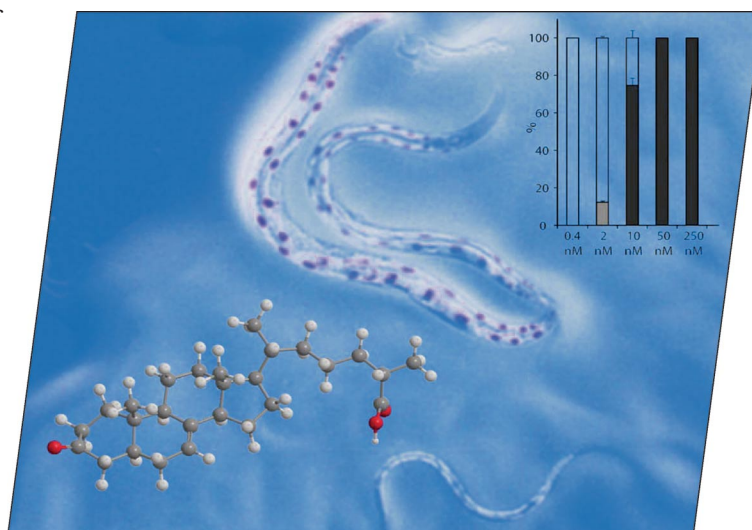


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further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

COVER PICTURE

The cover picture shows the bioactivity for rescue of diapause in *daf-9(dh6)* mutant worms using (25*S*)- Δ^7 -dafachronic acid (structure, bottom left). The fluorescence label (represented by purple spots) marks the *daf-9(dh6); dhEx24* mutant worms that develop into adults without the requirement of exogenous hormonally active steroidal acid. The *daf-9(dh6)* mutant worms (no fluorescence, at the bottom) can develop into adults by using (25*S*)- Δ^7 -dafachronic acid at concentrations down to 10 nM (top right). Details are discussed in the article by H.-J. Knölker et al. on p. 3703ff.



MICROREVIEW

Asymmetric Catalysis

S. Adachi, T. Harada* 3661–3671

Catalytic Enantioselective Aldol Additions to Ketones

Keywords: Aldol reactions / Asymmetric catalysis / Asymmetric synthesis / Ketones



This microreview presents an overview of progresses in catalytic enantioselective aldol addition to ketones. The reaction, once thought to be challenging owing to the lower reactivity and the decreased steric

discrimination of a ketone carbonyl group, has been realized recently based on the activation of acceptor ketones and/or nucleophile enolates.

SHORT COMMUNICATIONS

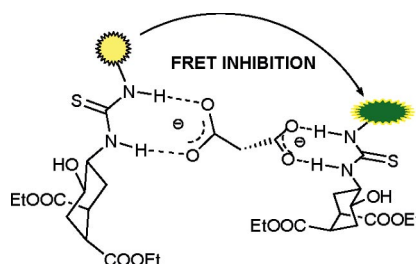
Fluorescent Chemosensors

A. M. Costero,* J. V. Colomer, S. Gil, M. Parra 3673–3677



Fluorescent Cyclohexyl-Based Chemosensors for Selective Sensing of TMA Malonate in DMSO/Water

Keywords: Host-guest systems / Molecular recognition / Fluorescent probes / Sensors / FRET (Fluorescence Resonance Energy Transfer)



A new cyclohexyl-based fluorescent system is able to recognize trimethylammonium (TMA) malonate through the inhibition of FRET in buffered DMSO/water solutions. Longer and shorter homologous dicarboxylates did not give rise to changes in the solution fluorescent properties.

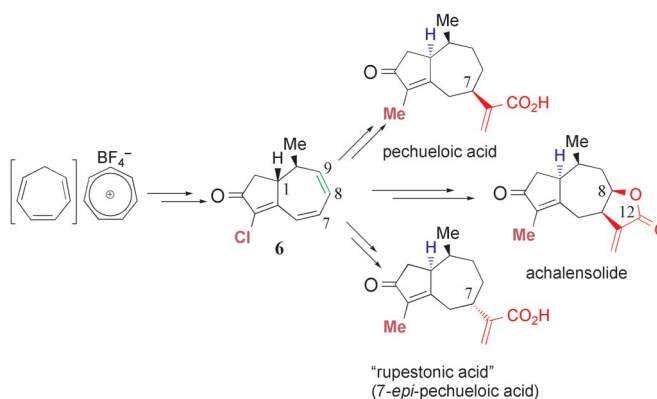
Stereocontrolled Transformations

T. Sainte-Luce Banchelin, S. Carret, A. Giannini, J.-P. Deprés* 3678–3682



Short and Stereoselective Total Synthesis of Δ -11,13-Didehydroguaianes and -guaianolides: Synthesis of (\pm)-Achalensolide and (\pm)-Pechueloic Acid; Revision of the Structure of (+)-Rupestonic Acid

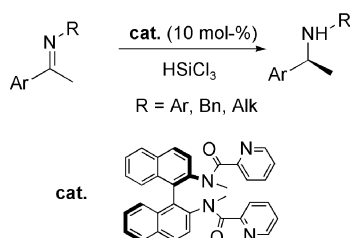
Keywords: Guaianes / Guaianolides / Conjugate addition / Isomerization / Total synthesis / Diastereoselectivity



The total synthesis of pechueloic acid (1) as well as the first syntheses of rupestonic acid (3) and achalensolide (5) were achieved in nine regio- and stereocontrolled steps, via hydroazulenone 6 (a versa-

tile intermediate), through efficient C-1 epimerization, selective C-8,9 hydrogenation and stereocontrolled 1,6-conjugate addition of an acrylate equivalent.

An organocatalyst, easily prepared in a single step by condensation of picolinic acid and readily available 1,1'-binaphthyldiamine, promoted the synthesis of chiral secondary and primary amines in high yield and stereoselectivity. These catalysts are able to promote the reduction not only of *N*-aryl but also of *N*-alkyl and *N*-benzyl ketimines, often in quantitative yields and up to 87% enantioselectivity.



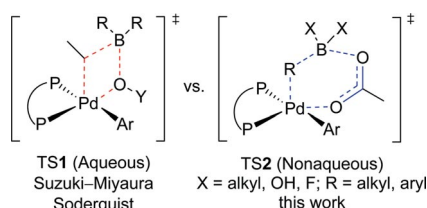
S. Guizzetti, M. Benaglia,*
G. Celentano 3683–3687

1,1'-Binaphthyldiamine-Based Lewis Bases as Readily Available and Efficient Organocatalysts for the Reduction of *N*-Aryl and *N*-Alkyl Ketimines

Keywords: Reduction / Lewis bases / Organocatalysis / Binaphthyldiamines / Enantioselectivity

Suzuki–Miyaura Cross-Coupling

CsOAc promotes Suzuki–Miyaura cross-coupling and related Pd-catalyzed reactions under anhydrous conditions as effectively as stronger bases. A neglected six-membered transition-state model was proposed to give alternative insight into the key process of transmetalation.



B. Wang,* H.-X. Sun,
Z.-H. Sun* 3688–3692

A General and Efficient Suzuki–Miyaura Cross-Coupling Protocol Using Weak Base and No Water: The Essential Role of Acetate

Keywords: Suzuki–Miyaura coupling / Cross-coupling / Boranes / Lewis bases / Palladium

Chiral Brønsted Acids

BINBAM [(*R*)-1,1'-binaphthyl-2,2'-bis(sulfon)amide] is the first member of a new generation of chiral Brønsted acids. It is easily accessible from commercially available BINOL and its 3,3'-derivatives. It shows higher Brønsted acidity than competing phosphoric acid derivatives like the TRIP family.

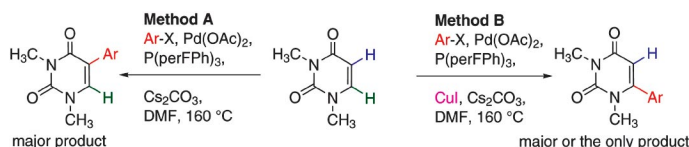


M. Treskow, J. Neudörfel,
R. Giernoth* 3693–3697

BINBAM – A New Motif for Strong and Chiral Brønsted Acids

Keywords: Chirality / Acidity / Sulfonamides / Organocatalysis

C–H Arylation



Direct C–H arylation of pyrimidine nucleobase proceeds regioselectively, and the selectivity (and mechanism) can be efficiently switched by copper iodide. In the absence

of CuI, the arylations of 1,3-dimethyluracil lead to 5-arylruracils, while in the presence of CuI, to 6-aryl derivatives.

M. Černová, R. Pohl,
M. Hocek* 3698–3701

Switching the Regioselectivity of Direct C–H Arylation of 1,3-Dimethyluracil

Keywords: Pyrimidines / C–H arylation / Regioselectivity / Cross-coupling / Copper

FULL PAPERS

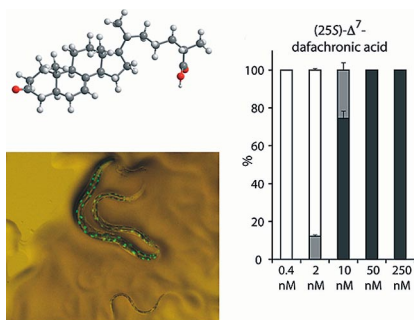
Steroid Hormones

R. Martin, E. V. Entchev, F. Däbritz,
T. V. Kurzchalia,
H.-J. Knölker* 3703–3714



Synthesis and Hormonal Activity of the (25*S*)-Cholesten-26-oic Acids – Potent Ligands for the DAF-12 Receptor in *Caenorhabditis elegans*

Keywords: Diastereoselectivity / Hormones / Oxidation / Protecting groups / Steroids



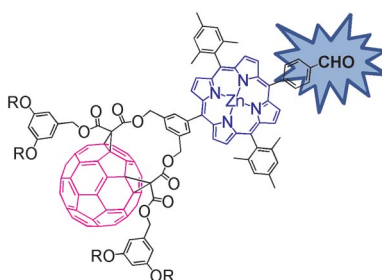
An elegant synthetic approach to the (25*S*)-cholesten-26-oic acids has been developed using a stereoselective Evans aldol reaction as key-step. These steroids are potent ligands for the hormonal receptor DAF-12 in *Caenorhabditis elegans*. Our biological studies confirm (25*S*)-Δ⁷-dafachronic acid (**1**) as the most active ligand known so far.

Porphyrin Chemistry

M. Urbani, J. Iehl, I. Osinska, R. Louis,
M. Holler,
J.-F. Nierengarten* 3715–3725

Formyl-Porphyrin and Formyl-Fullerenoporphyrin Building Blocks for the Construction of Multiporphyrin Arrays

Keywords: Fullerenes / Porphyrin / Atropisomerism / Restricted rotation / Molecular devices



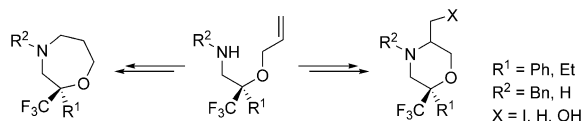
A formyl-fullerenoporphyrin building block has been prepared and used for the construction of a pentaporphyrin derivative surrounded by four peripheral C₆₀ units. By following a similar strategy, a nonaporphyrin array was prepared from a bis-porphyrin building block bearing an aldehyde function.

Heterocyclic Chemistry

J. Nonnenmacher, F. Grellepois,
C. Portella* 3726–3731

Synthesis of Enantiopure 2-Aryl(Alkyl)-2-trifluoromethyl-Substituted Morpholines and Oxazepanes

Keywords: Cyclization / Asymmetric synthesis / Fluorine / Heterocycles / Enantiopurity



Novel enantiopure morpholines and oxazepanes containing a quaternary trifluoromethyl substituent have been prepared

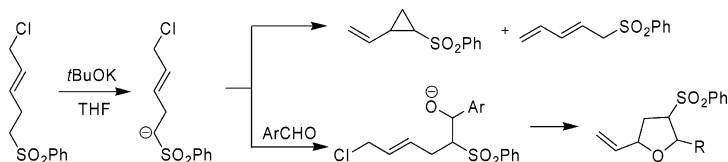
from a common *O*-allyl amino ether intermediate by a 6-*exo* or 7-*endo* nucleophilic cyclisation process.

γ-Halocarbanion Chemistry

A. Wojtasiewicz, B. Lewandowski, M. Judka,
M. Mąkosza* 3732–3740

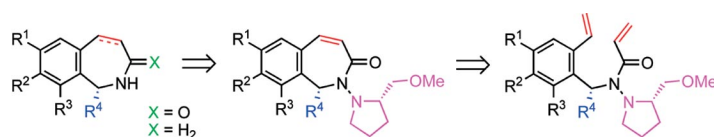
Reactions of Carbanions of 1-Chloro-5-(phenylsulfonyl)pent-2-enes: Synthesis of Vinyl-Substituted Tetrahydrofurans

Keywords: Carbanions / Sulfones / Nucleophilic substitution / Oxygen heterocycles



Carbanions of 1-chloro-5-(phenylsulfonyl)pent-2-enes can be considered as vinyl-oxides of γ-halocarbanions. They undergo intramolecular S_N2' 1,3-substitution and 1,5-elimination to produce 2-(phenylsul-

fonyl)-1-vinylcyclopropanes and 1-(phenylsulfonyl)penta-2,4-dienes. They also add rapidly to aromatic aldehydes to produce the corresponding 2-aryl-3-(phenylsulfonyl)-5-vinyl-tetrahydrofurans.



A flexible asymmetric synthesis of chiral (1*R*)-1-alkylated benzazepinone and benzazepine derivatives that combines a highly stereoselective 1,2-addition to SAMP-

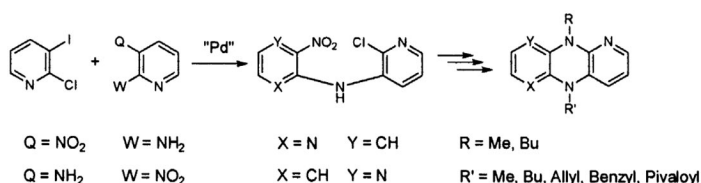
hydrazones with the ring-closing metathesis of styrenic enehydrazides has been achieved.

D. Dumoulin, S. Lebrun, E. Deniau,
A. Couture,*
P. Grandclaude 3741–3752

First Asymmetric Synthesis of (Un)saturated 1-Alkylbenzo[*c*]azepin-3-ones: Extension to the Corresponding Benzazepines

Keywords: Lactams / Chiral auxiliaries / Cyclization / Hydrazones / Fused-ring systems / Asymmetric synthesis

Heterocyclic Chemistry



Specific syntheses of each of the unsymmetrically substituted dihydrodipyridopyrazine isomers **A** and **B** have been completed. The novel strategy that was developed for their syntheses featured Pd cataly-

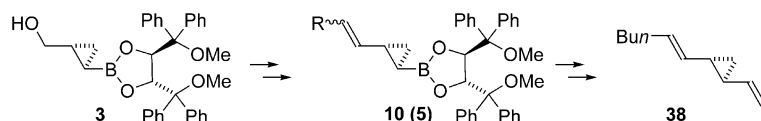
sis for key couplings, followed by a substitution/reduction/cyclization/substitution sequence of suitable nitro-substituted *N,N'*-dipyridinylamine products.

O.-I. Patriciu, A.-L. Fînar, S. Massip,
J.-M. Léger, C. Jarry,
G. Guillaumet* 3753–3764

Efficient and Selective Method for the Synthesis of Dihydrodipyridopyrazines Based on the Pd-Catalysed Amination of Halo-pyridines

Keywords: Dihydrodipyridopyrazines / Pd catalysis / Cross-coupling / Reduction / Cyclization

Cyclopropylboronic Esters



Isomerically pure vinylcyclopropanes (e.g., **10**) have been prepared from cyclopropylboronic esters (e.g., **3**). A number of alternative procedures for their synthesis via the corresponding alkyltrifluoroborates

have been established and they require relatively mild reaction conditions for their activation. The sequence has been applied to the synthesis of natural dictyptene **A** (**38**).

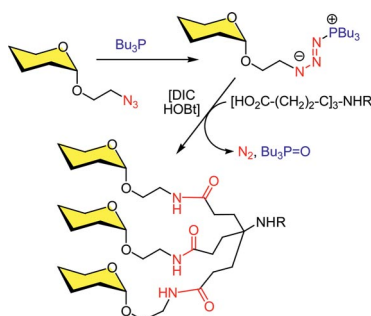
E. Hohn, J. Paleček, J. Pietruszka,*
W. Frey 3765–3782

Enantiomerically Pure Vinylcyclopropylboronic Esters

Keywords: Boron / Cyclopropane / Asymmetric synthesis / Palladium / Natural products

Staudinger-Ligated Glycoconjugates

Staudinger ligation can be utilized in the synthesis of multivalent glycomimetics such as glycoclusters and glycoamino acid building blocks.



A. Schierholt, H. A. Shaikh,
J. Schmidt-Lassen,
T. K. Lindhorst* 3783–3789

Utilizing Staudinger Ligation for the Synthesis of Glycoamino Acid Building Blocks and Other Glycomimetics

Keywords: Ligation / Amino acids / Glycomimetics / Glycoconjugates / Azides

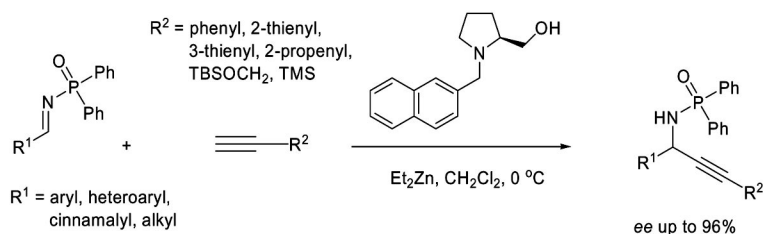
CONTENTS

Chiral Propargylamines

W. Yan, B. Mao, S. Zhu, X. Jiang, Z. Liu, R. Wang* 3790–3794



Asymmetric Addition of Terminal Alkynes to *N*-(Diphenylphosphinoyl)imines Promoted by Stoichiometric Amounts of a Proline-Derived β -Amino Alcohol



Keywords: Enantioselectivity / Asymmetric synthesis / Alkynylation / β -Amino alcohol / Propargylamines

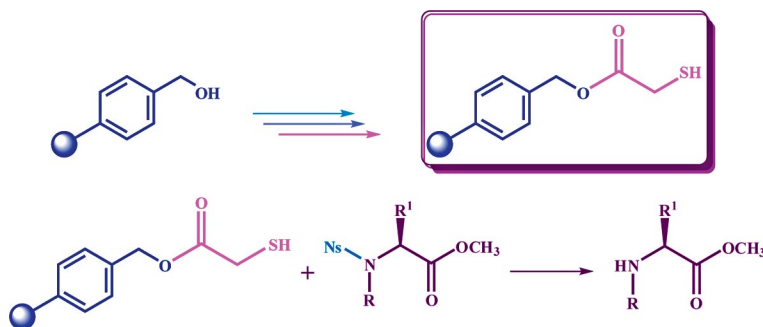
The highly enantioselective alkynylation of *N*-(diphenylphosphinoyl)imines has been

achieved by the use of a proline-derived β -amino alcohol and diethylzinc.

Supported Mercaptoacetic Acid

R. De Marco, M. L. Di Gioia, A. Leggio, A. Liguori,* M. C. Viscomi 3795–3800

Deprotection of *N*-Nosyl- α -amino Acids by Using Solid-Supported Mercaptoacetic Acid



Keywords: Supported reagents / Amino acids / Thiols / Solution-phase synthesis / Chirality / Protecting groups

A solid-supported thiol has been conveniently prepared by treating an *S*-protected mercaptoacetic acid with Wang resin. Deprotection of the thiol function pro-

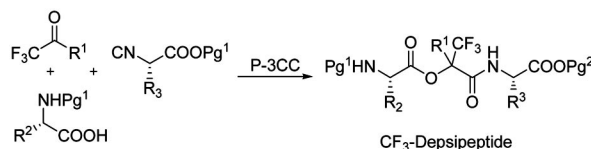
vided the supported nucleophile, which was used to remove the nosyl group from the α -amino function of nosyl- α -amino acids in a polymer-assisted solution-phase reaction.

Multicomponent Reactions

A. V. Gulevich, I. V. Shpilevaya, V. G. Nenajdenko* 3801–3808



The Passerini Reaction with CF_3 -Carbonyl Compounds – Multicomponent Approach to Trifluoromethyl Depsipeptides



Keywords: Multicomponent reactions / Peptidomimetics / Depsipeptide / Chiral resolution

The first detailed investigation of the Passerini reaction with CF_3 -carbonyl compounds is reported. The reaction provides

a new approach to trifluorolactic acid derivatives and CF_3 -substituted depsipeptides.

RETRACTION

I. Izquierdo,* M. T. Plaza, J. A. Tamayo, F. Sánchez-Cantalejo 3809

A New Synthetic Approach to (+)-Hyacinthacine A₁ and the First Total Synthesis and Absolute Configuration Assignment of Naturally Occurring (+)-Hyacinthacine A₆

Keywords: Alkaloids / Azasugars / Hyacinthacines / Enantioselectivity / Synthetic methods / Enzyme inhibitors

* 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 21 were published online on July 6, 2009