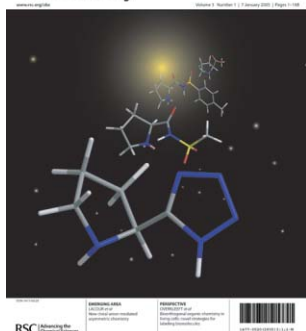


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ISSN 1477-0520 CODEN OBCRAK 3(1) 1–188 (2005)

Organic & Biomolecular Chemistry

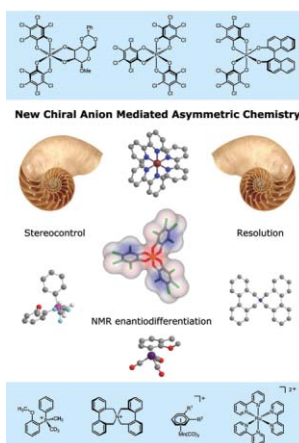


Cover

See Alexander J. A. Cobb, David M. Shaw, Deborah A. Longbottom, Johan B. Gold and Steven V. Ley, pp. 84–96.

The illustration represents the progression of asymmetric organocatalysis. Organocatalysts have been developed which have shown vast improvements on proline itself (in the background) in several reactions, most notably so far, the tetrazole compound (in the foreground).

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Inside Cover

See Jérôme Lacour and Richard Frantz, pp. 15–19.

The illustration depicts in its center the propeller structure of chiral TRISPHAT anion which is, along with the other members of the PHAT family (top banner), an effective NMR chiral solvating, resolving and asymmetry-inducing agent for chiral cations (bottom banner) of various shape and nature (organic, inorganic, organometallic).

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C1

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January 2005/Volume 2/Issue 1

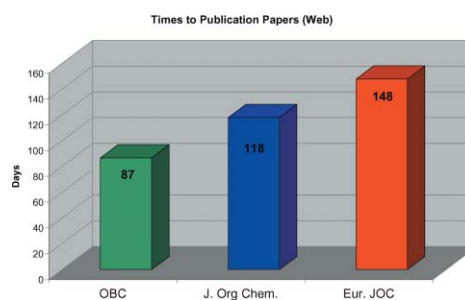
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EDITORIAL

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Editorial

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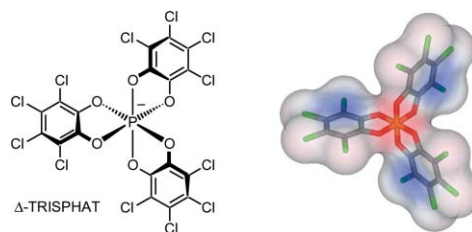
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New chiral anion mediated asymmetric chemistry

Jérôme Lacour* and Richard Frantz

Chiral cations can be effectively analyzed, resolved and stereocontrolled through an asymmetric ion pairing with enantiopure anions like TRISPHAT.



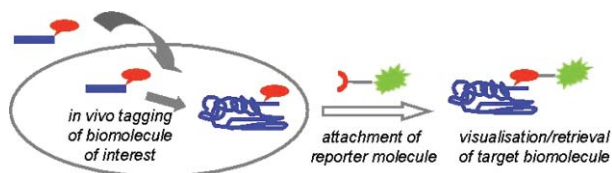
PERSPECTIVE

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Bioorthogonal organic chemistry in living cells: novel strategies for labeling biomolecules

Paul F. van Swieten, Michiel A. Leeuwenburgh, Benedikt M. Kessler and Herman S. Overkleeft*

Several approaches for the *in vivo* introduction of latent reactive functionalities into biomolecules for subsequent chemical modification are described.



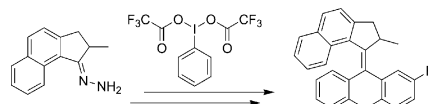
COMMUNICATIONS

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New procedure for the preparation of highly sterically hindered alkenes using a hypervalent iodine reagent

Matthijs K. J. ter Wiel, Javier Vicario, Stephen G. Davey, Auke Meetsma and Ben L. Feringa*

The sterically hindered central olefinic bond in new molecular motors could be effectively introduced using a hypervalent iodine reagent.

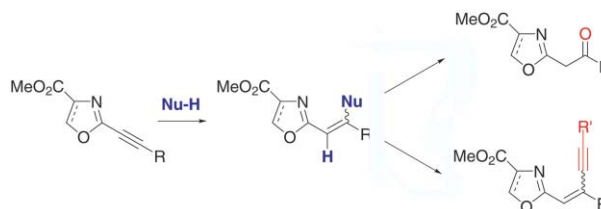


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Synthesis and hetero-Michael addition reactions of 2-alkynyl oxazoles and oxazolines

Peter Wipf* and Thomas H. Graham

Stereoselective conjugate addition of alcohols, amines, thiols, and halides to C(2)-alkynyl oxazoles and oxazolines provides a versatile approach to heterocyclic building blocks.

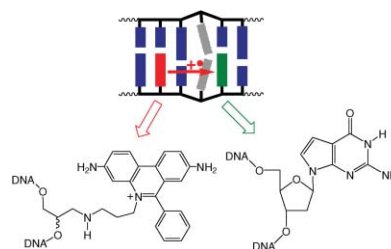


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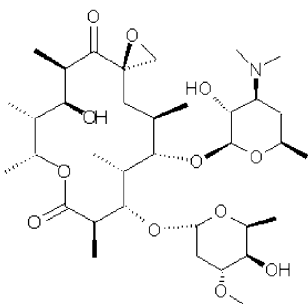
Detection of single base mismatches and abasic sites using phenanthridinium as an artificial DNA base and charge donor

Linda Valis, Nicole Amann and Hans-Achim Wagenknecht*

Combining the fluorescence properties of phenanthridinium as an artificial DNA base together with DNA-mediated charge transfer processes allows the homogeneous detection of DNA base mismatches and abasic sites.



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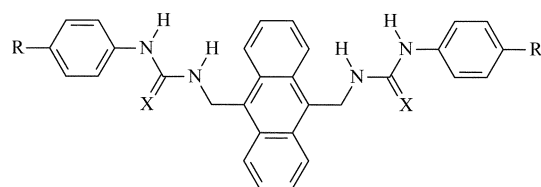


Conformational analysis of oleandomycin and its 8-methylene-9-oxime derivative by NMR and molecular modelling

Predrag Novak,* Zrinka Banić Tomišić,* Predrag Tepeš, Gorjana Lazarevski, Janez Plavec and Gordana Turkalj

A combination of experimental NMR data and molecular modelling techniques applied to antibiotic oleandomycin and its derivative has enabled new insight into the conformational behaviour and properties of macrolides.

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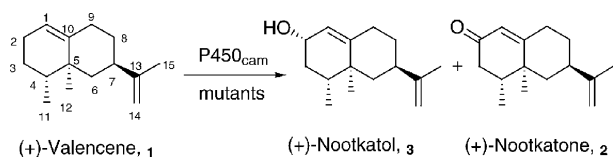
1: R = CF₃, X = S
2: R = H, X = S
3: R = CF₃, X = O

Synthesis and photophysical evaluation of charge neutral thiourea or urea based fluorescent PET sensors for bis-carboxylates and pyrophosphate

Thorfinnur Gunnlaugsson,* Anthony P. Davis, John E. O'Brien and Mark Glynn

Fluorescent PET chemosensors were developed for the recognition of anions flanked with two binding sites. The fluorescence emission was quenched upon anion sensing, but reversibly *switched on* upon addition of polar solvents such as water or ethanol.

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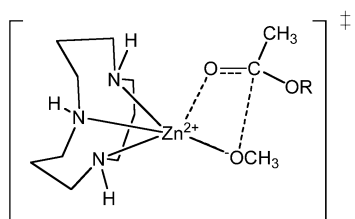


Biotransformation of the sesquiterpene (+)-valencene by cytochrome P450_{cam} and P450_{BM-3}

Rebecca J. Sowden, Samina Yasmin, Nicholas H. Rees, Stephen G. Bell and Luet-Lok Wong*

Cytochrome P450_{cam} from *Pseudomonas putida* has been engineered to oxidise (+)-valencene to (+)-nootkatol and (+)-nootkatone as the major (>85%) products.

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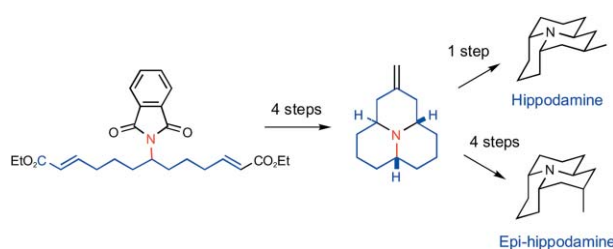


Metal ion promoted transesterifications of carboxylate esters. A structure/activity study of the efficacy of Zn²⁺ and La³⁺ to catalyze the methanolysis of some aryl and aliphatic esters

Alexei A. Neverov, N. E. Sunderland and R. Stan Brown*

The catalytic system comprising 1,5,9-triazacyclododecane : Zn²⁺(⁻OCH₃) promotes the methanolysis of activated and unactivated esters through bifunctional catalysis.

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Combining two-directional synthesis and tandem reactions: an efficient strategy for the total syntheses of (±)-hippodamine and (±)-epi-hippodamine

Martin Rejzek, Robert A. Stockman* and David L. Hughes

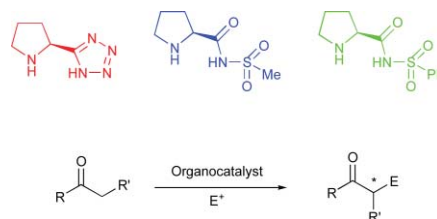
The combination of two-directional synthesis and tandem reaction strategies has resulted in concise syntheses of the Coccinellid alkaloids hippodamine and *epi*-hippodamine.

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Organocatalysis with proline derivatives: improved catalysts for the asymmetric Mannich, nitro-Michael and aldol reactions

Alexander J. A. Cobb, David M. Shaw, Deborah A. Longbottom, Johan B. Gold and Steven V. Ley*

Organocatalysts derived from proline have been shown to be highly effective in the catalysis of various enantioselective processes and have been shown to outperform proline itself.

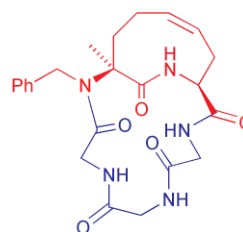


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Application of tandem Ugi multi-component reaction/ring closing metathesis to the synthesis of a conformationally restricted cyclic pentapeptide

Silvia Anthoine Dietrich, Luca Banfi,* Andrea Basso, Gianluca Damonte, Giuseppe Guanti and Renata Riva

A cyclic pentapeptide containing an unsaturated 9-membered lactam as a semi-rigid scaffold was prepared in a very convergent manner.

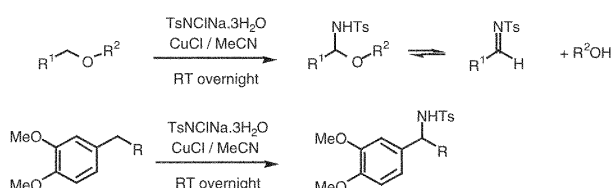


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Amination of ethers using chloramine-T hydrate and a copper(I) catalyst

David P. Albone, Stephen Challenger, Andrew M. Derrick, Shaun M. Fillery, Jacob L. Irwin, Christopher M. Parsons, Hiroya Takada, Paul C. Taylor* and D. James Wilson

Commercially available chloramine-T trihydrate with CuCl in acetonitrile as the catalyst is effective for amination, proceeding by concerted nitrenoid insertion.

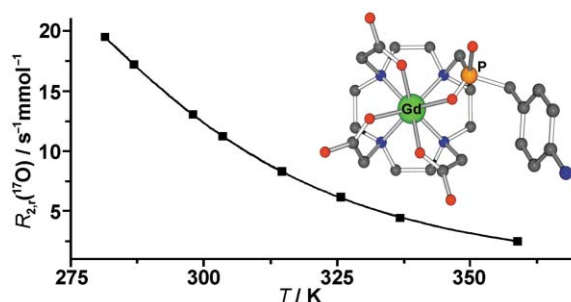


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Synthesis of a bifunctional monophosphinic acid DOTA analogue ligand and its lanthanide(III) complexes. A gadolinium(III) complex endowed with an optimal water exchange rate for MRI applications

Jakub Rudovský, Jan Kotek, Petr Hermann,* Ivan Lukeš, Valentina Mainero and Silvio Aime

Gadolinium(III) complex of monophosphinic acid derivative of DOTA exhibits a fast water exchange rate ($^{298}\tau_M = 16$ ns) as well as a high millimolar relaxivity ($^{298}r_1 = 6.7$ s mmol $^{-1}$; 10 MHz).



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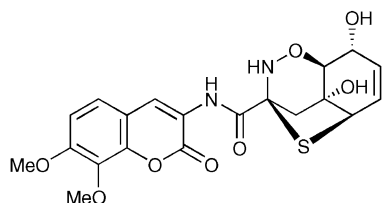
(+)-Echinobetaine B: isolation, structure elucidation, synthesis and preliminary SAR studies on a new nematocidal betaine from a southern Australian marine sponge, *Echinodictyum* sp.

Robert J. Capon,* Dat Vuong, Michelle McNally, Torsten Peterle, Nicholas Trotter, Ernest Lacey and Jennifer H. Gill

An Australian sponge *Echinodictyum* sp. yielded the potent nematocidal agent (+)-echinobetaine B. The structure was solved by spectroscopic analysis and total synthesis.



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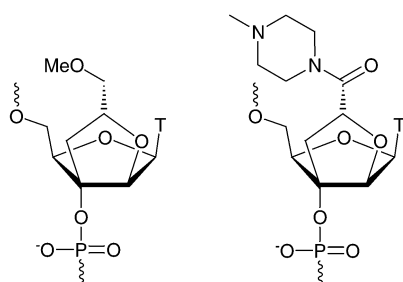


Aspergillazines A–E: novel heterocyclic dipeptides from an Australian strain of *Aspergillus unilateralis*

Robert J. Capon,* Ranjala Ratnayake, Michael Stewart, Ernest Lacey, Shaun Tennant and Jennifer H. Gill

An Australian strain of *Aspergillus unilateralis* yielded a series of highly modified dipeptides, aspergillazines A–E, including the first account of a fused oxazine–thiophane heterocycle.

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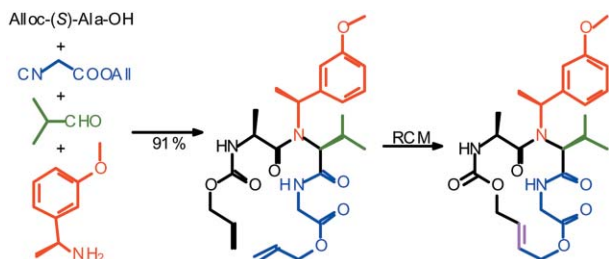


Synthesis and thermal denaturation studies of novel 2'-O,3'-C-linked bicyclic oligonucleotides with a methoxy or a piperazino group facing the major groove of nucleic acid duplexes

Michael Raunkjær, Mads D. Sørensen and Jesper Wengel*

Functionalized 2'-O,3'-C-linked bicyclic nucleic acid monomers are shown to be promising scaffolds for the attachment of groups facing the major groove of nucleic acid duplexes.

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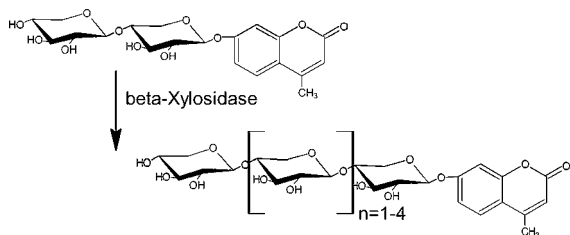


A straightforward approach towards cyclic peptides *via* ring-closing metathesis—scope and limitations

Uli Kazmaier,* Christina Hebach, Anja Watzke, Sabine Maier, Heike Mues and Volker Huch

N- and *C*-terminal diallylated peptides, obtained by several approaches, are suitable substrates for ring-closing metathesis.

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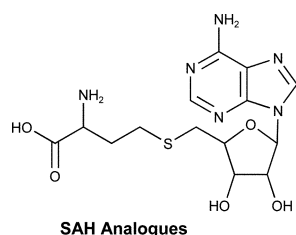


Chemo-enzymatic synthesis of 4-methylumbelliferyl β -(1 \rightarrow 4)-D-xylooligosides: new substrates for β -D-xylanase assays

Elena V. Eneyskaya, Dina R. Ivanen, Konstantin A. Shabalin, Anna A. Kulminskaya,* Leon V. Backinowsky, Harry Brumer III and Kirill N. Neustroev

Transglycosylation catalyzed by a β -D-xylosidase from *Aspergillus* sp. was used to synthesize a set of 4-methylumbelliferyl (MU) β -1 \rightarrow 4-D-xylooligosides having the common structure $[\beta$ -D-Xyl-(1 \rightarrow 4)]₂₋₅- β -D-Xyl-MU.

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SAH Analogues

Determinants of cofactor binding to DNA methyltransferases: insights from a systematic series of structural variants of *S*-adenosylhomocysteine

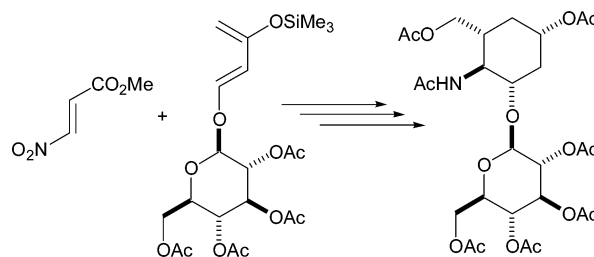
Helen M. Cohen, Andrew D. Griffiths, Dan S. Tawfik and David Loakes*

Analogues of *S*-adenosylhomocysteine were prepared, with single modifications to the adenine, ribose and methionine moieties in order to characterise the functional groups that allow cofactor recognition by DNA methyltransferases.

Studies related to carba-pyranoses: synthesis of acetylated derivatives of 4-amino-2,4-dideoxy-3-*O*-(β -D-glucopyranosyl)- β -L-(and β -D-) altrocarba-pyranose from a D-glucose template

Robin G. Pritchard, Richard J. Stoodley and Wai-Hung Yuen*

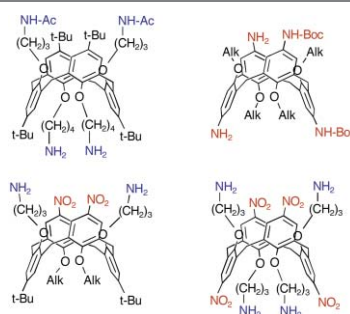
(1 \rightarrow 3) Acetal-linked aminomonocarba-disaccharides have been synthesised from the ketone prepared by the Diels–Alder reaction between methyl nitroacrylate and the glycopyranose diene. The conformation properties of the intermediate ketones have been studied and one of the ketone displays unexpected conformational properties affected by the glycopyranose moiety.



1,3-Alternate calix[4]arenes, selectively functionalized by amino groups

Crenguta Danila, Michael Bolte and Volker Böhmer*

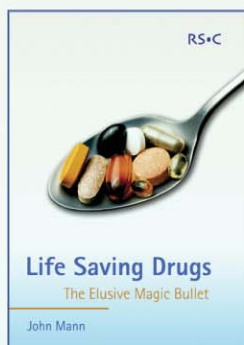
General strategies are described to synthesize calix[4]arenes which are fixed in the 1,3-alternate conformation and substituted selectively by amino groups on the narrow, wide or narrow and wide rims.



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John M. Sanderson (DOI: 10.1039/b415499a)

Total synthesis of the *Fusarium* toxin equisetin

Darren J. Dixon, Lisa T. Burke, Steven V. Ley and Félix Rodríguez (DOI: 10.1039/b411350k)

The chirality of dendrimer-based supramolecular complexes

Maarten A. C. Broeren, Bas F. M. de Waal, Joost L. J. van Dongen, Marcel H. P. van Genderen and E. W. Meijer (DOI: 10.1039/b413724h)

Rational design and synthesis of new quorum sensing inhibitors derived from acylated homoserine lactones and natural products from garlic

Tobias Persson, Thomas H. Hansen, Thomas B. Rasmussen, Mette E. Skindersø, Michael Givskov and John Nielsen (DOI: 10.1039/b415761c)

Solid-phase synthesis of serine-based glycosphingolipid analogues for preparation of glycoconjugate arrays

Fredrik K. Wallner, Henrik A. Norberg, Annika I. Johansson, Mickael Mogemark and Mikael Elofsson (DOI: 10.1039/b415436c)

Synthesis and stereochemistry of musacins isolated from *Streptomyces griseoviridis* (FH-S 1832)

Toshihiko Ueki and Takamasa Kinoshita (DOI: 10.1039/b415759c)

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Stephen G. Davies, Rebecca L. Nicholson and Andrew D. Smith (DOI: 10.1039/b415943c)

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