

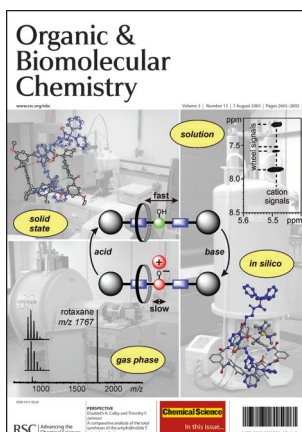
In this issue...

New linkers for solid phase synthesis

A new class of linkers that not only tether the substrate to a polymer support but also play a key role in product formation. See Procter *et al.* pp. 2805–2816.



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: www.rsc.org/chembiol



Cover

See Pradyut Ghosh, Guido Federwisch, Michael Kogej, Christoph A. Schalley, Detlev Haase, Wolfgang Saak, Arne Lützen and Ruth M. Gschwind, pp. 2691–2700. The cover depicts the combination of different methods for studying the rate of shuttling motions in [2]rotaxanes, controlled by electrostatic interactions.

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CHEMICAL SCIENCE

C57

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.

Chemical Science

August 2005/Volume 2/Issue 8

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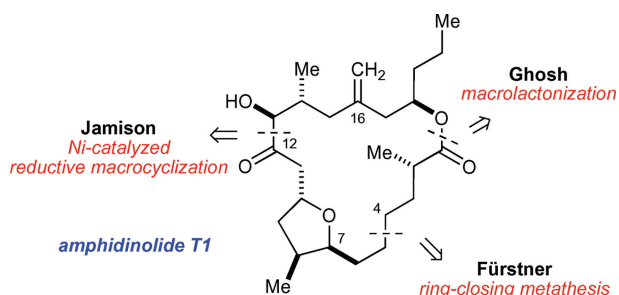
PERSPECTIVE

2675

A comparative analysis of the total syntheses of the amphidinolide T natural products

Elizabeth A. Colby and Timothy F. Jamison*

We compare and contrast the strategies and tactics used by three laboratories in syntheses of the amphidinolide T natural products.



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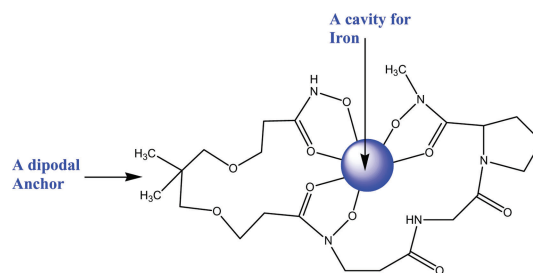
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2685

Synthesis and biological evaluation of lipophilic iron chelators as protective agents from oxidative stress

Eylon Yavin, Raghavendra Kikkiri, Shosh Gil, Rina Arad-Yellin, Ephraim Yavin and Abraham Shanzer*

Lipophilic iron(III) chelators were shown to protect oligodendrial cells from $\text{Fe}^{III}/\text{H}_2\text{O}_2$ -induced oxidative stress. In comparison to Desferal, one synthetic analog was significantly more effective according to a cell survival assay.

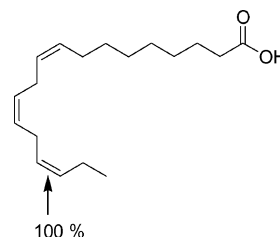


2688

Enantioselective epoxidation of linolenic acid catalysed by cytochrome P450_{BM3} from *Bacillus megaterium*

Ayhan Çelik, Davide Sperandio, Robert E. Speight and Nicholas J. Turner*

Linolenic acid is epoxidised with 100% regioselectivity and moderate (60% ee) enantioselectivity using cytochrome P450 from *Bacillus megaterium*.



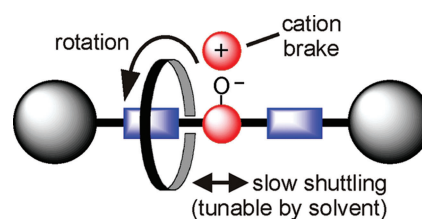
ARTICLES

2691

Controlling the rate of shuttling motions in [2]rotaxanes by electrostatic interactions: a cation as solvent-tunable brake

Pradyut Ghosh, Guido Federwisch, Michael Kogej, Christoph A. Schalley,* Detlev Haase, Wolfgang Saak, Arne Lützen* and Ruth M. Gschwind*

Solvent-tunable electrostatic interactions between a phenolate in the center of a rotaxane axle and the corresponding counterion permit control of the shuttling rate of the rotaxane wheel.

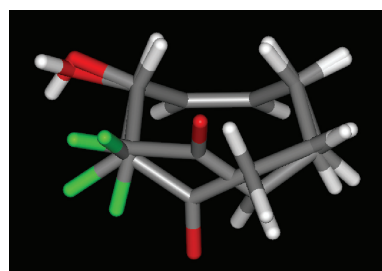


2701

Towards novel difluorinated sugar mimetics; syntheses and conformational analyses of highly-functionalised difluorinated cyclooctenones

Gerry A. Griffith, Jonathan M. Percy,* Stéphane Pintat, Clive A. Smith, Neil Spencer and Emi Uneyama

Difluorinated cyclooctenones adopted a remarkably limited range of conformers which were examined by VT NMR (NOESY/ROESY) and electronic structure calculations.

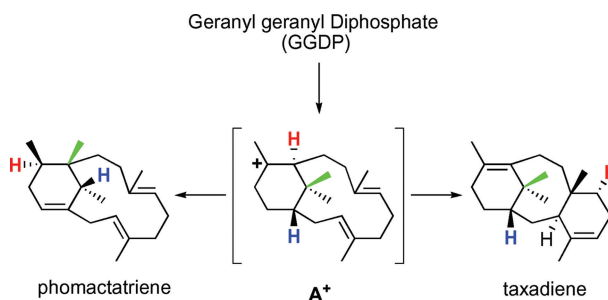


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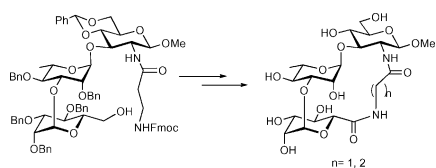
Proposed mechanism for diterpene synthases in the formation of phomactatriene and taxadiene

Tetsuo Tokiwano, Taeko Endo, Tae Tsukagoshi, Hitoshi Goto, Eri Fukushi and Hideaki Oikawa*

Mechanism of the GGDP cyclization to A^+ followed by the rearrangements providing phomactatriene and taxadiene is proposed based on the results of feeding experiments and the acid-catalyzed biomimetic reaction with verticillol.



2723

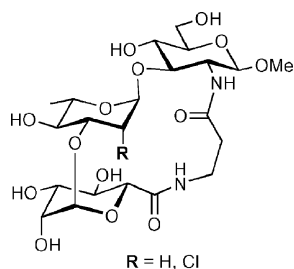


The design, synthesis and evaluation of high affinity macrocyclic carbohydrate inhibitors

Robert S. McGavin, Rod A. Gagne, Mary C. Chervenak and David R. Bundle*

Synthesis of trisaccharide inhibitors tethered in their bound conformation has been employed in an attempt to design high affinity carbohydrate ligands by minimization of free energy losses arising from conformational entropy.

2733

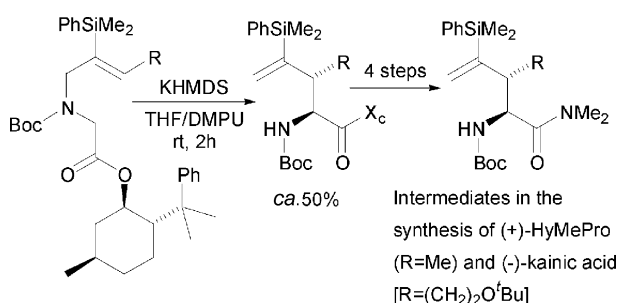


Developing high affinity oligosaccharide inhibitors: conformational pre-organization paired with functional group modification

Robert S. McGavin and David R. Bundle*

Trisaccharides constrained in their bound conformation via an intramolecular tether have been synthesized with one additional functional group modification. The impact of paired modifications on the thermodynamics of binding are reported.

2741

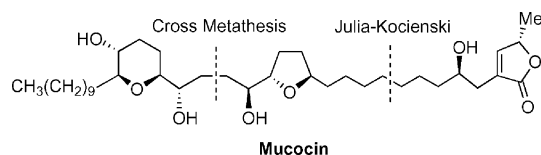


Asymmetric aza-[2,3]-Wittig sigmatropic rearrangements: chiral auxiliary control and formal asymmetric synthesis of (2*S*, 3*R*, 4*R*)-4-hydroxy-3-methylproline and (-)-kainic acid

James C. Anderson,* Julian M. A. O'Loughlin and James A. Tornos

After a survey of different strategies and chiral auxiliaries it was found that the (-)-8-phenylmenthol chiral auxiliary gave *ca.* 50% yields of enantiomerically pure products.

2750

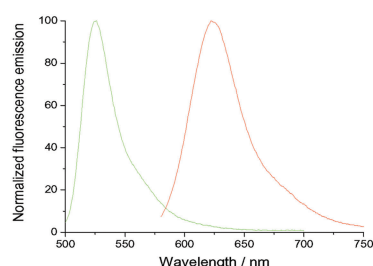
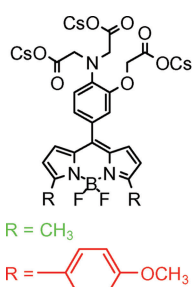


Synthesis of the non-classical acetogenin mucocin: a modular approach based on olefinic coupling reactions

Lei Zhu and David R. Mootoo*

A three component modular synthesis of the potent antitumor agent mucocin, using the olefin cross-metathesis and Julia-Kocienski olefination as the segment coupling reactions, is described.

2755



Synthesis and spectroscopic characterisation of BODIPY[®] based fluorescent off-on indicators with low affinity for calcium

Nikola Basarić, Mukulesh Baruah, Wenwu Qin, Bert Metten, Mario Smet, Wim Dehaen and Noël Boens*

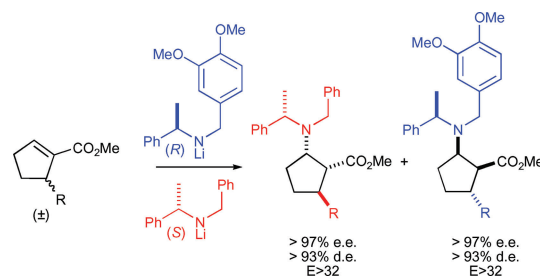
The two fluorescent indicators show a significant increase in the fluorescence quantum yield upon Ca²⁺ binding.

2762

Kinetic resolution and parallel kinetic resolution of methyl (\pm)-5-alkyl-cyclopentene-1-carboxylates for the asymmetric synthesis of 5-alkyl-cis-pentacin derivatives

Stephen G. Davies,* A. Christopher Garner, Marcus J. C. Long, Rachel M. Morrison, Paul M. Roberts, Edward D. Savory, Andrew D. Smith, Miles J. Sweet and Jonathan M. Withey

The efficient kinetic resolution and parallel kinetic resolution of a range of methyl (\pm)-5-alkyl-cyclopentene-1-carboxylates (alkyl = ⁱPr, Ph, ^tBu, mesityl) for the asymmetric synthesis of 5-alkyl-cis-pentacin derivatives are demonstrated.

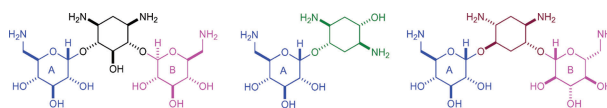


2776

Synthesis of a library of stereo- and regiochemically diverse aminoglycoside derivatives

Blandine Clique, Alan Ironmonger, Benjamin Whittaker, Jacqueline Colley, James Titchmarsh, Peter Stockley and Adam Nelson*

Forty diverse aminoglycoside derivatives were prepared which probe regions of conformational space unavailable to the natural products.

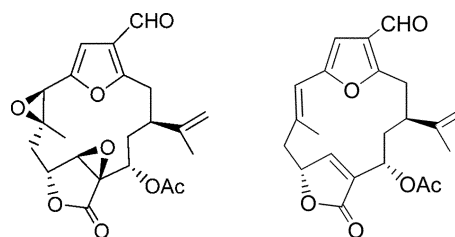


2786

Synthetic studies towards furanocembrane diterpenes. A total synthesis of bis-deoxylophotoxin

Manuel Cases, Felix Gonzalez-Lopez de Turiso, Maria S. Hadjisoteriou and Gerald Pattenden*

Synthetic approaches to the furanocembrane family of natural products are described. A total synthesis of bis-deoxylophotoxin, the probable biological precursor to the neurotoxin lophotoxin, is then presented.

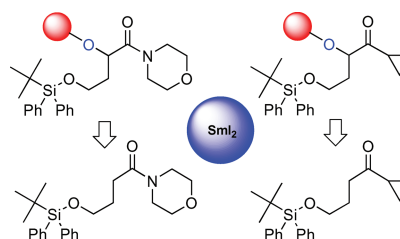


2805

Evaluation of a new linker system cleaved using samarium(II) iodide. Application in the solid phase synthesis of carbonyl compounds

Fiona McKerlie, Iain M. Rudkin, Graham Wynne and David J. Procter*

Insights into the mechanism of the samarium(II) iodide cleavage reaction are described and the potential of a sequential cleavage carbon-carbon bond forming process is assessed.

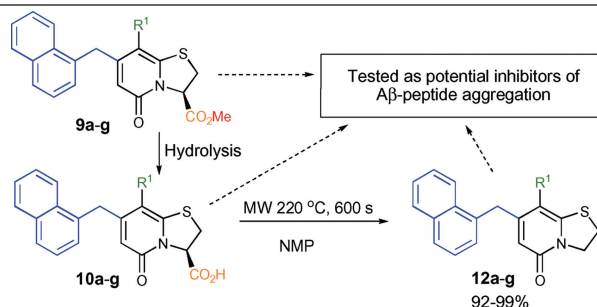


2817

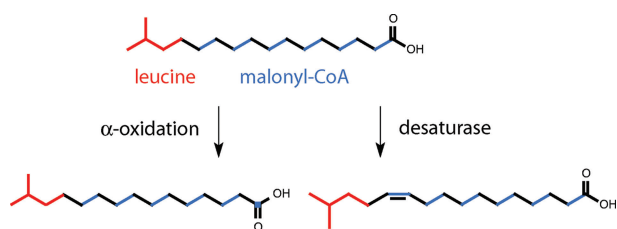
Microwave-assisted decarboxylation of bicyclic 2-pyridone scaffolds and identification of A β -peptide aggregation inhibitors

Veronica Åberg, Fredrik Norman, Erik Chorell, Andreas Westermark, Anders Olofsson, A. Elisabeth Sauer-Eriksson and Fredrik Almqvist*

A microwave-assisted decarboxylation of bicyclic 2-pyridones is described. Of the compounds synthesized, **10a** and **10e** proved to inhibit A β -peptide aggregation.



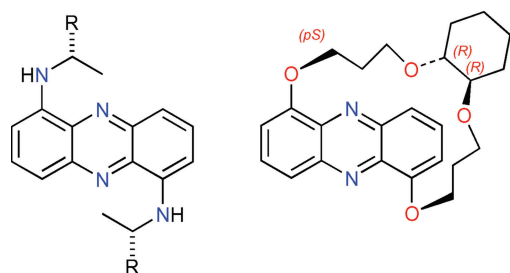
2824

**Biosynthesis of iso-fatty acids in myxobacteria**

Joeroen S. Dickschat, Helge B. Bode, Reiner M. Kroppenstedt, Rolf Müller and Stefan Schulz*

The unusual biosynthesis of methyl-branched fatty acids in myxobacteria proceeds *via* α -oxidation and participation of desaturases in some cases.

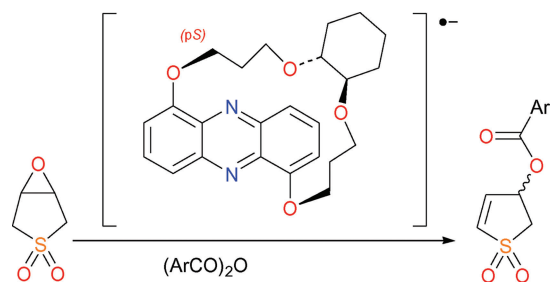
2832

**Synthesis of phenazine derivatives for use as precursors to electrochemically generated bases**

A. Mateo Alonso, Roberto Horcajada, Helen J. Groombridge, Reshma Chudasama (*née* Mandalia), Majid Motevalli, James H. P. Utley* and Peter B. Wyatt*

1,6-Disubstituted phenazine amines and ethers, including enantiomerically pure and planar chiral examples, have been prepared for use as precursors to strongly basic radical anions.

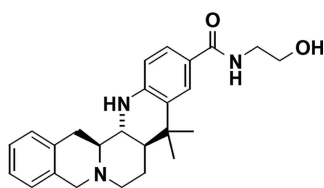
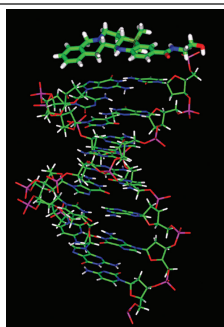
2842

**The reactivity, as electrogenerated bases, of chiral and achiral phenazine radical-anions, including application in asymmetric deprotonation**

A. Mateo Alonso, Roberto Horcajada, Majid Motevalli, James H. P. Utley* and Peter B. Wyatt*

The bases can induce asymmetry in the rearrangement of a *meso*-epoxide to an allylic alcohol.

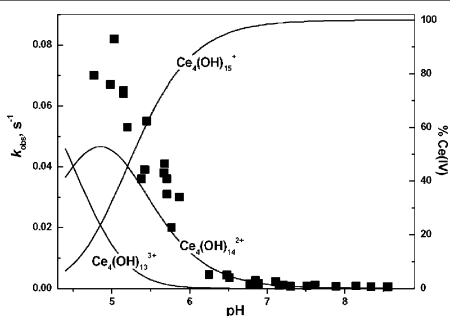
2848

**Synthesis and DNA binding properties of novel benzo[b]isoquino[2,3-*h*]-naphthyridines**

Oliver Koepler, Stefania Mazzini,* Maria Cristina Bellucci, Rosanna Mondelli, Angelika Baro, Sabine Laschat,* Marc Hotfilder, Christophle Viseur and Wolfgang Frey

Several benzo[b]isoquino[2,3-*h*]-naphthyridines were prepared in order to study their cytotoxicity properties and binding modes to DNA fragments by NMR and molecular dynamics simulations. Complexes to minor-groove and *cap*-complexes were detected.

2859

**Kinetics of phosphodiester cleavage by differently generated cerium(IV) hydroxo species in neutral solutions**

Ana L. Maldonado and Anatoly K. Yatsimirsky*

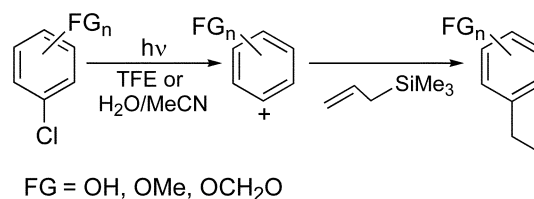
Complexes of Ce(IV) with neutral ligands, *e.g.* [Ce(BTP)₂(NO₃)₄].2H₂O (BTP = bis-tris propane), serve as precursors of polynuclear hydroxo species with high catalytic activity in phosphodiester hydrolysis.

2868

**Expedient synthesis of bioactive allylphenol constituents of the genus *Piper* through a metal-free photoallylation procedure**

Stefano Protti, Maurizio Fagnoni* and Angelo Albini

Nine bioactive derivatives from the plant *Piper* have been synthesised via a metal-free procedure. This involves the generation of aryl cations by irradiation in a polar solvent, in the presence of allyltrimethylsilane.

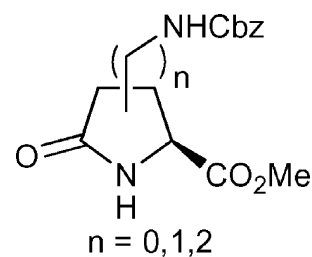


2872

Stereoselective synthesis of conformationally constrained ω -amino acid analogues from pyroglutamic acid

Emilie L. Bentz, Rajesh Goswami, Mark G. Moloney* and Susan M. Westaway

A bicyclic lactam derived from pyroglutamic acid provides a useful scaffold for modification of the ring periphery, allowing access to conformationally restricted amino acids.



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FORTHCOMING ARTICLES

Emerging Area: One-pot multi-step synthesis: a challenge spawning innovation

Steven J. Broadwater, Shoshannah L. Roth, Kristin E. Price, Muris Kobašija and D. Tyler McQuade
 (DOI: 10.1039/b506621m)

Communication: Titanocene(II)-promoted carbonyl allenation utilizing 1,1-dichloroalk-1-enes

Tomohiro Shono, Kenji Ito, Akira Tsubouchi and Takeshi Takeda (DOI: 10.1039/b508820h)

Communication: Anion recognition by α -aryloxy-*N*-confused calix[4]pyrroles

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Polyaza metacyclophanes as ditopic anion receptors

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Amino acid conjugates of 1,1'-diaminiferrocene. Synthesis and chiral organisation

Somenath Chowdhury, Khaled A. Mahmoud, Gabriele Schatte and Heinz-Bernhard Kraatz (DOI: 10.1039/b506178d)

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