Organic & Biomolecular Chemistry

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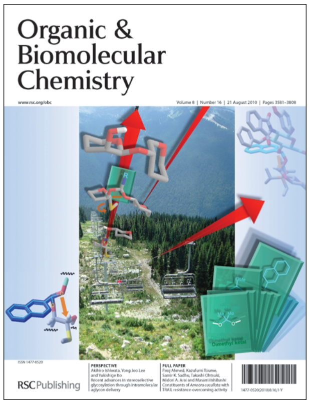
ISSN 1477-0520 CODEN OBCRAK 8(16) 3581–3808 (2010)



Cover
See Akihiro Ishiwata *et al.*,
pp. 3596–3608.
The article by Ishiwata *et al.* describes invention and evolution of intramolecular aglycon delivery (IAD) approach which has proven powerful in giving a variety of *O*-glycosides stereoselectively.

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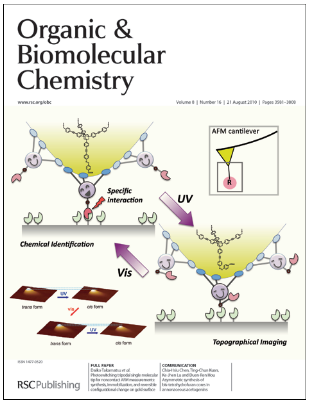

Inside cover
See Daiko Takamatsu *et al.*,
pp. 3655–3664.
Robust, stationary, and photoswitchable tripods were synthesized as single molecule AFM tips for combined chemical force microscopy and topographical imaging.

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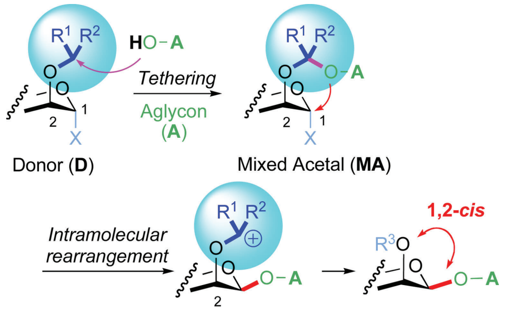
PERSPECTIVES

3596

Recent advances in stereoselective glycosylation through intramolecular aglycon delivery

Akihiro Ishiwata,* Yong Joo Lee and Yukishige Ito*

This account summarizes the newest naphthylmethyl (NAP) ether-mediated intramolecular aglycon delivery as well as all the types of mediations for stereospecific construction of various 1,2-*cis* linkages, not only for β-mannopyranoside, but also for other linkages almost without exception, including β-L-rhamnoside.

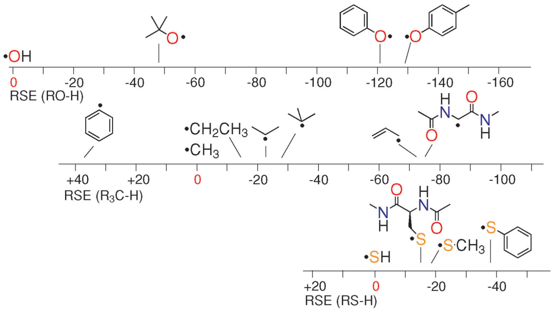


3609

Radical stability and its role in synthesis and catalysis

Johnny Hioe and Hendrik Zipse*

The use of Radical Stabilization Energy (RSE) values for the rationalization and analysis of radical reactions is demonstrated using four case studies from synthetic and biological chemistry: (a) Protecting Group/Radical Translocation (PRT) reactions; (b) Polarity Reversal Catalysis (PRC); (c) Biomimetic Oxidation Reactions; and (d) Class I Ribonucleotide Reductase (RNR I).



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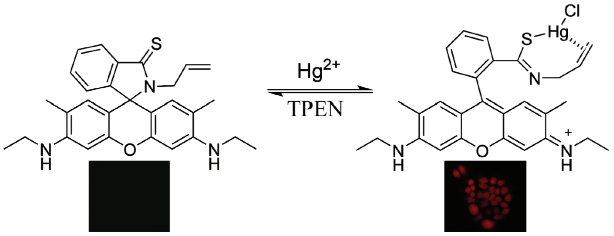
3618

A reversible fluorescent Hg^{2+} chemosensor based on a receptor composed of a thiol atom and an alkene moiety for living cell fluorescence imaging

Weiying Lin,* Xiaowei Cao, Yundi Ding, Lin Yuan and Quanxing Yu

A novel reversible fluorescence turn-on Hg^{2+} chemosensor was constructed based on a new receptor for fluorescence imaging in living cells.

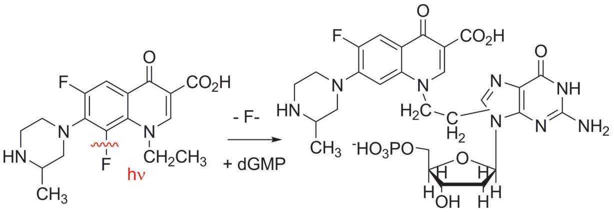


3621

Fluoroquinolones as potential photochemotherapeutic agents: covalent addition to guanosine monophosphate

Elisa Fasani,* Ilse Manet, Massimo L. Capobianco, Sandra Monti,* Luca Pretali and Angelo Albini*

The aryl cation photochemically generated from 8-fluoroquinolones forms a covalent bond with guanosine monophosphate ($k_r > 10^9$ $M^{-1}s^{-1}$).

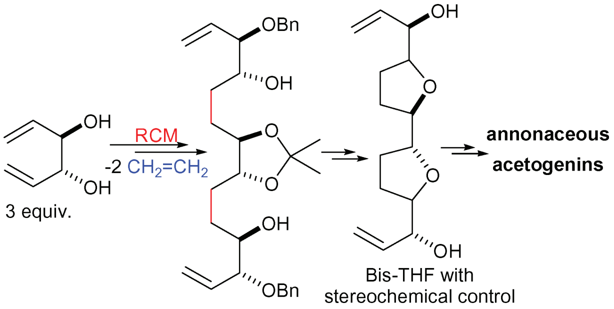


3624

Asymmetric synthesis of bis-tetrahydrofuran cores in annonaceous acetogenins

Chia-Hsiu Chen, Ting-Chun Kuan, Ke-Jhen Lu and Duen-Ren Hou*

The bis-THF cores were synthesized from (3*R*,4*R*)-1,5-hexadiene-3,4-diol, and the methylene acetal function was developed as a new linker for RCM.

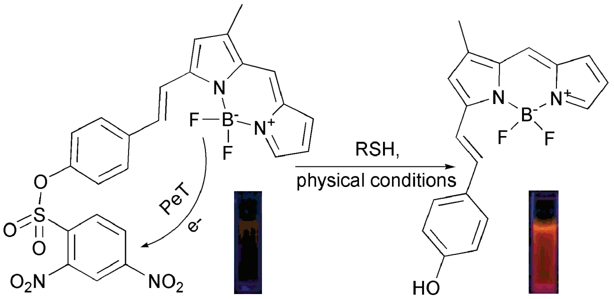


3627

Design and synthesis of a highly selective fluorescent turn-on probe for thiol bioimaging in living cells

Xin Li, Shijing Qian, Qiaojun He, Bo Yang, Jia Li and Yongzhou Hu*

A highly-selective fluorescent turn-on probe for the rapid optical sensing of thiols has been designed, synthesized and applied to imaging of thiols in living cells.



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Introducing Dr Tony Wood

Co-Editor-in-Chief

Tony was appointed Head of Worldwide Medicinal Chemistry at Pfizer in October 2008. Prior to this he was Head of Chemistry and Exploratory Medicinal Sciences in Sandwich from February 2007 and Head of Chemistry from April 2004. He joined Pfizer as a Scientist in the Department of Discovery Chemistry at Sandwich in 1992. He played a leading role in the discovery of Maraviroc, a CCR5 antagonist for the treatment of HIV, for which he was awarded the RSC Malcolm Campbell Prize in 2005, and was a co-recipient of the ACS Heroes of Chemistry Prize, the Prix Galien USA and Scripps awards in 2008 and the PhRMA Discoverers Award in 2010. He also led the team that discovered Lersivirine, a new non cross resistant non nucleoside reverse transcriptase inhibitor that is currently in Phase II.

Tony received his BSc in 1987 and PhD in 1990 from the University of Newcastle upon Tyne working with Professor Richard Jackson on amino synthesis before completing post-doctoral studies with Professor Steven Ley at Imperial College in London.

Tony has active interests in many areas of medicinal chemistry. He is currently a member of the EPSRC Council. He is an author or inventor on more than 50 scientific publications and patents and has given invited lectures at a number of International Conferences on Medicinal Chemistry. Tony is also a Visiting Professor at the University of Newcastle upon Tyne.

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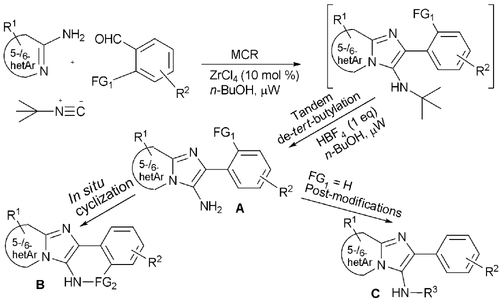
COMMUNICATIONS

3631

Towards molecular diversity: dealkylation of *tert*-butyl amine in Ugi-type multicomponent reaction product establishes *tert*-butyl isocyanide as a useful convertible isonitrile

Sankar K. Guchhait* and Chetna Madaan

Development of a novel tandem de-*tert*-butylation in an Ugi-type MCR product afforded for the first time *tert*-butyl isocyanide as a useful convertible isonitrile towards the generation of molecular diversity of N-fused imidazoles (**A**, **B** and **C**).

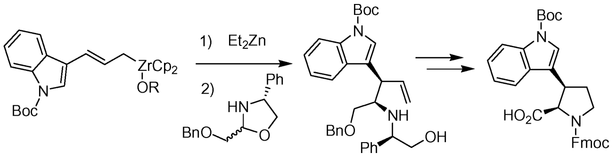


3635

Asymmetric synthesis of proline-based conformationally constrained tryptophan mimetic

Pierre-Olivier Delaye, Jean-Luc Vasse* and Jan Szymoniak

The stereoselective synthesis of a constrained tryptophan mimetic is described, based on the generation of an unprecedented indole-containing allylmetal.



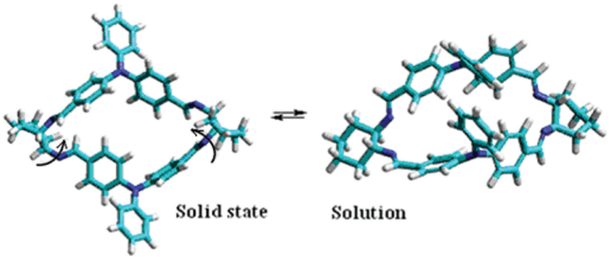
PAPERS

3638

Triphenylamine-based rhombimine macrocycles with solution interconvertable conformation

Mircea Grigoras,* Loredana Vacareanu, Teofilia Ivan and Gabriela Liliana Ailiesei

Three rhombimine macrocycles have been synthesized by [2+2] cyclocondensation reaction between (R,R)-1,2-diaminocyclohexane and 4,4′-*bis*formyl triphenylamine derivatives. Evidence from ^{1}H-NMR and UV suggests that there is a rotamer inversion in solution arising from the rotation of triphenylamine group around cyclohexyl–N single bonds.

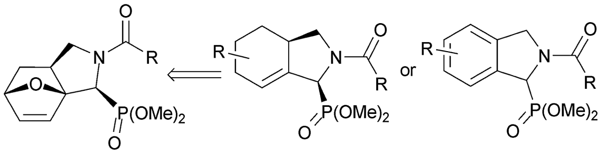


3644

Experimental and computational study of the ring opening of tricyclic oxanorbornenes to polyhydro isoindole phosphonates

Diederica D. Claeys, Christian V. Stevens,* Bart I. Roman, Pieter Van De Caveye, Michel Waroquier and Veronique Van Speybroeck*

Experimental and molecular modelling study of the ring opening of tricyclic α-amino phosphonates with Lewis-acid and clay-based catalysts.



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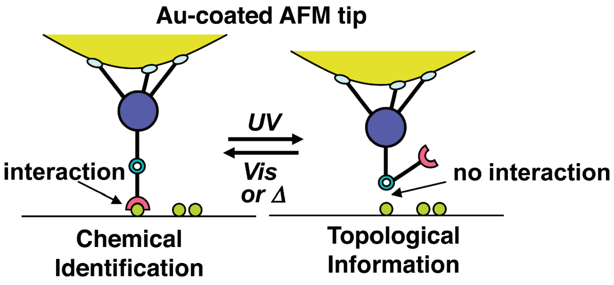
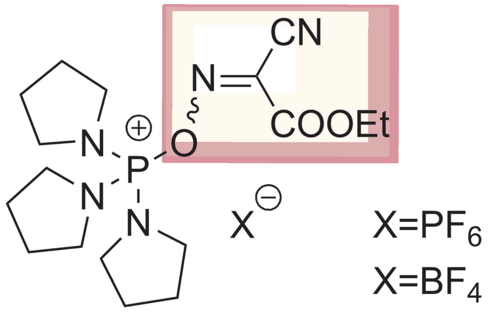


Photoswitching tripodal single molecular tip for noncontact AFM measurements: synthesis, immobilization, and reversible configurational change on gold surface

Daiko Takamatsu, Ken-ichi Fukui,* Safwan Aroua and Yoko Yamakoshi*

Photoswitching tripods were synthesized as molecular tips for chemical force microscopy. Stationary immobilized molecules on the gold surface provided reversible configurational changes indicating a great potential for both chemical and topographical imaging by AFM.

3665

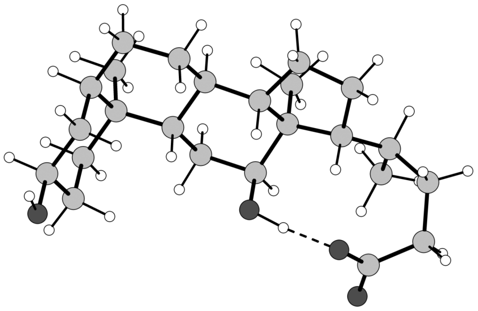


PyOxP and PyOxB: the Oxyma-based novel family of phosphonium salts

Ramon Subirós-Funosas, Ayman El-Faham* and Fernando Albericio*

Here we present the synthesis and evaluation of the phosphonium salts *O*-[(1-cyano-2-ethoxy-2-oxoethylidene)amino]-oxytri(pyrrolidin-1-yl) phosphonium hexafluorophosphate (PyOxP) and tetrafluoroborate (PyOxB).

3674

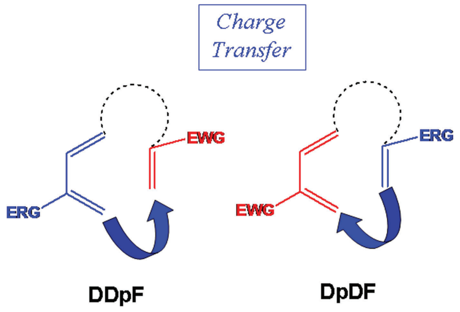


Relative acidity scale of bile acids through ESI-MS measurements

Olga Bortolini,* Giancarlo Fantin, Valeria Ferretti, Marco Fogagnolo, Pier Paolo Giovannini and Alessandro Medici

The anion proton affinity of the most important human bile acids and those of the corresponding keto bile acids have been examined in order to establish a true (intrinsic) relative acidity scale. The acidity of cholic and deoxycholic acids were confirmed to be significantly high. A rationale of the differences found for the various bile acids are discussed, also supported by theoretical calculations.

3678



Quantitative characterization of group electrophilicity and nucleophilicity for intramolecular Diels–Alder reactions

Jorge Soto-Delgado,* Luis R. Domingo and Renato Contreras*

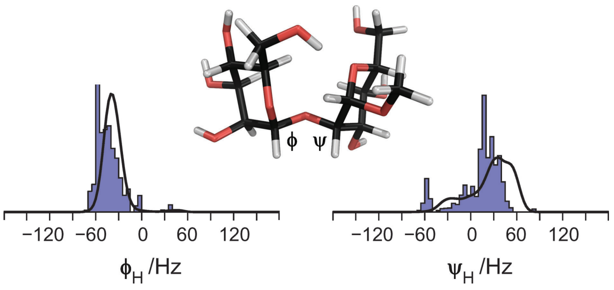
The transferability of the empirical reactivity rules established for the intermolecular DA cycloadditions to the intramolecular DA processes is discussed.

3684

Population distribution of flexible molecules from maximum entropy analysis using different priors as background information: application to the ϕ, ψ-conformational space of the α-(1→2)-linked mannose disaccharide present in *N*- and *O*-linked glycoproteins

Elin Säwén, Tariq Massad, Clas Landersjö, Peter Damberg* and Göran Widmalm*

Spectroscopy data and background information was used to determine solution conformational preferences at a glycosidic linkage.

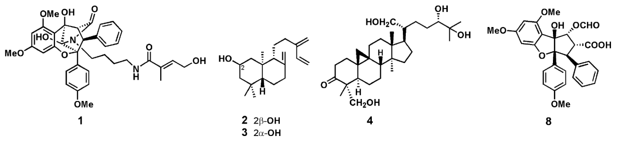


3696

Constituents of *Amoora cucullata* with TRAIL resistance-overcoming activity

Firoj Ahmed, Kazufumi Toume, Samir K. Sadhu, Takashi Ohtsuki, Midori A. Arai and Masami Ishibashi*

Bioassay-guided fractionation of mangrove, *Amoora cucullata*, led to the isolation of four new compounds (**1–4**) along with known compounds (**5–11**), among which **8** showed the most potent TRAIL resistance-overcoming activity.

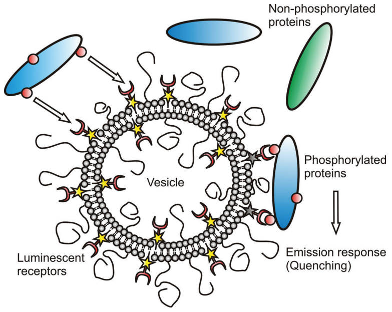


3704

Luminescent vesicular receptors for the recognition of biologically important phosphate species

Benjamin Gruber, Stefan Stadlbauer, Kristina Woinaroschy and Burkhard König*

Novel luminescent zinc complexes with affinity to phosphate ions have been prepared and incorporated into vesicle membranes. The obtained particles respond to phosphate binding by quenching of fluorescence emission and could be used for the selective recognition of phosphorylated proteins.

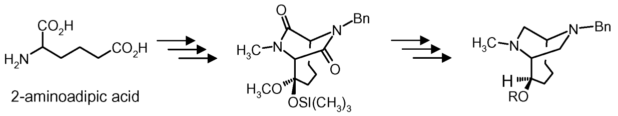


3715

Bicyclic σ receptor ligands by stereoselective Dieckmann analogous cyclization of piperazinebutyrate

Sunil Kumar Sunnam, Dirk Schepmann, Birgit Wibbeling and Bernhard Wünsch*

A Dieckmann analogous cyclization was used to obtain novel bicyclic systems representing conformationally restricted piperazine derivatives. The intermediate mixed methyl silyl ketal allows further introduction of substituents into the four-carbon bridge to modify receptor interactions.

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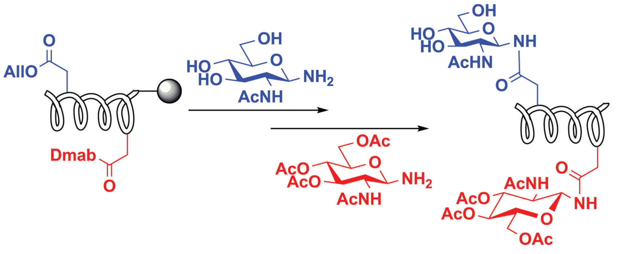
3723

Synthesis of *N*-linked glycopeptides *via* solid-phase aspartylation

Trent Conroy, Katrina A. Jolliffe and Richard J. Payne*

An efficient solid-phase strategy for the preparation of *N*-linked glycopeptides is described which utilises orthogonal side chain protection of aspartic acid residues with allyl or Dmab esters. Glycopeptides were prepared in high yield after selective deprotection followed by aspartylation with a glycosylamine. The orthogonality of the two protecting groups was exploited in the preparation of an *N*-linked glycopeptide bearing two different glycan moieties.

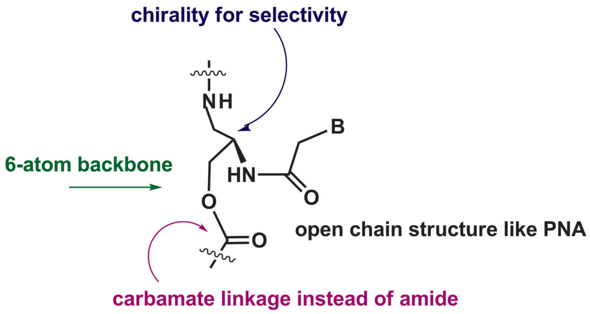


3734

Design, synthesis and DNA/RNA binding studies of nucleic acids comprising stereoregular and acyclic polycarbamate backbone: polycarbamate nucleic acids (PCNA)

Vangala Madhuri and Vaijayanti A. Kumar*

The designed, chiral, acyclic polycarbamate nucleic acids (PCNA) exhibited sequence and orientation specific binding to nucleic acids. Complexes of PCNA with DNA were as stable as PNA:DNA complexes and those with RNA were as stable as natural DNA:RNA complexes.

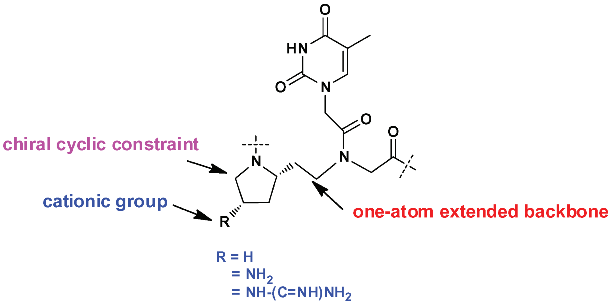


3742

Amino/guanidino-functionalized *N*-(pyrrolidin-2-ethyl)glycine-based pet-PNA: Design, synthesis and binding with DNA/RNA

Sachin S. Gokhale and Vaijayanti A. Kumar*

One atom extended, chiral, amino/guanidino functionalized pyrrolidin-2-ethyl PNA, pet-PNA, allows sequence specific and orientation selective binding to target DNA/RNA in either duplex or triplex modes.

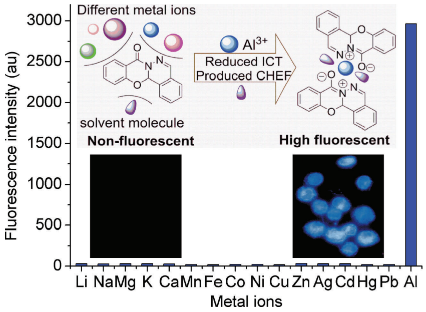


3751

A selective, cell-permeable fluorescent probe for Al^{3+} in living cells

Lina Wang, Wenwu Qin, Xiaoliang Tang, Wei Dou, Weisheng Liu,* Qingfeng Teng and Xiaojun Yao

A new chemosensor which could be used for Al^{3+} ion monitoring in environmental and biological systems was synthesized.



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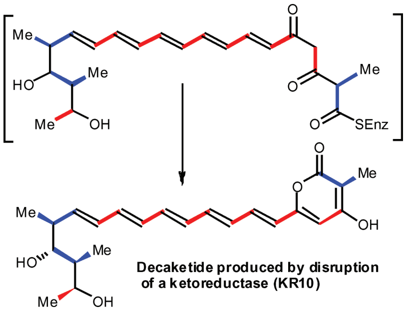
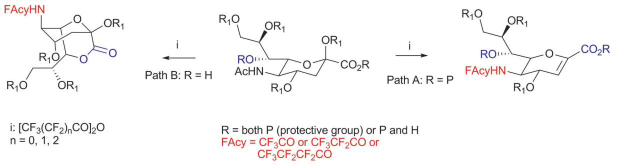


Isolation and characterisation of amphotericin B analogues and truncated polyketide intermediates produced by genetic engineering of *Streptomyces nodosus*

Barry Murphy, Katie Anderson, Charles Borissow, Patrick Caffrey, Gerald Griffith, Jessica Hearn, Odubunmi Ibrahim, Naseem Khan, Natalie Lamburn, Michael Lee, Katherine Pugh and Bernard Rawlings*

Genetic manipulation of *Streptomyces nodosus* has resulted in a wide range of amphotericin B analogues and truncated biosynthetic intermediates as linear polyenyl-pyrones.

3771

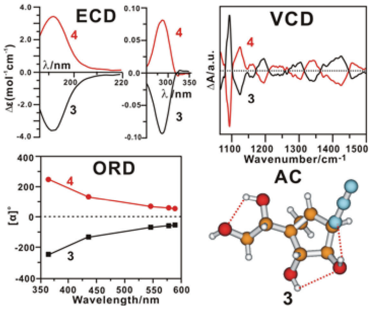


Reaction of *N*-acetylneuraminic acid derivatives with perfluorinated anhydrides: a short access to *N*-perfluoroacylated glycals with antiviral properties

Paola Rota, Pietro Allevi, Roberto Mattina and Mario Anastasia*

Reaction of sialic acids with perfluorinated anhydrides affords *N*-transacylated glycals (Path A) if the carboxy group and/or the 7-hydroxyl are protected, otherwise it affords 1,7-transacylate lactones (Path B).

3777

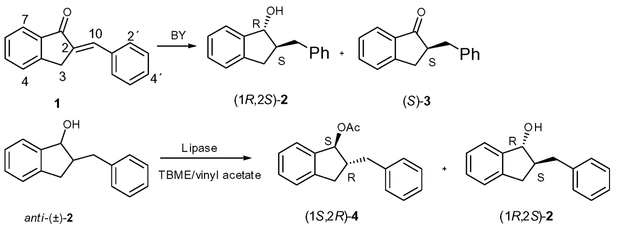


Determination of the absolute configurations of bicyclo[3.1.0]hexane derivatives *via* electronic circular dichroism, optical rotation dispersion and vibrational circular dichroism spectroscopy and density functional theory calculations

Guochun Yang, Jing Li, Yang Liu, Todd L. Lowary and Yunjie Xu*

The ACs of **3** and **4** by ECD, ORD, VCD and DFT.

3784



Biocatalytic preparation and absolute configuration of enantiomerically pure fungistatic *anti*-2-benzylindane derivatives. Study of the detoxification mechanism by *Botrytis cinerea*

Cristina Pinedo-Rivilla, Josefina Aleu, Manuel Grande Benito and Isidro G. Collado*

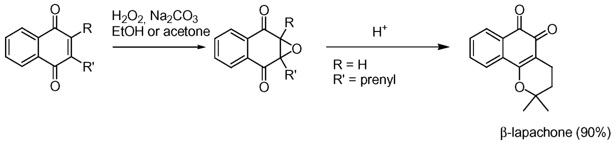
Enantiomerically pure 2-benzylindane derivatives were prepared using biocatalytic methods and their absolute configuration determined. The antifungal activity of these products against the phytopathogen *Botrytis cinerea* was tested.

3790

Synthesis of naturally occurring naphthoquinone epoxides and application in the synthesis of β-lapachone

Sven Claessens, Pascal Habonimana and Norbert De Kimpe*

Optimized epoxidation conditions of mono- and dialkylated naphthoquinones are presented making use of H_2O_2/Na_2CO_3. The optimized epoxidation conditions are applied in a short and high yielding synthesis of the pharmaceutically important β-lapachone.

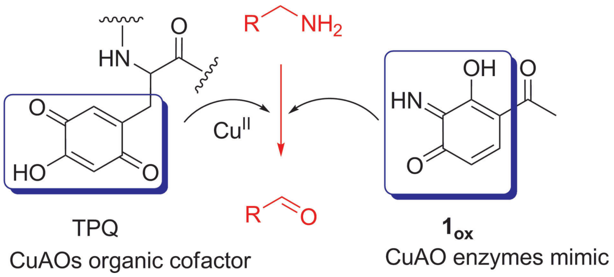


3796

A small molecule that mimics the metabolic activity of copper-containing amine oxidases (CuAOs) toward physiological mono- and polyamines

Martine Largeron,* Maurice-Bernard Fleury and Margherita Strolin Benedetti

Can a small molecule replicate the activity and specificity of copper-containing amine oxidase enzymes toward endogenous mono- and polyamines?

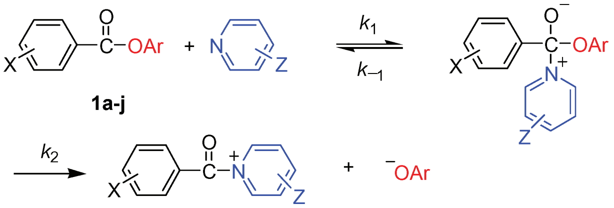


3801

Nonlinear Hammett plots in pyridinolysis of 2,4-dinitrophenyl X-substituted benzoates: change in RDS *versus* resonance contribution

Ik-Hwan Um,* Li-Ra Im, Eun-Hee Kim and Ji Hye Shin

The electronic nature of substituent X in the benzoyl moiety does not affect the rate-determining step.



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