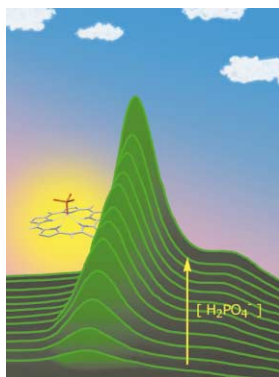


# Organic & Biomolecular Chemistry

FORMERLY PERKIN TRANSACTIONS 1 AND 2

Incorporating Acta Chemica Scandinavica

**Cover**

See Jonathan L. Sessler, Julian M. Davis, Vladimir Král, Thomas Kimbrough and Vincent Lynch, page 4113.

This picture depicts the fluorescence emission intensity enhancement observed when an aqueous solution (pH 7.0, 25 mM PIPES buffer, 150 mM NaCl) of a water soluble saphyrin is titrated with 0–180 mM sodium phosphate.

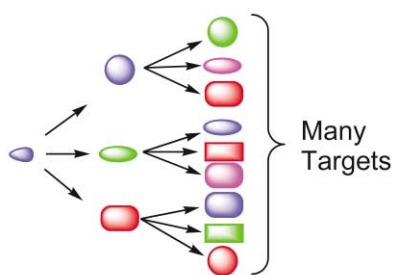
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## contents

## EMERGING AREA



3867 3870

**Diversity-oriented synthesis; a challenge for synthetic chemists**

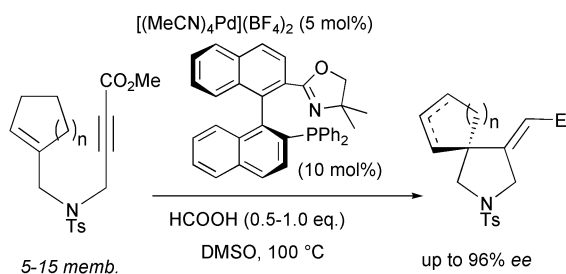
David R. Spring

The efficient, simultaneous synthesis of structurally diverse compounds, diversity-oriented synthesis (DOS) is not obvious, and remains a challenge.

## COMMUNICATIONS



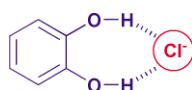
3871 3873

**Highly enantioselective alkaloid synthesis *via* ene-type cyclizations catalyzed by cationic chiral palladium(II) complexes of PN-ligands with an *achiral* oxazoline unit**

Manabu Hatano and Koichi Mikami

A highly efficient asymmetric alkaloid synthesis *via* ene-type cyclizations catalyzed by cationic chiral palladium(II) complexes of a PN-ligand with an *achiral gem*-dimethyl oxazoline unit is demonstrated.

3874 3877

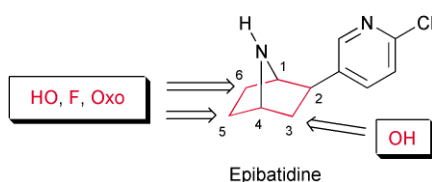


### Rapid NMR screening of chloride receptors: uncovering catechol as a useful anion binding motif

David K. Smith

Results of calibrated competitive NMR screening indicate that catechol is a surprisingly good host for chloride anions.

3878 3881

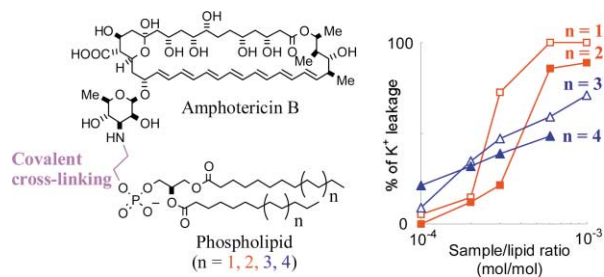


### Functionalization of the alicyclic skeleton of epibatidine: synthesis and nicotinic acetylcholine receptor binding affinities of epibatidine analogues

Zhi-Liang Wei, Yingxian Xiao, Clifford George, Kenneth J. Kellar and Alan P. Kozikowski

A novel method for the epimerization of *endo*-2-(6-chloro-3-pyridyl)-7-azabicyclo[2.2.1]heptan-3-one (**12**) on silica gel was developed and used as the key step to synthesize functionalized analogues of epibatidine which were evaluated for their nicotine receptor subtype selectivity in binding studies.

3882 3884



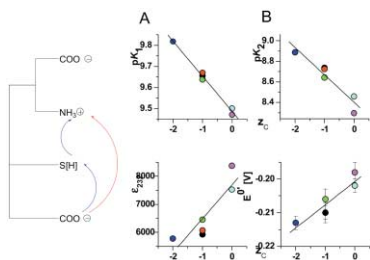
### Amphotericin B–phospholipid covalent conjugates: dependence of membrane-permeabilizing activity on acyl-chain length

Shigeru Matsuoka, Nobuaki Matsumori and Michio Murata

Amphotericin B–phospholipid conjugates elicit ion flux across a phospholipid membrane, and their dose–response relationship is greatly influenced by acyl chain length.

## ARTICLES

3885 3890

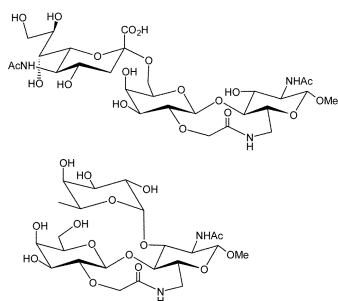


### Structure–function relationships in glutathione and its analogues

Artur Krężel and Wojciech Bal

Results are presented of measurements of protonation constants, UV spectroscopic properties and redox potentials of GSH and its five analogues, which are modified at the C-terminal glycine residue.

3891 3899



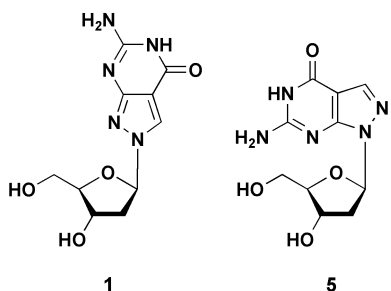
### Chemo-enzymatic synthesis of conformationally constrained oligosaccharides

M. Carmen Galan, Andre P. Venot, John Glushka, Anne Imberty and Geert-Jan Boons

An *N*-acetyllactosamine derivative, which has a methylene amide tether between C-6 and C-2', was enzymatically glycosylated using rat liver  $\alpha$ -2,6-sialyltransferase (ST6GalI) or recombinant human fucosyltransferase V (FucT-V) to give conformationally constrained trisaccharides, that are analogs of 6'-sialyllactosamine ( $\alpha$ Neu5Ac-(2–6) $\beta$ Gal(1–4) $\beta$ GlcNAc-OMe) and Lewis<sup>x</sup> ( $\beta$ Gal(1–4)-[ $\alpha$ Fuc-(1–3)] $\beta$ Glc-NAc-OMe).



3900 3908

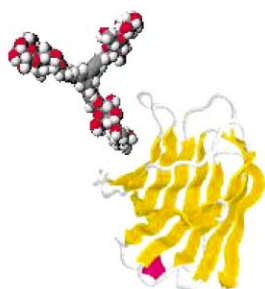


### Oligonucleotide duplexes containing N<sup>8</sup>-glycosylated 8-aza-7-deazaguanine and self-assembly of 8-aza-7-deazapurines on the nucleoside and the oligomeric level

Frank Seela and Rita Kröschel

Stable base pairs are formed between compound **1** with dC or m<sup>5</sup>iC<sub>d</sub>; dG aggregation is inhibited by compound **1** and **5**.

3909 3916

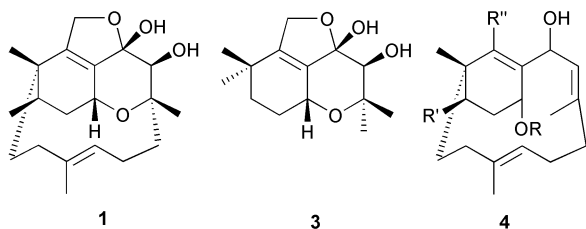


### First demonstration of differential inhibition of lectin binding by synthetic tri- and tetravalent glycoclusters from cross-coupling of rigidified 2-propynyl lactoside

Sabine André, Bingcan Liu, Hans-J. Gabius and René Roy

The lactoside-binding lectins involved in apoptosis, *i.e.* homodimeric galectins-1 and -7 vs chimera-type galectin-3 can be selectively targeted using rigidified glycoclusters of defined geometries and valencies.

3917 3948

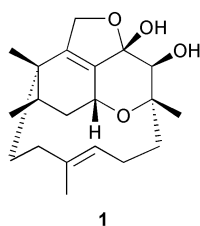


### Synthetic studies towards the phomactins. Concise syntheses of the tricyclic furanochroman and the oxygenated bicyclo[9.3.1]pentadecane ring systems in phomactin A

Kevin M Foote, Christopher J Hayes, Matthew P John and Gerald Pattenden

A concise synthesis of the tricyclic furanochroman unit **3** and of the bicyclo[9.3.1]pentadecane ring system **4** found in the PAF antagonist phomactin A (**1**) isolated from the marine fungus *Phoma* sp., is described.

3949 3956



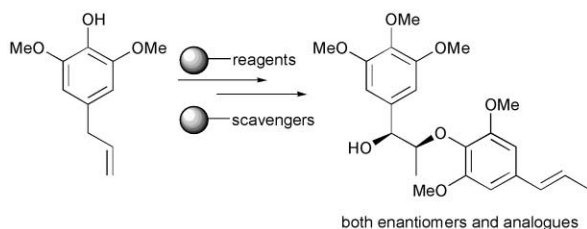
### A total synthesis of (±)-phomactin A

Christopher M. Diaper, William P. D. Goldring and Gerald Pattenden

A total synthesis of the PAF antagonist phomactin A (**1**), isolated from the marine fungus *Phoma* sp., is described.



3957 3966



### The synthesis of the anti-malarial natural product polysphorin and analogues using polymer-supported reagents and scavengers

Ai-Lan Lee and Steven V. Ley

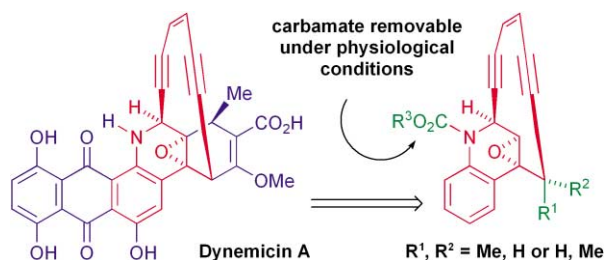
Synthesis of the natural product polysphorin and various analogues has been achieved using polymer-supported reagents and scavengers in a multi-step sequence. A novel enzymatic selective dihydroxylations using microencapsulated osmium tetroxide were also investigated during the course of this study.

3967 3976

**Simplified dynemicin analogues: diastereoselective synthesis and evaluation of their activity against plasmid DNA**

Giuseppe Guanti and Renata Riva

Diastereoselective synthesis of two epimeric enediynes with dynemicin *core*, showing promising DNA scission activity with a consistent double-strand cleavage.

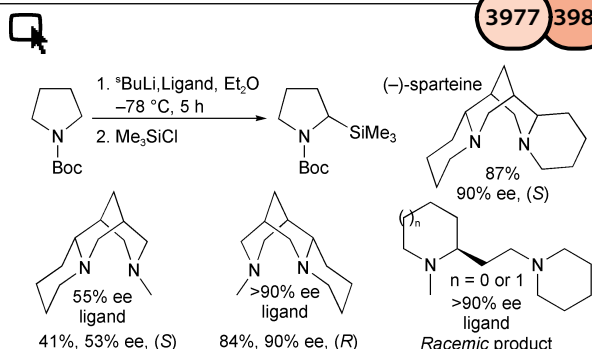


3977 3988

**Synthesis of sparteine-like chiral diamines and evaluation in the enantioselective lithiation–substitution of *N*-(*tert*-butoxy-carbonyl)pyrrolidine**

Jean-Paul R. Hermet, David W. Porter, Michael J. Dearden, Justin R. Harrison, Tobias Koplín, Peter O'Brien, Jérôme Parmene, Vladimir Tyurin, Adrian C. Whitwood, John Gilday and Neil M. Smith

A diamine with only three of the four rings of (–)-sparteine gives high enantioselectivity in the asymmetric deprotonation of *N*-Boc pyrrolidine.

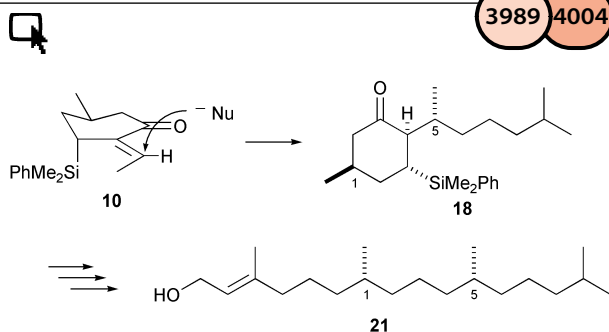


3989 4004

**Stereocontrol of 1,5-related stereocentres using an intermediate silyl group—the diastereoselectivity of nucleophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group**

Ian Fleming, Pranab Maiti and Chandrashekar Ramarao

Nucleophilic attack anti to the silyl group in the enone **10** leads to a high level of open-chain 1,5 stereocontrol.

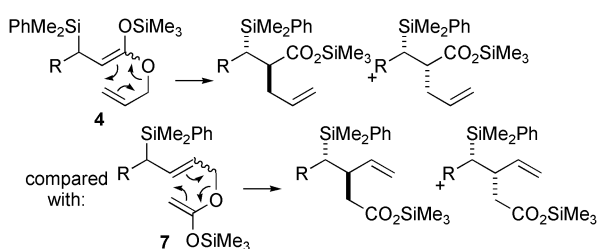


4005 4016

**The Ireland–Claisen rearrangement as a probe for the diastereoselectivity of nucleophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group**

Mark S. Betson and Ian Fleming

The electronically complementary Ireland–Claisen rearrangements **4** and **7** are selective for the new bond to form anti to the silyl group.

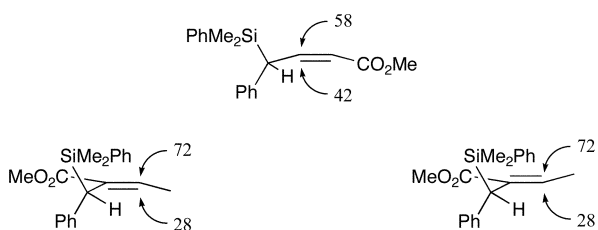


4017 4024

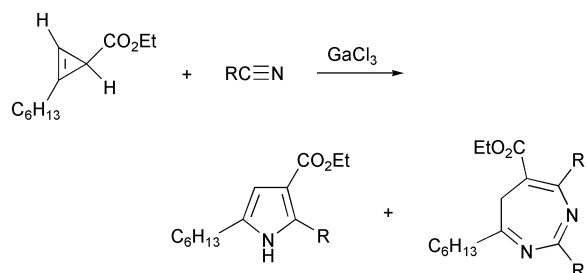
**Diastereocontrol in open-chain nucleophilic attack on a double bond adjacent to a stereogenic centre carrying a silyl group**

Mark S. Betson, Ian Fleming and Jacqueline V. A. Ouzman

Nucleophilic attack on the enones **37**, **38** and **39** appears to take place predominantly from the side syn to the silyl group.



4025 4029

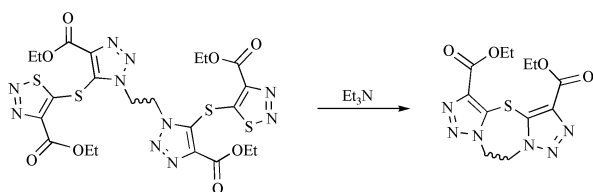


### A new synthesis of pyrroles by the condensation of cyclopropenes and nitriles mediated by gallium(III) and indium(III) salts

Shuki Araki, Takashi Tanaka, Shinya Toumatsu and Tsunehisa Hirashita

Gallium(III) and indium(III) halides mediate the condensation of cyclopropene with nitrile to yield pyrrole and diazepine derivatives.

4030 4038

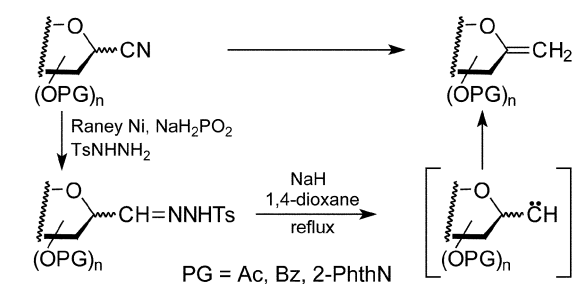


### Reaction of 5-halo-1,2,3-thiadiazoles with aliphatic diamines. Synthesis and intramolecular cyclization of bis(1,2,3-triazolyl-1,2,3-thiadiazolyl)sulfides

Natalya N. Volkova, Evgeniy V. Tarasov, Mikhail I. Kodess, Luc Van Meervelt, Wim Dehaen and Vasily A. Bakulev

Various vicinal diamines react with 5-halo-1,2,3-thiadiazoles to form the bis[1,2,3]triazolo[1,5-b:5',1'-f][1,3,6]thiadiazepine system. The mechanism of the transformation depends upon the reactivity of the diamine.

4039 4046

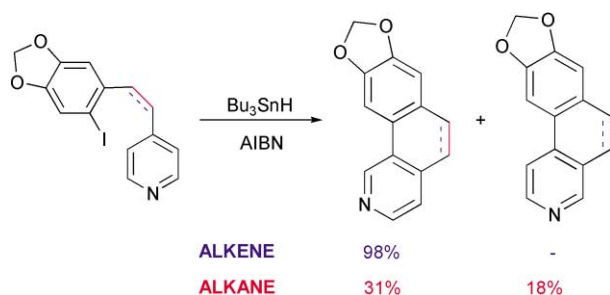


### C-Glycosylmethylene carbenes: synthesis of anhydro-aldose tosylhydrazones as precursors; generation and a new synthetic route to *exo*-glycals

Marietta Tóth, Katalin E. Kövér, Attila Bényei and László Somsák

The Bamford–Stevens reaction of anhydro-aldose tosylhydrazones prepared in one step from glycosyl cyanides represents a new synthesis of acylated *exo*-glycals.

4047 4057

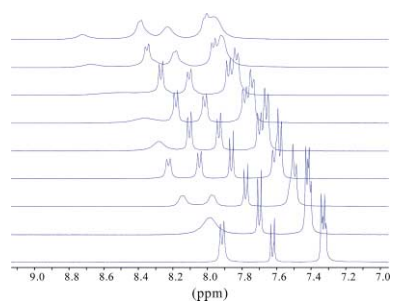


### Intramolecular radical additions to pyridines

David C. Harrowven, Benjamin J. Sutton and Steven Coulton

A survey of radical cyclisation reactions to pyridines has uncovered a number of synthetically useful transformations and an unprecedented rearrangement.

4058 4063

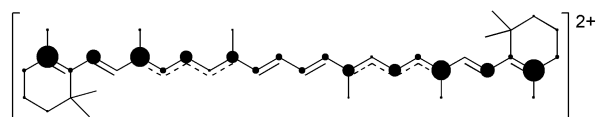


### Structure, modelling and dynamic behaviour of aza- and azaoxamacrocyclic ligands derived from (*R,R*)-1,2-diamino-cyclohexane

Sonia Pulacchini, Rima Nasser, Kevin F. Sibbons, Majid Motevalli, Geoffrey E. Hawkes, Romano T. Kroemer, Edson S. Bento and Michael Watkinson

A detailed structural solid and solution state analysis using molecular modelling, X-ray diffraction and VT-NMR of aza- and azaoxamacrocyclic ligands.

4064 4072

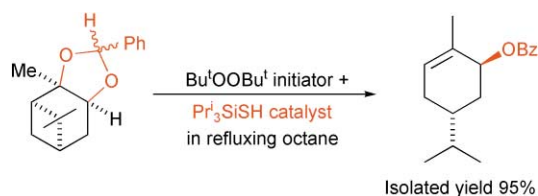


### The charge delocalised $\beta,\beta$ -carotene dication—preparation, structure elucidation by NMR and reactions with nucleophiles

Bjart Frode Lutnaes, Liv Bruås, Geir Kildahl-Andersen, Jostein Krane and Synnøve Liaaen-Jensen

The reaction between  $\beta,\beta$ -carotene and  $\text{BF}_3$ -etherates has been investigated, leading to structural elucidation of the blue product, as a symmetrical charge delocalised dication with considerable stability.

4073 4084

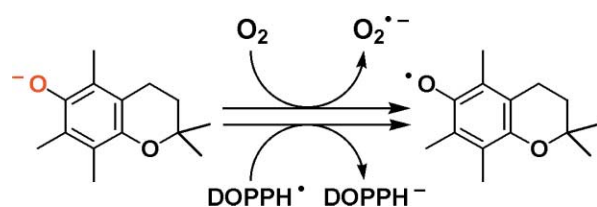


### Thiol-catalysed radical-chain redox rearrangement reactions of benzylidene acetals derived from terpenoid diols

Hai-Shan Dang, Brian P. Roberts and Derek A. Tocher

The thiol-catalysed radical-chain redox rearrangements of benzylidene acetals derived from 1,2- and 1,3-diols of terpene origin afford a variety of products of synthetic and mechanistic interest.

4085 4088

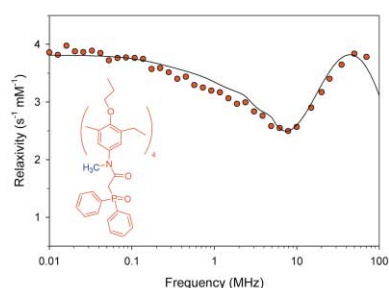


### Kinetic study of the electron-transfer oxidation of the phenolate anion of a vitamin E model by molecular oxygen generating superoxide anion in an aprotic medium

Ikuo Nakanishi, Kentaro Miyazaki, Tomokazu Shimada, Yuko Iizuka, Keiko Inami, Masataka Mochizuki, Shiro Urano, Haruhiro Okuda, Toshihiko Ozawa, Shunichi Fukuzumi, Nobuo Ikota and Kiyoshi Fukuhara

The phenolate anion of a vitamin E model can act as an electron donor to molecular oxygen ( $\text{O}_2$ ) to generate superoxide anion ( $\text{O}_2^{\cdot -}$ ), as well as an efficient scavenger of 2,2-bis(4-*tert*-octyl-phenyl)-1-picrylhydrazyl radical (DOPPH $^{\cdot}$ ).

4089 4096

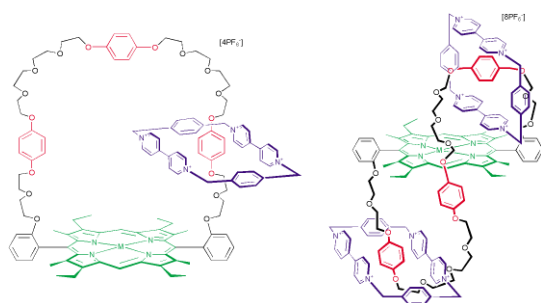


### Modification of calix[4]arenes with CMPO-functions at the wide rim. Synthesis, solution behavior, and separation of actinides from lanthanides

Christian Schmidt, Mohamed Saadioui, Volker Böhmer, Valéry Host, Marie-Rose Spirlet, Jean F. Desreux, Frédéric Brisach, Françoise Arnaud-Neu and Jean-François Dozol

Calix[4]arenes featuring  $\text{N}(\text{Me})\text{-CO-CH}_2\text{-P}(\text{O})\text{Ph}_2$  residues are synthesized from tetraamines. They are selective  $\text{Am}(\text{III})/\text{Eu}(\text{III})$  extractants and form aggregates as shown by relaxation dispersion.

4097 4112



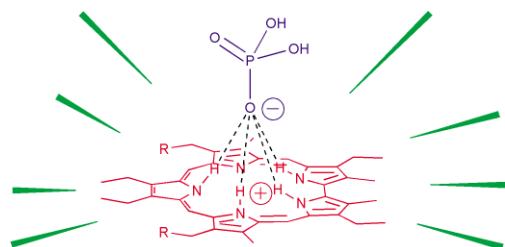
### Translational isomerism and dynamics in multi-hydroquinone derived porphyrin [2]- and [3]-catenanes

Maxwell J. Gunter, Sandra M. Farquhar and Tyrone P. Jaynes

The synthesis and dynamics are described of a series of porphyrin-containing [2]- and [3]catenanes, consisting of zinc porphyrins strappable by polyethylene glycol chain incorporating 2 or 3 central hydroquinone units, interlinked with bipyridinium macrocycles.



4113 4123

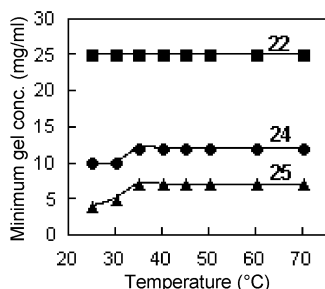


### Water soluble saphyrins: potential fluorescent phosphate anion sensors

Jonathan L. Sessler, Julian M. Davis, Vladimír Král, Thomas Kimbrough and Vincent Lynch

Addition of phosphate to aqueous solutions of aggregated saphyrin (low fluorescence) causes the release of highly fluorescent monomeric saphyrin.

4124 4131



### L-Lysine based gemini organogelators: their organogelation properties and thermally stable organogels

Masahiro Suzuki, Tomomi Nigawara, Mariko Yumoto, Mutsumi Kimura, Hirofusa Shirai and Kenji Hanabusa

New gemini organogelators linked by an oxalyl amide that can be easily, effectively, and cheaply synthesized have good organogelation abilities and their cyclohexane gels have superior thermal stabilities; that containing a 3,5,5-trimethylhexyl ester can gel at 0.7 wt% cyclohexane even at 70 °C.

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