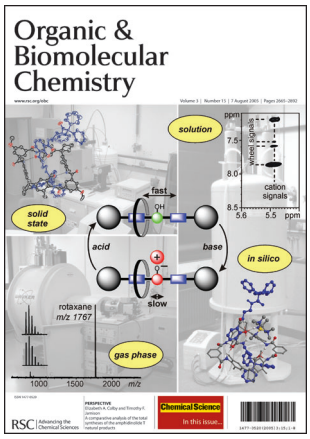
ISSN 1477-0520 CODEN OBCRAK 3(15) 2665–2884 (2005)

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.



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.

Image supplied by permission of Christoph Schalley and Arne Lützen.

CHEMICAL SCIENCE

C57

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Chemical Science

August 2005/Volume 2/Issue 8

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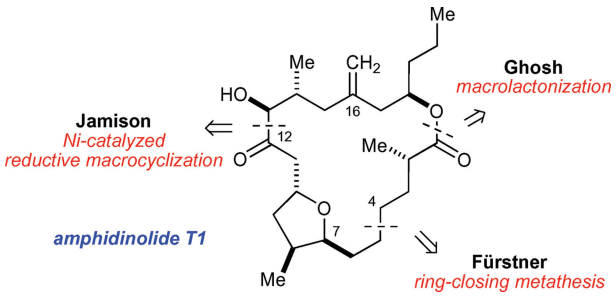
PERSPECTIVE

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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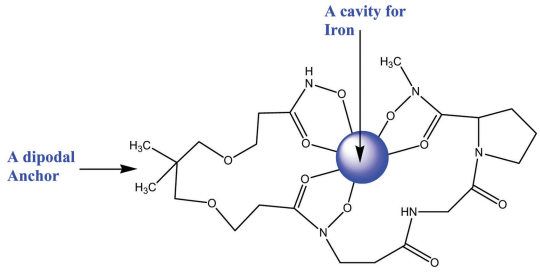
COMMUNICATIONS

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 Fe^{II}/H_2O_2-induced oxidative stress. In comparison to Desferal, one synthetic analog was significantly more effective according to a cell survival assay.

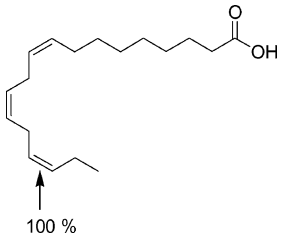


2688

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*.



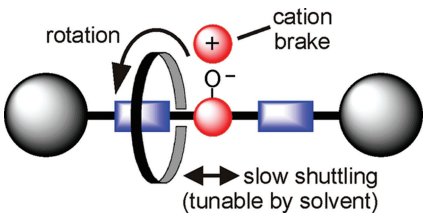
ARTICLES

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.

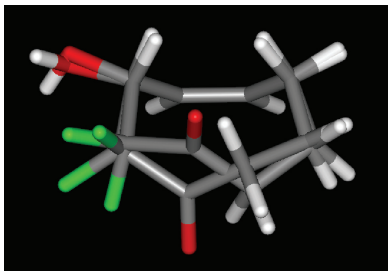


2701

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.

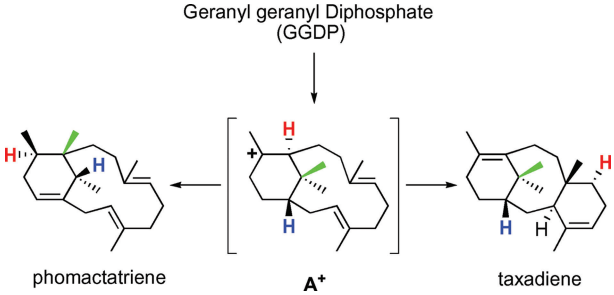


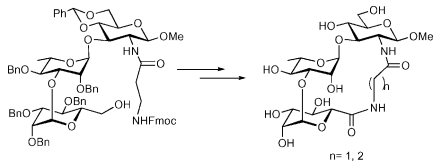
2713

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 $\mathbf{A}^+$ 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.

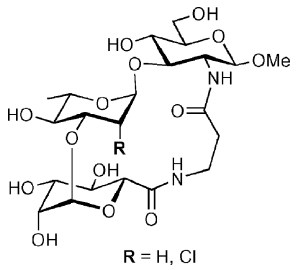




The design, synthesis and evaluation of high affinity macrocyclic carbohydrate inhibitors

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

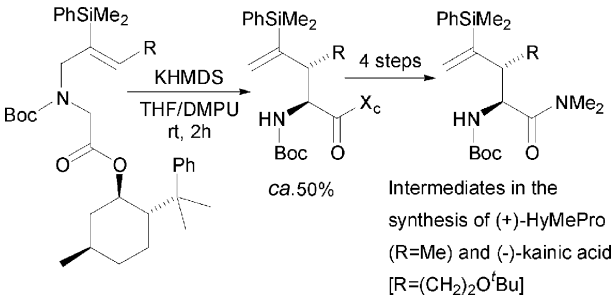
Synthesis of trisaccharide inhibitors tethered in their bound conformation has been employed in an attempt to design high affinity carbohydrate ligands by minimization of free energy losses arising from conformational entropy.



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

Robert S. McGavin and David R. Bundle*

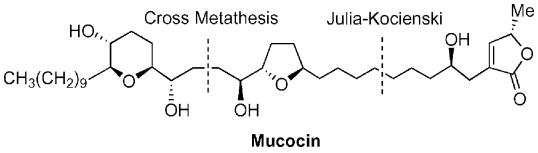
Trisaccharides constrained in their bound conformation via an intramolecular tether have been synthesized with one additional functional group modification. The impact of paired modifications on the thermodynamics of binding are reported.



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

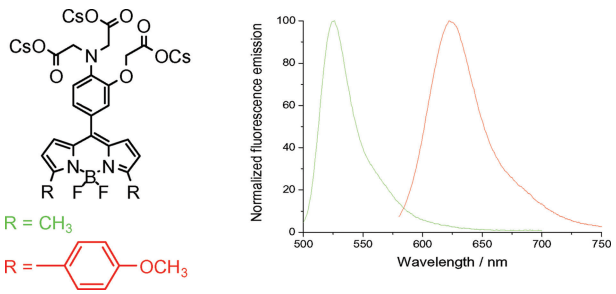
After a survey of different strategies and chiral auxiliaries it was found that the (−)-8-phenylmenthol chiral auxiliary gave *ca.* 50% yields of enantiomerically pure products.



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

Lei Zhu and David R. Mootoo*

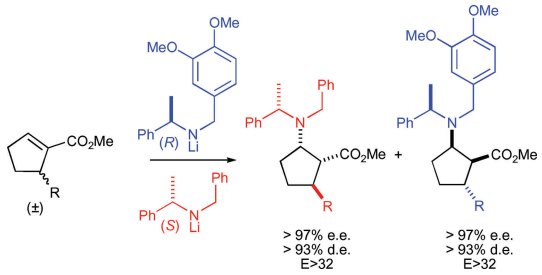
A three component modular synthesis of the potent antitumor agent mucocin, using the olefin cross-metathesis and Julia–Kocienski olefination as the segment coupling reactions, is described.

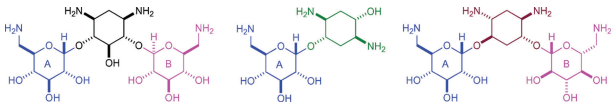


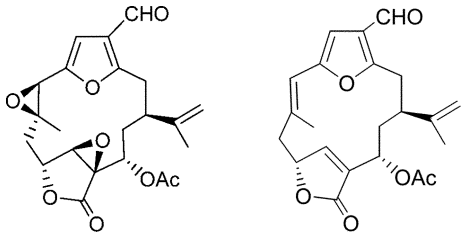
Synthesis and spectroscopic characterisation of BODIPY® based fluorescent off–on indicators with low affinity for calcium

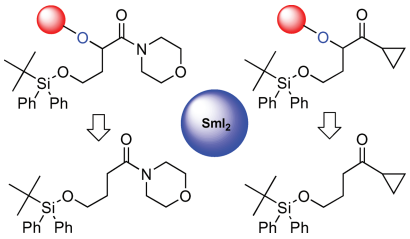
Nikola Basarić, Mukulesh Baruah, Wenwu Qin, Bert Metten, Mario Smet, Wim Dehaen and Noël Boens*

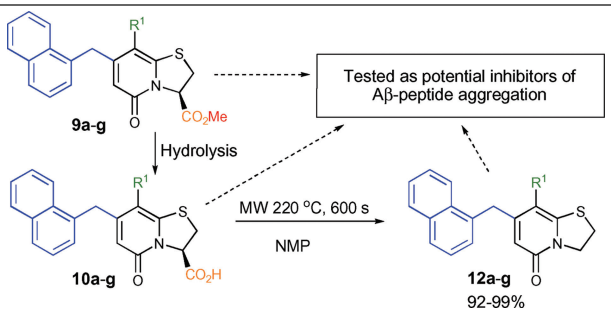
The two fluorescent indicators show a significant increase in the fluorescence quantum yield upon Ca^{2+} binding.

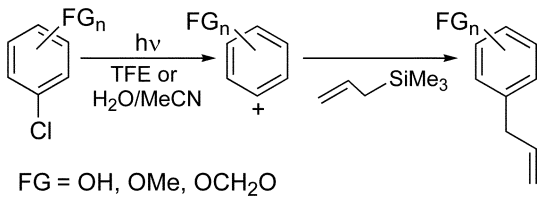


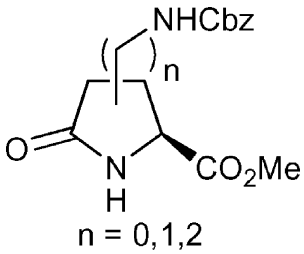


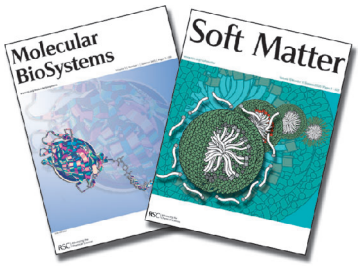












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FORTHCOMING ARTICLES

Emerging Area: One-pot multi-step synthesis: a challenge spawning innovation
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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-arylazo-*N*-confused calix[4]pyrroles
Rong Gu, Stefaan Depraetere, Jan Kotek, Jan Budka, Ewa Wagner-Wysiecka, Jan F. Biernat and Wim Dehaen (**DOI**: 10.1039/b507508d)

Two-stage enzyme mediated drug release from LMWG hydrogels
Kjeld J. C. van Bommel, Marc C. A. Stuart, Ben L. Feringa and Jan van Esch (**DOI**: 10.1039/b507157g)

Polyaza metacyclophanes as ditopic anion receptors
Christos A. Ilioudis and Jonathan W. Steed (**DOI**: 10.1039/b506828b)

Synthesis and stability of exocyclic triazine nucleosides
Michelle Hysell, Jay Siegel and Yitzhak Tor (**DOI**: 10.1039/b503757c)

Efficient terpene hydroxylation catalysts based upon P450 enzymes derived from actinomycetes
Ayhan Çelik, Sabine L. Flitsch and Nicholas J. Turner (**DOI**: 10.1039/b506159h)

Amino acid conjugates of 1,1′-diaminoferrocene. Synthesis and chiral organisation
Somenath Chowdhury, Khaled A. Mahmoud, Gabriele Schatte and Heinz-Bernhard Kraatz (**DOI**: 10.1039/b506178d)

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