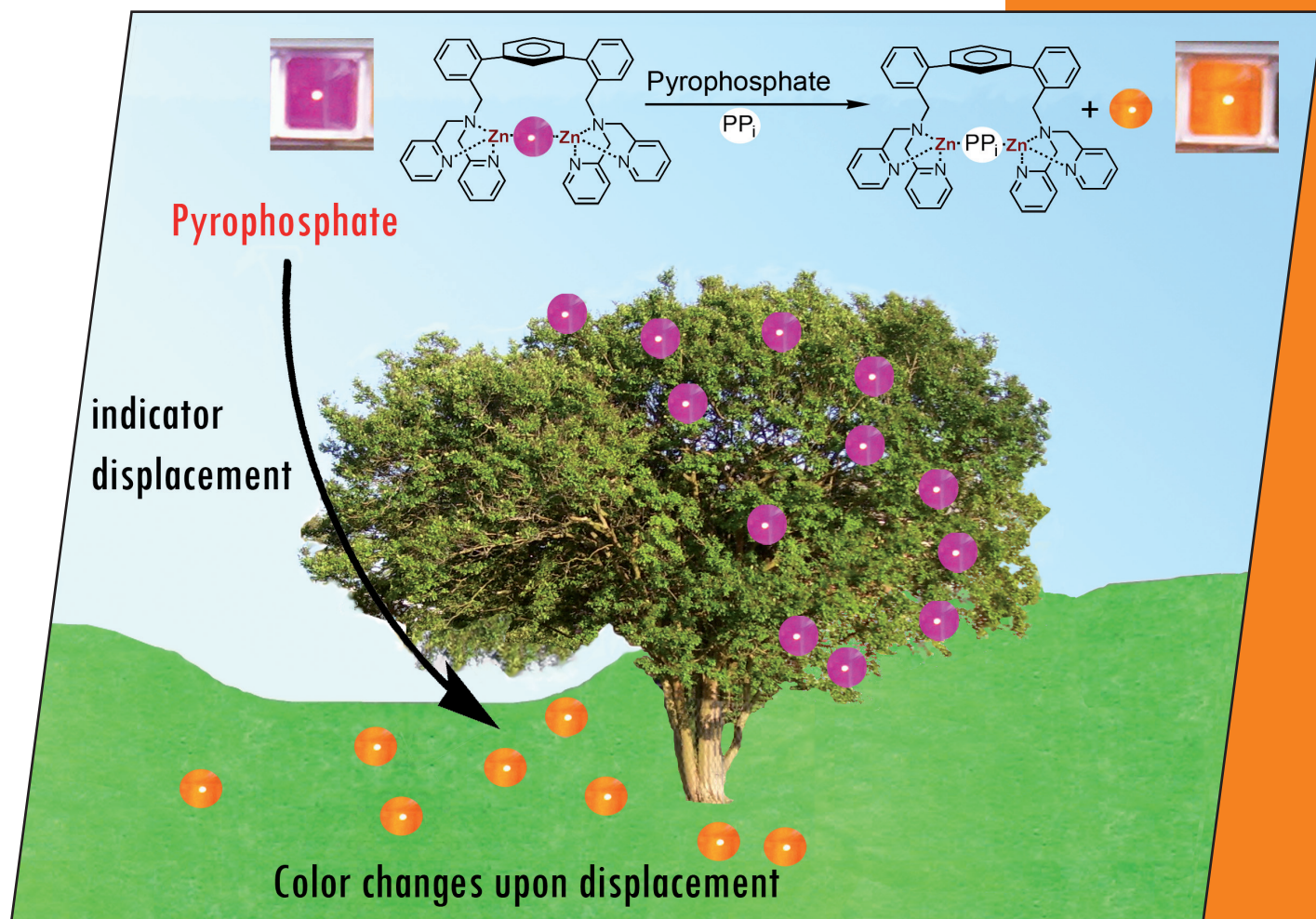


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**Cover Picture**

Rhett C. Smith et al.

Dizinc Phosphohydrolase Model

**Microreview**

Štefan Toma, Mária Mečiarová and Radovan Šebesta

Are Ionic Liquids Suitable Media for Organocatalytic Reactions?

**WILEY-VCH**

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A Journal of



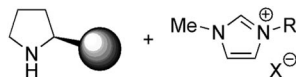
## MICROREVIEW

### Organocatalysis

Š. Toma,\* M. Mečiarová,  
R. Šebesta\* ..... 321–327

Are Ionic Liquids Suitable Media for Organocatalytic Reactions?

**Keywords:** Ionic liquids / Organocatalysis / Aldol reaction / Mannich reaction / Michael addition



Organocatalyzed reactions carried out in nonclassical solvents such as ionic liquids represent interesting alternatives to established procedures. This combination often leads to improved yields and selectivities, as well as to possible catalyst recycling.

## SHORT COMMUNICATIONS

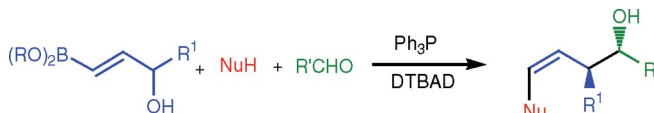
### Boron-Mediated Mitsunobu Reactions

F. Berrée,\* N. Gernigon, A. Hercouet,  
C. H. Lin, B. Carboni ..... 329–333



$S_N2'$  Boron-Mediated Mitsunobu Reactions – A New One-Pot Three-Component Synthesis of Substituted Enamides and Enol Benzoates

**Keywords:** Mitsunobu reaction / Boronic esters / Nucleophilic substitution / Allylboration



Substituted enamides and enol benzoates are readily prepared with a high diastereoselectivity in a one-pot procedure consisting of a regiocontrolled Mitsunobu reaction with convenient nucleophiles, followed by allylboration of aldehydes.

sisting of a regiocontrolled Mitsunobu reaction with convenient nucleophiles, followed by allylboration of aldehydes.

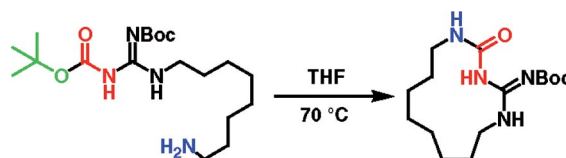
### Innovative Macrocycles

D. Castagnolo, F. Raffi, G. Giorgi,  
M. Botta\* ..... 334–337



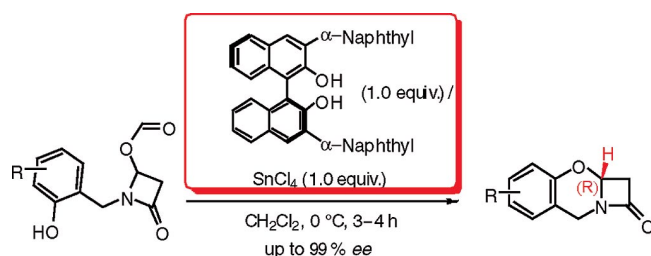
Macrocyclization of Di-Boc-guanidinoalkylamines Related to Guazatine Components: Discovery and Synthesis of Innovative Macrocyclic Amidinoureases

**Keywords:** Macrocyclization / Amidinourease / Aminoguanidine



Innovative macrocyclic amidinoureases were synthesised from linear di-Boc-guanidinoalkylamines related to guazatine. Macrocyclization proceeds under mild conditions affording 11- to 16-membered rings with a

new and previously undescribed structure in good yields. The synthesis of enantiomerically pure macrocyclic amidinoureases was also accomplished.



A short, enantioselective Lewis acid catalyzed synthesis of some 3,4-benzo-5-oxacephams is reported. The absolute configuration

of the title compounds was established by CD spectroscopy.

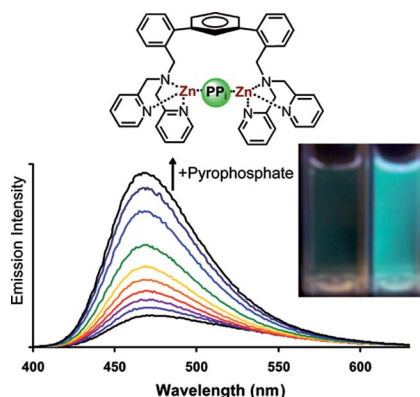
A. Koziol, J. Frelek, M. Woźnica,  
B. Furman, M. Chmielewski\* .... 338–341

An Enantioselective Synthesis of 3,4-Benzo-5-oxacephams

**Keywords:** Lactams / Asymmetric synthesis / Chiral Lewis acids / Cyclization

## FULL PAPERS

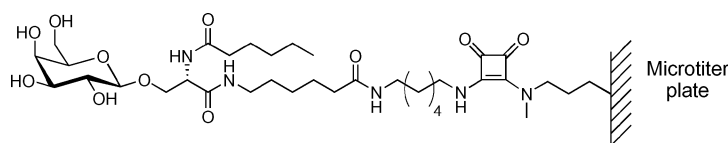
The dizinc complex of a dinucleating ligand built on a *m*-terphenyl scaffold was tested for binding to anions and complexometric indicators under physiological conditions. Colorimetric and fluorescence-based indicator displacement assays with selectivity for pyrophosphate over other anions were achieved with Zn<sub>2</sub>L2 as the receptor component.



M. K. Coggins, A. M. Parker,  
A. Mangalum, G. A. Galdamez,  
R. C. Smith\* ..... 343–348

Dizinc Phosphohydrolase Model Built on a *m*-Terphenyl Scaffold and Its Use in Indicator Displacement Assays for Pyrophosphate Under Physiological Conditions

**Keywords:** Biomimetic synthesis / N ligands / Enzyme models / Metalloenzymes / Receptors / Phosphohydrolase / Bimetallic complexes / Sensors / Pyrophosphate



Serine-based amino-functionalized neoglycolipids were prepared by solid-phase synthesis using a carbamate-linker strategy and monitoring with gel-phase <sup>19</sup>F NMR spectroscopy. The terminal amine obtained

after cleavage was conjugated to amino-functionalized microtiter plates using didecyl squarate and the array was successfully probed with a galactose-binding lectin.

S. Spjut, M. Pudelko, M. Hartmann,  
M. Elofsson\* ..... 349–357

Carbamate Linker Strategy in Solid-Phase Synthesis of Amino-Functionalized Glycoconjugates for Attachment to Solid Surfaces and Investigation of Protein-Carbohydrate Interactions

**Keywords:** Solid-phase synthesis / Glycoconjugates / Carbohydrates / Proteins / Carbohydrate protein interactions / Carbamate linker / Gel-phase <sup>19</sup>F NMR spectroscopy / Microtiter plates

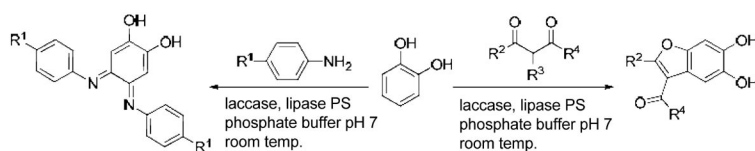
# CONTENTS

## Laccase-Lipase Cocatalytic System

S. Witayakran,  
A. J. Ragauskas\* ..... 358–363

Cocatalytic Enzyme System for the Michael Addition Reaction of in-situ-Generated *ortho*-Quinones

**Keywords:** Enzyme catalysis / Laccase / Lipase / Michael addition / Cascade reaction / Quinones



The use of laccase-lipase cocatalytic system to catalyze domino reaction of catechols and nucleophilic reagent, 1,3-dicarbonyl

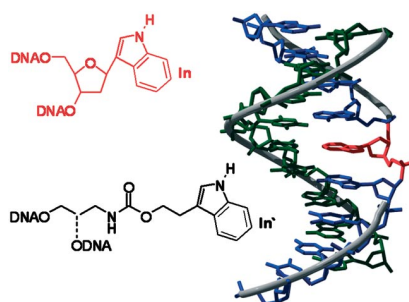
compounds and anilines, affords the corresponding products in a good yield in aqueous medium at room temperature.

## Artificial DNA Bases

J. Barbaric, C. Wanninger-Weiß,  
H.-A. Wagenknecht\* ..... 364–370

Indole in DNA: Comparison of a Nucleosidic with a Non-Nucleosidic DNA Base Substitution

**Keywords:** Nitrogen heterocycles / DNA / Oligonucleotides / Nucleosides



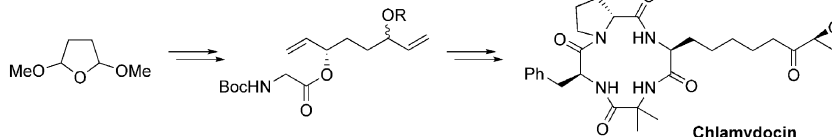
Linkage does not matter for indole as DNA base substitution: The synthetic incorporation of indole as an artificial DNA base into oligonucleotides by two different structural approaches is described. The natural-like indole nucleoside In destabilizes DNA duplexes as much as the non-nucleosidic surrogate In' that connects the phosphodiester bridges by a glycol unit.

## Cyclopeptides

C. Quirin, U. Kazmaier\* ..... 371–377

Synthesis of Chlamydocin by Chelate-Claisen Rearrangement

**Keywords:** Aoe / Chlamydocin / Cyclopeptides / Natural products / Rearrangement / Total synthesis



Chelate-Claisen rearrangement of a chiral allylic ester allows the synthesis of the unusual epoxyketo amino acid Aoe found in

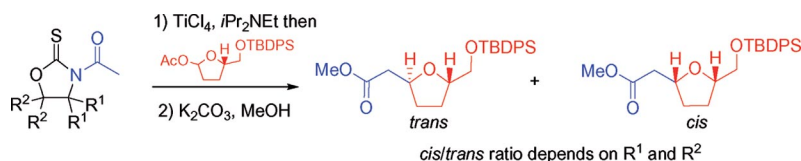
chlamydocin, one representative of a group of peptide-based HDAC inhibitors.

## C-Glycosylations

G. Jalce, X. Franck,  
B. Figadère\* ..... 378–386

Synthesis and Use of Achiral Oxazolidine-2-thiones in Selective Preparation of *trans* 2,5-Disubstituted Tetrahydrofurans

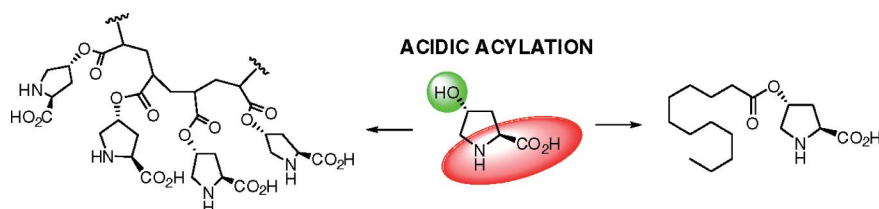
**Keywords:** Titanium / Diastereoselectivity / Natural products / Lactols / Furans / Glycosylation



2,5-Disubstituted tetrahydrofurans can be obtained in a *trans/cis* ratio of up to 93:7 by the addition of an achiral *N*-acetyl-

oxazolidine-2-thione to a lactol acetate. The diastereoselectivity depends on the nature of R<sup>1</sup> and R<sup>2</sup> on the achiral reagent.





A selective *O*-acylation of hydroxyproline in  $\text{CF}_3\text{CO}_2\text{H}$  makes a range of proline derivatives available on large-scale without any use of chromatographic purification or

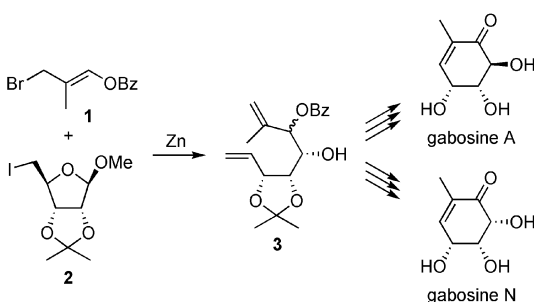
protecting groups, both catalytically active proline amphiphiles and an interesting new high-load proline polymer.

T. E. Kristensen, F. K. Hansen,  
T. Hansen\* ..... 387–395

The Selective *O*-Acylation of Hydroxyproline as a Convenient Method for the Large-Scale Preparation of Novel Proline Polymers and Amphiphiles

**Keywords:** Acylation / Polymerization / Amphiphiles / Amino acids / Immobilization

## Natural Products



Gabosine A and N were prepared in 8–9 steps from ribose. The key step is a zinc-mediated tandem reaction between **1** and **2** to afford diene **3**. Subsequent ring-closing

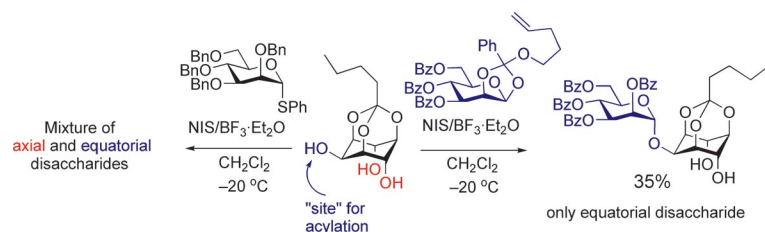
metathesis yields the corresponding cyclohexene which is then converted into the two natural products.

R. N. Monrad, M. Fanefjord,  
F. G. Hansen, N. M. E. Jensen,  
R. Madsen\* ..... 396–402

Synthesis of Gabosine A and N from Ribose by the Use of Ring-Closing Metathesis

**Keywords:** Carbohydrates / Cyclitols / Metathesis / Natural products / Total synthesis

## Regioselective Glycosylation



A mannose *n*-pentenyl orthoester (NPOE) glycosylates regioselectively *myo*-inositol orthopentenoate at the equatorial OH, whereas phenyl tetra-*O*-benzyl-*D*-mannose thioglycoside was less discriminant giving

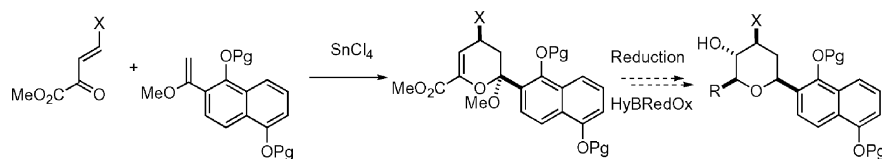
mixtures of axial and equatorial disaccharides. As noted previously, the preferred site for glycosylation of NPOEs coincides with that of selective acylation with the system  $\text{RCOCl/pyridine}$ .

C. Uriel, A. M. Gómez, J. C. López,\*  
B. Fraser-Reid\* ..... 403–411

Reciprocal Donor–Acceptor Selectivity: the Influence of the Donor O-2 Substituent in the Regioselective Mannosylation of *myo*-Inositol Orthopentanoate

**Keywords:** Carbohydrates / Glycosides / Regioselectivity / Glycosylation / *myo*-Inositol / *n*-Pentenyl orthoester / Thioglycoside / Donor-acceptor systems

## C-Aryl Glycosides



The *de novo* access to “projuglone” *C*-naphthyl glycosides has been investigated through a [4+2] heterocycloaddition route. Two original dienophiles, conveniently protected at phenolic positions, were synthe-

sized and stereoselectively led to the expected heteroadducts. This work presents the first attempts to apply the HyBRedOx sequence to the synthesis of projuglone *C*-naphthyl glycosides.

L. Maingot, N. Q. Vu, S. Collet,  
A. Guingant, A. Martel,  
G. Dujardin\* ..... 412–422

[4+2]/HyBRedOx Approach to *C*-Naphthyl Glycosides: Failure in the Projuglone Series and Reinvestigation of the HyBRedOx Sequence

**Keywords:** Tin / Cycloaddition / Dienophiles / Glycosides / Heterocycles

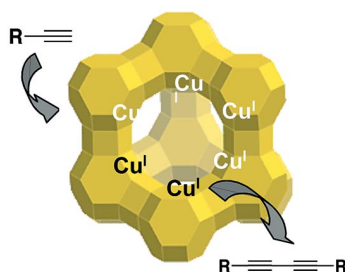
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## Metal–Zeolites in Organic Synthesis

P. Kuhn, A. Alix, M. Kumarraja, B. Louis,  
P. Pale,\* J. Sommer\* ..... 423–429

Copper–Zeolites as Catalysts for the Coupling of Terminal Alkynes: An Efficient Synthesis of Diynes

**Keywords:** Zeolites / Copper / Alkynes / Diynes / Glycosides



Cu<sup>I</sup>-modified zeolites were used for the first time as catalysts for the synthesis of diynes by homocoupling of terminal alkynes. Zeolites exhibiting internal large cage frames, Cu<sup>I</sup>–USY and Cu<sup>I</sup>–Y, proved to be the best catalysts. High and usually quantitative yields were obtained with a large variety of alkynes, including carbohydrate derivatives.

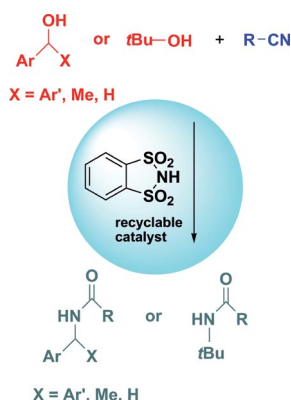
## Homogeneous Catalysis

M. Barbero, S. Bazzi, S. Cadamuro,  
S. Dughera\* ..... 430–436



*o*-Benzenedisulfonimide as a Reusable Brønsted Acid Catalyst for Ritter-Type Reactions

**Keywords:** Homogeneous catalysis / Amides / Nitriles / Ritter reaction / Brønsted acid



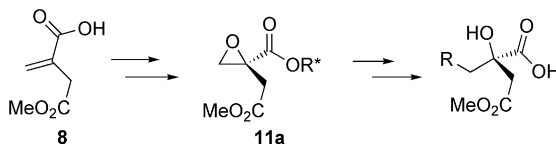
Reactions between benzyl alcohols or *tert*-butyl alcohol and nitriles carried out in the presence of catalytic amounts of *o*-benzenedisulfonimide are described. The catalyst was recovered with economic and ecological benefits.

## Cephalotaxus Alkaloid Side-Chains

F. Berhal, S. Tardy, J. Pérard-Viret,  
J. Royer\* ..... 437–443

Synthesis of Optically Active Monoacid Side-Chains of *Cephalotaxus* Alkaloids

**Keywords:** Alkaloids / Esters / Epoxides / Ring-opening / Chirality



Enantiopure monoacid side-chains of esters of cephalotaxine have been prepared. The strategy used as key intermediate the chiral nonracemic epoxide **11a** prepared from monomethyl itaconate (**8**). Ring-

opening of epoxide **11a** by using different organocuprate nucleophiles followed by hydrogenolysis gave the monoacid side-chains of the corresponding esters of cephalotaxine in moderate to good overall yields.

\* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 2 were published online on December 23, 2008