann, R. Manski, R. I. Sáez Díaz, W.-D. Stohrer, F.-P. Montforts\* ...... 249-257

Synthesis of an Enantiomerically Pure Building Block for the Synthesis of Hydroporphyrins

**Keywords:** Hydroporphyrins / Nitrogen heterocycles / Chiral resolution / Circular dichroism

OHOMAN 
$$3-5$$
 steps OHOMAN  $n = 1, 2$  OHOMAN  $n$ 

The preparation of  $\beta$ -hydroxyhydrindanones and  $\beta$ -hydroxyhydroazulenones

from  $\alpha,\beta$ -enone and isoxazoline precursors is described.

# Hydrindanones and Hydroazulenones

Preparation of Sixteen 3-Hydroxy-4- and 7-Hydroxy-1-hydrindanones and 3-Hydroxy-4- and 8-Hydroxy-1-hydroazulenones

**Keywords:** Alcohols / Diastereoselectivity / Elimination / Fused-ring systems / Isomerization / Ketones

$$H \xrightarrow{Q} R^{1} \xrightarrow{\begin{array}{c} L\text{-proline,} \\ DEAD \\ \text{up to 87\% yield,} \\ \text{up to 86\% } ee \end{array}} H \xrightarrow{Q} NR_{2} \xrightarrow{R^{1}} R^{1}, R^{2} = Alkyl, Aryl HO \xrightarrow{R^{1}} R^{2}$$

An efficient access to configurationally stable  $\alpha$ , $\alpha$ -disubstituted  $\alpha$ -amino aldehydes, oxazolidinones, and  $\alpha$ -amino acids is presented. Starting from easily available racemic aldehydes, the  $\alpha$ -aminated products were obtained using azodicarboxyl-

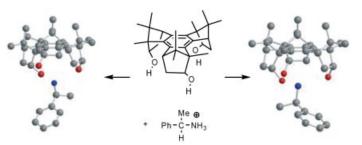
ates as the nitrogen source in up to 86% ee and moderate to excellent yield. These products could further be converted into the corresponding  $\alpha$ -amino alcohols, oxazolidinones, and into  $\alpha$ -alkylated phenylglycines.

#### **Asymmetric Amination**

The Proline-Catalyzed Asymmetric Amination of Branched Aldehydes

**Keywords:** Amination / Amino acids / Organocatalysis / Aldehydes / Asymmetric synthesis

# **Chiral Recognition**



(+)-syn-Benzotriborneol was obtained in eight steps from enantiopure (-)-bornyl acetate. This  $C_3$ -symmetric enantiopure tripodal ligand demostrated to act as an

efficient chiral solvating agent with (1-phenethyl)ammonium ion, affecting appreciable splitting of <sup>1</sup>H and <sup>13</sup>C NMR resonances of this chiral ion.

A Novel  $C_3$ -Symmetric Triol as Chiral Receptor for Ammonium Ions

**Keywords:** Chirality / Host-guest systems / Enantioselective recognition / Cyclotrimerization / Tripodal ligand

# **CONTENTS**

#### **Absolute Configuration**

H. Hussain, K. Krohn,\* U. Floerke, B. Schulz, S. Draeger, G. Pescitelli, S. Antus, T. Kurtán ................................ 292–295

Absolute Configurations of Globosuxanthone A and Secondary Metabolites from *Microdiplodia* sp. – A Novel Solid-State CD/TDDFT Approach

**Keywords:** Fungal secondary metabolites / *Microdiplodia* sp. / Dihydroxanthenone / Single-crystal X-ray analysis / TDDFT CD calculations / Solid-state CD

The absolute configuration of the potent new antitumor antibiotic, globosuxanthone A is established by a combination of X-ray structure analysis, quantum-mechanic calculatation of the theoretical CD spectrum from the X-ray coordinates and comparison with the solid-state CD spectrum.

#### **Absolute Configuration**

G. Kerti, T. Kurtán,\* T.-Z. Illyés, K. E. Kövér, S. Sólyom, G. Pescitelli, N. Fujioka, N. Berova,

S. Antus\* ...... 296-305

Enantioselective Synthesis of 3-Methylisochromans and Determination of Their Absolute Configurations by Circular Dichroism

**Keywords:** Chirality / Configuration determination / Kinetic resolution

Seven (S)-3-methylisochromans with different substitution patterns on their aromatic rings were synthesized from (S)-1-arylpropan-2-ol derivatives, and a CD study was performed on the effect of their achiral ring substituents. By oxidation of isochromans, dihydroisocoumarins and 1-methoxy-3-methylisochroman derivatives were also prepared.

#### Polyfluoroquinolines

N-Acetylation as a Means to Activate Polyfluoroarylamines for Selective *ortho*-Hydrodefluorination by Zinc in Aqueous Ammonia: A Concise Route to Polyfluorobenzo Azaheterocycles

**Keywords:** Amides / Hydrodefluorination / Ab initio calculations / Nitrogen heterocycles / Zinc

$$\begin{array}{c|c}
NHCOCH_3 & NHCOCH_3 \\
\hline
F & F & H & X \\
X & X = F, CF_3, H & X
\end{array}$$

Reduction of *N*-acetyl derivatives of polyfluoroarylamines by zinc in aqueous ammonia and subsequent Skraup heterocyclization of their *ortho*-hydrodefluori-

nated analogs thus prepared furnish an expeditious approach to quinolines polyfluorinated in the benzene moiety.



A new strategy toward the important class of benzomorphans is described. The key bond formation is based on an intramolecular Buchwald—Hartwig arylation reaction. After removal of the *N*-protecting group from the tricyclic benzomorphan derivatives, derivatization reactions are possible.

$$\begin{array}{c|c} & & & & \\ & O \\ Br & & & \\ \hline O \\ Br & & & \\ \hline O \\ CO_2Et \\ \hline & & \\ D \\ Bn & & \\ \hline & & \\ \hline & & \\ CO_2Et \\ \hline \\ & & \\ \hline & & \\ \hline \\ & & \\ \hline \\$$

#### Benzomorphan Synthesis

A. S. Khartulyari, M. E. Maier\* 317-324

Synthesis of Benzomorphan Analogues by Intramolecular Buchwald-Hartwig Cyclization

**Keywords:** Cyclization / Benzomorphan / Pd catalysis / Scaffold / Arylation

The fragmentation of primary alkoxyl radicals is usually a minor process with respect to other competing reactions. However, when  $\beta$ -amino alcohols were used as substrates, the scission proceeded in good to excellent yields. The fragmentation can be coupled with an allylation or alkylation reaction, to give alkaloid analogues and functionalized nitrogen heterocycles.

#### Alkaloids by Radical Fragmentation

Synthesis of Alkaloid Analogues from β-Amino Alcohols by β-Fragmentation of Primary Alkoxyl Radicals

**Keywords:** Alkaloids / Amino alcohols / Radical reactions / Nitrogen heterocycles / Cleavage reactions

# HO OH HO OH 1-step

#### **Chiral Ligands for Catalysis**

L. Finet, M. Dakir, I. Castellote, T. Kaoudi, L. Toupet, S. Arseniyadis\* ....... 335-341

Synthesis of Chiral Ligands from Hydrindene Diols with a Consecutive Heterodomino Transformation as the Key Reaction Step

**Keywords:** Chirality / Ligand design / Domino reactions / Bicyclo[2.2.2]octane

The threefold different oxygenation pattern of a domino product is used to generate bi-, tri- and polydentate ligands. The

inexpensive chirality was derived from (S)-(+)-Hajos-Parrish ketone in early steps.

New taxoid C-ring precursors, designed to minimize post-coupling elaboration are synthesized. The key feature of their preparation is a consecutive heterodomino reaction.

#### **Fully Functional Taxoid C-Ring Construction**

Practical Construction of Taxoid C-Ring Segments with a Consecutive Heterodomino Transformation as the Key Reaction Step

**Keywords:** Taxoid construction / Domino reactions / Bicyclo[2.2.2]octane / Oxidation

## **CONTENTS**

#### **Synthesis of Butenolides**

 OSiMe<sub>3</sub> OSiMe<sub>3</sub> + OCI HOME

Synthesis of γ-Alkylidenebutenolides by Formal [3+2] Cyclizations of 1,5- and 2,4-Bis(trimethylsilyloxy)-1,3,5-hexatrienes with Oxalyl Chloride

 $\gamma$ -Alkylidenebutenolides were regioselectively prepared by cyclization of 1,5- and

2,4-bis(trimethylsilyloxy)-1,3,5-hexatrienes with oxalyl chloride.

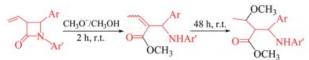
**Keywords:** Butenolides / Cyclizations / O-Heterocycles / Regioselectivity / Silyl enol ethers

#### Amino Esters from β-Lactams

L. De Vitis, L. Troisi,\* C. Granito, E. Pindinelli, L. Ronzini ............ 356-362

Tandem-Selective Bond Cleavage of the Lactam Nucleus and Michael Reaction

**Keywords:** Lactams / Amino esters / Cleavage reactions / Michael addition



Ar = phenyl; 4-methylthiazol-2-yl; Ar' = phenyl; thiazol-2-yl; 2-phenylethyl

Ring opening reactions were performed on 3-allyl- $\beta$ -lactams with CH<sub>3</sub>O<sup>-</sup>/CH<sub>3</sub>OH at room temperature and/or reflux. The lactam nucleus isomerization followed by the N1–C2 bond cleavage and the methanol

Michael addition affords substituted amino esters. The ring opening path is highlighted depending on the substituent at the lactam nitrogen atom, to C3 and C4, respectively.

#### **Asymmetric Oxidation**

S. Colonna,\* V. Pironti, F. Zambianchi,

G. Ottolina, N. Gaggero,

Diastereoselective Synthesis of  $\beta$ -Hydroxy Sulfoxides: Enzymatic and Biomimetic Approaches

**Keywords:** Sulfoxides / Cyclohexanone monooxygenase / Kinetic resolution / Bovine serum albumin / Enzyme catalysis / Asymmetric oxidation

An enzymatic route to enantiomerically enriched β-hydroxy sulfoxides is described.



#### **Total Synthesis**

An efficient enantioselective synthesis of (-)-(3S,6R)-3,6-dihydroxy-10-methylundecanoic acid from epichlorohydrin is described. The key steps include Jacobsen's hy-

drolytic kinetic resolution, Sharpless asymmetric dihydroxylation, regioselective opening of epoxide and cyclic sulfate.

S. Kumar Pandey, P. Kumar\* .... 369-373

Efficient Total Synthesis of (-)-(3S,6R)-3,6-Dihydroxy-10-methylundecanoic Acid

**Keywords:** Jacobsen's hydrolytic kinetic resolution (HKR) / Grignard reaction / Hydroboration—oxidation / Dihydroxylation / Regioselective / Cyclic sulfate

# RSH + R<sup>1</sup> EWG Borax (10 mol-%) r.t., water 5-180 min / 70-97 % R<sup>3</sup> NH + EWG Borax (10 mol-%) R<sup>4</sup> EWG R<sup>3</sup> EWG R<sup>3</sup> EWG R<sup>4</sup> R<sup>4</sup> R<sup>4</sup> R<sup>4</sup> R<sup>4</sup> R<sup>5</sup> R<sup>8</sup> R<sup>4</sup> R<sup>8</sup> R<sup>8</sup>

Borax very efficiently catalyzes the conjugate addition of thiols, dithiols and amines to  $\alpha,\beta$ -unsaturated ketones, nitriles,

amides, aldehydes and esters in water at room temperature.

#### **Clean Hetero-Michael Reactions**

S. Hussain, S. K. Bharadwaj, M. K. Chaudhuri,\* H. Kalita .... 374–378

Borax as an Efficient Metal-Free Catalyst for Hetero-Michael Reactions in an Aqueous Medium

**Keywords:** Borax / Thiols / Amines / Water / Michael addition

The geminal diacylates of a variety of aldehydes were prepared in good yields without any catalysts or solvent by simply refluxing the aldehydes with aliphatic acid anhydrides. The scope of the reactions and relative reactivities of aldehydes and acid anhydrides were examined.

$$\begin{array}{c} (R'CO)_2O \\ \hline \\ reflux, 1-6 \text{ h} \end{array} \qquad \begin{array}{c} R-CH(OCOR')_2 \\ R=\text{alkyl and substd.} \\ \text{phenyl, and furyl} \\ R'=CH_3, CH_2CH_3 \end{array}$$

**Geminal Diacylates** 

Preparation of Geminal Diacylates (Acylals) of Aldehydes — Scope and Reactivity of Aldehydes with Acid Anhydrides

**Keywords:** Geminal diacylate / Aldehydes / Acylals / Green chemistry

If not otherwise indicated in the article, papers in issue 1 were published online on December 15, 2006