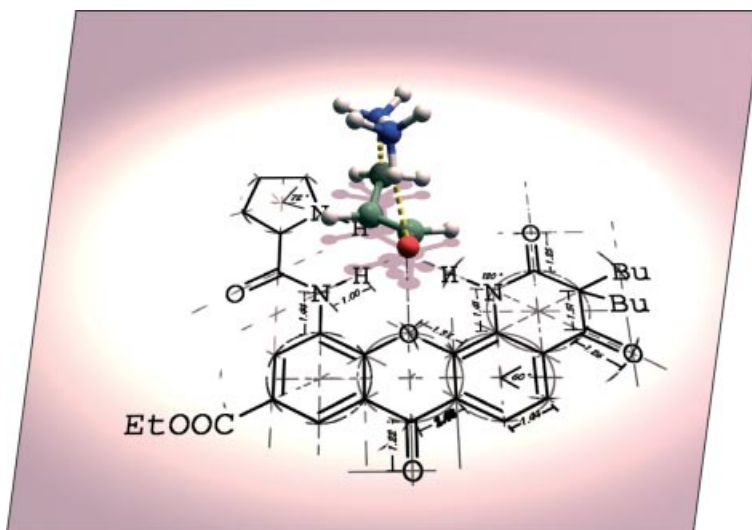




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic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

## COVER PICTURE

The cover picture shows the design of molecular receptors with enzyme-like catalytic activity for the Michael addition of pyrrolidine to an  $\alpha,\beta$ -unsaturated lactam. The picture emphasizes the design process of these receptors by using a draft-like style for the receptor structure. This design is based on a model for the transition state (represented as a high-quality 3-D model) that is obtained from theoretical study of the reaction mechanism. In the paper, we use both kinetic experiments and molecular modeling studies to assist the design of the H-bonding catalyst. From these studies we concluded that the presence of an auxiliary amine group could improve the catalytic activity of previous catalysts that resemble the oxyanion hole structure found in many enzymes. A simple modeling procedure is used to predict the catalytic activity of the tested catalyst, that in some cases shows  $k_{\text{cat}}/k_{\text{uncat}}$  values close to the range of values observed for many catalytic antibodies. Details are discussed in the article by L. Simón et al. on p. 4821ff.



# CONTENTS

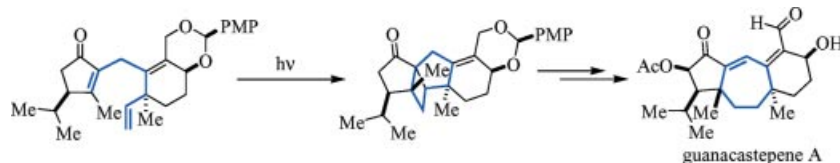
## MICROREVIEW

### Photochemistry

J. Iriando-Alberdi,  
M. F. Greaney\* ..... 4801–4815

Photocycloaddition in Natural Product  
Synthesis

**Keywords:** Natural products / Photochem-  
istry / Cycloaddition / Total synthesis



The application of photocycloaddition to natural product synthesis continues to produce innovative strategies for key bond constructions in the complex molecule environment. This Microreview surveys

the recent literature for photocycloaddition key steps in natural product synthesis, examining both completed routes and those in progress.

## SHORT COMMUNICATION

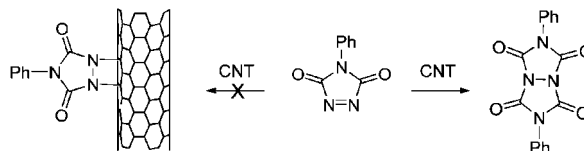
### Carbon Nanotubes

C. Ménard-Moyon, M. Gross,  
M. Bernard, P. Turek, E. Doris,\*  
C. Mioskowski ..... 4817–4819



Unexpected Outcome in the Reaction of  
Triazolidinedione with Carbon Nanotubes

**Keywords:** Carbon nanotubes / ESR /  
Triazolidinedione / Electron donors / Dimeri-  
zation



The reactivity of triazolidinedione (TAD) was investigated in the Diels–Alder reaction with carbon nanotubes. However, an unexpected conversion of TAD into its de-

aza dimer was observed. ESR spectroscopy suggested that the process was initiated by electron transfer from the nanotubes.

## FULL PAPERS

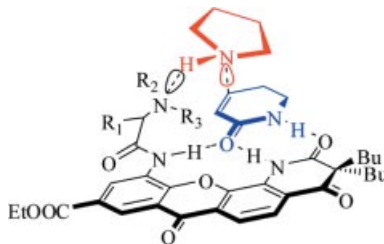
### Supramolecular Catalyst Design

L. Simón,\* F. M. Muñoz, S. Sáez,  
C. Raposo, J. R. Morán ..... 4821–4830

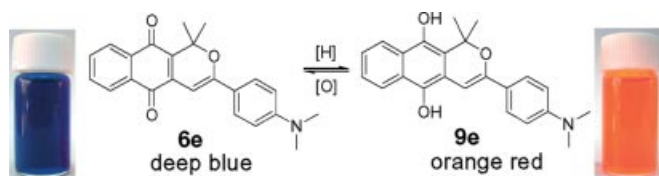


From Theozymes to Artificial Enzymes:  
Enzyme-Like Receptors for Michael Ad-  
ditions with Oxyanion Holes and Active  
Amino Groups

**Keywords:** Homogeneous catalysis / Supra-  
molecular chemistry / Hydrogen bonds /  
Reaction mechanisms / Molecular model-  
ling



The theozyme concept has been used in the design of artificial enzymes that show  $k_{\text{cat}}/k_{\text{uncat}}$  values of up to  $10^4$  in Michael addition reactions of pyrrolidine to  $\alpha,\beta$ -unsaturated lactams. The receptors combine “oxyanion hole” structures with amino groups responsible for the proton transport of the nucleophile. Computational chemistry applications in the catalyst design are also investigated.



Trisubstituted naphthopyrandione derivatives were prepared; quinone **6e** instantly changed from deep blue to orange red when treated with NaBH<sub>4</sub> in MeOH. Hydroquinone **9e** reverted back to its

original color when the reducing agent was removed. Quinone **6e** did not show fluorescence prior to reduction, but hydroquinone **9e** emitted red fluorescence.

T.-L. Shie, C.-H. Lin, S.-L. Lin,  
D.-Y. Yang\* ..... 4831–4836

Synthesis of 1,1,3-Trisubstituted Naphtho-  
[2,3-*c*]pyran-5,10-dione Derivatives as  
Potential Redox Switches

**Keywords:** Quinones / Redox chemistry /  
Fluorescence / Donor–acceptor systems

### Stereoselectivity and Li Anions

Qualitative modeling indicates that the observed stereoselectivity in Michael additions is due to steric requirements of the reagents at VDW distances, Ph–Li<sup>+</sup> bonding in the carbanion, and electrostatic factors.



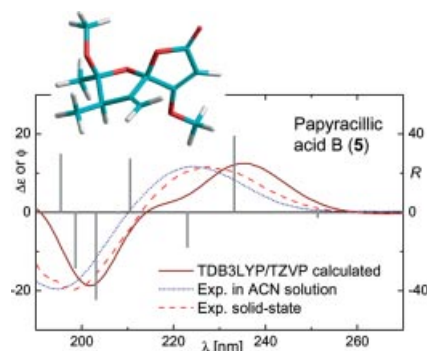
A. M. Belostotskii\* A. Albeck,  
A. Hassner\* ..... 4837–4844

Asymmetric Induction by a Remote Chiral  
Substituent – Computationally Deter-  
mined Stereodifferentiation in Michael  
Additions of  $\alpha$ -Lithiated Allyl Sulfones

**Keywords:** Michael addition / Carbanions /  
Diastereoselectivity / Conformational  
analysis

### Fungal Metabolites

Five new metabolites, palmarumycin M<sub>1</sub> (**1a**) and M<sub>2</sub> (**3**), papyracillic acid C (**6**) and the microsphaeropsins A (**7**) and B (**8**) were isolated from the fungus *Microsphaeropsis* sp. The absolute configuration of palmarumycin M<sub>1</sub> (**1a**) was determined by single-crystal X-ray analysis of the bis(4-bromobenzoate) **1c** and the relationship between **1a**, **2** and **3** established by chemical transformation. The relative configuration of papyracillic acids A–C (**4–6**) was revised and their absolute configuration determined by comparison of TDDFT calculated and experimental solid-state CD spectra.



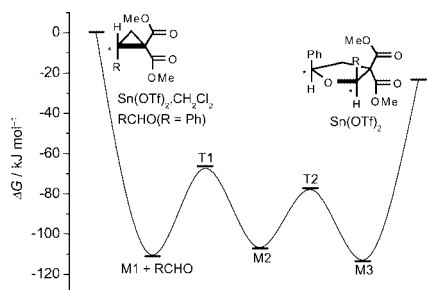
J. Dai, K. Krohn,\* B. Elsässer, U. Flörke,  
S. Draeger, B. Schulz, G. Pescitelli,  
P. Salvadori, S. Antus, T. Kurtán .....  
..... 4845–4854

Metabolic Products of the Endophytic  
Fungus *Microsphaeropsis* sp. from *Larix  
decidua*

**Keywords:** Fungal secondary metabolites /  
Palmarumycins M / Papyracillic acids /  
Microsphaeropsins / *Microsphaeropsis* sp. /  
Solid-state CD / Exciton chirality

### Mechanistic Studies

The Sn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>-catalyzed synthesis of 2,5-disubstituted tetrahydrofuran from a donor–acceptor cyclopropane cycloaddition reaction with benzaldehyde proceeds in a regio- and diastereoselective manner; the S<sub>N</sub>2 mechanism was confirmed by density functional calculations.



J. Zhang, W. Shen,  
M. Li\* ..... 4855–4866

DFT Study on the Sn<sup>II</sup>-Catalyzed Dia-  
stereoselective Synthesis of Tetrahydrofu-  
ran from D–A Cyclopropane and Benzal-  
dehyde

**Keywords:** Density functional calcu-  
lations / Tin / Donor–acceptor systems /  
Synthesis / Cycloaddition

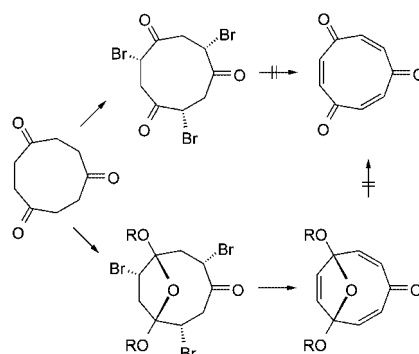
# CONTENTS

## Tris-homobenzenes

A. Pleschke, J. Geier,\* M. Keller, J. Wörth, L. Knothe, H. Prinzbach\* ..... 4867–4880

In Pursuit of *cis,cis,cis*-Cyclonona-2,5,8-triene-1,4,7-trione – An Adventure in Medium-Sized Ring Chemistry

**Keywords:** Tris  $\sigma/\pi$ -Homobenzenes / Cyclononanes, highly functionalized, bridged / Calculations



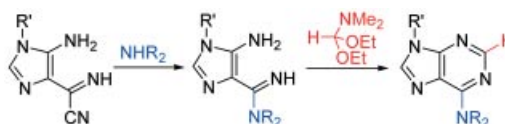
Why did the attempts to prepare *cis,cis,cis*-2,5,8-cyclononatriene-1,4,7-trione, a long soughtafter tris- $\pi$ -homobenzene, from cyclononane-1,4,7-trione fail? The answer is given in this paper.

## Adenine Derivatives

M. J. Alves, M. A. Carvalho, S. Carvalho, A. M. Dias, F. H. Fernandes, M. F. Proença\* ..... 4881–4887

A New Approach to the Synthesis of *N,N*-Dialkyladenine Derivatives

**Keywords:** Adenine derivatives / Amines / Imidazoles / Purines



*N,N*-Disubstituted adenine derivatives were prepared by a clean and efficient reaction

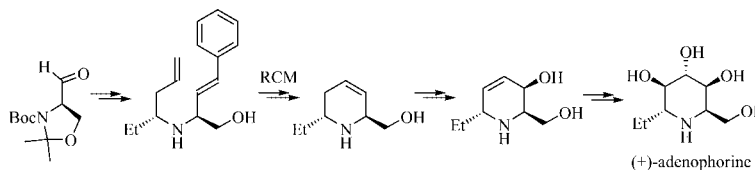
from substituted imidazoles and dimethylformamide diethyl acetal.

## Iminosugars

M. S. M. Pearson, M. Evain, M. Mathé-Allainmat, J. Lebreton\* ..... 4888–4894

First Total Synthesis of (+)-Adenophorine, a Naturally Occurring Inhibitor of Glycosidases

**Keywords:** Iminosugars / Adenophorine / RCM / Allylation / Imine / Epoxidation



The total synthesis of the naturally occurring iminosugar (+)-adenophorine, in 14 steps from the (+)-enantiomer of Garner's aldehyde, is reported. The synthesis takes

advantage of several key reactions, including a diastereoselective allylation of a chiral imine, stereoselective epoxidation, and RCM.

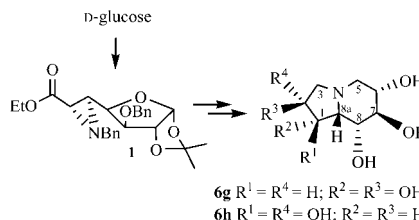
## Iminosugars

K. S. Ajish Kumar, V. D. Chaudhari, V. G. Puranik, D. D. Dhavale\* ..... 4895–4901



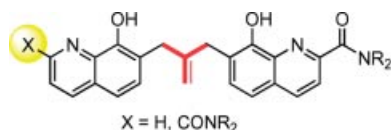
Synthesis and Glycosidase Inhibitory Studies of Pentahydroxyindolizidines: D-Glucose-Derived Aziridine-2-carboxylate Approach

**Keywords:** Iminosugars / Indolizidine / Asymmetric dihydroxylation (AD) / *N*-Methylmorpholine *N*-oxide (NMO)

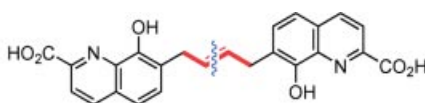


An efficient synthesis of pentahydroxyindolizidine alkaloids **6g** and **6h** from the amina obtained from the sugar-derived aziridine-2-carboxylate **1** and a preliminary study of their glycosidase inhibitory activity is presented.

## Ditopic Hydroxyquinolines




Homo- and heterotopic bischelating 8-hydroxyquinoline-based ligands with different spacer lengths can be prepared by utilizing a Claisen rearrangement as



a central reaction step. The tandem Hiratani–Claisen reaction proved to be especially useful in this respect.

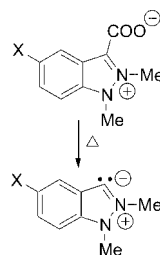
**M. Albrecht,\* O. Osetska,**  
**R. Fröhlich ..... 4902–4908**

Synthesis of Homo- and Heteroditopic 8-Hydroxyquinoline Ligands 


**Keywords:** Quinolines / Ligands / Rearrangement / Metathesis

## Nucleophilic Carbenes

5-Fluoro-, chloro- bromo-, and iodo-substituted 1,2-dimethyl indazolium-3-carboxylates, members of the class of pseudo-cross-conjugated heterocyclic mesomeric betaines, undergo thermal decarboxylation to 5-halo-1,2-dimethyl-indazol-3-ylidenes. Physical analyses and trapping reactions with sulfur and 2,4-dichlorophenylisocyanate, respectively, are reported.



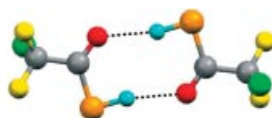
**A. Schmidt,\* B. Snovydyovych,**  
**T. Habeck, P. Dröttboom,**  
**M. Gjika, A. Adam ..... 4909–4916**

N-Heterocyclic Carbenes of 5-Haloindazoles Generated by Decarboxylation of 5-Haloindazolium-3-carboxylates 


**Keywords:** Thermogravimetric analysis / Betaines / Carbenes / Differential scanning calorimetry

## Halothioacetic Acid Chemistry

The novel thiocarboxylic acid  $\text{CF}_2\text{ClC}(\text{O})\text{SH}$  can be prepared from either  $\text{CF}_2\text{ClC}(\text{O})\text{Cl}$  or  $[\text{CF}_2\text{ClC}(\text{O})]_2\text{O}$ . Its most stable form has a synperiplanar orientation of the  $\text{C}=\text{O}$  double bond with respect to the  $\text{S}-\text{H}$  single bond whereas the *gauche* orientation of the  $\text{ClC}-\text{C}=\text{O}$  moiety is preferred in the chlorodifluoroacetyl group. The crystal structure is formed from cyclic dimers bonded by weak hydrogen bonds.



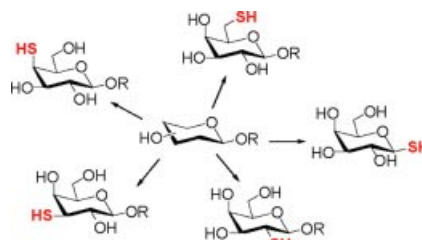
**M. F. Erben, R. Boese, H. Willner,**  
**C. O. Della Védova\* ..... 4917–4926**

Chlorodifluorothioacetic Acid,  $\text{CF}_2\text{ClC}(\text{O})\text{SH}$ : Synthesis, Characterization, X-ray Structure and Conformational Properties 

**Keywords:** Sulfur / Thiocarboxylic acids / Conformation analysis / Structure elucidation / Ab initio calculations

## Carbohydrate Synthesis

Systematic synthetic strategies to all positional thiol analogs of  $\beta$ -D-galactopyranose is presented.

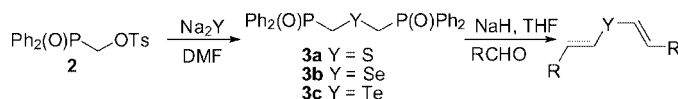


**Z. Pei, H. Dong, R. Caraballo,**  
**O. Ramström\* ..... 4927–4934**

Synthesis of Positional Thiol Analogs of  $\beta$ -D-Galactopyranose

**Keywords:** Thiosaccharides / Galactose / Lattrell–Dax / Inversion


## Divinylic Chalcogenides



The preparation of bis[(diphenylphosphinoyl)methyl] sulfides, selenides, and tellurides is described. The title compounds are subjected to Horner–Wittig-type reac-

tions with aldehydes and ketones to give symmetrical and unsymmetrical divinylic sulfides, selenides, and tellurides with preferential (*E*) stereochemistry.

**C. C. Silveira,\* F. Rinaldi,**  
**R. C. Guadagnin ..... 4935–4939**

Preparation and Reactivity of Chalcogenyl Phosphonates and Phosphane Oxides 

**Keywords:** Horner–Wittig reaction / Chalcogens / Phosphane oxides / Selenium / Tellurium



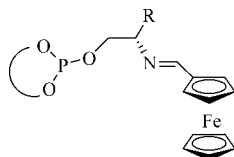
# CONTENTS

## Asymmetric Catalysis

K. N. Gavrilov,\* M. G. Maksimova,  
S. V. Zheglov, O. G. Bondarev,  
E. B. Benetsky, S. E. Lyubimov,  
P. V. Petrovskii, A. A. Kabro,  
E. Hey-Hawkins, S. K. Moiseev,  
V. N. Kalinin, V. A. Davankov ... 4940–4947

Ferrocenyliminophosphites as Easy-to-Modify Ligands for Asymmetric Catalysis

**Keywords:** Asymmetric catalysis / N,P ligands / Hydrogenation / Allylation



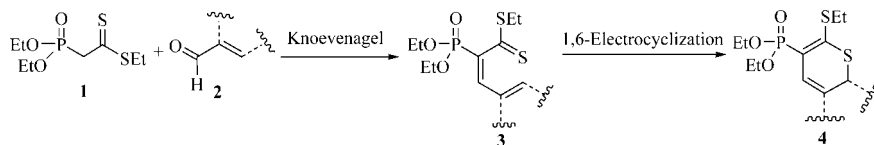
A family of ferrocenyliminophosphite ligands were successfully used in Rh-catalysed hydrogenations and Pd-catalysed allylic substitutions with enantiomeric excesses up to 97 %. Systematic variation of the ligand parameters indicates that enantioselectivities are determined by the nature of the phosphocentre and also by the substituent in the C\*HN fragment.

## Thiopyrans by Electrocyclization

A. Riu, A. Harrison-Marchand,\*  
J. Maddaluno, M. Gulea,\* H. Albadri,  
S. Masson ..... 4948–4952

A Domino Knoevenagel/1,6-Heteroelectrocyclization Sequence to Access Phosphono-2*H*-thiopyrans

**Keywords:** Domino reaction / Heteroelectrocyclization / Knoevenagel reaction / Phosphonodithioester / Thiopyran



Knoevenagel-type condensations between phosphonodithioacetate **1** and  $\alpha,\beta$ -unsaturated aldehydes **2** directly afford 5-phosphono-substituted 2*H*-thiopyrans **4**. Use of heteroaromatic aldehydes permit the consecutive heteroelectrocyclization of the triene intermediate **3**, provided that the

aromatic character of the C5–C6 double bond is sufficiently decreased, which is the case for electron-deficient indole nuclei. This Knoevenagel/1,6-heteroelectrocyclization sequence represents a new domino process.

## Isomerization Metathesis

J.-L. Panayides, R. Pathak,  
C. B. de Koning,  
W. A. L. van Otterlo\* ..... 4953–4961

Synthesis of Substituted 2,3-Dihydro-1*H*-2-benzazepines and 1,2-Dihydroisoquinolines Using an Isomerization-Ring-Closing Metathesis Strategy: Scope and Limitations

**Keywords:** Isomerization / Ring-closing metathesis / Benzazepines / Dihydroisoquinolines



This study investigates the scope and limitations of an isomerization-RCM approach which was used for the synthesis of substituted 2,3-dihydro-1*H*-2-benzazepines and 1,2-dihydroisoquinolines.

If not otherwise indicated in the article, papers in issue 28 were published online on September 14, 2007