

**Cover**  
Illustration of the principle of taking snapshots of a polymerisation reaction over a catalytic solid *in situ*.

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# contents

## FEATURE ARTICLE

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### Snapshots of a working catalyst: possibilities and limitations of *in situ* spectroscopy in the field of heterogeneous catalysis

Bert M. Weckhuysen



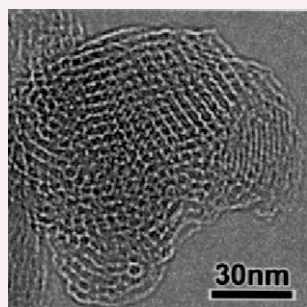
The use of *in situ* spectroscopic techniques, including the design of spectroscopic-reaction cells, to monitor real time catalytic events is reviewed.

## COMMUNICATIONS

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### Synthesis of a novel mesoporous tin phosphate, SnPO<sub>4</sub>

Nawal Kishor Mal, Satoshi Ichikawa and Masahiro Fujiwara

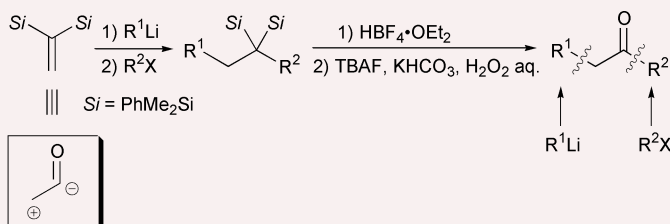


Mesoporous tin phosphates, SnPO<sub>4</sub>, have been synthesized using cationic surfactants (alkyltrimethylammonium bromide). The resulting calcined material (alkyl = C<sub>16</sub>H<sub>33</sub>) is stable at 500 °C and possesses a surface area of 230 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.21 cm<sup>3</sup> g<sup>-1</sup>.

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### Facile synthesis of ketones from 1,1-disilylalkenes *via* oxidation of *gem*-disilylalkanes

Atsushi Inoue, Junichi Kondo, Hiroshi Shinokubo and Koichiro Oshima

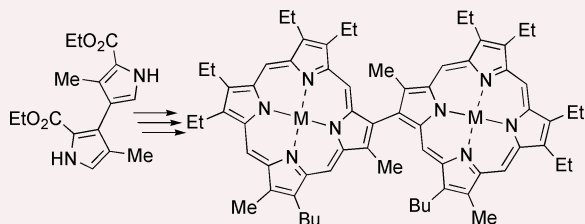


The oxidation of *gem*-disilylalkanes, which can be derived from 1,1-disilylalkene, alkyllithiums and alkyl halides, affords the corresponding ketones.

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**Novel preparation of  $\beta,\beta'$ -connected porphyrin dimers**

Hidemitsu Uno, Yukiko Kitawaki and Noboru Ono

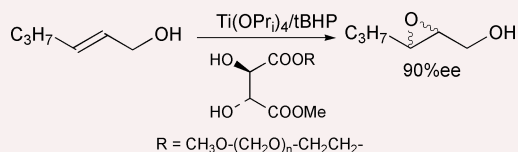


Porphyrin dimers were prepared from  $\beta,\beta'$ -dipyrrole derivatives *via* the double pyrrolylmethylation followed by double [2+2] MacDonald porphyrin synthesis.

118

**Efficient soluble polymer-supported Sharpless alkene epoxidation catalysts**

Hongchao Guo, Xueyan Shi, Zhen Qiao, Shicong Hou and Min Wang

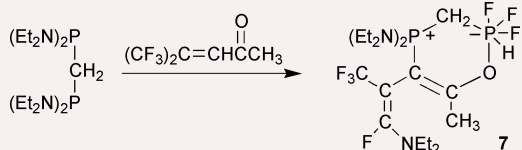


High chemical yields and good enantiomeric excesses are obtained by using soluble polymer-supported tartrate ester in the epoxidation of *trans*-hex-2-en-1-ol using  $\text{Ti}(\text{OPr}^i)_4$ /*tert*-butyl hydroperoxide.

120

**A novel type of formation of zwitterionic compounds, containing two phosphorus atoms of opposite charge and different coordination number**

Igor Shevchenko, Vasyl Andrushko, Enno Lork and Gerd-Volker Rösenthaler



The unexpected formation of zwitterionic compound **7** is a result of an unusual exchange between diethylamino groups at phosphorus atom and fluorine atoms of  $\text{CF}_3$  group.

122

**Synthesis and application of chiral bisphosphines through lithiation–conjugate addition tandem cyclization of chiral  $\alpha,\beta,\psi,\omega$ -unsaturated bisphosphine oxide**

Yasuo Nagaoka, Hideki Inoue, Nawal El-Koussi and Kiyoshi Tomioka

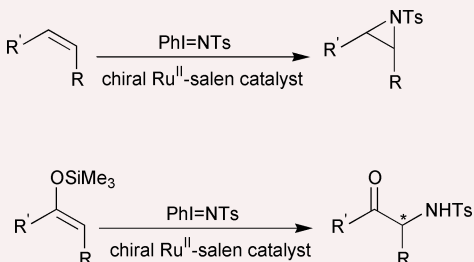


Treatment with lithium diisopropylamide and chiral  $\alpha,\beta,\psi,\omega$ -unsaturated bisphosphine oxides and sequential reductions afforded the corresponding cyclic bisphosphines.

124

**Amidation of silyl enol ethers and cholesteryl acetates with chiral ruthenium(II) Schiff-base catalysts: catalytic and enantioselective studies**

Jiang-Lin Liang, Xiao-Qi Yu and Chi-Ming Che

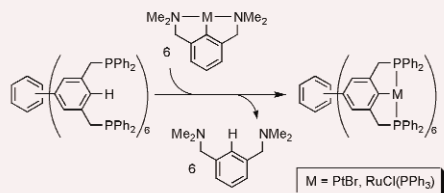


Chiral ruthenium(II)–salen complexes  $[\text{Ru}^{\text{II}}(\text{salen})(\text{PPh}_3)_2]$  catalyse asymmetric aziridination of alkenes with up to 83% ees, asymmetric amidation of silyl enol ethers with up to 97% ees, and allylic amidation of cholesteryl acetates with good regioselectivity.

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### Transcyclometalation, a versatile methodology for multiple metal–carbon bond formation with multisite ligands

Harm P. Dijkstra, Martin Albrecht and Gerard van Koten

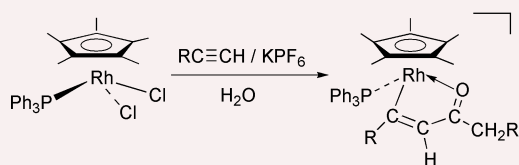


Application of the transcyclometalation reaction as a selective and unique method for the multi-platination and -ruthenation of cartwheel-type ligand systems containing six potential metal binding sites.

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### One-step synthesis of alkenyl ketone complexes from $\text{Cp}^*\text{RhCl}_2(\text{PPh}_3)$ , alkyne and $\text{H}_2\text{O}$ in the presence of $\text{KPF}_6$

Kenichi Ogata, Katsuaki Kuge, Kazuyuki Tatsumi and Yasuhiro Yamamoto

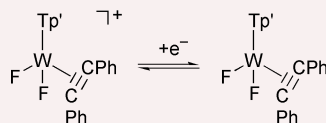


A convenient one-pot synthesis of alkenyl ketone complexes from metal halide bearing pentamethylcyclopentadienyl group, alkynes and water is described.

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### The $d^2/d^3$ alkyne redox pair $[\text{WF}_2(\text{PhC}\equiv\text{CPh})\text{Tp}']^z$ ( $z = +1$ or $0$ ): missing links in a 'redox family tree'

Christopher J. Adams, Kirsty M. Anderson, Neil G. Connelly, David J. Harding, A. Guy Orpen, Elena Patron and Philip H. Rieger

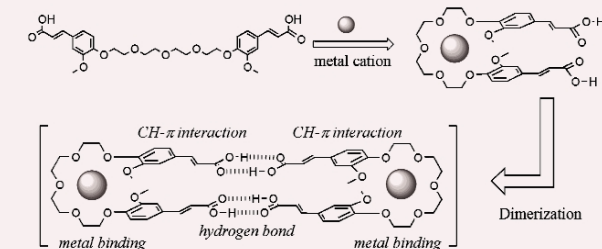


The  $d^2/d^3$  redox pair  $[\text{WF}_2(\text{PhC}\equiv\text{CPh})\text{Tp}']^z$  [ $z = +1$  or  $0$ ,  $\text{Tp}' = \text{hydrotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$ ] is the missing link in a 'redox family tree' relating the  $d^6$  tricarbonyls  $[\text{M}(\text{CO})_3\text{L}]^-$  to the  $d^2$  trihalides  $[\text{MX}_3\text{L}]$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ,  $\text{L} = \text{Cp}$  or  $\text{Tp}'$ ) by a series of stepwise reactions involving sequential one-electron oxidation followed by ligand substitution.

132

### A novel molecular assembly mode of ferulic acid derivatives

Yasuhiro Miyake, Asao Hosoda, Masafumi Takagaki, Eisaku Nomura and Hisaji Taniguchi

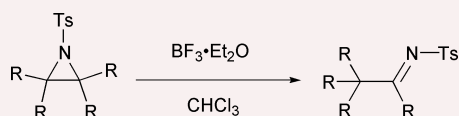


Ferulic acid derivative assembles with three kinds of non-covalent interactions, *i.e.*, metal coordination, hydrogen bonding and  $\text{CH}-\pi$  interaction.

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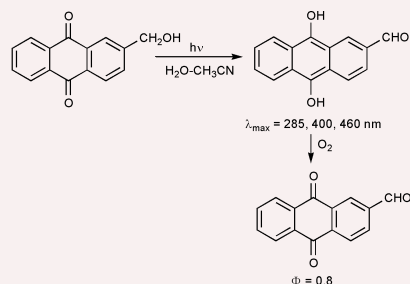
### Aza-pinacol rearrangement: acid-catalyzed rearrangement of aziridines to imines

Yoshiaki Sugihara, Shinya Iimura and Juzo Nakayama



A series of di-, tri-, and tetra-substituted *N*-tosylaziridines was found to undergo a  $\text{BF}_3$ -catalyzed rearrangement under mild conditions to give the corresponding *N*-tosylimines generally in satisfactory yields.

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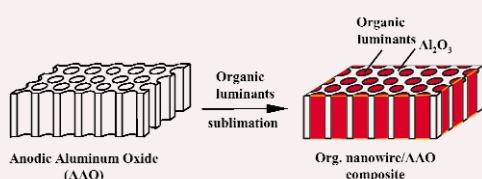


### Excited state intramolecular redox reaction of 2-(hydroxymethyl)anthraquinone in aqueous solution

Matthew Lukeman, Musheng Xu and Peter Wan

The title compound undergoes a novel excited state intramolecular redox reaction in which the 'distal' side chain benzylic alcohol is oxidized to the aldehyde and the carbonyl moieties of anthraquinone reduced, with evidence suggesting that the primary photochemical process is a deprotonation of the benzylic C–H proton (by water) mediated by the solvent.

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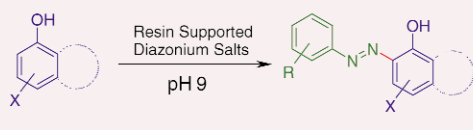


### Novel synthesis of organic nanowires and their optical properties

Jin-Kyu Lee, Weon-Kyu Koh, Weon-Sik Chae and Yong-Rok Kim

Aligned nanowires of organic materials were prepared by introducing the organic luminants into nanochannels of variable size in an anodic aluminum oxide membrane, and the emission spectra from these nanowire arrays exhibited novel size-dependent luminescent properties.

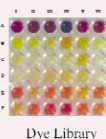
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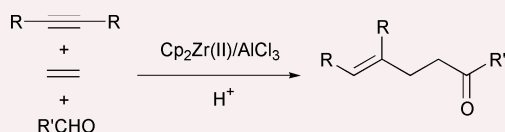
### Supported diazonium salts—convenient reagents for the combinatorial synthesis of azo dye

James Merrington, Mark James and Mark Bradley

Resin supported diazonium salts were synthesised. These were observed to be stable to storage and to provide a convenient means of compound handling and were employed in the solution synthesis of a  $6 \times 6$  azo dye library.



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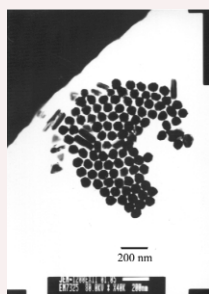


### One-pot synthetic route to homoallylketones *via* selective combination of alkyne, ethylene and aldehyde mediated by AlCl<sub>3</sub> and zirconocene

Changjia Zhao, Tao Yu and Zhenfeng Xi

Three different components of aldehyde, alkyne and ethylene are selectively combined in one-pot to afford homoallylketones in high yields mediated by AlCl<sub>3</sub> and zirconocene.

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### Seed-mediated growth of large, monodisperse core-shell gold-silver nanoparticles with Ag-like optical properties

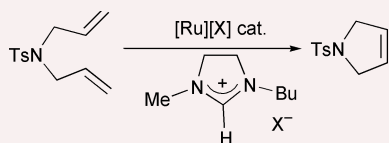
Lehui Lu, Haishui Wang, Yonghui Zhou, Shiquan Xi, Hongjie Zhang, Jiawen Hu and Bing Zhao

Large, monodisperse core-shell Au–Ag nanoparticles with Ag-like optical properties have been prepared using the seeding method.

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### Alkene metathesis catalysis in ionic liquids with ruthenium allenylidene salts

David Sémeril, H  l  ne Olivier-Bourbigou, Christian Bruneau and Pierre H. Dixneuf

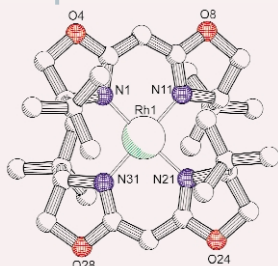


Ring closing metathesis of dienes in 1-butyl-3-methylimidazolium salts in the presence of ruthenium allenylidene salts as catalyst.

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### Spontaneous disproportionation of rhodium(I) bisoxazolates to rhodium(II)

Sander T. H. Willems, Jaap C. Russcher, Peter H. M. Budzelaar, Bas de Bruin, Ren   de Gelder, Jan M. M. Smits and Anton W. Gal

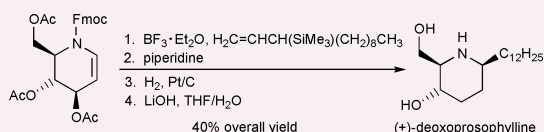


Mononuclear  $[\text{Rh}^{\text{II}}(\text{t-Bu}_2\text{-boxate})_2]$  was obtained by spontaneous disproportionation of  $[\text{Rh}^{\text{I}}(\text{t-Bu}_2\text{-boxate})(\text{C}_2\text{H}_4)_2]$ ; its X-ray structure reveals a remarkable coordination geometry between square planar and tetrahedral.

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### Divergent approach to imino sugar C-glycosides using imino glycals: application to the stereocontrolled synthesis of (+)-deoxoprosophylline

Paul J. Dransfield, Paul M. Gore, Michael Shipman and Alexandra M. Z. Slawin

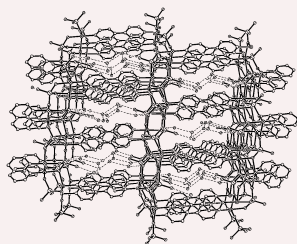


A variety of nucleophiles react, under Lewis acid mediated conditions, with a common imino glycal intermediate providing a stereoselective, divergent approach to imino sugar C-glycosides.

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### A three-dimensional zeolite-like organic–inorganic hybrid material constructed from $\{\text{CuMo}_2\text{O}_8\text{N}\}_n$ double helical chains linked via $[\text{Cu}(4,4'\text{-bpy})_n]$ fragments

Can-Zhong Lu, Chuan-De Wu, Shao-Fang Lu, Jia-Cheng Liu, Qiang-Jin Wu, Hong-Hui Zhuang and Jin-Shun Huang

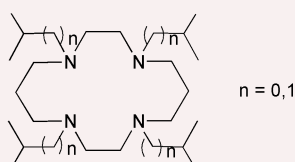


The three-dimensional microporous compound  $[\text{Cu}_2\text{Mo}_2\text{O}_8(4,4'\text{-bpy})_n]_n \cdot 3n\text{H}_2\text{O}$  contains  $\{\text{CuMo}_2\text{O}_8\text{N}\}$  double helical chains, which are further connected to each other by 4,4'-bpy coordinated  $\{\text{Cu}^{\text{II}}\text{O}_5\text{N}\}$ ; the study of the physical properties demonstrates that it is a paramagnetic semiconductor and a zeolite material.

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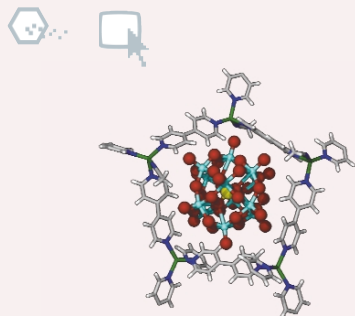
### Lipophilic derivatives of cyclam as new inhibitors of tumor cell growth

John W. Sibert, Ann H. Cory and Joseph G. Cory



Two new lipophilic tetraazamacrocycles were prepared and, in contrast to non-lipophilic analogs, found to be potent inhibitors of tumor cell growth *in vitro* with  $\text{IC}_{50}$  values below 10 micromolar.

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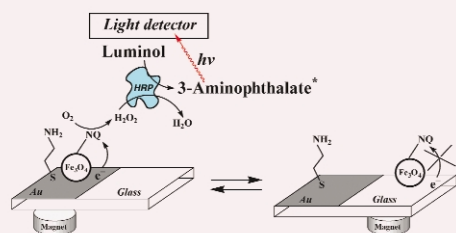


### A polyoxometallate-templated coordination polymer: synthesis and crystal structure of $[\text{Cu}_3(4,4'\text{-bipy})_5(\text{MeCN})_2]\text{PW}_{12}\text{O}_{40}\cdot 2\text{C}_6\text{H}_5\text{CN}$

Chad Inman, Jacqueline M. Knaust and Steven W. Keller

The spherical phosphotungstate ion,  $\text{PW}_{12}\text{O}_{40}^{3-}$ , has been used as a non-coordinating anionic template for the construction of a novel, three-dimensional Cu(I) coordination polymer.

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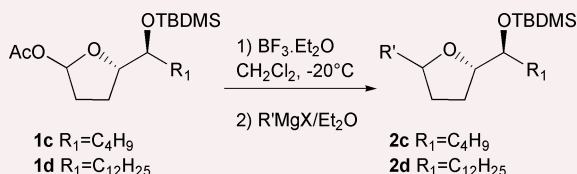


### Magneto-switchable electrogenerated biochemiluminescence

Laila Sheeney-Haj Ichia, Eugenio Katz, Julian Wasserman and Itamar Willner

Magnetic-field-stimulated 'ON' and 'OFF' biochemiluminescence is accomplished by electrocatalyzed reduction of naphthoquinone-functionalized magnetic particles in the presence of a biocatalytic peroxidase/luminol system.

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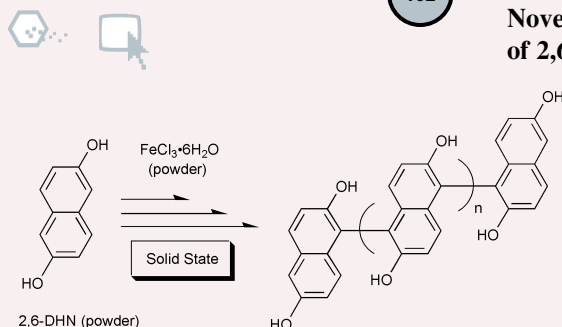


### Access to 2,5-disubstituted tetrahydrofurans from Grignard reagents and hemiacetal derivatives

Xavier Franck, Reynald Hocquemiller and Bruno Figadère

2,5-Disubstituted tetrahydrofurans are readily prepared in dichloromethane, for the first time, from Grignard reagents and lactol acetates with good yields and stereoselectivities. A dramatic solvent effect was observed.

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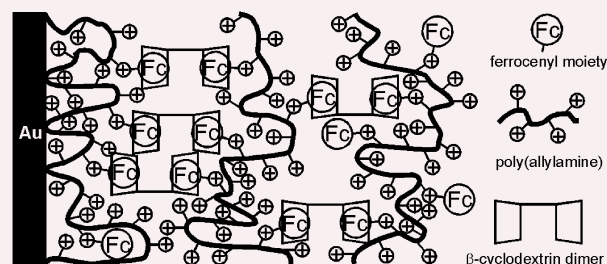


### Novel solid-state polycondensation I. Oxidative-coupling polymerization of 2,6-dihydroxynaphthalene

Masato Suzuki and Yutaka Yatsugi

The oxidative-coupling polymerization of 2,6-dihydroxynaphthalene effectively took place at rt by grinding the crystals of its benzylamine complex with  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  powder in a mortar. The polymerizability was much improved by the crystalline arrangement of the monomer.

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### Construction of positively-charged layered assemblies assisted by cyclodextrin complexation

Iwao Suzuki, Yuya Egawa, Yosuke Mizukawa, Tomonori Hoshi and Jun-ichi Anzai

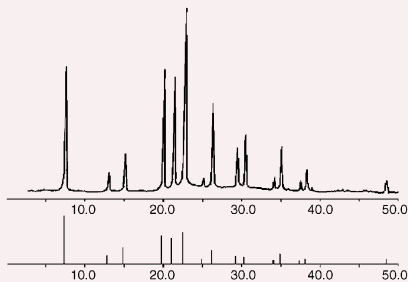
Positively charged ferrocene-modified poly(allylamine) multilayer was successfully deposited on the gold surface with the assistance of the  $\beta$ -cyclodextrin dimer.

166

### Synthesis of high silicon content SAPO<sub>4</sub>-5 using anionic surfactants in a hexanol/aqueous two phase media

Xue S. Han, Craig D. Williams, Darren F. Lee and Catherine I. Round

Siliceous SAPO<sub>4</sub>-5 (with silicon content up to 0.511 atoms per unit cell) has been synthesised using anionic species as surfactants from aqueous/hexanol two phase media.

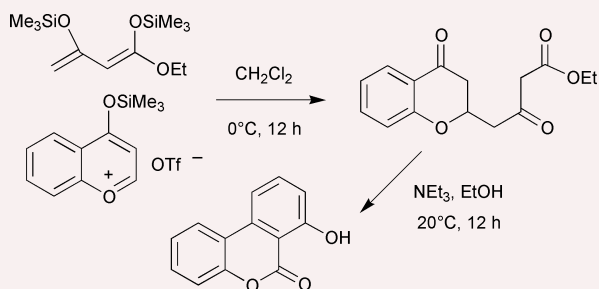


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### Efficient synthesis of biaryl lactones by domino retro-Michael–aldol–lactonization reactions

Peter Langer, Nehad N. R. Saleh and Ilia Freifeld

Biaryl lactones were prepared by novel domino retro-Michael–aldol–lactonization reactions of 2,3-dihydropyrans.

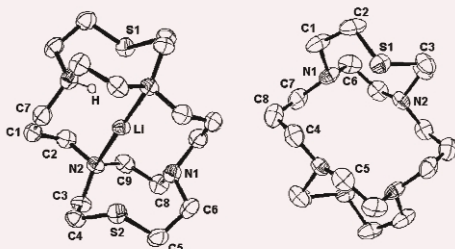


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### Synthesis and structure of a new macrotricyclic ligand that encapsulates lithium and transition metal ions

Tosha M. Barclay, Alex McAuley and S. Subramanian

A macrocycle, L<sup>3</sup>, capable of encapsulating transition metal ions has been synthesized; structures of [Li(HL<sup>3</sup>)](ClO<sub>4</sub>)<sub>2</sub> and [H<sub>2</sub>L<sup>3</sup>](ClO<sub>4</sub>)<sub>2</sub> are described. In both these structures, L<sup>3</sup> adopts a *trans*-IV conformation.

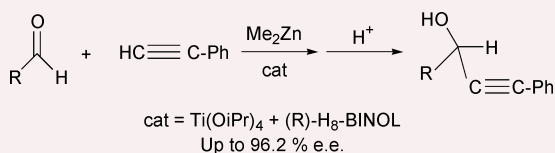


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### Titanium-catalyzed enantioselective alkylation of aldehydes

Gui Lu, Xingshu Li, Wing Lai Chan and Albert S. C. Chan

A simple and practical method to make chiral propargylic alcohols has been developed: in the presence of a titanium alkoxide catalyst prepared *in situ* from titanium tetraisopropoxide and (*R*)-H<sub>8</sub>-binaphthol, a variety of aromatic aldehydes were converted to the corresponding chiral propargylic alcohols with very good enantioselectivities (up to 96.2% e.e.) and yields.

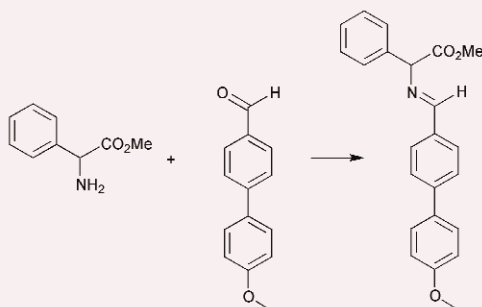


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### Colour indicator for enantiomeric excess and assignment of the configuration of the major enantiomer of an amino acid ester

Richard A. van Delden and Ben L. Feringa

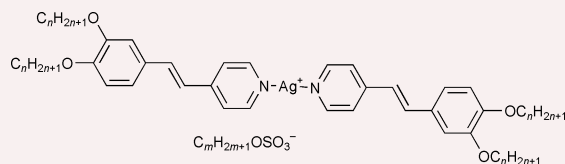
A colour indicator for the full range of enantiomeric excess based on visual colour inspection of a liquid crystal doped with the analyte is reported. This new method provides the enantiomeric excess and allows the assignment of the major enantiomer.



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**Lyotropic mesomorphism in some thermotropic, polycatenar complexes of silver(I)**

Antonina I. Smirnova and Duncan W. Bruce

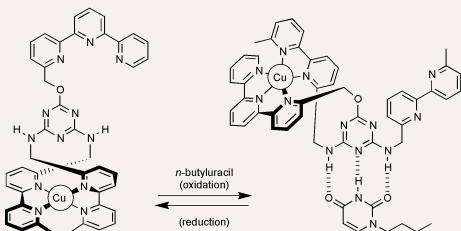


Polycatenar mesogens, such as the one shown here, are found to exhibit lyotropic liquid crystal phases in a variety of solvents.

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**Controlling allostery using redox chemistry**

Mohammad H. Al-Sayah and Neil R. Branda

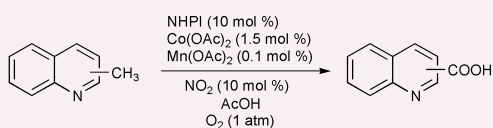


The binding of a hydrogen-bonding receptor to its substrate is reversibly regulated by varying the oxidation state of a copper allosteric cofactor.

180

**Remarkable effect of nitrogen dioxide for *N*-hydroxyphthalimide-catalyzed aerobic oxidation of methylquinolines**

Satoshi Sakaguchi, Akihiro Shibamoto and Yasutaka Ishii



Aerobic oxidation of methylquinolines was successfully achieved by the use of *N*-hydroxyphthalimide/Co(OAc)<sub>2</sub>/Mn(OAc)<sub>2</sub> as catalyst in the presence of a small amount of NO<sub>2</sub>.

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Supplementary crystallographic data are available: see article for further information.



Electronic supplementary information is available on <http://www.rsc.org/esi>: see article for further information.



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