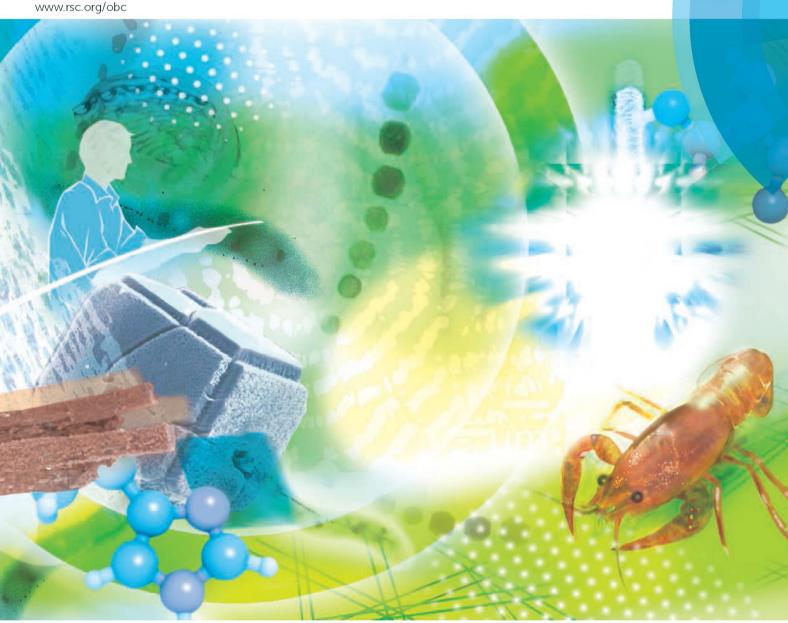
Organic & Biomolecular Chemistry



ISSN 1477-0520



REVIEW ARTICLE

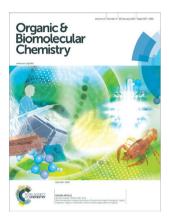
Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry www.rsc.org/obc

The Royal Society of Chemistry is the world's leading chemistry community. Through our high impact journals and publications we connect the world with the chemical sciences and invest the profits back into the chemistry community.

IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 13(4) 957-1266 (2015)



See Atsushi Arakaki. Takashi Kato et al., pp. 974-989.

Image reproduced by permission of Takashi Kato from Org. Biomol. Chem., 2015, **13**, 974.



Inside cover

See P. Ballester et al., pp. 1022-1029.

Image reproduced by permission of P. Ballester from Org. Biomol. Chem., 2015, 13, 1022.

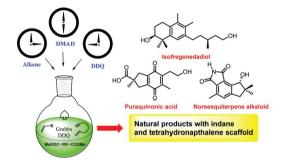
PERSPECTIVE

970

One-pot quadruple/triple reaction sequence: a useful tool for the synthesis of natural products

K. Kashinath and D. Srinivasa Reddy*

Multiple reactions in one pot has always been a useful technique for synthetic organic chemists, as it can minimizes solvent usage, time and the number of purification steps when compared to individual multi-step syntheses.



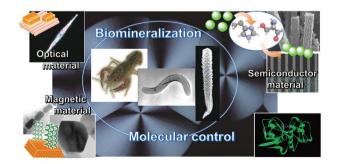
REVIEW

974

Biomineralization-inspired synthesis of functional organic/inorganic hybrid materials: organic molecular control of self-organization of hybrids

Atsushi Arakaki,* Katsuhiko Shimizu, Mayumi Oda, Takeshi Sakamoto, Tatsuya Nishimura and Takashi Kato*

Biomineralization-inspired synthesis of functional organic/ inorganic hybrid materials. Molecularly controlled mechanisms of biomineralization and application of the processes towards future material synthesis are introduced.



Editorial staff

Editor

Richard Kelly

Deputy editor

Marie Cote

Editorial production manager

Development editor

James Anson

Publishing editors

Nicola Burton, Zoe Karthauser, Elisa Meschini, Roxane Owen, Simon Rankmore, Donna Smith

Publishing assistants

Emily Finney, Rosalind Searle

Emma Wilson

For gueries about submitted papers, please contact Helen Saxton, Editorial production manager 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 Order Department, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, UK Tel +44 (0)1223 432398; E-mail orders@rsc.org

2015 Annual (print+electronic) subscription price: £4572; US\$8534. 2015 Annual (electronic) subscription price: £4343; US\$8107 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.

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. Broad in scope, it publishes research and reviews on topics across organic synthesis, physical organic chemistry, supramolecular chemistry and chemical biology

Editorial board

Andrei Yudin, University of Toronto, Canada

Associate editors

Margaret Brimble, University of Auckland, New Zealand Jin-Quan Yu, Scripps Research Institute, La Jolla, CA, USA

Editorial board members

Ashraf Brik, Ben-Gurion University of the Negey Israel Pauline Chiu, University of Hong Kong, China Jonathan Clayden, University of Manchester, UK Anthony Davis, University of Bristol,

Christian Hertweck, Leibniz-Institute Jena Germany Kenichiro Itami, Nagoya University, Qi-Lin Zhou, Nankai University,

Advisory board

Kyo Han Ahn, Pohang University of Science and Technology, Korea Fredrik Almqvist, Umeå University, Sweden

Barry Carpenter, Cardiff University, UK Krishna Kaliappan, IITB, India David Chen, Seoul National University, Korea

Shunsuke Chiba, Nanyang Technological University, Singapore Sheng-Hsien Chiu, National Taiwan

University, Chinese Taipei Luiz Carlos Dias,

State University of Campinas, Brazil Antonio Echavarren, Autonomous University of Madrid, Spain

Jonathan Ellman, Yale University, USA Margaret Faul, Amgen, USA Ben Feringa, University of Groningen,

The Netherlands Amar Flood, Indiana University Bloomington, USA

Nobutaka Fujii, Kyoto University,

Carmen Galan, University of Bristol,

Sam Gellman, University of Wisconsin, USA

Christian Hackenberger, Free University Berlin, Germany Mimi Hii, Imperial College London,

Steven V. Ley, University of Cambridge, UK Shih-Yuan Liu, University of Oregon,

Stephen Loeb, University of Windsor,

David Lupton, Monash University,

llan Marek, Israel Institute of Technology, Israel

Keiji Maruoka, Kyoto University, Japan Cristina Nevado, University of Zürich, Switzerland

Dhevalapally B. Ramachary, University Peter Wipf, University of Pittsburgh, of Hyderabad, India

Viresh Rawal, University of Chicago, 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

Tibor Soos, Hungarian Academy of Sciences, Hungary Corev Stephenson

University of Michigan, USA Mark Taylor, University of Toronto,

Dirk Trauner, Ludwig-Maximilian University Munich, Germany Bruce Turnbull, University of Leeds,

Georgios Vassilikogiannakis, University of Crete, Greece Helma Wennemers, University of Basel, Switzerland

Shuli You, Shanghai Institute of Organic Chemistry, China Li He Zhang, Peking University, China Jian Zhou, East China Normal 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 2015. Apart from fair dealing for the purposes of research or private study for non-commercial purposes, or criticism or Registered Charity No. 207890. 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)

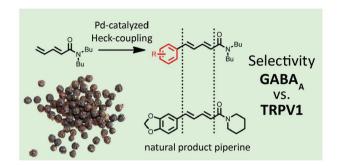
COMMUNICATIONS

990

Developing piperine towards TRPV1 and GABA_A receptor ligands — synthesis of piperine analogs *via* Heck-coupling of conjugated dienes

Laurin Wimmer, David Schönbauer, Peter Pakfeifer, Angela Schöffmann, Sophia Khom, Steffen Hering and Marko D. Mihovilovic*

Synthetic analogs of piperine, the pungent alkaloid of black pepper, were identified as selective ligands for either $GABA_A$ or TRPV1 receptors.

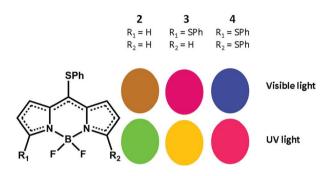


995

Unprecedented one-pot sequential thiolate substitutions under mild conditions leading to a red emissive BODIPY dye 3,5,8-tris(PhS)-BODIPY

Robinson I. Roacho, Alejandro Metta-Magaña, Eduardo Peña-Cabrera and Keith Pannell*

Phenylthiol performs a thiol exchange with 8-MeS-BODIPY and activates/substitutes the 3,5 positions forming a tri-thiolated BODIPY.



1000

An expedient approach to 1,2-dihydroisoquinoline derivatives *via* cobalt catalysed 6-*endo dig* cyclization followed by Mannich condensation of *o*-alkynylarylaldimines

Urvashi, Gaurav K. Rastogi, Sandeep K. Ginotra, Alka Agarwal and Vibha Tandon*

A highly effective 6-endo dig cyclisation of o-alkynyl aldimines to 1,2-dihydroisoquinolines has been described via direct and nitro Mannich condensation using inexpensive and readily available cobalt chloride as catalyst.

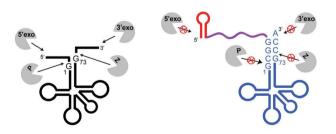
L-Proline, R₃-NH₂ CoCl₂ (30 mol%) Nu (X = H or OH and Y = H or CH₃) R₁ CoCl₂ (30 mol%) Nu=CH₃NO₂ Or C₂H₅NO₂ R₂

1008

Investigation of end processing and degradation of premature tRNAs and their application to stabilization of *in vitro* transcripts in wheat germ extract

Atsushi Ogawa* and Yasunori Doi

We investigated the end processing and degradation of premature tRNAs in wheat germ extract (left), which led to the findings of end protectors for efficiently stabilizing an *in vitro* transcript (purple, right).



COMMUNICATIONS

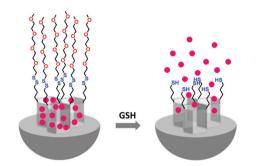
1013

A chiral borane catalyzed asymmetric hydrosilylation of imines

Xiaxia Zhu and Haifeng Du*

An enantioselective hydrosilylation of imines was achieved using an in situ generated chiral borane to furnish amines with up to 82% ee.

1017

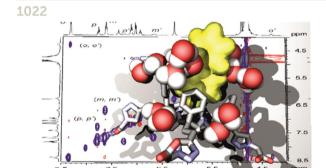


Highly selective and sensitive detection of glutathione using mesoporous silica nanoparticles capped with disulfide-containing oligo(ethylene glycol) chains

S. El Sayed, C. Giménez, E. Aznar, R. Martínez-Máñez,* F. Sancenón and M. Licchelli*

Mesoporous silica nanoparticles loaded with safranin O and capped with disulfide-containing oligo(ethylene glycol) chains were used for the selective and sensitive fluorimetric detection of GSH.

PAPERS

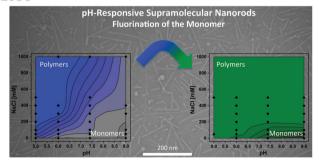


Water-soluble aryl-extended calix[4]pyrroles with unperturbed aromatic cavities: synthesis and binding studies

D. Hernández-Alonso, S. Zankowski, L. Adriaenssens and P. Ballester*

An aryl-extended calix[4]pyrrole receptor with four carboxylic groups at the lower rim binds N-oxides in water with high stability constants.

1030



Tuning the pH-triggered self-assembly of dendritic peptide amphiphiles using fluorinated side chains

Ralph Appel, Sebastian Tacke, Jürgen Klingauf and Pol Besenius*

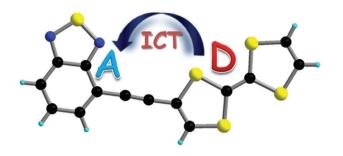
We report the synthesis of a series of anionic dendritic peptide amphiphiles of increasing hydrophobic character and describe their self-assembly into supramolecular nanorods using pH and ionic strength dependent state diagrams.

1040

Modulation of the charge transfer and photophysical properties in non-fused tetrathiafulvalene-benzothiadiazole derivatives

Flavia Pop. Sabine Seifert, Jihane Hankache, Jie Ding. Andreas Hauser* and Narcis Avarvari*

Stille and Sonogashira coupling strategies allowed the preparation of luminescent TTF-benzothiadiazole donor-acceptor compounds with direct linkage or an acetylenic spacer.

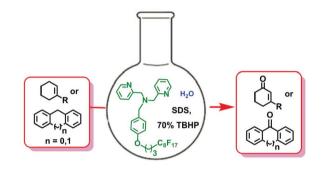


1048

Allylic and benzylic sp³ C-H oxidation in water

Wei Jie Ang and Yulin Lam*

A copper-catalyzed method for the oxidation of allylic and benzylic sp³ C-H by aqueous tert-butyl hydroperoxide (T-Hydro) in water using a recyclable fluorous ligand has been developed.



1053

Synthesis and tautomerization of hydroxylated isoflavones bearing heterocyclic hemi-aminals

Mykhaylo S. Frasinyuk, Svitlana P. Bondarenko, Volodymyr P. Khilya, Chunming Liu, David S. Watt and Vitaliy M. Sviripa*

Aminomethylation of 7-hydroxy isoflavones with C_2-C_5 ω -aminoalcohols led to tautomers 4 and 5 that were interconverted as confirmed by NMR studies.

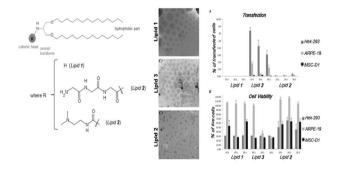
1068

Niosomes based on synthetic cationic lipids for gene delivery: the influence of polar head-groups on the transfection efficiency in HEK-293, ARPE-19 and MSC-D1 cells

E. Ojeda, G. Puras, M. Agirre, J. Zárate, S. Grijalvo, R. Pons, R. Eritja, G. Martinez-Navarrete,

C. Soto-Sanchez, E. Fernández and J. L. Pedraz*

We designed niosomes based on three lipids that differed only in the polar-head group to analyze their influence on the transfection efficiency.



1082

$$R^{2} = OMe, NHR$$

$$BF_{3} \cdot OEt_{2}$$

$$Lowis Acid$$

$$BF_{3} \cdot OEt_{2}$$

$$R^{2} = OMe, NHR$$

$$R^{3} \cdot OEt_{2}$$

$$R^{2} = OMe, NHR$$

$$R^{3} \cdot OEt_{2}$$

$$R^{3} \cdot OE$$

1,4 Addition of unprotected pyrrole onto chiral acrylamides: toward synthesis of new polypeptidic architectures

Alexander Gratais, Xavier Pannecoucke and Samir Bouzbouz*

A variety of new chiral functionalized pyrroloamides have been synthesized by a simple and robust process involving Lewis acids. Unprotected pyrrole could be selectively monoalkylated or dialkylated.

Anionic glycolipids related to glucuronosyldiacylglycerol inhibit protein kinase Akt

Maria Vetro, Barbara Costa, Giulia Donvito, Noemi Arrighetti, Laura Cipolla, Paola Perego,* Federica Compostella, Fiamma Ronchetti and Diego Colombo*

Long chain GlcADG analogues synthesized as PI3P mimics inhibited isolated Akt and proliferation of human ovarian carcinoma IGROV-1 cells.

1100 **RSH** Activated bleomycin TRANS LIPIDS

Bleomycin-induced trans lipid formation in cell membranes and in liposome models

Aysegul Cort, Tomris Ozben, Anna Sansone, Sebastian Barata-Vallejo, Chryssostomos Chatgilialoglu and Carla Ferreri*

Bleomycin-iron complexes cause lipid cis-trans isomerisation through thiyl radical formation and reactivity with unsaturated phospholipids, revealing membranes as a relevant and novel site of drug effect.

1106

Determination of the absolute configuration of phosphinic analogues of glutamate

Bruno Commare, Delphine Rigault, Isabelle A. Lemasson, Patrick Deschamps, Alain Tomas, Pascal Roussel, Isabelle Brabet, Cyril Goudet, Jean-Philippe Pin, Frédéric R. Leroux,* Françoise Colobert* and Francine C. Acher*

Stereomers of LSP1-2111 have been separated, their absolute configuration and agonist activity at mGlu4R determined.

1113

The synthesis of [18F]pitavastatin as a tracer for hOATP using the Suzuki coupling

Yusuke Yagi, Hiroyuki Kimura,* Kenji Arimitsu, Masahiro Ono, Kazuya Maeda, Hiroyuki Kusuhara, Tetsuya Kajimoto, Yuichi Sugiyama and Hideo Saji*

Fluorine-18 labeled radiotracers, such as [18F]fluorodeoxyglucose, can be used as practical diagnostic agents in positron emission tomography (PET).

1122

Cationic dialkylarylphosphates: a new family of bio-inspired cationic lipids for gene delivery

Stéphanie S. Le Corre, Nawal Belmadi, Mathieu Berchel, Tony Le Gall, Jean-Pierre Haelters, Pierre Lehn, Tristan Montier and Paul-Alain Jaffrès*

The synthesis of mono- and di-cationic lipophosphates is reported. These cationic lipids were formulated as liposomal solutions, and their capacity to transfect cells was evaluated on three cell lines.

1133

The development of a complementary pathway for the synthesis of aliskiren

Le-Le Li, Jin-Ying Ding, Lian-Xun Gao and Fu-She Han*

We present an alternative pathway for the synthesis of aliskiren by applying the Evans chiral auxiliary-aided asymmetric allylation and the Julia-Kocienski olefination as the key transformations.

1141

Design and synthesis of Tröger's base ditopic receptors: host-quest interactions, a combined theoretical and experimental study

M. B. Reddy, M. Shailaja, A. Manjula, * J. R. Premkumar, G. N. Sastry,* K. Sirisha and A. V. S. Sarma

The host-guest interaction between flexible ditopic receptors and bisammonium ion has been investigated experimentally and computationally. The conformation folding of guest bisammonium ion molecules leads to the oscillation of the host-guest interaction.

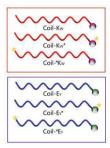
1150

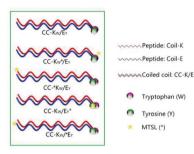
Catalyst-free synthesis of 2-aryl-1,2-dihydroquinazolin-4(1H)-thiones from 2-aminobenzothioamides and aldehydes in water

Stefan Oschatz, Tom Brunzel, Xiao-Feng Wu* and Peter Langer*

A convenient and facile procedure for the synthesis of dihydroquinazolinthiones from 2-aminobenzothioamide with aldehydes has been developed. The reactions took place in water without the need of any additive.

1159





Probing coiled-coil assembly by paramagnetic **NMR** spectroscopy

TingTing Zheng, Aimee Boyle, Hana Robson Marsden, Dayenne Valdink, Giuliana Martelli, Jan Raap and Alexander Kros*

Here a new method to determine the orientation of coiled-coil peptide motifs is described.

1169

Gold-catalyzed spiro-N,O-ketal synthesis

M. Grammatikopoulou, S. Thysiadis and V. Sarli*

An efficient method for the synthesis of spiro-N,O-ketals with 5- and 6-membered rings was developed via a goldcatalyzed spiroamidoketalization of alkynyl amidoalcohols under mild conditions.

1179



Enantioselective synthesis of benzoindolizidine derivatives using chiral phase-transfer catalytic intramolecular domino aza-Michael addition/ alkylation

Jiajia Guo and Shouyun Yu*

An efficient and enantioselective strategy to synthesize benzoindolizidines via domino intramolecular aza-Michael addition/alkylation was developed.

1187

Synthesis of isoxazolidine-containing uridine derivatives as caprazamycin analogues

Mayumi Yamaguchi, Akira Matsuda and Satoshi Ichikawa*

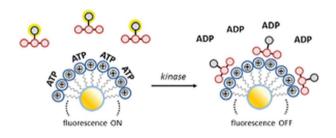
Simplification of caprazamycins was conducted by scaffold-hopping of the structurally complex diazepanone moiety to the isoxazolidine scaffold.

1198

Label-free fluorescence detection of kinase activity using a gold nanoparticle based indicator displacement assay

Cristian Pezzato, Davide Zaramella, Massimiliano Martinelli, Grégory Pieters, Mario A. Pagano* and Leonard J. Prins*

A straightforward fluorescence indicator-displacement assay (IDA) has been developed for the quantitative analysis of ATP→ADP conversion.



1204

Fluorescent organic nanoparticles of dihydropyrimidone derivatives for selective recognition of iodide using a displacement assay: application of the sensors in water and biological fluids

Amanpreet Kaur, Tilak Raj, Simanpreet Kaur, Narinder Singh* and Navneet Kaur*

Fluorescent organic nanoparticles (FON's) derived from dihydropyrimidone derivatives (1-4) were developed and evaluated for their sensor properties.

1213

γ-Cyclodextrin modulates the chemical reactivity by multiple complexation

J. Fernández-Rosas, M. Pessêgo, M. Cepeda-Plaza, N. Basilio, M. Parajó, P. Rodríguez-Dafonte and L. García-Río*

Multiple recognition by cooperative/competitive mechanisms to form a 1:1:1 inclusion complex plays a crucial role in determining the chemical reactivity in the γ-CD cavity.

1225

$$M = Cu$$
path a
$$M = R'$$

$$M = Au, In$$
path b
$$0$$

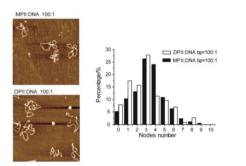
$$R$$
2,4-CHD
$$1,3-CHD$$

Metal-catalyzed formation of 1,3-cyclohexadienes: a catalyst-dependent reaction

Shifa Zhu,* Xiaobing Huang, Tian-Qi Zhao, Tongmei Ma and Huanfeng Jiang

A metal-dependent and complementary catalytic method to synthesize the cyclohexadienes has been developed. When gold or indium salts were used as catalysts, 1,3cyclohexadiene (1,3-CHD) could be obtained; when Cu(OTf)₂ was used as the catalyst, however, another isomer 2,4-cyclohexadiene (2,4-CHD) was furnished instead.

1234



Characterizations of cationic y-carbolines binding with double-stranded DNA by spectroscopic methods and AFM imaging

Tao Jia,* Jing Wang, Peng Guo and Junping Yu*

Because of differences in their structures, cationic γ-carbolines intercalate into DNA with different activities.

1243

Palladium-catalyzed oxidative cross-coupling of azole-4-carboxylates with indoles: an approach to the synthesis of pimprinine

Haipin Zhou, Kuo Gai, Aijun Lin, Jinyi Xu, Xiaoming Wu* and Heguan Yao*

A palladium-catalyzed oxidative cross-coupling reaction between azole-4-carboxylates and indoles forming 5-(3-indolyl)azoles with excellent regioselectivity has been developed.

1249

Tunneling in tocopherol-mediated peroxidation of 7-dehydrocholesterol

H. Muchalski, L. Xu and N. A. Porter*

We report here that H-atom tunneling facilitates the propagation step in the tocopherol-mediated peroxidation (TMP) of 7-dehydrocholesterol. This process likely becomes a major propagation pathway when radical intermediates are isolated in cellular organelles or lipid particles such as low-density lipoproteins. In TMP of 7-DHC and deuterium-reinforced 7-DHC, the KIE of removing hydrogen/deuterium at C9 was found to be 21 ± 1 .

1254

Ruthenium-catalyzed direct C3 alkylation of indoles with α,β -unsaturated ketones

Shuai-Shuai Li, Hui Lin, Xiao-Mei Zhang and Lin Dong*

In this paper, a simple and highly efficient ruthenium-catalyzed direct C3 alkylation of indoles with various $\alpha,\beta\text{-}\text{unsaturated}$ ketones without chelation assistance has been developed.