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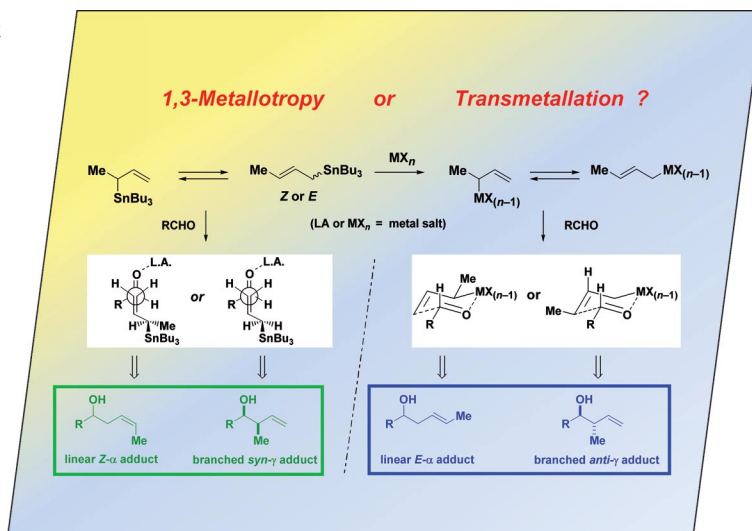


NETHERLANDS

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 different pathways that can be involved in the reaction of crotylins with aldehydes in the presence of metal salts. Depending on the experimental conditions, the crotylins can isomerize through 1,3-metallotropy or transmetallate with metal salts. The ratio of *E/Z* linear homoallylic alcohols and the ratio of *syn/anti* branched homoallylic alcohols are used to discriminate between these pathways. Details are discussed in the article by F. Zammattio, J.-P. Quintard et al. on p. 1681ff.



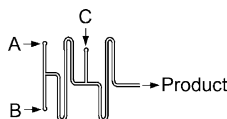
## MICROREVIEW

### Synthetic Methodology

C. Wiles, P. Watts\* ..... 1655–1671

Continuous Flow Reactors, a Tool for the Modern Synthetic Chemist

**Keywords:** Microreactors / Flow reactors / Methodology / Organic synthesis



It is the aim of this Microreview to provide the reader with an overview of recent advances made within the field of continuous-flow synthesis and highlight, in particular for those new to the field, examples that illustrate the intrinsic benefits associated with this rapidly growing area of organic synthesis.

## SHORT COMMUNICATIONS

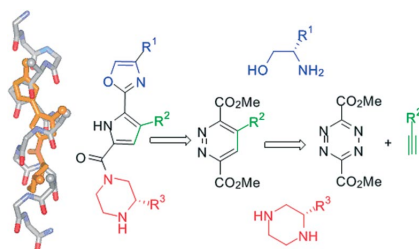
### $\alpha$ -Helix Mimetics

L. Moisan, S. Odermatt, N. Gombosuren, A. Carella, J. Rebek Jr.\* .....1673–1676



Synthesis of an Oxazole–Pyrrole–Piperazine Scaffold as an  $\alpha$ -Helix Mimetic

**Keywords:** Helical structures / Mimetics / Inverse electron demand Diels–Alder reactions / Nitrogen heterocycles



The design and synthesis of nonpeptidic  $\alpha$ -helix mimetics based on a tricyclic oxazole–pyrrole–piperazine scaffold is described. The scaffolds present both a hydrophobic surface for recognition and a hydrophilic edge that is rich in hydrogen-bond donors and acceptors.

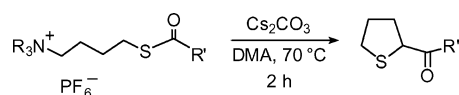
### Functionalized Tetrahydrothiophenes

S. Voltrova, J. Srogl\* ..... 1677–1679



Reaction of Thioesters with Nitrogen Ylides

**Keywords:** Thioesters / Ylides / Ammonium salts / Sulfur heterocycles



A novel intramolecular reaction of thioesters with nitrogen ylides is presented, which leads to the formation of a functionalized

tetrahydrothiophene skeleton through a 1,2-thiolate shift.

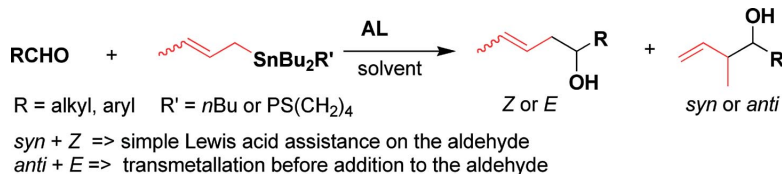
## FULL PAPERS

### Crotylation Mechanisms

V. Fargeas, F. Zammattio,\*  
J.-M. Chrétien, M.-J. Bertrand, M. Paris,  
J.-P. Quintard\* .....1681–1688

Crotylation of Aldehydes by Crotyltins: Discrimination between Mechanisms Involving Transmetalation or Simple Lewis Acid Assistance through the Consideration of the Stereochemistry of the Corresponding Homoallylic Alcohols

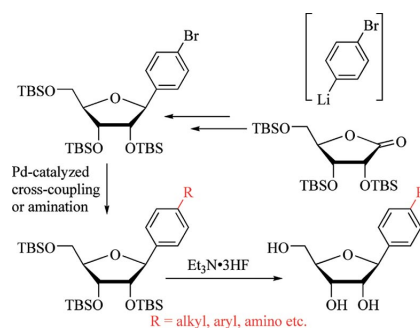
**Keywords:** Aldehydes / Allylation / Diastereoselectivity / Regioselectivity / Reaction mechanisms



The crotylation of aldehydes by crotyltins is highly dependent on the nature of the aldehyde, metal salt and solvent. By using CeCl<sub>3</sub>/7H<sub>2</sub>O/NaI, Z-linear  $\alpha$  adducts (crotyltributyltin) and syn-branched  $\gamma$  adducts (polymer-supported crotyltin) are ob-

tained. By using InX<sub>3</sub>, the reaction is Lewis acid assisted in CH<sub>2</sub>Cl<sub>2</sub> but moves to a transmetalation process in MeCN with a preference for the E- $\alpha$  adduct and the anti- $\gamma$  adduct.

A modular and efficient synthesis of a series of diverse 4- and 3-substituted benzene and aniline C-ribonucleosides was developed on the basis of Pd-catalyzed cross-coupling and amination reactions of protected bromophenyl C-nucleosides.

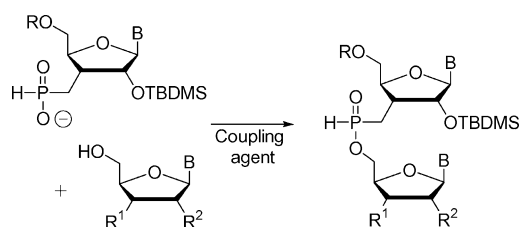


**M. Štefko, R. Pohl, B. Klepetářová, M. Hocek\*** ..... 1689–1704

A Modular Methodology for the Synthesis of 4- and 3-Substituted Benzene and Aniline C-Ribonucleosides

**Keywords:** Nucleosides / Cross-coupling / Amination / Arene

**Oligonucleotide Analogues**



Several classes of coupling agents for the formation of dinucleoside 3'-C-methylene-

phosphinates were investigated with respect to rate and side reactions.

**A. Winqvist, R. Strömberg\*** .... 1705–1714

Investigation on Condensing Agents for Phosphinate Ester Formation with Nucleoside 5'-Hydroxyl Functions

**Keywords:** Oligonucleotides / Nucleotides / Phosphinates / Phosphonates / Methylene-phosphonates / Condensation reactions

**Anti-Apiophilic Phosphoranes**



Diastereomeric anti-Apiophilic phosphoranes (*O*-equatorial phosphoranes) have been found to undergo stereospecific

pseudorotation to different *O*-apical diastereomers.

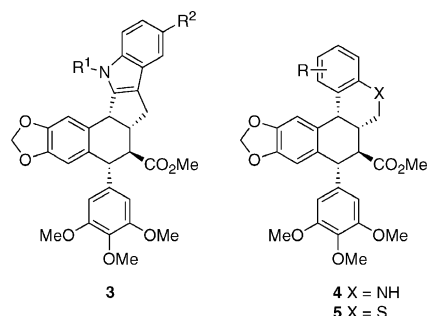
**S. Kojima,\* M. Nakamoto, K.-y. Akiba\*** ..... 1715–1722

Stereospecific Pseudorotation of Diastereomeric Anti-Apiophilic Spirophosphoranes: A Novel Stereochemical Transformation Involving 10-P-5 Phosphoranes

**Keywords:** Anti-Apiophilicity / Pseudorotation / Phosphoranes / Stereospecificity / Oxidation

**Friedel–Crafts-Type Cyclization**

The synthesis of a 1-aryltetralin privileged-structure-based library of novel angular heterocyclic lignans is described. Indolo-tetralins **3**, tetrahydroquinolinotetralins **4**, and thiochromanotetralins **5** were obtained from the methyl ester of thuriferic acid **2** according to a three-step procedure involving an InCl<sub>3</sub>-catalyzed Friedel–Crafts-type cyclization as the key step.



**M. Dorbec, J.-C. Florent,\* C. Monneret, M.-N. Rager, C. Fosse, E. Bertounesque\*** ..... 1723–1731

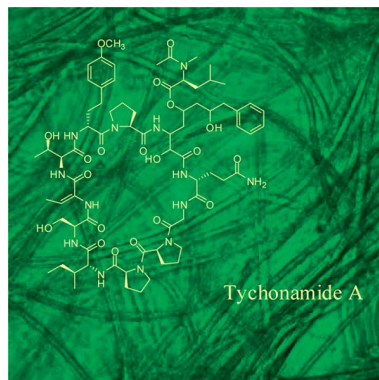
Synthesis of Novel Angular Heterocyclic Lignans by an InCl<sub>3</sub>-Catalyzed Friedel–Crafts-Type Cyclization

**Keywords:** Friedel–Crafts cyclization / Heterocyclic lignans / Indium / Michael addition / Privileged structures


# CONTENTS

## Cyclic Peptides from Cyanobacteria

C. Mehner, D. Müller, A. Krick,  
S. Kehraus, R. Löser, M. Gütschow,  
A. Maier, H.-H. Fiebig, R. Brun,  
G. M. König\* ..... 1732–1739



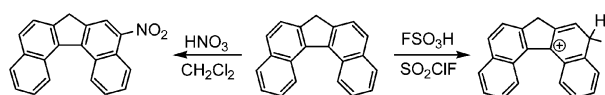
From the cyanobacterium *Tychonema* sp. two new cyclic peptides (tychonamide A and B) were obtained, both of which contain the novel  $\beta$ -amino acid Atpoa (3-amino-2,5,7-trihydroxy-8-phenyloctanoic acid). The peptides are distinguished by their cytotoxicity and interesting antiprotozoal activity.


 A Novel  $\beta$ -Amino Acid in Cytotoxic Peptides from the Cyanobacterium *Tychonema* sp.

**Keywords:** Natural products / Peptides / Cyanobacteria / Structure elucidation / Configuration determination

## Novel PAH Carbocations

K. K. Laali,\* T. Okazaki, F. Sultana,  
S. D. Bunge, B. K. Banik,  
C. Swartz ..... 1740–1752



 Stable-Ion NMR and GIAO-DFT Study of the Carbocations from Benzo- and Dibenzofluorenes; Synthesis of Nitro Derivatives; Mutagenicity Assay and X-ray Analysis

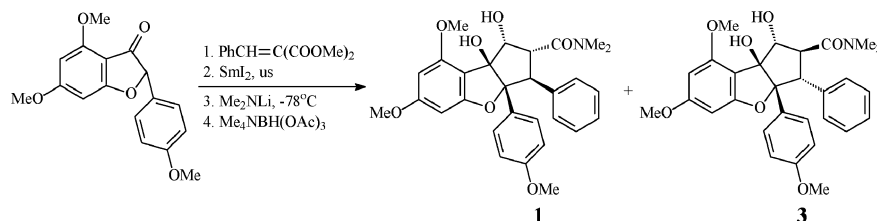
Stable carbocations derived from substituted benzo- and dibenzofluorenes were studied by NMR and DFT methods. Sev-


eral nitro derivatives were synthesized. Comparative mutagenicity assay and X-ray analysis were performed.

**Keywords:** Carbocations / Benzo- and Dibenzofluorenes / Nitro derivatives / Mutagenicity / NMR and DFT

## Natural Insecticides

H. S. Li, B. Fu, M. A. Wang, N. Li,  
W. J. Liu, Z. Q. Xie, Y. Q. Ma,  
Z. H. Qin\* ..... 1753–1758



 Total Synthesis and Biological Activity of ( $\pm$ )-Rocaglamide and Its 2,3-Di-*epi* Analogue

**Keywords:** Rocaglamides / Michael addition / Reductive coupling / Total synthesis / Insecticidal activity

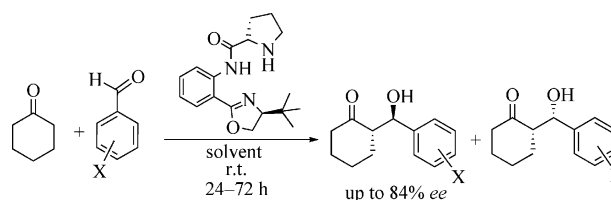
An efficient synthetic method to rocaglamide **1** and its 2,3-di-*epi* analogue **3** in racemic form was set up with 14.3 and 5.6%

total yield, respectively, starting from benzofuranone **4**. Several reactions were highly stereoselective or even stereospecific.

## Asymmetric Organocatalysis

S. Doherty,\* J. G. Knight,\* A. McRae,  
R. W. Harrington, W. Clegg .... 1759–1766

Oxazoline-Substituted Prolinamide-Based Organocatalysts for the Direct Intermolecular Aldol Reaction between Cyclohexanone and Aromatic Aldehydes

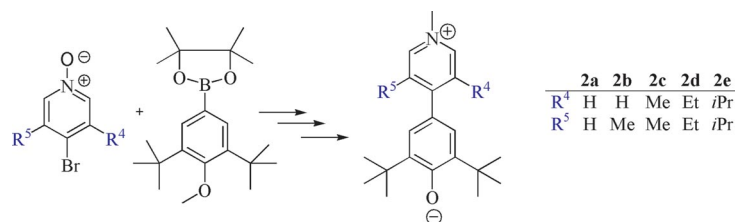


**Keywords:** Prolinamide / Oxygen heterocycles / Nitrogen heterocycles / Organocatalysis / Aldol reaction / Absolute configuration

Oxazoline-substituted prolinamides catalyze the direct asymmetric aldol reaction between cyclohexanone and a range of aldehydes to give excellent conversions and enantioselectivities up to 84% under opti-

imum conditions. Reactions were highly substrate-specific with electron-deficient aldehydes giving the highest yields and *ee* values.

## Pyridinium Phenolate Betaines



Efficient syntheses of chromophores for quadratic optics by using a Suzuki cross-coupling reaction between 4-bromo-

pyridine *N*-oxides and *tert*-butylated boronic ester are described.

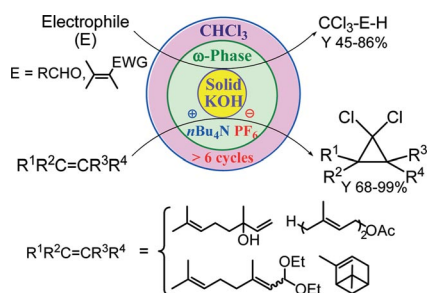
V. Diemer, H. Chaumeil,\* A. Defoin,  
A. Fort, A. Boeglin, C. Carré ... 1767–1776

Syntheses of Sterically Hindered Zwitterionic Pyridinium Phenolates as Model Compounds in Nonlinear Optics

**Keywords:** Donor–acceptor systems / Zwitterions / Nonlinear optics / Cross-coupling / Chromophores / N heterocycles

## Recoverable Phase-Transfer Catalyst

Tetraalkylammonium salts bearing PF<sub>6</sub><sup>−</sup> and BF<sub>4</sub><sup>−</sup> anions have been recognized as recoverable phase-transfer catalysts for the synthesis of 1,1-dichlorocyclopropane and α-(trichloromethyl)carbinol derivatives from alkenes or aldehydes in the heterogeneous system KOH(s)/CHCl<sub>3</sub>. The catalysts retained their catalytic activity over several reaction cycles.



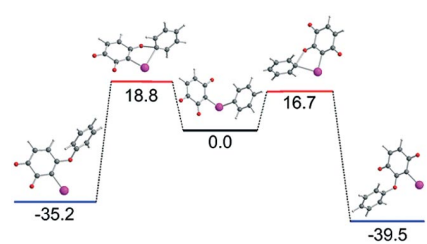
G. V. Kryshal, G. M. Zhbankina,  
S. G. Zlotin\* ..... 1777–1782

Recoverable Phase-Transfer Catalysts with Fluorinated Anions: Generation and Reactions of Dichlorocarbene and CCl<sub>3</sub> Anion in the Heterogeneous System KOH(s)/CHCl<sub>3</sub>/nBu<sub>4</sub>NPF<sub>6</sub>

**Keywords:** Phase-transfer catalysis / Dichlorocyclopropanation / Ionic liquids / Fluorinated anions / Heterogeneous reactions

## Ylide Rearrangements

Theoretical calculations predict that ketene formation in phenyliodonium ylides of hydroxyquinones is a more favorable reaction path than the phenyl-group migration path observed in analogous cyclic ylides. This is in excellent agreement with experimental data. Both rearrangements follow a single-step concerted mechanism via different transition states.



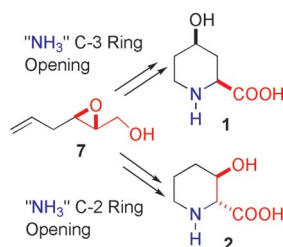
E. G. Bakalbassis,\* S. Spyroudis,  
C. A. Tsipis ..... 1783–1788

Ketene Formation or Phenyl-Group Migration as the Favorable Intramolecular Rearrangement in Phenyliodonium Ylides of Hydroxyquinones

**Keywords:** Density functional calculations / Transition states / Ylides / Quinones

## Chiral Unsaturated Epoxides

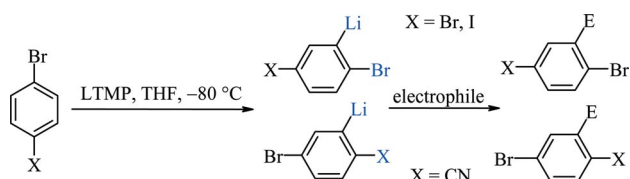
Enantioselective routes to both enantiomers of *cis*-4-hydroxypipercolic acid (**1**) and *trans*-3-hydroxypipercolic acid (**2**) are described. The regioselective C-3 ring opening of **7** leads to **1**, whereas C-2 ring opening leads to **2**. This chemistry was also used in the preparation of *trans*-3-hydroxy-2-hydroxymethylpiperidine and the natural product baikian.



C. Alegret, X. Ginesta,  
A. Riera\* ..... 1789–1796

Asymmetric Synthesis of *cis*-4- and *trans*-3-Hydroxypipercolic Acids

**Keywords:** Epoxidation / Asymmetric synthesis / Ring-opening / Natural products



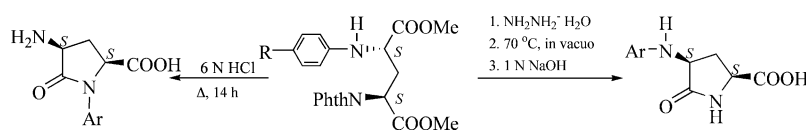
Regioselective lithiation of synthetically important activated bromobenzenes  $\text{XC}_6\text{H}_4\text{Br}$  ( $\text{X} = 4\text{-Br}, 4\text{-I}, 4\text{-CN}, 2\text{-CN}$ ) is reported. Treatment of the resultant aryl-

lithiums with a number of electrophiles provided functionalized derivatives with good yields.

S. Luliński,\* J. Serwatowski,  
M. Szczerbińska ..... 1797–1801

Regioselective Generation of Aryllithiums from Substituted Bromobenzenes  $\text{XC}_6\text{H}_4\text{Br}$  ( $\text{X} = 4\text{-Br}, 4\text{-I}, 4\text{-CN}, 2\text{-CN}$ )

**Keywords:** Lithiation / Arenes / Lithium / Halides / Cyanides



Acidic hydrolysis of (2*S*,4*S*)-4-arylamino-glutamates results in the formation of lactams in which ring closure occurs with the participation of the  $\gamma$ -amino and  $\alpha$ -COOH groups; lactams resulting from  $\alpha$ -amino

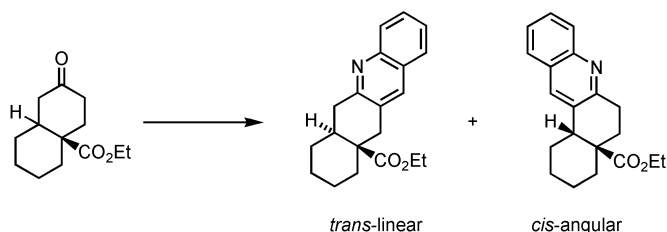
and  $\gamma$ -COOH group participation are not formed. Isomeric lactams can be easily converted in acidic medium into more stable 4-amino-1-aryl-5-oxoprolines.

Cyclization of 4-Arylamino Glutamates

V. P. Krasnov,\* I. A. Nizova, A. Y. Vigorov,  
T. V. Matveeva, G. L. Levit,  
P. A. Slepukhin, M. A. Ezhikova,  
M. I. Kodess ..... 1802–1810

Structure and Properties of 4-Amino Derivatives of 5-Oxoproline

**Keywords:** Amino acids / Lactams / Cyclization / NMR spectroscopy / Structure elucidation



Depending on the relative configuration of starting bicyclic ketones (*cis* or *trans*),

either linear or angular quinoline annulation can take place with high selectivity.

Regioselective Quinoline Synthesis

C. L. Diedrich, D. Haase, W. Saak,  
J. Christoffers\* ..... 1811–1816

Regioselectivity of Friedländer Quinoline Syntheses

**Keywords:** Annulation / Quinoline derivatives / Heterocycles / Regioselectivity / Friedländer synthesis

CORRECTION

**Keywords:** Asymmetric catalysis / Chiral pool / Palladium / Pyridine ligands / Zinc

Pyridyl Phosphinites and Pyridyl Phosphites from Chiral Pyridyl Alcohols – A Modular Approach

F. Rahm, A. Fischer, C. Moberg\* ..... 1817

If not otherwise indicated in the article, papers in issue 9 were published online on March 4, 2008