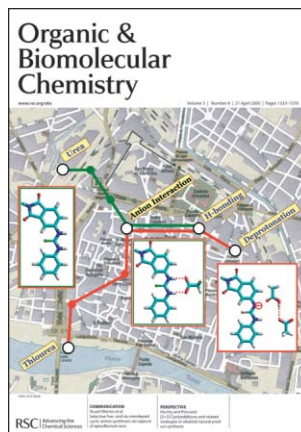
**Cover**

See Joseph P. A. Harrity and Olivier Provoost, pp. 1349–1358
Combining complementary three-atom fragments via a formal cycloaddition process provides an efficient means of generating functionalized piperidines that can be further exploited in target synthesis.

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**Inside Cover**

See David Esteban Gómez, Luigi Fabbri, Maurizio Licchelli and Enrico Monzani, pp. 1495–1500
A thiourea based receptor first forms a genuine H-bond complex with acetate, then, on further anion addition, undergoes deprotonation; the less acidic urea containing receptor stops at the complex formation.

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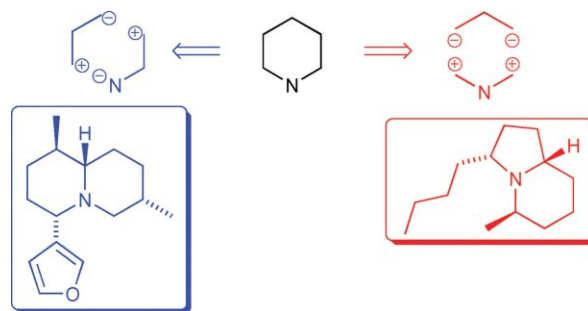
PERSPECTIVE

1349

[3 + 3] Cycloadditions and related strategies in alkaloid natural product synthesis

Joseph P. A. Harrity* and Olivier Provoost

A strategically unusual approach to piperidines *via* formal [3 + 3] cycloaddition reactions is described for the synthesis of alkaloid natural products.



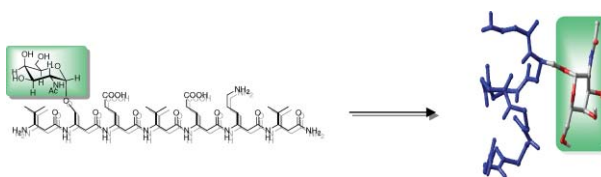
COMMUNICATIONS

1359

Functionalized foldamers: synthesis and characterization of a glycosylated β -peptide 3_{14} -helix conveying the T_N-antigen

Anna S. Norgren and Per I. Arvidsson*

The concept of a novel conjugate, a functional foldamer, composed of an artificial biomimetic backbone functionalized with a natural biologically active ligand, is exemplified by the design, synthesis, and structural investigation of a β -heptapeptide carrying a GalNAc-carbohydrate residue.



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1362

A chiral molecular recognition approach to the formation of optically active quaternary centres in aza-Henry reactions

Kristian Rahbek Knudsen and Karl Anker Jørgensen*

High yields, diastereo- and excellent enantioselectivity are obtained in aza-Henry reactions by the combination of chiral organo- and Lewis acid catalysis.

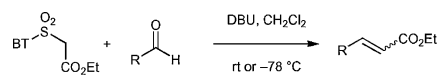


1365

Ethyl (benzothiazol-2-ylsulfonyl)acetate: a new reagent for the stereoselective synthesis of α,β -unsaturated esters from aldehydes

Paul R. Blakemore,* Danny K. H. Ho and W. Mieke Nap

The title reagent engaged in the modified Julia olefination with aldehydes under mild reaction conditions to afford α,β -unsaturated esters stereoselectively.



BT = benzothiazol-2-yl

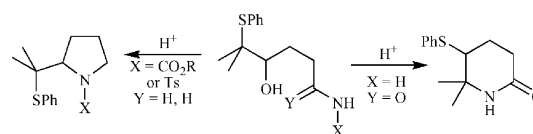
R	yield (%)	E:Z
1-naphthyl	86	96:4
Et ₂ CH	88	> 98:2
<i>n</i> -C ₆ H ₁₁	47	8:92

1369

Selective five- and six-membered cyclic amine syntheses *via* capture of episulfonium ions

David J. Fox, Thomas J. Morley, Sarah Taylor and Stuart Warren*

Amide nitrogens open episulfonium ions to form pyrrolidines or piperidines selectively, depending on the nitrogen substituent, in either reversible or irreversible reactions.

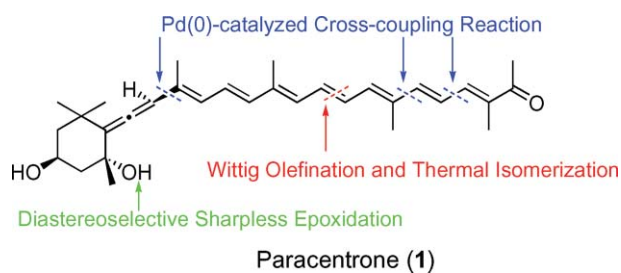


1372

Total synthesis of paracentrone, C₃₁-allenic *apo*-carotenoid

Yusuke Murakami, Masayuki Nakano, Takuya Shimofusa, Noriyuki Furuichi and Shigeo Katsumura*

The stereocontrolled total synthesis of a C₃₁-allenic *apo*-carotenoid, paracentrone, is described.



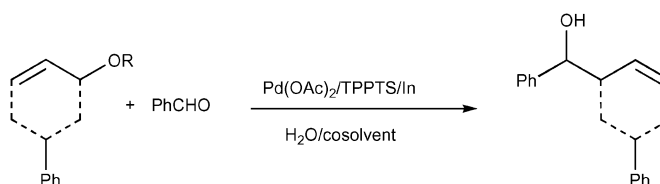
ARTICLES

1375

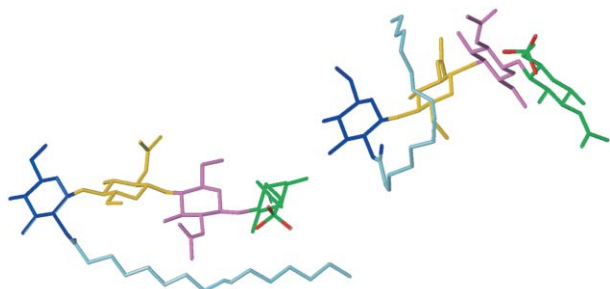
Investigation of the aqueous transmetalation of π -allylpalladium with indium salt: the use of the Pd(OAc)₂-TPPTS catalyst

Gianfranco Fontana, André Lubineau and Marie-Christine Scherrmann*

π -Allylpalladium complexes generated in water by the palladium(0) water soluble catalyst prepared *in situ* from palladium acetate and TPPTS were transmetalated with indium to react with benzaldehyde.



1381

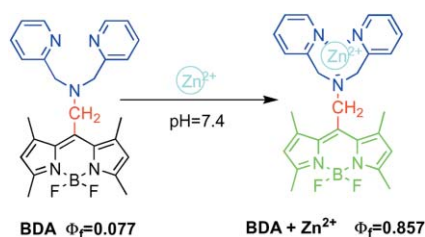


The relative orientation of the lipid and carbohydrate moieties of lipochitooligosaccharides related to nodulation factors depends on lipid chain saturation

Patrick Groves, Stefanie Offermann, Martin Ohsten Rasmussen, F. Javier Cañada, Jean-Jacques Bono, Hugues Driguez, Anne Imberty* and Jesús Jiménez-Barbero*

One additional double bond (right) provides a natural Nod factor with a distinct structural conformation compared to its synthetic analogue.

1387

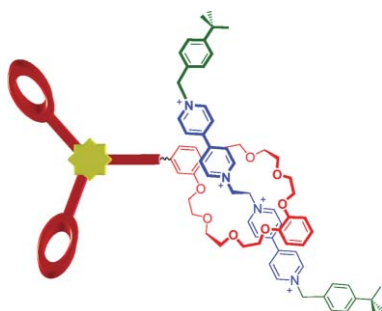


Boron dipyrromethene fluorophore based fluorescence sensor for the selective imaging of Zn(II) in living cells

Yunkou Wu, Xiaojun Peng,* Binchen Guo, Jiangli Fan, Zhichao Zhang, Jingyun Wang, Aijun Cui and Yunling Gao

A boron dipyrromethene fluorophore based fluorescence sensor has been developed as a new Zn(II) sensor suitable for biological application.

1393

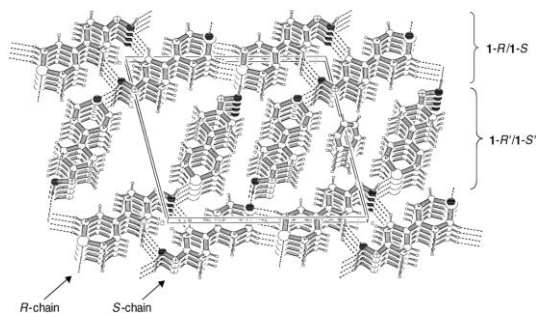


Branched [n]rotaxanes (n = 2–4) from multiple dibenzo-24-crown-8 ether wheels and 1,2-bis(4,4'-dipyridinium)ethane axles

Stephen J. Loeb* and David A. Tramontozzi

The 1,2-bis(pyridinium)ethane_{24C8} rotaxane motif can be incorporated into macromolecules employing multiple dibenzo-24-membered crown ether wheels with various aromatic core structures and the 1,2-bis(4,4'-dipyridinium)ethane axle.

1402

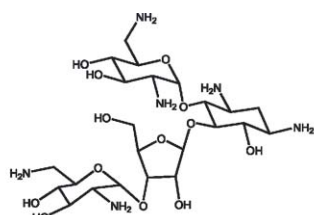


4-(Tetrahydro-4H-thiopyran-1-oxide-4-ylidene)-cyclohexanone oxime in the solid-state. A two-dimensional network of enantiomorphous chains interconnected by weak hydrogen bonds

Albert W. Marsman, Bart L. A. van Poecke, Leonardus W. Jenneskens,* Anthony L. Spek, Egbertus T. G. Lutz and Joop H. van der Maas

In the solid-state 4-(tetrahydro-4H-thiopyran-1-oxide-4-ylidene)-cyclohexanone oxime gives a two-dimensional network of enantiomorphous chains interconnected by weak hydrogen bonds.

1410



Neomycin Biosynthetic Gene Cluster in *Streptomyces fradiae*



The neomycin biosynthetic gene cluster of *Streptomyces fradiae* NCIMB 8233: characterisation of an aminotransferase involved in the formation of 2-deoxystreptamine

Fanglu Huang, Stephen F. Haydock, Tatiana Mironenko, Dieter Spiteller, Yanyan Li and Jonathan B. Spencer*

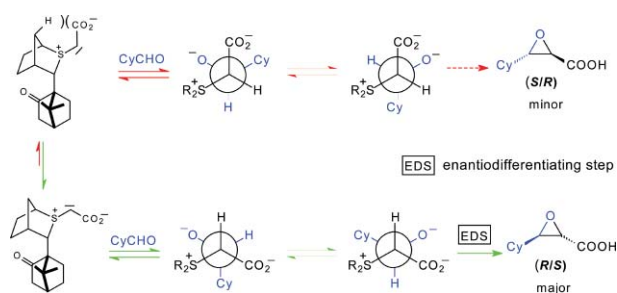
The gene cluster for neomycin has been sequenced, giving a clear insight into the biosynthesis of this clinically useful antibiotic.

1419

Carboxylate-stabilised sulfur ylides (thetin salts) in asymmetric epoxidation for the synthesis of glycidic acids. Mechanism and implications

Varinder K. Aggarwal* and Christina Hebach

The reaction of carboxylate-stabilised chiral sulfur ylides (thetin salts) with aldehydes and ketones has been investigated but low ee was observed due to reversibility in betaine formation.

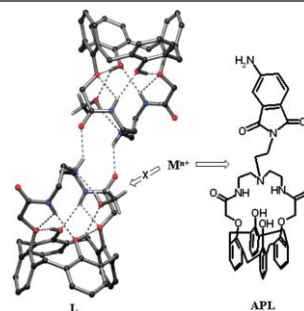


1428

Calix[4]azacrown and 4-aminophthalimide-appended calix[4]azacrown: synthesis, structure, complexation and fluorescence signaling behaviour

Sandip Banthia and Anunay Samanta*

Calix[4]azacrown framework serving as potential hosts for selective recognition of transition metal ions.

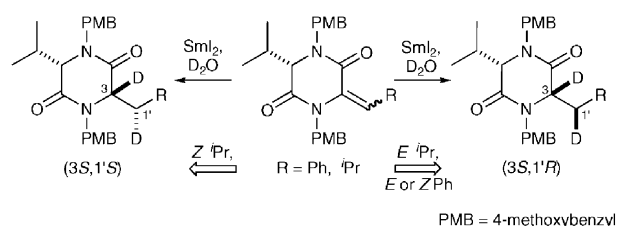


1435

Asymmetric conjugate reductions with samarium diiodide: asymmetric synthesis of (2*S*,3*R*)- and (2*S*,3*S*)[2-²H,3-²H]-leucine-(*S*)-phenylalanine dipeptides and (2*S*,3*R*)-[2-²H,3-²H]-phenylalanine methyl ester

Stephen G. Davies,* Humberto Rodríguez-Solla, Juan A. Tamayo, Andrew R. Cowley, Carmen Concellón, A. Christopher Garner, Alastair L. Parkes and Andrew D. Smith

The highly diastereoselective samarium diiodide-D₂O promoted conjugate reduction of homochiral 3-ylidene diketopiperazines has been demonstrated and the stereospecificity of the process is determined by the ylidene substitution.



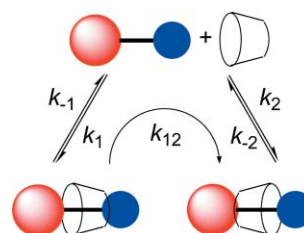
PMB = 4-methoxybenzyl

1448

Orientational isomers of α -cyclodextrin [2]semi-rotaxanes with asymmetric dicationic threads

Andrew J. Baer and Donal H. Macartney*

The threading of α -cyclodextrin by asymmetric dicationic threading molecules results in kinetically and thermodynamically preferred orientational isomers of the resulting [2]semi-rotaxanes.

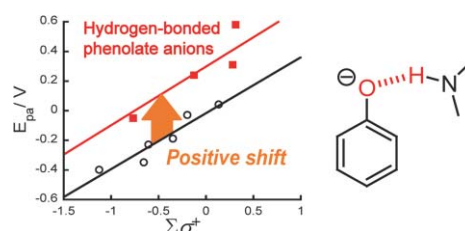


1453

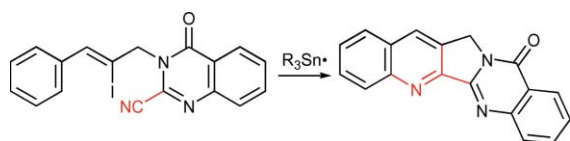
Contribution of the intramolecular hydrogen bond to the shift of the p*K*_a value and the oxidation potential of phenols and phenolate anions

Daisuke Kanamori, Atsushi Furukawa, Taka-aki Okamura, Hitoshi Yamamoto and Norikazu Ueyama*

Hydrogen bonding to phenolate anions positively shifts the oxidation potential of the phenolate anion.



1460

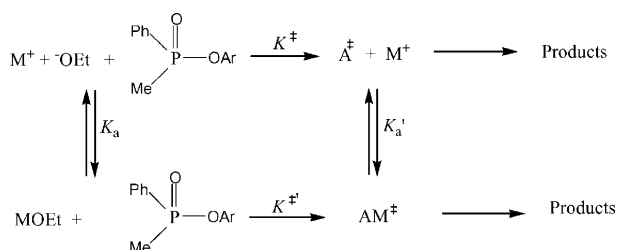


Synthesis of heteroarenes using cascade radical cyclisation via iminyl radicals

W. Russell Bowman,* Martin O. Cloonan, Anthony J. Fletcher and Tobias Stein

Cascade radical cyclisation *via* iminyl radicals involving homolytic aromatic substitution has been used to synthesise new tetracycles including the biologically active alkaloids mappicine and luotonin A.

1468

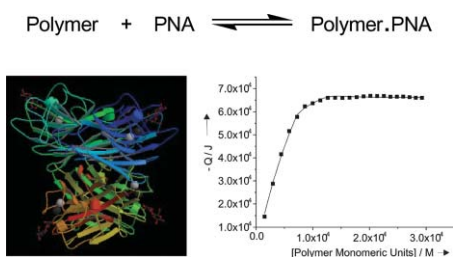


Catalysis of the ethanolsis of aryl methyl phenyl phosphinate esters by alkali metal ions: transition state structures for uncatalyzed and metal ion-catalyzed reactions

Ikenna Onyido,* Kendall Albright and Erwin Buncel*

Transition state and ground state stabilization in metal ion catalysis of the ethanolsis of aryl methylphenyl phosphinates.

1476

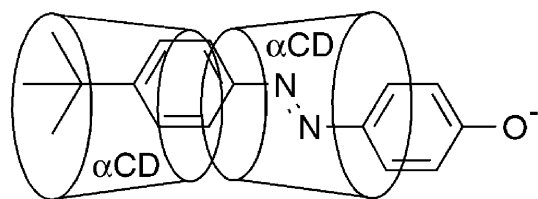


Investigation of the interaction between peanut agglutinin and synthetic glycopolymeric multivalent ligands

Moira Ambrosi, Neil R. Cameron,* Benjamin G. Davis* and Snjezana Stolnik

Binding of a β -D-galactose-bearing polymer to the lectin PNA is around 50 times stronger than D-galactose and is entropically driven.

1481

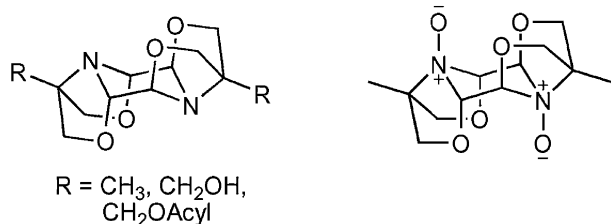


Cyclodextrin and modified cyclodextrin complexes of *E*-4-*tert*-butylphenyl-4'-oxyazobenzene: UV-visible, ¹H NMR and *ab initio* studies

Bruce L. May, Jacobus Gerber, Philip Clements, Mark A. Buntine, David R. B. Brittain, Stephen F. Lincoln* and Christopher J. Easton

α - and β -cyclodextrin form 1 : 1 and 2 : 1 isomeric complexes (includomers) with *E*-4-*tert*-butylphenyl-4'-oxyazobenzene which is also complexed by linked cyclodextrins.

1489



Polycyclic compounds from aminopolyols and α -dicarbonyls: structure and application in the synthesis of exoditopic ligands

Giovanni B. Giovenzana,* Giovanni Palmisano,* Erika Del Grosso, Lorella Giovannelli, Andrea Penoni and Tullio Pilati

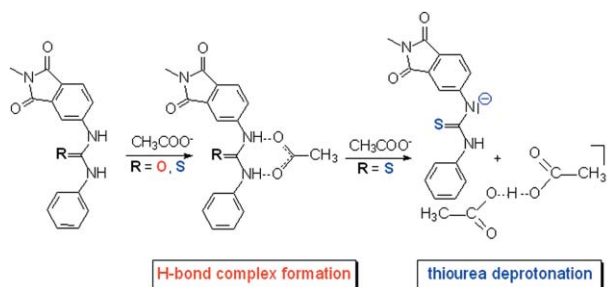
The reaction between aminopolyols and α -dicarbonyls is surveyed; the corresponding products are useful in the preparation of potential exoditopic ligands.

1495

Urea vs. thiourea in anion recognition

David Esteban Gómez, Luigi Fabbrizzi,* Maurizio Licchelli and Enrico Monzani

In the presence of an X^- anion excess, thiourea and urea containing receptors may release an HX fragment, with the formation of the deprotonated receptor and anion self-complex $[HX_2]^-$.

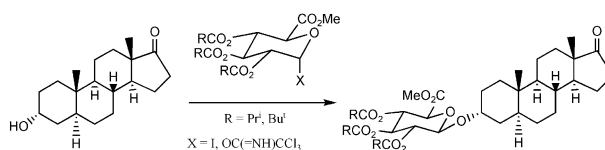


1501

Glucuronidation of steroidal alcohols using iodosugar and imidate donors

John R. Harding, Clare D. King, Jennifer A. Perrie, Deborah Sinnott and Andrew V. Stachulski*

A number of steroidal alcohols (androsterone shown) have been glucuronidated using both our recently described glycosyl iodide and the trichloroacetimidate method. The iodosugar has given good results: most yields are from 60 to 75% and $\beta : \alpha$ ratios generally from 95 : 5 to 100 : 0.

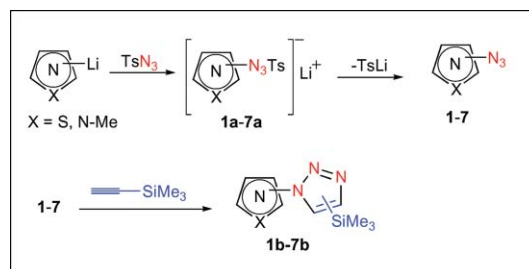


1508

On the utility of the azido transfer protocol: synthesis of 2- and 5-azido *N*-methylimidazoles, 1,3-thiazoles and *N*-methylpyrazole and their conversion to triazole-azole bisheteroaryls

Paolo Zanirato* and Stefano Cerini

Preparation of azidoazoles and silylated triazole-azole bisheteroaryls can be achieved by the azido transfer protocol.

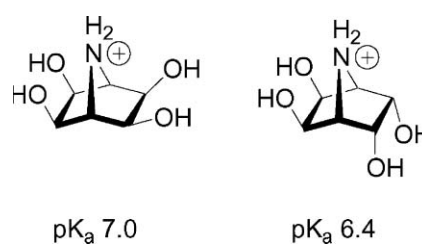


1514

On the electronic effects of OH groups. Synthesis and investigation of tetrahydroxylated azabicycloheptanes

Anette Gregersen, Christian Marcus Pedersen, Henrik Helligsø Jensen and Mikael Bols*

In the [2.2.1]azabicycloheptane system an *endo*-hydroxyl group is found to be more electron-withdrawing than an *exo*-OH group.

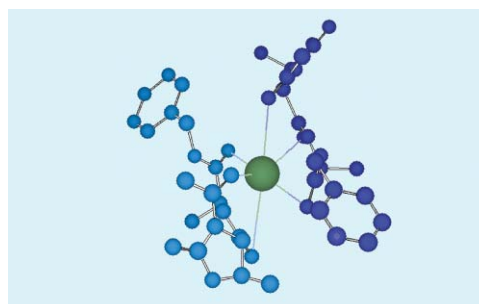


1520

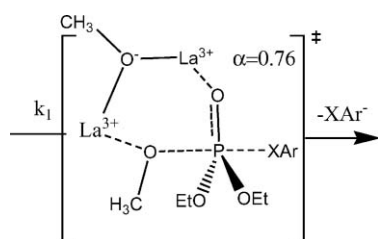
Development of new calcium receptors based on oxazolidin-2-ones containing pseudopeptides

Gianluigi Luppi, Andrea Garelli, Luca Prodi, Quirinus B. Broxterman, Bernard Kaptein and Claudia Tomasini*

Ac-L-Oxd-L-Ala-OBn was identified as a promising new calcium receptor compound by MS-ESI analysis and by photoluminescence spectroscopy.



1525

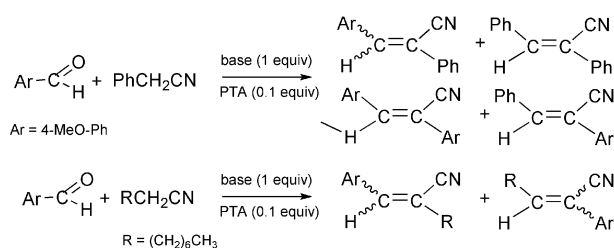


Mechanistic studies of La^{3+} - and Zn^{2+} -catalyzed methanolysis of aryl phosphate and phosphorothioate triesters. Development of artificial phosphotriesterase systems

Tony Liu, Alexei A. Neverov, Josephine S. W. Tsang and R. Stan Brown*

A concerted transition state for $(\text{La}^{3+})_2(-\text{OCH}_3)_2$ catalyzed methanolysis of phosphate triester is proposed.

1534

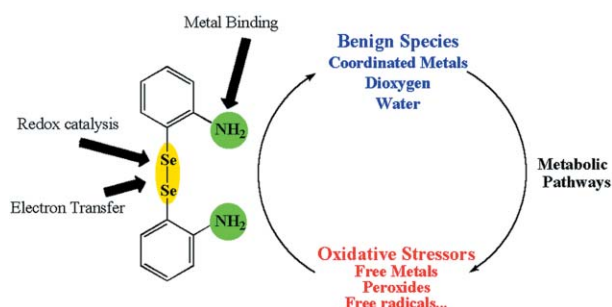


Solvent-free condensation of phenylacetonitrile and nonanenitrile with 4-methoxybenzaldehyde: optimization and mechanistic studies

André Loupy,* Michèle Pellet, Alain Petit and Giang Vo-Thanh

Condensation can be performed using neat powdered KOH at room temperature or K_2CO_3 in the presence of a phase transfer agent at 130°C .

1541

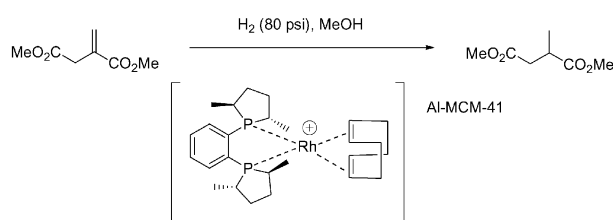


Towards multifunctional antioxidants: synthesis, electrochemistry, *in vitro* and cell culture evaluation of compounds with ligand/catalytic properties

Catriona A. Collins, Fiona H. Fry, Andrea L. Holme, Anthe Yiakouvakaki, Abdullah Al-Qenaei, Charareh Pourzand and Claus Jacob*

Agents that combine the catalytic activity of glutathione peroxidase with metal binding properties provide the basis for the design of effective antioxidants.

1547

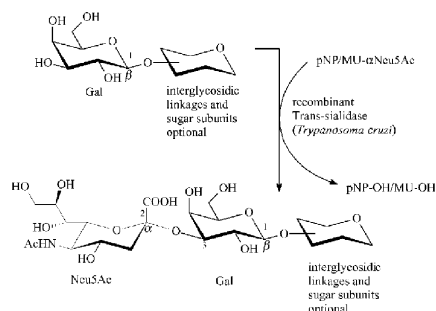


Asymmetric hydrogenation using chiral Rh complexes immobilised with a new ion-exchange strategy

William P. Hems, Paul McMorn, Stewart Riddell, Simon Watson, Frederick E. Hancock and Graham J. Hutchings*

Immobilized rhodium diphosphine complexes give comparable catalytic performances to the non-immobilised complexes for asymmetric hydrogenation of dimethyl itaconate, and can be recovered and reused without loss of performance.

1551



Preparation of sialylated oligosaccharides employing recombinant trans-sialidase from *Trypanosoma cruzi*

Björn Neubacher, Dirk Schmidt, Patrick Ziegelmeüller and Joachim Thiem*

Terminally sialylated oligosaccharides are synthesised, employing a recombinant trans-sialidase from *Trypanosoma cruzi*.

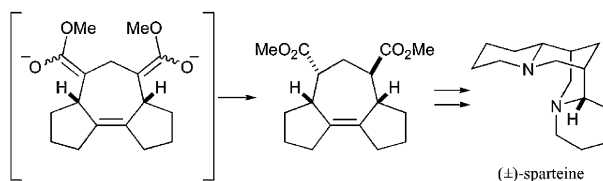
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A synthesis of (±)-sparteine

Thomas Buttler, Ian Fleming,* Sabine Gonsior, Bo-Hye Kim, A.-Young Sung and Hee-Gweon Woo

(±)-Sparteine has been synthesised with chirality introduced relatively late using the protonation of a meso dienolate.

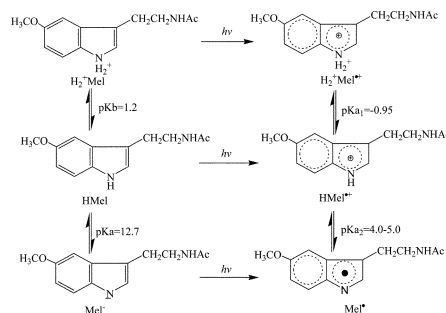


1568

The formation and properties of the melatonin radical: a photolysis study of melatonin with 248 nm laser light

Hui He, Mingzhang Lin, Zhenhui Han, Yusa Muroya, Hisaaki Kudo and Yosuke Katsumura*

The melatonin radical in solution exhibits three characteristic absorption bands at 340, 460 and 560 nm and the radical exists in the solution as various species based on the acid–base equilibrium.



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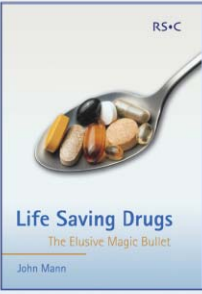
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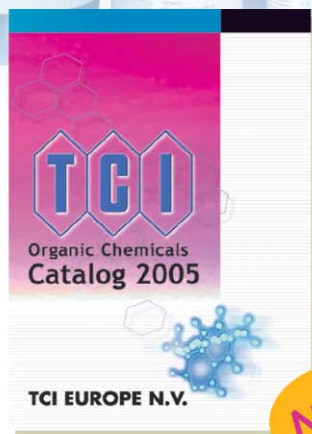
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