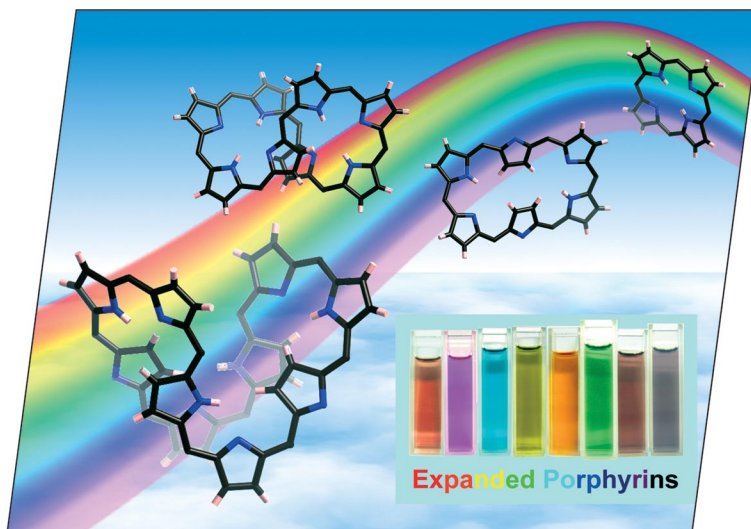


The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows the crystal structures and colors of *meso*-pentafluorophenyl-substituted expanded porphyrins. [18]Porphyrin, [26]hexaphyrin, [36]octaphyrin, [44]decaphyrin, [52]dodecaphyrin, [62]tetradecaphyrin, [72]hexadecaphyrin, and [80]octadecaphyrin were synthesized and characterized. As indicated, the absorption bands of these expanded porphyrins are redshifted as their size increases, and [80]octadecaphyrin shows its absorption maximum at 953 nm. Their solutions exhibit various colors, reflecting the macrocyclic conjugation like a rainbow. Details are discussed in the article by A. Osuka et al. on p. 1341ff.



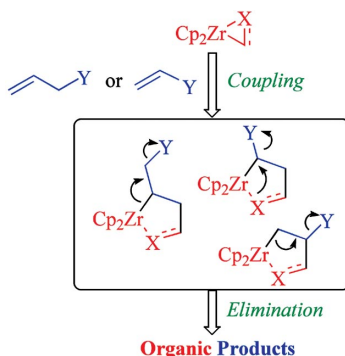
## MICROREVIEW

### Zirconocene Chemistry

F. J. Fañanás,\* F. Rodríguez\* .... 1315–1329

Cross-Coupling–Elimination Reactions Mediated or Catalyzed by Zirconium Complexes: A Valuable Tool in Organic Synthesis

**Keywords:** Cross-coupling / Elimination / Insertion / Migratory insertion / Zirconium



The tandem zirconocene-mediated or -catalyzed cross-coupling–elimination reaction is a powerful tool for the construction of scaffolds that in many cases are difficult to access by traditional organic chemistry. In this Microreview we discuss the reactivity of alkyne-, aryne-, alkene- and iminezirconocene complexes towards alkenes containing a heteroatom functionality at an appropriate position.

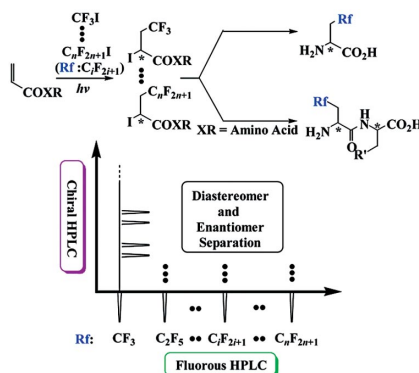
## SHORT COMMUNICATIONS

### Fluorous Amino Acids

T. Tono, A. Nishikawa, T. Yajima,\*  
H. Nagano, K. Mikami\* ..... 1331–1335

Fluorous Substituent-Based Enantiomer and Diastereomer Separation: Orthogonal Use of HPLC Columns for the Synthesis of Nonproteinogenic Polyfluoro Amino Acids and Peptides

**Keywords:** Fluorine / Racemates / Amino acids / Peptides



A fluorous racemic mixture synthesis (FRMS) of nonproteinogenic polyfluoro amino acid and peptide precursors was developed by the orthogonal use of fluorous and chiral HPLC columns.

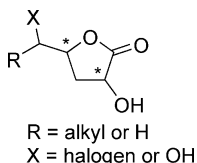
### 3'-Deoxyribolactones

D. J. Vugts, H. Aktas, K. Al-Mafraji,  
F. J. J. de Kanter, E. Ruijter, M. B. Groen,  
R. V. A. Orru\* ..... 1336–1339



Synthesis of 3'-Deoxyribolactones using a Hydrolysis-Induced Lactonization Cascade Reaction of Epoxy Cyanohydrins

**Keywords:** 3-Deoxyribolactone / Cascade reaction / Cyclization / Cyanohydrin

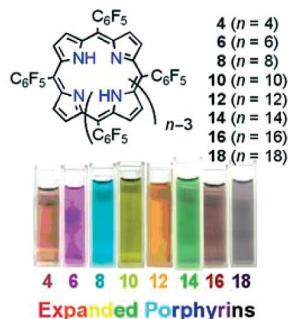


In this communication a one-pot hydrolysis-induced four-reaction lactonization cascade is described for the synthesis of 3'-deoxyribolactones. These  $\gamma$ -lactones are useful synthetic intermediates towards biologically active chiral 4-butanolides.


## FULL PAPERS

### Expanded Porphyrins

Large expanded porphyrins up to [80]octadecaphyrin **18** were synthesized and characterized. The solid-state structure of **10** was revealed by X-ray diffraction analysis to be a crescent-like conformation. The absorption bands of the porphyrins are redshifted as their sizes increase.



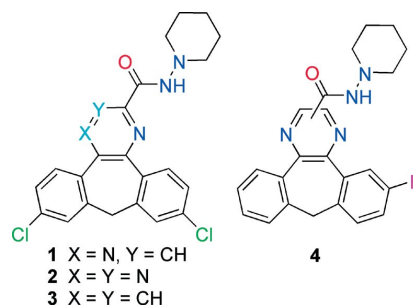
Y. Tanaka, J.-Y. Shin,  
A. Osuka\* ..... 1341–1349

Facile Synthesis of Large *meso*-Pentafluorophenyl-Substituted Expanded Porphyrins 

**Keywords:** Porphyrinoids / Expanded porphyrins / Conjugation / Macrocycles

### Synthesis of Rimona-bant Analogues

A synthesis of methylene-bridged analogs of rimona-bant is presented. The preparation of the desired compounds is based on a cyclocondensation reaction of tricyclic 1,2-diketones.

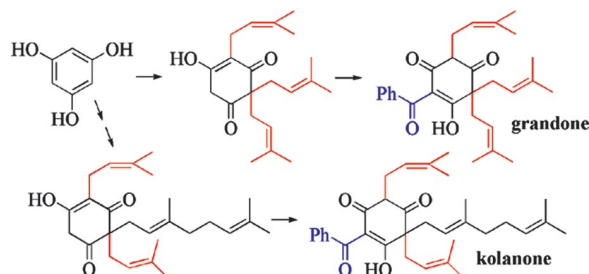


M. Ślusarczyk, W. M. De Borggraeve,\*  
G. Hoornaert, F. Deroose,  
J. T. M. Linders ..... 1350–1357

Synthesis and Biological Evaluation of Methylene-Bridged Analogs of the Potent Cannabinoid Receptor Antagonist Rimona-bant

**Keywords:** Heterocycles / Cyclocondensation / Diels–Alder reaction


### Phloroglucinol Prenylation



C-Alkylation of phloroglucinol with prenyl bromide in water provided a *gem*-disubstituted triprenylated derivative. Starting from geranyl- and isolavandulylphloroglucinol, compounds possessing a prenyl and a C<sub>10</sub> chain at the same position were

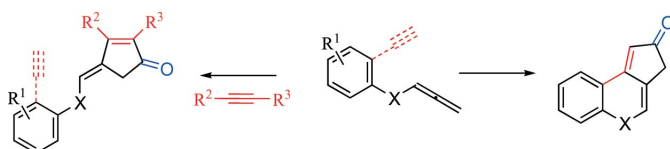
obtained. Subsequent C-benzoylation allowed the synthesis of natural products. Biomimetic-like electrophilic cyclization reactions were attempted with the aim of constructing polycyclic polyprenylated acylphloroglucinols (PPAPs).

S. B. Raikar, P. Nuhant,\* B. Delpech,\*  
C. Marazano ..... 1358–1369

Synthesis of Polyprenylated Benzoylphloroglucinols by Regioselective Prenylation of Phloroglucinol in an Aqueous Medium 

**Keywords:** Phloroglucinols / Prenylation / C-Benzoylation / Electrophilic cyclization / Natural products / Biomimetic synthesis


### Allenic Pauson–Khand Reactions



Pauson–Khand reactions of functionalized allenes with different alkynes give monocyclic cyclopentenones with generally high regio- and stereoselectivities. The allenes react with the external double bonds,

giving cyclopentenones with exocyclic double bonds at their  $\beta$  positions, mainly with *E* stereochemistry. Some intramolecular reactions with allenes connected through aromatic rings are described.

Á. González-Gómez, L. Añorbe,  
A. Poblador, G. Domínguez,  
J. Pérez-Castells\* ..... 1370–1377

Intermolecular and Intramolecular Pauson–Khand Reactions of Functionalized Allenes 

**Keywords:** Pauson–Khand reactions / Allenes / Cyclizations / Allenamides

# CONTENTS

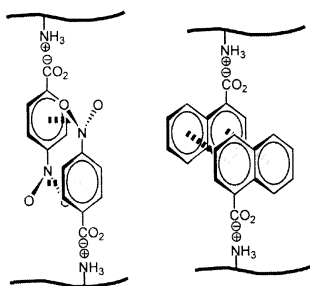
## Chemomechanical Polymers

K. Kato, H.-J. Schneider\* ..... 1378–1382



Dispersive Effects in Chemomechanical Reactions with Polyallylamine-Derived Hydrogels

**Keywords:** Supramolecular chemistry / Chemomechanical polymers / Hydrogels / Actuators / Dispersive interactions / Non-covalent interactions



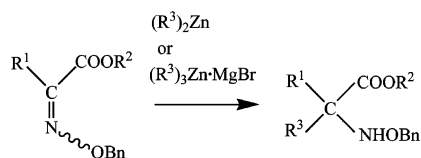
Van der Waals interactions between effector molecules in aqueous solution lead to contraction of polyallylamine gel particles, which for benzoic acids increase from about 18% to 70% by the presence of nitro groups, and to 67% with naphthalene derivatives. The observed cooperativity indicates dispersive forces as major driving factor for volume changes in such intelligent materials.

## $\alpha,\alpha$ -Disubstituted $\alpha$ -Amino Acids

M. Mitani,\* Y. Tanaka, A. Sawada, A. Misu, Y. Matsumoto ..... 1383–1391

Preparation of  $\alpha,\alpha$ -Disubstituted  $\alpha$ -Amino Acid Derivatives via Alkyl Addition to  $\alpha$ -Oxime Esters with Organozinc Species

**Keywords:** Amino acids / Trialkylzincate / Dialkylzinc / Oxime ethers / Alkylation



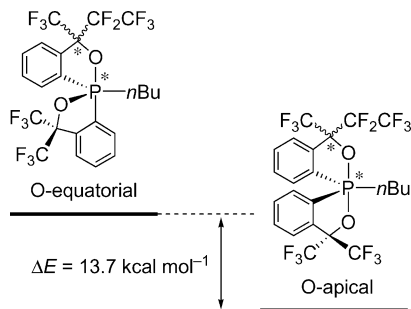
The Lewis acid-promoted reaction of  $\alpha$ -oxime esters with trialkylzincate or dialkylzinc reagents afforded *C*-alkylation of the oxime group. Subjection of the thus obtained adducts to hydrogenolysis catalyzed by palladium-on-carbon brought about the cleavage of the C–N bond to give  $\alpha,\alpha$ -disubstituted  $\alpha$ -amino esters.

## Stereomutation of Spirophosphoranes

X.-D. Jiang, S. Matsukawa, H. Yamamichi, K.-i. Kakuda, S. Kojima, Y. Yamamoto\* ..... 1392–1405

Stereomutation and Experimental Determination of the Relative Stability of Diastereomeric *O*-Equatorial Anti-Apicophilic Spirophosphoranes

**Keywords:** Diastereomers / Hypervalent compounds / Isomerization



By using a bidentate ligand derived from 1,1,1,3,3,4,4,4-octafluoro-2-phenyl-2-butanol, diastereomeric pairs of *O*-equatorial and *O*-apical spirophosphoranes were synthesized. Kinetic measurements of the stereomutation of the two isomers revealed that the *O*-equatorial phosphoranes are less stable than the *O*-apical isomers by 13.7 kcal mol<sup>−1</sup>.

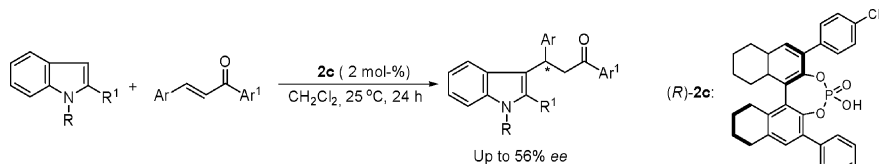
## Asymmetric Friedel–Crafts Alkylation

H.-Y. Tang, A.-D. Lu, Z.-H. Zhou,\* G.-F. Zhou, L.-N. He,\* C.-C. Tang ..... 1406–1410



Chiral Phosphoric Acid Catalyzed Asymmetric Friedel–Crafts Alkylation of Indoles with Simple  $\alpha,\beta$ -Unsaturated Aromatic Ketones

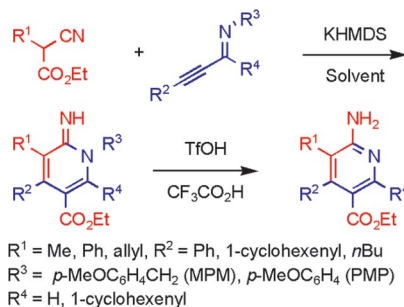
**Keywords:** Indoles /  $\alpha,\beta$ -Unsaturated aromatic ketones / Asymmetric Friedel–Crafts alkylation / Chiral phosphoric acids / Organocatalysis



An efficient H<sub>8</sub>-BINOL-based chiral phosphoric acid catalyzed asymmetric Michael-type Friedel–Crafts alkylation has been de-

veloped to provide the products in good yields and with moderate enantioselectivities.

Multi-substituted 2-iminopyridines can be synthesized by conjugate addition of ethyl cyanoacetate derivatives to alkynyl imines. Deprotection of the substituent on the nitrogen of 2-iminopyridines under acidic conditions gives 2-aminopyridines.

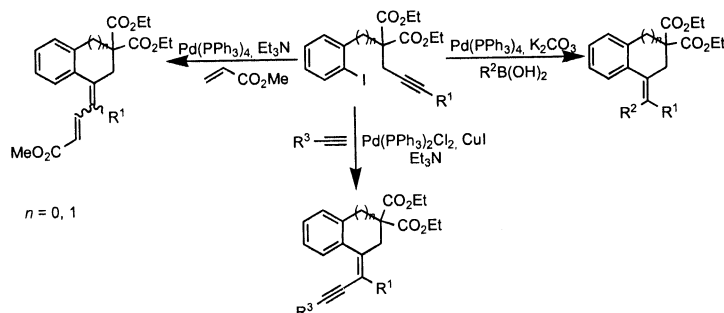


**I. Hachiya, Y. Minami, T. Aramaki, M. Shimizu\*** ..... 1411–1417

Synthesis of Multi-Substituted 2-Iminopyridine by Conjugate Addition of Ethyl Cyanoacetate Derivatives to Alkynyl Imines

**Keywords:** Conjugate addition / Imines / Pyridine / Ring-opening / Amines / Alkynes

## Pd-Catalyzed Domino Reactions



**L.-N. Guo, X.-H. Duan, J. Hu, H.-P. Bi, X.-Y. Liu, Y.-M. Liang\*** ..... 1418–1425

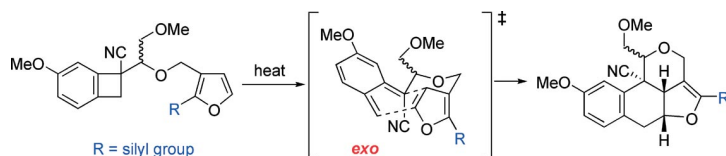
Synthesis of Indene and Naphthalene Derivatives by a Palladium-Catalyzed Domino Carbopalladation/Cyclization/Coupling Process

**Keywords:** Domino reactions / Carbopalladation / Cyclization / C-C coupling

Highly substituted indene and naphthalene derivatives have been readily prepared in good-to-high yields by a palladium-

catalyzed domino reaction. This domino reaction involves a Heck carbopalladation/cyclization/coupling process.

## Tandem Pericyclic Reactions



**Y. Matsuya,\* Y. Imamura, T. Miyahara, H. Ochiai, H. Nemoto\*** ..... 1426–1430

Approach to a New Dihydrofuran-Fused Cyclic System by a Remarkable Switching of *endo/exo* Selectivity of a [4+2] Cycloaddition Reaction

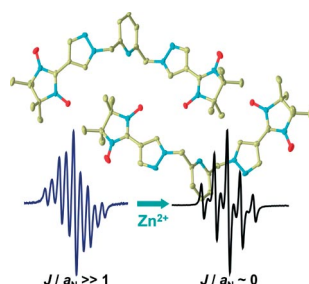
**Keywords:** Cycloaddition / Quinodimethanes / Pericyclic reaction / Diastereoselectivity / Anti-influenza agent

A new class of furan-fused tetracyclic compounds, which have an oxa-furanosteroidal framework, have been synthesized via an *o*-quinodimethane generated by thermal electrocyclic ring-opening of benzocyclobutene derivatives. The stereo-

selectivity could be controlled by preinstallation of a bulky silyl substituent onto the furan ring, enforcing an *exo* transition state. Preliminary biological evaluation of these compounds suggests they have potential as new anti-influenza agents.

## Stable Biradical Systems

The novel nitronyl nitroxide biradical system based on the 2,6-bis(pyrazolylmethyl)pyridine unit exhibits a through-bond ferromagnetic interaction ( $0.06 \text{ cm}^{-1} < \Delta E_{\text{ST}} = 2J/k_B < 0.6 \text{ cm}^{-1}$ ) which vanishes ( $2J/k_B \approx 0$ ) upon coordination with  $\text{Zn}^{2+}$  metal ions.



**G. Zoppellaro, A. Geies, K. K. Andersson, V. Enkelmann, M. Baumgarten\*** ..... 1431–1440

Synthesis, Optical Properties and Magnetic Studies of 2,6-Bis(pyrazolylmethyl)pyridine Functionalized with Two Nitronyl Nitroxide Radicals

**Keywords:** High-spin molecules / Radicals / EPR spectroscopy / Bis(pyrazolylmethyl)pyridine / NMR spectroscopy



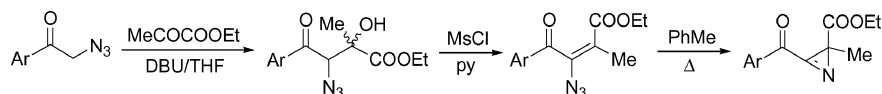
# CONTENTS

## C–C Coupling of $\alpha$ -Azido Ketones

T. Patonay,\* J. Jekő,  
É. Juhász-Tóth ..... 1441–1448

Synthesis of Highly Substituted 2*H*-Azirine-2-carboxylates via 3-Azido-4-oxobut-2-enates

**Keywords:** Azides / Azirines / C–C coupling / Nitrenes / Thermolysis



Phenacyl azides can be transformed into ethyl 4-aryl-3-azido-2-methyl-4-oxobut-2-enates by base-induced coupling of  $\alpha$ -azido ketones with an  $\alpha$ -oxo ester followed by elimination from the mesylate generated in situ from the labile aldol-type interme-

diates ethyl 4-aryl-3-azido-2-hydroxy-2-methyl-4-oxobutanoates. Thermolysis of the ethyl 4-aryl-3-azido-2-methyl-4-oxobut-2-enates gives the hitherto unknown 3-aryl-2-ethoxycarbonyl-2-methyl-2*H*-azirines.

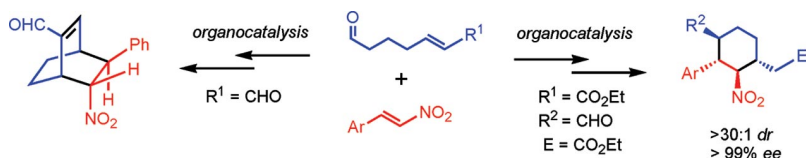
## Tandem Reactions

B.-C. Hong,\* R. Y. Nimje, M.-F. Wu,  
A. A. Sadani ..... 1449–1457



Organocatalytic Double Michael Reaction of 7-Oxohept-2-enates and Nitrostyrene – Formal Synthesis of (–)- $\alpha$ - and (–)- $\beta$ -Lycorane

**Keywords:** Asymmetric synthesis / Organocatalysis / Michael additions / Domino reactions / Tandem reactions



Organocatalytic conjugate addition of 7-oxohept-2-enate and nitrostyrene followed by intramolecular cyclization affords the highly functionalized cyclohexane car-

booster with four stereogenic centers with high diastereoselectivity and high enantioselectivity (>99% *ee*).

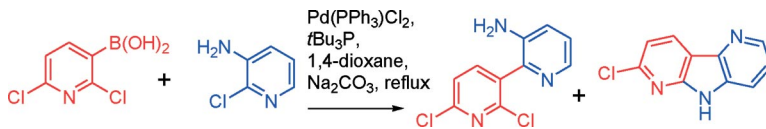
## Functionalised Heterocycles

A. E. Smith, K. M. Clapham,  
A. S. Batsanov, M. R. Bryce,\*  
B. Tarbit ..... 1458–1463



(Dimethoxy- and Dihalopyridyl)boronic Acids and Highly Functionalized Heteroarylpyridines by Suzuki Cross-Coupling Reactions

**Keywords:** Pyridine / Lithiation / Boronic acid / Cross-coupling / Diazacarbazole



Functionalised heteroarylpyridines have been synthesized by Suzuki methodology using (2,6-dimethoxy-3-pyridyl)boronic acid, (2,3-dimethoxy-4-pyridyl)boronic

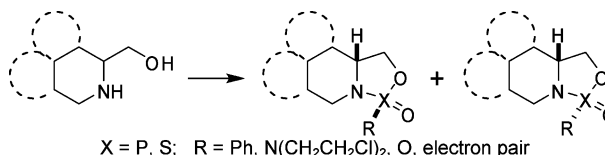
acid, (2,6-difluoro-3-pyridyl)boronic acid, (2,6-dichloro-3-pyridyl)boronic acid and (2,3-dichloro-4-pyridyl)boronic acid as key reagents.

## Phosphorus and Sulfur Heterocycles

I. Schuster, A. Koch, M. Heydenreich,  
E. Kleinpeter,\* E. Forró, L. Lázár,  
R. Sillanpää, F. Fülöp\* ..... 1464–1472

Synthesis and Conformational Analysis of Tetrahydroisoquinoline-Fused 1,3,2-Oxazaphospholidines and 1,2,3-Oxathiazolidines

**Keywords:** Phosphorus heterocycles / Sulfur heterocycles / Fused-ring systems / Conformational analysis / Molecular modelling



The cyclizations of tetrahydroisoquinoline 1,2-amino alcohols with phenylphosphonic dichloride, bis(2-chloroethyl)phosphoramidic dichloride, thionyl chloride and sulfonyl chloride were utilized to synthesize 5-

membered O,P,N- and O,S,N-heterocycles. NMR spectroscopic analysis revealed the existence of conformational equilibria that are fast on the NMR timescale.

If not otherwise indicated in the article, papers in issue 7 were published online on February 13, 2008