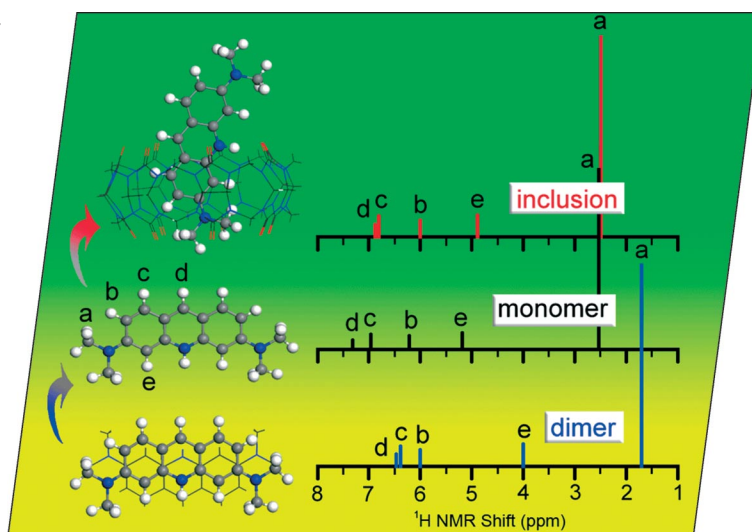




A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture shows the formation of the inclusion complex of acridine orange (AO) with cucurbit[7]uril (CB[7]) and the unusual downfield NMR shifts of the proton resonances. This shift is the net result of large downfield shifts arising from the deaggregation of AO aggregates followed by small upfield shifts resulting from the inclusion of AO into the CB[7] cavity. The background shows the color change of the aqueous AO solution from yellow to green in the absence and presence of CB[7]. Details are discussed in the article by J. Ma, X. Du et al. on p. 4931ff.



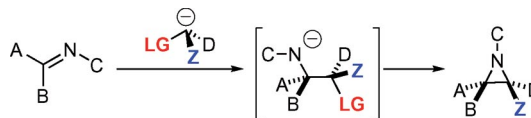
## MICROREVIEW

### Modern Aziridination Methods

J. Sweeney\* ..... 4911–4919

Aziridine Synthesis via Nucleophilic Attack of Carbene Equivalents on Imines: the Aza-Darzens Reaction

**Keywords:** Nitrogen heterocycles / Carbene equivalent / Cyclization / Ylides / Asymmetric synthesis



The aza-Darzens reaction (younger sibling of the homonymous epoxidation process) has recently burgeoned as a practical method

for aziridinations of imines. This Microreview summarizes the pertinent features and recent developments of the reaction.

## SHORT COMMUNICATIONS

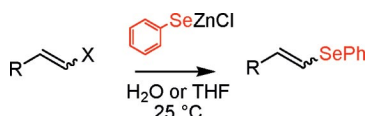
### Vinyl Selenides

S. Santoro, B. Battistelli, L. Testaferri, M. Tiecco, C. Santi\* ..... 4921–4925



Vinyl Substitutions Promoted by PhSeZnCl: Synthetic and Theoretical Investigations

**Keywords:** Selenium / Zinc / Vinylic substitution / Nucleophilic substitution / DFT calculations



Vinyl selenides can be easily obtained through nucleophilic substitution of the corresponding halides by using PhSeZnCl in THF as well as in water suspension. Retention of the olefin geometry is generally observed. A mechanism involving the zinc atom has been studied by DFT calculations.

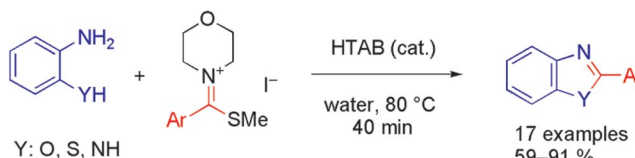
### All Compounds in Aqueous Media

H. Zali Boeini,\* K. Hajibabaei Najafabadi ..... 4926–4929



Efficient One-Step Synthesis of Benzazoles in Aqueous Media

**Keywords:** Heterocycles / Organic salts / Acid derivatives / Onium compounds



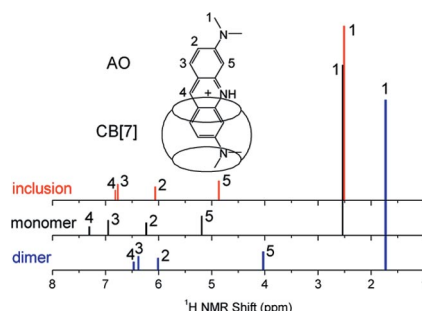
Aquatic reaction of thioamidinium salts and 2-aminophenol, 2-aminothiophenol, and *o*-phenylenediamine was successfully employed for the synthesis of benzoxazole, benzothiazole, and benzimidazole derivatives, respectively. The method represents a

promising alternative as an environmentally safe synthesis of 2-aryl-substituted benzazoles, which are extremely important compounds in medicinal and industrial chemistry.

## FULL PAPERS

### Supramolecular Chemistry

The unusual downfield NMR shifts of the proton resonances of the inclusion complex of acridine orange (AO) with cucurbit[7]uril (CB[7]) were the net result of large downfield shifts arising from the deaggregation of AO aggregates followed by small upfield shifts resulting from the inclusion of AO in the CB[7] cavity.

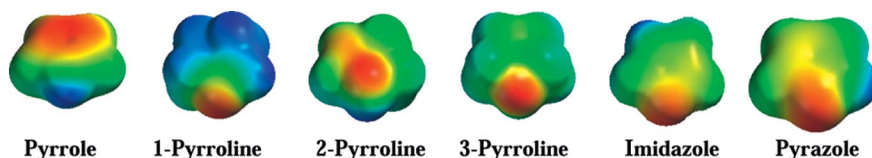


J. Liu, N. Jiang, J. Ma,\*  
X. Du\* ..... 4931–4938

Insight into Unusual Downfield NMR Shifts in the Inclusion Complex of Acridine Orange with Cucurbit[7]uril

**Keywords:** Cucurbiturils / Competitive binding / NMR spectroscopy / Host–guest systems / Supramolecular chemistry

### Hydrogen-Bond Basicity



The hydrogen-bond properties of five-membered nitrogen heterocycles are reported. These compounds were found to act either as very weak  $\pi$  bases or strong imino or amino bases, depending on the

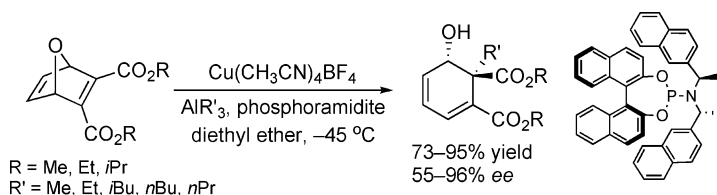
immediate surrounding of the nitrogen atom. The individual hydrogen-bond basicity of the pyrrolic and pyridinic nitrogen atoms of myosmine derivatives have been determined.

V. Arnaud, M. Berthelot, F.-X. Felpin,  
J. Lebreton, J.-Y. Le Questel,  
J. Graton\* ..... 4939–4948

Hydrogen-Bond Accepting Strength of Five-Membered N-Heterocycles: The Case of Substituted Phenylpyrrolines and Myosmines

**Keywords:** Density functional calculations / IR spectroscopy / Nitrogen heterocycles / Hydrogen-bond basicity /  $pK_{\text{BHX}}$  scale

### Asymmetric Synthesis



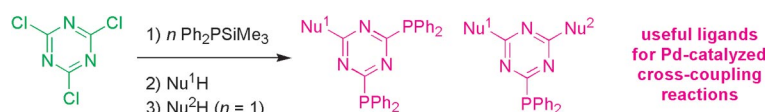
The asymmetric conjugate addition of trialkylaluminum to oxacyclic substrates in the presence of a copper catalyst with phosphoramidite ligands allows the simultaneous formation of two stereocenters.

The addition occurs *syn* to the bridging oxygen atom, and the corresponding products were obtained in good yields and with good to excellent enantioselectivities.

C. Ladjel, N. Fuchs, J. Zhao,  
G. Bernardinelli,  
A. Alexakis\* ..... 4949–4955

New Bifunctional Substrates for Copper-Catalyzed Asymmetric Conjugate Addition Reactions with Trialkylaluminum

**Keywords:** Conjugation / Copper / P ligands / Aluminium / Oxygen heterocycles



Mono- and diphosphanyltriazines with a variety of substituents on the triazine ring were selectively synthesized from cyanuric chloride by the one-pot step-by-step reaction. Polymer-supported and water-soluble

ligands can be obtained by the same procedure. Phosphanyltriazine Pd complexes are active catalysts in the Mizorogi–Heck reaction and the Suzuki–Miyaura coupling.

M. Hayashi,\* T. Yamasaki, Y. Kobayashi,  
Y. Imai, Y. Watanabe ..... 4956–4962

Selective Syntheses of Mono- and Diphosphanyltriazines as Novel Ligands for Transition Metal Catalysts

**Keywords:** Synthetic methods / Phosphorus / Nucleophilic substitution / P ligands / Cross-coupling

# CONTENTS

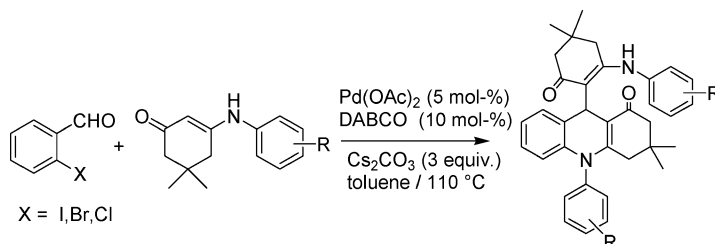
## 1,4-Dihydroquinoline Derivatives

X.-J. Wu, X.-P. Xu, X.-M. Su, G. Chen,  
Y. Zhang, S.-J. Ji\* ..... 4963–4970



A Novel, Highly Efficient, One-Pot Synthesis of 1,4-Dihydroquinoline Derivatives in the Presence of a Pd(OAc)<sub>2</sub>/DABCO Catalytic System

**Keywords:** Aldehydes / Enaminones / Nitrogen heterocycles / Cross-coupling / Synthetic methods



We have developed a novel and efficient method for the synthesis of various 1,4-dihydroquinoline derivatives from *o*-halo-benzaldehyde and a wide range of  $\beta$ -enaminones with the use of a Pd(OAc)<sub>2</sub>/DABCO

catalytic system. Noteworthy, the catalytic system was employed in the C–N cross-coupling reaction for the first time and showed outstanding performance.

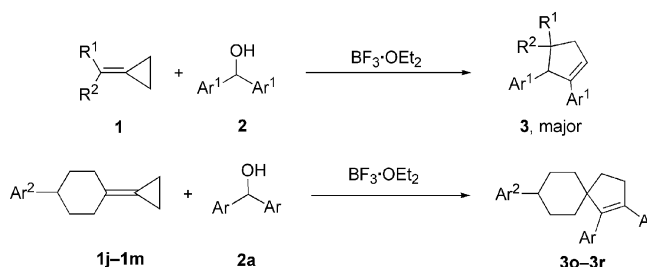
## Methylenecyclopropane Chemistry

L.-F. Yao, M. Shi\* ..... 4971–4982



Lewis-Acid-Catalyzed Reactions of Bis(4-alkoxyphenyl)methanol with (Diarylmethylene)- and (Dialkylmethylene)cyclopropanes

**Keywords:** Lewis acids / Synthetic methods / Cycloalkenes / Strained molecules



Cyclopentene derivatives can be obtained by a Lewis-acid-catalyzed protocol in good yield from readily accessible (arylmeth-

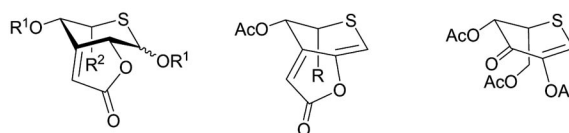
ylene)cyclopropanes **1** and bis(4-alkoxyphenyl)methanol (**2**) under mild conditions.

## Highly Functionalized Thiosugars

N. M. Xavier, P. J. A. Madeira,  
M. H. Florêncio,  
A. P. Rauter\* ..... 4983–4991

Synthetic Approaches to Novel Thiosugar Scaffolds Containing  $\alpha,\beta$ -Unsaturated Carbonyl Groups

**Keywords:** Carbohydrates / Sulfur heterocycles / Lactones / Enones / Ring expansion / Thiosugars



The synthesis of new thiosugar scaffolds containing unsaturated carbonyl systems – namely 5-thiopyranose-fused butenolides and a 1-eno-5-thiopentopyran-3-ulose – from easily available starting furan-3-uloses

was accomplished. Methods used included the introduction of sulhydryl groups at C-5 on appropriate furanose intermediates and took advantage of furanose–pyranose conversion.

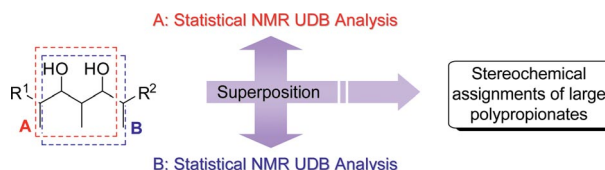
## Polypropionate Configurations

E. Fleury, M.-I. Lannou, O. Bistri,  
F. Sautel, G. Massiot, A. Pancrazi,\*  
J. Ardisson\* ..... 4992–5001



Advances in the Universal NMR Database: Toward the Determination of the Relative Configurations of Large Polypropionates

**Keywords:** NMR spectroscopy / Polypropionates / Configuration determination / Computer chemistry / Databases / Statistical approach

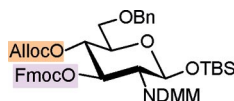


A general method for the determination of the configurations of large polypropionates, based on NMR spectroscopic investigation of intact molecules, is proposed. The procedure, an extension of Kishi's original

<sup>13</sup>C NMR UDB approach based on a statistical process, was applied to the stereochemical determination of different pentads and hexads.

## Orthogonal Protecting Groups

The Fmoc/phenoxyacetyl, Fmoc/levulinoyl and Fmoc/allyloxy carbonyl pairs have been studied as potential orthogonal ester protecting groups for vicinal diols. Selective access to the 3-hydroxy group or the 4-hydroxy group of glucosamine has been investigated.

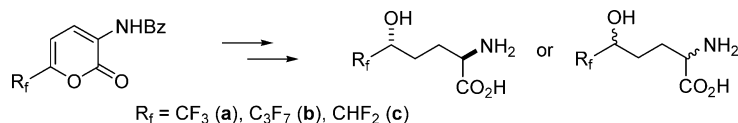


S. D. Markad,  
R. R. Schmidt\* ..... 5002–5011

Temporary Carbohydrate Diol Protection with Ester Groups – Orthogonality under Solid-Phase Oligosaccharide Synthesis Conditions

**Keywords:** Protecting groups / Carbohydrates / Glucosamine / Diols, vicinal / Solid-phase synthesis / Oligosaccharides

## Fluorinated Amino Acids



Several new  $\delta$ -(polyfluoroalkyl)- $\delta$ -hydroxy- $\alpha$ -amino acids were synthesized starting

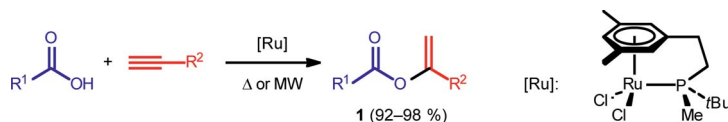
from corresponding 6-(polyfluoroalkyl)-pyrones.

N. A. Tolmacheva, I. I. Gerus\*,  
V. G. Dolovanyuk, I. S. Kondratov,  
G. Haufe\* ..... 5012–5019

Synthesis of New  $\delta$ -(Polyfluoroalkyl)- $\delta$ -hydroxy- $\alpha$ -amino Acids

**Keywords:** Amino acids / Polyfluoroalkyl groups / 2-Pyrones / Hydrogenation / Ring-opening / Fluorine

## Vinyl Esters



Tethered ( $\eta^1$ : $\eta^6$ -phosphanoarene)ruthenium complexes, such as **5**, are efficient catalyst precursors (up to 5000 turnovers!) for the highly regioselective synthesis of

Markovnikov vinyl esters **1** through the addition of carboxylic acids to terminal alkynes.

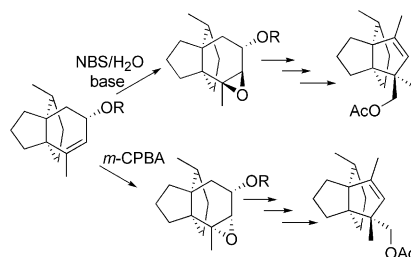
F. Nicks, R. Aznar, D. Sainz, G. Muller,  
A. Demonceau\* ..... 5020–5027

Novel, Highly Efficient and Selective Ruthenium Catalysts for the Synthesis of Vinyl Esters from Carboxylic Acids and Alkynes

**Keywords:** Alkynes / Carboxylic acids / Homogeneous catalysis / Microwave chemistry / Ruthenium / Vinyl esters

## Natural Product Synthesis

Facile entry to the [4.3.3]propellane structure through a tandem radical cyclization reaction of a dienyne set the stage for stereoselective epoxide formation followed by stereospecific Lewis acid catalyzed ring contraction to an oxygenated modhephene structure and led to the total synthesis of (–)-13-acetoxymodhephene and (+)-14-acetoxymodhephene.



H.-Y. Lee,\* R. N. Murugan,  
D. K. Moon ..... 5028–5037

Total Synthesis of (–)-13-Acetoxymodhephene and (+)-14-Acetoxymodhephene

**Keywords:** Total synthesis / Epoxidation / Enantioselectivity / Polycycles / Radical reactions



# CONTENTS

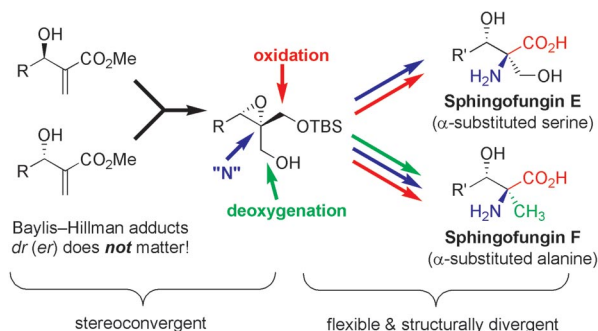
## Amino Acid Synthesis

B. Wang,\* G.-Q. Lin\* ..... 5038–5046



A Flexible Common Approach to  $\alpha$ -Substituted Serines and Alanines: Diastereoconvergent Syntheses of Sphingofungins E and F

**Keywords:** Amino acids / Asymmetric synthesis / Epoxides / Natural products / Quaternary stereocenters



A flexible common approach for the synthesis of sphingofungins E and F is reported. Steric effects of 2-substituents in diastereoselective dihydroxylations of (*E*)-2-hydroxymethyl-2,3-alkenoates were ob-

served, and control over the configurations of quaternary stereocenters in  $\alpha$ -substituted amino acids through adjustment of oxidation states was achieved.

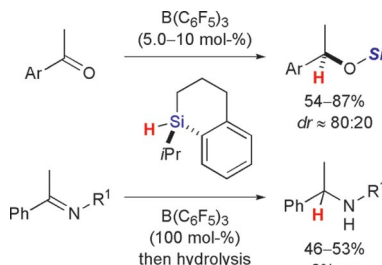
## Lewis Acid Catalysis

D. T. Hog, M. Oestreich\* ..... 5047–5056



$B(C_6F_5)_3$ -Catalyzed Reduction of Ketones and Imines Using Silicon-Stereogenic Silanes: Stereoinduction by Single-Point Binding

**Keywords:** Asymmetric catalysis / Chirality transfer / Hydrosilylation / Lewis acids / Reduction



Probed with silicon: Chirality at Si induces decent diastereoselectivity in the  $B(C_6F_5)_3$ -catalyzed carbonyl reduction whereas no stereoselection is observed in the related imine reduction. Mechanisms of action are suggested for the irreversible, stereochemistry-determining hydride transfer from a borohydride. Moreover, an unusual 1,6-reduction with a borohydride is disclosed for a sterically congested ketone.

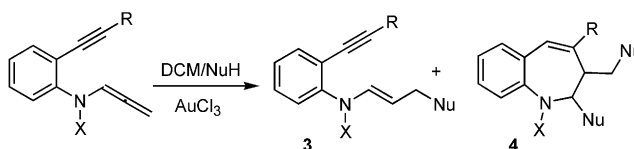
## Gold-Catalysed Cyclizations

Á. González-Gómez, G. Domínguez, J. Pérez-Castells\* ..... 5057–5062



Synthesis of Benzazepines by Gold-Catalysed Reactions of *N*-Allenylamides

**Keywords:** Gold / Cyclization / Allenes / Nitrogen heterocycles



Gold(III)-catalysed reactions of allenylamides give benzazepines in the presence of nucleophiles. This sequential process may follow two different reaction pathways, and these are discussed. Metal coordination to

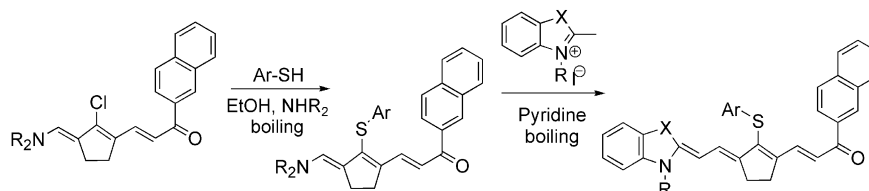
the allene and addition of NuH to give 3, which can decompose into other products and also form 4, is postulated as the best explanation for these results.

## Reactivity of Merocyanine Dyes

T. Gospodova, J. Rashkova, D. Ivanova, L. Viteva,\* C. Duprat, M.-R. Mazières, S. Bakalova, J. Kaneti ..... 5063–5071

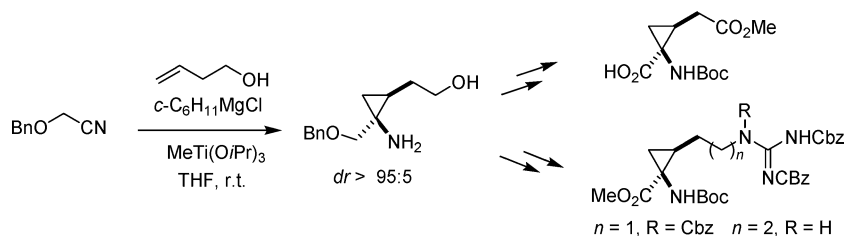
Synthetic Potentials of Heptamethine Merocyanine Dyes Containing an Active Chlorine Atom: Reactivity towards Nucleophiles

**Keywords:** Dyes/Pigments / Cyanines / Reaction mechanisms / UV/Vis spectroscopy / Photophysics



Heptamethine merocyanines containing a nucleofugal chlorine atom react with aromatic and heteroaromatic thiols with formation of ramified dyes. The reactivity differs from that of analogous cationic cyan-

ines and is consistent with a  $S_NAr$  addition–elimination pathway. The stability of the new dyes is significantly improved as a result of the elongation of the polymethine chain.



A short and stereoselective synthetic pathway to synthesize cyclopropane amino

acids derived from proteinogenic  $\alpha$ -amino acids or analogues has been developed.

T. K. Pradhan, A. Joosten, J.-L. Vasse,  
 P. Bertus, P. Karoyan,  
 J. Szymoniak\* ..... 5072–5078

A Concise Stereoselective Synthesis of 2-Substituted 1-Aminocyclopropanecarboxylic Acids



**Keywords:** Amino acids / Peptidomimetics / Diastereoselectivity / Small ring systems / Titanium

\* 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 28 were published online on September 15, 2009