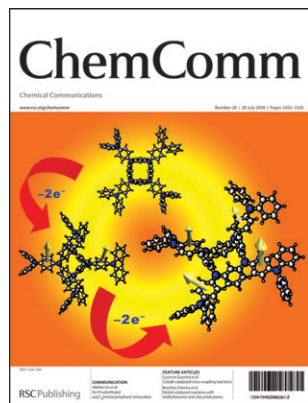


## IN THIS ISSUE

ISSN 1359-7345 CODEN CHCOFS (28) 3205-3320 (2008)



### Cover

See Akihiro Ito *et al.*, pp. 3242–3244.  
*N*-substituted aza[1.4]metacyclophane tetracation: a spin-quintet tetradical having four *para*-phenylenediamine-based semi-quinone moieties. Image reproduced by permission of Akihiro Ito, Syuuzi Inoue, Yasukazu Hirao, Ko Furukawa, Tatsuhisa Kato and Kazuyoshi Tanaka from *Chem. Commun.*, 2008, 3242.



### Inside cover

See Heather D. Maynard *et al.*, pp. 3245–3247.  
Reduction of a siRNA–polymer conjugate synthesized by RAFT polymerization releases the free RNA duplex. Image reproduced by permission of Karina L. Heredia, Thi H. Nguyen, Chien-Wen Chang, Volga Bulmus, Thomas P. Davis and Heather D. Maynard from *Chem. Commun.*, 2008, 3245.

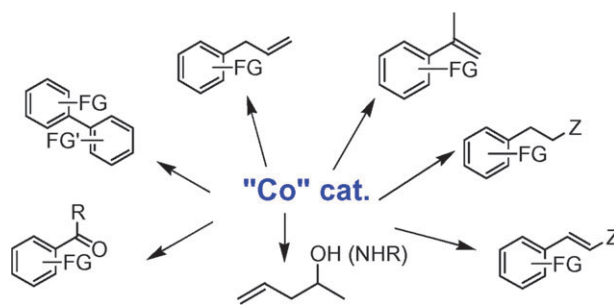
## FEATURE ARTICLES

3221

### Cobalt-catalyzed cross-coupling reactions

Corinne Gosmini,\* Jeanne-Marie Bégouin and Aurélien Moncombe

Economical cobalt salts can advantageously replace expensive and toxic catalysts for cross coupling reactions and these cobalt-catalyzed reactions have considerably extended the range of functionalized compounds in which a variety of sensitive functional groups can be tolerated. Here, we describe our contributions in this area for the preparation of a broad range of functionalized compounds from organometallic species or by direct cross-coupling.

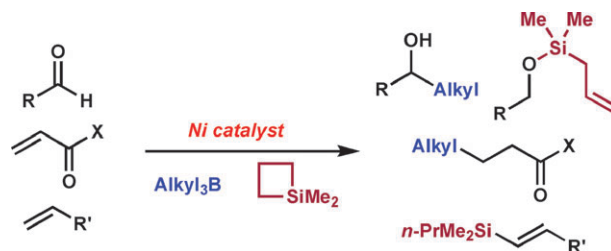


3234

### Nickel-catalysed reactions with trialkylboranes and silacyclobutanes

Koji Hirano, Hideki Yorimitsu\* and Koichiro Oshima\*

This feature article describes nickel-catalysed reactions with trialkylboranes and silacyclobutanes of modest reactivity, including alkylation of carbonyl compounds with various trialkylboranes, ring opening of silacyclobutanes with aldehydes, and silylation of terminal alkenes with silacyclobutane.



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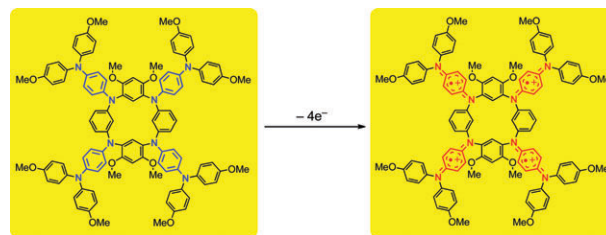
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3242

### An *N*-substituted aza[1<sub>4</sub>]metacyclophane tetracation: a spin-quintet tetradical with four *para*-phenylenediamine-based semi-quinone moieties

Akihiro Ito,\* Syuuzi Inoue, Yasukazu Hirao, Ko Furukawa, Tatsuhisa Kato and Kazuyoshi Tanaka

A fully dianisylaminophenylated aza[1<sub>4</sub>]metacyclophane has been synthesized that exhibits four reversible two-electron oxidation processes, and its dicationic and tetracationic species have been found to be in triplet and quintet states.

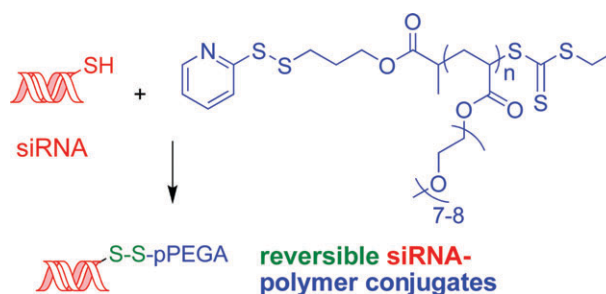


3245

### Reversible siRNA–polymer conjugates by RAFT polymerization

Karina L. Heredia, Thi H. Nguyen, Chien-Wen Chang, Volga Bulmus,\* Thomas P. Davis and Heather D. Maynard\*

A straightforward method to produce reversible siRNA–polymer conjugates is described. RAFT polymerization with a designed pyridyl disulfide-functionalized chain transfer agent results in well-defined polymers for efficient conjugation to siRNA.

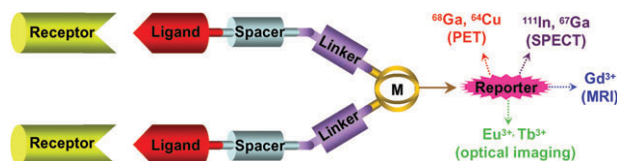


3248

### Novel DOTA-based prochelator for divalent peptide vectorization: synthesis of dimeric bombesin analogues for multimodality tumor imaging and therapy

Keelara Abiraj, Hugues Jaccard, Martin Kretzschmar, Lothar Helm and Helmut R. Maecke\*

Dimeric peptidic vectors, obtained by the divalent grafting of bombesin analogues on a newly synthesized DOTA-based prochelator, showed improved qualities as tumor targeted imaging probes in comparison to their monomeric analogues.

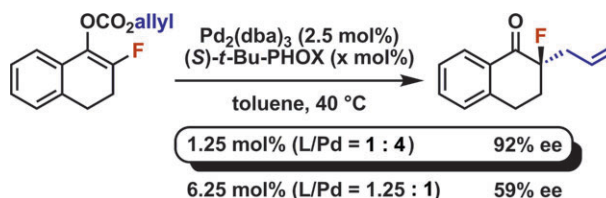


3251

### Unexpected effect of the fluorine atom on the optimal ligand-to-palladium ratio in the enantioselective Pd-catalyzed allylation reaction of fluorinated enol carbonates

Étienne Bélanger, Clément Houzé, Nicolas Guimond, Katy Cantin and Jean-François Paquin\*

The enantioselective Pd-catalyzed allylation reaction of fluorinated allyl enol carbonates is presented; a key feature is the important effect of the ligand-to-palladium ratio on the enantioselectivity of the  $\alpha$ -fluoroketones.





# Chemistry-Biology Interface

## Chemistry-Biology Interface theme issue

This theme issue covers topical areas at the chemistry–biology interface from a chemical perspective. The biological consequences of specific molecular interactions have long been a part of scientific (and non-scientific) activities throughout human history. The last century witnessed a myriad of discoveries in the life sciences at molecular detail, and the associated growth of the pharmaceutical and biotech industries. This century has seen a further growth in the field with a resultant increase in publications and journals.

### Reviews include:

#### **Nucleic acid encoding to program self-assembly in chemical biology**

Zbigniew L. Pianowski and Nicolas Winssinger

#### **Chemical technologies for probing embryonic development**

Ilya A. Shestopalov and James K. Chen

#### **Interspecies and interkingdom communication mediated by bacterial quorum sensing**

Colin A. Lowery, Tobin J. Dickerson and Kim D. Janda

#### **Small molecule inhibition of microbial natural product biosynthesis—an emerging antibiotic strategy**

Justin S. Cisar and Derek S. Tan

#### **Identification of the cellular targets of bioactive small organic molecules using affinity reagents**

Benjamin J. Leslie and Paul J. Hergenrother

#### **Expanding dialogues: from natural autoinducers to non-natural analogues that modulate quorum sensing in Gram-negative bacteria**

Grant D. Geske, Jennifer C. O'Neill and Helen E. Blackwell

### Guest editor:



**David Spring**  
University of Cambridge, UK

"The interface with biology is a fertile scientific pursuit for chemists"

060833

### See also:

*Molecular BioSystems* issue 6, 2008 – Emerging Investigators theme issue

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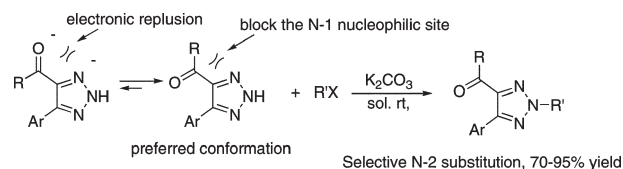
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3254

### Conformational control in the regioselective synthesis of N-2-substituted-1,2,3-triazoles

Yunfeng Chen, Yuxiu Liu, Jeffrey L. Petersen and Xiaodong Shi\*

An effective strategy for the synthesis of N-2-substituted-1,2,3-triazoles with excellent yields and regioselectivity has been developed.

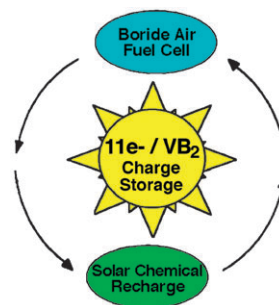


3257

### Renewable highest capacity $\text{VB}_2$ /air energy storage

Stuart Licht,\* Huiming Wu, Xingwen Yu and Yufei Wang

The first renewable energy system which stores more energy than gasoline is presented. With ten-fold lithium-ion's capacity,  $\text{VB}_2$  opens a pathway towards electric vehicles with a viable driving range.

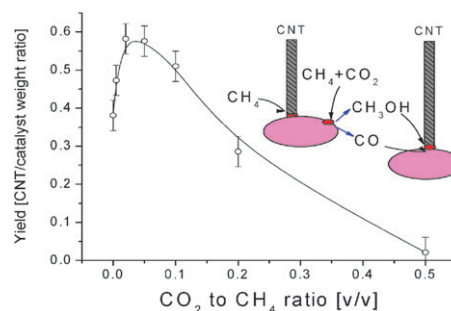


3260

### $\text{CO}_2$ enhanced carbon nanotube synthesis from pyrolysis of hydrocarbons

Zhongrui Li,\* Yang Xu, Xiaodong Ma, Enkeleda Dervishi, Viney Saini, Alexandru R. Biris, Dan Lupu and Alexandru S. Biris\*

The authors report on the role of  $\text{CO}_2$  in improving carbon nanotube yield and crystallinity from catalytic chemical vapor deposition of hydrocarbons. This approach is also valid for the synthesis of any carbon nanotube species while using various types of hydrocarbon.

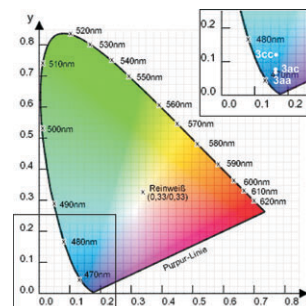


3263

### Blue phosphorescent emitters: new N-heterocyclic platinum(II) tetracarbene complexes

Yvonne Unger, Alexander Zeller, Sebastian Ahrens and Thomas Strassner\*

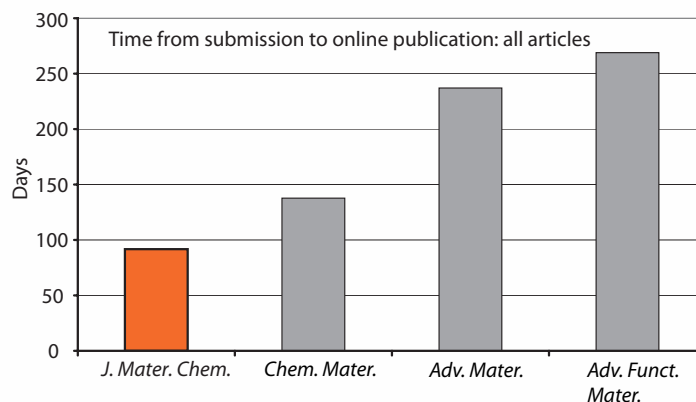
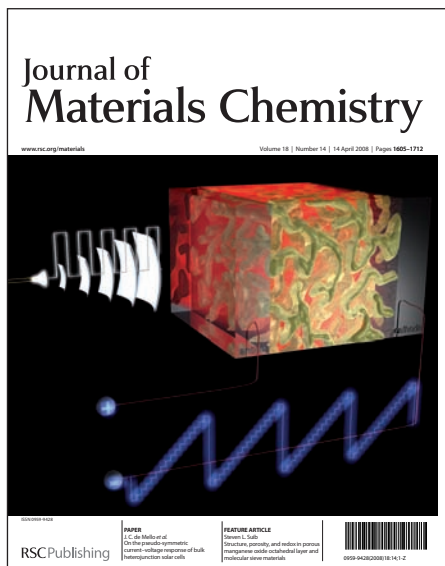
Photoluminescence measurements show that platinum(II) tetracarbene complexes, which could be obtained *via* different synthetic routes, are an interesting class of compounds for the development of blue emitters for PhOLEDs with good quantum yields and high photostability.



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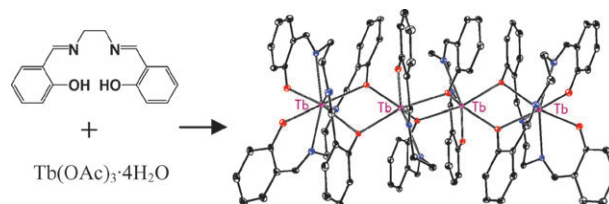
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3266

### Anion dependant self-assembly and the first X-ray structure of a neutral homoleptic lanthanide salen complex $Tb_4(salen)_6$

Xiaoping Yang, Richard A. Jones\* and Wai-Kwok Wong\*

Reaction of  $H_2salen$  ( $H_2L$ ) with  $Tb(OAc)_3 \cdot 4H_2O$  (3 : 2) in MeOH–MeCN under reflux gives homoleptic  $Tb_4L_6$  (**1**) which has been structurally characterized for the first time. ( $H_2L = N,N'$ -ethylenebis(salicylideneimine)).

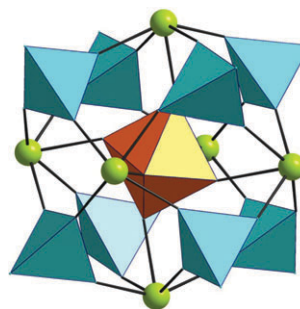


3269

### Cerium(IV)-containing oxomolybdenum cluster with a unique $Ce_6Mo_9O_{38}$ core structure

Xiao-Yi Yi, Herman H. Y. Sung, Ian D. Williams and Wa-Hung Leung\*

Interaction of  $[Ce(L_{OEt})_2(NO_3)_2]$  ( $L_{OEt}^- = [Co(\eta^5-C_5H_5)\{P(O)(OEt)_2\}_3]^-$ ) with  $(NH_4)_6[Mo_7O_{24}]$  in water affords the cerium(IV)-containing oxomolybdenum cluster  $[H_4(CeL_{OEt})_6Mo_9O_{38}]$ , which exhibits a unique  $Ce_6Mo_9O_{38}$  core structure.

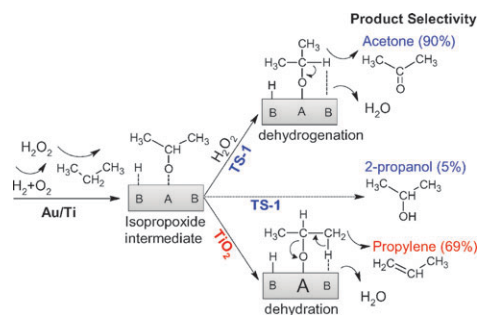


3272

### Propane reacts with $O_2$ and $H_2$ on gold supported TS-1 to form oxygenates with high selectivity

J. J. Bravo-Suárez, K. K. Bando, T. Akita, T. Fujitani, T. J. Fuhrer and S. T. Oyama\*

Gold nanoparticles supported on a microporous titanosilicate (TS-1) have been found to be active and highly selective towards the formation of acetone and isopropanol from propane,  $O_2$ , and  $H_2$ . The conversion is believed to occur *via* an isopropoxy intermediate.

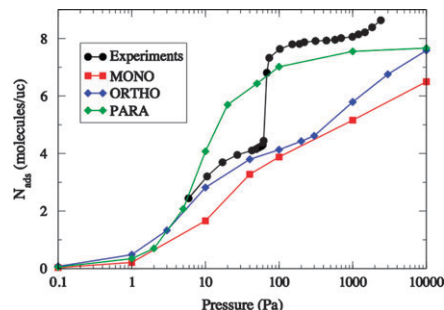


3275

### Structural changes in nanoporous solids due to fluid adsorption: thermodynamic analysis and Monte Carlo simulations

Marie Jeffroy, Alain H. Fuchs and Anne Boutin\*

A thermodynamic analysis based on the osmotic ensemble scheme enables the prediction of structural changes occurring in silicalite-1 zeolite upon halocarbon molecule adsorption.



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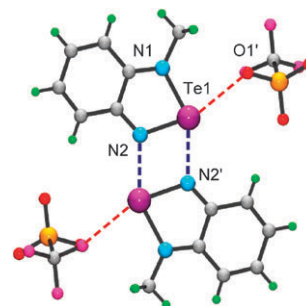


3278

### Self-association of the *N*-methyl benzotellurodiazolium cation: implications for the generation of super-heavy atom radicals

Maarit Risto, Robert W. Reed, Craig M. Robertson, Raija Oilunkaniemi, Risto S. Laitinen\* and Richard T. Oakley\*

The *N*-methyl benzotellurodiazolium cation self-associates in the solid state *via* short (2.471(3) Å) 4-center Te...N' intermolecular contacts; electrochemical data and the results of DFT calculations suggest that the dimers persist in solution.

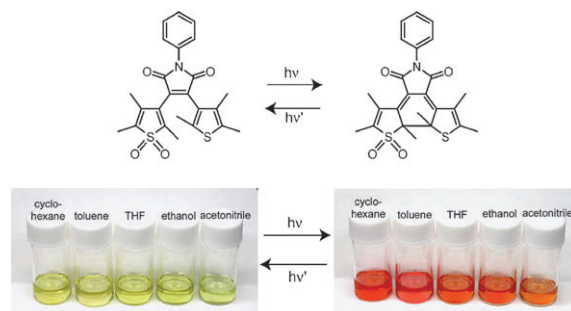


3281

### Photocyclization reaction of a diarylmaleimide derivative in polar solvents

Masato Ohsumi, Masaki Hazama, Tuyoshi Fukaminato\* and Masahiro Irie\*

The photochromic reactivity of a diarylmaleimide derivative in polar solvents was improved by the oxidation of the sulfur atom on the aryl moiety.

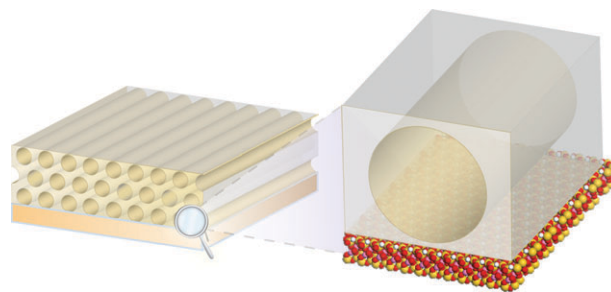


3284

### Facile unidirectional alignment of mesochannels in a mesoporous silica film on a freshly cleaved mica surface

Takashi Suzuki, Yosuke Kanno, Yuji Morioka and Kazuyuki Kuroda\*

The alignment of mesochannels in a mesoporous silica film on a freshly cleaved mica surface, prepared by an evaporation-induced self-assembly process, is unexpectedly found to be unidirectional with the narrowest directional distribution.

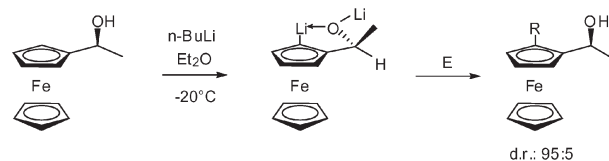


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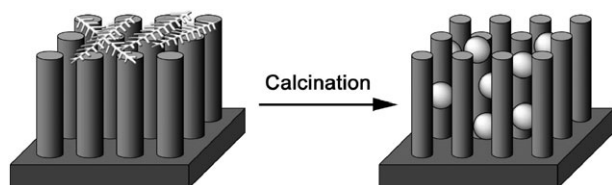
### *Ortho*-lithiation of free ferrocenyl alcohols: a new method for the synthesis of planar chiral ferrocene derivatives

Bernhard J. Ueberbacher,\* Herfried Griengl and Hansjörg Weber

An *ortho*-metalation method for free ferrocenyl alcohols has been developed, which allows preparation of planar chiral ferrocene derivatives in high yields and diastereoselectivities.



3290

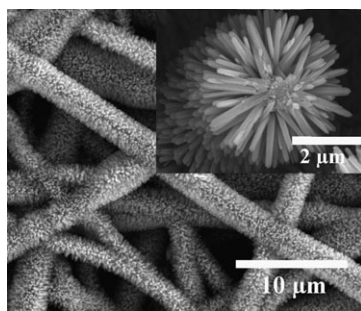


### Ag microparticles embedded in Si nanowire arrays: a novel catalyst for gas-phase oxidation of high alcohol to aldehyde

Chenxi Zhang, Ping Chen, Jian Liu, Yahong Zhang, Wei Shen, Hualong Xu\* and Yi Tang\*

A novel catalyst of silver microparticles embedded in a silicon nanowire array support (Ag@SiNW) was prepared by an *in situ* electroless metal deposition method; it exhibited high selectivity and stability for gas-phase oxidation of high alcohol to its corresponding aldehyde.

3293

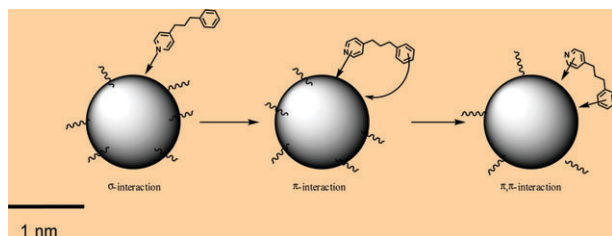


### Preparation of self-supporting hierarchical nanostructured anatase/rutile composite TiO<sub>2</sub> film

Chenghua Sun, Nuanxia Wang, Shiyi Zhou, Xiujie Hu, Shuyun Zhou\* and Ping Chen\*

Via the combination of an electrospinning method with a hydrothermal reaction, a large-scale cedar-like hierarchical nanostructured TiO<sub>2</sub> film with an anatase/rutile composite phase was fabricated.

3296

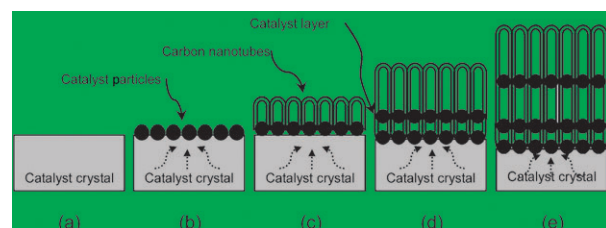


### A new and specific mode of stabilization of metallic nanoparticles

Isabelle Favier, Stéphane Massou, Emmanuelle Teuma, Karine Philippot, Bruno Chaudret and Montserrat Gómez

A new mode of stabilization for metal nanoparticles is depicted here. Due to its specific structure, 4-(3-phenylpropyl)pyridine interacts at the ruthenium particles surface by  $\pi$ -interactions.

3299



### A multi-stage growth model leading to high-yield production of carbon nanotubes

Yajun Tian,\* Huaixin Yang, Yanbin Cui, Shuanglin Zhan and Yunfa Chen

A novel growth model leading to the high-yield production of multi-walled carbon nanotubes is presented. It consists of quasi-periodically separating the reactive flakes from parent catalyst and growing carbon nanotubes from both sides of the flakes.

3302

### Asymmetric multifunctional organocatalytic Michael addition of nitroalkanes to $\alpha,\beta$ -unsaturated ketones

Pengfei Li, Yongcan Wang, Xinmiao Liang\* and Jinxing Ye\*

Cinchona alkaloid derived primary amine thioureas organocatalyzed Michael addition of nitroalkanes to enones in good yield and up to 98% ee and offered a new way to construct chiral quaternary stereocenters from enones and nitroalkanes.

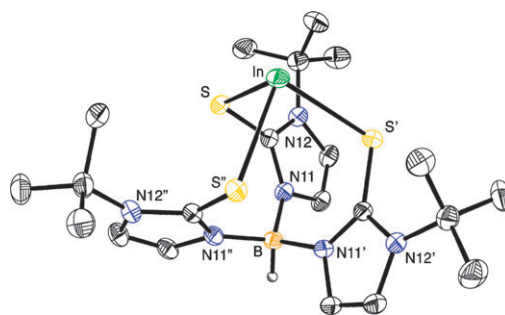


3305

### Monovalent indium in a sulfur-rich coordination environment: synthesis, structure and reactivity of *tris*(2-mercapto-1-*tert*-butylimidazolyl)hydroborato indium, [Tm<sup>Bu</sup>]<sup>+</sup>In

Kevin Yurkerwich, Daniela Buccella, Jonathan G. Melnick and Gerard Parkin\*

[Tm<sup>Bu</sup>]<sup>+</sup>In, a monovalent indium compound that features a sulfur-rich coordination environment, exhibits a structure and reactivity that is distinct from its thallium counterpart.

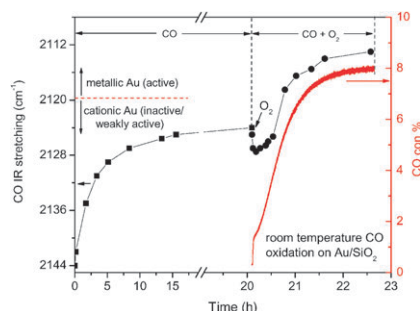


3308

### Oxygen-assisted reduction of Au species on Au/SiO<sub>2</sub> catalyst in room temperature CO oxidation

Zili Wu, Shenghu Zhou, Haoguo Zhu, Sheng Dai and Steven H. Overbury\*

Oxygen unusually assists the reduction of cationic Au species by CO at room temperature on Au/SiO<sub>2</sub> catalyst; the reduced metallic Au species plays a major role in CO oxidation.

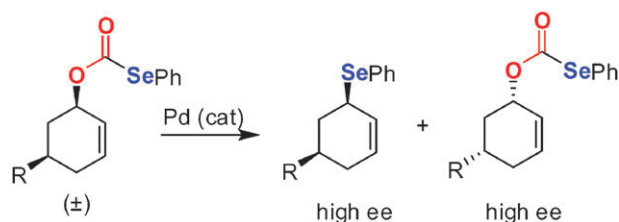


3311

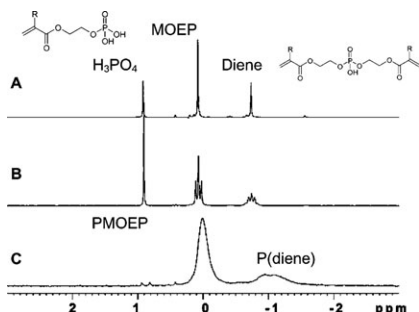
### Synthesis of allyl selenides by palladium-catalyzed decarboxylative coupling

Shelli R. Waetzig and Jon A. Tunge\*

Decarboxylative coupling allows the catalytic synthesis of enantioenriched allyl selenides under neutral conditions. Subsequent [2,3]-sigmatropic rearrangements provide access to enantioenriched allylic chlorides and amines.



3314



### Influence of a diene impurity on the molecular structure of phosphate-containing polymers with medical applications

Lisbeth Grøndahl,\* Shuko Suzuki and Edeline Wentrup-Byrne\*

$^{31}\text{P}$  NMR proved a key tool in clarifying the polymerisation processes observed for MOEP containing a previously unacknowledged high level of impurities.

3317



### $\text{Me}_2\text{Zn}$ mediated, *tert*-butylhydroperoxide promoted, catalytic enantioselective Reformatsky reaction with aldehydes

Pier Giorgio Cozzi,\* Fides Benfatti, Montse Guiteras Capdevila and Alessandro Mignogna

A practical and highly enantioselective (up to 93% ee) catalytic Reformatsky reaction with aldehydes promoted by *t*BuOOH, and catalyzed by a cheap, commercially available aminoalcohol, is described.

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## AUTHOR INDEX

- Abiraj, Keelara, 3248  
 Ahrens, Sebastian, 3263  
 Akita, T., 3272  
 Bando, K. K., 3272  
 Bégouin, Jeanne-Marie, 3221  
 Bélanger, Étienne, 3251  
 Benfatti, Fides, 3317  
 Biris, Alexandru R., 3260  
 Biris, Alexandru S., 3260  
 Boutin, Anne, 3275  
 Bravo-Suárez, J. J., 3272  
 Buccella, Daniela, 3305  
 Bulmus, Volga, 3245  
 Cantin, Katy, 3251  
 Chang, Chien-Wen, 3245  
 Chaudret, Bruno, 3296  
 Chen, Ping, 3290, 3293  
 Chen, Yunfa, 3299  
 Chen, Yunfeng, 3254  
 Cozzi, Pier Giorgio, 3317  
 Cui, Yanbin, 3299  
 Dai, Sheng, 3308  
 Davis, Thomas P., 3245  
 Dervishi, Enkeleda, 3260  
 Favier, Isabelle, 3296  
 Fuchs, Alain H., 3275  
 Fuhrer, T. J., 3272  
 Fujitani, T., 3272  
 Fukaminato, Tuyoshi, 3281  
 Furukawa, Ko, 3242  
 Gómez, Montserrat, 3296  
 Gosmini, Corinne, 3221  
 Griengl, Herfried, 3287  
 Grøndahl, Lisbeth, 3314  
 Guimond, Nicolas, 3251  
 Guiteras Capdevila, Montse, 3317  
 Hazama, Masaki, 3281  
 Helm, Lothar, 3248  
 Heredia, Karina L., 3245  
 Hirano, Koji, 3234  
 Hirao, Yasukazu, 3242  
 Houzé, Clément, 3251  
 Hu, Xiujie, 3293  
 Inoue, Syuuzi, 3242  
 Irie, Masahiro, 3281  
 Ito, Akihiro, 3242  
 Jaccard, Hugues, 3248  
 Jeffroy, Marie, 3275  
 Jones, Richard A., 3266  
 Kanno, Yosuke, 3284  
 Kato, Tatsuhisa, 3242  
 Kretschmar, Martin, 3248  
 Kuroda, Kazuyuki, 3284  
 Laitinen, Risto S., 3278  
 Leung, Wa-Hung, 3269  
 Li, Pengfei, 3302  
 Li, Zhongrui, 3260  
 Liang, Xinmiao, 3302  
 Licht, Stuart, 3257  
 Liu, Jian, 3290  
 Liu, Yuxiu, 3254  
 Lupu, Dan, 3260  
 Ma, Xiaodong, 3260  
 Maecke, Helmut R., 3248  
 Massou, Stéphane, 3296  
 Maynard, Heather D., 3245  
 Melnick, Jonathan G., 3305  
 Mignogna, Alessandro, 3317  
 Moncomble, Aurélien, 3221  
 Morioka, Yuji, 3284  
 Nguyen, Thi H., 3245  
 Oakley, Richard T., 3278  
 Ohsumi, Masato, 3281  
 Oilunkaniemi, Raija, 3278  
 Oshima, Koichiro, 3234  
 Overbury, Steven H., 3308  
 Oyama, S. T., 3272  
 Paquin, Jean-François, 3251  
 Parkin, Gerard, 3305  
 Petersen, Jeffrey L., 3254  
 Philippot, Karine, 3296  
 Reed, Robert W., 3278  
 Risto, Maarit, 3278  
 Robertson, Craig M., 3278  
 Saini, Viney, 3260  
 Shen, Wei, 3290  
 Shi, Xiaodong, 3254  
 Strassner, Thomas, 3263  
 Sun, Chenghua, 3293  
 Sung, Herman H.Y., 3269  
 Suzuki, Shuko, 3314  
 Suzuki, Takashi, 3284  
 Tanaka, Kazuyoshi, 3242  
 Tang, Yi, 3290  
 Teuma, Emmanuelle, 3296  
 Tian, Yajun, 3299  
 Tunge, Jon A., 3311  
 Ueberbacher, Bernhard J., 3287  
 Unger, Yvonne, 3263  
 Waetzig, Shelli R., 3311  
 Wang, Nuanxia, 3293  
 Wang, Yongcan, 3302  
 Wang, Yufei, 3257  
 Weber, Hansjörg, 3287  
 Wentrup-Byrne, Edeline, 3314  
 Williams, Ian D., 3269  
 Wong, Wai-Kwok, 3266  
 Wu, Huiming, 3257  
 Wu, Zili, 3308  
 Xu, Hualong, 3290  
 Xu, Yang, 3260  
 Yang, Huaixin, 3299  
 Yang, Xiaoping, 3266  
 Ye, Jinxing, 3302  
 Yi, Xiao-Yi, 3269  
 Yorimitsu, Hideki, 3234  
 Yu, Xingwen, 3257  
 Yurkerwich, Kevin, 3305  
 Zeller, Alexander, 3263  
 Zhan, Shuanglin, 3299  
 Zhang, Chenxi, 3290  
 Zhang, Yahong, 3290  
 Zhou, Shenghu, 3308  
 Zhou, Shiyi, 3293  
 Zhou, Shuyun, 3293  
 Zhu, Haoguo, 3308

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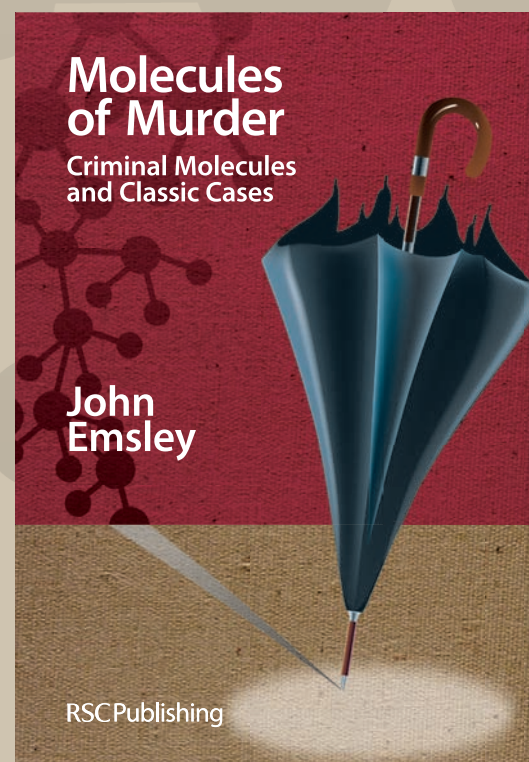
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