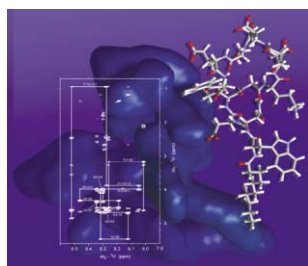


Organic & Biomolecular Chemistry

INDEXED IN MEDLINE

Incorporating Acta Chemica Scandinavica

**Cover**

See Lee-Jon Ball, Catherine M. Gault, James A. Donarski, Jason Micklefield and Vasudevan Ramesh, pp. 1872–1878

The cover diagram illustrates the 3D structure of daptomycin, a calcium dependent lipopeptide antibiotic recently approved for clinical use, based on NMR spectral data. The acidic residues (Asp and MeGlu) in the structure are not in close proximity which suggests that Ca^{2+} may serve as a neutralising bridge between daptomycin molecules during assembly into a larger complex.

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contents

C49 C56

Chemical Science

July 2004/Volume 1/Issue 7

www.rsc.org/chemicalscience

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a 'snapshot' of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

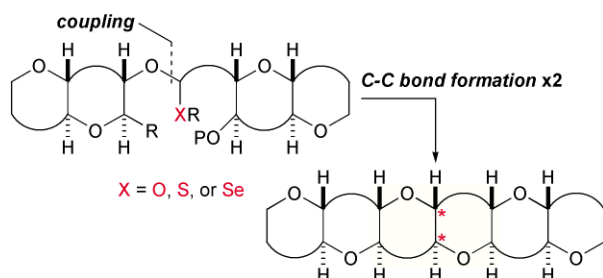
1811 1817

PERSPECTIVE

Convergent syntheses of polycyclic ethers. Illustrations of the utility of acetal-linked intermediates

Masayuki Inoue

Application of convergent methodology using an acetal-linkage as a key motif culminated in the total syntheses of gambierol and ciguatoxin CTX3C.

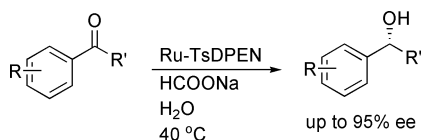


1818 1821

Accelerated asymmetric transfer hydrogenation of aromatic ketones in water

Xiaofeng Wu, Xiaoguang Li, William Hems, Frank King and Jianliang Xiao

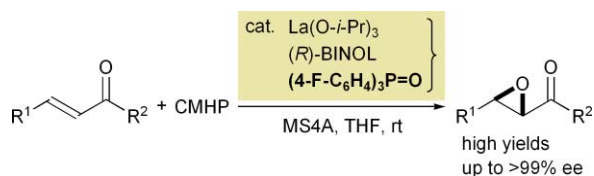
Water is shown to be an excellent solvent for the asymmetric transfer hydrogenation of aromatic ketones by Noyori's Ru-TsDPEN catalyst.



1822 1824

Remarkable effect of tris(4-fluorophenyl)phosphine oxide on the stabilization of chiral lanthanum complex catalysts. A new and practical protocol for the highly enantioselective epoxidation of conjugated enones

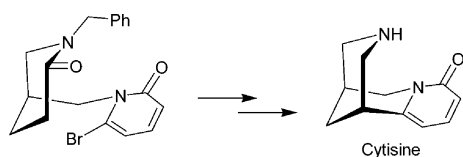
Rie Kino, Kazuhiro Daikai, Toshio Kawanami, Hiroshi Furuno and Junji Inanaga

A new and efficient chiral La-catalyst system was developed for highly enantioselective epoxidation of α,β -unsaturated ketones.

1825 1826

A short synthesis of (\pm)-cytisine

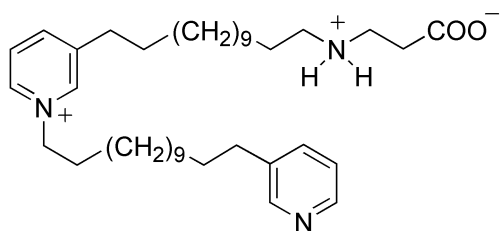
Candice Botuha, Carl M. S. Galley and Timothy Gallagher

The synthesis of racemic cytisine has been achieved using a Pd(0) mediated intramolecular lactam to α -arylation as a key step.

1827 1830

Viscosaline: new 3-alkyl pyridinium alkaloid from the Arctic sponge *Haliclona viscosa*

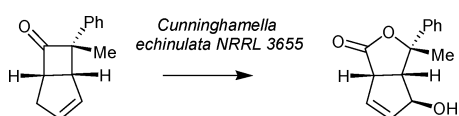
Christian A. Volk and Matthias Köck

The chemical investigation of the Arctic sponge *Haliclona viscosa* and structure elucidation of the acyclic 1,3-dialkyl pyridinium alkaloid viscosaline is described. A novel structural motif of viscosaline is that β -alanine is covalently bound to one alkyl chain.

1831 1833

A one-pot remote allylic hydroxylation and Baeyer–Villiger oxidation of a bicyclo[3.2.0]hept-2-en-6-one by *Cunninghamella echinulata* NRRL 3655

Ian J. S. Fairlamb, Stephanie Grant, Gideon Grogan, David A. Maddrell and Josephine C. Nichols

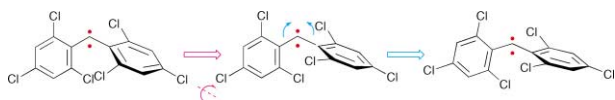
7-*exo*-Methyl-7-*endo*-phenylbicyclo[3.2.0]hept-2-en-6-one undergoes Baeyer–Villiger and allylic oxidation, to yield a novel hydroxylactone in good yield by *Cunninghamella echinulata* NRRL 3655, representing a one step biocatalytic access to a cyclopentanoid scaffold with three chiral centres. Interestingly, allylic oxidation occurs with transposition of the double bond.

1834 1837

An ESR insight into the thermally activated structural relaxation of the bis(2,4,6-trichlorophenyl)carbene in relation to the molecular mobility of the immediate surroundings

Boris P. Makarov and Hideo Tomioka

Sterically congested triplet diphenylcarbene undergoes geometrical relaxation in a rigid matrix upon warming, first by twisting the phenyl rings, followed by expanding the central carbenic angle.

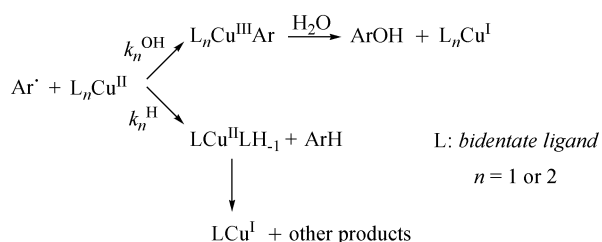


1838 1855

Promotion of Sandmeyer hydroxylation (homolytic hydroxydediazoniatio) and hydrodediazoniatio by chelation of the copper catalyst: bidentate ligands

Peter Hanson, Simon C. Rowell, Paul H. Walton and Allan W. Timms

Equatorial ligands on a Cu(II) ion hinder the interaction of its SOMO with that of an attacking aryl radical.

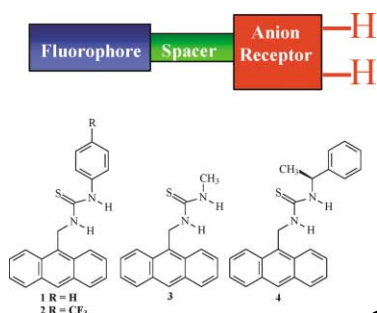


1856 1863

Design, synthesis and photophysical studies of simple fluorescent anion PET sensors using charge neutral thiourea receptors

Thorfinnur Gunnlaugsson, Anthony P. Davis, Gillian M. Hussey, Juliann Tierney and Mark Glynn

The fluorescent PET chemosensors 1–4 were developed for the detection of anions such as acetate, fluoride and phosphate in organic solvents. The anion recognition occurs through hydrogen bonding between the anion and the thiourea moiety, giving rise to PET quenching of the anthracene excited state.

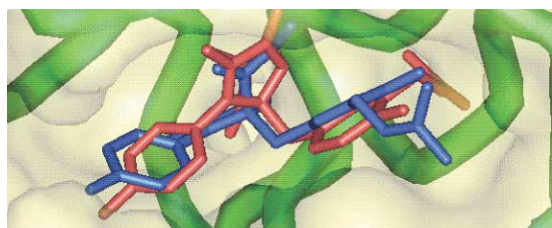


1864 1871

Synthesis and biological evaluation of analogues of butyrolactone I and molecular model of its interaction with CDK2

Miguel F. Braña, M. Luisa García, Berta López, Beatriz de Pascual-Teresa, Ana Ramos, Jose M. Pozuelo and M. Teresa Domínguez

Analogues of butyrolactone I have been synthesized and a molecular model of its interaction with CDK2 has been built.

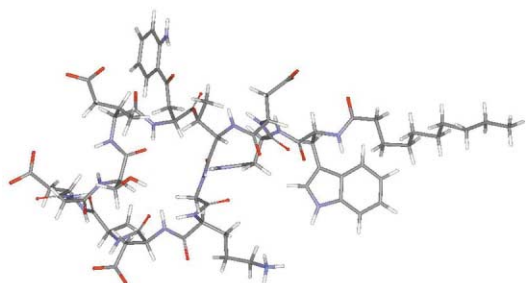


1872 1878

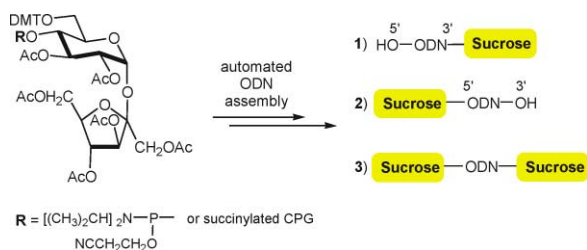
NMR structure determination and calcium binding effects of lipopeptide antibiotic daptomycin

Lee-Jon Ball, Catherine M. Goult, James A. Donarski, Jason Micklefield and Vasudevan Ramesh

The first NMR structure of daptomycin and calcium induced spectral perturbations highlight the role of aggregation in the antibiotic's activity.



1879 1886

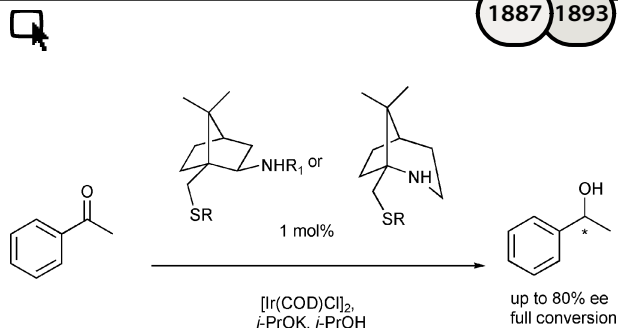


Modulating the activity of oligonucleotides by carbohydrate conjugation: solid phase synthesis of sucrose-oligonucleotide hybrids

Matteo Adinolfi, Lorenzo De Napoli, Giovanni Di Fabio, Alfonso Iadonisi and Daniela Montesarchio

The sucrose units at both ends of selected oligonucleotide sequences were shown to increase their chemical and enzymatic stability, while not interfering with duplex formation and with the ability of G-rich sequences to adopt a quadruplex structure.

1887 1893

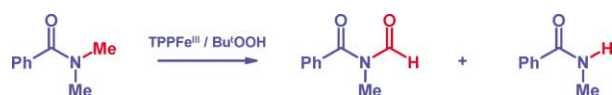


Development of new camphor based N,S chiral ligands and their application in transfer hydrogenation

Arnaud Gayet, Christelle Bolea and Pher G. Andersson

This work describes the preparation of new classes of chiral N,S-containing ligands and their evaluation in transfer hydrogenation.

1894 1900

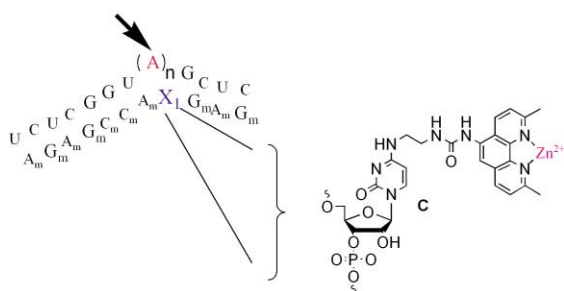


Oxidation of tertiary benzamides by 5,10,15,20-tetraphenylporphyrinatoiron^{III} chloride-*tert*-butylhydroperoxide

Luis Constantino and Jim Iley

The major reaction products are *N*-acylamides, although small amounts of secondary amides, the products of dealkylation, are also formed. We propose that these reactions proceed *via* hydrogen atom abstraction to form an α -carbon-centred radical.

1901 1907

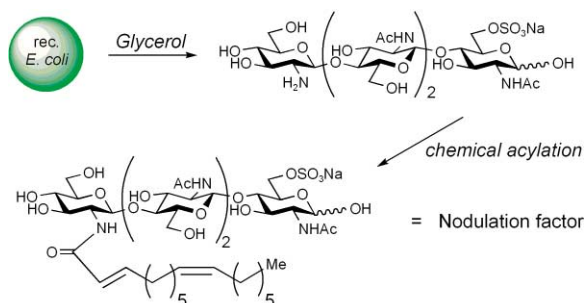


Synthesis of new OBAN's and further studies on positioning of the catalytic group

Hans Åström and Roger Strömberg

The current study is a continuation of our efforts to evaluate linkers and the syntheses of two new OBAN's are described.

1908 1910

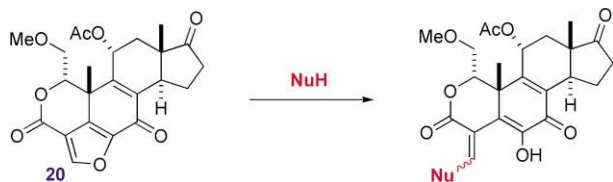


New access to lipo-chitooligosaccharide nodulation factors

Martin Ohsten Rasmussen, Bridget Hogg, Jean-Jacques Bono, Eric Samain and Hugues Driguez

Sulfonated and non-sulfonated lipo-chitooligosaccharides involved in *Sinorhizobium meliloti*-legume symbiosis are efficiently obtained on a multi mg scale by a 2-step procedure combining biotechnological and chemical approaches.

1911 1920

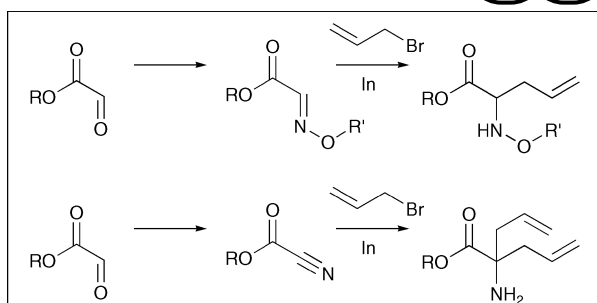


Synthesis and biological evaluation of synthetic viridins derived from C(20)-heteroalkylation of the steroidal PI-3-kinase inhibitor wortmannin

Peter Wipf, Daniel J. Minion, Robert J. Halter, Margareta I. Berggren, Caroline B. Ho, Gary G. Chiang, Lynn Kirkpatrick, Robert Abraham and Garth Powis

Several subnanomolar PI-3-kinase inhibitors with lower liver toxicity and greater promise for inhibition of tumor cell growth than wortmannin were discovered among a library of 99 viridin analogs prepared by nucleophilic addition at C(20) of the natural product.

1921 1933

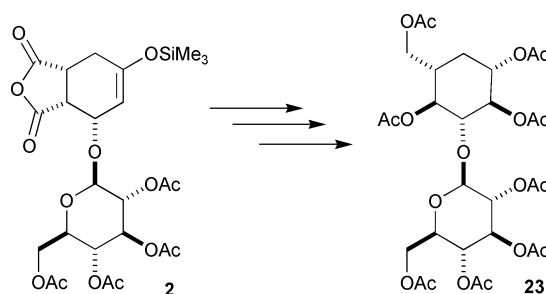


Indium mediated allylation of glyoxylate oxime ethers, esters and cyanofornates

Dougal J. Ritson, Russell J. Cox and John Berge

An indium mediated procedure has been developed for the allylation of activated *O*-functionalised oximes and nitriles as exemplified by a variety of glyoxylate derivatives.

1934 1942

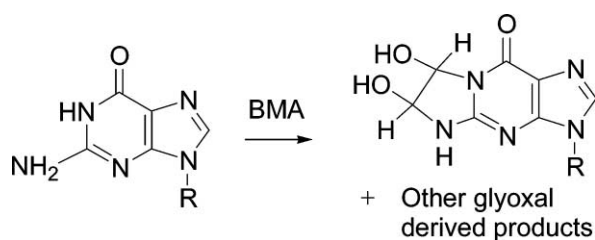


Studies related to carba-pyranoses: a radical decarboxylation approach to monocarba-disaccharides

David S. Larsen, Roger J. Lins, Richard J. Stoodley and Nicholas S. Trotter

(1→1), (1→3) and (1→4) acetal-linked monocarba-disaccharides have been synthesised from cycloadduct **2** using radical decarboxylation of intermediary γ - and δ -lactonic acids in the key step.

1943 1950



Reactions of 9-substituted guanines with bromomalondi-aldehyde in aqueous solution predominantly yield glyoxal-derived adducts

Anne-Mari Ruohola, Niangoran Koissi, Sanna Andersson, Iona Lepistö, Kari Neuvonen, Satu Mikkola and Harri Lönnberg

The main products were isolated and characterized by ^1H and ^{13}C NMR and mass spectroscopy. The final products formed under acidic and basic conditions were different, but they shared the common feature of being derived from glyoxal.

1951

Caroline D. Cox, John R. Malpass, John Gordon and Alan Rosen

Synthesis of epibatidine isomers: *endo*-5- and 6- (6'-chloro-3'-pyridyl-2-azabicyclo[2.2.1]heptanes



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