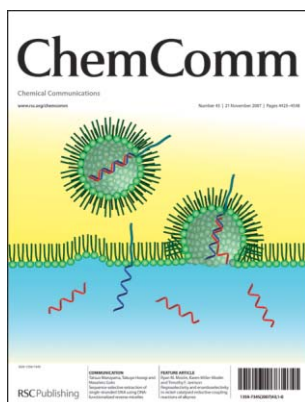


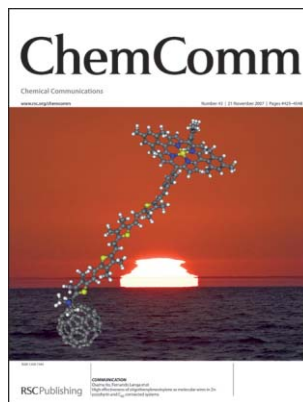
## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (43) 4425-4548 (2007)



### Cover

See Tatsuo Maruyama, Takuya Hosogi and Masahiro Goto, page 4450.  
DNA-surfactant allows selective transport of the target DNA to an organic phase from a mixture of DNA oligonucleotides.  
Image reproduced by permission of Tatsuo Maruyama, Takuya Hosogi and Masahiro Goto from *Chem. Commun.*, 2007, 4450.



### Inside cover

See Osamu Ito, Fernando Langa *et al.*, page 4498.  
High effectiveness of oligothiénylenevinylene as molecular wires in Zn-porphyrin and C<sub>60</sub> connected systems.  
Image reproduced by permission of Frédéric Oswald, D.-M. Shafiqul Islam, Yasuyuki Araki, Vincent Troiani, Ruben Caballero, Pilar de la Cruz, Osamu Ito and Fernando Langa from *Chem. Commun.*, 2007, 4498.

## CHEMICAL SCIENCE

C81

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.

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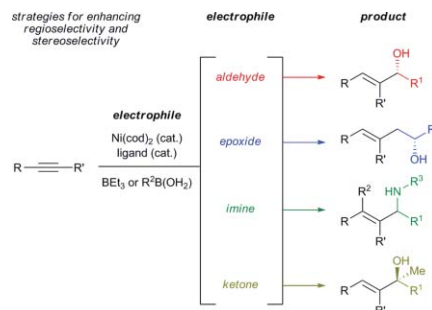
## FEATURE ARTICLE

4441

### Regioselectivity and enantioselectivity in nickel-catalysed reductive coupling reactions of alkynes

Ryan M. Moslin, Karen Miller-Moslin and Timothy F. Jamison\*

Nickel-catalysed reductive coupling reactions of alkynes have emerged as powerful synthetic tools for the selective preparation of functionalized alkenes. Recent work from our laboratory has provided an improved understanding of several of the factors governing regioselectivity in these reactions.



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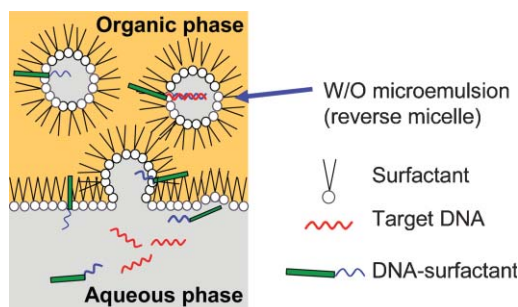
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4450

### Sequence-selective extraction of single-stranded DNA using DNA-functionalized reverse micelles

Tatsuo Maruyama,\* Takuya Hosogi and Masahiro Goto\*

The authors report sequence-specific liquid/liquid extraction of single-stranded DNA using reverse micelles, in which a DNA-surfactant transports a target DNA selectively to an organic phase from a mixture of DNA oligonucleotides.

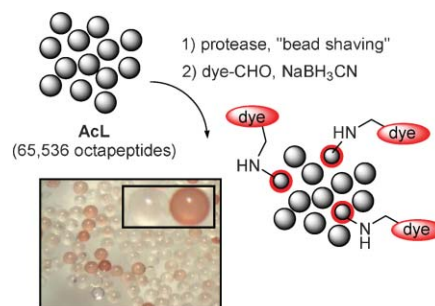


4453

### Identification of protease substrates by combinatorial profiling on TentaGel beads

Jacob Kofoed and Jean-Louis Reymond\*

Bead shaving of a solid-supported combinatorial peptide library and selective staining of free amino termini allows the rapid identification of protease substrates.

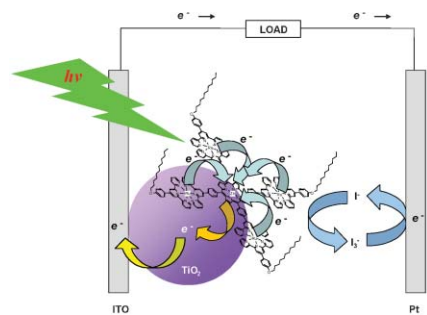


4456

### 5,10,15,20-Tetrakis[4'-(terpyridinyl)phenyl]porphyrin and its Ru<sup>II</sup> complexes: Synthesis, photovoltaic properties, and self-assembled morphology

Tae Joon Cho, Carol D. Shreiner, Seok-Ho Hwang, Charles N. Moorefield, Brandy Courneya, Luis A. Godínez, Juan Manríquez, Kwang-Un Jeong, Stephen Z. D. Cheng and George R. Newkome\*

A tetrakis(terpyridinyl)porphyrin derivative and its Ru<sup>II</sup> complexes were efficiently synthesized by a microwave assisted reaction and shown to possess photovoltaic properties. TEM and SAED revealed its nanowire assembly.

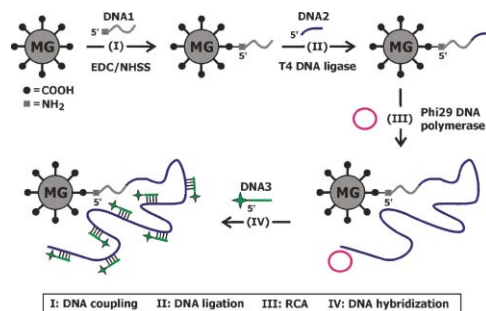


4459

### Enzymatic manipulations of DNA oligonucleotides on microgel: towards development of DNA-microgel bioassays

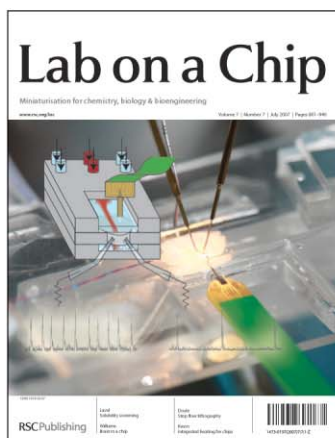
Md Monsur Ali, Shunxing Su, Carlos D. M. Filipe, Robert Pelton and Yingfu Li\*

DNA oligonucleotides coupled to colloid microgel (MG) can be manipulated by T4 DNA ligase for DNA ligation and by Phi29 DNA polymerase for rolling circle amplification (RCA); the long single-stranded RCA product can generate intensive fluorescence upon hybridization with complementary fluorescent DNA probe.



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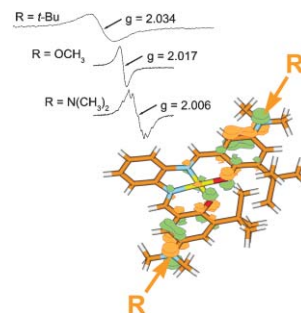
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4462

### A versatile electronic hole in one-electron oxidized Ni<sup>II</sup> bis-salicylidene phenylenediamine complexes

Olaf Rotthaus, Olivier Jarjayes,\* Carlos Perez Del Valle, Christian Philouze and Fabrice Thomas\*

A versatile “delocalized radical” character is induced in nickel-salen complexes: it could be modulated by the electron-donating properties of the phenolate *para*-substituent.

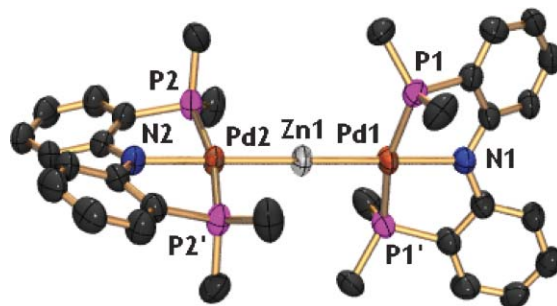


4465

### Covalent palladium–zinc bonds and their reactivity

Claudia M. Fafard, Chun-Hsing Chen, Bruce M. Foxman and Oleg V. Ozerov\*

Photolysis of (F<sup>-</sup>PNP)Pd–Et in the presence of Et<sub>2</sub>Zn leads to the formation of (F<sup>-</sup>PNP)Pd–Zn–Pd(PNP<sup>F-</sup>), the first example of a compound with a covalent Pd–Zn bond.

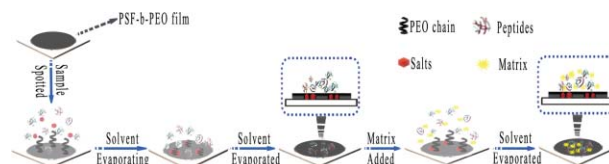


4468

### Wash-free *in-situ* self-desalting and peptide enrichment by block copolymer analyzed with MALDI-TOFMS

Ying Zhang, Jianhua Fang, Yongbo Kuang, Xiaoxia Guo, Haojie Lu\* and Pengyuan Yang\*

A novel technique of simultaneous peptide enrichment and wash-free *in-situ* self-desalting for MALDI analysis is reported.

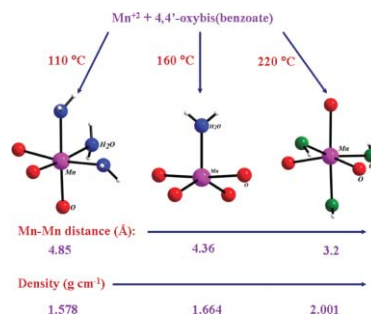


4471

### The role of temperature on the structure and dimensionality of MOFs: an illustrative study of the formation of manganese oxy-bis(benzoate) structures

Partha Mahata, A. Sundaresan and Srinivasan Natarajan\*

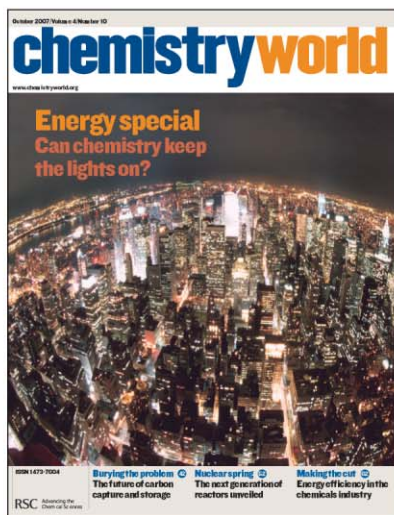
A possible entropy driven process, employing temperature as the variable, gives rise to products of higher dimensionality under hydrothermal conditions.



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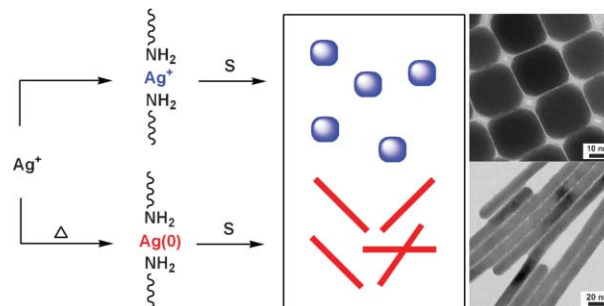
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4474

### Shape-controlled synthesis of silver sulfide nanocrystals by understanding the origin of mixed-shape evolution

Kwonho Jang, So Yeon Kim, Kang Hyun Park, Eunjoon Jang, Shinae Jun and Seung Uk Son\*

The origin of the mixed-shape problem in the shape-controlled synthesis of silver sulfide nanomaterials was investigated. Amine reduction during the dissolution of silver nitrate can generate zerovalent silver species, which can be the origin of the mixed-shape problem in the synthesis of silver sulfide nanomaterials.

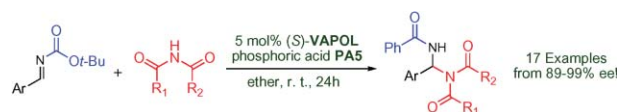


4477

### VAPOL phosphoric acid catalysis: the highly enantioselective addition of imides to imines

Yuxue Liang, Emily B. Rowland, Gerald B. Rowland, Jason A. Perman and Jon C. Antilla\*

The first highly enantioselective catalytic method for the preparation of chiral aminals *via* the addition of imide nucleophiles to imines is reported. The aminal products were formed in up to 94% yield and up to 99% ee.

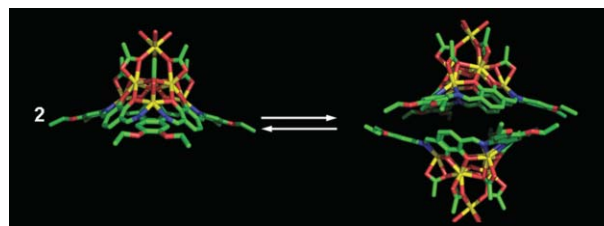


4480

### Capsule formation in novel cadmium cluster metallocavitands

Peter D. Frischmann and Mark J. MacLachlan\*

A heptanuclear cadmium cluster formed in a Schiff base macrocycle self-assembles into capsules in the solid state and in solution, where thermodynamic studies indicate that the reversible dimerization is entropy-driven.

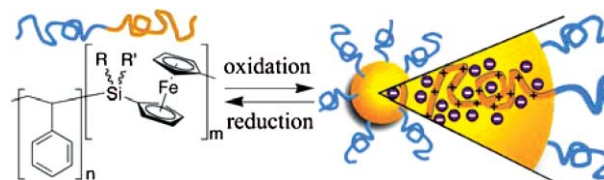


4483

### Redox-controlled micellization of organometallic block copolymers

David A. Rider, Mitchell A. Winnik\* and Ian Manners\*

Polystyrene-*block*-polyferrocenylsilane (**PS-*b*-PFS**) diblock copolymers were reversibly oxidized in solution with tris(4-bromophenyl)-ammoniumyl salts and self-assembled into well-defined spherical micelles due to the redox-induced polarity change for the **PFS** block.



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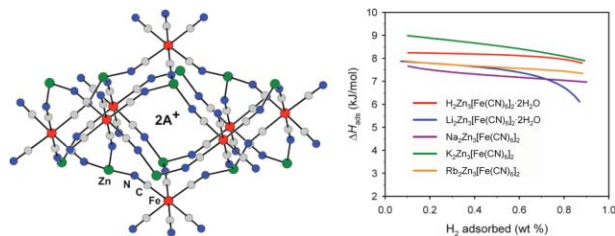


4486

### Hydrogen adsorption in dehydrated variants of the cyano-bridged framework compounds $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$ (A = H, Li, Na, K, Rb)

Steven S. Kaye and Jeffrey R. Long\*

The hydrogen storage properties are investigated for a series of microporous cyano-bridged framework compounds,  $A_2Zn_3[Fe(CN)_6]_2 \cdot xH_2O$  (A = H, Li, Na, K, Rb), containing coordinatively-unsaturated alkali metal cations. The results reveal an enhancement in the initial  $H_2$  adsorption enthalpies, with the unusual trend  $K^+ > (H_3O)^+ > Rb^+ \approx Li(H_2O)^+ > Na^+$ .

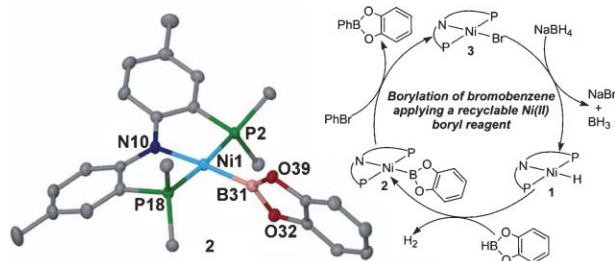


4489

### Structural elucidation of a nickel boryl complex. A recyclable borylation Ni(II) reagent of bromobenzene

Debashis Adhikari, John C. Huffman and Daniel J. Mindiola\*

A novel nickel boryl complex,  $(PNP)Ni[B(\text{catechol})]$  (PNP =  $N[2\text{-P}(\text{CHMe}_2)_2\text{-4-methylphenyl}]_2^-$ ), has been prepared, structurally characterized, and analyzed by DFT. This complex is a recyclable compound for the borylation of bromobenzene.

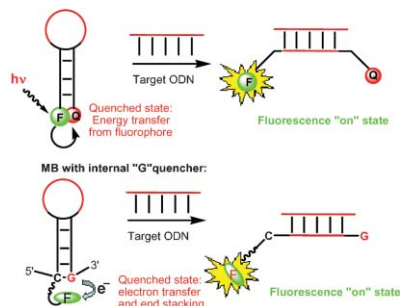


4492

### Design of a novel G-quenched molecular beacon: A simple and efficient strategy for DNA sequence analysis

Yoshio Saito,\* Erika Mizuno, Subhendu Sekhar Bag, Isamu Suzuka and Isao Saito\*

Novel G-quenched molecular beacons in which the fluorophores are attached *via* a six-carbon alkylamino linker at the 5'-end, are capable of sensing specific DNA sequence with high efficiency.

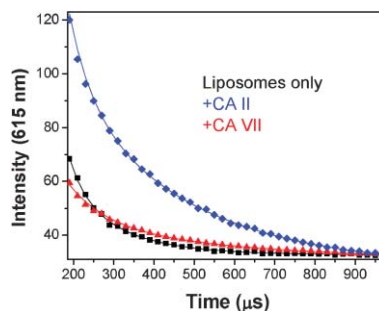


4495

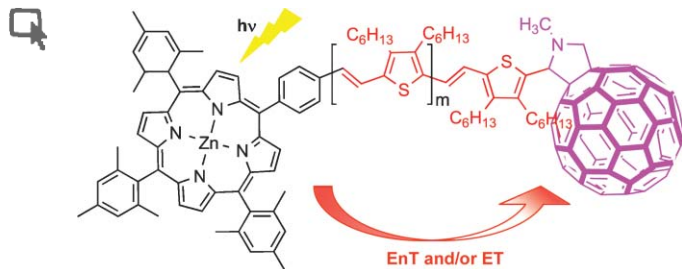
### Recognition of isozymes *via* lanthanide ion incorporated polymerized liposomes

Adekunle I. Elegbede, Manas K. Haldar, Sumathra Manokaran, Sanku Mallik\* and D. K. Srivastava\*

We report the selective recognition of carbonic anhydrase isozymes based on the excited-state lifetimes of chelated  $Eu^{3+}$  ions incorporated in polymerized liposomes.



4498

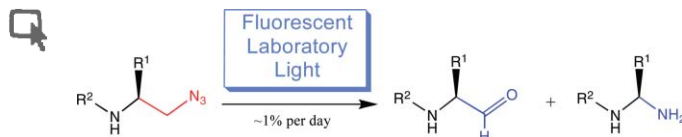


### High effectiveness of oligothiénylenevinylene as molecular wires in Zn-porphyrin and C<sub>60</sub> connected systems

Frédéric Oswald, D.-M. Shafiqul Islam, Yasuyuki Araki, Vincent Troiani, Ruben Caballero, Pilar de la Cruz, Osamu Ito\* and Fernando Langa\*

Photo-induced energy and electron transfer processes have been found between the excited singlet state of Zn-porphyrin and C<sub>60</sub> via thiénylenevinylene (*n*TV) bridges depending on the length of the *n*TV and solvent polarity.

4501

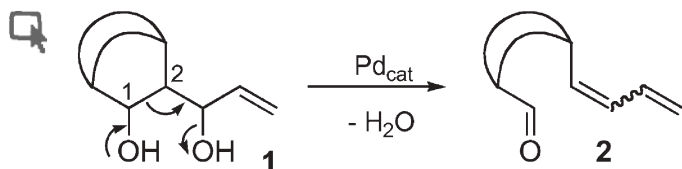


### Unexpected photolytic decomposition of alkyl azides under mild conditions

Giovanni Abbenante, Giang T. Le and David P. Fairlie\*

Alkyl azides are shown to be susceptible to photolysis under very mild conditions (laboratory light) giving aldehyde and monoacyl aminal decomposition products.

4504

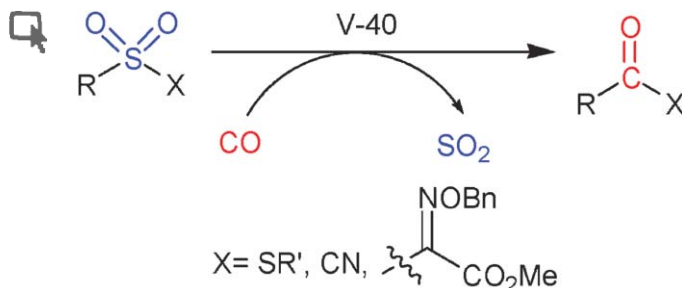


### Palladium-catalyzed 1,3-diol fragmentation: synthesis of ω-dienyl aldehydes

Masanari Kimura, Masahiko Mori and Yoshinao Tamaru\*

1,3-Diols **1**, undergo dehydrative C1–C2 bond cleavage and provide ω-dienyl aldehydes **2** under the catalysis of Pd(0) and 9-phenyl-9-borabicyclo[3.3.1]nonane.

4507



### A novel approach for the direct conversion of alkylsulfonyl derivatives into alkylcarbonyl derivatives via tin-free radical carbonylation

Sangmo Kim, Kyoung-Chan Lim and Sunggak Kim\*

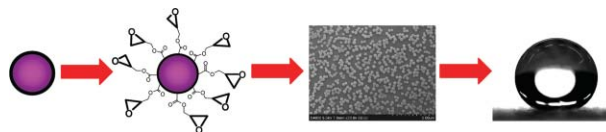
A novel radical approach for the direct conversion of RSO<sub>2</sub>X into RCOX in a single step is devised. The present approach is very simple, highly efficient, and minimizes formation of by-products.

4510

**Ultrahydrophobic textile surface via decorating fibers with monolayer of reactive nanoparticles and non-fluorinated polymer**

Karthik Ramaratnam, Volodymyr Tsyalkovsky, Viktor Klep and Igor Luzinov\*

The hydrophobicity and miniature protrusions of the lotus leaves are mimicked using a monolayer of non-fluorinated hydrophobic polymer and functionalized nanoparticles, to form a permanent nanocoating that generates ultrahydrophobic fibers/textiles with excellent water repellency and self-cleaning ability.

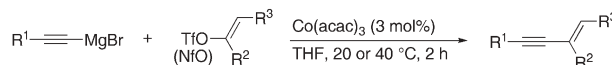


4513

**Cobalt-catalyzed cross-coupling of alkynyl Grignard reagents with alkenyl triflates**

Eiji Shirakawa,\* Takahiro Sato, Yusuke Imazaki, Takahiro Kimura and Tamio Hayashi\*

A practically useful and widely applicable alkynyl–alkenyl coupling is presented, where only a readily available  $\text{Co}(\text{acac})_3$  and THF respectively as a catalyst and a solvent are required to couple alkynyl Grignard reagents with alkenyl triflates.

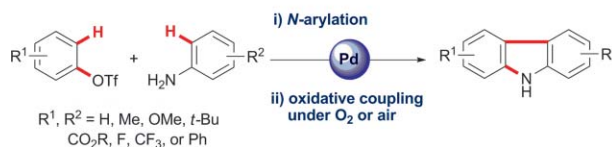


4516

**One-pot synthesis of carbazoles by palladium-catalyzed *N*-arylation and oxidative coupling**

Toshiaki Watanabe, Satoshi Ueda, Shinsuke Inuki, Shinya Oishi, Nobutaka Fujii\* and Hiroaki Ohno\*

One-pot *N*-arylation and oxidative coupling were promoted by a common palladium catalyst in the presence of appropriate additives to afford various types of functionalized carbazoles in good to excellent yields.

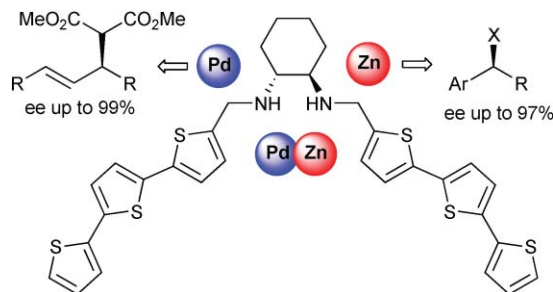


4519

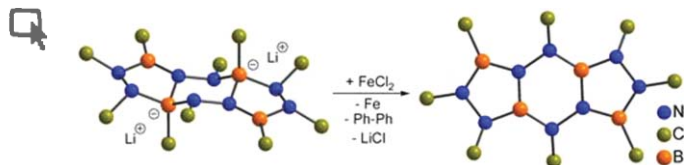
**New chiral diamino-bis(*tert*-thiophene): an effective ligand for Pd- and Zn-catalyzed asymmetric transformations**

Marco Bandini,\* Manuela Melucci, Fabio Piccinelli, Riccardo Sinisi, Simona Tommasi and Achille Umani-Ronchi\*

Chiral diamino-bis(*tert*-thiophene) as a valuable motif for organometallic asymmetric catalysis.



4522

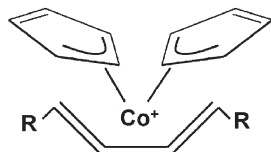


### Assembly of a planar, tricyclic B<sub>4</sub>N<sub>8</sub> framework with *s*-indacene structure

Hanh V. Ly, Heikki M. Tuononen, Masood Parvez and Roland Roesler\*

A tricyclic B<sub>4</sub>N<sub>8</sub><sup>2-</sup> diborate was prepared by self-assembly of two anionic boron–nitrogen rings, and subsequently oxidized with FeCl<sub>2</sub> to biphenyl and a planar, formally 16π-electron tricycle with B<sub>4</sub>N<sub>8</sub> framework.

4525

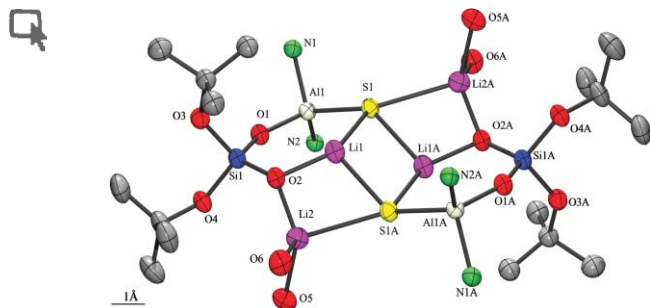


### Reactive MALDI mass spectrometry: application to high mass alkanes and polyethylene

William E. Wallace

A long standing analytical problem pertinent to the petroleum and polyolefin industries has been solved using an innovative bimolecular MALDI matrix where a reactive species is sequestered by intercalation into a host fullerene matrix.

4528

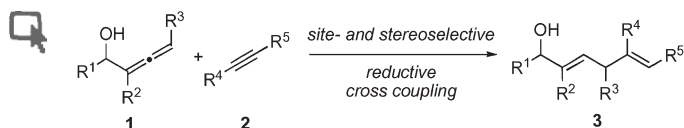


### Soluble, reactive and stable – unique aluminosilicate ligands and a heterobimetallic derivative [LAl(SLi)(μ-O)Si(OLi·2thf)(O'Bu)<sub>2</sub>]<sub>2</sub>

Vojtech Jancik, Fernando Rascón-Cruz, Raymundo Cea-Olivares\* and Rubén A. Toscano

The reaction of LAl(SH)<sub>2</sub> with (tBuO)<sub>2</sub>Si(OH)<sub>2</sub> yielded the novel aluminosilicate ligand LAl(SH)(μ-O)Si(OH)(O'Bu)<sub>2</sub>, which was used for the preparation of the heterobimetallic aluminosilicate [LAl(SLi)(μ-O)Si(OLi·2thf)(O'Bu)<sub>2</sub>]<sub>2</sub> and the dihydroxide LAl(OH·thf)(μ-O)Si(OH)(O'Bu)<sub>2</sub>.

4531



### An alkoxide-directed alkyne–allene cross-coupling for stereoselective synthesis of 1,4-dienes

Heidi L. Shimp and Glenn C. Micalizio\*

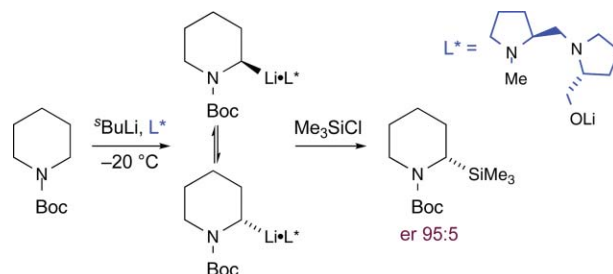
A titanium alkoxide-mediated convergent coupling between internal alkynes and allenes is described for the regio- and stereocontrolled synthesis of substituted acyclic 1,4-dienes.

4534

### Dynamic kinetic and kinetic resolution of *N*-Boc-2-lithiopiperidine

Iain Coldham,\* Jignesh J. Patel, Sophie Raimbault and David T. E. Whittaker

The *2R* and *2S* organolithium complexes interconvert at  $-20\text{ }^{\circ}\text{C}$  and react at different rates, allowing a dynamic kinetic resolution.



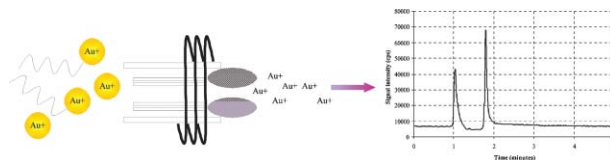
Resolution of the organolithiums based on their relative rate of reaction.

4537

### Nano-particle labelling of nucleic acids for enhanced detection by inductively-coupled plasma mass spectrometry (ICP-MS)

Samantha Louise Kerr and Barry Sharp\*

Oligonucleotides containing a biotin functionality were successfully labelled with a streptavidin nanogold conjugate and subsequently separated and analysed by HPLC-ICP-MS.

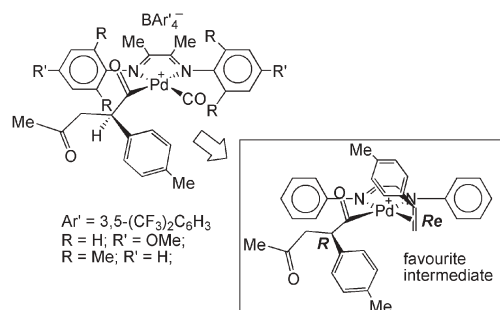


4540

### Stereocontrol mechanism in CO/*p*-methylstyrene copolymerisation catalysed by aryl- $\alpha$ -diimine Pd(II) complexes

Carla Carfagna,\* Giuseppe Gatti, Luca Mosca, Alessandra Passeri, Paola Paoli and Annalisa Guerri

Structural analysis of the first steps of isotactic CO/*p*-methylstyrene copolymerisation, catalysed by aryl- $\alpha$ -diimine Pd(II) complexes, highlights the influence of steric effects on the stereoselectivity of olefin insertion.

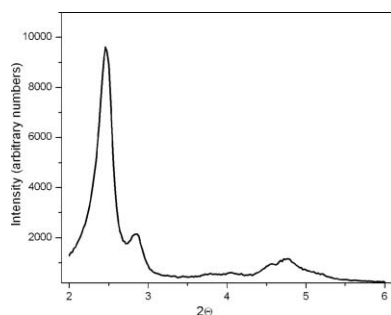


4543

### Rapid and facile synthesis of siliceous MCM-48 mesoporous materials

Brett Boote, Hariharaputhiran Subramanian and Koodali T. Ranjit\*

A rapid and facile synthesis of cubic MCM-48 mesoporous material based on the modification of Stöber synthesis in as little time as 30 minutes at room temperature is possible by careful control of stirring rate and aging time.



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