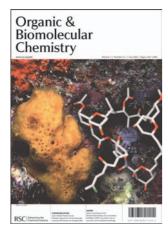
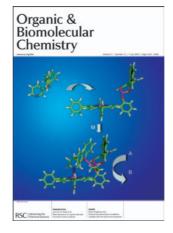
ISSN 1477-0520 CODEN OBCRAK 3(13) 2361-2484 (2005)



Cover

See Ian Paterson et al., pp. 2399-2409 See Ian Paterson et al., pp. 2410-2419 See Ian Paterson et al., pp. 2420-2430 See Ian Paterson et al., pp. 2431-2440 The figure shows the challenging 3D-structure of altohyrtin A, a potent anticancer agent of marine sponge origin, synthesised by the Paterson group using boron aldol methodology to enable its further preclinical development. Sponge photograph taken by Dr Andrew Flowers and provided by Dr Mary Garson.

Image reproduced by permission of Ian Paterson from Org. Biomol. Chem., 2005, 3, 2399 & 2410 & 2420 & 2431.



Inside Cover

See Matthew J. Wilkinson, Piet W. N. M. van Leeuwen and Joost N. H. Reek, pp. 2371-2383 The figure shows how two monodentate ligands can be assembled to form a bidentate chelating ligand to be used in transition metal catalysis. This is just one of the new strategies in the area of supramolecular catalysis assembly.

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C49

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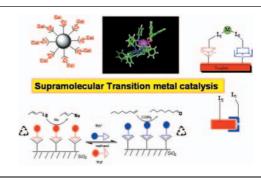
PERSPECTIVE

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New directions in supramolecular transition metal catalysis

Matthew J. Wilkinson, Piet W. N. M. van Leeuwen and Joost N. H. Reek*

This perspective describes new approaches to transition metal catalyst development that evolve from a combination of supramolecular strategies and rational ligand design.



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2384

Near IR emitting isothiocyanato-substituted fluorophores: their synthesis and bioconjugation to monoclonal antibodies

Wubiao Duan, Karen Smith, Huguette Savoie, John Greenman and Ross W. Boyle*

Two near IR active fluorophores suitable for bioconjugation to proteins have been synthesised and conjugated to monoclonal antibodies

2387

Oxidation of *N*-substituted dopamine derivatives: irreversible formation of a spirocyclic product

Edward J. Land, Almudena Perona, Christopher A. Ramsden* and Patrick A. Riley

ortho-Quinones with 4-ethyl sidechains carrying amidine or thiourea functional groups rapidly cyclise to give novel cyclic products in high yield.

2389

Enhancing selectivity in oxidation catalysis with sol-gel nanocomposites

Pamela Gancitano, Rosaria Ciriminna, Maria Luisa Testa, Alexandra Fidalgo, Laura M. Ilharco and Mario Pagliaro*

Synthesis of valuable compounds such as α-hydroxy acids using a sol-gel hydrophobized nanostructured silica matrix doped with the organocatalyst TEMPO.

$$\begin{array}{c} \text{RuCl}_3, \, \text{NaIO}_4 & \text{ormosil-TEMPO, NaOCI} \\ \text{CH}_3\text{CN/ EtOAC/H}_2\text{O} & \text{CH}_3\text{CN/NaHCO}_3 \, 5\% \\ \hline \text{R1} & 0 \, ^{\circ}\text{C, 0.5-3 min.} & \text{R1} & 0 \, ^{\circ}\text{C} & \text{R1} & \text{O} \\ \text{R2} & & \text{HO} & \text{OH} & & \text{HO} & \text{OH} \\ \end{array}$$

2393

Divalent ligand for intramolecular complex formation to streptavidin

Joan-Antoni Farrera,* Pedro Hidalgo-Fernández, Jurry M. Hannink, Jurriaan Huskens, Alan E. Rowan, Nico A. J. M. Sommerdijk and Roeland J. M. Nolte

Monovalent ligand 4 and divalent ligand 8 have been synthesized, and their thermodynamic parameters of complexation to avidin and streptavidin have been analyzed in terms of multivalent binding.

2396

New odourless protocols for efficient Pauson-Khand annulations

Jack A. Brown, Stephanie Irvine, William J. Kerr* and Colin M. Pearson

An inexpensive and odourless additive, dodecyl methyl sulfide, has been shown to be an effective promoter of Pauson-Khand cyclisations.

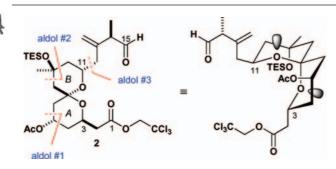
$$R = \frac{1. \text{ Co}_2(\text{CO})_8}{\text{Or}}$$

$$R = \text{NTs}, O, C(\text{CO}_2\text{R})$$

$$R = 1,2$$

$$R = \text{NTs}, O = 1,2$$

2399

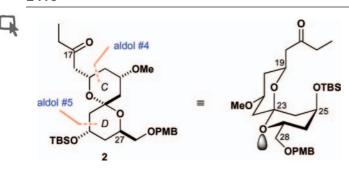


The stereocontrolled total synthesis of altohyrtin A/spongistatin 1: the AB-spiroacetal segment

Ian Paterson,* Mark J. Coster, David Y.-K. Chen, Renata M. Oballa, Debra J. Wallace and Roger D. Norcross

A stereocontrolled synthesis of the C1–C15 subunit of altohyrtin A/spongistatin 1, relying on matched boron aldol reactions of chiral methyl ketones, has been developed.

2410

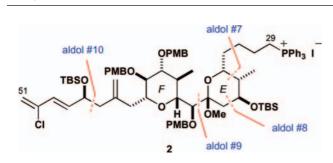


The stereocontrolled total synthesis of altohyrtin A/spongistatin 1: the CD-spiroacetal segment

Ian Paterson,* Mark J. Coster, David Y.-K. Chen, Karl R. Gibson and Debra J. Wallace

Stereocontrolled syntheses of the C16-C28 subunit of altohyrtin A/spongistatin 1, relying on kinetic and thermodynamic control of the spiroacetal formation, have been developed.

2420

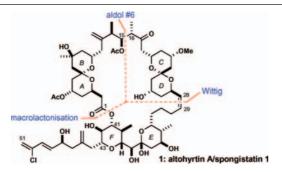


The stereocontrolled total synthesis of altohyrtin A/spongistatin 1: the southern hemisphere EF segment

Ian Paterson,* Mark J. Coster, David Y.-K. Chen, José L. Aceña, Jordi Bach, Linda E. Keown and Thomas Trieselmann

The C29-C51 segment of altohyrtin A/spongistatin 1 has been synthesised in a convergent and stereocontrolled manner, involving four highly diastereoselective, substrate-controlled, boron aldol reactions as key stereodetermining steps.

2431

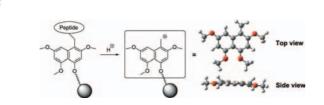


The stereocontrolled total synthesis of altohyrtin A/spongistatin 1: fragment couplings, completion of the synthesis, analogue generation and biological evaluation

Ian Paterson,* David Y.-K. Chen, Mark J. Coster, José L. Aceña, Jordi Bach and Debra J. Wallace

The antimitotic marine macrolide altohyrtin A/spongistatin 1, and two close structural analogues, have been synthesised and evaluated as growth inhibitory agents against a range of human tumour cell lines.

2441



Substituent effects on the stability of extended benzylic carbocations: a computational study of conjugation

Michael Pittelkow, Jørn B. Christensen and Theis I. Sølling*

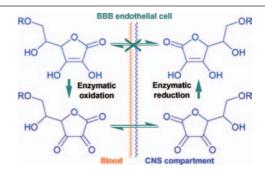
When methoxy substituents are forced out of the plane of the aromatic core by steric congestion then the carbocation stabilization via conjugation is sometimes completely lost.

2450

Enhanced delivery of γ-secretase inhibitor DAPT into the brain via an ascorbic acid mediated strategy

Gilles Quéléver, Philippe Kachidian, Christophe Melon, Cédrik Garino, Younes Laras, Nicolas Pietrancosta, Mahmoud Sheha and Jean Louis Kraus*

We report the synthesis of a γ -secretase inhibitor whose scaffold bears an ascorbic acid moiety allowing an enhanced distribution into the brain through the blood brain barrier.

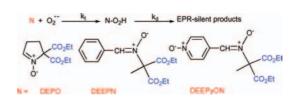


2458

Spin trapping of superoxide by diester-nitrones

Ahmad Allouch, Valérie Roubaud, Robert Lauricella, Jean-Claude Bouteiller and Béatrice Tuccio*

The rate constants k_t and k_d determined for DEPO, DEEPN and DEEPyON were compared to those obtained with analogous monoester-nitrones.



2463

Expansion of repertoire of modified DNAs prepared by PCR using KOD Dash DNA polymerase

Tsutomu Ohbayashi, Masayasu Kuwahara, Masatoshi Hasegawa, Toshiyuki Kasamatsu, Takehiro Tamura and Hiroaki Sawai*

Thymidine analogues bearing various functional groups were accepted by the polmerase enzyme, forming the modified DNA by PCR.

R: functional group(pyridine, imidazole, biotin, guanidinium, amino, mercaptopyridyl, phenanthrolne, --)

2469

Iodo- and bromo-enolcyclization of 2-(2-propenyl)cyclohexanediones and 2-(2-propenyl)cyclohexenone derivatives using iodine in methanol and pyridinium hydrobromide perbromide in dichloromethane

Malose J. Mphahlele* and Thwanthwadi B. Moekwa

The combined electrophilic and oxidative properties associated with iodine were exploited to construct diversely substituted tetrahydrobenzofuranones and dihydrobenzofuran derivatives.

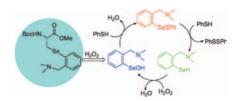
2476



Internally stabilized selenocysteine derivatives: syntheses, ⁷⁷Se NMR and biomimetic studies

Prasad P. Phadnis and G. Mugesh*

Aryl-substituted seleno-cysteine/-cystine derivatives are synthesized from L-serine. Oxidation-elimination reactions in Sec derivatives could be used for the generation of biologically active selenols with internally stabilizing substituents.





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