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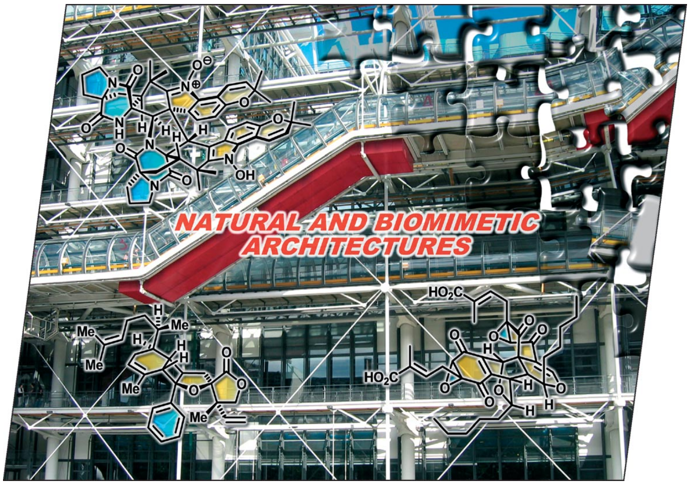
## COVER PICTURE

**The cover picture shows** three representative structures of complex natural products. They exemplify the main topic discussed in the Microreview by E. Gravel and E. Poupon on p. 27 ff: To what extent can natural substances be assembled spontaneously in nature? The modular architecture of the Pompidou Centre for modern art and creation in Paris has been chosen as a background. Indeed, this masterpiece of architectural design has obvious references to the complexity of living systems.



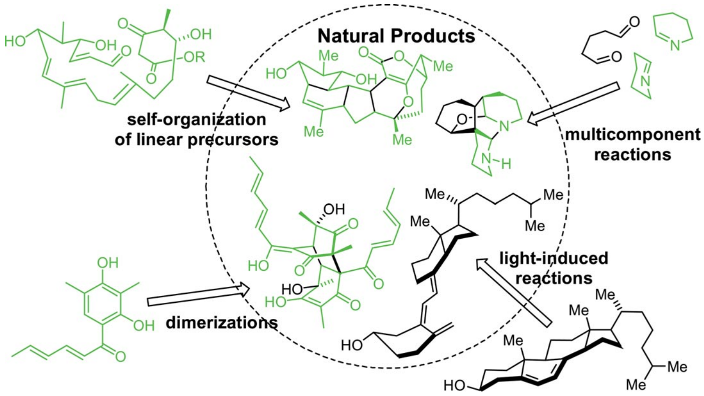
## MICROREVIEW

### Biomimetic Chemistry

**E. Gravel, E. Poupon*** ................... 27–42

Biogenesis and Biomimetic Chemistry: Can Complex Natural Products Be Assembled Spontaneously?

**Keywords:** Natural products / Biogenesis / Biomimetic synthesis / Molecular complexity / Molecular diversity



In some cases, complex structures of natural products can be generated with surprising spontaneity, through self-construction mechanisms. Rearrangements of linear molecules, light-induced reactions, dimerizations and multi-component reactions can explain the formation of secondary metabolites through the intrinsic reactivity of their precursors.

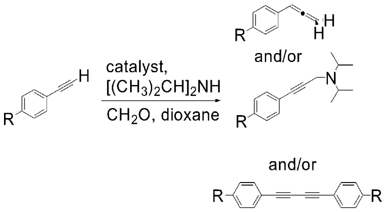
## SHORT COMMUNICATIONS

### Allenes from Arylacetylenes

**V. Kumar, A. Chipeleme,**
**K. Chibale*** ................................... 43–46

Effect of Varying the Anionic Component of a Copper(I) Catalyst on Homologation of Arylacetylenes to Allenes by the Mannich Reaction

**Keywords:** Allene / Homologation / Mannich reaction / Copper(I) catalyst / Alkyne dimerization



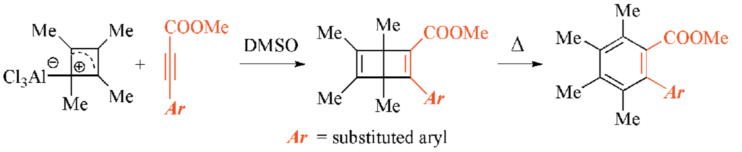
The effect of varying the anionic component of a copper(I) catalyst in the homologation of terminal arylacetylenes to allenes by the Mannich reaction was investigated. Varying amounts of allenes, Mannich bases and dimers were obtained depending on the nature of the anionic component of the copper catalyst.

### Dewar Benzenes

**Š. Janková, M. Dračínský, I. Císařová, M. Kotora*** .................................. 47–51

Synthesis and Rearrangement of Dewar Benzenes Into Biaryls: Experimental Evidence for Conrotatory Ring Opening

**Keywords:** Dewar benzene / Biaryls / Alkynes / Hammett / Rearrangement



Rearrangement of aryl-substituted Dewar benzenes into the corresponding biaryls may serve as an alternative pathway for the synthesis of sterically hindered biaryls. The kinetic data obtained from thermal rearrangements of Dewar benzenes provide experimental evidence for the proposed orbital-symmetry-controlled electrocyclic ring opening.

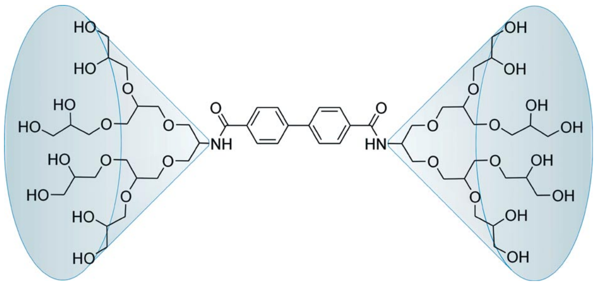
## FULL PAPERS

### Bifunctional Dendrons

**M. Wyszogrodzka, K. Möws, S. Kamlage, J. Wodzińska, B. Plietker,* R. Haag*** .................................... 53–63

New Approaches Towards Monoamino Polyglycerol Dendrons and Dendritic Triblock Amphiphiles

**Keywords:** Polyglycerol dendrimers / Amphiphiles / Nile Red / Fluorescence / UV/Vis spectroscopy



A new class of triblock amphiphiles is described that was synthesized by a straightforward convergent approach. For the synthesis of monoamino dendrons a simple iterative two-step process was applied based on allylation and dihydroxylation. After linkage to a biphenyl core, the transport behavior of these designed triblock amphiphiles was investigated with the dye Nile Red.

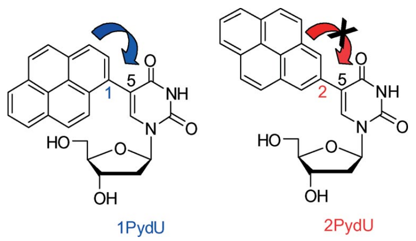
### DNA

**C. Wanninger-Weiß, H.-A. Wagenknecht*** .................... 64–71

Synthesis of 5-(2-Pyrenyl)-2′-deoxyuridine as a DNA Modification for Electron-Transfer Studies: The Critical Role of the Position of the Chromophore Attachment

**Keywords:** Electron transfer / Fluorescence / Iridium / Oligonucleotides / Palladium / Pyrene

Electronically coupled or not? The position of the chromophore attachment in pyrene-modified uridines is critical for the optical properties of this nucleoside label.

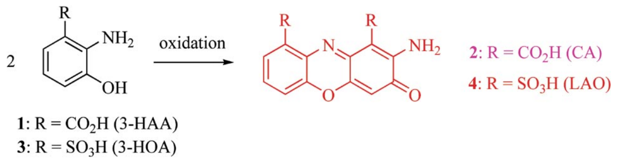


### Water-Soluble Fluorochromophores

**F. Bruyneel, E. Enaud, L. Billottet, S. Vanhulle, J. Marchand-Brynaert*** ................ 72–79

Regioselective Synthesis of 3-Hydroxyorthanilic Acid and Its Biotransformation into a Novel Phenoxazinone Dye by Use of Laccase

**Keywords:** Laccase / Phenoxazinone / Lithiation / Biotransformation / Aromatic sulfonation reaction



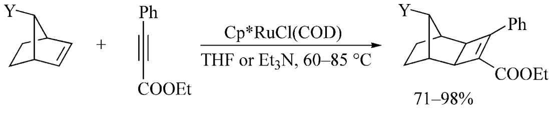
The regioselective sulfonation of 2-hydroxyaniline was investigated for the synthesis of 3-hydroxyorthanilic acid (**3**), which was then subjected to laccase oxidation in order to mimic the synthesis of cinnabarinic acid (**2**). The major product of biotransformation was isolated and identified as the novel dye 2-amino-3-oxo-3*H*-phenoxazine-1,9-disulfonic acid (**4**).

## Ruthenium-Catalyzed Cycloadditions

**R. W. Jordan, P. Le Marquand,**
**W. Tam* ....................................... 80−86**

Ruthenium(II)-Catalyzed [2+2] Cycloadditions of *anti* 7-Substituted Norbornenes

**Keywords:** Ruthenium / Catalysis / Cycloaddition / Reactivity / Norbornenes



Relative rate of cycloaddition: Y = OAc < OTBS < O*t*Bu < H < Ph
1 5 6 29 40

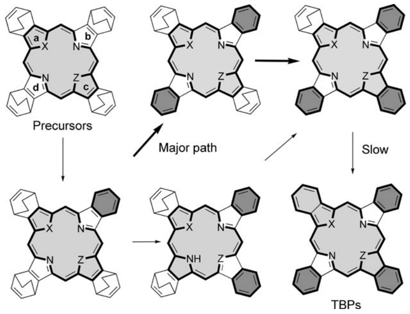
The ruthenium(II)-catalyzed [2+2] cycloadditions of *anti* 7-substituted norbornenes with an alkyne were found to proceed with a high degree of stereoselectivity, giving only the *exo* stereoisomers in moderate to good yields using an improved protocol. Comparative rate studies between a variety of *anti* 7-substituted norbornenes and an alkyne revealed that the reactivity of the alkene component decreases dramatically as the alkene becomes more electron deficient.

## Fused Porphyrinoids

**H. Uno,* Y. Shimizu,**
**H. Uoyama, Y. Tanaka, T. Okujima,**
**N. Ono ........................................... 87−98**

Thermal Behavior of Free-Base and Core-Modified Bicyclo[2.2.2]octadiene-Fused Porphyrins

**Keywords:** Porphyrinoids / Retro reactions / Aromatic ring current



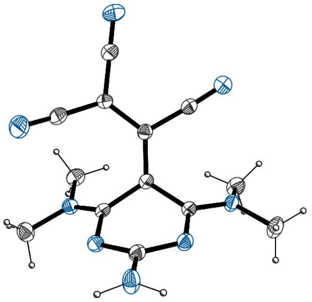
*opp*-Dibenzoporphyrins were preferentially formed during the thermal fragmentation of quadruply bicyclo[2.2.2]octadiene-fused porphyrins to tetrabenzoporphyrins. The fourth extrusion of an ethylene molecule was very slow and tribenzoporphyrin derivatives were obtained in good selectivity.

## Donor−Acceptor Systems

**A. Ortíz, B. Insuasty,* M. R. Torres,**
**M. Á. Herranz, N. Martín,* R. Viruela,**
**E. Ortí* ...................................... 99−108**

Aminopyrimidine-Based Donor−Acceptor Chromophores: Push−Pull versus Aromatic Behaviour

**Keywords:** 2-Aminopyrimidines / Push−pull / Aromaticity / Nonplanar



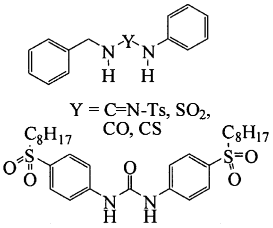
Novel 2-aminopyrimidines substituted with two electron-donor dialkylamino groups and one dicyanovinyl (**4a**−**d**) or tricyanovinyl (**7a**−**d**) electron-acceptor group have been synthesized, and the balance between their push−pull character and their aromatic behaviour has been studied by experimental (spectroscopic, electrochemical and X-ray analysis) and theoretical (DFT/B3LYP/6-31G**) methods.

## Ureas as Hosts

**L. Pescatori, A. Arduini, A. Pochini,**
**F. Ugozzoli, A. Secchi* .............. 109−120**

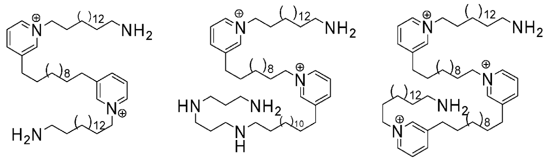
Design, Synthesis and Recognition Properties of Urea-Type Anion Receptors in Low Polar Media

**Keywords:** Anion recognition / Lipophilic EWG / Complexation studies / Solvent effects / Urea derivatives / Receptors



The binding efficiency of acyclic anion receptors of formula BnNH−Y−NHPh has been evaluated in chloroform by using $^1H$ NMR spectroscopy. MM and DFT calculations revealed that the nature of the spacer Y affects both the host's preorganisation and the electronic effects exerted on the NH binding groups. The synthesis and binding properties of new lipophilic urea receptors bearing electron-withdrawing $SO_2R$ substituents are also reported.

## Natural Products



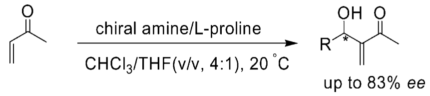
Three 3-alkylpyridinium salts, pachychalines A (**1**), B (**2**) and C (**3**), were isolated from the Caribbean marine sponge *Pachychalina* sp. (order Haplosclerida). They are the first examples of 3-aminoalkylpyridinium salts. The total synthesis of **1** allowed the confirmation of the unusual C–C connection between both pyridinium moieties.

**R. Laville, O. P. Thomas,* F. Berrue, F. Reyes, P. Amade* .................. 121–125**

### Pachychalines A–C: Novel 3-Alkylpyridinium Salts from the Marine Sponge *Pachychalina* sp.

**Keywords:** Natural products / Alkaloids / Pyridinium salts / Marine sponge

## Asymmetric MBH Reaction



Several chiral amines in combination with L-proline have been found to be efficient cocatalysts for the asymmetric Morita–Baylis–Hillman (MBH) reaction between methyl vinyl ketone (MVK) and aromatic aldehydes. The corresponding adducts were formed in reasonable chemical yields and with good enantioselectivities (up to 83% *ee*). These chiral amines have been successfully applied in combination with L-proline as efficient cocatalysts

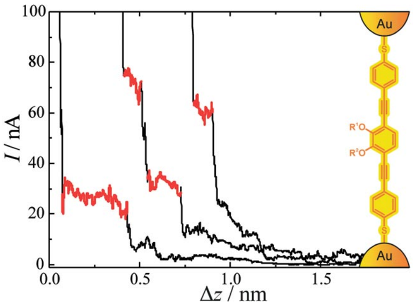
**H. Tang, G. Zhao, Z. Zhou,* P. Gao, L. He,* C. Tang ........................ 126–135**

### Chiral Tertiary Amine/L-Proline Cocatalyzed Enantioselective Morita–Baylis–Hillman (MBH) Reaction

**Keywords:** Chirality / Amines / Organocatalysis / Asymmetric catalysis / Morita–Baylis–Hillman reactions / Enantioselectivity

## Molecular Electronics

Several molecular rods comprising variously protected catechol subunits have been synthesized and investigated as potential precursors of a catechol-functionalized molecular rod. Furthermore, molecular junctions formed by the dimethyl-protected catechol-functionalized rod in an electrochemical STM set-up allowed preliminary single-molecule transport measurements.



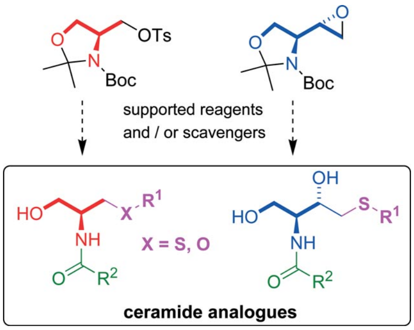
**N. Weibel, A. Błaszczyk, C. von Hänisch, M. Mayor,* I. Pobelov, T. Wandlowski,* F. Chen, N. Tao* ...................... 136–149**

### Redox-Active Catechol-Functionalized Molecular Rods: Suitable Protection Groups and Single-Molecule Transport Investigations

**Keywords:** Molecular electronics / Protecting groups / Electrochemistry / Molecular rods / Catechol / Single-molecule conductance

## Ceramide Analogues

A simple solution-phase protocol for the synthesis of ceramide analogues from enantiopure scaffolds is disclosed. Nucleophilic thiolates or phenoxides and appropriate supported reagents or scavengers are used to give the target compounds in good overall yields. The method is adaptable to combinatorial protocols for the generation of small-to-medium-sized libraries.



**S. Grijalvo, X. Matabosch, A. Llebaria, A. Delgado* .............................. 150–155**

### A Straightforward Protocol for the Solution-Phase Parallel Synthesis of Ceramide Analogues

**Keywords:** Ceramide analogues / Amino alcohols / Scavengers / Supported reagents / Combinatorial chemistry

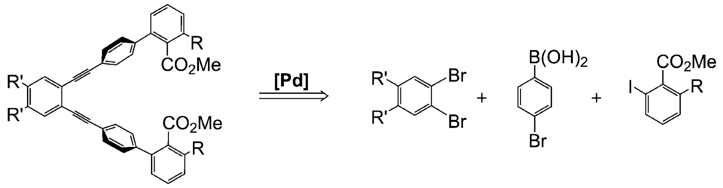
# CONTENTS

## Cross-Coupling

**E. Reisner, S. J. Lippard* .......... 156–163**

Synthesis of Dicarboxylate "C-Clamp" 1,2-Diethynylarene Compounds as Potential Transition-Metal Ion Hosts

**Keywords:** Cross-coupling / C–C coupling / Carboxylate ligands / Bridging ligands / Chelates



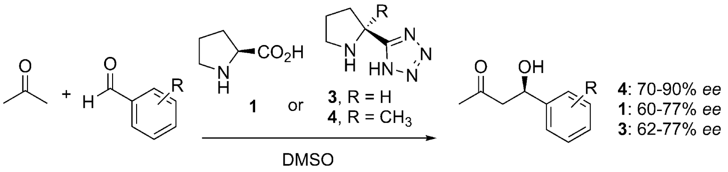
C-clamp molecules were prepared by an efficient convergent synthesis involving Sonogashira, Suzuki, and Heck cross-coupling reactions (see graphic). The dicarboxylate groups are potential dinucleating hosts for transition-metal ions. X-ray crystal structure analysis reveals that the C-clamp acid can accommodate two water molecules in its *endo*-binding pocket with strong hydrogen-bonding interactions.

## Asymmetric Organocatalysis

**S.-T. (A.) Tong, P. W. R. Harris, D. Barker, M. A. Brimble* ........ 164–170**

Use of (*S*)-5-(2-Methylpyrrolidin-2-yl)-1*H*-tetrazole as a Novel and Enantioselective Organocatalyst for the Aldol Reaction

**Keywords:** Aldol / Enantioselectivity / Methylproline / Organocatalysis / Tetrazole



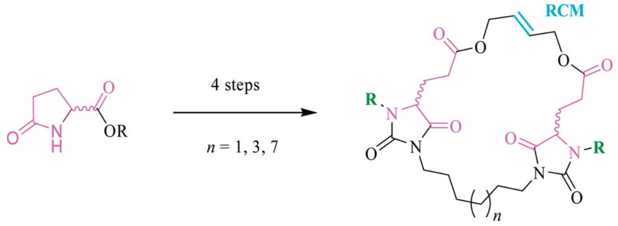
The novel organocatalyst (*S*)-5-(2-methylpyrrolidin-2-yl)-1*H*-tetrazole catalyzes the aldol reaction between acetone and various aldehydes with superior enantioselectivity over the known organocatalysts (*S*)-proline and (*S*)-5-(pyrrolidin-2-yl)-1*H*-tetrazole.

## RCM Macrocyclisation

**D. D. Claeys, C. V. Stevens,* N. Dieltiens ............................... 171–179**

The Formation of *trans*-Fused Macrocycles from $N^3$,$N^{3'}$-Polymethylenebis(hydantoins) by Ring-Closing Metathesis

**Keywords:** Nitrogen heterocycles / Lactams / Macrocycles / Rearrangement / Pyroglutamates / Hydantoins / Ring-closing metathesis / Isocyanates



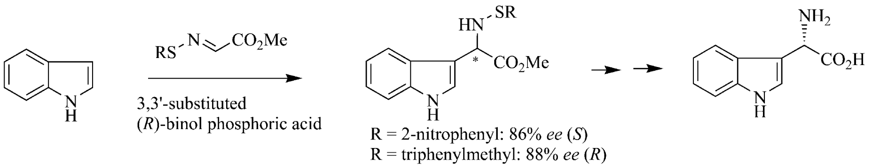
The synthesis of bis(hydantoins) as potent anticancer drugs from pyroglutamates and diisocyanates by rearrangement is described. The macrocyclisation of these products by ring-closing metathesis has been shown by undecoupled HSQC to yield only the *E* diastereoisomers.

## Organocatalysis

**M. J. Wanner, P. Hauwert, H. E. Schoemaker, R. de Gelder, J. H. van Maarseveen, H. Hiemstra* ........................... 180–185**

Synthesis of Enantiopure (*S*)-Indolylglycine by Organocatalyzed Friedel–Crafts Alkylation of Indole

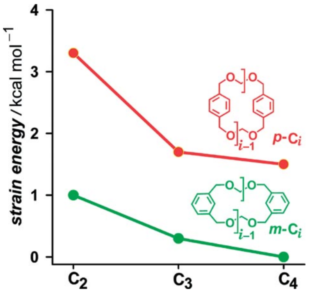
**Keywords:** Friedel–Crafts reaction / Chirality / Phosphoric acids / Amino acids / Sulfenamides / Organocatalysis



Tritylsulfenyl- and 2-nitrophenylsulfenyl-substituted glyoxyl imines were used in chiral phosphoric acid catalyzed Friedel–Crafts reactions with indole. Products with 99.5%*ee* and 71% yield were readily obtained by crystallization. Removal of the Nps protecting group under mild acidic conditions provided (*S*)-indolylglycine in ≥98% *ee.*

## Dynamic Covalent Chemistry (DCC)

Strain energies from DCC of interconverting macrocycles: Dynamic libraries of cyclophane formaldehyde acetals were used as valuable sources of *EM* data, which in turn were translated into ring strain energies. Molecular mechanics calculations provided insights into the origin of such strain.

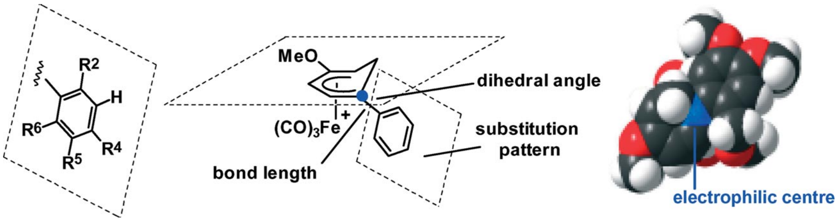


**R. Cacciapaglia, S. Di Stefano,**
**L. Mandolini,* P. Mencarelli,***
**F. Ugozzoli*** .............................. **186–195**

Metathesis Reactions of Formaldehyde Acetals – Experimental and Computational Investigation of Isomeric Families of Cyclophanes under Dynamic Conditions

**Keywords:** Cyclooligomerization / Dynamic covalent chemistry / Effective molarity / Molecular modeling / Transacetalation

## Aryl-Substituted Electrophiles



Manipulating the substitution pattern on the aryl substituent flattens the dihedral angle and permits regiocontrol in synthetic applications. Five X-ray structures of (1-arylcyclohexadienyl)iron electrophiles are described.

**C. E. Anson, A. V. Malkov,**
**C. Roe, E. J. Sandoe,**
**G. R. Stephenson*** ..................... **196–213**

Stereomanipulation of ($\eta^5$-1-Arylcyclohexadienyl)iron Complexes

**Keywords:** Iron / Cations / X-ray structure characterisation / Nucleophilic addition / Regioselectivity