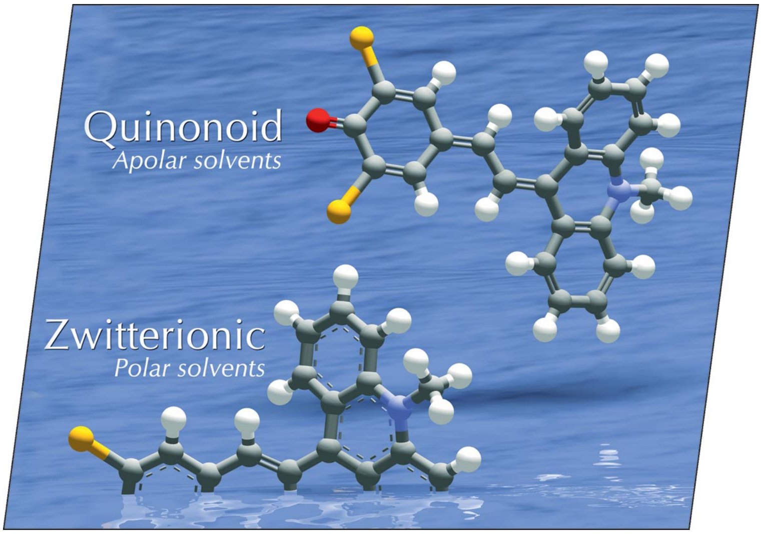
HUNGARY
ITALY
GERMANY
GREECE
BELGIUM
FRANCE
EUChemSoc
SWEDEN
CZECH REPUBLIC
AUSTRIA
PORTUGAL
SPAIN
NETHERLANDS

**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** the quinonoid and zwitterionic limiting formulas of the solvatochromic probe MeAMBr$_2$ [(*E*)-2,6-dibromo-2-(1-methylacridinium-4-yl)ethenyl phenolate]. The solvatochromic behavior is influenced by the solvent-dependent contributions of the two limiting formulas to the ground and excited states of the probe. Details are discussed in the article by O. A. El Seoud et al. on p. 1165 ff. The artwork for the cover picture was prepared by E. L. Bastos.



# CONTENTS

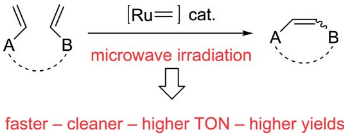
## MICROREVIEWS

### Olefin Metathesis

**Y. Coquerel,* J. Rodriguez* .... 1125–1132**

Microwave-Assisted Olefin Metathesis

**Keywords:** Homogeneous catalysis / Heterogeneous catalysis / Alkenes / Metathesis / Microwave / C=C bond formation



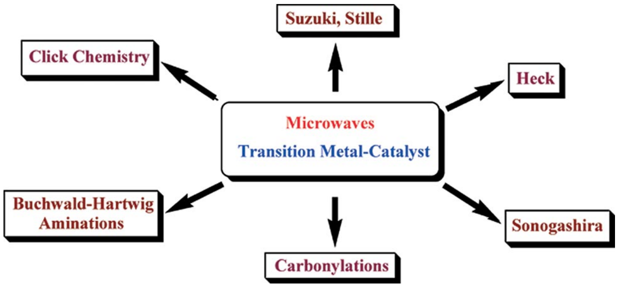
The beneficial effect of microwave irradiation instead of classical thermal conditions in olefin metathesis reactions is illustrated through a series of literature examples of ring-closing-metathesis and cross-metathesis reactions.

### Microwave-Assisted Transformations

**P. Appukkuttan,**
**E. Van der Eycken* ................ 1133–1155**

Recent Developments in Microwave-Assisted, Transition-Metal-Catalysed C–C and C–N Bond-Forming Reactions

**Keywords:** Microwave reactions / Transition metals / Cross-coupling / C–C coupling / Palladium



A selective survey on the recent developments of microwave-assisted transition-metal-catalysed C–C and C–N bond-forming reactions is presented. This review encompasses the advances in the last three years of Suzuki, Stille, Heck and Sonogashira couplings, carbonylations, Buchwald–Hartwig aminations, click chemistry and some other related areas.

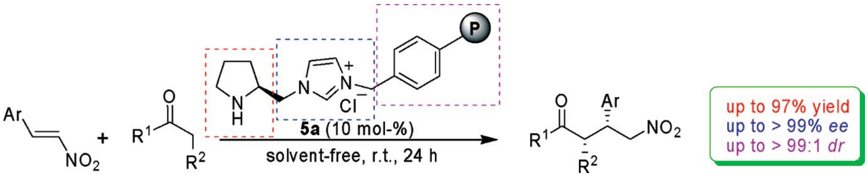
## SHORT COMMUNICATIONS

### Immobilized Chiral Ionic Liquids

**P. Li, L. Wang,* M. Wang,**
**Y. Zhang ................................ 1157–1160**

Polymer-Immobilized Pyrrolidine-Based Chiral Ionic Liquids as Recyclable Organocatalysts for Asymmetric Michael Additions to Nitrostyrenes under Solvent-Free Reaction Conditions

**Keywords:** Immobilized chiral ionic liquids / Asymmetric Michael additions / Organocatalysis / Nitrostyrenes / Solvent-free reactions

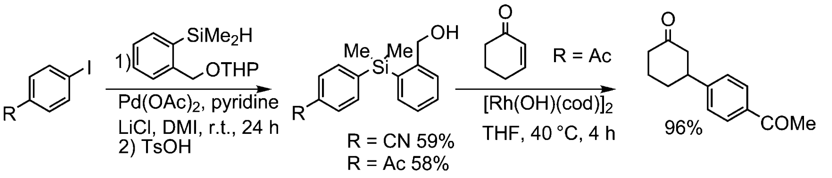


A polymer-immobilized pyrrolidine-based chiral ionic liquid **5a** was found as a highly efficient catalyst for the Michael additions of ketones and aldehydes to nitrostyrenes. The reactions afforded the corresponding adducts in good yields (up to 97%), excellent enantioselectivities (up to >99% *ee*) and high diastereoselectivities (up to >99:1 *dr*) under solvent-free reaction conditions. Furthermore, **5a** could be reused at least eight times without a significant loss of its catalytic activity and stereoselectivity.

### Functionalized Arylsilane

**M. Iizuka, Y. Kondo*** ............ **1161–1163**

Palladium-Catalyzed Silylation of Electron-Deficient Aryl Iodides Using Triorganosilane in the Presence of Pyridine and LiCl



Palladium-catalysed silylation of aryl iodides with electron-withdrawing groups was efficiently achieved using pyridine and lithium chloride as additives and conducting the reaction at room temperature.

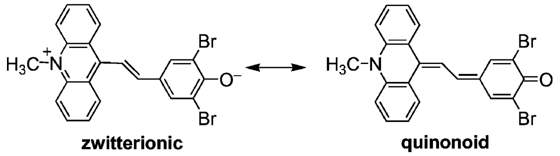
**Keywords:** Silylation / Palladium / Aryl iodides / Pyridine / Lithium chloride

## FULL PAPERS

### Solvatochromism of Merocyanines

**C. T. Martins, M. S. Lima, E. L. Bastos,
O. A. El Seoud*** .................... **1165–1180**

Thermo-Solvatochromism of Merocyanine Polarity Probes – What Are the Consequences of Increasing Probe Lipophilicity through Annelation?



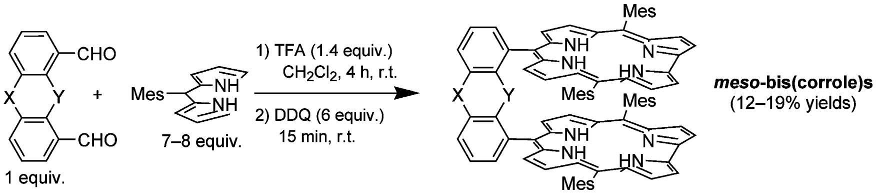
The effect of annelation on solvatochromism of merocyanines is interpreted in terms of structure- and solvent-dependent contributions of zwitterionic and quinonoid limiting structures to the probe resonance hybrid. Increasing probe lipophilicity by annelation affects solvatochromic responses more than increasing the length of the alkyl chain in the pyridinium moiety.

**Keywords:** Solvatochromism / Thermo-solvatochromism / Merocyanine dyes / Binary solvent mixtures

### Bis(corroles)

**M. El Ojaimi, C. P. Gros,
J.-M. Barbe*** ......................... **1181–1186**

Efficient Two-Step Synthesis of Face-to-Face *meso*-Substituted Bis(corrole) Dyads



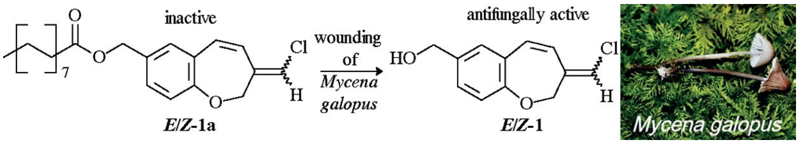
*meso*-Substituted bis(corrole) dyads were obtained in good yields from a dialdehyde linker and dipyrromethane in a one-step reaction. The best reaction conditions required a decreased amount of TFA catalyst and a large excess of dipyrromethane.

**Keywords:** Macrocycles / Corroles / Synthetic methods

### Chemical Defence

**S. Peters, R. J. R. Jaeger,
P. Spiteller*** ........................... **1187–1194**

Benzoxepine Esters as Precursors of the Wound-Activated Chemical Defence of *Mycena galopus*



A metabolic profiling of intact and injured fruiting bodies of *Mycena galopus* revealed that intact fruiting bodies contain previously unknown fatty acid esters, such as ***E*/*Z*-1a**, of the benzoxepine benzyl alcohols ***E***- and ***Z*-1**. Upon injury the inactive esters are cleaved, yielding the antifungally active free alcohols ***E***- and ***Z*-1**, thus probably protecting the fruiting bodies of *M. galopus* from yeasts and other fungi.

**Keywords:** Benzoxepines / Chemical defence / Fungi / Metabolic profiling / Natural products

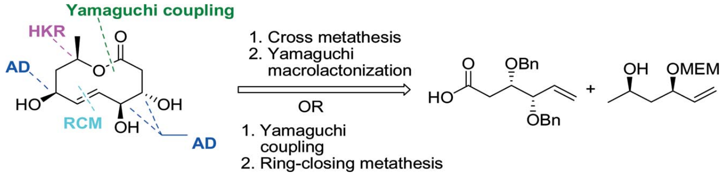
# CONTENTS

## Asymmetric Synthesis

**P. Gupta, P. Kumar*** .............. **1195–1202**

An Efficient Total Synthesis of Decarestrictine D

**Keywords:** Macrolides / Hydrolytic kinetic resolution / Sharpless asymmetric dihydroxylation / Cross metathesis / Ring-closing metathesis



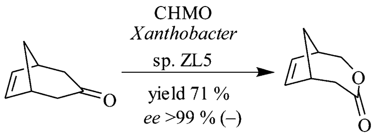
An efficient total synthesis of decarestrictine D has been achieved using cross-metathesis or ring-closing metathesis and Yamaguchi macrolactonization as key steps. The stereogenic centres were generated by means of hydrolytic kinetic resolution (HKR) and Sharpless asymmetric dihydroxylation (AD).

## Biooxidation

**D. V. Rial, D. A. Bianchi, P. Kapitanova, A. Lengar, J. B. van Beilen, M. D. Mihovilovic*** ................ **1203–1213**

Stereoselective Desymmetrizations by Recombinant Whole Cells Expressing the Baeyer–Villiger Monooxygenase from *Xanthobacter* sp. ZL5: A New Biocatalyst Accepting Structurally Demanding Substrates

**Keywords:** Biotransformation / Enzymes / Substrate profile / Baeyer–Villiger reaction / Epoxidation / Biocatalytic cascade reactions / *Xanthobacter* sp.



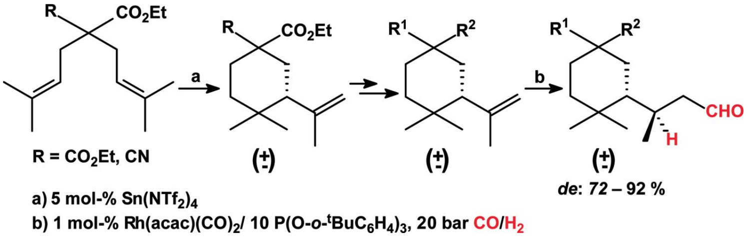
About 40 prochiral ketones of different sizes and substitution patterns were successfully desymmetrized with very good to excellent enantiomeric excesses by the CHMO from *Xanthobacter* sp. ZL5. This biocatalyst is able to convert sterically demanding ketones and thus enlarges the number of lactones accessible through biotransformation processes. Furthermore, the epoxidation of non-activated C=C bonds is achieved by this catalyst.

## Selective Hydroformylation

**F. Grau, J. C. Bayón,* P. A. Aguirre, T. Parella, E. Duñach*** .......... **1214–1223**

New Aldehydes by Catalytic Diene Cycloisomerisations

**Keywords:** Hydroformylation / Aldehydes / Isopropylidenecyclohexane / Stereochemistry / NMR spectroscopy



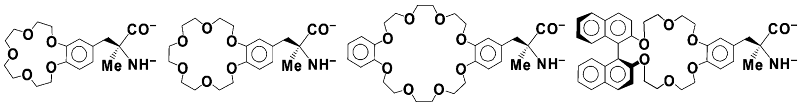
Rhodium-catalysed hydroformylation of isopropylidenecyclohexane derivatives, obtained by Sn(NTf$_2$)$_4$-catalysed intramolecular diene cyclisations, affords the corresponding aldehydes in good yields, with complete chemo- and regioselectivities, and with *de*s between 72 and 92%.

## Peptides and Crown Ethers

**K. Wright,* R. Anddad, J.-F. Lohier, V. Steinmetz, M. Wakselman, J.-P. Mazaleyrat, F. Formaggio, C. Peggion, M. De Zotti, T. A. Keiderling, R. Huang, C. Toniolo*** ............................ **1224–1241**

Synthesis, Ion Complexation Study, and 3D-Structural Analysis of Peptides Based on Crown-Carrier, $C^{\alpha}$-Methyl-L-DOPA Amino Acids

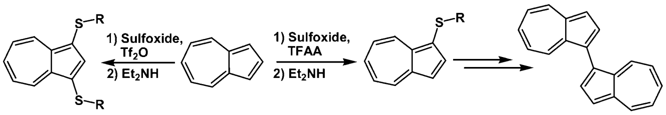
**Keywords:** Crown ethers / Peptides / DOPA / Solution peptide synthesis / Electronic circular dichroism / Vibrational circular dichroism



**L-Mdp[15-C-5]** **L-Mdp[18-C-6]** **L-Mdp[benzo-24-C-8]** **L-Mdp[*(S)*-Binol-20-C-6]**

Terminally protected peptides to the hexamer level, based on crown-ether-containing $C^{\alpha}$-methyl-L-DOPA (L-Mdp) amino acid residues, were prepared. Their alkali metal cation complexation ability was determined by ESI-MS analysis. Their FTIR absorption, $^1$H NMR, ECD, and VCD spectroscopic properties suggest that all of these crowned amino acids are strong inducers of (left-handed) β-turns and $3_{10}$-helical structures.

## Azulene Chemistry



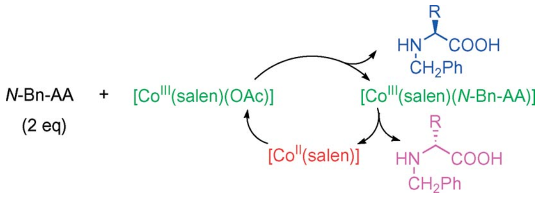
Azulene was treated with several sulfoxides in the presence of acid anhydrides to afford the corresponding 1-azulenylsulfonium and 1,3-azulenediyldisulfonium ions. Reaction of the 1-azulenylsulfonium ions with diethylamine gave 1-azulenyl sulfides which were readily converted into 1-azulenyl sulfoxides by reaction with MCPBA. The azulenyl sulfoxides were used to prepare 1,1′-biazulene derivatives under acidic conditions. The redox behavior of the 1-azulenyl sulfides, 1,3-bis(methyl- and phenylthio)azulenes, and 1,1′-biazulene derivatives bearing a methylthio or phenylthio substituent on each azulene ring was examined by cyclic voltammetry (CV).

**T. Shoji,* J. Higashi, S. Ito, K. Toyota, T. Asao, M. Yasunami, K. Fujimori, N. Morita*** ........................... **1242−1252**

### Synthesis and Redox Behavior of 1-Azulenyl Sulfides and Efficient Synthesis of 1,1′-Biazulenes

**Keywords:** Azulene / 1,1′-Biazulene / Electrophilic substitution / Electrochemistry / Cyclic voltammetry

## Enantioselective Extractions



Racemic *N*-benzyl α-amino acids (*N*-Bn-AA) are resolved in excellent yield and high enantiomeric excess by liquid-liquid extraction using a lipophilic chiral [Co$^{III}$(salen)(OAc)] complex. The amino acid extracted into the organic phase by coordination to cobalt can then be released by reductive counter-extraction. The original chiral cobalt(III) complex is restored and re-used with no loss of reactivity and selectivity.

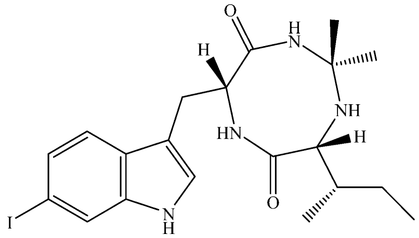
**P. Dzygiel, T. B. Reeve, U. Piarulli,* M. Krupicka, I. Tvaroska, C. Gennari*** .......................... **1253−1264**

### Resolution of Racemic *N*-Benzyl α-Amino Acids by Liquid-Liquid Extraction: A Practical Method Using a Lipophilic Chiral Cobalt(III) Salen Complex and Mechanistic Studies

**Keywords:** Amino acids / Cobalt / Recognition / Resolution / Salen ligands

## Hicksoanes A−C from Gorgonians

Eight-membered heterocyclic hicksoanes A−C were isolated from the gorgonian *Subergorgia hicksoni*. Their structures were determined by UV, IR, 1D and 2D NMR spectroscopy, MS, and chemical degradation. Their unique structures contain a triazocane cycle substituted by isoleucine and tryptophan moieties.



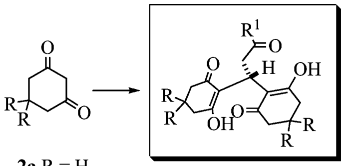
**T. Řezanka,* L. O. Hanuš, V. M. Dembitsky, K. Sigler** .... **1265−1270**

### Identification of the Eight-Membered Hetero-cycles Hicksoanes A−C from the Gorgonian *Subergorgia hicksoni*

**Keywords:** Gorgonians / Nitrogen heterocycles / Hicksoanes A−C / Natural products

## Atropisomerism

The design and selective synthesis of four atropisomers by a tandem-Michael/Michael addition of 1,3-cyclohexanediones to alkynes with the assistance of L-proline is reported. The reaction mechanism and the associated tautomerism of these compounds are also discussed.



**2a** R = H
**2b** R = CH$_3$

**1a** R = H, R$^1$ = OCH$_3$
**1b** R = H, R$^1$ = CH$_3$
**1c** R = CH$_3$, R$^1$ = OCH$_3$
**1d** R = CH$_3$, R$^1$ = CH$_3$

**L. E. Luna, G. Seoane, R. M. Cravero*** ..................... **1271−1277**

### Synthesis and Characterization of Atropisomers Arising from 1,3-Cyclohexanediones by Intermolecular Tandem-Michael/Michael Additions

**Keywords:** Tandem reactions / Michael addition / Cyclohexanediones / Alkynes / Chirality / Atropisomerism

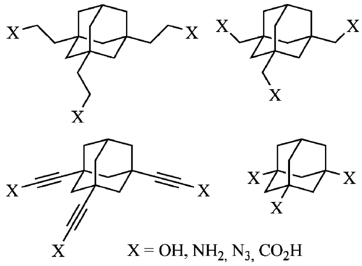
# CONTENTS

## $C_3$-Symmetric Scaffolds

**N. Pannier, W. Maison* ......... 1278–1284**

Rigid $C_3$-Symmetric Scaffolds Based on Adamantane

**Keywords:** $C_3$-Symmetry / Multivalency / Molecular recognition / Adamantane / Bioorganic chemistry



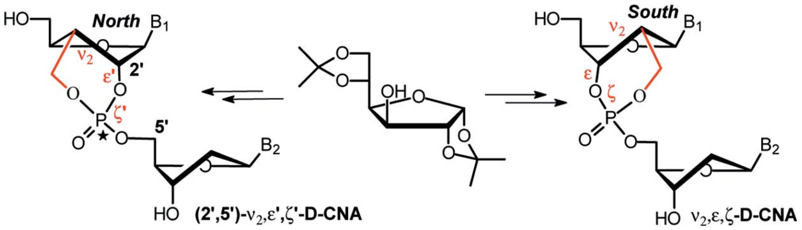
Efficient syntheses of rigid $C_3$-symmetric scaffolds based on adamantane are described. The scaffolds have been designed for conjugation to various natural products. They are valuable for the construction of strictly defined molecular architectures with threefold geometry for applications in bioorganic chemistry, catalysis or material science.

## Constrained Nucleotides

**C. Dupouy, P. Lavedan,**
**J.-M. Escudier* ..................... 1285–1294**

Synthesis and Structure of Dinucleotides with S-Type Sugar Puckering and Non-canonical ε and ζ Torsion Angle Combination (ν,ε,ζ-D-CNA)

**Keywords:** Strained molecules / Nucleotides / DNA structure / Phosphorus heterocycles / Conformation analysis



The diastereomeric $\nu_2$,ε,ζ-D-CNA dinucleotide building units of nucleic acids and their (2′,5′)-$\nu_2$,ε′,ζ′-D-CNA analogues where prepared from a common 3-deoxy-3-(hydroxymethyl)-D-allofuranose intermediate; torsional angles are stereocontrolled by a dioxaphosphorinane ring structure (D-CNA family), and sugar puckering can be restricted to the North or South conformation.