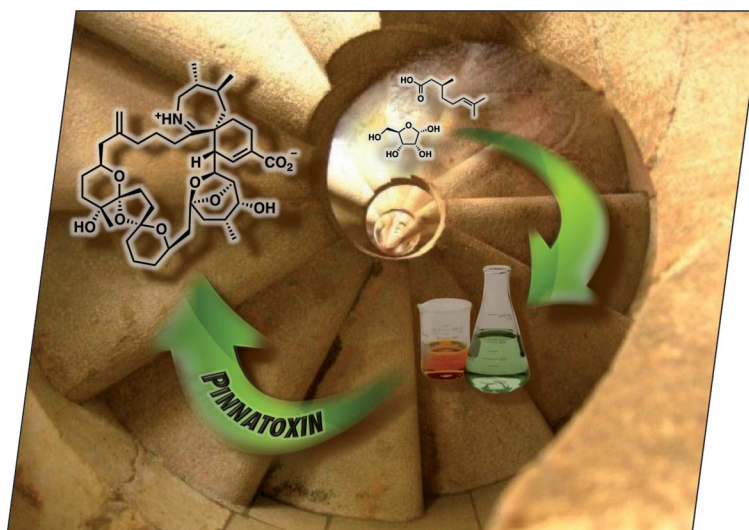


EurJOC is co-owned by 11 societies of ChemPubSoc Europe, a union of European chemical societies for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Organic Chemistry* and the *European Journal of Inorganic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

## COVER PICTURE

The cover picture shows the building blocks for the total synthesis of pinnatoxin A as the focal point, culminating with the marine natural product at the top of the stairs. The background reflects a highlight of the Santa Barbara Mission, located in Santa Barbara, California. Founded by Franciscan Friar Fermin de Lasuen on the Feast of St. Barbara in 1786, the mission is the principal cultural and historic landmark of the city. The spiral symbolizes the universal pattern of growth and evolution, as well as the ongoing process of discovery. Details of the total synthesis of pinnatoxin A are presented in the Microreview by A. Zakarian et al. on p. 3743ff.



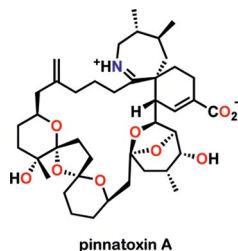
## MICROREVIEW

### Natural Product Synthesis

S. Beaumont, E. A. Ilardi, N. D. C. Tappin,  
A. Zakarian\* ..... 5743–5765

Marine Toxins with Spiroimine Rings: Total Synthesis of Pinnatoxin A

**Keywords:** Natural products / Total synthesis / Marine toxins / Spiroimine natural products / Pinnatoxin / Spiro compounds



This microreview provides a compilation of synthetic approaches and total syntheses of pinnatoxin A, a single representative member of a fascinating group of potent marine toxins that share a spiroimine subunit as a unifying structural element. The literature is surveyed up to early 2010.

## SHORT COMMUNICATIONS

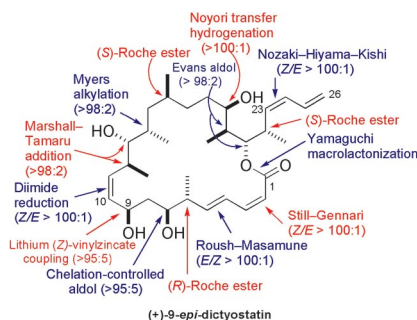
### Asymmetric Total Synthesis

C. Zanato, L. Pignataro, A. Ambrosi,  
Z. Hao, C. Gennari\* ..... 5767–5771



A Highly Stereoselective Total Synthesis of (+)-9-*epi*-Dictyostatin

**Keywords:** Antitumor agents / Asymmetric synthesis / Macrocycles / Natural products / Total synthesis



Eleven stereogenic centers and four stereogenic double bonds were obtained with a high level of stereocontrol in the total synthesis of (+)-9-*epi*-dictyostatin, a diastereomer of the antimitotic marine-sponge-derived macrolide (–)-dictyostatin.

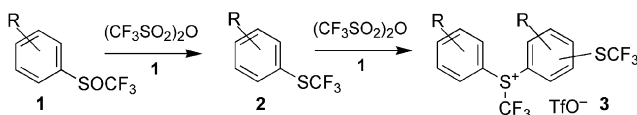
### Trifluoromethyl Sulfoxide Reduction

Y. Macé, J.-C. Blazejewski,\* C. Pradet,  
E. Magnier ..... 5772–5776



Self-Immulative Reduction of Trifluoromethyl Sulfoxides Promoted by Trifluoromethanesulfonic Anhydride

**Keywords:** Reduction / Anhydrides / Fluorine / Reaction mechanisms / Sulfur



Trifluoromethanesulfonic anhydride acts twice as a promoter for the conversion of aryl trifluoromethyl sulfoxides **1** into sulfonium salts **3**. We showed that this reaction occurs by prior reduction of sulfoxide

**1** to its corresponding sulfane induced by sulfoxide **1** itself. Further reaction of sulfane with sulfoxide **1** activated again by the anhydride gave rise to sulfonium salt **3**.

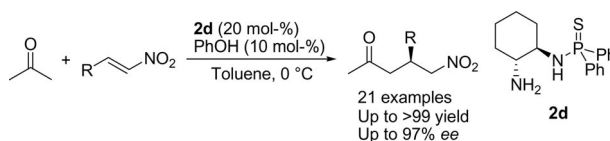
### Asymmetric Michael Addition

A. Lu, T. Liu, R. Wu, Y. Wang,\* Z. Zhou,\*  
G. Wu, J. Fang, C. Tang ..... 5777–5781



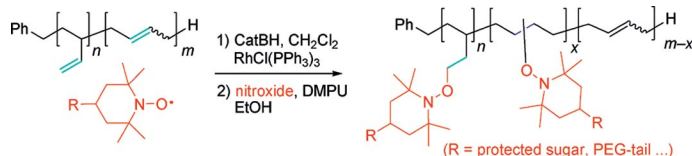
Highly Enantioselective Michael Addition of Acetone to Nitro Olefins Catalyzed by Chiral Bifunctional Primary Amine-Thiophosphoramidate Catalyst

**Keywords:** Enantioselectivity / Michael addition / Nitro olefins / Chiral thiophosphoramidate



A novel chiral phosphoramidate functions well as an efficient bifunctional organocatalyst for the asymmetric Michael addition of acetone, one of the most challenge substrate in Michael addition, to nitro olefins

to afford the corresponding synthetic valuable  $\gamma$ -nitro ketones in good to excellent yield with high levels of enantioselectivities (up to 97% ee, respectively).



Functionalized poly(butadiene)s can be prepared by a reaction sequence comprising olefin hydroboration and nitroxide induced oxidation to give poly(alkoxyamines). If the nitroxide is charged with an

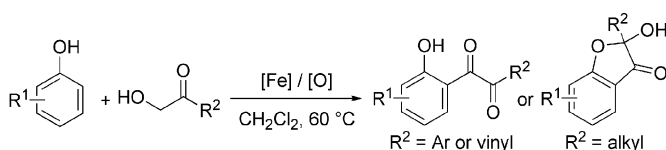
interesting functional moiety such as a sugar derivative or a polyethylene glycol tail, the trapping process delivers the corresponding functionalized chemically modified poly(olefins) in a one-pot process.

C. B. Wagner, A. Studer\* ..... 5782–5786

Oxidation of Alkylcatecholboranes with Functionalized Nitroxides for Chemical Modification of Cyclohexene, Perallylated Polyglycerol and of Poly(butadiene)

**Keywords:** Polymers / Hydroboration / Polymer modification / Boron / Radicals / Nitroxides

## Synthetic Methods



An iron-catalyzed *ortho*-functionalization of phenols was developed. The reactions of simple phenols with  $\alpha$ -hydroxy ketones

provide a novel and efficient method to construct 2'-hydroxyphenyl-1,2-dione derivatives.

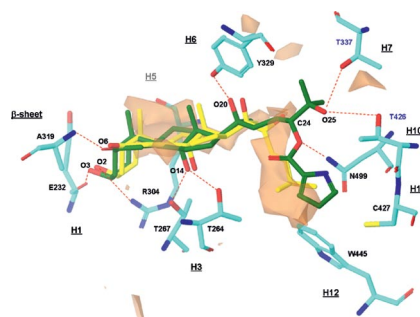
X. Guo, W. Li, Z. Li\* ..... 5787–5790

Iron-Catalyzed *ortho*-Selective Functionalization of Phenols: A Straightforward Strategy towards the 2'-Hydroxyphenyl-1,2-dione Skeleton

**Keywords:** Iron / C-H activation / Ketones / Fused-ring systems / Phenols

## FULL PAPERS

Plant-derived ecdysteroids are chemically related to insect steroid hormones, which are generally non-selective towards ecdysteroid receptors (EcRs) from different species. In contrast, the phytoecdysteroid canescensterone shows a remarkable selectivity towards non-lepidopteran EcRs. The full stereochemical assignment of canescensterone was determined using 1D and 2D solution NMR experiments, leading to a better understanding of the molecular basis of its receptor selectivity

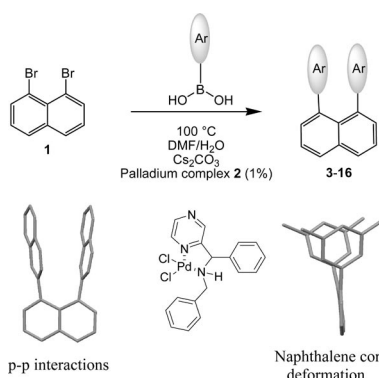


H. Sun, L. Dinan, R. Lafont, A. Suksamrarn, C. Griesinger, U. Reinscheid,\* S. Lapenna\* ..... 5791–5799

Absolute Configuration and Docking Study of Canescensterone, a Potent Phytoecdysteroid, with Non-Lepidopteran Ecdysteroid Receptor Selectivity

**Keywords:** Steroids / Receptors / NMR spectroscopy / Structure–activity relationships / Molecular docking

The synthesis of substituted 1,8-diarylnaphthalenes using bis-Suzuki coupling of 1,8-dibromonaphthalene is described. Molecular structures in the solid state for six new compounds were analyzed. The influence of several parameters on naphthalene core deformation are described.



G. Pieters, V. Terrasson, A. Gaucher,\* D. Prim,\* J. Marrot ..... 5800–5806

Synthesis and Molecular Structure of Symmetrical 1,8-Diarylnaphthalenes

**Keywords:** Conformation analysis / N ligands / Palladium / Stacking interactions / Structure elucidation

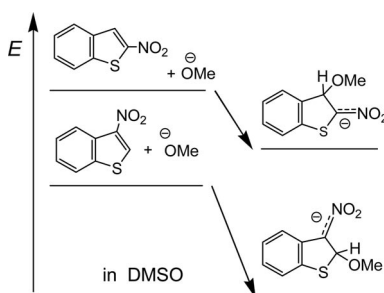
# CONTENTS

## Nucleophilic Aromatic Substitution

G. Consiglio, B. Cosimelli, S. Guernelli,  
C. Z. Lanza, F. Sancassan,\* D. Spinelli,\*  
M. Stenta ..... 5807–5816



A Novel Approach to the Evaluation of the Importance of Steric and Electronic Effects in  $S_NAr$  Reactions: A Computational, Thermodynamic and  $^1H$  and  $^{13}C$  NMR Study of “Meisenheimer-Type” Adducts in the Benzo[*b*]thiophene Series



$^{13}C$  NMR chemical shifts can contribute to evaluations of whether or not steric effects are important in  $S_NAr$  reactions. Provided that electronic effects prevail, Meisenheimer-type adducts at the C atom in  $\alpha$  position to S also exhibit the larger stability constants when the thiophene ring is benzo[*b*]-fused. Benzo[*b*]-condensation causes a dramatic decrease in the aromatic character of the thiophene ring.

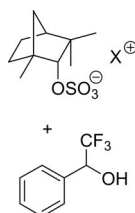
**Keywords:** Reaction mechanisms / Aromatic substitution / Meisenheimer adducts / Sulfur heterocycles

## Chiral Ionic Liquids

A. Winkel, R. Wilhelm\* ..... 5817–5824

New Chiral Ionic Liquids Based on Enantiopure Sulfate and Sulfonate Anions for Chiral Recognition

**Keywords:** Ionic liquids / Chirality / Anions / Green chemistry / Chiral recognition



Novel chiral ionic liquids based on chiral anions have been prepared. The new salts were explored as chiral shift reagents with a neutral alcohol.

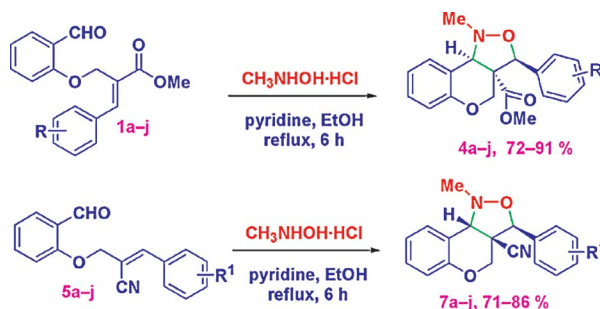
## Nitrone Cycloaddition

M. Bakthadoss,\* G. Murugan ... 5825–5830



Highly Stereoselective Synthesis of Tricyclic Chromenoisoxazolidines by Intramolecular 1,3-Dipolar Cycloadditions

**Keywords:** Heterocycles / Cycloaddition / Fused-ring systems / Chirality



The development of a novel synthetic method for the stereoselective synthesis of fused tricyclic chromenoisoxazolidines with

angular substitution through a [3+2] nitrone cycloaddition reaction by utilizing Baylis–Hillman derivatives is described.

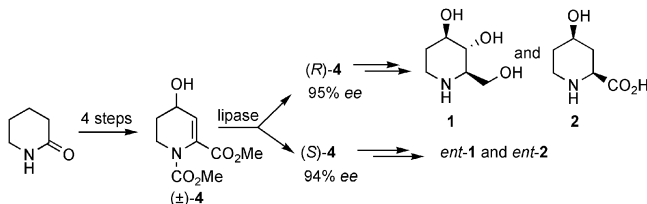
## Chemoenzymatic Synthesis

L. Bartali, A. Casini, A. Guarna,  
E. G. Occhiato,\* D. Scarpi ..... 5831–5840



Enantiodivergent Chemoenzymatic Synthesis of 4-Hydroxypiperidine Alkaloids

**Keywords:** Alkaloids / Enzyme catalysis / Kinetic resolution / Lipase / Supported catalysts

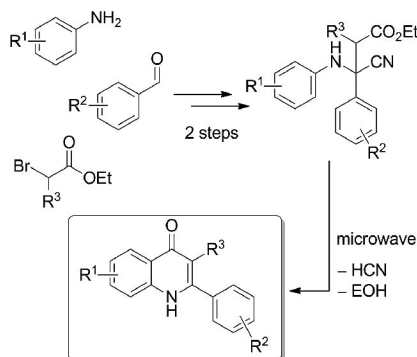


The lipase-catalyzed kinetic resolution of a racemic alcohol, readily obtained from commercial  $\delta$ -valerolactam, is the key step

of an enantiodivergent synthesis of D- and L-fagomine as well as *cis*- and *trans*-4-hydroxypipercolic acid.



The  $\alpha$ -alkylation of deprotonated *N*-aryl- $\alpha$ -aminonitriles with  $\alpha$ -bromoesters furnishes intermediates that can be cyclized to 4-quinolones upon microwave irradiation. Alternatively, base-induced dehydrocyanation of the alkylation products furnishes enaminesters, which can, for example, be converted into quinoline-3-carboxylates.

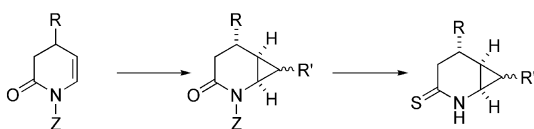


**A. Romek, T. Opatz\*** ..... 5841–5849

Microwave-Assisted Synthesis of Polysubstituted 4-Quinolones from Deprotonated  $\alpha$ -Aminonitriles

**Keywords:** Nitrogen heterocycles / Cyclization / Alkylation / Microwave chemistry

## Stereoselective Cyclopropanation



Unsaturated  $\delta$ -lactams are cyclopropanated with the aid of diazo compound decomposition catalysed by metal complexes. A study of the reaction conditions, stereochemical outcome and group protection is

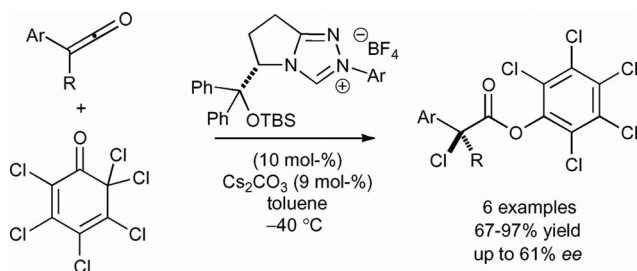
reported. Transformation into thiolactams assists in separation of the different isomers obtained and removal of the protecting group.

**I. S. Suárez del Villar, A. Gradillas, J. Pérez-Castells\*** ..... 5850–5862

Synthesis of 2-Azabicyclo[4.1.0]heptanes through Stereoselective Cyclopropanation Reactions

**Keywords:** Nitrogen heterocycles / Cyclopropanation / Polycycles / Lactams / Diastereoselectivity

## Asymmetric Catalysis



NHCs promote the efficient chlorination of unsymmetrical disubstituted ketenes with

up to 61% *ee* observed using 2,3,4,5,6,6-hexachlorocyclohexa-2,4-dienone.

**J. Douglas, K. B. Ling, C. Concellón, G. Churchill, A. M. Z. Slawin, A. D. Smith\*** ..... 5863–5869

NHC-Mediated Chlorination of Unsymmetrical Ketenes: Catalysis and Asymmetry

**Keywords:** Homogeneous catalysis / Asymmetric synthesis / *N*-Heterocyclic carbene / Ketenes / Chlorination

## Polar Diels–Alder Reaction

A comprehensive study of the Diels–Alder reaction mechanism of 2*H*-pyran-2-ones and non-symmetrically substituted electron-rich and electron-pure alkynes using both experimental and computational approaches is presented.



**B. Štefane,\* A. Perdih, A. Pevec, T. Šolmajer, M. Kočevár** ..... 5870–5883

The Participation of 2*H*-Pyran-2-ones in [4+2] Cycloadditions: An Experimental and Computational Study

**Keywords:** Cycloaddition / Density functional calculations / Donor-acceptor systems / Pyranones / Reaction mechanisms

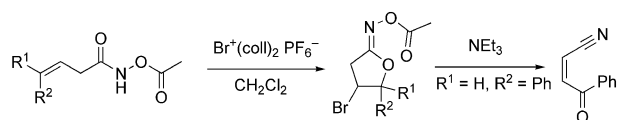
# CONTENTS

## Formation of Imino Lactones

H. Trabulsi, R. Guillot,  
G. Rousseau\* ..... 5884–5896

Preparation of Imino Lactones by Electrophilic Cyclization of  $\beta,\gamma$ -Unsaturated Hydroxamates: Formation of 3-Cyano-prop-2-en-1-ones through Fragmentation Reactions

**Keywords:** Nitriles / Lactams / Lactones / Bromonium ions / Electrophilic cyclization



Reactions between hydroxamates and bromonium ion led not to *N*-alkoxy lactams but to the thermodynamically more stable imino lactones. If  $R^1 = H$  and  $R^2 =$

Ph, subsequent treatment with triethylamine led to (*Z*)-4-oxo-4-phenylbut-2-enitrile through Beckman fragmentation.

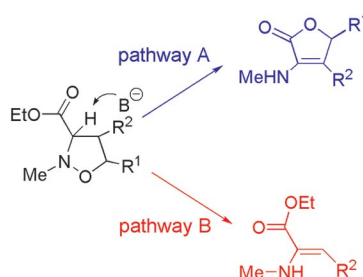
## Competitive Chemistry

D. Iannazzo,\* E. Brunaccini, S. V. Giofrè,  
A. Piperno, G. Romeo, S. Ronsisvalle,  
M. A. Chiacchio, G. Lanza,\*  
U. Chiacchio ..... 5897–5905



Competitive Formation of  $\beta$ -Enaminones and 3-Amino-2(5*H*)-furanones from the Isoxazolidine System: A Combined Synthetic and Quantum Chemical Study

**Keywords:** 1,3-Dipolar cycloaddition / Density function calculations / Isoxazolidines /  $\beta$ -Enaminones / 2(5*H*)-Furanones



Substituted isoxazolidines afford  $\beta$ -enaminones and/or 3-methylamino-2(5*H*)-furanones by treatment with tetrabutylammonium fluoride according to the nature of the substituents at  $C^4$  and  $C^5$ . Two alternative mechanisms (lactonization and retroaldolization) have been rationalized by DFT quantum chemical methods.

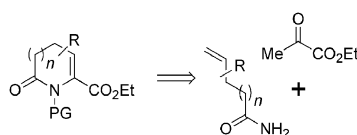
## Synthesis of Piperidines

S. A. M. W. van den Broek,  
P. G. W. Rensen, F. L. van Delft,  
F. P. J. T. Rutjes\* ..... 5906–5912



Expedient Pathway into Optically Active 2-Oxopiperidines

**Keywords:** Nitrogen heterocycles / Alkaloids / Ring-closing metathesis / Amino acids / Dehydroamino acids



A ring-closing metathesis (RCM)-mediated approach for the formation of highly substituted cyclic dehydroamino esters has been developed. These cyclic enamides represent valuable intermediates en route to substituted pipercolic acids as well as more elaborate heterocycles.

## CORRECTION

F. Alonso,\* Y. Moglie, G. Radivoy,  
M. Yus ..... 5913

Unsupported Copper Nanoparticles in the 1,3-Dipolar Cycloaddition of Terminal Alkynes and Azides

**Keywords:** Click chemistry / Cycloaddition / Alkynes / Azides / Copper / Nanoparticles

\* 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 29 were published online on October 5, 2010