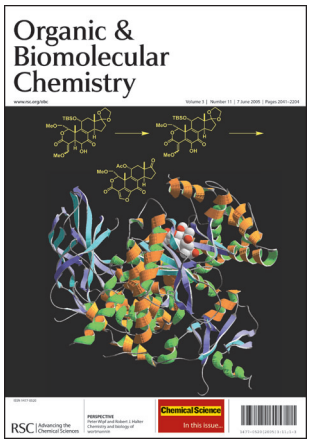
ISSN 1477-0520 CODEN OBCRAK 3(11) 2041–2204 (2005)



Cover
See Peter Wipf and Robert J. Halter, pp. 2053–2061.
End game of the total synthesis of (±)-wortmannin by the Shibasaki group, on top of the X-ray structure of wortmannin bound to PI-3 kinase.

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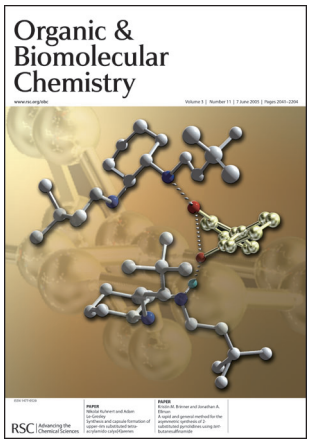


Inside Cover
See Hideki Takagi, Tadashi Mizutani, Takuya Horiguchi, Susumu Kitagawa and Hisanobu Ogoshi, pp. 2091–2094.
The chart shows that the axial chirality is induced in biphenyldiol (highlighted in gold) by complex formation with chiral diamine. The proton transfer equilibrium in the hydrogen-bonding diamine–diol complex drives the formation of a ternary complex, resulting in effective chiral induction.

Image reproduced by permission of Tadashi Mizutani from *Org. Biomol. Chem.*, 2005, **3**, 2091.

CHEMICAL SCIENCE

C41

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.

Chemical Science

June2005/Volume 2/Issue 6

www.rsc.org/chemicalscience

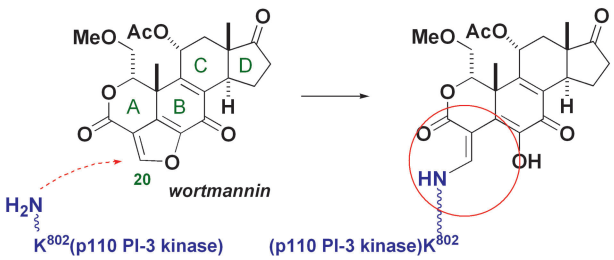
PERSPECTIVE

2053

Chemistry and biology of wortmannin

Peter Wipf* and Robert J. Halter

Wortmannin is the parent member of the viridin class of steroidal furans and a potent enzyme inhibitor that binds to the ATP site of important regulatory kinases.



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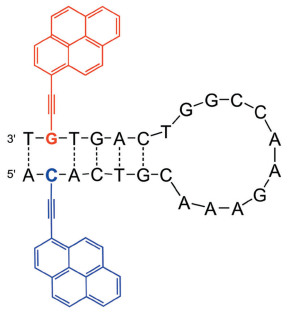
2062

1-Ethynylpyrene-modified guanine and cytosine as optical labels for DNA hybridization

Clemens Wagner, Manuela Rist, Elke Mayer-Enthart and Hans-Achim Wagenknecht*

Incorporation of 1-ethynylpyrene at different sites of DNA tunes the energy donor–acceptor properties as molecular beacons.

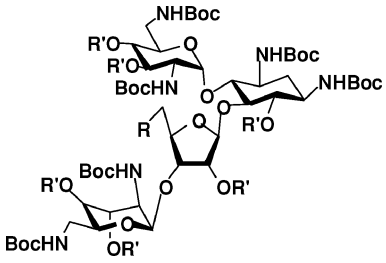


2064

Introduction of a substituent at the 5″-position of *N*-Boc neomycin B under Mitsunobu reaction conditions

Angelica Hernandez Linares, Dominique Fourmy, Jean-Louis Fourrey* and Ali Loukaci

Because of the peculiar reactivity of the idose part of *N*-Boc neomycin B **3**, special care must be exercised to introduce a substituent at the 5″-position of the antibiotic when using Mitsunobu reaction conditions.

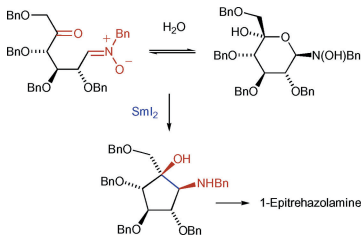


2067

***cis*-Stereoselective SmI_2-promoted reductive coupling of keto-nitrones: first synthesis of 1-epitrehazolamine**

Géraldine Masson, Christian Philouze and Sandrine Py*

An expeditious (four steps, 42% overall yield) synthesis of 1-epitrehazolamine is presented, involving a *cis*-selective SmI_2-promoted reductive cyclization of a masked keto-nitrone.

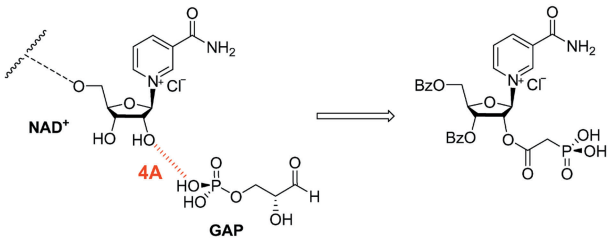


2070

Selective inhibition of *Trypanosoma cruzi* GAPDH by "bi-substrate" analogues

Sylvain Ladame,* Régis Fauré, Colette Denier, Faouzi Lakhdar-Ghazal and Michèle Willson

The synthesis and biological activity of "bi-substrate" analogues as specific inhibitors of the GAPDH from *Trypanosoma cruzi* are described.

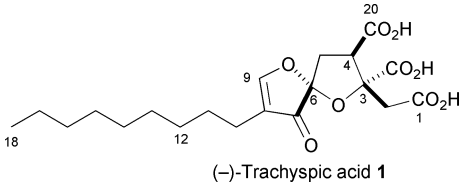


2073

Enantiospecific synthesis of (−)-trachyspic acid

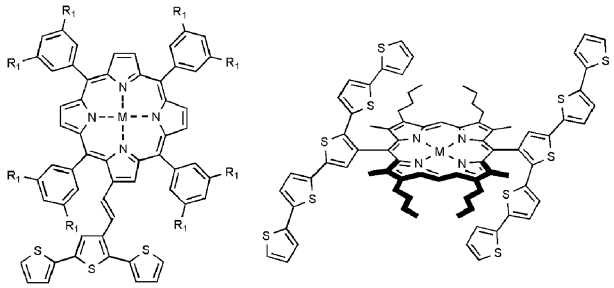
Steven C. Zammit, Jonathan M. White and Mark A. Rizzacasa*

The enantiospecific synthesis of (−)-trachyspic acid (**1**) is described.



(–)-Trachyspic acid **1**

2075

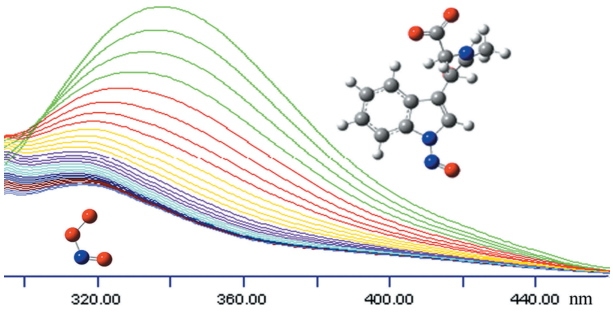


The design and synthesis of porphyrin/oligiothiophene hybrid monomers

Gavin E. Collis, Wayne M. Campbell, David L. Officer* and Anthony K. Burrell*

A series of porphyrin/oligothiophene hybrid monomers with defined architecture have been synthesised for photovoltaic studies.

2085

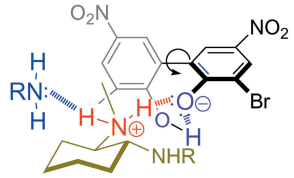


Generation of peroxynitrite from reaction of *N*-acetyl-*N*-nitrosotryptophan with hydrogen peroxide over a wide range of pH values

Michael Kirsch* and Manfred Lehnig

The *in situ* generation of peroxynitrite from *N*-acetyl-*N*-nitrosotryptophan-dependent transnitrosation of hydrogen peroxide is introduced.

2091

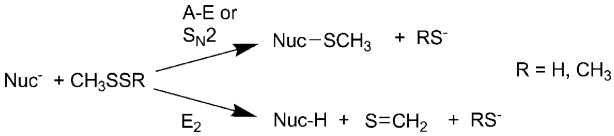


Efficient axial chirality induction in biphenyldiol triggered by proton-transferred hydrogen bonding with chiral amine

Hideki Takagi, Tadashi Mizutani,* Takuya Horiguchi, Susumu Kitagawa and Hisanobu Ogoshi

Proton transferred hydrogen bonds are formed between biphenyldiol and diamine resulting in highly efficient chiral induction.

2095

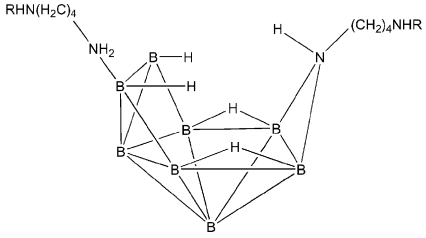


Competing elimination and substitution reactions of simple acyclic disulfides

Steven M. Bachrach* and Andrey Pereverzev

MP2/aug-cc-pVDZ and B3LYP/aug-cc-pVDZ computations are used to compare the elimination *vs.* substitution reactions with different nucleophiles (F^-, HO^-, allyl anion).

2102



Synthesis and characterization of a novel functionalized azanonaborane cluster for boron neutron capture therapy

Afaf R. Genady*

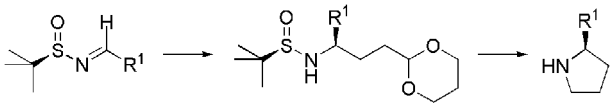
The reductive amination of some carbonyl compounds led to the formation of new functionalized derivatives of the $\{B_8N\}$ cluster to be used in BNCT.

2109

A rapid and general method for the asymmetric synthesis of 2-substituted pyrrolidines using *tert*-butanesulfinamide

Kristin M. Brinner and Jonathan A. Ellman*

A general three-step method for the asymmetric synthesis of 2-substituted pyrrolidines using *tert*-butanesulfinamide is described.

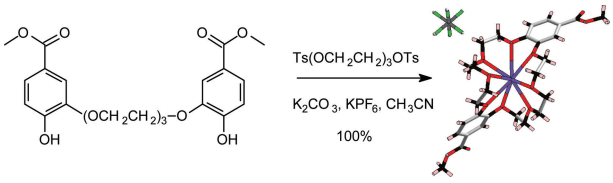


2114

Regioselective routes to disubstituted dibenzo crown ethers and their complexations

Harry W. Gibson,* Hong Wang, Klaus Bonrad, Jason W. Jones, Carla Slebodnick, Lev N. Zackharov, Arnold L. Rheingold, Bradley Habenicht, Peter Lobue and Amy E. Ratliff

We report regiospecific, K-templated synthesis of *cis*-bis(carbomethoxybenzo)-24-crown-8, the synthesis of its *trans*-isomer and their pseudorotaxane complexes with dibenzylammonium hexafluorophosphate.

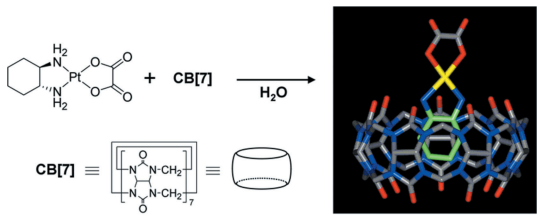


2122

Novel molecular drug carrier: encapsulation of oxaliplatin in cucurbit[7]uril and its effects on stability and reactivity of the drug

Young Jin Jeon, Soo-Young Kim, Young Ho Ko, Shigeru Sakamoto, Kentaro Yamaguchi and Kimoon Kim*

The inclusion phenomenon of oxaliplatin, a drug recently approved for the treatment of colorectal cancer, into cucurbit[7]uril is investigated; encapsulation of the drug results in a large enhancement of stability, a moderate decrease in reactivity toward guanosine but a much larger decrease in reactivity toward L-methionine.

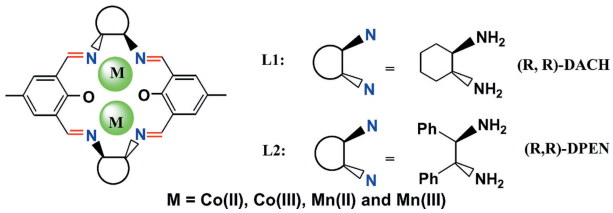


2126

Catalytic asymmetric cyclopropanation at a chiral platform

Jian Gao,* F. Ross Woolley and Ralph A. Zingaro

Novel chiral Robson-type Schiff base–dimetallic Mn(II), Mn(III), Co(II) and Co(III) complexes are shown to be highly effective catalysts for the asymmetric cyclopropanation of styrene and diazoacetate with high enantioselectivity.

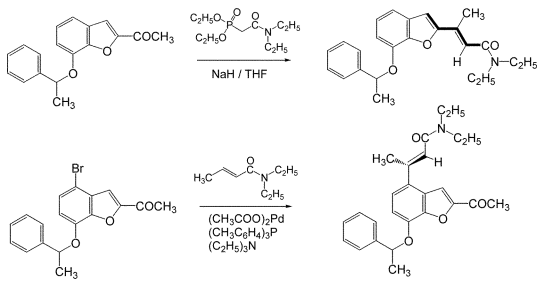


2129

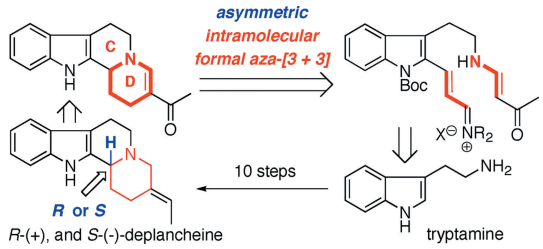
Synthesis of 2-, 4- and 5-(2-alkylcarbamoyl-1-methylvinyl)-7-alkyloxybenzo[*b*]furans and their leukotriene B_4 receptor antagonistic activity

Kumiko Ando, Eriko Tsuji, Yuko Ando, Jun-ichi Kunitomo, Reina Kobayashi, Takehiko Yokomizo, Takao Shimizu, Masayuki Yamashita, Shunsaku Ohta, Takeshi Nabe, Shigekatsu Kohno and Yoshitaka Ohishi*

2-Alkylcarbamoyl-1-methylvinyl groups substituted on benzo[*b*]furan at C-2, C-4 and C-5 had different conformations which caused characteristic LTB_4 receptor antagonistic activity.



2140

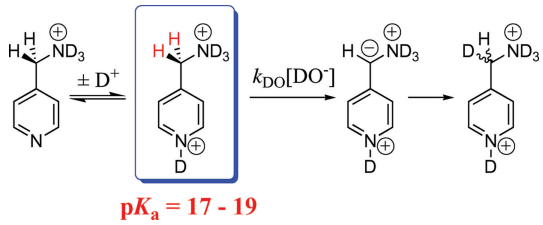


Total syntheses of enantiomerically enriched *R*-(+)- and *S*-(−)-deplancheine

Nadiya Sydorenko, Craig A. Zificsak, Aleksey I. Gerasyuto and Richard P. Hsung*

Total syntheses of indoloquinolizidine alkaloid (±)-, *R*-(+)-, and *S*-(−)-deplancheine are described here. The synthesis features an enantioselective intramolecular formal aza-[3 + 3] cycloaddition for the construction of the quinolizidine CD-ring.

2145

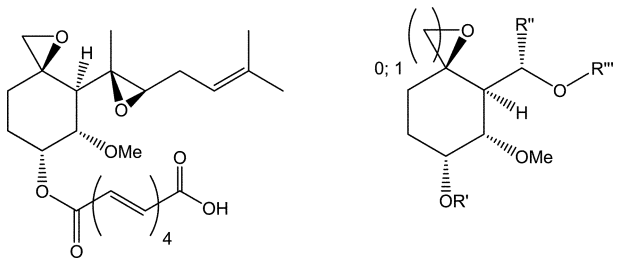


Carbon acidity of the α-pyridinium carbon of a pyridoxamine analog

Juan Crugeiras, Ana Rios, Tina L. Amyes and John P. Richard*

The effect of an α-pyridinium substituent on the acidity of a simple carbon acid in water has been examined.

2150

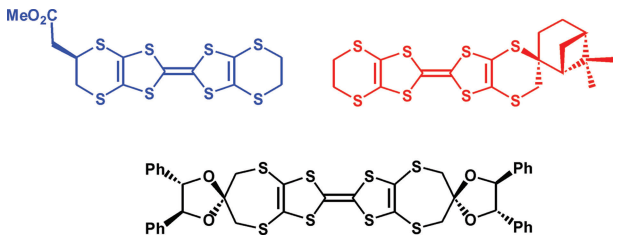


Synthesis and biological evaluation of novel fumagillin and ovalicin analogues

Ralph Mazitschek,* Axel Huwe and Athanassios Giannis*

Fumagillin and ovalicin are potent inhibitors of tumour angiogenesis. A series of analogues lacking the epoxy functionalities linked to harmful side-effects were tested for their anti-angiogenic activity.

2155

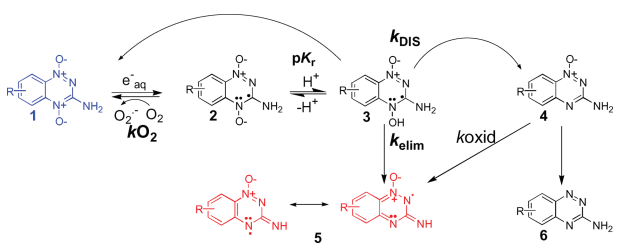


Synthetic strategies to chiral organosulfur donors related to bis(ethylenedithio)tetrathiafulvalene

Jon-Paul Griffiths, Hui Nie, R. James Brown, Peter Day and John D. Wallis*

Syntheses are reported for three enantiopure organosulfur donors which are substrates for preparing chiral electroactive materials.

2167



Radical properties governing the hypoxia-selective cytotoxicity of antitumor 3-amino-1,2,4-benzotriazine 1,4-dioxides

Robert F. Anderson,* Sujata S. Shinde, Michael P. Hay, Swarna A. Gamage and William A. Denny

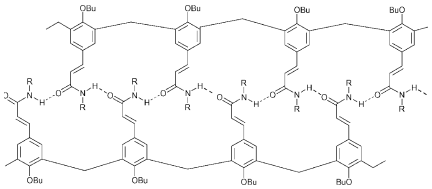
Hypoxic and aerobic cytotoxicity of tirapazamine analogues depend on reduction potentials of the benzotriazinyl radical and the reduced metabolite, maximizing the differential ratio will produce more efficacious hypoxia-selective anticancer drugs.

2175

Synthesis and capsule formation of upper rim substituted tetra-acrylamido calix[4]arenes

Nikolai Kuhnert* and Adam Le-Gresley

Upper rim substituted tetra-acrylamido calix[4]arenes have been synthesised. The compounds display solvent dependent aggregation to form dimeric capsules stabilised by eight hydrogen bonds and π–π interactions.

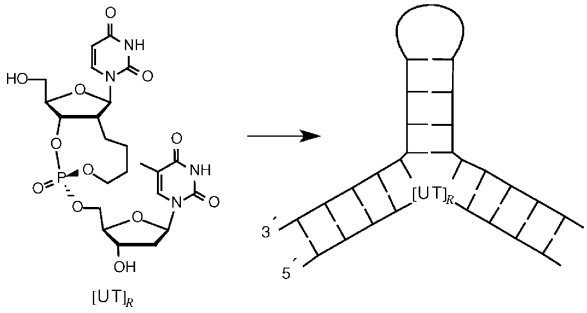


2183

Stabilisation of a nucleic acid three-way junction by an oligonucleotide containing a single 2′-*C* to 3′-*O*-phosphate butylene linkage prepared by a tandem RCM-hydrogenation method

Philip Børsting, Katrine E. Nielsen and Poul Nielsen*

One of two epimeric cyclic dinucleotides was incorporated into an oligodeoxynucleotide which was found to stabilise a three-way junction.

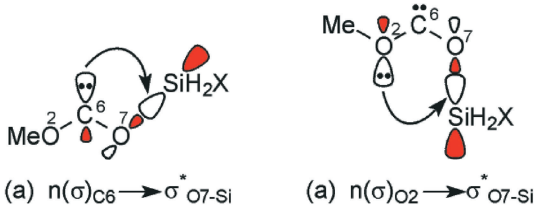


2191

Substituent effects and the role of negative hyperconjugation in siloxycarbene rearrangements

Paul G. Loncke and Gilles H. Peslherbe*

Quantum chemical calculations and natural bond orbital analysis have been used to assess the role of negative hyperconjugation in methoxy(substituted-siloxy)carbenes.



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Recent experimental and theoretical developments towards the observation of parity violation (PV) effects in molecules by spectroscopy
Jeanne Crassous, Christian Chardonnet, Trond Saue and Peter Schwerdtfeger (**DOI**: 10.1039/b504212g)

"Click chemistry" *en route* to pseudo-starch
Laurence Marmuse, Sergey A. Nepogodiev and Robert A. Field (**DOI**: 10.1039/b504293c)

Fluorous click chemistry as a practical tagging method
Zoltán Kaleta, Orsolya Egyed and Tibor Soós (**DOI**: 10.1039/b504973c)

First total synthesis of cichorine and zinnimidine
Anne Moreau, Axel Couture, Eric Deniau, Pierre Grandclaudon and Stéphane Lebrun (**DOI**: 10.1039/b504602e)

The dimethyldioxirane-mediated oxidation of phenylethyne
Klaus-Peter Zeller, Meike Kowallik and Peter Haiss (**DOI**: 10.1039/b504296h)

Parallel *vs.* anti-parallel orientation in a curdlan/oligo(dA) complex as estimated by a FRET technique
Munenori Numata, Kazuya Koumoto, Masami Mizu, Kazuo Sakurai and Seiji Shinkai (**DOI**: 10.1039/b500156k)

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Heather M. E. Duggan, Peter B. Hitchcock and Douglas W. Young (**DOI**: 10.1039/b503014e)

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Romute Yu Garlyauskayte, Alexander N. Chernega, Christophe Michot, Michel Armand, Yurii L. Yagupolskii and Lev M. Yagupolskii (**DOI**: 10.1039/b503286p)

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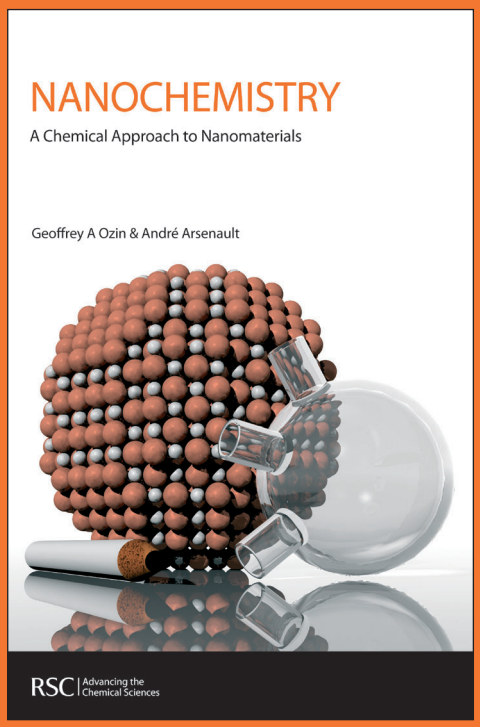

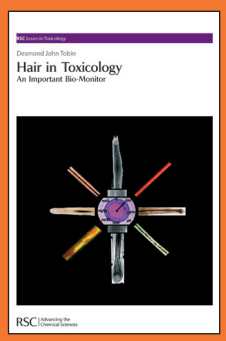

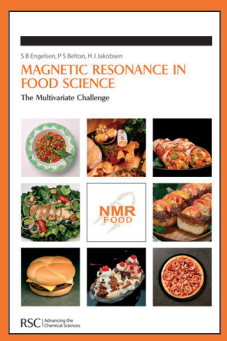

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