

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 photochemically promoted acylation of alcohols under very mild conditions. The experimental protocol is extremely simple, thanks to the use of a benchtop photochemical reactor based on UV LEDs. The acyl transfer proceeds well for primary, secondary and even tertiary alcohols. The choice of a long wavelength (up to 420 nm) allows the presence of otherwise photosensitive groups, which can later be photolyzed at a higher energy. Details are discussed in the article by C. G. Bochet et al. on p. 2073 ff.



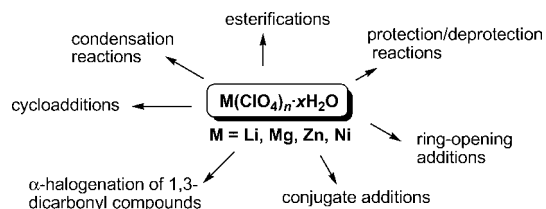
## MICROREVIEW

### Safe Use of Metal Perchlorates

G. Bartoli, M. Locatelli, P. Melchiorre,  
L. Sambri\* ..... 2037–2049

Taking Up the Cudgels for Perchlorates: Uses and Applications in Organic Reactions under Mild Conditions

**Keywords:** Lewis acids / Organic syntheses / Perchlorates / Safety



More than just rocket science: the most commonly employed metal perchlorates – among them being  $\text{LiClO}_4$ ,  $\text{Mg}(\text{ClO}_4)_2$ ,  $\text{Zn}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ , and  $\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$  –

are efficient Lewis acids for modern and mild organic transformations. This micro-review reports an overview of recent applications of these salts in organic synthesis.

## SHORT COMMUNICATIONS

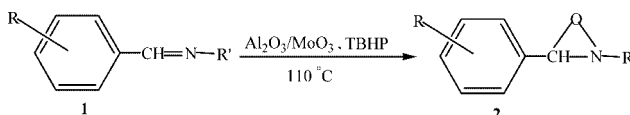
### Oxygenation Reactions

S. Singhal, S. L. Jain, V. V. D. N. Prasad,  
B. Sain\* ..... 2051–2054



An Environmentally Friendly Oxidation System for the Selective Oxygenation of Aldimines to Oxaziridines with Anhydrous TBHP and Alumina-Supported  $\text{MoO}_3$  as a Recyclable Heterogeneous Catalyst

**Keywords:** Oxygenation / Supported catalysts / Heterogeneous catalysis / Imines



Alumina-supported  $\text{MoO}_3$  was found to be an efficient heterogeneous recyclable catalyst for the oxygenation of imines to

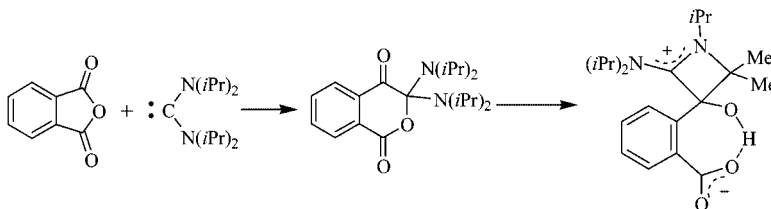
oxaziridines in excellent yields with the use of anhydrous TBHP as the oxidant under mild reaction conditions.

### Stable Carbenes

D. Poliakov,  
I. Shevchenko\* ..... 2055–2057

C–O Insertion Reaction of Nucleophilic Carbene: Facile Synthesis of Isochromane Cage

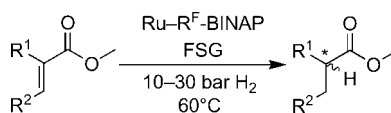
**Keywords:** Carbenes / Insertion / Isochromane / Zwitterions / Hydrogen bonds




Bis(diisopropylamino)carbene easily reacts with phthalic anhydride to give quantitatively the isochromane derivative which un-

dergoes unusual isomerization with the formation of a strained azetidinium ring and a very short intramolecular hydrogen bond.

A fluorous chiral BINAP–Ru complex was used in the asymmetric hydrogenation of olefins. Successful recovery and reuse of the complex was accomplished by means of noncovalent immobilisation on FSG. Additionally, the accelerating effect of porous silica gel on the asymmetric hydrogenations was investigated.

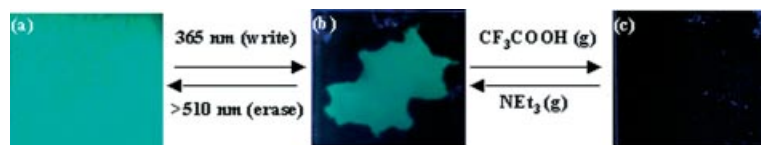


**J. Horn, W. Bannwarth\*** ..... 2058–2063

Repetitive Application of a Fluorous Chiral BINAP–Ru Complex in the Asymmetric Hydrogenation of Olefins 

**Keywords:** Asymmetric catalysis / Biphasic catalysis / Supported catalysts / Green chemistry / Hydrogenation

### Molecular Switches



A photo- and proton-dual-responsive fluorescence switch based on a bisthiényl-ethene–naphthalimide dimer was described. On the basis of fluorescence with

the use of light and proton sources, the overall write–conceal–display process of information in security data storage was successfully demonstrated.

**G. Jiang, S. Wang, W. Yuan, Z. Zhao, A. Duan, C. Xu, L. Jiang, Y. Song,\* D. Zhu** ..... 2064–2067

Photo- and Proton-Dual-Responsive Fluorescence Switch Based on a Bisthiényl-ethene-Bridged Naphthalimide Dimer and Its Application in Security Data Storage

**Keywords:** Fluorescence / Photochromism / Dual-responsive / Security data storage

### Asymmetric Catalysis



Catalysts generated from  $\text{B}(\text{OPh})_3$  and the vanol and vapol ligands are highly effective in the catalytic asymmetric aziridination of diazomethyl vinyl ketones with ethyl

diazooacetate to give high asymmetric inductions and high diastereoselectivity for *cis*-aziridines.

**Y. Deng, Y. R. Lee, C. A. Newman, W. D. Wulff\*** ..... 2068–2071

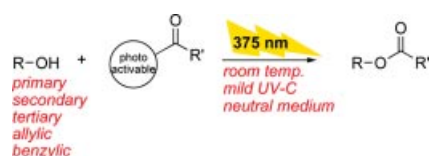
Aziridinyl Vinyl Ketones from the Asymmetric Catalytic Aziridination Reaction 

**Keywords:** Aziridines / Asymmetric catalysis / Lewis acids

## FULL PAPERS

### Photoacylation

The efficient preparation of esters from alcohols by a photoacylation reaction is now possible. The reaction conditions, both chemical and photochemical, are very mild, thanks to the use of monochromatic LEDs.



**J.-L. Débieux, A. Cosandey, C. Helgen, C. G. Bochet\*** ..... 2073–2077

Photoacylation of Alcohols in Neutral Medium 

**Keywords:** Alcohols / Esters / Acylation / Protecting groups / Photochemistry

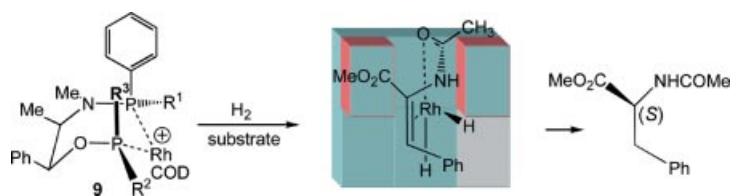
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## Asymmetric Hydrogenation

C. Darcel,\* D. Moulin, J.-C. Henry,  
M. Lagrelette, P. Richard, P. D. Harvey,  
S. Jugé\* ..... 2078–2090

Modular P-Chirogenic Aminophosphane-  
Phosphinite Ligands for Rh-Catalyzed  
Asymmetric Hydrogenation: A New Model  
for Prediction of Enantioselectivity

**Keywords:** Rhodium / P ligands / Amino-  
phosphane-phosphinites / Hydrogenation /  
Asymmetric catalysis



A series of P-chirogenic AMPP ligands has been synthesized from (+)-ephedrine by a versatile three-step methodology and tested in catalyzed hydrogenations of methyl  $\alpha$ -acetamidocinnamate by Rh complexes. Variation of the substituent on a P-center

of the ligand affords the phenylalanine derivatives with *ee* values ranging from 99 % (*S*) to 88 % (*R*). A new model for the enantioselectivity, taking into consideration the boat conformation in the AMPP-RhH<sub>2</sub> substrate complex, has been proposed.

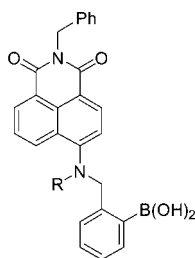
## Fluorescent Probes

J. Wang, S. Jin, S. Akay,  
B. Wang\* ..... 2091–2099



Design and Synthesis of Long-Wavelength  
Fluorescent Boronic Acid Reporter Com-  
pounds

**Keywords:** Carbohydrates / Boronic acid /  
Fluorescence spectroscopy



R = benzyl, methyl, H

Three new fluorescent probes based on the 4-amino-1,8-naphthalimide structure were synthesized, and their sugar binding properties were studied in 0.1 M phosphate buffer at pH 7.4.

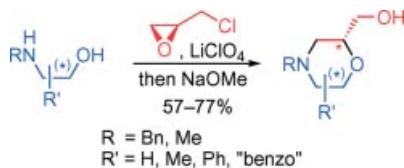
## Chiral Morpholines

M. Breuning,\* M. Winnacker,  
M. Steiner ..... 2100–2106



Efficient One-Pot Synthesis of Enantio-  
merically Pure 2-(Hydroxymethyl)morpho-  
lines

**Keywords:** Asymmetric synthesis / Nitro-  
gen heterocycles / Cyclization / Morpho-  
lines / Epichlorohydrin



Convenience is the key! An efficient one-pot procedure for the stereoselective synthesis of 2-(hydroxymethyl)morpholines is presented. LiClO<sub>4</sub>-induced ring opening of (*S*)- or (*R*)-epichlorohydrin with chiral  $\beta$ -amino alcohols and subsequent cyclization under basic conditions delivered the target molecules in good yields (57–77 %).

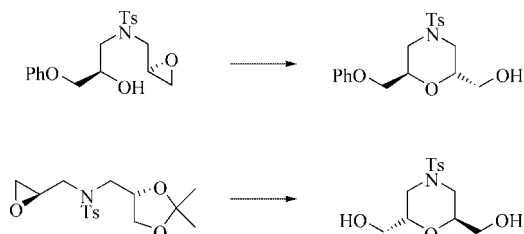
## Morpholine Derivatives

D. Albanese,\* M. Salsa, D. Landini,  
V. Lupi, M. Penso ..... 2107–2113



Concise Synthesis of 2,6-Disubstituted  
Morpholines by Cyclization of Epoxy  
Alcohols

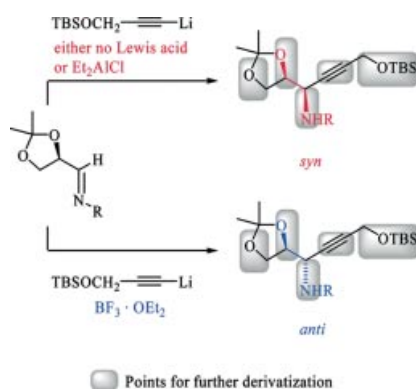
**Keywords:** Phase-transfer catalysis /  
Cyclization / Sulfonamides / Epoxy  
alcohols / Morpholines



A novel, straightforward and high yielding synthesis of enantiomerically pure 2,6-disubstituted morpholines was developed

by acid-catalyzed cyclization of epoxy alcohols.

The *syn/anti* diastereoselectivity of the addition of the lithium derivative of *tert*-butyldimethylsilyl propargyl ether to *N*-benzylimines derived from (*R*)-glyceraldehyde can be controlled and reversed by the appropriate use of Lewis acids as imine precomplexing agents. Double stereodifferentiation processes occur with total stereocontrol.

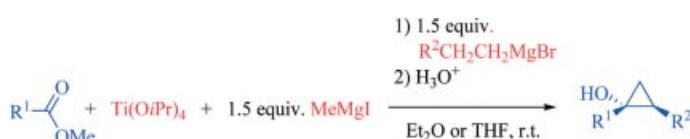


**R. Díez, R. Badorrey,  
M. D. Díaz-de-Villegas,\*  
J. A. Gálvez\*** ..... 2114–2120

Highly Stereoselective Synthesis of Stereochemically Defined Polyhydroxylated Propargylamines by Alkylation of *N*-Benzylimines Derived from (*R*)-Glyceraldehyde

**Keywords:** Amino alcohols / Asymmetric synthesis / Diastereoselectivity / Schiff bases / Nucleophilic addition

### Cyclopropanation



An improved procedure for the preparation of *cis*-1,2-dialkylcyclopropanols, minimizing the formation of side products that are not readily separable, has been elaborated. Inhibitory action of carboxylic esters towards the reduction of titanium(IV)

isopropoxide with alkylmagnesium halides and some other observations were explained in the context of the specified ate complex mechanism for the titanium-mediated cyclopropanation of carboxylic esters with Grignard reagents.

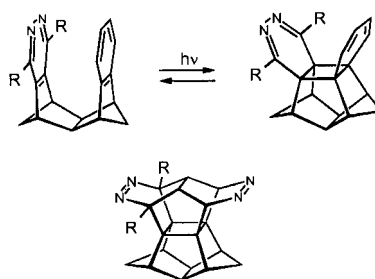
**O. G. Kulinkovich,\*  
D. G. Kananovich** ..... 2121–2132

Advanced Procedure for the Preparation of *cis*-1,2-Dialkylcyclopropanols – Modified Ate Complex Mechanism for Titanium-Mediated Cyclopropanation of Carboxylic Esters with Grignard Reagents

**Keywords:** Reaction mechanisms / Titanium / Cyclopropanols / Titanacyclopropanes / Carboxylic esters

### Photochemical Transformations

Are [6+6]photocycloadditions between highly proximate and (nearly) perfectly face-to-face oriented benzene and pyridazine rings possible? Are the respective cycloadducts useful for the construction of azapagodane-type cage molecules? The answers are given in this article.

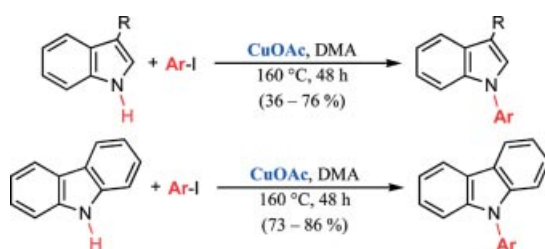


**T. Mathew,\* J. Tonne, G. Sedelmeier,  
C. Grund, M. Keller, D. Hunkler,  
L. Knothe, H. Prinzbach\*** ..... 2133–2146

[6+6]Photocycloadditions in Face-to-Face Benzo/Pyridazino Substrates – En Route to Azapagodanes

**Keywords:** Photocycloadditions / Polycycles / Polyelectron cycloadditions / Heterocycles

### Ullmann Reaction



CuOAc-Mediated *N*-arylation of 1*H*-indoles and 1*H*-carbazole with aryl iodides under base-free and ligandless conditions provides a variety of *N*-arylazoles with com-

plete *N*-selectivity and an unprecedented tolerance of functional groups in moderate to good yields.

**F. Bellina,\* C. Calandri, S. Cauteruccio,  
R. Rossi\*** ..... 2147–2151

Selective, Efficient and Functional Group-Tolerant CuOAc-Mediated *N*-Arylation of 1*H*-Indoles and 9*H*-Carbazole with Aryl Iodides Under Base-Free and Ligandless Conditions

**Keywords:** C–N coupling / Copper / Selectivity / Synthetic methods / Indoles / Carbazole

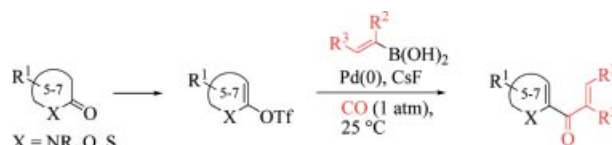
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## Carbonylative Cross-Coupling

L. Bartali, A. Guarna, P. Larini,  
E. G. Occhiato\* ..... 2152–2163

Carbonylative Suzuki–Miyaura Coupling Reaction of Lactam-, Lactone-, and Thiolactone-Derived Enol Triflates for the Synthesis of Unsymmetrical Dienones

**Keywords:** Carbonylation / Cross-coupling / Boronic acids / Triflates / Enones



The carbonylative Suzuki–Miyaura coupling reaction of enol triflates derived from lactams, lactones, and thiolactones with alkenylboronic acids provides unsymmetrical dienones in 50–86% overall yields. The

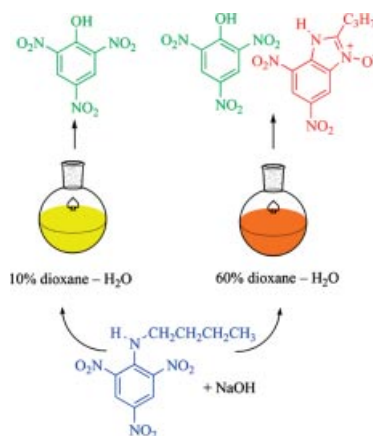
coupling reaction occurs at room temperature under CO pressure with palladium catalyst and allows for a rapid preparation of substrates useful in conjugate additions and Nazarov reactions.

## Kinetics

M. L. Salum, R. H. de Rossi,  
E. I. Buján\* ..... 2164–2174

Medium Effect on the Reaction of *N*-Butyl-2,4,6-trinitroaniline with NaOH

**Keywords:** Aromatic substitution / Cyclization / Kinetics / Reaction mechanisms / Solvent effects



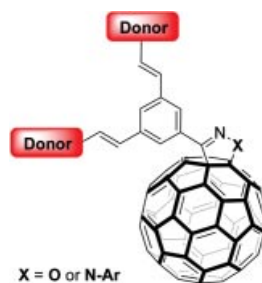
*N*-Butyl-2,4,6-trinitroaniline in 10% dioxane/H<sub>2</sub>O in basic media leads quantitatively to substitution of the amino group, whereas in 60% dioxane/H<sub>2</sub>O the observed rate constant for this reaction decreases by about one order of magnitude making the cyclization reaction leading to benzimidazole *N*-oxide a competitive pathway.

## Electron Transfer

L. Perez, M. E. El-Khouly,  
P. de la Cruz, Y. Araki, O. Ito,\*  
F. Langa\* ..... 2175–2185

Comparison between the Photophysical Properties of Pyrazolo- and Isoxazolo[60]-fullerenes with Dual Donors (Ferrocene, Aniline and Alkoxyphenyl)

**Keywords:** Fullerenes / Electron transfer / Dual-donor-C<sub>60</sub> systems / Electrochemistry / Laser spectroscopy



Two series of new pyrazolo- and isoxazolo-[60]fullerenes covalently linked to vinylene-phenylene and bearing two donors have been synthesized. A charge separation process takes place in the bis(ferrocene)–pyrazolo-C<sub>60</sub> system more efficiently than in the isoxazolo-C<sub>60</sub> triads.

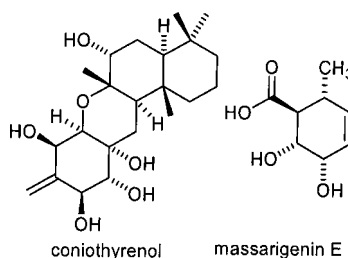
## Fungal Metabolites

I. Kock, K. Krohn,\* H. Egold, S. Draeger,  
B. Schulz, J. Rheinheimer ..... 2186–2190



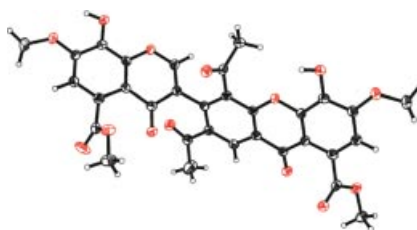
New Massarilactones, Massarigenin E, and Coniothyrenol, Isolated from the Endophytic Fungus *Coniothyrium* sp. from *Carpobrotus edulis*

**Keywords:** Fungal metabolites / *Coniothyrium* sp. / Massarilactone / Massarigenin / Coniothyrenol



New lactone-type natural products, among them massarigenin E and coniothyrenol, were isolated from *Coniothyrium* sp. together with other known lactones. The relative configuration of coniothyrenol with an unprecedented benzo[*a*]xanthene skeleton and ten chirality centers was determined by 1D- and 2D-NMR spectroscopy.

Three new fungal polyketide metabolites, chaetocyclinone A (**1**) to C (**5**), were produced by cultures of *Chaetomium* sp. (strain Gö 100/2), which was isolated from marine algae. The structures of the novel compounds were established by detailed spectroscopic analysis. Additionally, an X-ray analysis of **5** was performed (red = O). The biosynthesis of **1** and **5** was studied by feeding <sup>13</sup>C-labelled acetate and the biological activity of all compounds is reported.

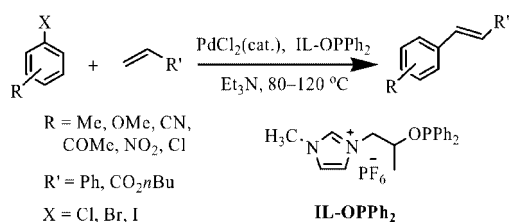


S. Lösger, O. Schlörke,  
K. Meindl, R. Herbst-Irmer,  
A. Zeeck\* ..... 2191–2196

Structure and Biosynthesis of Chaetocyclinones, New Polyketides Produced by an Endosymbiotic Fungus

**Keywords:** Chaetocyclinone / Secondary metabolites / Polyketides / Biosynthesis / *Chaetomium* sp.


### Reusable Reaction Medium



A new imidazolium-based phosphinite ionic liquid is reported as an effective reusable medium and suitable Pd<sup>II</sup> ligand for C–C bond formation through Heck coupling reactions of aryl iodides, bro-

mides and also chlorides with styrene and *n*-butyl acrylate. The ionic liquid, still containing its corresponding Pd<sup>II</sup> complex, was easily recovered and reused in several runs without losing its efficiency.

N. Iranpoor,\* H. Firouzabadi,\*  
R. Azadi ..... 2197–2201

An Imidazolium-Based Phosphinite Ionic Liquid (IL-OPPh<sub>2</sub>) as a Reusable Reaction Medium and Pd<sup>II</sup> Ligand in Heck Reactions of Aryl Halides with Styrene and *n*-Butyl Acrylate 

**Keywords:** Ionic liquid / Heck reaction / Palladium / Aryl halide

## CORRECTIONS

**Keywords:** Cycloaddition / Diastereoselectivity / Chiral auxiliaries / Oxyallyl cations

Diastereoselective [4+3] Cycloadditions of Enantiopure Nitrogen-Stabilized Oxyallyl Cation

D. I. MaGee,\* E. Godineau, P. D. Thornton,  
M. A. Walters, D. J. Sponholtz ..... 2203

**Keywords:** Allylic alcohols / Cross-coupling / Conjugated dienes / Metallacycles / Titanium

Titanocene(II)-Promoted Cross-Coupling of Unsaturated Compounds

A. Ogata, M. Nemoto, K. Arai,  
K. Kobayashi, A. Tsubouchi,  
T. Takeda\* ..... 2204

If not otherwise indicated in the article, papers in issue 12 were published online on March 27, 2007