

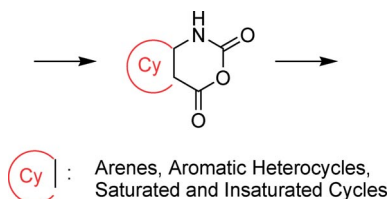
MICROREVIEW

Heterocyclic Chemistry

Y. Brouillette, J. Martinez,
V. Lisowski* 3487–3503

Chemistry of Ring-Fused Oxazine-2,4-diones

Keywords: Heterocycles / Diones / Anhydrides / Synthetic methods / Fused-ring systems



A survey of the latest methods of preparation of all known ring-fused oxazine-2,4-diones is given. The reactivity scope of this class of attractive compounds is exhaustively depicted.

SHORT COMMUNICATIONS

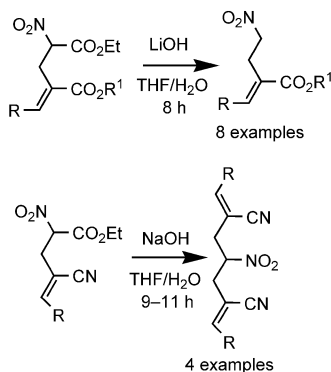
Homoallyl Nitroalkanes

M. Nayak, S. Batra* 3505–3507



Stereoselective Synthesis of Homoallyl Nitroalkane Derivatives through Base-Promoted Regioselective Decarboxylation of Baylis–Hillman Derivatives

Keywords: Nitroalkanes / Regioselectivity / Baylis–Hillman / Decarboxylation / Allylic compounds



Base-promoted decarboxylative protonation of the dialkanoates afforded from the S_N2' -reaction of Baylis–Hillman acetates of acrylates with ethyl nitroacetate provides a general route for the synthesis of homoallyl nitroalkanes. A similar reaction of substrates derived from Baylis–Hillman acetates of acrylonitrile results in the formation of bisallyl nitroalkanes.

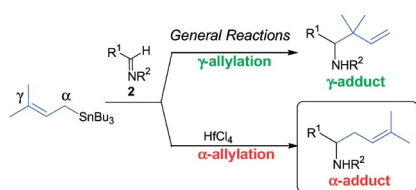
Regioselective α -Prenylation

I. Shibata,* S. Miyamoto, S. Tsunoi,
K. Sakamoto, A. Baba 3508–3511



Generation of Prenylhafnium and α -Selective Addition to Imines

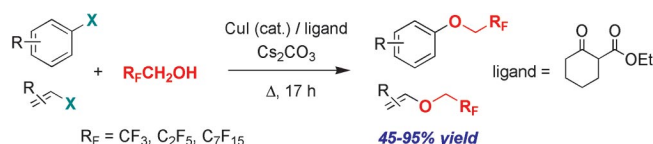
Keywords: Allylation / Regioselectivity / Hafnium / Tin / Transmetalation / Imines



Highly α -selective addition reaction can be achieved by using the prenyltributyltin/ $HfCl_4$ system. In situ generated allylhafnium plays an important role for the reactivity and regioselectivity.

FULL PAPERS

Fluorinated Ethers



Fluorinated aryl and vinyl ethers are easily obtained by copper-catalysed cross-coupling reactions between fluoro alcohols

(R_F-CH_2OH type) and the corresponding halides.

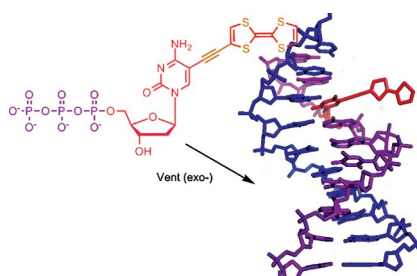
**D. Vuluga, J. Legros,* B. Crousse,*
D. Bonnet-Delpon 3513–3518**

Facile Access to Fluorinated Aryl and Vinyl Ethers through Copper-Catalysed Reaction of Fluoro Alcohols

Keywords: Fluorine / Alcohols / Enols / Ethers / Copper

DNA Labelling

DNA labelling by tetrathiafulvalene has been attempted. TTF-modified nucleoside triphosphates were prepared and tested as substrates for DNA polymerases. Their enzymatic incorporation was inefficient and at higher concentrations they totally inhibited the polymerase.



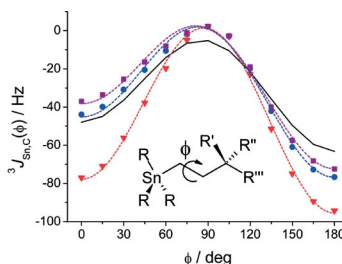
**J. Riedl, P. Horáková, P. Šebest, R. Pohl,
L. Havran, M. Fojta,*
M. Hocek* 3519–3525**

Tetrathiafulvalene-Labelled Nucleosides and Nucleoside Triphosphates: Synthesis, Electrochemistry and the Scope of Their Polymerase Incorporation into DNA

Keywords: Nucleosides / Nucleotides / Nucleic acids / Cross-coupling / DNA polymerase / Tetrathiafulvalene

DFT Study on Organotin Couplings

Unrolling Tin Conformations: The Karplus-type dependence on the dihedral angle θ of vicinal spin-spin couplings involving ^{119}Sn in organotin(IV) derivatives has been studied computationally at the scalar ZORA relativistic and at non-relativistic DFT levels. Several factors influencing the shape of the curve have been highlighted.

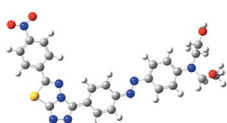


**G. Casella, F. Ferrante,
G. Saielli* 3526–3534**

Karplus-Type Dependence of Vicinal $^{119}Sn-^{13}C$ and $^{119}Sn-^1H$ Spin-Spin Couplings in Organotin(IV) Derivatives: A DFT Study

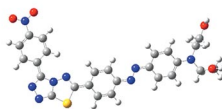
Keywords: Relativistic effects / Density functional calculations / NMR spectroscopy / Tin

Isomeric NLO Chromophores



$$\mu\beta = 430 \cdot 10^{-48} \text{ esu}$$

The synthesis and quadratic non-linear optical activities of bent azo-chromophores containing the 10-electron heterocycle *s*-triazolo[3,4-*b*]thiadiazole is presented. Attaching electron-withdrawing groups to



$$\mu\beta = 980 \cdot 10^{-48} \text{ esu}$$

either the thiadiazole or the triazole ring results in a strong variation of the ground-state dipole moment and the quadratic NLO activity.

**R. Centore,* S. Fusco, A. Peluso,
A. Capobianco, M. Stolte, G. Archetti,
H.-G. Kuball* 3535–3543**

Push–Pull Azo-Chromophores Containing Two Fused Pentatomic Heterocycles and Their Nonlinear Optical Properties

Keywords: Chromophores / Heterocycles / EOA spectroscopy / Isomerization / Non-linear optics / Density functional calculations

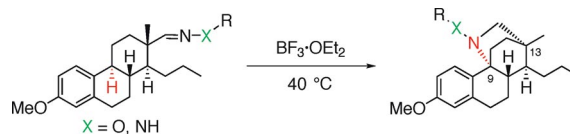
CONTENTS

Bridged Steroidal Heterocycles

É. Frank,* G. Schneider, Z. Kádár,
J. Wölfling 3544–3553

Intramolecular Hydro-*N*-alkylation of Hydrazones and Oxime Ethers: Synthesis of Novel D-Secoestrone Isoquinuclidines via Domino 1,5-Hydride Shift/Cyclization

Keywords: Domino reactions / 1,5-Hydride shift / Hydrazones / Oxime ethers / Lewis acids



Steroidal hydrazones and oxime ethers have been demonstrated to possess enough electrophilic force in the presence of a stoichiometric amount of $\text{BF}_3 \cdot \text{OEt}_2$ to induce 1,5-hydride shift from the activated benzylic

carbon C-9. The subsequent intramolecular cyclization led to novel 9,13-bridged azaestrone derivatives stereo- and regioselectively.

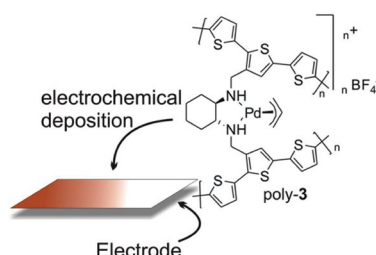
Heterogeneous Catalysis

M. Bandini,* A. Pietrangelo, R. Sinisi,
A. Umani-Ronchi,
M. O. Wolf 3554–3561



New Electrochemically Generated Polymeric Pd Complexes as Heterogeneous Catalysts for Suzuki Cross-Coupling Reactions

Keywords: Cross-coupling / Electropolymerization / Heterogeneous catalysis / Palladium / Sulfur heterocycles



Recoverable heterogeneous catalyst
for Suzuki reactions!!

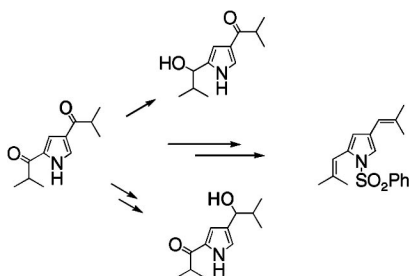
Catalytic films of (oligothienyl)Pd complexes are electrochemically deposited onto inert surfaces and are used as a recoverable, reusable Suzuki cross-coupling catalyst.

Pyrrole Chemistry

Y. Li, D. Dolphin* 3562–3566

Regioselective Reduction of 2,4-Diacetylpyrroles and the Synthesis of a 2,4-Divinylpyrrole

Keywords: N Heterocycles / Pyrroles / Reduction / Regioselectivity



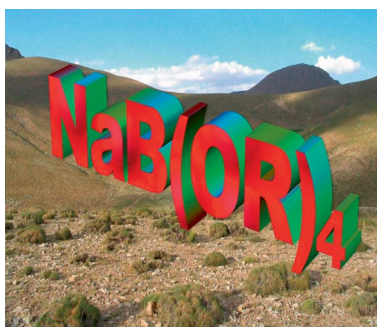
Starting from 2,4-diacetylpyrrole, a series of reduction, dehydration, *N*-protection and *N*-deprotection reactions have been explored. 2- and 4-Carbinols were obtained with complete regioselectivity and 2,4-divinylpyrrole was synthesized in the presence of a *N*-phenylsulfonyl group.

Tetraalkoxyborates

M. R. Naimi-Jamal,* J. Mokhtari,
M. G. Dekamin, G. Kaupp* 3567–3572

Sodium Tetraalkoxyborates: Intermediates for the Quantitative Reduction of Aldehydes and Ketones to Alcohols through Ball Milling with NaBH_4

Keywords: Alcohols / Sustainable chemistry / Carbonyl compounds / Hydrogen transfer / Borates




Elusive sodium tetraalkoxyborates are easily obtained by anhydrous ball milling of aldehydes and ketones with $1/4\text{NaBH}_4$. They are versatile solid precursors of alcohols. This quantitative new technique specifically provides allylic alcohols from conjugated aldehydes, which solves a long-standing synthetic problem. The inorganic sodium borate originating from desert mines is easily recycled.



Cyanogen azide was found to be an efficient reagent for the synthesis of readily purified substituted tetrazoles from second-

ary amines under noncatalytic mild conditions.

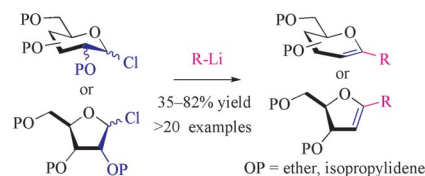
Y.-H. Joo, J. M. Shreeve* 3573–3578

Functionalized Tetrazoles from Cyanogen Azide with Secondary Amines 


Keywords: Tetrazole / Cyclization / Azides / Nitrogen heterocycles

C-1 Glycols from Chlorides

Pyranosyl and furanosyl chlorides, with ether or acetal protecting groups, can be conveniently transformed into C-1 glycols by treatment with organolithium reagents (R-Li) at low temperature.

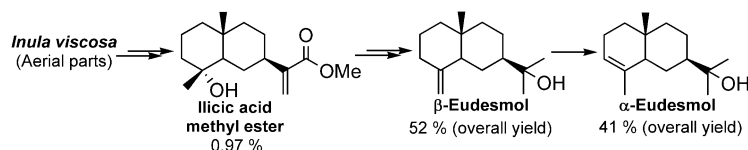


A. M. Gómez,* A. Pedregosa, M. Casillas, C. Uriel, J. C. López* 3579–3588

Synthesis of C-1 Alkyl and Aryl Glycols from Pyranosyl or Furanosyl Chlorides by Treatment with Organolithium Reagents 

Keywords: Lithium / Carbohydrates / C-Glycosides / Protecting groups

Synthesis of β- and α-Eudesmol



The enantiospecific synthesis of β- and α-eudesmol was carried out from the new

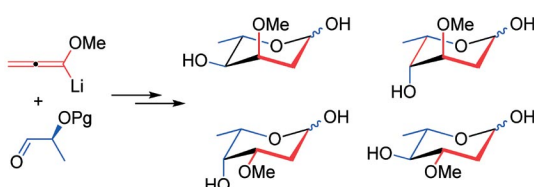
natural quiron ilicic acid in six and seven steps, respectively.

A. F. Barrero,* M. M. Herrador,* P. Arteaga, J. V. Catalán 3589–3594

Ilicic Acid as a Natural Quiron for the Efficient Preparation of Bioactive α- and β-Eudesmol

Keywords: Enantioselectivity / Synthetic methods / Biological activity / Terpenoids / Natural products


Rare Deoxy Sugars



Stereodivergent toward four rare 2,6-dideoxyhexoses! Starting from lithiated methoxyallene and (S)-lactaldehyde derivatives,

a C₃ + C₃ approach allows the efficient synthesis of L-cymarose, L-sarmentose, L-diginose and L-oleandrose.

M. Brasholz, H.-U. Reifbig* ... 3595–3604

Alkoxyallene-Based De Novo Synthesis of Rare Deoxy Sugars: New Routes to L-Cymarose, L-Sarmentose, L-Diginose and L-Oleandrose 

Keywords: Total synthesis / Carbohydrates / Deoxy sugars / Glycosylation / Gold catalysis / Allenes / Oxygen heterocycles / Furans

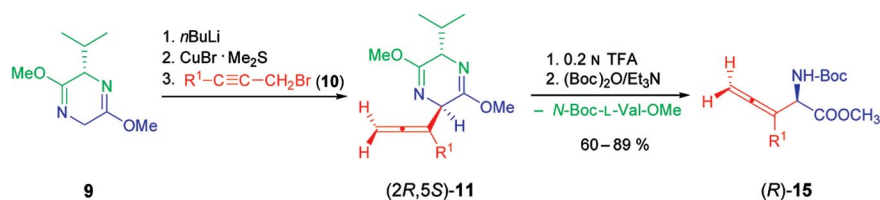
CONTENTS

Asymmetric Synthesis

C. Bucuroaia, U. Groth,* T. Huhn,
M. Klinge 3605–3612

Asymmetric Synthesis of α -Allenylglycines

Keywords: Asymmetric synthesis / Amino acids / Cuprates / Allenes / Alkynes



A highly enantioselective synthesis of α -allenylglycines **15** is described. The methodology is based on the diastereoselective

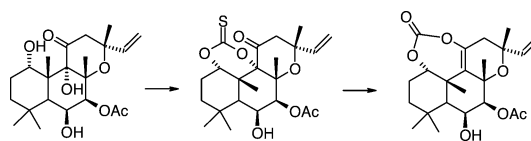
coupling of the homocuprate of bislactim ether **9** with primary propargyl halides **10**.

Forskolin Analogues

M. Egger, P. Maity, M. Hübner,
R. Seifert, B. König* 3613–3618

Synthesis and Pharmacological Properties of New Tetracyclic Forskolin Analogues

Keywords: Medicinal chemistry / Biological activity / Fused-ring systems / Carbenes / Rearrangement



The preparation and pharmacological properties of new tetracyclic forskolin analogues are reported. The new tetracyclic analogues were obtained via radical and carbene intermediates by an unprecedented

rearrangement. The activity of the new forskolin analogues towards adenylyl cyclases 1, 2 and 5 were tested and found to be partial agonists of the enzyme.

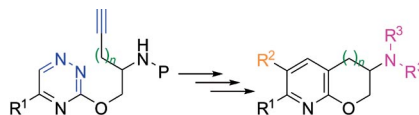
Heterocyclic Chemistry

E. Badarau, F. Suzenet,* A.-L. Finaru,
G. Guillaumet 3619–3627



Synthesis of 3-Amino-8-azachromans and 3-Amino-7-azabenzofurans via Inverse Electron Demand Diels–Alder Reaction

Keywords: Heterocycles / Cycloaddition / Polycycles



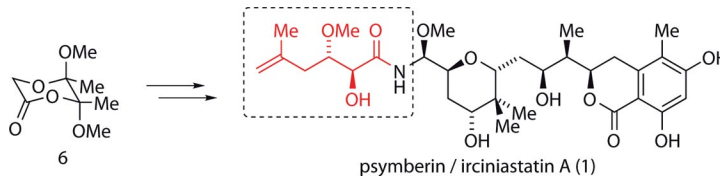
A series of chroman isosteres was synthesized by using an intramolecular inverse electron demand Diels–Alder reaction as key step. This approach allows the modulation of the pyridin core of the amine moiety and of the nonaromatic ring size.

Chemoenzymatic Synthesis

J. Pietruszka,* R. C. Simon ... 3628–3634

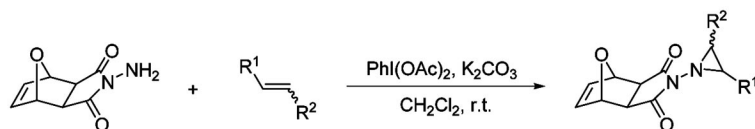
Chemoenzymatic Synthesis of (Protected) Psymberic Acid

Keywords: Antitumor agents / Natural products / Diastereoselectivity / Enzymes / Kinetic resolution



Two syntheses of the unique side-chain of psymberin (**1**) are presented starting from either the racemic or enantiomerically pure protected glycolic acid **6**. A key building


block ready for coupling is provided by a chemoenzymatic approach. The enzymatic step was optimized, furnishing the desired intermediate in high selectivity ($E > 100$).



N-Amino-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalimide demonstrated high activity towards addition to alkenes, giving access to stable aminoaziridine derivatives in good

yields. Although the aminoaziridination agent contained a highly reactive double bond, no products of self-aziridination were detected.

M. Zibinsky, T. Stewart, G. K. S. Prakash,
M. A. Kuznetsov* 3635–3642

N-Amino-*exo*-3,6-epoxy-1,2,3,6-tetrahydrophthalimide as an Active Aminoaziridinating Agent 

Keywords: Nitrogen heterocycles / Amines / Alkenes / Synthons

* Author to whom correspondence should be addressed.

 Supporting information on the WWW (see article for access details).

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