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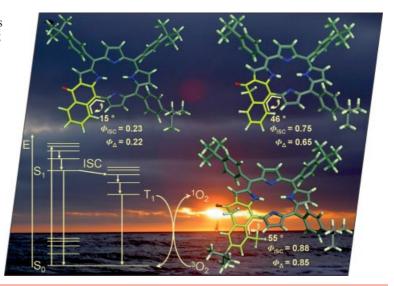




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further EUChemSoc Societies (Austria, Czech Republic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

# **COVER PICTURE**

The cover picture shows three tetraphenylporphyrins that possess an exocyclic keto-group-bearing ring connecting the central chromophore with one of the phenyl rings. Depending on the size of the exocyclic ring and on the additional steric strain induced by a methyl group on the substituted phenyl ring, the dihedral angle between the central chromophore and the phenyl ring varies between 15 and 55°. These topological changes have a dramatic influence on, for example, the singlet-oxygen quantum yield. As the generation of  ${}^{1}O_{2}$  is induced by red light, the setting sun (taken at San Diego beach in 2003 by Michael Köhl) seemed to be an appropriate background for the porphyrins. Details of the syntheses and characterization are reported in the article by N. Jux, B. Röder et al. on p. 1075ff.



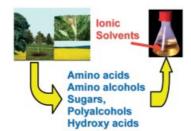
## **MICROREVIEW**

## **Green Chemistry**

G. Imperato, B. König, C. Chiappe\* ...... 1049–1058

Ionic Green Solvents from Renewable Resources

**Keywords:** Ionic liquids / Amino acids / Natural products / Solvent effects / Carbohydrates / Green chemistry



Non-toxic, biodegradable materials arising from biorenewable resources may be used to prepare room-temperature ionic liquids. The development of ionic solvents from natural products is an emerging area of intensive research. This Microreview presents recent advances in this area.

## SHORT COMMUNICATIONS

#### **Radical-Ion Rearrangement**

M. D. Roydhouse, J. C. Walton\* ...... 1059–1063

Formation of a Tetracyclic Isoquinoline
Derivative by Rearrangement of a [(Bromophenyl)butyryl]oxazolidinone

**Keywords:** Rearrangement / Cyclisation / Heterocycles / Radical ions / EPR spectroscopy

Treatment of a [(bromophenyl)butyryl]-oxazolidinone with LDA in THF launched an intricate cascade rearrangement ending in the assembly of a tetracyclic cyclopenta-oxazolo-isoquinolin-6-one derivative.

#### Carbamate-Linked Oligosaccharides

D. Sawada, S. Sasayama, H. Takahashi, S. Ikegami\* ...... 1064-1068

Novel Synthesis of Carbamate-Linked Oligosaccharides by a Modified Curtius Rearrangement

**Keywords:** Carbamates / Carbohydrates / Dendrimers / Rearrangements / Stereospecific synthesis

We describe a novel stereospecific synthesis of various carbamate-linked disaccharides using sugar carboxylic acids and sugar alcohols by a modified Curtius rearrangement. Furthermore, we applied this method to the synthesis of carbamate-linked oligosaccharides including a dendritic molecule.



#### Diels-Alder Reactions

Lactone-based dienolates were [4+2]annulated with high and contrasteric asymmetric induction to oxocyclohexenecarboxylates. Subsequently, a novel tandem fragmentation of the (silylmethyl)lactone and silylated  $\beta$ -oxo ester moieties led to an allyl and a ketone group, respectively.

#### T. Tricotet, R. Brückner\* ..... 1069-1074

Enantio- and Diastereomerically Pure Decalins by Deslongchamps-Type Annulation of Dienolates Containing a Chiral Lactone Substituent

**Keywords:** 1,3-Asymmetric induction / Bicyclo[4.4.0]decane / De(alkoxycarbonylation) / Homoallyl anion equivalent /  $\gamma$ -Lactone fragmentation / Stereoselective synthesis / Tandem reaction

## **FULL PAPERS**

Three novel porphyrins that carry an exocyclic ketone-bearing ring have been prepared. Owing to hindered rotation, stable atropisomers exist that possess axial chirality. Photophysical investigations of these compounds show moderate-to-high singlet oxygen quantum yields.

## **New Porphyrinoid Photosensitizers**

Novel Synthetic Cycloketo-Tetraphenyl-porphyrins

**Keywords:** Porphyrinoids / Photosensitizer / Fluorescence / Chirality

2-Trifluoromethyl-1,2,3-triol compounds can be synthesised by asymmetric trifluoromethylation of enantiomerically pure  $\alpha$ -monosubstituted 1,3-dioxan-5-ones. Additionally, starting from the corresponding

 $\alpha,\alpha,\alpha'$ -trisubstituted dioxanones a highly stereoselective access to trifluoromethylated alcohols bearing two neighbouring quaternary stereocenters is possible.

### **Stereoselective Trifluoromethylation**

D. Enders,\* C. Herriger ...... 1085-1090

Asymmetric Synthesis of 2-Trifluoromethyl-1,2,3-triols

**Keywords:** Trifluoromethylation / Asymmetric synthesis / Nucleophilic addition / Ruppert reagent

A catalytic, asymmetric  $\alpha$ -bromination of acid chlorides to produce highly versatile, optically active  $\alpha$ -bromo esters is described.

### Catalytic, Asymmetric α-Bromination

C. Dogo-Isonagie, T. Bekele, S. France,

J. Wolfer, A. Weatherwax,

A. E. Taggi, D. H. Paull, T. Dudding,

T. Lectka\* ...... 1091-1100

A Mechanistic Study on the Catalytic, Asymmetric  $\alpha$ -Bromination of Acid Chlorides

**Keywords:** Catalytic / Asymmetric /  $\alpha$ -Bromination / Enantioselective

# **CONTENTS**

#### **Chiral Building Blocks**

A. Baeza, C. Nájera,\*
J. M. Sansano ...... 1101-1112

S<sub>N</sub>2' Alkylation of Chiral Allylic Cyanohydrin *O*-Phosphates with Organocuprates

**Keywords:** Copper / Allylic substitution / Asymmetric synthesis / Unsaturated nitriles / Cyanophosphates

$$R^{1} \xrightarrow{OP} CN \xrightarrow{R^{2}MgCl} CN \xrightarrow{R^{2}MgCl} CN \xrightarrow{R^{2}CN} R^{2} \xrightarrow{R^{2}CN} CN \xrightarrow{R^{2}CN} CN \xrightarrow{R^{2}CO_{2}Me} CN$$

Enantiomerically enriched cyanohydrin O-phosphates react regioselectively with organocuprates derived from alkyl Grignard reagents and CuCN to give  $\gamma$ -alkyl-substituted  $\alpha,\beta$ -unsaturated nitriles in a

S<sub>N</sub>2' process. This new evidence of the versatility of these cyanophosphates as chiral building blocks is demonstrated by the synthesis of the sex pheromone of the yellow mealworm *Tenebrio molitor* L.

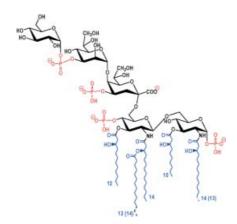
### Glycolipid from Marine Bacteria

S. Leone, A. Molinaro,\* L. Sturiale, D. Garozzo, E. L. Nazarenko, R. P. Gorshkova, E. P. Ivanova,

L. S. Shevchenko, R. Lanzetta, M. Parrilli ...... 1113-1122

The Outer Membrane of the Marine Gram-Negative Bacterium *Alteromonas addita* is Composed of a Very Short-Chain Lipopolysaccharide with a High Negative Charge Density

**Keywords:** *Alteromonas addita /* Marine bacteria / Lipooligosaccharide



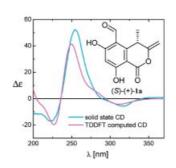
The complete structure of the lipopolysaccharide isolated from the Gram-negative marine bacterium *Alteromonas addita*, type strain KMM 3600T = R10SW13T, has been elucidated by means of state-of-the-art NMR and MS analyses. The structure is made up of a novel, highly negatively charged, deep-rough lipopolysaccharide in which a phosphodiester bridge connects two monosaccharides.

### **Absolute Configuration of Ascochin**

K. Krohn,\* I. Kock, B. Elsässer, U. F. B. Schulz, S. Draeger, G. Pescitelli, S. Antus, T. Kurtán ...... 1123–1129

Bioactive Natural Products from the Endophytic Fungus *Ascochyta* sp. from *Meliotus dentatus* — Configurational Assignment by Solid-State CD and TDDFT Calculations

**Keywords:** Biological activity / Natural products / Isocoumarins / Quantum-mechanical calculation of CD spectra



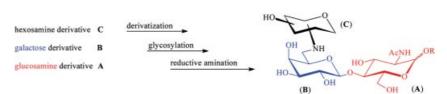
Two new metabolites, (4S)-(+)-ascochin (1a) and (S,S)-(+)-ascodiketone (3) were isolated from the endophytic fungus *Ascochyta* sp. The structure of the antifungal isocoumarin 1a was confirmed by X-ray diffraction and its absolute configuration determined by solid-state TDDFT CD methodology. The measured and TDDFT-calculated CD spectra enabled studies on the correlation between absolute configuration and  $n-\pi^*$  transition CD.

#### **Novel Glycomimetics**

J. Neumann, S. Weingarten,
J. Thiem\* ...... 1130-1144

Synthesis of Novel Di- and Trisaccharide Mimetics with Non-Glycosidic Amino Bridges

**Keywords:** Carbohydrates / Saccharide mimetics / Enzymatic glycosylation / Reductive amination / Dess—Martin oxidation / Non-glycosidically amino-bridged saccharides



Synthesis of novel di- and trisaccharides using enzymatic glycosylation, Dess-Martin oxidation and reductive amination allows rapid access to the target structures.

Thus, a novel class of glycomimetics was obtained having nitrogen inserted as bridging atom between two non-anomeric positions.



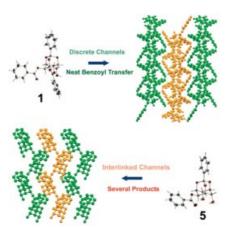
### Sesquiterpene Lactone Models

In order to study the reactivity of sesquiterpene lactones in biological systems, an efficient stereoselective synthesis of a simple model was developed.

A Highly Stereoselective Divergent Synthesis of Bicyclic Models of Photoreactive Sesquiterpene Lactones

Keywords:  $\alpha$ -Methylene- $\gamma$ -butyrolactones / Asymmetric synthesis / Palladium / Allylic substitution / Enantioselectivity / Diastereoselectivity

Neat transesterification reaction takes place in crystals of 1, while a similar reaction in crystals of 5 and 6 is not clean. These reactivities are correlated with crystal structures. Illustrated are compounds 1 and 5; crystals of 1 contain discretely packed helices with favourable electrophile—nucleophile short contacts and other weak interactions which favour the reaction, whereas 5 have interlinked helices that lack these favourable interactions.



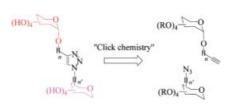
### **Right Organization Matters!**

C. Murali, M. S. Shashidhar,\*
R. G. Gonnade,
M. M. Bhadbhade\* ...... 1153-1159

Investigating Organization of Molecules that Facilitates Intermolecular Acyl Transfer in Crystals: Reactivity and X-ray Structures of *O*-Benzoyl-*myo*-inositol 1,3,5-Orthoesters

**Keywords:** Inositol / Solid-state reaction / Transesterification / Weak interactions / Molecular self assembly

Carbohydrates bearing alkyne and azide substituents in different positions have been connected by click chemistry techniques. The high solubilities of the protected sugars in DMF allowed us to add water to the mixtures, which accelerates the reaction. One example demonstrates the possibilities for modulating the distance between triazole-linked saccharide units.



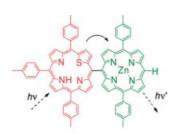
### **Connecting Carbohydrates**

S. G. Gouin, L. Bultel, C. Falentin, J. Kovensky\* ...... 1160–1167

A Simple Procedure for Connecting Two Carbohydrate Moieties by Click Chemistry Techniques

**Keywords:** Carbohydrates / Dipolar cycloaddition / Click chemistry

The synthesis of eight novel compounds with *meso*-5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin as a key synthon under mild Pd-coupling conditions is reported.



## **Asymmetrical Porphyrin Oligomers**

S. Punidha, N. Agarwal, I. Gupta, M. Ravikanth\* ...... 1168–1175

*meso*-5-Bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin as a Precursor for the Synthesis of Novel Compounds

**Keywords:** 21-Thiaporphyrin / Building blocks / Palladium(0) coupling / *mesomeso*-Linked dyad / Energy transfer

## **CONTENTS**

#### Vitamin E Chemistry

Tocopherols by Hydride Reduction of Dialkylamino Derivatives

**Keywords:** Natural products / Vitamins / Reduction / Aminomethylation / Deuteriated tocopherols

$$R^{1} \longrightarrow 0$$

$$R^{1} \longrightarrow 0$$

$$R^{2} \longrightarrow 0 \stackrel{\times}{=} R^{*}$$

$$R^{1} = H, D$$

$$R^{2} = II, CII_{3}$$

$$R^{*} = H_{2}C$$

$$R^{1} \longrightarrow 0$$

$$R^{1} \longrightarrow 0$$

$$R^{1} = H, D$$

$$R^{2} = II, CII_{3}$$

Aminomethylation – the hydride reduction route for the preparation of labelled

and unlabelled  $\alpha$ - and  $\beta$ -tocopherol is disclosed.

#### **Transannular Aldol Reactions**

A. D. Payne, B. W. Skelton, D. Wege, A. H. White ...... 1184–1195

Approaches to Cyclopropazulenes: Transannular Aldol Reactions of Some Derivatives of 1,10-Dibromobicyclo[8.1.0]undecane-3,8-dione

**Keywords:** Strained molecules / Azulenes / Cyclopropazulenes / Aldol reactions / Ozonolysis

$$\bigcup_{O}^{O} \bigcup_{Br}^{Br} \longrightarrow \bigcup_{HO}^{O} \bigcup_{Br}^{H} \bigcup_{Br}^{Br}$$

 $\bigcap_{O} \bigcap_{Br} \bigcap_{Br} OH$ 

The direction of transannular aldol reaction within a benzo-fused derivative of 1,10-dibromobicyclo[8.1.0]undecane-3,8-dione was altered by insertion of a transannular epoxy bridge.

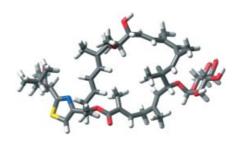
## Macrolide Conformation—Activity Study

D. Menche,\* J. Hassfeld, H. Steinmetz, M. Huss, H. Wieczorek,

F. Sasse ...... 1196-1202

Archazolid-7-*O*-β-D-glucopyranoside – Isolation, Structural Elucidation and Solution Conformation of a Novel V-ATPase Inhibitor from the Myxobacterium *Cystobacter violaceus* 

**Keywords:** Natural products / Polyketides / Inhibitors / Glycosides / Archazolide



The first archazolid-glycoside, archazolid C, from the myxobacterium *Cystobacter violaceus*, and simplified synthetic analogues are reported. The V-ATPase activity of this novel polyketide macrolide was studied in detail and is discussed in relation to its 3D solution conformation.

# **CORRECTION**

B. R. Buckley, J. Y. Boxhall, P. C. B. Page,

Y. Chan, M. R. J. Elsegood, H. Heaney,\*

K. E. Holmes, M. J. McIldowie,

V. McKee, M. J. McGrath, M. Mocerino,

A. M. Poulton, E. P. Sampler,

B. W. Skelton, A. H. White ...... 1203

Mannich and O-Alkylation Reactions of Tetraalkoxyresorcin[4]arenes – The Use of Some Products in Ligand Assisted Reactions

**Keywords:** Axial chirality / Chiral auxiliaries / Configuration determination / Diastereoselectivity / Mannich reactions / Resorcinarenes

If not otherwise indicated in the article, papers in issue 6 were published online on January 30, 2007