

Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

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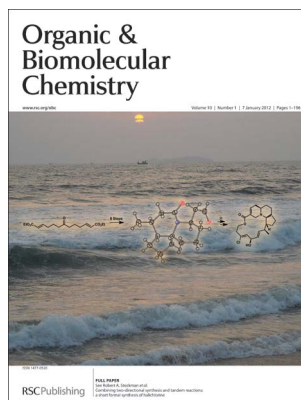
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Cover

See Brian M. Stoltz *et al.*, pp. 56–59.

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Inside cover

See Robert A. Stockman *et al.*, pp. 67–69.

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EDITORIAL

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Happy New Year from *Organic & Biomolecular Chemistry*

On behalf of the *OB*C Editorial Board and Editorial Team, we welcome you to this first issue of 2012, *OB*C's 10th year of publication

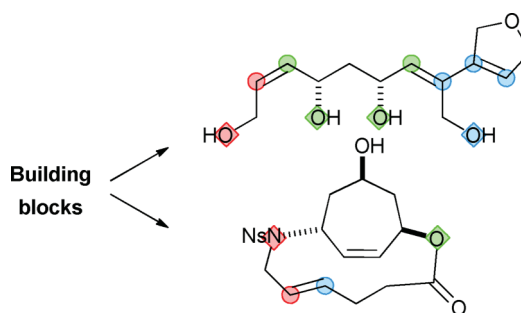
PERSPECTIVE

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Towards the systematic exploration of chemical space

Mark Dow, Martin Fisher, Thomas James, Francesco Marchetti and Adam Nelson*

This article describes synthetic strategies that have emerged that may allow chemical space to be explored more systematically.



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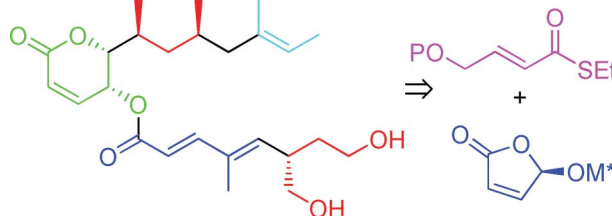
COMMUNICATIONS

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A concise asymmetric synthesis of (–)-rasfonin

Yange Huang, Adriaan J. Minnaard* and Ben L. Feringa*

A very efficient total synthesis of the apoptosis inducer (–)-rasfonin has been developed using asymmetric conjugate addition and Feringa's butenolide.

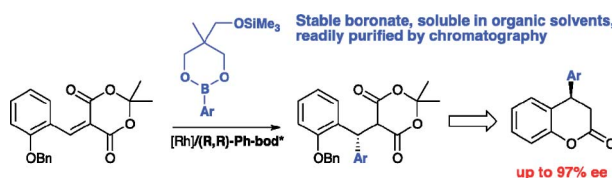


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Rhodium-catalysed enantioselective synthesis of 4-arylchroman-2-ones

Joseph C. Allen, Gabriele Kociok-Köhn and Christopher G. Frost*

The rhodium-catalysed enantioselective 1,4-addition of organoboron reagents to arylidene Meldrum's acids as acceptors, allows convenient access to 4-arylchroman-2-ones with good to excellent levels of enantioselectivity. The use of silyl-protected dioxaborinanes as donors was found to be advantageous to achieving good yields of product under anhydrous conditions.

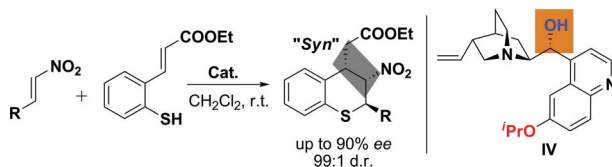


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Expeditious diastereoselective construction of a thiochroman skeleton via a cinchona alkaloid-derived catalyst

Zhiyun Du, Chenggang Zhou, Yaojun Gao, Qiao Ren, Kun Zhang, Hansong Cheng,* Wei Wang* and Jian Wang*

An example of diastereoselective and enantioselective synthesis of thiochroman derivatives through a sulfa-Michael–Michael cascade sequence is disclosed.

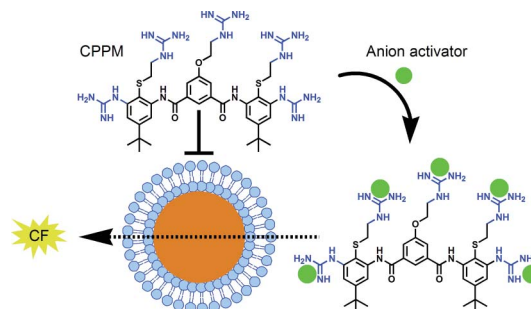


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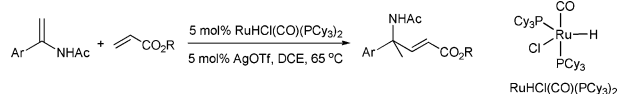
Anion mediated activation of guanidine rich small molecules

Abhigyan Som, Yongjiang Xu, Richard W. Scott and Gregory N. Tew*

Here we report that guanidine rich small molecules can be potential membrane transporters in the presence of hydrophobic counteranion activators.



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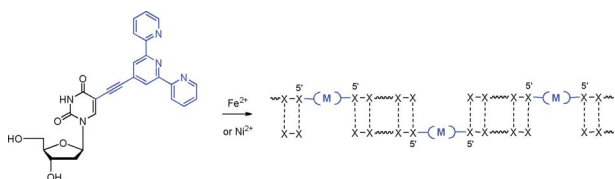


Synthesis of α,β -unsaturated γ -amino esters with a quaternary center by ruthenium-catalyzed codimerization of *N*-acetyl α -arylenamines and acrylates

Qiu-Shi Wang, Jian-Hua Xie, Lu-Chuan Guo and Qi-Lin Zhou*

Ruthenium-catalyzed codimerization of *N*-acetyl- α -arylenamines with ethyl acrylates provides a new method for the synthesis of α,β -unsaturated γ -aminoesters with a quaternary center.

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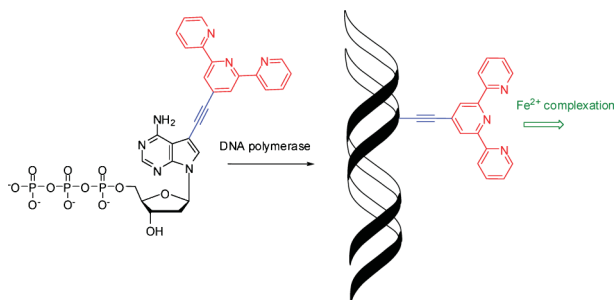


Metal-mediated DNA assembly using the ethynyl linked terpyridine ligand

Thomas Ehrenschwender, Anna Barth, Holger Puchta and Hans-Achim Wagenknecht*

The terpyridine ligand directly attached to the 5-position of a uridine allows metal-mediated DNA assembly towards potentially electronically coupled DNA conjugates.

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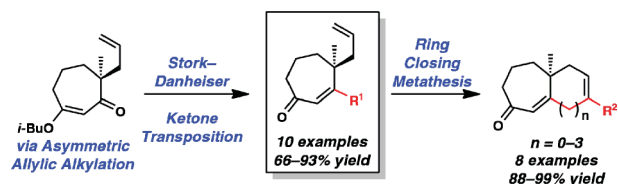


Synthesis of nucleoside mono- and triphosphates bearing oligopyridine ligands, their incorporation into DNA and complexation with transition metals

Lubica Kalachova, Radek Pohl and Michal Hocek*

Oligopyridine-linked 5-substituted cytosine or 7-substituted 7-deazaadenine 2'-deoxyribonucleoside triphosphates were prepared and used for polymerase incorporation to DNA. The resulting bpy- or tpy-substituted DNA was used for complexation with Fe^{2+} .

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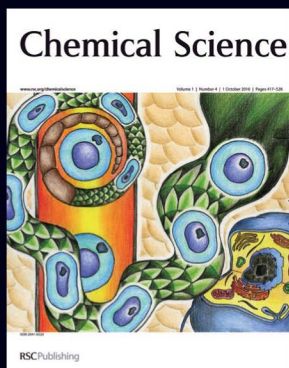


Synthesis of enantioenriched γ -quaternary cycloheptenones using a combined allylic alkylation/Stork–Danheiser approach: preparation of mono-, bi-, and tricyclic systems

Nathan B. Bennett, Allen Y. Hong, Andrew M. Harned and Brian M. Stoltz*

A general method for the synthesis of β -substituted and unsubstituted cycloheptenones bearing enantioenriched all-carbon γ -quaternary stereocenters is reported.

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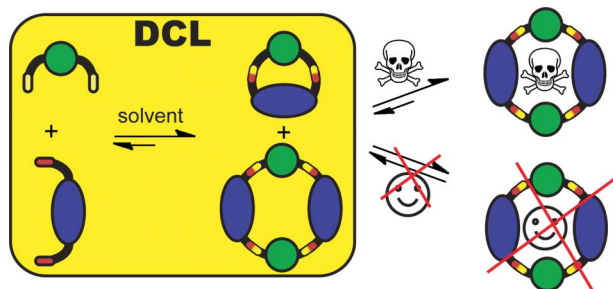
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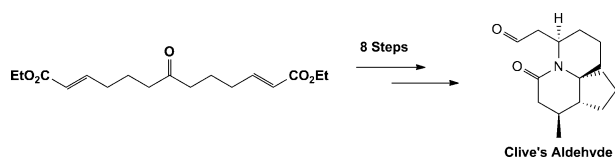


Dynamic combinatorial libraries for the recognition of heavy metal ions

Jörg M. Klein, Vittorio Saggiomo, Lisa Reck, Ulrich Lüning* and Jeremy K. M. Sanders*

Selection of toxic metal ions: Dynamic Combinatorial Libraries (DCLs) create receptors that selectively bind to Ba^{2+} and Sr^{2+} . A route to new receptors that facilitate the extraction of toxic metals?

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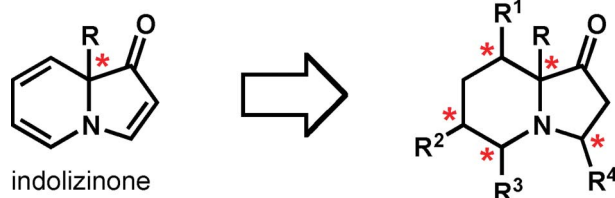


Combining two-directional synthesis and tandem reactions: a short formal synthesis of halichlorine

Camille Gignoux, Annabella F. Newton, Alexandre Barthelme, William Lewis, Marie-Lyne Alcaraz and Robert A. Stockman*

A short and efficient synthesis of an advanced intermediate (1) in the Clive route to halichlorine has been achieved in 12 steps and 13.2% yield by a combined two-directional synthesis/tandem reaction strategy.

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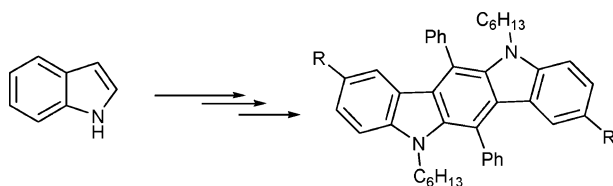


Indolizones as synthetic scaffolds: fundamental reactivity and the relay of stereochemical information

Alison R. Hardin Narayan and Richmond Sarpong*

The innate reactivity of indolizones is explored, revealing the exquisite chemo- and stereoselectivity of these underutilized *N*-heterocycles.

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Synthesis of novel 2,8-disubstituted indolo[3,2-*b*]carbazoles

Sven Van Snick and Wim Dehaen*

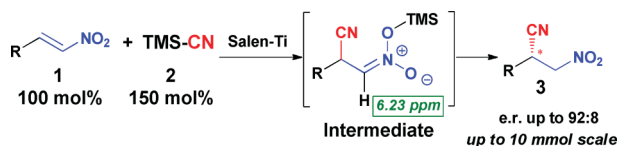
A new synthetic pathway towards 2,8-difunctionalised indolo[3,2-*b*]carbazoles was investigated.

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Asymmetric cyanation of nitroalkenes catalyzed by a salen–titanium catalyst

Li Lin, Wen Yin, Xu Fu, Jinlong Zhang, Xiaojuan Ma and Rui Wang*

The salen–Ti complex catalyzed cyanation of nitroolefins was accomplished *via* the silyl nitronate intermediate for the synthesis of chiral β -nitronitriles with e.r. up to 92:8 and high yields (up to 90%). The catalyst also kept a high turnover frequency at room temperature. The yield and enantioselectivity of the protocol were slightly affected even in a 10 mmol scale.

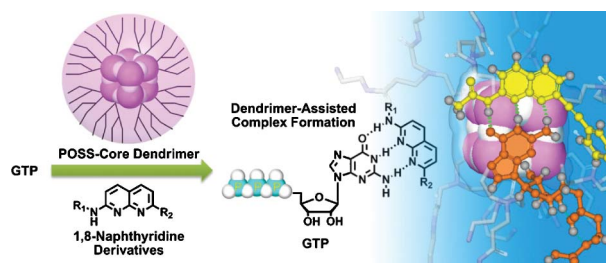


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Enhancement of affinity in molecular recognition *via* hydrogen bonds by POSS-core dendrimer and its application for selective complex formation between guanosine triphosphate and 1,8-naphthyridine derivatives

Kazuo Tanaka, Masahiro Murakami, Jong-Hwan Jeon and Yoshiki Chujo*

Selective recognition of guanosine triphosphate was accomplished using a 1,8-naphthyridine ligand and the POSS-core dendrimer by enhancing the binding affinity *via* hydrogen bonds.

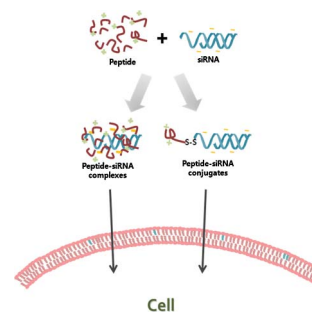


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Complexation and conjugation approaches to evaluate siRNA delivery using cationic, hydrophobic and amphiphilic peptides

Jung Woo Park, Eun-Kyoung Bang, Eun Mi Jeon and Byeang Hyeon Kim*

Both the complexation and conjugation methods were nontoxic and allowed the delivery of siRNA into the cytoplasm.

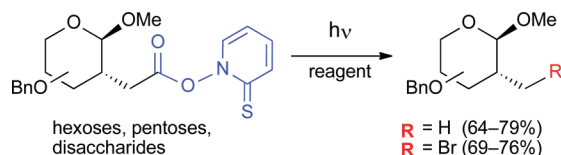


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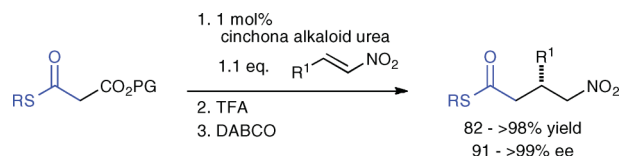
Barton radical reactions of 2-C-branched carbohydrates

Tukaram M. Pimpalpal, Jian Yin and Torsten Linker*

The side chain of various carbohydrates was functionalized by photoreaction of hitherto unknown Barton esters, which were synthesized from glycals in only a few steps.



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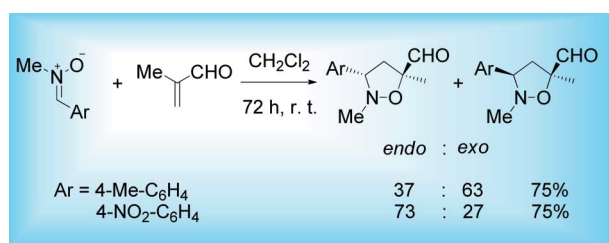


Mono thiomalonates as thioester enolate equivalents—enantioselective 1,4-addition reactions to nitroolefins under mild conditions

Paolo Clerici and Helma Wennemers*

Mono thiomalonates are introduced as versatile thioester enolate equivalents. Asymmetric organocatalyzed conjugate addition reactions to nitroolefins proceed under mild conditions to afford synthetically useful γ -nitrothioesters with excellent yields and enantioselectivities.

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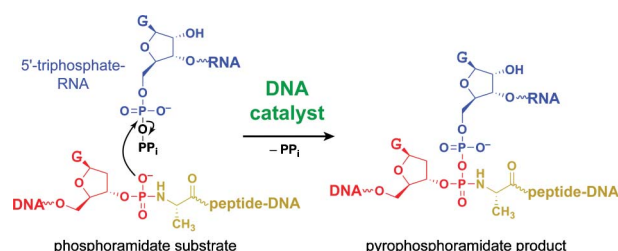


Electronic effects in 1,3-dipolar cycloaddition reactions of *N*-alkyl and *N*-benzyl nitrones with dipolarophiles

Andrei Bădoiu and E. Peter Kündig*

In 1,3-dipolar cycloadditions between nitrones and enals, the electronic properties of the substituents in the nitrones define the activity of the dipoles and dominate diastereoselectivity.

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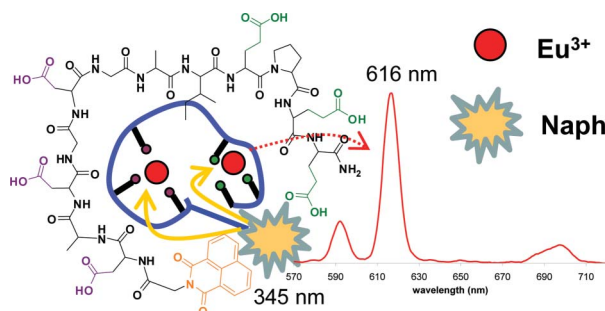


DNA-catalyzed reactivity of a phosphoramidate functional group and formation of an unusual pyrophosphoramidate linkage

Amit Sachdeva and Scott K. Silverman*

A deoxyribozyme is identified that catalyzes nucleophilic attack of a phosphoramidate functional group at a 5'-triphosphate-RNA, forming an unusual pyrophosphoramidate linkage.

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Luminescent lanthanide-binding peptides: sensitising the excited states of Eu(III) and Tb(III) with a 1,8-naphthalimide-based antenna

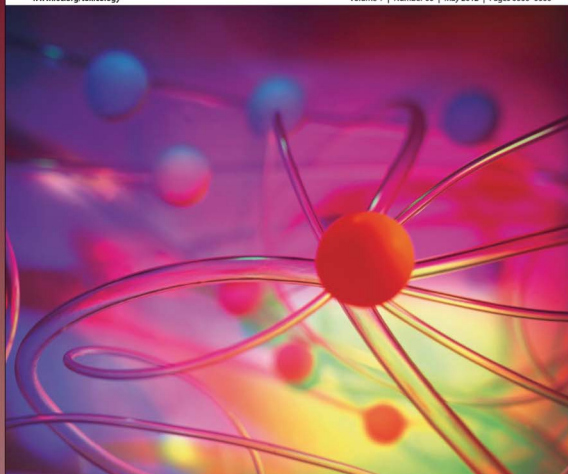
Célia S. Bonnet,* Marc Devocelle and Thorfinnur Gunnlaugsson*

The synthesis and structure of a lanthanide-binding peptide possessing a 1,8 naphthalimide chromophore are described. The luminescence properties and the selectivity over Ca(II) of the Eu(III) and Tb(III) complexes are studied.

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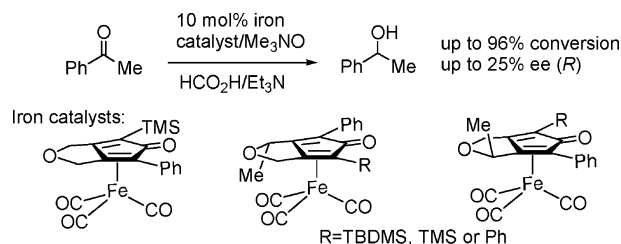
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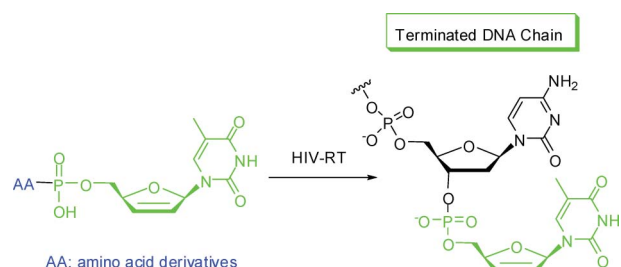


Developing asymmetric iron and ruthenium-based cyclone complexes; complex factors influence the asymmetric induction in the transfer hydrogenation of ketones

Jonathan P. Hopewell, José E. D. Martins, Tarn C. Johnson, Jamie Godfrey and Martin Wills*

The preparation of a range of asymmetric iron and ruthenium-cyclone complexes, and their application to the asymmetric reduction of a ketone, are described.

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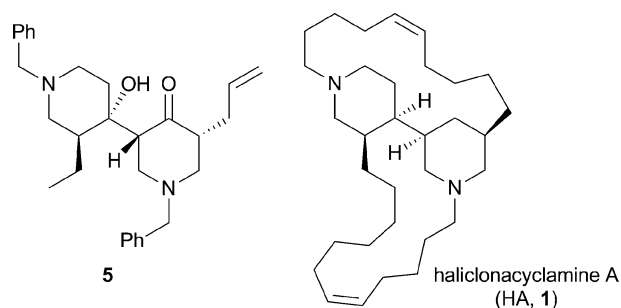


Synthesis and *in vitro* enzymatic and antiviral evaluation of phosphoramidate d4T derivatives as chain terminators

Shiqiong Yang, Christophe Pannecouque, Eveline Lescrinier, Anne Giraut and Piet Herdewijn*

A series of phosphoramidate d4T derivatives have been synthesized and evaluated as substrates for HIV-1 RT, and also tested for their *in vitro* anti-HIV activity in the cells.

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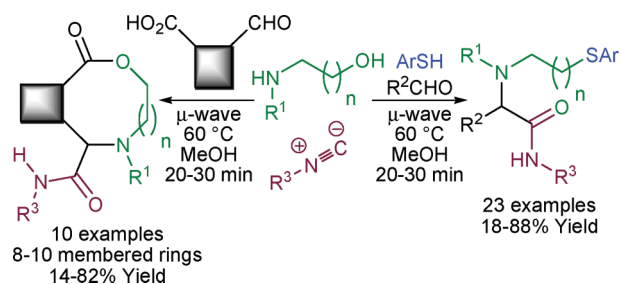


3,4'-Linked bis(piperidines) related to the haliclonaclamine class of marine alkaloids: synthesis using crossed-aldol chemistry and preliminary biological evaluations

M. G. Banwell,* M. J. Coster, N. L. Hungerford, M. J. Garson, S. Su, A. C. Kotze and M. H. G. Munro

Compounds such as **5** incorporating the 3,4'-bis(piperidine) core of the marine alkaloid haliclonaclamine A (HA, **1**) have been prepared using crossed-aldol processes. They retain most of the biological properties of the parent.

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Rapid synthesis of highly functionalised α -amino amides and medium ring lactones using multicomponent reactions of amino alcohols and isocyanides

Martin Bachman, Sam E. Mann and Tom D. Sheppard*

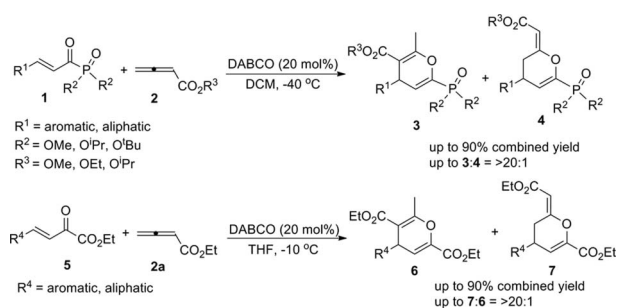
Multicomponent reactions of amino alcohols and isocyanides take place in 20–30 min under microwave irradiation without the need for a catalyst.

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DABCO-catalyzed regioselective cyclization reactions of β,γ -unsaturated α -ketophosphonates or β,γ -unsaturated α -ketoesters with allenic esters

Cheng-Kui Pei, Lei Wu, Zhong Lian and Min Shi*

Highly efficient DABCO-catalyzed [4 + 2] cycloaddition of β,γ -unsaturated α -ketophosphonates or β,γ -unsaturated α -ketoesters with allenic esters.

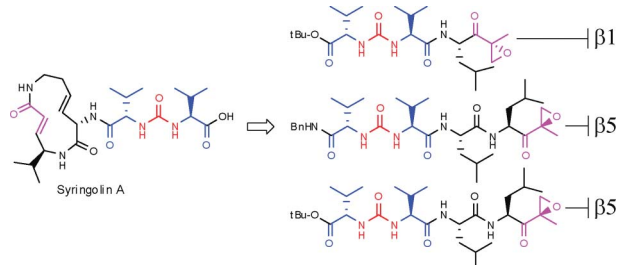


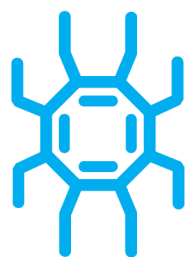
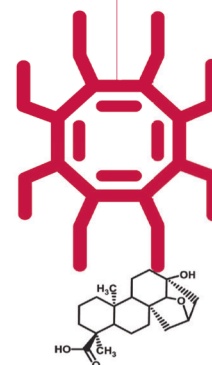
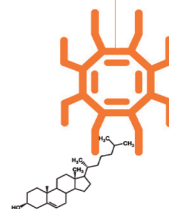
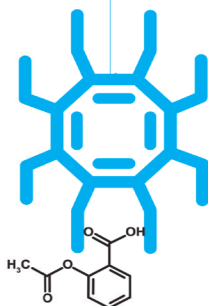
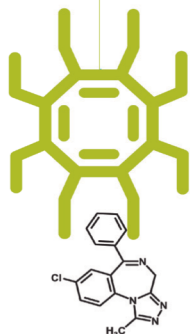
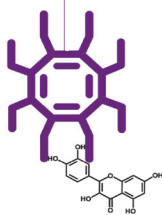
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Discovery of a potent and highly $\beta 1$ specific proteasome inhibitor from a focused library of urea-containing peptide vinyl sulfones and peptide epoxyketones

Wouter A. van der Linden, Lianne I. Willems, Tamer B. Shabaneh, Nan Li, Mark Ruben, Bogdan I. Florea, Gijs A. van der Marel, Markus Kaiser, Alexei F. Kisselev* and Herman S. Overkleeft*

Syringolins are natural product proteasome inhibitors with a macrolactam and an urea as structural features. This work reveals that the relative position of the urea in peptide vinyl sulfones and peptide epoxyketones has a major impact on proteasome inhibition potency and selectivity.





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