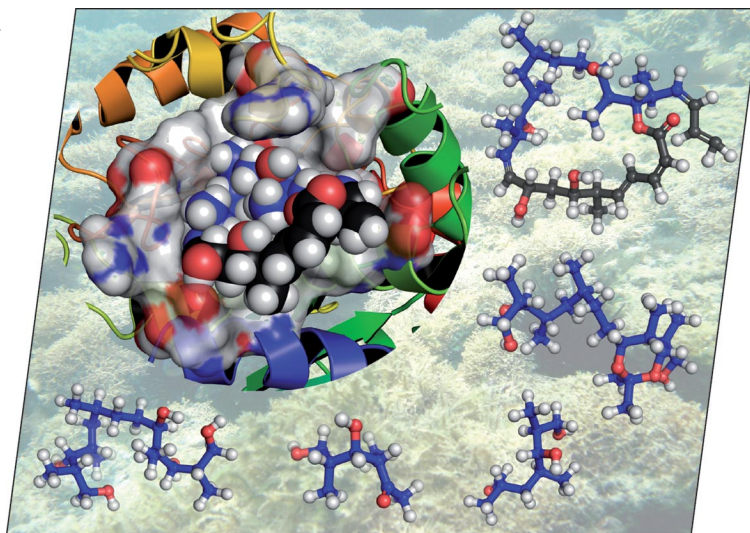


## COVER PICTURE

The cover picture shows the intermolecular interactions between the marine-derived dictyostatin and the  $\beta$ -tubulin binding site, as well as some important molecular fragments of the required 15-step sequence to produce the C11–C23 fragment (highlighted in blue) of dictyostatin in good overall yield. Dictyostatin, an unsaturated 22-membered macrolactone containing 11 stereocenters, a (Z)-alkene, and two diene systems, exhibits potent antitumoral activity as a consequence of its reversible and specific binding to the  $\beta$ -tubulin cavity and modulation of microtubule function. Details of the synthesis and characterization of the C11–C23 fragment are reported in the Short Communication by L. C. Dias et al. on p. 1491ff. The authors thank Ms. Livia B. Salum for her contribution to the design of the cover picture.



## EDITORIAL SURVEY

L. Bornmann,\* W. Marx,  
H. Schier ..... 1471–1476

Hirsch-Type Index Values for Organic  
Chemistry Journals: A Comparison of New  
Metrics with the Journal Impact Factor

**Keywords:** Journal Impact Factor / Hirsch-  
type indices / *h* index / *g* index / *h*(2) index /  
*a* index / *r* index

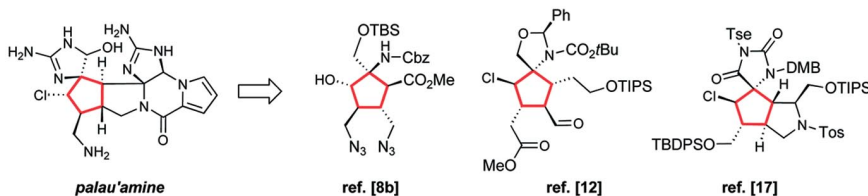
## MICROREVIEW

### Total Synthesis

B. Heasley\* ..... 1477–1489

Stereocontrolled Preparation of Fully Sub-  
stituted Cyclopentanes: Relevance to Total  
Synthesis

**Keywords:** Natural products / Carbocycles /  
Cyclopentane / Total synthesis / Asym-  
metric synthesis / Diels–Alder reaction /  
Palau'amine

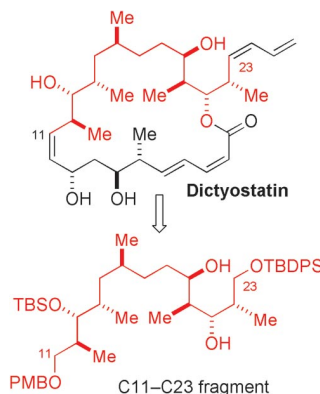


A hexa-substituted chlorocyclopentane  
framework is common to a variety of di-  
meric marine alkaloids of the oroidin fam-  
ily. In the pursuit of synthons for oroidin  
dimers such as palau'amine, the stereo-

controlled synthesis of complex C<sub>5</sub> rings  
has seen a renaissance in recent years.  
Stereochemical challenges posed by these  
intricate and densely functionalized cyclo-  
pentanes will be discussed.

## SHORT COMMUNICATIONS

The synthesis of the C11–C23 fragment of dictyostatin proceeded in good overall yield after 15 steps for the longest linear sequence.



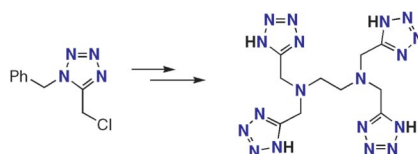
### Antitumor Agents

L. C. Dias,\* D. J. P. Lima,  
C. C. S. Gonçalves,  
A. D. Andricopulo ..... 1491–1494

Synthesis of the C11–C23 Fragment of the Potent Antitumor Agent Dictyostatin

**Keywords:** Total synthesis / Natural products / Aldol reactions / Lactones / Olefination

A synthon for the convergent introduction of a protected tetrazole moiety into nucleophile-bearing molecules is presented. Benzyl deprotection is accomplished under neutral conditions. The usual in situ establishment of the tetrazole moiety is thus avoided, as is the lack of regioselective control during subsequent protection. The exemplary synthesis of a new isoelectronic analogue of EDTA is presented.



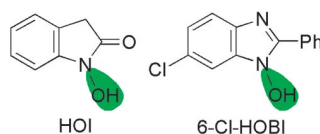
### Tetrazolyl Synthons

F. Touti, P. Maurin,  
J. Hasseroth\* ..... 1495–1498

A Tetrakis(tetrazolyl) Analogue of EDTA

**Keywords:** Nitrogen heterocycles / Protecting groups / Isosteres / N ligands

Cheap and convenient replacement additives for the explosive HOBt are reported to be used in peptide synthesis.

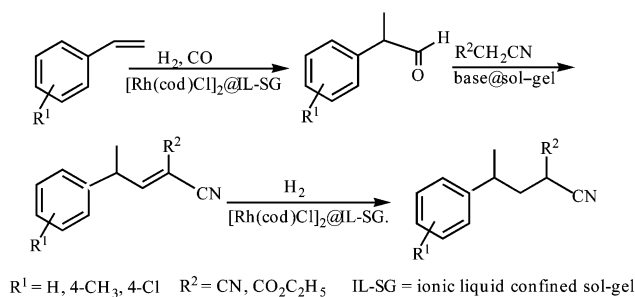


### HOBt Replacements

A. El-Faham,\* F. Albericio\* ... 1499–1501

Synthesis and Application of *N*-Hydroxylamine Derivatives as Potential Replacements for HOBt

**Keywords:** Amino acids / Coupling reagents / *N*-Hydroxylamine derivatives / Peptides / Racemization



### One-Pot Reactions

K. Hamza, H. Schumann,\*  
J. Blum\* ..... 1502–1505

One-Pot, Selective Hydroformylation, Condensation, and Hydrogenation Processes by a Sol–Gel Entrapped Rhodium Complex, an Immobilized Base, and an Ionic Liquid

**Keywords:** Hydroformylation / Hydrogenation / Ionic liquids / Rhodium

In the presence of  $[\text{Rh}(\text{cod})\text{Cl}]_2$  that has been entrapped within an ionic liquid confined silica sol–gel, styrene derivatives were hydroformylated at 80° C to selectively give branched aldehydes that undergo, within

the same pot, condensation with active methylene compounds followed by hydrogenation of the resulting unsaturated products.

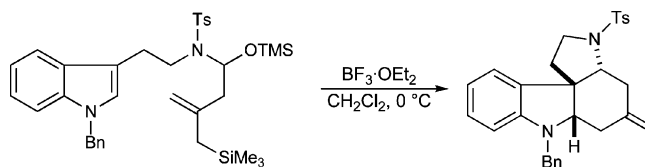
# CONTENTS

## Synthetic Methods

R. Delgado, S. B. Blakey\* ..... 1506–1510



Cascade Annulation Reactions To Access the Structural Cores of Stereochemically Unusual Strychnos Alkaloids



**Keywords:** Malagashanine / Strychnos / Alkaloids / Iminium / Cascade / Annulation / Reaction mechanisms / Polycycles / Natural products

A versatile cascade sequence provides rapid access to the core structure of the stereochemically unusual Malagashanine

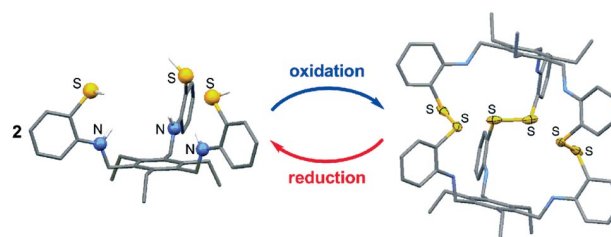
alkaloids. Amide reduction provides access to particularly sensitive iminium ions, facilitating this cascade process.

## Dynamic Covalent Chemistry

Y.-C. Horng,\* T.-L. Lin, C.-Y. Tu,  
T.-J. Sung, C.-C. Hsieh, C.-H. Hu,  
H. M. Lee, T.-S. Kuo ..... 1511–1514



Preparation of a Reversible Redox-Controlled Cage-Type Molecule Linked by Disulfide Bonds



**Keywords:** Dimerization / Self-assembly / Sulfur / Preorganization

A trithiol macromolecule, comprising an intrinsic conformational propensity for dimerization (molecular capsule) as opposed to oligomerization upon oxidation, was effortlessly prepared through rational design.

The X-ray structure of the molecular capsule represents the first successful example of a redox-controlled reversible dimeric capsule linked through covalent disulfide bonds.

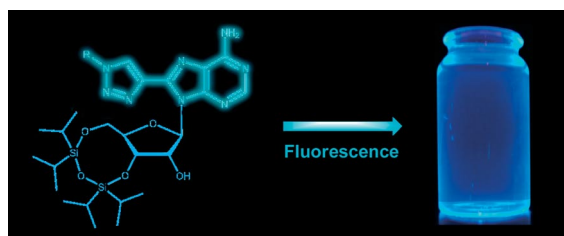
# FULL PAPERS

## Fluorescent Nucleoside Analogues

C. Dyrager, K. Börjesson, P. Dinér, A. Elf,  
B. Albinsson, L. M. Wilhelmsson,  
M. Grötl\* ..... 1515–1521



Synthesis and Photophysical Characterisation of Fluorescent 8-(1*H*-1,2,3-Triazol-4-yl)adenosine Derivatives



**Keywords:** Nucleoside derivatives / Click chemistry / Sonogashira coupling / Fluorescence / Triazoles / Nitrogen heterocycles / Density functional calculations

Substituted adenosine derivatives have been synthesised by using Sonogashira cross-coupling and click chemistry. The nu-

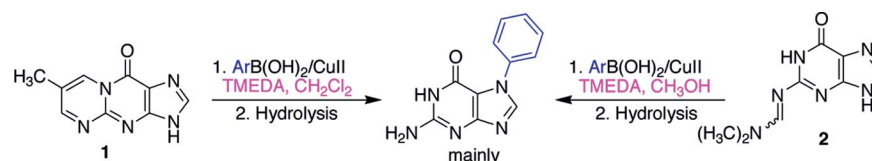
cleoside analogues show high absorptivities and high fluorescence quantum yields in organic as well as in water solution.

## N<sup>7</sup>-Arylguanines and -Adenines

R. Keder, H. Dvořáková,  
D. Dvořák\* ..... 1522–1531



New Approach to the Synthesis of N<sup>7</sup>-Arylguanines and N<sup>7</sup>-Aryladenines

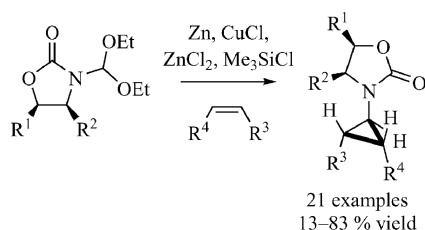


**Keywords:** Nucleobases / Nitrogen heterocycles / Copper / Boron

The copper-mediated arylation of 7-methylpyrimido[1,2-*a*]purin-10(3*H*)-one (**1**) in dichloromethane or of N<sup>2</sup>-(dimethylamino)methyleneguanine (**2**) in methanol

in the presence of TMEDA and subsequent hydrolysis leads to the preferential formation of 7-arylguanines. 7-Aryladenines can similarly be prepared.

A versatile method is described for the synthesis of a range of enantiopure amino- and amido-cyclopropanes, through the generation of organozinc carbenoids from *N*-(diethoxymethyl)oxazolidinones.



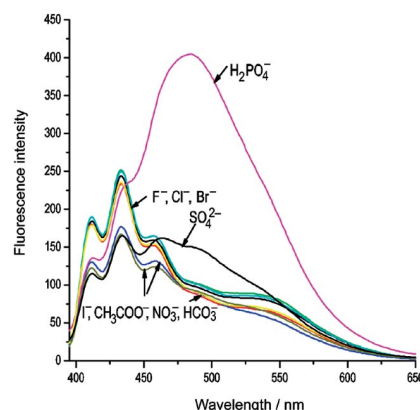
G. Bégis, D. E. Cladingboel, L. Jerome,  
W. B. Motherwell,\*  
T. D. Sheppard ..... 1532–1548

Asymmetric Synthesis of Aminocyclopropanes and *N*-Cyclopropylamino Alcohols Through Direct Amidocyclopropanation of Alkenes Using Chiral Organozinc Carbenoids

**Keywords:** Cyclopropanes / Chiral auxiliaries / Alkenes / Carbenoids / Zinc

## Fluorescent Chemosensors

The recognition ability of novel receptor 1·2Zn towards various anions has been studied. The receptor displays an excellent selective fluorescent enhancement of the excimer emissive peak with H<sub>2</sub>PO<sub>4</sub><sup>−</sup> that is absent with other inorganic anions in water.

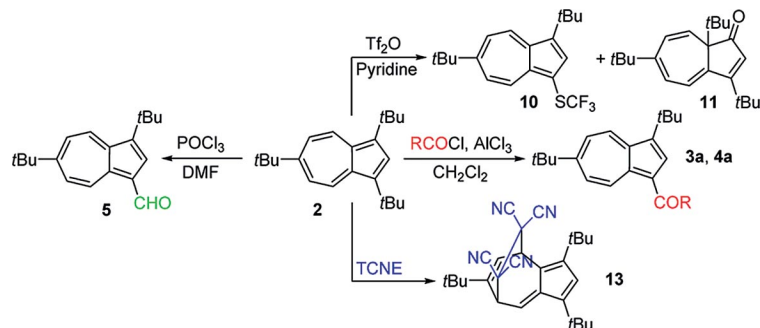


X.-H. Huang, Y.-B. He,\* C.-G. Hu,  
Z.-H. Chen ..... 1549–1553

A Selective Metal–Ligand Fluorescent Chemosensor for Dihydrogen Phosphate via Intermolecular Excimer Formation in Water

**Keywords:** Anions / Receptors / Fluorescence / Sensors / Chemosensors / Supramolecular chemistry

## Azulene Chemistry



T. Shoji,\* S. Ito, T. Okujima, J. Higashi,  
R. Yokoyama, K. Toyota, M. Yasunami,  
N. Morita\* ..... 1554–1563

Electrophilic *ipso*-Substitution and Some Unique Reaction Behavior of 1,3,6-Tri-*tert*-butylazulene

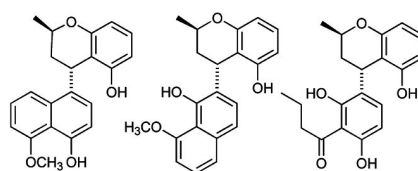
**Keywords:** Azulenes / *ipso*-Substitution / Cycloaddition / Electrochemistry / Aromatic substitution

Friedel–Crafts and Vilsmeier reactions of 1,3,6-tri-*tert*-butylazulene (2) gave the corresponding *ipso*-substitution products 3a, 4a and 5, respectively, in moderate to excellent yields. Treatment of 2 with TPT unexpectedly afforded 1-(trifluoromethyl)thio-

azulene 10 and 1(8*H*)-azulenone 11. Compound 2 also reacted with TCNE to give cycloaddition product 13 in excellent yield, rather than the *ipso*-substitution reaction product.

## Fungal Natural Products

The hitherto unknown nodulisporins D–F were isolated from the culture broth of *Nodulisporium* sp. A naphthalene moiety is coupled to different sites of a chroman or an open-chain analogue. Interestingly, the “monomeric” parts or closely related compounds were also isolated. This example demonstrates the increase of quantity and quality of chemical diversity by coupling of monomeric units.



J. Dai, K. Krohn,\* S. Draeger,  
B. Schulz ..... 1564–1569

New Naphthalene-Chroman Coupling Products from the Endophytic Fungus, *Nodulisporium* sp. from *Erica arborea*

**Keywords:** Natural products / Fungal secondary metabolites / Nodulisporins D–F / *Nodulisporium* sp. / Structural elucidation / Bioactivity

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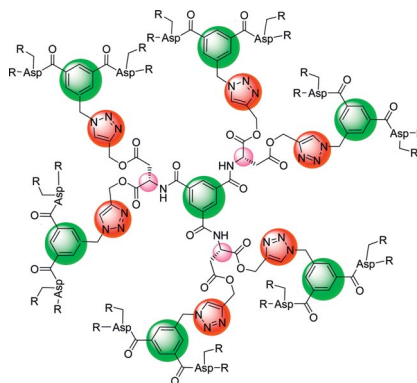
## Designer Dendrimers

V. Haridas,\* Y. K. Sharma,  
S. Naik ..... 1570–1577



Multi-Tier Dendrimers with an Aromatic Core

**Keywords:** Dendrimers / Click reactions / Heterocycles / Amino acids



Multi-tier designer dendritic molecules that incorporate an aromatic core and heterocyclic and peptide units have been synthesized. The versatility of the synthesis has been illustrated by the synthesis of various symmetrical, unsymmetrical and cationic dendrimers on an aromatic core. The synthesis of such dendrimers will be useful for generating molecules with various functions.

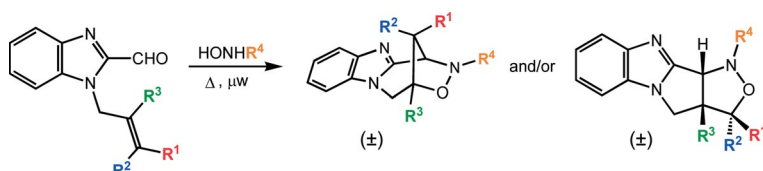
## Intramolecular Dipolar Cycloadditions

L. Meng, S. C. Wang, J. C. Fetting,  
M. J. Kurth,\* D. J. Tantillo\* ... 1578–1584



Controlling Selectivity for Cycloadditions of Nitrones and Alkenes Tethered by Benzimidazoles: Combining Experiment and Theory

**Keywords:** Nitrones / Cycloaddition / Quantum chemical calculations / Stereoselectivity / Substituent effects / Transition states



Theory and experiment were used synergistically to pinpoint the effects of substituents on intramolecular cycloadditions of alkenes with in-situ generated nitrones that

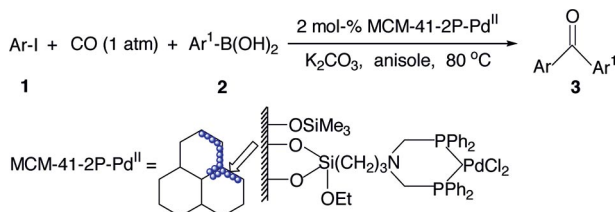
can produce two different polyheterocyclic scaffolds that position their arrays of functional groups in well-defined but different orientations.

## Carbonylative Coupling Reactions

M. Cai,\* G. Zheng, L. Zha,  
J. Peng ..... 1585–1591

Carbonylative Suzuki–Miyaura Coupling of Arylboronic Acids with Aryl Iodides Catalyzed by the MCM-41-Supported Bidentate Phosphane Palladium(II) Complex

**Keywords:** Carbonylation / Cross coupling / Supported catalysts / Palladium / Ketones



An MCM-41-supported bidentate phosphane palladium(II) complex (MCM-41-2P-Pd<sup>II</sup>) exhibits higher activity and selectivity than [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] in the carbo-

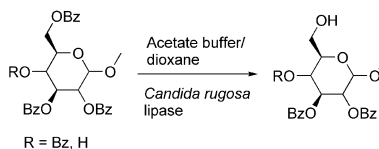
nylative Suzuki–Miyaura cross-coupling reactions of arylboronic acids with aryl iodides and can be reused at least 10 times without any decrease in activity.

## Regioselective Hydrolysis

A. Esmurziev, E. Sundby,  
B. H. Hoff\* ..... 1592–1597

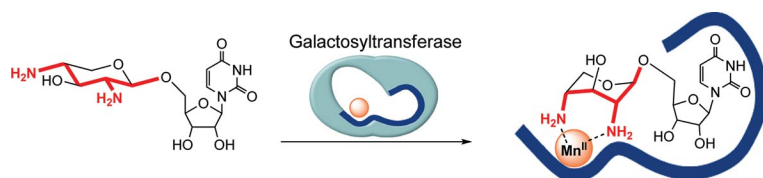
Regioselective C-6 Hydrolysis of Methyl *O*-Benzoyl-pyranosides Catalysed by *Candida Rugosa* Lipase

**Keywords:** Carbohydrates / Glycosides / Biocatalysis / Hydrolysis / Enzyme catalysis / *Candida rugosa* lipase



The first examples of enzymatic regioselective hydrolysis of methyl *O*-benzoyl-pyranosides are reported. Using *Candida rugosa* lipase as catalyst, the gluco-, galacto-, and mannopyranosides were hydrolysed regioselectively at C-6. The reaction rate was dependant among others on pyranoside structure. The highest yields were obtained for the  $\alpha$ -D-galacto-,  $\beta$ -D-galacto- and  $\alpha$ -D-glucopyranosides





Conjugates of 2,4-diamino sugars and uridine have been synthesized as galactosyltransferase inhibitors. Their inhibition activities appear to be influenced by their

conformational flexibility and thus their chelation abilities towards  $\text{Mn}^{\text{II}}$  within the structure of GalT.

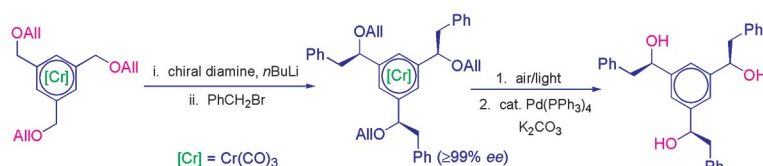
N. Mitsuhashi, H. Yuasa\* ..... 1598–1605

A Novel Galactosyltransferase Inhibitor with Diamino Sugar as a Pyrophosphate Mimic



**Keywords:** Bioorganic chemistry / Inhibitors / Glycoconjugates / Enzymes / Chelation

## Asymmetric Synthesis



The tricarbonylchromium(0) complexes of benzyl allyl ethers undergo enantioselective deprotonation/alkylation reactions to give

enantioenriched imidazole alcohols, a triol and a tertiary alcohol after removal of the allyl group.

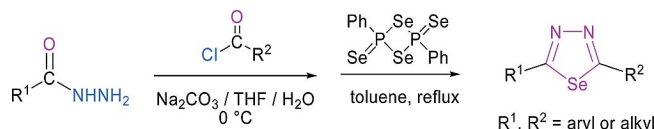
K. Abecassis, S. E. Gibson,\*  
M. Martin-Fontecha ..... 1606–1611

Synthesis of Enantioenriched Secondary and Tertiary Alcohols via Tricarbonylchromium(0) Complexes of Benzyl Allyl Ethers



**Keywords:** Alcohols / Allylic compounds / Chiral base / Chromium / Enantioselectivity / Alkylation

## Organoselenium Chemistry



An efficient two-step method for the preparation of a series of novel 2,5-disubstituted 1,3,4-selenadiazoles by selenating with Woollins' reagent (**WR**) is reported. Six

examples, representing the first of this class, have been characterised crystallographically.

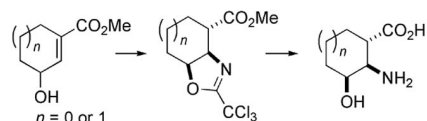
G. Hua, Y. Li, A. L. Fuller,  
A. M. Z. Slawin,  
J. D. Woollins\* ..... 1612–1618

Facile Synthesis and Structure of Novel 2,5-Disubstituted 1,3,4-Selenadiazoles

**Keywords:** Selenium / Organoselenium chemistry / 1,3,4-Selenadiazoles / Woollins' reagent

## Intramolecular Conjugate Additions

Trichloroacetimidates undergo stereoselective intramolecular conjugate addition reactions to produce oxazolines. The resulting oxazolines can in a very concise way be converted into 2-amino-3-hydroxycycloalkanecarboxylic acids.



Y. Matsushima,\* J. Kino ..... 1619–1624

New Concise Route to 2-Amino-3-hydroxycycloalkanecarboxylic Acids by Imidate-Mediated Intramolecular Conjugate Addition



**Keywords:** Amino acids / Heterocycles / Intramolecular conjugate addition / Stereoselectivity

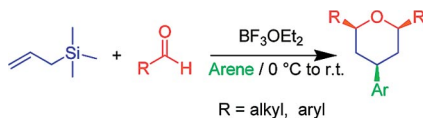
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## Substituted Aryltetrahydropyrans

U. C. Reddy, S. Bondalapati,  
A. K. Saikia\* ..... 1625–1629



Stereoselective Synthesis of 2,6-Disubstituted-4-Aryltetrahydropyrans Using Sakurai–Hosomi–Prins–Friedel–Crafts Reaction



The reaction of aldehydes with allyltrimethylsilane afforded 2,6-disubstituted-4-aryltetrahydropyrans through a Sakurai–Hosomi–Prins–Friedel–Crafts sequence. The reaction was highly stereoselective.

**Keywords:** Multicomponent reactions / Diastereoselectivity / Cyclization / Oxygen heterocycles

## CORRECTION

J. J. Eisch,\* P. O. Fregene ..... 1631

Vanadium(I) Chloride and Lithium Vanadium(I) Dihydride as Selective Epimetalating Reagents for  $\pi$ - and  $\sigma$ -Bonded Organic Substrates

**Keywords:** Vanadium(I) chloride / Lithium vanadium(I) dihydride / Epimetallation / Cleavage of carbon-heteroatom bonds / Reductive dimerization

\* 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 9 were published online on March 2, 2009