

# Organic & Biomolecular Chemistry

INDEXED IN MEDLINE

Incorporating Acta Chemica Scandinavica

**Cover**

See Remco W. A. Havenith, Leonardus W. Jenneskens, Patrick W. Fowler and Alessandro Soncini, pp. 1281–1286. The cover art shows computed current density maps of cyclooctatetraene (top) and benzene (bottom) clamped with unsaturated 3,4-dimethylenecyclobuteno “petal groups”.

Image reproduced by permission of Leonardus W. Jenneskens. © Leonardus W. Jenneskens 2004



Chemical biology articles published in this journal also appear in the *Chemical Biology Virtual Journal*: [www.rsc.org/chembiol](http://www.rsc.org/chembiol)

# contents

C33 C40

## Chemical Science

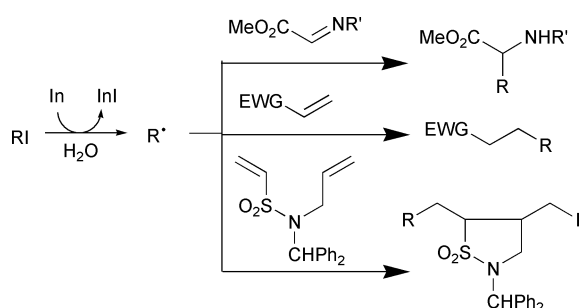
May 2004/Volume 1/Issue 5

[www.rsc.org/chemicalscience](http://www.rsc.org/chemicalscience)

Drawing together the research highlights and news from all RSC publications, *Chemical Science* provides a ‘snapshot’ of the latest developments across the chemical sciences showcasing newsworthy articles, as well as the most significant scientific advances.

### EMERGING AREA

1267 1270



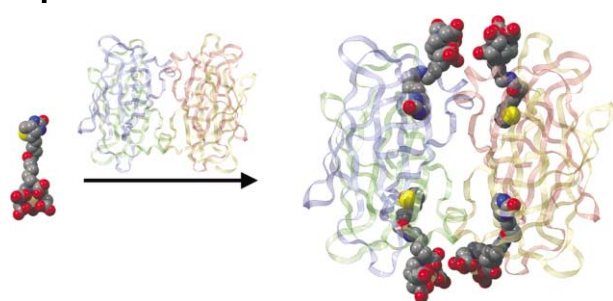
#### The utility of indium in aqueous medium radical reactions

Hideto Miyabe and Takeaki Naito

Employed as a Single Electron Transfer initiator, indium looks SET to transform carbon–carbon bond formation in aqueous media.



1271 1273

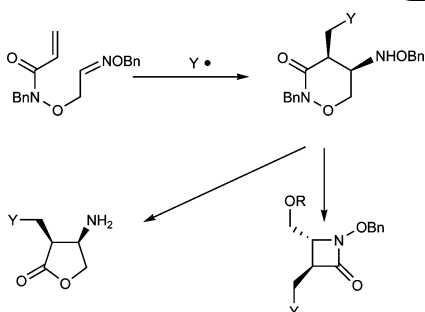


### Probing the interaction of the biotin–avidin complex with the relaxivity of biotinylated Gd-DTPA

Sander Langereis, Homme-Auke T. Kooistra, Marcel H. P. van Genderen and E. W. Meijer

A biotinylated Gd-DTPA complex is designed to study the biotin–avidin complexation using the longitudinal relaxivity of this new MRI label.

1274 1276



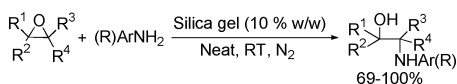
### A novel synthesis of amino-1,2-oxazinones as a versatile synthon for $\beta$ -amino acid derivatives

Okiko Miyata, Megumi Namba, Masafumi Ueda and Takeaki Naito

The radical addition–cyclisation of  $\alpha,\beta$ -unsaturated hydroxamates containing an oxime ether provides a novel method for the stereoselective synthesis of amino-1,2-oxazinones.

## ARTICLES

1277 1280

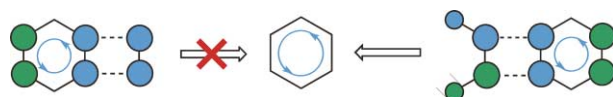


### An efficient synthesis of 2-amino alcohols by silica gel catalysed opening of epoxide rings by amines

Asit K. Chakraborti, Santosh Rudrawar and Atul Kondaskar

Silica gel catalyses the opening of epoxide rings by amines at rt.

1281 1286

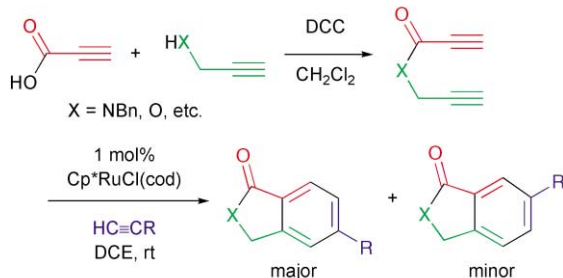


### Which $\pi$ -clamped conjugated monocycles exhibit ring currents?

Remco W. A. Havenith, Leonardus W. Jennekens, Patrick W. Fowler and Alessandro Soncini

Parity match or mismatch of frontier orbitals is the key to quenching and survival of ring currents in  $\pi$ -clamped annulenes.

1287 1294

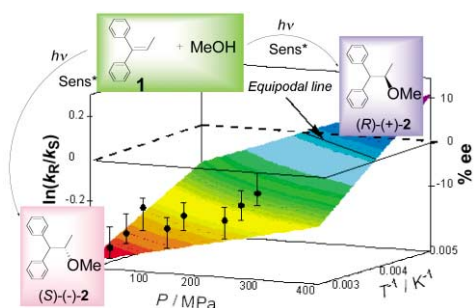


### Synthesis of benzo-fused lactams and lactones *via* Ru(II)-catalyzed cycloaddition of amide- and ester-tethered $\alpha,\omega$ -diynes with terminal alkynes: electronic directing effect of internal conjugated carbonyl group

Yoshihiko Yamamoto, Keisuke Kinpara, Tomoaki Saigoku, Hisao Nishiyama and Kenji Itoh

In the presence of a catalytic amount of  $\text{Cp}^*\text{RuCl}(\text{cod})$ , 1,6- and 1,7-diynes connected by an amide or an ester tether underwent cycloaddition with terminal alkynes at room temperature to give rise to cycloadducts in 40–93% yields with 63 : 37–83 : 17 regioisomer ratios.

1295 1303

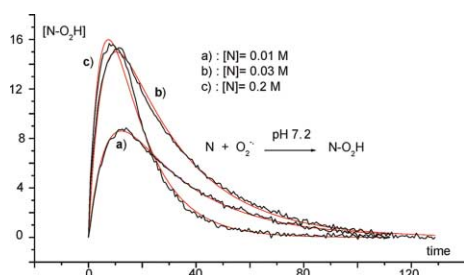


### Pressure control of enantiodifferentiating polar addition of 1,1-diphenylpropene sensitized by chiral naphthalenecarboxylates

Masayuki Kaneda, Yasuhiro Nishiyama, Sadayuki Asaoka, Tadashi Mori, Takehiko Wada and Yoshihisa Inoue

Combined use of pressure and temperature serves as a powerful tool for controlling the yield, chirality and enantiomeric excess in this photosensitized enantiodifferentiating polar addition of methanol to 1,1-diphenylpropene.

1304 1309

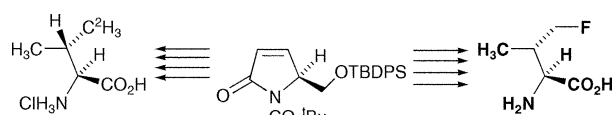


### A new kinetic approach to the evaluation of rate constants for the spin trapping of superoxide/hydroperoxyl radical by nitrones in aqueous media

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

Computer simulation of the kinetic curves led to rate constants for the trapping of superoxide by the nitrene N and for decay of the adduct.

1310 1314

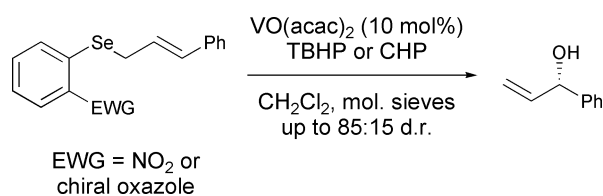


### Synthesis of (2*S*,3*R*)-[3',3',3'-<sup>2</sup>H<sub>3</sub>]-valine and (2*S*,3*S*)-4-fluorovaline

Jean-Damien Charrier, Peter B. Hitchcock and Douglas W. Young

A new synthesis of (2*S*,3*R*)-[3',3',3'-<sup>2</sup>H<sub>3</sub>]-valine has been completed and (2*S*,3*S*)-4-fluorovaline has been synthesised for the first time.

1315 1329

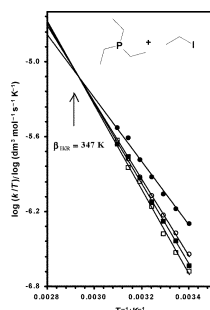


### Vanadium-catalyzed selenide oxidation with *in situ* [2,3] sigmatropic rearrangement (SOS reaction): scope and asymmetric applications

T. Campbell Bourland, Rich G. Carter and Alexandre F. T. Yokochi

The first metal-catalyzed method for the SOS reaction has been developed. Its application to the synthesis of enantiomerically enriched allylic alcohols has been studied on a series of chiral oxazole-containing systems with a diastereomeric ratio (d.r.) of up to 85 : 15.

1330 1338



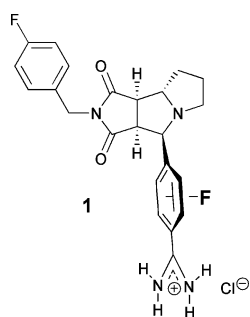
### The quaternisation reaction of phosphines and amines in aliphatic alcohols. A similarity analysis using the isokinetic, isosolvent and isoselective relationships

Lídia M. V. Pinheiro, António R. T. Calado and João Carlos R. Reis

The quaternisation of tertiary phosphines is a much better model reaction for the S<sub>N</sub>2 mechanism than the Menshutkin reaction.



1339 1352

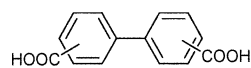


### A fluorine scan of the phenylamidinium needle of tricyclic thrombin inhibitors: effects of fluorine substitution on $pK_a$ and binding affinity and evidence for intermolecular C-F $\cdots$ CN interactions

Jacob Olsen, Paul Seiler, Björn Wagner, Holger Fischer, Thomas Tschopp, Ulrike Obst-Sander, David W. Banner, Manfred Kansy, Klaus Müller and François Diederich

Substitution of H- by F-atoms in the phenylamidinium needle of inhibitor **1** and linear free energy relationships revealed that binding affinity against thrombin is more affected by a decreasing amidinium  $pK_a$  than the affinity against trypsin.

1353 1358



$$\Delta_c U_m^\circ, \Delta_{cr}^g H_m^\circ, \Delta_f H_m^\circ$$

### Thermochemistry of biphenylcarboxylic and dicarboxylic acids. A combined experimental and theoretical study

M. Agostinha R. Matos, Margarida S. Miranda, Diana V. S. S. Martins, Natália A. B. Pinto, Victor M. F. Morais and Joel F. Liebman

Thermochemistry of the biphenylcarboxylic and dicarboxylic acids: a combined experimental and theoretical investigation of enthalpies and energies.

1359 1363



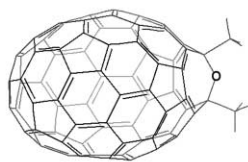
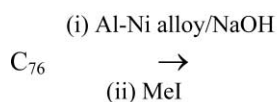
### Aminoxyl radicals as crosslinks for macromolecules of polyvinylpyrrolidone

Evgenii Ya. Davydov, Elena N. Afanas'eva, Irina S. Gaponova and Georgii B. Pariiskii

Photoreactions of nitrogen trioxide produced during photolysis of ceric ammonium nitrate initiate crosslinking of macromolecules via aminoxyl radical formation.



1364 1367



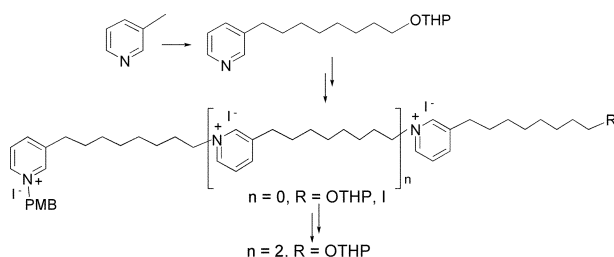
C<sub>76</sub>Me<sub>2</sub> (5 isomers),  
C<sub>76</sub>(CH<sub>2</sub>)<sub>n</sub> (n = 2-4),  
C<sub>76</sub>Me<sub>2</sub>O, C<sub>76</sub>Me<sub>4</sub>O<sub>2</sub>

### Methylation of [76]fullerene and [84]fullerenes; the first oxahomo derivatives of a higher fullerene

Adam D. Darwish, Natalia Martsinovich and Roger Taylor

Methylation of [76]fullerene gives polymethyl and polymethylene derivatives, the first oxahomo[76]fullerene and bis oxahomo[76]fullerene. Methylation of [84]fullerene gives four C<sub>84</sub>Me<sub>2</sub> isomers.

1368 1375



### Synthesis and bioactivity of linear oligomers related to polymeric alkylpyridinium metabolites from the Mediterranean sponge *Reniera sarai*

Ines Mancini, Adriana Sicurelli, Graziano Guella, Tom Turk, Peter Maček and Kristina Sepčić

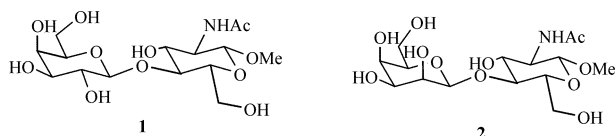
Synthetic analogues of the natural 3-octyl pyridinium polymers have shown antibacterial and anti-acetylcholinesterase activities, increasing with the degree of oligomerization.

1376 1380

**The design and synthesis of a selective inhibitor of fucosyltransferase VI**

M. Carmen Galan, Andre P. Venot, Robert S. Phillips and Geert-Jan Boons

Inversion of configuration of the C-2' hydroxyl of methyl LacNAc led to a compound **2** that was not glycosylated by  $\alpha$ -(2,6)- and  $\alpha$ -(2,3)-ST and fucosyltransferase III, V and VI. However, this derivative showed exquisite selectivity for inhibition of fucosyltransferase VI.

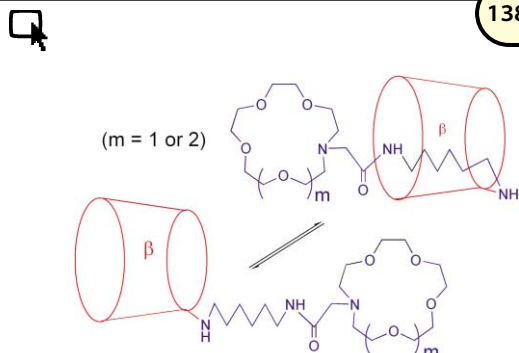


1381 1386

**Intra- and intermolecular complexation in C(6) monoazacoronand substituted cyclodextrins**

Julia S. Lock, Bruce L. May, Philip Clements, Stephen F. Lincoln and Christopher J. Easton

$\beta$ -Cyclodextrin, with an azacoronand appended at C(6) through a flexible link, undergoes intramolecular complexation unlike its smaller  $\alpha$ -cyclodextrin analogue.

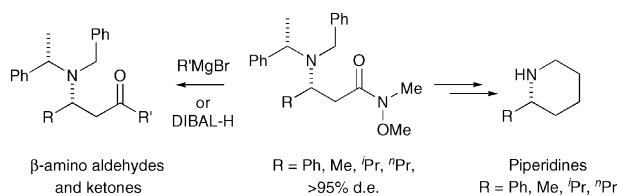


1387 1394

**Asymmetric synthesis and applications of  $\beta$ -amino Weinreb amides: asymmetric synthesis of (*S*)-coniine**

Anthony J. Burke, Stephen G. Davies, A. Christopher Garner, Tom D. McCarthy, Paul M. Roberts, Andrew D. Smith, Humberto Rodriguez-Solla and Richard J. Vickers

$\beta$ -Amino Weinreb amides are versatile intermediates for the asymmetric synthesis of  $\beta$ -amino aldehydes and ketones; chain extension and subsequent functional group manipulation offers an efficient route to homochiral  $\delta$ -amino acid derivatives and 2-substituted piperidines.

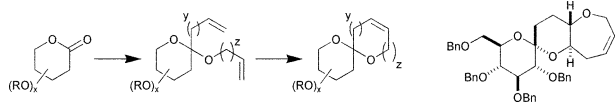


1395 1403

**Synthesis and elaboration of functionalised carbohydrate-derived spiroketals**

Peter A. V. van Hoof, Farid El Oualid, Herman S. Overkleeft, Gijsbert A. van der Marel, Jacques H. van Boom and Michiel A. Leeuwenburgh

Functionalised spiroketals, generated from glyconolactones *via* sequential Grignard reaction, ketoglycosidation and ring-closing metathesis, can be elaborated towards complex ring systems.



1404 1412

**Aqueous solutions that model the cytosol: studies on polarity, chemical reactivity and enzyme kinetics**

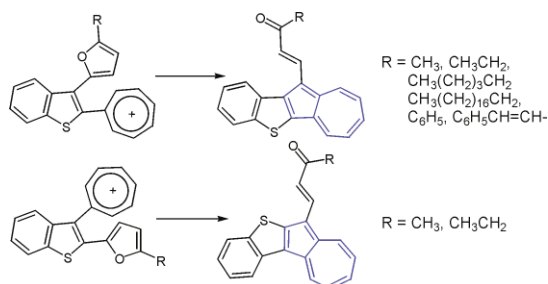
Nabil Asaad, Marie Jetta den Otter and Jan B. F. N. Engberts

Changes in solution polarity and rates of chemical and enzyme reactions have been assessed as a function of solute concentration (up to 400 g l<sup>-1</sup>) in order to model the effects of the cellular environment on chemistry.





1413 1418

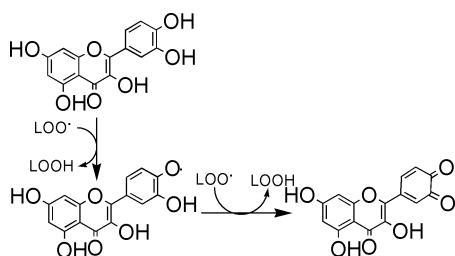


**An efficient novel synthesis of  $\beta$ -(azuleno[1,2-*b*]benzothienyl)- and  $\beta$ -(azuleno[2,1-*b*]benzothienyl)- $\alpha,\beta$ -unsaturated ketones by the tropylium ion-mediated intramolecular furan ring-opening reaction and X-ray investigation of methyl ketone derivative**

Kimiaki Yamamura, Yuuko Houda, Masao Hashimoto, Takatomo Kimura, Makoto Kamezawa and Takehiko Otani

Intramolecular reaction of 2-tropylio-3-(5-substituted 2-furyl)-benzothiophenes and 3-tropylio-2-(5-substituted 2-furyl)benzothiophenes afforded the  $\beta$ -(azuleno[1,2-*b*]benzothienyl)- $\alpha,\beta$ -unsaturated ketones and  $\beta$ -(azuleno[2,1-*b*]benzothienyl)- $\alpha,\beta$ -unsaturated ketones, respectively.

1419 1423



**Inhibition of free radical initiated peroxidation of human erythrocyte ghosts by flavonols and their glycosides**

Lifen Hou, Bo Zhou, Li Yang and Zhong-Li Liu

The flavonols bearing *ortho*-dihydroxyl groups possess significantly higher antioxidative activity than those bearing no such functionalities and the glycosides are less active than their parent aglycones.

## CONFERENCE DIARY

ix

Dates, venues and contact details of forthcoming events.

## COPIES OF CITED ARTICLES

The Library and Information Centre (LIC) of the RSC offers a first class Document Delivery Service for items in Chemistry and related subjects. Contact the LIC, The Royal Society of Chemistry, Burlington House, Piccadilly, London W1V 0BN, UK; Tel: +44 (0) 20 7437 8656; Fax: +44 (0) 20 7287 9798; E-mail: library@rsc.org

This service is only available from the LIC in London and not the RSC in Cambridge.

## FREE E-MAIL ALERTS

Contents lists in advance of publication are available on the web via [www.rsc.org/obc](http://www.rsc.org/obc) – or take advantage of our free e-mail alerting service ([www.rsc.org/ej\\_alert](http://www.rsc.org/ej_alert)) to receive notification each time a new list becomes available.

## ADVANCE ARTICLES AND ELECTRONIC JOURNAL

Free site-wide access to Advance Articles and the electronic form of this journal is provided with a full-rate institutional subscription. See [www.rsc.org/ejs](http://www.rsc.org/ejs) for more information.

\* Indicates the author for correspondence: see article for details.



Electronic supplementary information (ESI) is available *via* the online article (see <http://www.rsc.org/esi> for general information about ESI)