













AUSTRIA



SPAIN





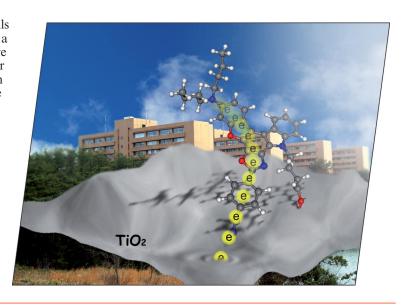




A union formed by chemisocieties in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the European Journal of Inorganic Chemistry and the European Journal of Organic Chemistry. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## **COVER PICTURE**

The cover picture shows dye-sensitized solar cells (DSSCs) based on organic dyes adsorbed on a nanocrystalline TiO2 electrode. DSSCs have received considerable attention because of their high incident solar-light-to-electricity conversion efficiency and low cost of production. To create high-performance DSSCs, it is necessary to design and synthesize new and efficient organic dye photosensitizers with effective chromophores and substituents for the performance of DSSCs, which will be made possible by the exquisite molecular design and synthetic strategy of organic chemists. The background shows the architecture of the Department of Engineering, Hiroshima University, which is associated with the arrangement of organic dyes adsorbed on TiO<sub>2</sub> electrodes. The designs and synthesis of organic dyes for DSSCs are presented in the Microreview by Y. Ooyama and Y. Harima on p. 2903ff.



# **MICROREVIEW**

### **Dye-Sensitized Solar Cells**

Y. Ooyama,\* Y. Harima\* ...... 2903-2934

Molecular Designs and Syntheses of Organic Dyes for Dye-Sensitized Solar Cells

Keywords: Dye-sensitized solar cells / Dyes/ pigments / Energy conversion / Photochemistry / Photosensitizers / Photovoltaic performances



Dye-sensitized solar cells (DSSCs) based on organic dyes adsorbed on nanocrystalline TiO2 electrodes have received considerable attention because of their high incident solar light-to-electricity conversion efficiencies and low costs of production. The aim of this microreview is to highlight the designs and syntheses of organic dyes for DSSCs based on recent work of organic chemists.

## SHORT COMMUNICATIONS

#### **Trifluoromethylated Fullerene**

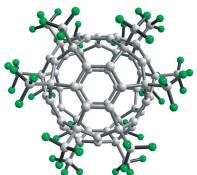
N. A. Samokhvalova, P. A. Khavrel, V. Yu. Markov, P. S. Samokhvalov, A. A. Goruynkov, E. Kemnitz,

L. N. Sidorov, S. I. Troyanov\* ... 2935-2938



Isolation and Structural Characterization of the Most Stable, Highly Symmetric Isomer of C<sub>60</sub>(CF<sub>3</sub>)<sub>18</sub>

Keywords: Fullerenes / Trifluoromethylation / NMR spectroscopy / Structure elucidation



The energetically most stable isomer of  $C_{60}(CF_3)_{18}$  with molecular  $C_3v$  symmetry has been obtained by isolation from a complex C<sub>60</sub>(CF<sub>3</sub>)<sub>n</sub> isomer mixture and characterized by means of <sup>19</sup>F NMR spectroscopy and single-crystal X-ray crystallography.

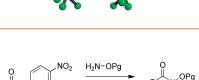
#### **Hydroxamic Acid Synthesis**

T. Kurz,\* M. K. Pein, L. Marek, C. T. Behrendt, L. Spanier, K. Kuna, K. Brücher ...... 2939-2942



Microwave-Assisted Conversion of 4-Nitrophenyl Esters into O-Protected Hydroxamic Acids

Keywords: Acylation / 4-Nitrophenyl esters / Hydroxamic acids / Microwave-assisted synthesis



Reactions of 4-nitrophenyl esters with differently O-protected hydroxylamines under microwave irradiation led to the corresponding O-protected hydroxamic acids in good yields and short reaction times.

## **One-Pot Oxidation—Wittig Reaction**

E. Y. Lee, Y. Kim, J. S. Lee, J. Park\* ...... 2943-2946

$$R \cap OH + Ph_3P=CHCO_2R'$$

$$Ru/AIO(OH) (1)$$

$$O_2 (1 atm), toluene, 110 °C$$



Ruthenium-Catalyzed, One-Pot Alcohol Oxidation-Wittig Reaction Producing α,β-Unsaturated Esters

**Keywords:** Heterogeneous catalysis / Wittig reactions / Ruthenium / Oxidation

By a one-pot process,  $\alpha,\beta$ -unsaturated esters were synthesized in high yield through the Ru-catalyzed oxidation of primary alcohols and the coupling of the resulting aldehydes and stabilized Wittig reagents. The ruthenium catalyst is composed of ruthenium nanoparticles embedded in aluminum oxyhydroxide and can be recovered simply by filtration or decantation.



### **Telescoped Alkenyl-Oxindole Synthesis**

A one-pot enolate arylation/HWE procedure has been developed to provide rapid access to a range of 3-alkenyl-oxindoles

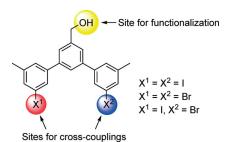
and employed to achieve the first synthesis of Soulieotine, a constituent of a traditional Chinese medicine.

Telescoped Enolate Arylation/HWE Procedure for the Preparation of 3-Alkenyl-Oxindoles: The First Synthesis of Soulie-otine

**Keywords:** Horner-Wadsworth-Emmons olefination / Phosphonates / Enolate arylation / Palladium catalysis / Oxindoles / Telescoped reactions

#### Versatile *m*-Terphenylenes

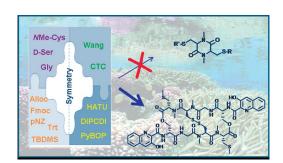
According to the increasing interest in oligo- and polyphenylene-based nanostructures, a set of versatile *m*-terphenylenes has been designed. Their easy and multigramscale syntheses are described. These compounds are considered key building blocks for the synthesis of new macrocycles, foldamers as well as other polymers using transition-metal mediated cross-coupling reactions.



An Easy and Multigram-Scale Synthesis of Versatile AA- and AB-Type *m*-Terphenylenes as Building Blocks for Kinked Polyphenylenes

**Keywords:** Cross-coupling / Masking / Macrocycles / Foldamers / Polymers

# **FULL PAPERS**



Investigations into the synthesis of oxathiocoraline revealed a number of unexpected side-reactions that could not be circumvented by classical or standard means. General points that should be addressed when attempting the synthesis of a cyclodepsipeptide – such as strategies to prevent or minimize diketopiperazine formation,  $\beta$ -elimination and oxidation byproducts – are described.

## Waking Up from a DKP Nightmare!

N. Bayó-Puxan, J. Tulla-Puche,\* F. Albericio\* ...... 2957-2974

Oxathiocoraline: Lessons to be Learned from the Synthesis of Complex *N*-Methylated Depsipeptides

**Keywords:** Thiocoraline / Peptides / Solidphase synthesis / Cysteine / Diketopiperazines / Synthesis design

#### Natural Products

Eleven new metabolites, including nine lovastatin analogues, one linear furanopolyketide and a monoterpene named dihydroxysabinane were isolated from the endophytic fungal strain *Phomopsis* sp. XZ-26 of

Camptotheca acuminate. Their structures were elucidated by spectroscopic methods and X-ray single-crystal analysis. A hypothetical biosynthetic pathway is proposed for oblongolides.

T. Lin, X. Lin, C. Lu, Z. Hu, W. Huang, Y. Huang, Y. Shen\* ...... 2975–2982

Secondary Metabolites of *Phomopsis* sp. XZ-26, an Endophytic Fungus from *Camptotheca acuminate* 

**Keywords:** Camptotheca acuminate / *Phomopsis* sp. / Polyketides / Natural products / Oblongolide

## **CONTENTS**

### **Homoallylation of Carbonyls**

Y. Zhang, X. Jia, J.-X. Wang\* ... 2983-2986

The Solvent-Free Addition Reaction of Allylzinc Bromide and Carbonyl Compounds

**Keywords:** Green chemistry / Allylic compounds / Zinc / Alcohols / Carbonyl compounds

$$ZnBr$$
 +  $R$   $R^1$   $R^1$ 

A variety of homoallylic alcohols were prepared in good to excellent yield under catalyst- and solvent-free conditions by the addition of allylzinc bromide to carbonyl compounds in an open atmosphere at room temperature.

### **Toxic Sesquiterpenoids**

Studies towards the Total Synthesis of (-)-Caulerpenynol, a Toxic Sesquiterpenoid of the Green Seaweed *Caulerpa taxifolia* 

**Keywords:** Natural products / Total synthesis / Biological activity / Terpenoids



The first diastereoselective synthesis of the antimicrobial and cytotoxic agent (-)-caulerpenynol (2) was achieved in relatively few steps from commercially available (S)-malic acid. Highlights of this synthesis include the nonracemization of the sensitive  $\alpha$ -hydroxy ketone moiety and the correct choice of protecting groups for the critical last deprotection step.

#### **Metalla-Antibiotics**



Synthesis of 2-Azetidinones Incorporating Carbenechromium(0) Moieties and Their Use in the Preparation of Penicillin- and Cephalosporin-Containing Peptides

**Keywords:** Chromium / Peptides / Lactams / Photochemistry / Carbonylation / Carbenes

#### METALLA-2-AZETIDINONES

#### β-LACTAM CONTAINING PEPTIDES

β-Lactams incorporating a carbenechromium(0) moiety in their structures are suitable precursors for the preparation of α-amino esters, dipeptides and tripeptides

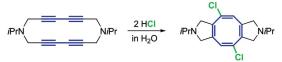
tethered to a 2-azetidinone ring. Penicillin and cephalosporin derivatives are also available by this approach.

#### **Transannular Reactions**

R. Gleiter,\* K. Hövermann, B. Esser, A. Bandyopadhyay ...... 3006–3010

Transannular Ring Closure of a 1,8-Diazacyclotetradeca-3,5,10,12-tetrayne to a Tricyclic System with a Central Cyclooctatetraene Ring

**Keywords:** Alkynes / Butadiynes / Cyclization / Medium-ring compounds / Structure elucidation / Transannular reactions



On treatment with aqueous HCl the two butadiyne units in 14-membered cyclic systems perform a transannular reaction leading to 5-8-5 patterned tricyclic systems. The positioning of the chlorine atoms depends on the number of nitrogen atoms in the cycle.



### **Heterocyclic Chemistry**

Two different methods have been employed to prepare the hexahydropyrido[2,1-a]isoind-olone framework in good overall yield.

New Efficient Route to Fused Aryltetrahydroindolizinones via *N*-Acyliminium Intermediates

**Keywords:** Iminium / Indolizinones / Carbonylation / Lithiation / Nitrogen heterocycles

## **Carbonylative Suzuki Couplings**

$$R = CH_3, OCH_3, Br$$

$$R^1 = CH_3, OCH_3, No_2, Br$$

$$X = N, S$$

$$n = 1 \text{ or } 2$$

$$R = CH_3, OCH_3, No_2, Br$$

$$R^1 = CH_3, OCH_3, No_2, Br$$

$$R^1 = CH_3, OCH_3, No_2, Br$$

$$R^1 = CH_3, OCH_3, No_2, Br$$

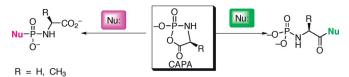
A facile protocol was developed for the synthesis of biaryl ketones through a carbonylative Suzuki coupling reaction with the use of Pd(tmhd)<sub>2</sub>/Pd(OAc)<sub>2</sub> as a phos-

phane-free catalyst. The catalytic system is applicable to carbonylative couplings of both aromatic and heteroaromatic aryl iodides with various phenylboronic acids.

Phosphane-Free Palladium-Catalyzed Carbonylative Suzuki Coupling Reaction of Aryl and Heteroaryl Iodides

**Keywords:** Carbonylation / Cross-coupling / Palladium / Boron

## Cyclic Acylphosphoramidates



Nu: =  $H_2O$ ,  $HPO_4^{2-}$ ,  $NH_2CHRCOOH$ ,  $CH_3OH$ 

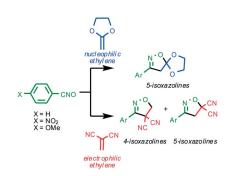
The bielectrophilicity of  $\alpha$ -CAPAs, phosphomimics of  $\alpha$ -NCAs, was identified by isotopic analysis ( $^{18}$ O,  $^{15}$ N) and further proved by trapping  $\alpha$ -CAPA with nucleo-

philes such as water, amino acids, phosphate and methanol in alkaline media, which yielded interesting phosphorylated products.

On the Electrophilicity of Cyclic Acylphosphoramidates (CAPAs) Postulated as Intermediates

**Keywords:** Amino acids / Bielectrophilicity / NMR spectroscopy / Phosphorus

Whereas the cycloaddition reactions of benzonitrile *N*-oxides with electron-rich ethylenes are completely regioselective, yielding 5-isoxazolines, the reactions with electron-deficient ethylenes give a mixture of 4- and 5-isoxazolines.



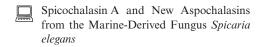
An Analysis of the Regioselectivity of 1,3-Dipolar Cycloaddition Reactions of Benzonitrile *N*-Oxides Based on Global and Local Electrophilicity and Nucleophilicity Indices

**Keywords:** Nitrile *N*-oxides / Cycloaddition / Regioselectivity / Electrophilicity / Nucleophilicity / Heterocycles

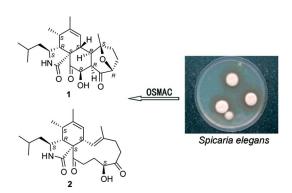
## CONTENTS

### **Natural Products Chemistry**

Z. Lin, T. Zhu, H. Wei, G. Zhang, H. Wang, Q. Gu\* ...... 3045-3051



Keywords: Spicochalasin A / Cytochalasans / Antibiotics / Natural products / Marine fungi / Antitumor agents



Different culture conditions directed by the OSMAC (one strain-many compounds) approach yielded a novel spicochalasin A (1) and five new aspochalasins M-Q (2-6). Their absolute configurations were determined by X-ray diffraction and the Mosher

ester method. Spicochalasin A (1) has a unique pentacyclic system and was found to be moderately cytotoxic towards human leukemic HL-60 cells with an IC50 value of 19.9 µm.

#### **Xanthene Derivatives**

L. E. Luna, R. M. Cravero\* R. Faccio, H. Pardo, Á. W. Mombrú, G. Seoane ...... 3052-3057

Synthesis of 9-Substituted-1,8-Dioxooctahydroxanthenes by an Efficient Iodine-Catalyzed Cyclization

Keywords: Oxygen heterocycles / Iodine / Cyclization / Alkynes / Fused-ring systems



A simple, practical, and efficient method for the synthesis of 1,8-dioxooctahydroxanthenes with substituents in the 2-, 3-, and 9-positions was developed by employing a sequential tandem Michael-iodine-cata-

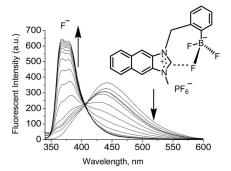
lyzed cyclization. The isolation and the Xray molecular structure of the 4a-hydroxyxanthene intermediate verify the proposed mechanistic pathways.

#### Ratiometric Fluoride Probe

Z. Xu, S. K. Kim, S. J. Han, C. Lee, G. Kociok-Kohn, T. D. James,\* J. Yoon\* ...... 3058-3065

Ratiometric Fluorescence Sensing of Fluoride Ions by an Asymmetric Bidentate Receptor Containing a Boronic Acid and Imidazolium Group

Keywords: Anions / Fluorides / Boron / Heterocycles / Fluorescence



An asymmetric bidentate receptor containing boronic acid and an imidazolium group can recognize F-, as evidenced by ratiometric fluorescence responses in aqueous solution.

### **Bis(oxy)iminium Ion Chemistry**

V. O. Smirnov, A. S. Sidorenkov,

Y. A. Khomutova, S. L. Ioffe,\*

V. A. Tartakovsky ...... 3066-3074

Five-Membered Cyclic Nitronates in C-C Coupling with 1-(tert-Butyldimethylsilyloxy)-1-methoxyethylene

**Keywords:** Nitronates / C-C coupling / Acetals / Heterocycles / Iminium ions

Five-membered cyclic nitronates undergo C-C coupling reactions with a silyl ketene acetal in the presence of trialkylsilyl triflate to give isoxazolidines that are inaccessible by conventional methods. The reaction

proceeds via a bis(oxy)iminium ion as intermediate. Some transformations of the obtained N-silyloxyisoxazolidines have been examined.



**Organocatalysis** 

Chiral cyclopropanes with three stereocenters are easily synthesized from  $\alpha,\beta$ -unsaturated aldehydes and 2-bromo keto esters in

high yields and good to excellent diastereoand enantioselectivities.

Asymmetric Organocatalytic Cyclopropanation – Highly Stereocontrolled Synthesis of Chiral Cyclopropanes with Quaternary Stereocenters

**Keywords:** Cyclopropanation / Organocatalysis / Enantioselectivity / Diastereoselectivity / Quaternary centers

cis-Bicyclo[3.3.0]octane-3,7-diones

An easy access to *cis*-3,7-dimethylenebicyclo[3.3.0]octane-1,5-dicarboximides by double methylenecyclopentane annulation of *N*-substituted succimides is described. Ozonization of these compounds gave the corresponding 3,7-dioxo derivatives; these kinds of compounds have never been obtained through the Bertz-Weiss-Cook reaction.

$$H_2C$$
 $NR$ 
 $CH_2$ 

P. Camps,\* J. A. Fernández, J. Rull, S. Vázquez ....... 3081–3087

Double Methylenecyclopentane Annulation of Succinimides: Easy Access to 3,7-Dioxobicyclo[3.3.0]octane-1,5-dicarboximides

**Keywords:** Alkylation / Annulation / Carbocycles / Lithiation / Ozonolysis

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

If not otherwise indicated in the article, papers in issue 17 were published online on May 25, 2009

<sup>\*</sup> Author to whom correspondence should be addressed.