

Organic & Biomolecular Chemistry

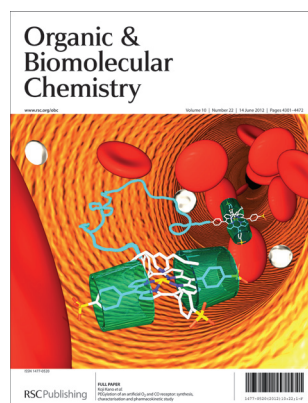
An international journal of synthetic, physical and biomolecular organic chemistry

www.rsc.org/obc

RSC Publishing is a not-for-profit publisher and a division of the Royal Society of Chemistry. Any surplus made is used to support charitable activities aimed at advancing the chemical sciences. Full details are available from www.rsc.org

IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 10(22) 4301–4472 (2012)



Cover

See Koji Kano *et al.*, pp. 4337–4347.

Image reproduced by permission of Koji Kano from *Org. Biomol. Chem.*, 2012, **10**, 4337.



Inside cover

See Sebastian Klimczyk, Nuno Maulide *et al.*, pp. 4327–4329.

Image reproduced by permission of Nuno Maulide from *Org. Biomol. Chem.*, 2012, **10**, 4327.

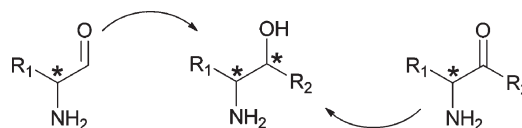
PERSPECTIVE

4311

Diastereoselective synthesis of vicinal amino alcohols

Oskari K. Karjalainen and Ari M. P. Koskinen*

In this era of enantioselective catalysis, diastereoselective synthesis still remains a central objective. In this Perspective the general issues determining diastereoselectivity in the synthesis of vicinal amino alcohols are discussed.



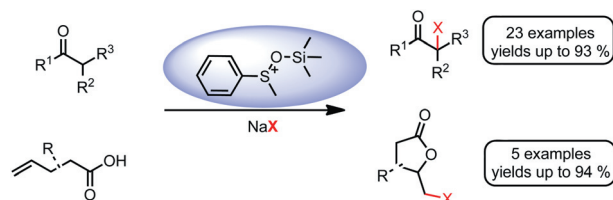
COMMUNICATIONS

4327

Sulfoxide-mediated Umpolung of alkali halide salts

Sebastian Klimczyk, Xueliang Huang, Christophe Farès and Nuno Maulide*

A new protocol for the direct two-electron oxidative Umpolung of alkali halide salts is reported.



EDITORIAL STAFF

Editor

Richard Kelly

Deputy editor

Marie Cote

Development editor

James Anson

Senior publishing editor

Helen Saxton

Publishing editors

Mark Archibald, Andrea Banham, Nicola Burton, Sarah Dixon, Frances Galvin, Elisa Meschini, Roxane Owen

Publishing assistants

Aliya Anwar, Nathalie Horner

Publisher

Emma Wilson

For queries about submitted papers, please contact Helen Saxton, Senior publishing editor in the first instance. E-mail: obc@rsc.org

For pre-submission queries please contact Richard Kelly, Editor. Email: obc-rsc@rsc.org

Organic & Biomolecular Chemistry (print: ISSN 1477-0520; electronic: ISSN 1477-0539) is published 48 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF. All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Distribution Services, c/o Portland Customer Services, Commerce Way, Colchester, Essex, UK CO2 8HP. Tel +44 (0)1206 226050; E-mail sales@rscdistribution.org

2012 Annual (print+electronic) subscription price: £3950; US\$7373. 2012 Annual (electronic) subscription price: £3752; US\$7004. Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT. If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at www.rsc.org/ip. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank. Periodicals postage paid at Rahway, NJ, USA and at additional mailing offices. Airfreight and mailing in the USA by Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001, USA.

US Postmaster: send address changes to Organic & Biomolecular Chemistry (OBC) c/o Mercury Airfreight International Ltd., 365 Blair Road, Avenel, NJ 07001. All despatches outside the UK by Consolidated Airfreight.

The Royal Society of Chemistry takes reasonable care in the preparation of this publication but does not accept liability for the consequences of any errors or omissions. Inclusion of an item in this publication does not imply endorsement by The Royal Society of Chemistry of the content of the original documents to which that item refers.

Advertisement sales: Tel +44 (0) 1223 432246; Fax +44 (0) 1223 426017; E-mail advertising@rsc.org

For marketing opportunities relating to this journal, contact marketing@rsc.org

Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

www.rsc.org/obc

Organic & Biomolecular Chemistry brings together molecular design, synthesis, structure, function and reactivity in one journal. It publishes fundamental work on synthetic, physical and biomolecular organic chemistry as well as all organic aspects of: chemical biology, medicinal chemistry, natural product chemistry, supramolecular chemistry, macromolecular chemistry, theoretical chemistry, and catalysis.

EDITORIAL BOARD

Chair

Jeffrey Bode, ETH Zürich, Switzerland

Associate Editors

Jin-Quan Yu, Scripps Research

Institute, La Jolla, CA, USA

Andrei Yudin, University of Toronto,

Canada

Ashraf Brik, Ben-Gurion University of the Negev, Israel

Margaret Brimble, University of Auckland, New Zealand

Pauline Chiu, University of Hong Kong, China

Anthony Davis, University of Bristol, UK

Veronique Gouverneur, University of Oxford, UK

Christian Hertweck, Leibniz-Institute Jena, Germany

Kenichiro Itami, Nagoya University, Japan

Stephen Kent, University of Chicago, USA

Paolo Scrimin, University of Padova, Italy

Qi-Lin Zhou, Nankai University, China

ADVISORY BOARD

Helen Blackwell, University of Wisconsin-Madison, USA

Barry Carpenter, Cardiff University, UK

Michael Crimmins, University of North Carolina, USA

Antonio Echavarren, Autonomous University of Madrid, Spain

Jonathan Ellman, Yale University, USA

Kurt Faber, University of Graz, Austria

Ben Feringa, University of Groningen, Netherlands

Nobutaka Fujii, Kyoto University, Japan

Jan Kihlberg, Umeå University, Sweden

Philip Kocienski, University of Leeds, UK

Steven V Ley, University of Cambridge, UK

Stephen Loeb, University of Windsor, Canada

Ilan Marek, Israel Institute of Technology, Israel

Manuel Martín Lomas, CCRB, San Sebastián, Spain

Keiji Maruoka, Kyoto University, Japan

Heather Maynard, University of California, Los Angeles, USA

E W 'Bert' Meijer, Eindhoven University of Technology, Netherlands

Eiichi Nakamura, University of Tokyo, Japan

Ryoji Noyori, Nagoya University, Japan

Mark Rizzacasa, University of Melbourne, Australia

Richmond Sarpong, University of California, Berkeley, USA

Oliver Seitz, Humboldt University of Berlin, Germany

Jay Siegel, University of Zürich, Switzerland

Bruce Turnbull, University of Leeds, UK

Chris Welch, Merck & Co., Rahway, NJ, USA

Helma Wennemers, University of Basel, Switzerland

Peter Wipf, University of Pittsburgh, USA

Henry N C Wong, Chinese University of Hong Kong, China

Shuli You, Shanghai Institute of Organic Chemistry, China

Sam Zard, Ecole Polytechnique, France

Li He Zhang, Peking University, China

INFORMATION FOR AUTHORS

Full details on how to submit material for publication in *Organic & Biomolecular Chemistry* are given in the Instructions for Authors (available from <http://www.rsc.org/authors>). Submissions should be made *via* the journal's homepage: <http://www.rsc.org/obc>.

Authors may reproduce/republish portions of their published contribution without seeking permission from the RSC, provided that any such republication is accompanied by an acknowledgement in the form: (Original Citation)—Reproduced by permission of The Royal Society of Chemistry.

This journal is © The Royal Society of Chemistry 2012. Apart from fair dealing for the purposes of research or private study for non-commercial purposes, or criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the Copyright and Related Rights Regulation 2003, this publication may only be reproduced, stored or transmitted, in any form or by any means, with the prior permission in writing of the Publishers or in the case of reprographic reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK. US copyright law is applicable to users in the USA.

The Royal Society of Chemistry takes reasonable care in the preparation of this publication but does not accept liability for the consequences of any errors or omissions.

Ⓢ The paper used in this publication meets the requirements of ANSI/NISO Z39.48–1992 (Permanence of Paper).

Royal Society of Chemistry: Registered Charity No. 207890.

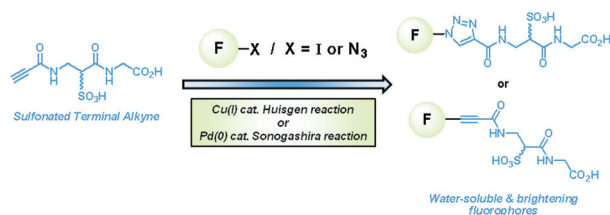
COMMUNICATIONS

4330

New insights into the water-solubilisation of fluorophores by post-synthetic “click” and Sonogashira reactions

Cédrik Massif, Sébastien Dautrey, Alexandre Haefele, Raymond Ziessel, Pierre-Yves Renard and Anthony Romieu*

Transition-metal-mediated reactions, namely the copper-catalysed Huisgen 1,3-dipolar cycloaddition (“click” reaction) and the Sonogashira cross-coupling, work “hand in hand” with a sulfonated terminal alkyne to convert azido- or iodo-fluorophores into water-soluble fluorescent derivatives.



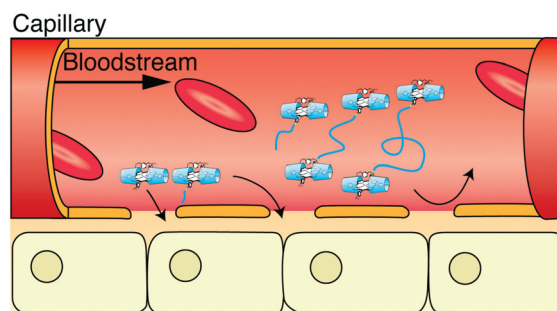
PAPERS

4337

PEGylation of an artificial O₂ and CO receptor: synthesis, characterisation and pharmacokinetic study

Takunori Ueda, Hiroaki Kitagishi and Koji Kano*

Poly(ethylene glycol) (PEG) chains with four different lengths were covalently attached to a supramolecular O₂ and CO receptor composed of an iron(II)porphyrin and a per-*O*-methylated β-cyclodextrin dimer with a pyridine ligand to control the circulation time of the receptor in the bloodstream.

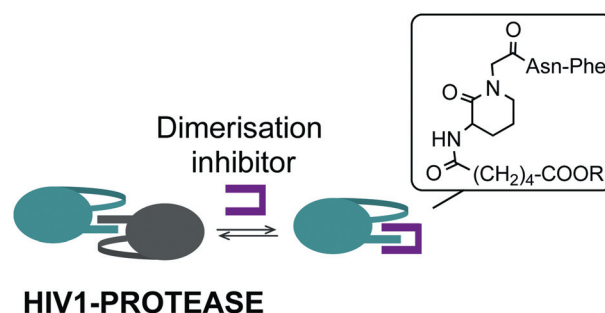


4348

Applications of 3-aminolactams: design, synthesis, and biological evaluation of a library of potential dimerisation inhibitors of HIV1-protease

Eulàlia Pinyol, Silvia Frutos, Dolors Grillo-Bosch, Ernest Giralt, Bonaventura Clotet, Jose A. Esté and Anna Diez*

In the context of our studies on 3-aminolactams, we report here the synthesis of a library of potential dimerisation inhibitors of HIV-1 protease.

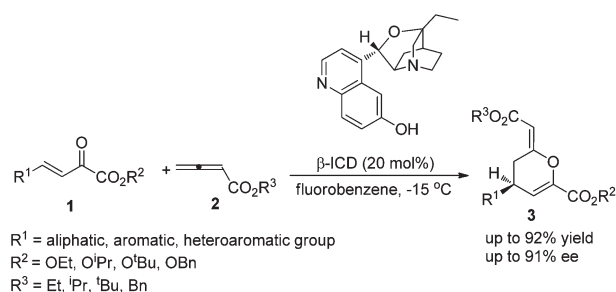


4355

Synthesis of optically active dihydropyrans from asymmetric [4 + 2] cycloaddition of β,γ-unsaturated α-ketoesters with allenic esters

Cheng-Kui Pei, Yu Jiang and Min Shi*

β-Isocupreidine (β-ICD) catalyzed asymmetric [4 + 2] cycloaddition of β,γ-unsaturated α-ketoesters with allenic esters to afford ester-substituted functionalized dihydropyran derivatives in high yields along with high enantioselectivities under mild conditions.



RSC e-membership

Chemical science at your fingertips

£20
for 12 months



RSC e-membership enables you to...

- **ACCESS** expert knowledge and keep current with 12 digital editions of the award-winning *Chemistry World* magazine
- **INTERACT** with specialists in your field and discuss the science that matters to you by joining an RSC Interest Group
- **ENGAGE** with tens of thousands of users worldwide on MyRSC, the online professional community for chemical scientists

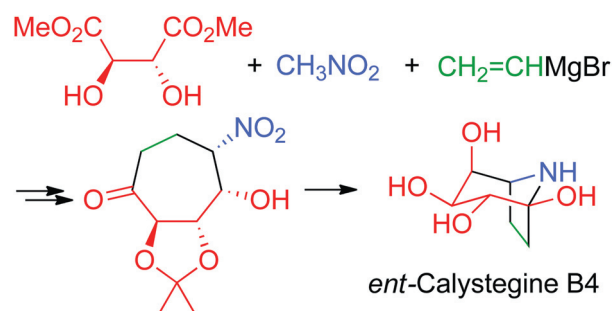
Join today and connect with the global scientific community through the RSC, the central hub for chemical science www.rsc.org/emembership

PAPERS

4362

Total synthesis of *ent*-calystegine B4 via nitro-Michael/aldol reaction

Akio Kamimura,* Koichiro Miyazaki, Shuzo Suzuki, Shingo Ishikawa and Hidemitsu Uno

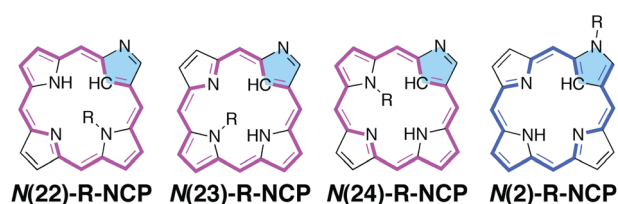
Optically active *ent*-calystegine B4 was prepared in 13 steps from commercially available chiral L-dimethyl tartrate.

4367

Regulation of NH-tautomerism in N-confused porphyrin by N-alkylation

Motoki Toganoh, Takaaki Yamamoto, Takayoshi Hihara, Hisanori Akimaru and Hiroyuki Furuta*

NH-Tautomerization in N-confused porphyrins is regulated by N-alkylation, which allowed us to obtain discrete information on each NH-tautomer of an N-confused porphyrin.

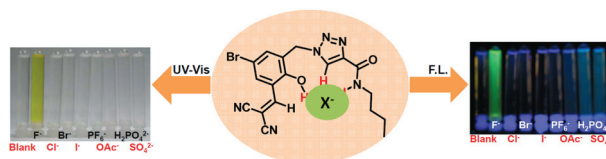


4375

A receptor incorporating OH, NH and CH binding motifs for a fluoride selective chemosensor

Liang Xu, Yongjun Li,* Yanwen Yu, Taifeng Liu, Songhua Cheng, Huibiao Liu and Yuliang Li*

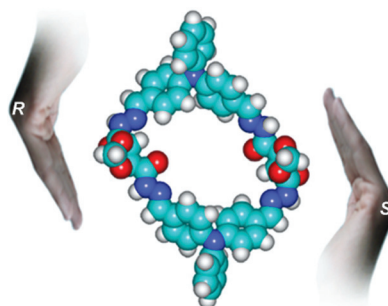
A receptor incorporating OH, NH and CH binding motifs has been constructed for colorimetric and fluorescent sensing of fluoride anion.



4381

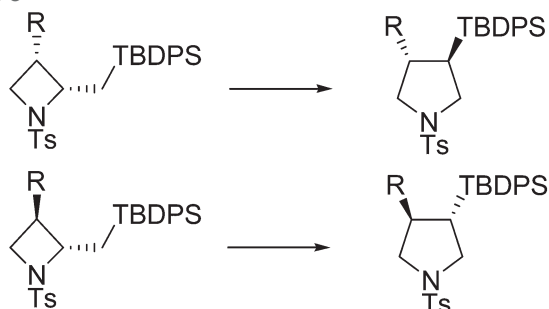
Synthesis of novel enantiomerically pure tetra-carbohydrazide cyclophane macrocycles

Hany F. Nour, Nadim Hourani and Nikolai Kuhnert*

A total of twelve novel enantiomerically pure tetra-carbohydrazide cyclophane macrocycles have been synthesised in quantitative yields by reacting chiral (4*R*,5*R*)- and (4*S*,5*S*)-1,3-dioxolane-4,5-dicarbohydrazides with aromatic bis-aldehydes in a [2 + 2]-cyclocondensation reaction.

PAPERS

4390

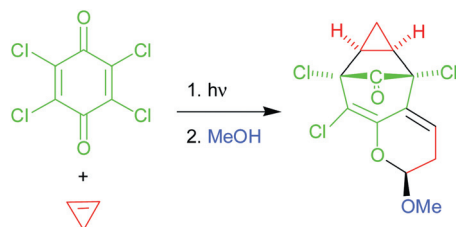


A smooth rearrangement of *N*-*p*-toluenesulfonyl 2-*tert*-butyldiphenylsilylmethyl-substituted azetidines into *N*-*p*-toluenesulfonyl 3-*tert*-butyldiphenylsilyl-substituted pyrrolidines

Bharat D. Narhe, Vardhineedi Sriramurthy and Veejendra K. Yadav*

On exposure to $\text{BF}_3 \cdot \text{OEt}_2$, the azetidine \rightarrow pyrrolidine transformation proceeds through a non-concerted $\sigma_{\text{C-N}}$ cleavage, silyranium ion formation and an intramolecular $\text{S}_{\text{N}}2$ reaction.

4400

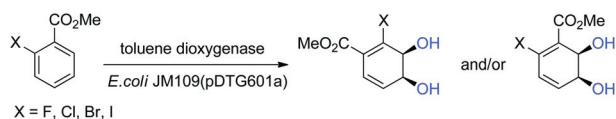


Photocycloadditions of tetrachloro-1,4-benzoquinone (chloranil) onto cyclobutene and cyclopropene. Expected and unexpected products

Max Braun and Manfred Christl*

The photocycloaddition of cyclopropene onto chloranil followed by methanolysis gives rise to a tetracyclic acetal, whereas cyclobutene behaves more conventionally.

4407

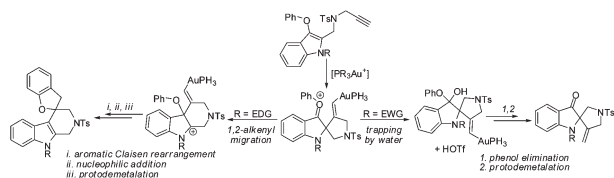


Toluene dioxygenase mediated oxidation of halogen-substituted benzoate esters

Vladislav Semak, Thomas A. Metcalf, Mary Ann A. Endoma-Arias, Pavel Mach and Tomas Hudlicky*

Whole-cell fermentation of *o*-halo methyl benzoates provided new *cis*-dihydrodiol metabolites.

4417



Mechanism of the *N*-protecting group dependent annulations of 3-aryloxy alkynyl indoles under gold catalysis: a computational study

Bing Cheng, Genping Huang, Liang Xu and Yuanzhi Xia*

The mechanism of regiodivergent gold-catalyzed annulations of alkynyl indoles from the Tu group was better understood by DFT calculations.

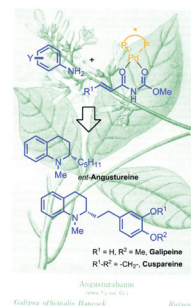
PAPERS

4424

Asymmetric synthesis of 2-alkyl-substituted tetrahydroquinolines by an enantioselective aza-Michael reaction

Laura L. Taylor, Frederick W. Goldberg and King Kuok (Mimi) Hii*

Three *Galipea* alkaloids (angustureine, galipeine and cuspareine) were derived from an enantiomerically pure tetrahydroquinoline intermediate, prepared by a Pd-catalysed aza-Michael reaction.

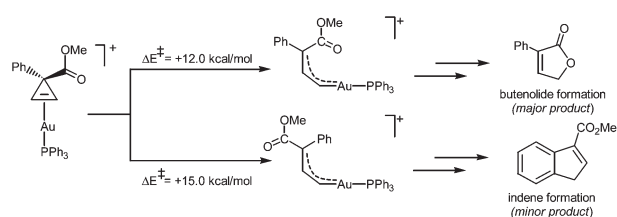


4433

Computational studies on the mechanism of the gold(I)-catalysed rearrangement of cyclopropenes

Maximillian S. Hadfield, L. Jonas L. Haller, Ai-Lan Lee,* Stuart A. Macgregor,* James A. T. O'Neill and Ashley M. Watson

Density functional theory calculations have been employed to investigate the mechanism of gold(I)-catalysed rearrangements of cyclopropenes.

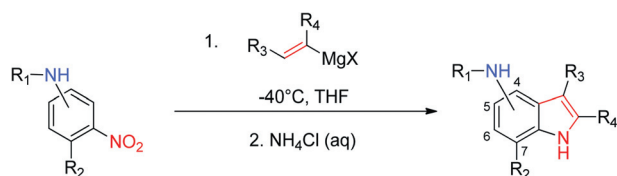


4441

Synthesis of amino-substituted indoles using the Bartoli reaction

Laura Wylie, Paolo Innocenti, Daniel K. Whelligan and Swen Hoelder*

We report herein the concise preparation of a range of functionalised aminoindoles *via* a new application of the Bartoli reaction.

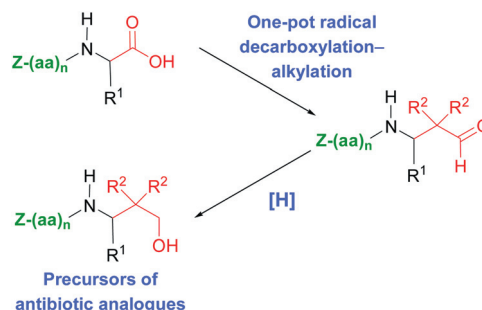


4448

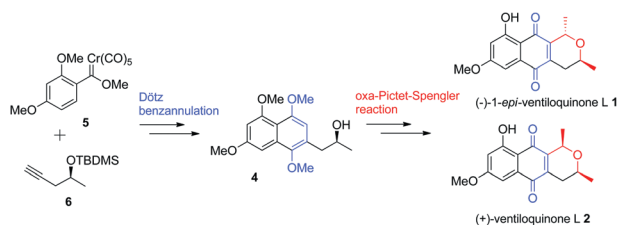
Preparation of modified peptides: direct conversion of α -amino acids into β -amino aldehydes

Carlos J. Saavedra, Alicia Boto* and Rosendo Hernandez*

The direct conversion of α -amino acids into β -amino aldehydes was developed, providing peptide aldehydes, which are precursors of peptaibol antibiotic analogues.



4462

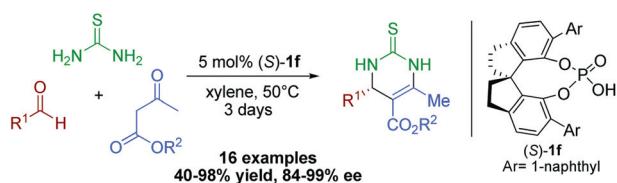


Stereoselective synthesis of (-)-1-*epi*-ventiloquinone L and (+)-ventiloquinone L, the monomeric unit of cardinalin 3

Rodney A. Fernandes,* Arun B. Ingle and Vijay P. Chavan

A stereoselective synthesis of (-)-1-*epi*-ventiloquinone L and (+)-ventiloquinone L, the monomeric unit of cardinalin 3 has been described using Dötz benzannulation and oxa-Pictet-Spengler reactions as key steps. The synthesis is completed in 7 steps with 10.5% and 13% overall yields for (-)-1-*epi*-ventiloquinone L and (+)-ventiloquinone L respectively.

4467



Highly enantioselective Biginelli reaction catalyzed by SPINOL-phosphoric acids

Fangxi Xu, Dan Huang, Xufeng Lin* and Yanguang Wang*

A highly enantioselective Biginelli reaction promoted by chiral spirocyclic SPINOL-phosphoric acids has been developed. Under the optimized conditions a wide range of optically active dihydropyrimidinethiones were obtained in high yields with good to excellent enantioselectivities. The synthetic utility of this method was demonstrated by the synthesis of chiral precursors of three drugs, including (*S*)-Monastrol, (*S*)-L-771688 and (*S*)-SQ 32926.

Looking for free content?

Then register for an RSC Publishing personal account. Giving you access to all free content on the RSC Publishing platform, it includes:

- All content of our newest journals for the first 2 volumes
- Any articles that are part of a special free access promotion
- A sample chapter from each book in the RSC eBook Collection

and much more.

With your username and password you can access the free content any time, any place – all you need is internet access.

So don't delay – register today.

RSC Publishing

www.rsc.org/personalregistration

Registered Charity Number 207890