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MINIREVIEW

5105

Configurationally stable, enantioenriched organometallic nucleophiles in stereospecific Pd-catalyzed cross-coupling reactions: an alternative approach to asymmetric synthesis

Chao-Yuan Wang, Joseph Derosa and Mark R. Biscoe*

Several research groups have recently developed methods to employ configurationally stable, enantioenriched organometallic nucleophiles in stereospecific Pd-catalyzed cross-coupling reactions.



EDGE ARTICLES

5114

Selective glycoprotein detection through covalent templating and allosteric *click*-imprinting

Alexander Stephenson-Brown, Aaron L. Acton, Jon A. Preece, John S. Fossey^{*} and Paula M. Mendes^{*}

A hierarchical bottom-up route exploiting reversible covalent interactions with boronic acids and so-called click chemistry for selective glycoprotein detection is described. The self-assembled and imprinted surfaces confer high binding affinities, nanomolar sensitivity, exceptional glycoprotein specificity and selectivity.



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NKT cell-dependent glycolipid-peptide vaccines with potent anti-tumour activity

Regan J. Anderson, Benjamin J. Compton, Ching-wen Tang, Astrid Authier-Hall, Colin M. Hayman, Gene W. Swinerd, Renata Kowalczyk, Paul Harris, Margaret A. Brimble, David S. Larsen, Olivier Gasser, Robert Weinkove, Ian F. Hermans* and Gavin F. Painter*

Glycolipid–peptide conjugates designed to release vaccine components within target cells ensuring potent CD1d dependent T cell responses.

5128

Triple aryne–tetrazine reaction enabling rapid access to a new class of polyaromatic heterocycles

Sung-Eun Suh, Stephanie A. Barros and David M. Chenoweth*

We report the triple aryne-tetrazine reaction for rapid access to a new class of dibenzocinnoline heteroaromatics.





5133

Fluorescence spectroscopy and microscopy as tools for monitoring redox transformations of uranium in biological systems

Debbie L. Jones, Michael B. Andrews, Adam N. Swinburne, Stanley W. Botchway, Andrew D. Ward, Jonathan R. Lloyd and Louise S. Natrajan*

Luminescence spectroscopy, microscopy and lifetime image mapping offers new insights into the bioreduction of *Geobacter sulfurreducens* with uranyl.

5139

Biomimetic *versus* enzymatic high-potential electrocatalytic reduction of hydrogen peroxide on a functionalized carbon nanotube electrode

Bertrand Reuillard, Solène Gentil, Marie Carrière, Alan Le Goff^{*} and Serge Cosnier

We report the non-covalent functionalization of a multi-walled carbon nanotube (MWCNT) electrode with a biomimetic model of the horseradish peroxidase (HRP) active site.









Enhancing electron affinity and tuning band gap in donor-acceptor organic semiconductors by benzothiadiazole directed C-H borylation

D. L. Crossley, I. A. Cade, E. R. Clark, A. Escande, M. J. Humphries, S. M. King, I. Vitorica-Yrezabal, M. J. Ingleson^{*} and M. L. Turner^{*}

Electrophilic borylation using BCl_3 and benzothiadiazole to direct the C-H functionalisation of an adjacent aromatic unit produces fused boracyclic materials with minimally changed HOMO energies but significantly reduced LUMO energies.





5172



Methanol-to-hydrocarbons conversion over MoO₃/ H-ZSM-5 catalysts prepared *via* lower temperature calcination: a route to tailor the distribution and evolution of promoter Mo species, and their corresponding catalytic properties

B. Liu, L. France, C. Wu, Z. Jiang, V. L. Kuznetsov, H. A. Al-Megren, M. Al-Kinany, S. A. Aldrees, T. Xiao* and P. P. Edwards*

A series of MoO_3/H -ZSM-5 catalysts were prepared *via* calcination at a lower-than-usual temperature and evaluated.

Enantioselective palladium(0)-catalyzed intramolecular cyclopropane functionalization: access to dihydroquinolones, dihydroisoquinolones and the BMS-791325 ring system

J. Pedroni, T. Saget, P. A. Donets and N. Cramer*

Enantioselective palladium(0)-catalyzed C–H arylations of cyclopropanes provide efficient access to dihydroquinolones, dihydroisoquinolones and the BMS-791325 indolobenzazepine core.

Water stabilization of Zr₆-based metal-organic frameworks *via* solvent-assisted ligand incorporation

Pravas Deria, Yongchul G. Chung, Randall Q. Snurr, Joseph T. Hupp* and Omar K. Farha*

Water stability in metal–organic frameworks (MOFs) is critical for several practical applications; we report here fundamental understanding how capillary forces induce damage to MOFs and highlight that metal node functionalization as a strategy to create vapor-stable and recyclable MOFs.

CO₂ induced phase transitions in diamine-appended metal-organic frameworks

Bess Vlaisavljevich, Samuel O. Odoh, Sondre K. Schnell, Allison L. Dzubak, Kyuho Lee, Nora Planas, Jeffrey B. Neaton, Laura Gagliardi^{*} and Berend Smit^{*}

Using a combination of density functional theory and lattice models, we study the effect of CO₂ adsorption in an amine functionalized metal–organic framework.

5186

Impacts of gold nanoparticle charge and ligand type on surface binding and toxicity to Gram-negative and Gram-positive bacteria

Z. Vivian Feng,^{*} Ian L. Gunsolus, Tian A. Qiu, Katie R. Hurley, Lyle H. Nyberg, Hilena Frew, Kyle P. Johnson, Ariane M. Vartanian, Lisa M. Jacob, Samuel E. Lohse, Marco D. Torelli, Robert J. Hamers, Catherine J. Murphy and Christy L. Haynes^{*}

Higher cationic charge density on nanoparticles is correlated with higher toxicity to bacteria.

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Redox reaction induced Ostwald ripening for sizeand shape-focusing of palladium nanocrystals

Zhaorui Zhang, Zhenni Wang, Shengnan He, Chaoqi Wang, Mingshang Jin* and Yadong Yin*

Size- and shape-focusing of palladium nanocrystals have been successfully achieved through the Ostwald ripening process induced by a redox reaction.





5204

Facet selectivity in gold binding peptides: exploiting interfacial water structure

Louise B. Wright, J. Pablo Palafox-Hernandez, P. Mark Rodger,* Stefano Corni* and Tiffany R. Walsh*

We demonstrate that surface hydration is a key factor in dictating the free energy of non-covalent peptide-materials recognition.





5230

5235

misfolded protein

ABP A3





Directed radical fluorination

Proteasome

aggresome

MG132

Beyond a solvent: the roles of 1-butyl-3methylimidazolium chloride in the acid-catalysis for cellulose depolymerisation

Heitor Fernando Nunes de Oliveira, Christophe Farès and Roberto Rinaldi^{*}

1-Butyl-3-methylimidazolium chloride plays other roles in the acid-catalysed depolymerisation of cellulose rather than being `merely' a solvent for the biopolymer. The ionic liquid species enhances the Hammett acidity of the catalyst, thus improving the kinetics of cellulose depolymerisation.

Unstrained C–C bond activation and directed fluorination through photocatalytically-generated radical cations

Cody Ross Pitts, Michelle Sheanne Bloom, Desta Doro Bume, Qinze Arthur Zhang and Thomas Lectka*

Unstrained C–C activation *via* putative radical cation formation promotes a directed radical fluorination event using Selectfluor, catalytic 9-fluorenone, and light.

A soluble molecular variant of the semiconducting silicondiselenide

Kartik Chandra Mondal, Sudipta Roy, Birger Dittrich,* Bholanath Maity, Sayan Dutta, Debasis Koley,* Suresh Kumar Vasa, Rasmus Linser, Sebastian Dechert and Herbert W. Roesky*

Silicondiselenide is a semiconductor and exists as an insoluble polymer (SiSe₂)_n which is prepared by reacting elemental silicon with selenium powder in the temperature range of 400–850 °C.

An inhibitor of ubiquitin conjugation and aggresome formation

Heeseon An and Alexander V. Statsyuk*

An inhibitor of ubiquitin activating E1 enzyme inhibits ubiquitin conjugation and aggresome formation.



F1 E2 E3

Fluorine teams up with water to restore inhibitor activity to mutant BPTI

Shijie Ye, Bernhard Loll, Allison Ann Berger, Ulrike Mülow, Claudia Alings, Markus Christian Wahl and Beate Koksch*

Fluorinated derivatives of aminobutyric acid engage in unique interactions with structural waters within the BPTI/trypsin interface and restore inhibitor activity.

5255

Vibrational properties and bonding nature of Sb₂Se₃ and their implications for chalcogenide materials

Volker L. Deringer, Ralf P. Stoffel, Matthias Wuttig and Richard Dronskowski*

There is more to chemical bonding in chalcogenides than the shortest, strongest bonds, as revealed by microscopic quantum-chemical descriptors.

5263

Self-assembly of a mesoporous ZnS/mediating interface/CdS heterostructure with enhanced visible-light hydrogen-production activity and excellent stability

Kui Li, Rong Chen, Shun-Li Li, Min Han, Shuai-Lei Xie, Jian-Chun Bao,* Zhi-Hui Dai and Ya-Qian Lan*

We designed and successfully fabricated a ZnS/CdS 3D mesoporous heterostructure with a mediating $Zn_{1-x}Cd_xS$ interface.

5269

Heterometallic titanium–gold complexes inhibit renal cancer cells *in vitro* and *in vivo*

Jacob Fernández-Gallardo, Benelita T. Elie, Tanmoy Sadhukha, Swayam Prabha, Mercedes Sanaú, Susan A. Rotenberg, Joe W. Ramos^{*} and María Contel^{*}

Heterometallic compounds as anticancer agents demonstrating *in vivo* potential for the first time. Titanocene–gold derivatives: promising candidates for renal cancer.







TBAF(1-Adamantanol)4

Tetracoordinate



Overcoming aggregation in indium salen catalysts for isoselective lactide polymerization

D. C. Aluthge, J. M. Ahn and P. Mehrkhodavandi*

A methodology for controlling aggregation in highly active and isoselective indium catalysts for the ring opening polymerization of racemic lactide is reported.

Coordination diversity in hydrogen-bonded homoleptic fluoride-alcohol complexes modulates reactivity

Keary M. Engle, Lukas Pfeifer, George W. Pidgeon, Guy T. Giuffredi, Amber L. Thompson, Robert S. Paton, John M. Brown and Véronique Gouverneur*

The X-ray structures of fourteen novel fluoride–alcohol complexes with tetrabutylammonium as the counterion show coordination diversity varying from four to two depending on the steric bulk of the alcohol.

Cucurbit[8]uril directed stimuli-responsive supramolecular polymer brushes for dynamic surface engineering

Chi Hu, Feng Tian, Yu Zheng, Cindy Soo Yun Tan, Kevin R. West and Oren A. Scherman*

Dual stimuli-responsive supramolecular polymer brushes are attached to the surface with cucurbit[8]uril-rotaxanes for dynamic surface engineering.



TBAF(Diphenylmethanol)₃

Tricoordinate

TBAF(Triphenylmethanol)2

Dicoordinate