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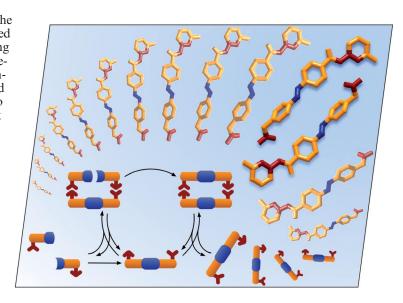
Portugal



A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by meraina 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 in the lower left corner the schematic representation of a recognition-mediated autocatalytic cycle that is capable of producing multiple copies of a single molecule in a templatedirected manner. The molecular recognition inherent in this cycle (red) leads to the accelerated formation of an imine bond (blue) between two building blocks through a ternary complex that renders the reaction between them pseudointramolecular. After bond formation, the product duplex dissociates and returns two molecules to the start of the autocatalytic cycle. The structure in the upper right corner represents the product duplex as determined by single-crystal X-ray diffraction ([18·18], taken from ref.<sup>[28]</sup>). The multiple copies of the reaction product shown highlight the exponential increase in the concentration of the product inherent in selfreplicating systems. Details are presented in the Microreview by A. Vidonne and D. Philp on p. 593ff.



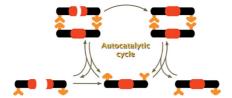
## **MICROREVIEW**

#### **Self-Replication**

A. Vidonne, D. Philp\* ...... 593-610

Making Molecules Make Themselves – the Chemistry of Artificial Replicators

**Keywords:** Hydrogen bonds / Molecular recognition / Self-replication / Supramolecular chemistry / Systems chemistry / Template synthesis



"Is the structural complexity of nucleic acids necessary to store and transmit information at a molecular level?". In this Microreview, we describe the design and implementation of systems based on small, synthetic organic molecules that can reproduce themselves.

# SHORT COMMUNICATION

#### Stereoselectivity

Stereoselectivity of Glycosylation May Change During the Reaction Course: Highly  $\alpha$ -Stereoselective Sialylation Achieved by Supramer Approach

**Keywords:** Glycosylation / Stereoselectivity / Sialic acids / Hydrogen bonds / Amides

Regular sialylation
(3 h)
$$\alpha/\beta = 7:1$$
Optimized sialylation
(15 min)
 $\alpha/\beta = 27:1$ 

Highly α-stereoselective sialylation of 1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranose (ROH) with sialic acid thioglycoside 1 was achieved by very simple means: (a) addition of non-reacting compound (DAMA), (b) decrease of reaction time (from 3 h to 15 min).

# **FULL PAPERS**

#### **Multicomponent Reactions**

M. J. Arévalo, N. Kielland, C. Masdeu, M. Miguel, N. Isambert,

R. Lavilla\* ...... 617-625



Multicomponent Access to Functionalized Mesoionic Structures Based on TFAA Activation of Isocyanides: Novel Domino Reactions

**Keywords:** Multicomponent reactions / Domino reactions / Isocyanides / Nitrogen heterocycles / Mesoionic compounds

Teamwork! Each component cooperatively participates in these new domino processes thereby allowing the formation of five to seven bonds. Unexpected reaction pathways become feasible thanks to the manifold roles played by the three distinct reagents in a precise sequence. Functionalized dipolar compounds are prepared in a single operation that requires only the mixing of the substrates.



#### **Scavenging Phenolic Antioxidants**

Syringaldehyde or methyl syringate substitute the 4-nitro group of 2,2-diphenyl-1picrylhydrazyl (DPPH). By contrast, the complexed sodium salt of syringaldehyde substitutes one of the phenyl groups of DPPH yielding another product.

MeO
$$R$$
 $NO_2$ 
 $NO_2$ 
 $R = CHO, CO_2Me$ 
 $NO_2$ 

E. N. Hristea,\* I. C. Covaci-Cimpeanu, G. Ionită, P. Ionită, C. Draghici, M. T. Căproiu, M. Hillebrand, T. Constantinescu, A. T. Balaban\* ...... 626-634

Reactions of 2,2-Diphenyl-1-picrylhydrazyl (DPPH) with Two Syringylic Phenols or One Aroxide Derivative

**Keywords:** Radical reactions / Hydrazyls / Aroxyls / EPR spectroscopy / Reaction mechanisms

#### **Synthetic Methods**

$$R \xrightarrow{\text{II}} X + NHR^{1}R^{2} \xrightarrow{\text{oxalyldihydrazide (50 mol-\%)} \\ + NHR^{1}R^{2} \xrightarrow{\text{hexane-2,5-dione}} R \xrightarrow{\text{II}} NR^{1}R^{2}$$

$$25-140 \text{ °C}$$

X=Br I NHR<sup>1</sup>R<sup>2</sup>: Aryl Amines, Alphatic Amines, imidazoles

Copper catalysis in water: Aryl bromides and aryl iodides could be aminated in water by a variety of amines and imidazoles under catalysis of a novel CuO/oxalyldihydrazide/hexane-2,5-dione system at room temperature or with heating to afford very good isolated yields.

A Facile and Efficient Oxalyldihydrazide/ Ketone-Promoted Copper-Catalyzed Amination of Aryl Halides in Water

**Keywords:** Amination / Cross-coupling / Copper / Water chemistry / Sustainable chemistry

# huperzine A

target compounds

huprine X target compounds

6,8-Bridged tetrahydro-1,6-naphthyridines were synthesised and evaluated as inhibitors of acetylcholinesterase. In a first approach, C3-bridged naphthyridines were constructed from 2-chloro-3-(1-piperidinylmethyl)pyridine precursors. Alternatively,

ring-closing metathesis was applied to construct an unsaturated C<sub>4</sub> bridge. Inhibition activities could be rationalised by comparative docking simulation studies based on the crystal structure of the acetylcholinesterase-huperzine A complex.

#### **Bridged Tetrahydro-1,6-naphthyridines**

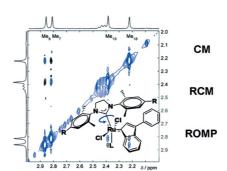
S. Vanlaer, A. Voet, C. Gielens, M. De Maever. F. Compernolle\* ...... 643-654

Bridged 5,6,7,8-Tetrahydro-1,6-naphthyridines, Analogues of Huperzine A: Synthesis, Modelling Studies and Evaluation as Inhibitors of Acetylcholinesterase

Keywords: Tetrahydro-1,6-naphthyridines / Nucleophilic substitution / Ring-closing metathesis / Pyridines / Acetylcholinesterase / Inhibitors

#### Olefin Metathesis

The performance of six 2<sup>nd</sup>-generation indenylidene catalysts with formula Cl<sub>2</sub>Ru(NHC)(L)(3-phenylinden-1-ylidene), where NHC is SIMes (R = Me) or SIMe (R = H) and L is  $PCy_3$ ,  $PPh_3$  or Py is reported, with complete NMR assignments and characterization of the rotameric behavior in solution. The results highlight the influence of N-aryl substitution patterns on the catalytic activity.



S. Monsaert, E. De Canck, R. Drozdzak, P. Van Der Voort, F. Verpoort,\* J. C. Martins,\* P. M. S. Hendrickx ...... 655-665

Indenylidene Complexes of Ruthenium Bearing NHC Ligands - Structure Elucidation and Performance as Catalysts for Olefin Metathesis

**Keywords:** Ruthenium / Olefin metathesis / Conformation analysis / Homogeneous catalysis / Indenylidene

# **CONTENTS**

#### **Nucleophilic Substitution**

#### H. Yang, L. Fang, M. Zhang, C. Zhu\* ...... 666-672

An Efficient Molybdenum(VI)-Catalyzed Direct Substitution of Allylic Alcohols with Nitrogen, Oxygen, and Carbon Nucleo-philes

**Keywords:** Molybdenum / Nucleophilic substitution / Allylic compounds / Alcohols

Readily available MoO<sub>2</sub>(acac)<sub>2</sub> is a highly effective catalyst for the nucleophilic substitution of allylic alcohols, which provides a

practical protocol for C-C, C-N, and C-O bond formation.

#### **Natural Amino Acid Synthesis**

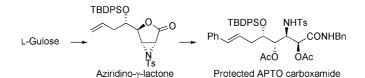
A. Tarrade-Matha, M. S. Valle, P. Tercinier, P. Dauban,\*

R. H. Dodd\* ...... 673–686



Enantiospecific Synthesis of a Protected Equivalent of APTO, the  $\beta$ -Amino Acid Fragment of Microsclerodermins C and D, by Aziridino- $\gamma$ -lactone Methodology

**Keywords:** Microsclerodermins / Amino acids / Aziridines / Synthesis design / Nucleophilic ring-opening



The efficient synthesis of a protected form of APTO, the  $\alpha$ -hydroxy  $\beta$ -amino acid component of microsclerodermins C and D, starting from L-gulose is reported. The

strategy is based on treatment of aziridino- $\gamma$ -lactones with soft nucleophiles, which regioselectively affords  $\alpha$ -substituted  $\beta$ -amino acids.

#### **Dinitro Tröger's Bases**

M. D. H. Bhuiyan, A. B. Mahon, P. Jensen, J. K. Clegg, A. C. Try\* ...... 687–698



Synthesis of Symmetric Dinitro-Functionalised Tröger's Base Analogues

**Keywords:** Tröger's base / Chirality / Aromatic substitution / Nitroanilines

More than 20 nitroanilines were converted into dinitro Tröger's base analogues for the first time.

#### 1,3-Asymmetric Induction

F. F. Fleming,\* W. Liu ...... 699-708



Metalated Nitriles: Internal 1,3-Asymmetric Induction

**Keywords:** Nitrile / Conformation analysis / Alkylation / Diastereoselectivity

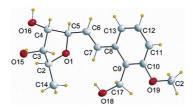
Stereoselective alkylations of substituted pentanenitriles reveal the fundamental requirements for 1,3-asymmetric induction and provide a predictive model based on the more stable diamond lattice confor-

mation. Using this strategy, metalated pentanenitriles selectively intercept a diverse range of electrophiles to install new quaternary centers in flexible metalated nitriles having a defined shape.



#### **Natural Product Synthesis**

The total synthesis of natural (+)-varitriol was accomplished by starting from dimethyl L-tartrate. The absolute configu-



ration of the target was confirmed by single-crystal X-ray analysis for the first time.

M. Palík, O. Karlubíková, A. Lásiková, J. Kožíšek, T. Gracza\* ...... 709-715

Total Synthesis of (+)-Varitriol

**Keywords:** Natural products / Total synthesis / Homogeneous catalysis / Palladium

#### **Pinacol Coupling Reactions**

The pinacol coupling reaction of ferrocene-carbaldehyde 1 was smoothly mediated by  $Sm(OTf)_2$  to give (R,R)-diol 2a predominantly (58% de), whereas the use of  $SmI_2$  resulted in low selectivity. The rhodium complexes of 2a were good catalysts for the asymmetric hydrogenation of  $\alpha$ -acetamidocinnamic acid, and the product was obtained quantitatively with up to 92% ee.

Divalent Samarium Triflate Mediated Stereoselective Pinacol Coupling of Planar Chiral Phosphanyl and Phosphoryl Ferrocenecarbaldehyde

**Keywords:** Samarium / Sandwich complexes / Radical reactions / Phosphanes / Pligands

#### Reaction Mechanism Elucidation

The elimination of a lithium methoxide from  $\beta$ -lithiated acetal **3A** most likely takes place through a second deprotonation with an excess of nBuLi. The resulting 1,3-di-

lithio intermediate 3ALi is transformed into *gem*-dilithio 9, which undergoes spontaneous  $\beta$ -elimination of a lithium methoxide.

Is the Elimination of Lithium Alkoxide Easier from a Vinyllithium or from an Alkyllithium? A DFT Study of the Aromatization of 3-Vinylidene-2,3-dihydrobenzofurans to Benzofurans

**Keywords:** Reaction mechanism / Density functional calculations / Elimination / Aromatization / Lithium / Acetals

### Polysubstituted Diphenylalkanes

The two acetylenic ends of untethered  $\alpha, \omega$ -diyne scaffold have been functionalized in a stepwise manner to construct polysubstituted diphenylalkane derivatives by a stra-

tegic utilization of [2+2+2] cyclotrimerization, cross-enyne metathesis and Diels—Alder reaction as key steps.

A Diversity-Oriented Approach to Diphenylalkanes by Strategic Utilization of

[2+2+2] Cyclotrimerization, Cross-Enyne

S. Kotha,\* P. Khedkar ...... 730-738

Metathesis and Diels—Alder Reaction

Keywords: Cyclotrimerization / Diels—Alder reaction / Diphenylalkanes / Diversity

# **CONTENTS**

#### **Organocatalysis**

J. N. Moorthy,\* S. Saha ...... 739-748



Highly Diastereo- and Enantioselective Aldol Reactions in Common Organic Solvents Using *N*-Arylprolinamides as Organocatalysts with Enhanced Acidity

**Keywords:** Asymmetric synthesis / Aldol reactions / Organocatalysis / Proline / Amides / C-C bond formation



Among a variety of *N*-arylamides, *N*-(pentafluorophenyl)prolinamide (8) is found to catalyze aldol reactions in highly nonpolar as well as polar solvents including brine to afford high yields of aldols with excellent diastereo- as well as enantio-

selectivity. The molecular structures of 8 and its 3,5-dinitrophenyl analog 7, determined by X-ray crystallography, reveal that the former may bind the electrophilic aldehydes better in the transition state via hydrogen bonding.

#### **Natural Products**

H. Hussain, N. Akhtar,

S. Draeger, B. Schulz, G. Pescitelli,

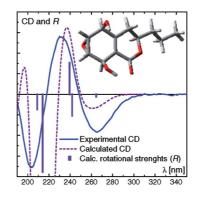
P. Salvadori, S. Antus, T. Kurtán,

K. Krohn\* ...... 749-756



New Bioactive 2,3-Epoxycyclohexenes and Isocoumarins from the Endophytic Fungus *Phomopsis* sp. from *Laurus Azorica* 

**Keywords:** Endophytic fungi / *Phomopsis* sp. / Biological activity / Natural products / Cycloepoxylactone / Cycloepoxytriol / Phomolactones / Circular dichroism / TDDFT calculations



The relative configuration of new biologically active epoxycyclohexenediols and isocoumarins, isolated from the endophytic fungus *Phomopsis* sp., were elucidated by extensive NMR spectroscopy. Their absolute configurations were determined by circular dichroism and comparison of solution CD spectra with TDDFT-calculated ones.

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

If not otherwise indicated in the article, papers in issue 4 were published online on January 13, 2009

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