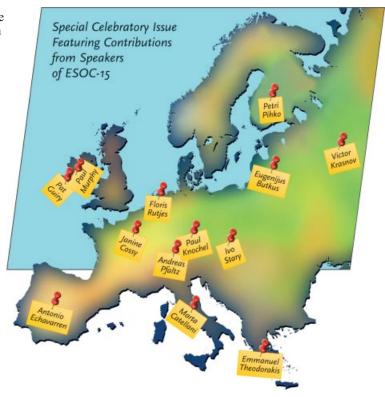
## **COVER PICTURE**

The cover picture shows that the contributors of the decennial celebratory issue of EurJOC come from all areas of Europe, thus highlighting the European heritage of the journal. The names of the corresponding authors are pinpointed in the region of Europe in which they conduct their research. The cover was conceptualised by Haymo Ross and designed by Denis Ott and Margitta Schmitt, both from the production department at Wiley-VCH.



# **CONFERENCE REPORT**

G C. Lloyd-Jones,\* M. Paz Muñoz, G. Owen-Smith ...... 4146-4150 15th European Symposium on Organic Chemistry (ESOC 15), Dublin, Ireland

## **MICROREVIEWS**

### **Aryl Coupling Reactions**

M. Catellani,\* E. Motti, N. Della Ca', R. Ferraccioli ....... 4153-4165

Recent Developments in Catalytic Aryl Coupling Reactions

**Keywords:** Aryl coupling / Homogeneous catalysis / Metallacycles / Palladium / Transition metals

Pd(OAc)<sub>2</sub> K<sub>2</sub>CO<sub>3</sub>, NMP 105 °C, 24 h

This microreview highlights recent advancements in catalytic aryl coupling methodologies, which provide powerful tools for the synthesis of compounds that are of interest to the fine chemical industry.



$$R^{2}-MgCI$$

$$R^{2}=Ar$$

$$R^{2}=Ar$$

$$R^{3}=Ar$$

$$R^{4}=Ar$$

$$R^{1}=Ar$$

$$R^{1}=Ar$$

$$R^{2}=Ar$$

$$R^{2}=Ar$$

$$R^{3}=Ar$$

$$R^{4}=Ar$$

$$R^{1}=Ar$$

$$R^{1}=Ar$$

$$R^{2}=Ar$$

Modern synthetic methods for the synthesis of primary, secondary, and tertiary amines are presented. Metal-catalyzed and

electrophilic amination reactions are covered, as well as the oxidative coupling of lithium amidocuprates.

Modern Amination Reactions

**Keywords:** Amines / C-N bond formation / Electrophilic amination / Oxidative couplings

## **Polyhydroxylated Scaffolds**

Saccharides, due to their multiple hydroxy groups and availability as chiral building blocks have been investigated as scaffolds for the synthesis of peptidomimetics, structurally constrained bivalent ligands and in the generation of novel scaffolds.

Peptidomimetics, Glycomimetics and Scaffolds from Carbohydrate Building Blocks

**Keywords:** Peptidomimetics / Macrocyclic scaffolds / Hybrid compounds / Multivalent ligands / Drug discovery

## SHORT COMMUNICATIONS

### Asymmetric Catalysis

Iridium complexes derived from chiral phosphane—oxazolines (phox ligands) are efficient catalysts for intramolecular Pauson—Khand reactions. Under optimized conditions high yields and enantioselectivities of > 90 % ee were

obtained with 2 mol-% of catalyst. The influence of the CO pressure and the anion were studied. The structure of a dicarbonyl(phox)iridium complex was determined by X-ray analysis.

Asymmetric Catalytic Intramolecular Pauson-Khand Reactions with Ir(phox) Catalysts

**Keywords:** Pauson—Khand reactions / Asymmetric catalysis / N,P ligands / Phosphane—oxazolines / Iridium

#### **Natural Products Synthesis**

A novel acid-mediated cyclopropylcarbinol ring expansion methodology has been explored for the construction of the AB ring framework of lancifodilactone F and related terpenoids of the *Schisandraceae* family of natural products. We found that this rearrangement, represented by the

conversion of 32 to 33, proceeds with good stereochemical control defined by inversion of the configuration at the C10 cyclopropyl center. These studies pave the way for a potentially bioinspired synthetic entry to the *Schisandraceae* metabolites.

Studies on the Synthesis of *Schisandraceae* Natural Products: Exploring a Cyclopropylcarbinol Ring Expansion Strategy

**Keywords:** Synthesis design / Cyclopropanation / Synthetic methods / Baeyer-Villiger oxidation / Ring expansion

## **FULL PAPERS**

### **Affinity Separation**

B. W. T. Gruijters, J. M. M. Verkade,

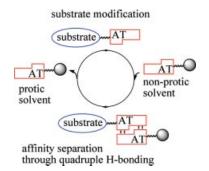
F. L. van Delft, R. P. Sijbesma,

P. H. H. Hermkens,

F. P. J. T. Rutjes\* ...... 4197-4204

A Novel Purification Method in Organic Synthesis Using Hydrogen Bonding

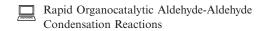
**Keywords:** Affinity separation / Hydrogen bonding / Ureidopyrimidinone / Parallel synthesis / Non-covalent linking



A new workup and purification method based on quadruple hydrogen-bonding interactions is reported. Substrates with a hydrogen-bonding affinity tag were conveniently separated from a reaction mixture and purified using a resin with self-complementary affinity tags. Ugi reaction products and substitution products were successfully purified by this affinity separation protocol.

#### **Amine Catalysis**

A. Erkkilä, P. M. Pihko\* ...... 4205-4216



**Keywords:** Aldehydes / Amines / Synthetic methods / Kinetics / Linear free energy relationships

An efficient secondary amine catalyst/acid co-catalyst combination has been identified, allowing the preparation of  $\alpha$ -substituted acroleins and  $\alpha,\beta$ -unsaturated aldehydes in a matter of minutes.

#### **Enyne Rearrangements**

N. Cabello, E. Jiménez-Núñez,

E. Buñuel, D. J. Cárdenas,

A. M. Echavarren\* ...... 4217-4223



On the Mechanism of the Puzzling "Endocyclic" Skeletal Rearrangement of 1,6-Enynes

**Keywords:** Gold / Platinum / Enynes / Rearrangement / DFT Calculations

$$Z \xrightarrow{AuL} R'$$

$$Z \xrightarrow{H} R$$

$$Z \xrightarrow{R'} R'$$

$$Z \xrightarrow{R'} R'$$

Gold(I) behaves differently from platinum(II) or (IV) as a catalyst in the skeletal rearrangement of enynes. With gold(I), formation of six-membered rings by a rearrangement that proceeds by a new type of single cleavage is also possible.

### **Ring Expansion Reactions**

I. Déchamps, D. Gomez Pardo,

J. Cossy\* ...... 4224-4234

Ring Expansion Induced by DAST: Synthesis of Substituted 3-Fluoropiperidines from Prolinols and 3-Fluoroazepanes from 2-Hydroxymethylpiperidines

**Keywords:** Ring expansion / Rearrangement / Fluorine / Aziridinium / Nitrogen heterocycles

$$R" \xrightarrow{n} R' OH \xrightarrow{\text{Et}_2 \text{NSF}_3} R" \xrightarrow{R'} F \\ P \xrightarrow{\text{DAST}} R \xrightarrow{\text{DAST}} R \xrightarrow{\text{R}} R$$

Optically active prolinols can be converted into optically active 3-fluoropiperidines by treatment with DAST. The reaction often produces the 2-fluoromethylpyrrolidines as byproducts. The rearrangement proceeds via an aziridinium intermediate.



#### **Asymmetric Allylation of Aldehydes**

Ligands with an oxazoline ring linked by an amide bond to a chiral protected proline unit were prepared and used in the enantioselective Nozaki-Hiyama-Kishi allylation of benzaldehyde to give enantioselectivities up to 57 %. Diastereomeric ligand pairs were prepared to determine the role of each chiral centre in enantioselection

New Proline-Oxazoline Ligands and Their Application in the Asymmetric Nozaki-Hiyama-Kishi Reaction

**Keywords:** Asymmetric catalysis / Oxazolines / Proline / Ligands / Allylation

Helicenes

$$CH_3O$$
 $CH_3O$ 
 $R^1 = CH_3O \text{ or } H$ 
 $R^2 = OH \text{ or } H$ 

2-Hydroxy- and 2,15-dihydroxyhexahelicene were synthesised from simple benzene and naphthalene building blocks by intramolecular Co<sup>1</sup>- or Ni<sup>0</sup>-catalysed [2+2+2] cycloisomerisation of CH<sub>3</sub>O-substituted

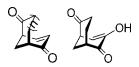
aromatic triynes. This approach avoids vexing photodehydrocyclisation of stilbenetype precursors, providing thus a useful alternative to classical procedures.

A Convenient Route to 2-Hydroxy- and 2,15-Dihydroxyhexahelicene

**Keywords:** Alkynes / Arenes / Cyclotrimerisation / Fused-ring systems

**Enantiospecific Synthesis** 

A series of enantiomerically pure bicyclo-[3.3.1]nonane  $\alpha,\beta$ -enones were synthesized, and the  $\alpha,\beta$ -enone chromophore was studied by circular dichroism. The chiroptical properties of the enantiomerically pure compounds were investigated. The circular dichroism spectra provided evidence for interchromophoric interaction in dichromophoric molecules.



E. Orentas, G. Bagdžiūnas, U. Berg, A. Žilinskas, E. Butkus\* ...... 4251–4256

Enantiospecific Synthesis and Chiroptical Properties of Bicyclic Enones

**Keywords:** Chirality / CD spectroscopy / Chromophores / Enantiospecific synthesis / Enones

Modification of Amino Acids

$$\begin{array}{c} \text{Br} \swarrow \overset{CO_2Me}{\longleftarrow} \overset{H}{\underset{PhthN}{\longleftarrow}} \overset{R'RN}{\longleftarrow} \overset{CO_2Me}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{CO_2Me}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{CO_2H}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{CO_2H}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{R'R}{\longleftarrow} \overset{R'R}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{R'RN}{\longleftarrow} \overset{R'R$$

We have shown that by using dimethyl (2S,4RS)-4-bromo-N-phthaloylglutamate as the starting material we obtain diastereomeric racemates of 4-amino-5-oxo-

proline and 4-aminoglutamic acid derivatives. In the case of secondary arylamines, the individual stereoisomers of the target products can be prepared.

Synthesis of 4-Amino Derivatives of 5-Oxoproline

**Keywords:** Amino acids / Nucleophilic substitution / Hydrolysis /  $\gamma$ -Lactams / Diastereoselectivity

If not otherwise indicated in the article, papers in issue 24 were published online on August 2, 2007