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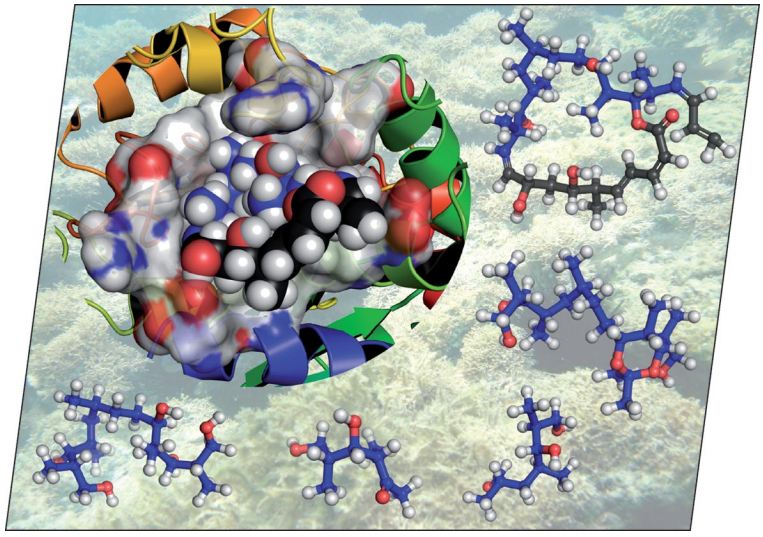
COVER PICTURE

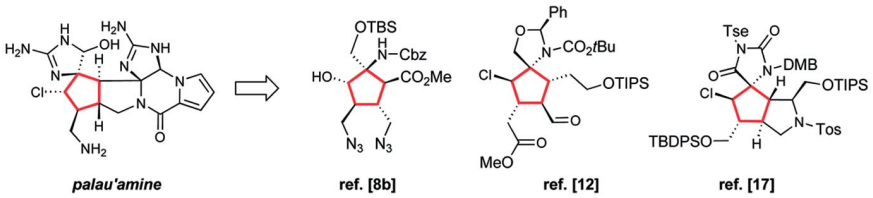
The cover picture shows the intermolecular interactions between the marine-derived dictyostatin and the β-tubulin binding site, as well as some important molecular fragments of the required 15-step sequence to produce the C11−C23 fragment (highlighted in blue) of dictyostatin in good overall yield. Dictyostatin, 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 β-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. Lívia B. Salum for her contribution to the design of the cover picture.



EDITORIAL SURVEY

MICROREVIEW

Total Synthesis



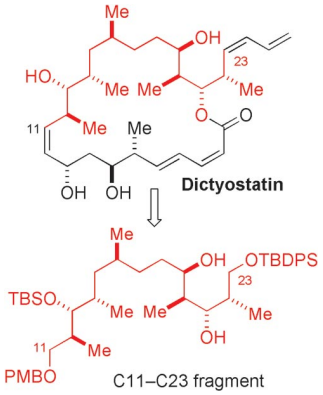
A hexa-substituted chlorocyclopentane framework is common to a variety of dimeric marine alkaloids of the oroidin family. In the pursuit of synthons for oroidin dimers such as palau'amine, the stereocontrolled synthesis of complex C_5 rings has seen a renaissance in recent years. Stereochemical challenges posed by these intricate and densely functionalized cyclopentanes will be discussed.

EurJOC European Journal of Organic Chemistry

SHORT COMMUNICATIONS

Antitumor Agents

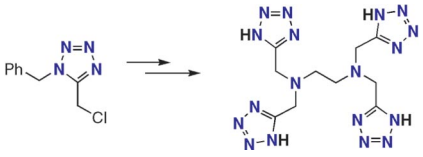
The synthesis of the C11−C23 fragment of dictyostatin proceeded in good overall yield after 15 steps for the longest linear sequence.



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

Tetrazolyl Synthons

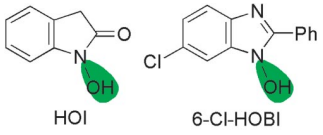
A synthon for the convergent introduction of a protected tetrazole moiety into nucleophile-bearing molecules is presented. Benzyl deprotection is accomplished under neutral conditions. The usual in situ establishment of the tetrazole moiety is thus avoided, as is the lack of regioselective control during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



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

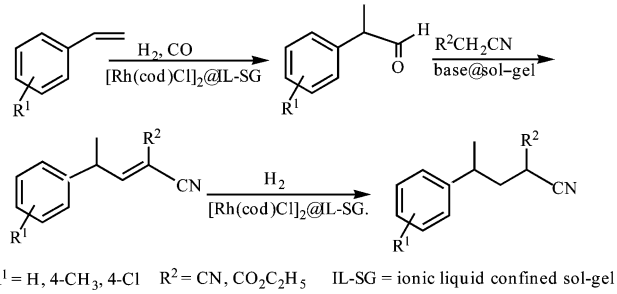
HOBt Replacements

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



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

One-Pot Reactions



In the presence of $[Rh(cod)Cl]_2$ 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.

Keywords: Hydroformylation / Hydrogenation / Ionic liquids / Rhodium

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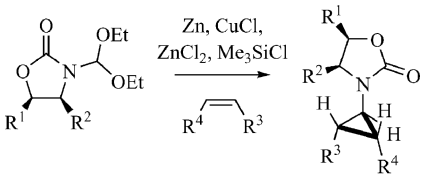
FULL PAPERS

Chiral Aminocyclopropanes

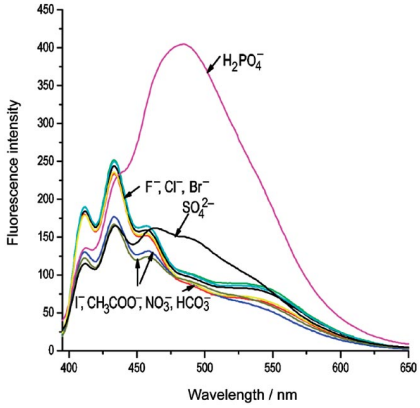
A versatile method is described for the synthesis of a range of enantiopure amino- and amido-cyclopropanes, through the generation of organozinc carbenoids from *N*-(diethoxymethyl)oxazolidinones.



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

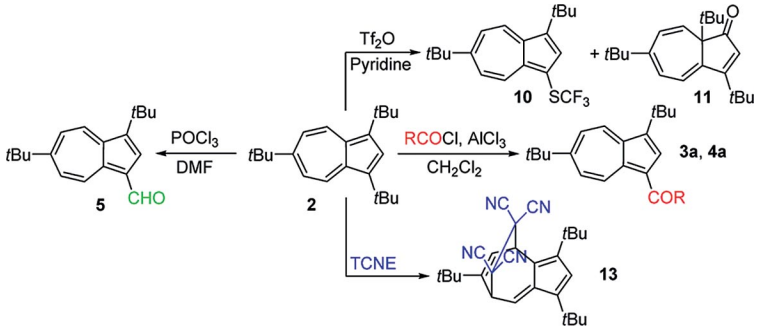
Fluorecent Chemosensors

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 $H_2PO_4^-$ that is absent with other inorganic anions in water.



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

Azulene Chemistry

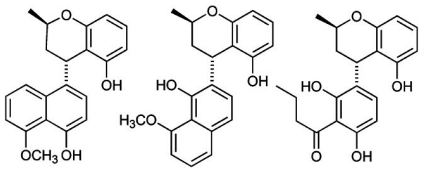


Friedel–Crafts and Vilsmeier reactions of 1,3,6-tri-*tert*-butylazulene (**2**) gave the corresponding *ipso*-substitution products **3a**, **4a** and **5**, respectively, in moderate to excellent yields. Treatment of **2** with TPT unexpectedly afforded 1-(trifluoromethyl)thioazulene **10** and 1(8*H*)-azulenone **11**. Compound **2** also reacted with TCNE to give cycloaddition product **13** in excellent yield, rather than the *ipso*-substitution reaction product.

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

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.



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

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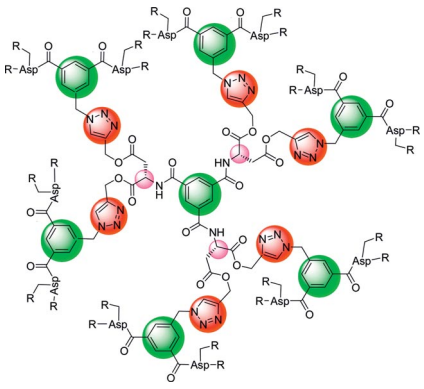
Designer Dendrimers

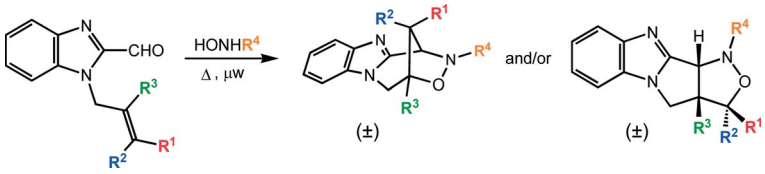
Keywords: Dendrimers / Click reactions / Heterocycles / Amino acids



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

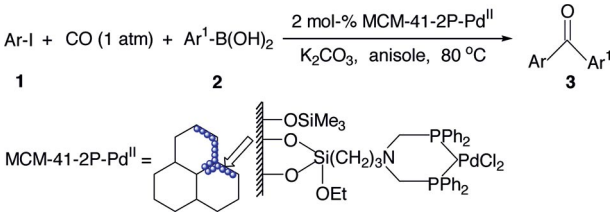
Keywords: Nitrones / Cycloaddition / Quantum chemical calculations / Stereoselectivity / Substituent effects / Transition states



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

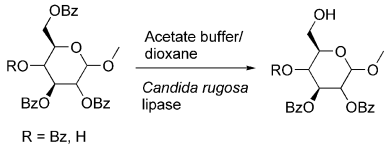
Keywords: Carbonylation / Cross coupling / Supported catalysts / Palladium / Ketones



An MCM-41-supported bidentate phosphane palladium(II) complex (MCM-41-2P-Pd^{II}) exhibits higher activity and selectivity than $[PdCl_2(PPh_3)_2]$ in the carbonylative Suzuki–Miyaura cross-coupling reactions of arylboronic acids with aryl iodides and can be reused at least 10 times without any decrease in activity.

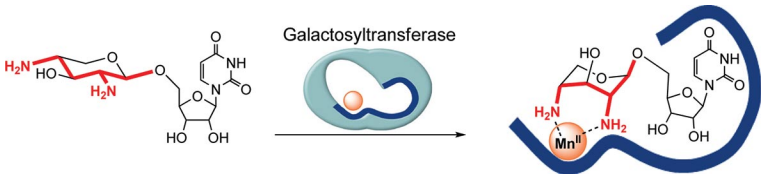
Regioselective Hydrolysis

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 α-D-galacto-, β-D-galacto- and α-D-glucopyranosides

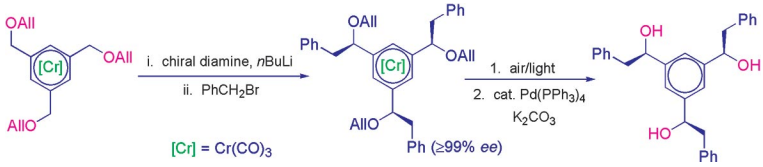
Enzyme Inhibition



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

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 Mn^{II} within the structure of GalT.

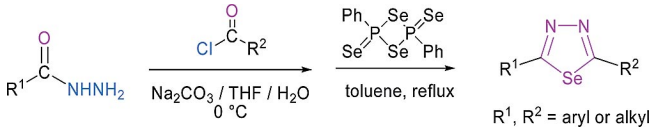
Asymmetric Synthesis



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

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.

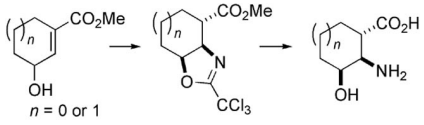
Organoselenium Chemistry



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

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.

Intramolecular Conjugate Additions



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

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

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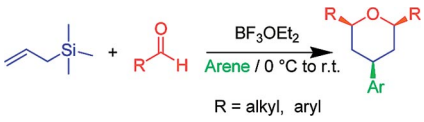
Substituted Aryltetrahydropyrans



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

CORRECTION

* 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

