Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

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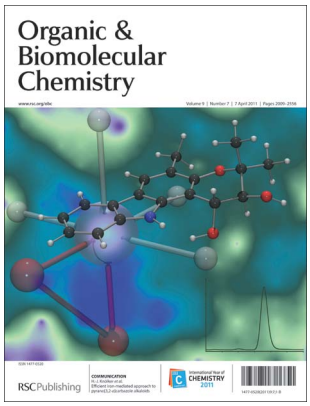
IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 9(7) 2009–2556 (2011)

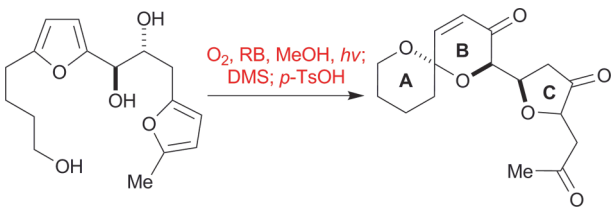


Cover

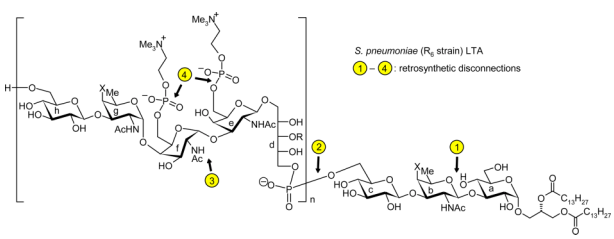
See Knölker *et al.*, pp. 2057–2061. The cover picture shows in the background the active titanium–peroxo species proposed for the asymmetric catalytic epoxidation and in the front (–)-*trans*-dihydroxygirinimbine and a plot of the chiral HPLC confirming the high degree of asymmetric induction (98% ee).

Image reproduced by permission of Hans-Joachim Knölker from *Org. Biomol. Chem.*, 2011, **9**, 2057.

EMERGING AREA



PERSPECTIVE



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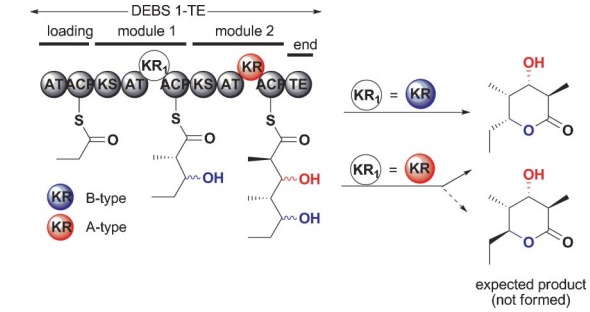
2053

Insights into the stereospecificity of ketoreduction in a modular polyketide synthase

David H. Kwan, Manuela Tosin, Nadin Schläger, Frank Schulz and Peter F. Leadlay*

Active site-directed mutagenesis in a ketoreductase domain from the erythromycin polyketide synthase alters the stereochemistry of reduction with pantetheinyl ester substrates but does not prevent the intact synthase from maintaining its original stereocontrol *in vivo*.

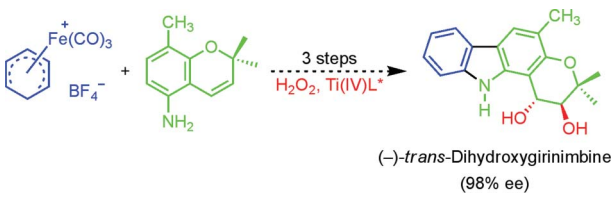


2057

Efficient iron-mediated approach to pyrano[3,2-*a*]carbazole alkaloids—first total syntheses of *O*-methylmurrayamine A and 7-methoxymurrayacine, first asymmetric synthesis and assignment of the absolute configuration of (–)-*trans*-dihydroxygirinimbine

Konstanze K. Gruner, Thomas Hopfmann, Kazuhiro Matsumoto, Anne Jäger, Tsutomu Katsuki and Hans-Joachim Knölker*

Using an Fe-mediated oxidative cyclisation, we report improved routes to girinimbine and murrayacine, and the first total syntheses of *O*-methylmurrayamine A and 7-methoxymurrayacine.

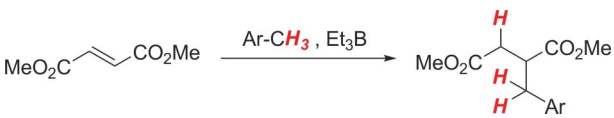


2062

Benzyl radical addition reaction through the homolytic cleavage of a benzylic C–H bond

Masafumi Ueda, Eiko Kondoh, Yuta Ito, Hiroko Shono, Maiko Kakiuchi, Yuki Ichii, Takahiro Kimura, Tetsuya Miyoshi, Takeaki Naito and Okiko Miyata*

Direct generation of a benzyl radical by C–H bond activation of toluenes and the addition reaction were developed.

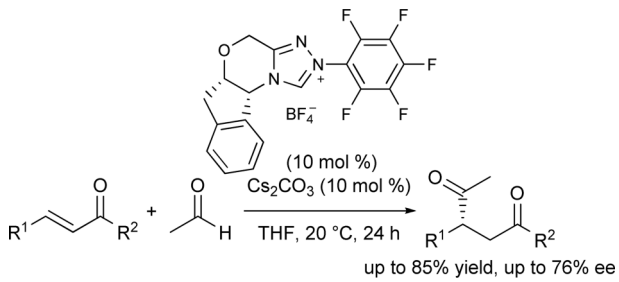


2065

Microwave promoted C6-alkylation of purines through S_NAr-based reaction of 6-chloropurines with 3-alkyl-acetylacetone

Hai-Ming Guo,* Yu Zhang, Hong-Ying Niu, Dong-Chao Wang, Zhi-Liang Chu and Gui-Rong Qu*

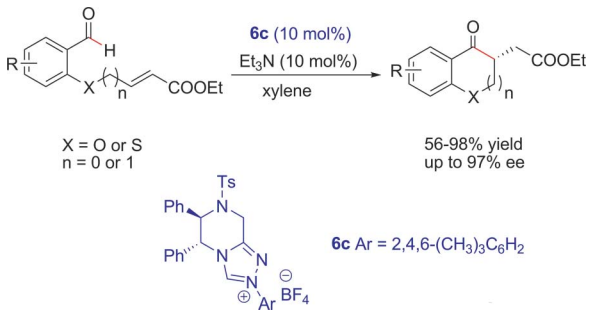
C6-Alkylated purine analogues were obtained selectively in good to excellent yields and short reaction times by S_NAr reaction of 6-chloropurine derivatives with 3-alkyl-acetylacetone under microwave irradiation. This work is complementary to classical coupling reactions for synthesis of C6-alkylated purines.



N-Heterocyclic carbene-catalysed intermolecular Stetter reactions of acetaldehyde

Sun Min Kim, Ming Yu Jin, Mi Jin Kim, Yan Cui, Young Sug Kim, Liqiu Zhang, Choong Eui Song, Do Hyun Ryu* and Jung Woon Yang*

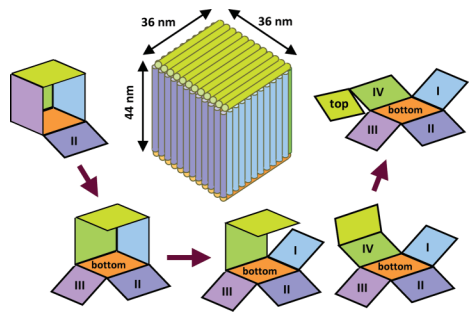
A facile method for the intermolecular Stetter reaction of various Michael acceptors with acetaldehyde as a biomimetic acylanion source was realized using *N*-heterocyclic carbene catalysis.



Synthesis of (1*R*,2*R*)-DPEN-derived triazolium salts and their application in asymmetric intramolecular Stetter reactions

Min-Qiang Jia, Yi Li, Zi-Qiang Rong and Shu-Li You*

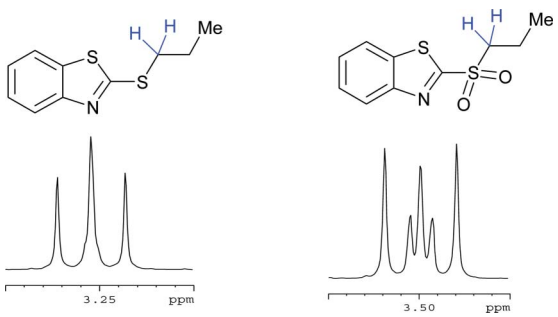
Novel chiral triazolium salts were synthesized and applied successfully in catalytic intramolecular Stetter reactions in excellent yields with up to 97% ee.



Direct AFM observation of an opening event of a DNA cuboid constructed *via* a prism structure

Masayuki Endo,* Kumi Hidaka and Hiroshi Sugiyama*

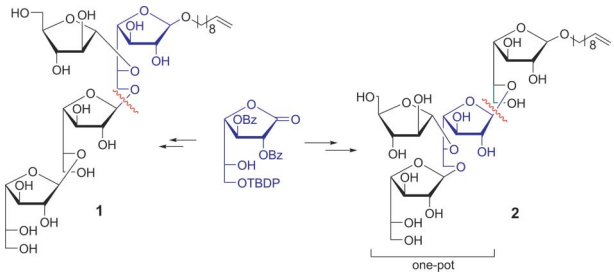
A cuboid DNA structure was designed and constructed, and the opening of the cuboid was directly observed by high-speed AFM.

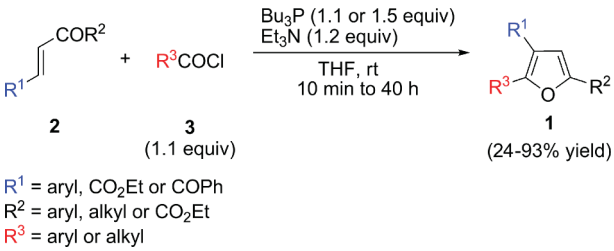


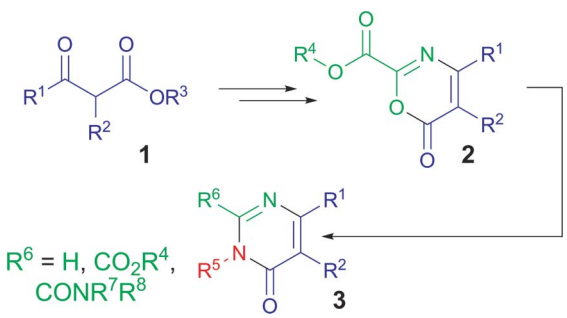
Second-order NMR spectra at high field of common organic functional groups

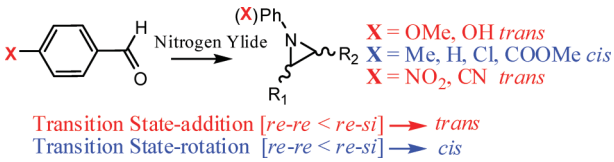
Paul J. Stevenson*

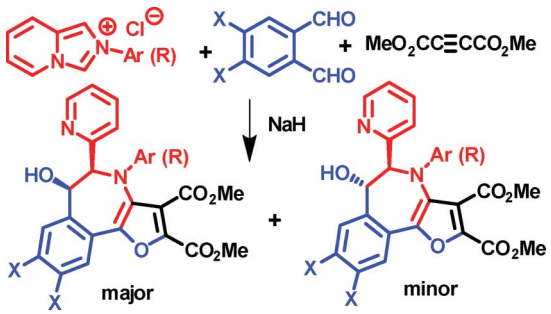
Second-order proton NMR spectra at high field due to magnetic non-equivalence, of achiral alkyl sulfones, alkyl phosphonium salts and SES-protecting groups lead to very distinctive AA′XX′ splitting patterns for the α-methylene signal.

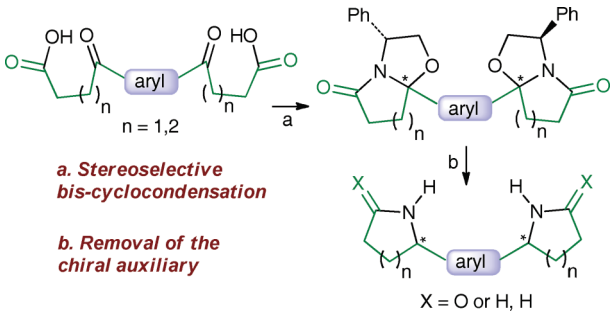


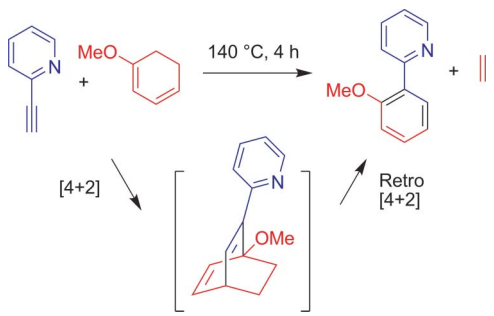


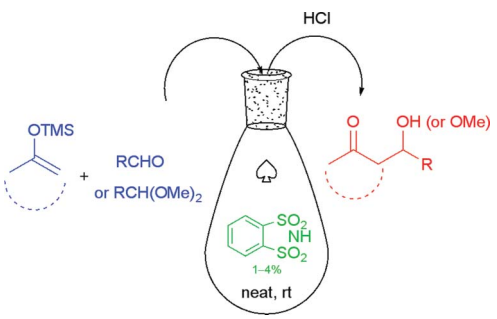




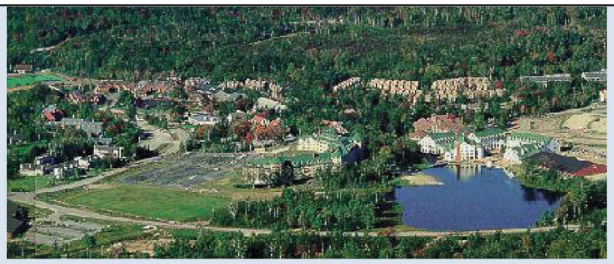


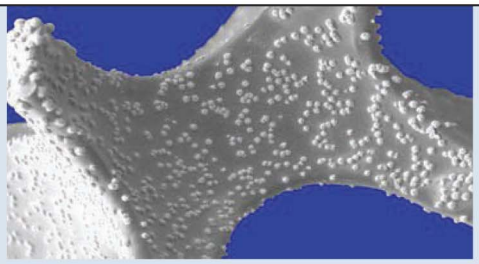






Gordon Research Conference on
Environmental Nanotechnology





Announcing the **2011 Gordon Research Conference on Environmental Nanotechnology**, Waterville Valley Resort, Waterville Valley, NH, USA, May 29 - June 3, 2011.

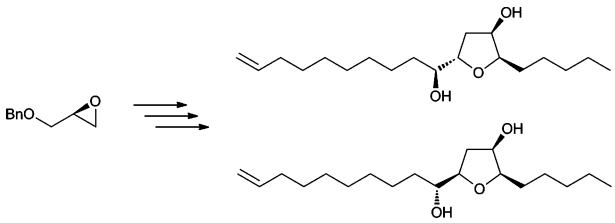
Conference Chair: **Wunmi A. Sadik**, SUNY-Binghamton Conference Vice Chair: **Nora Savage**, US-EPA

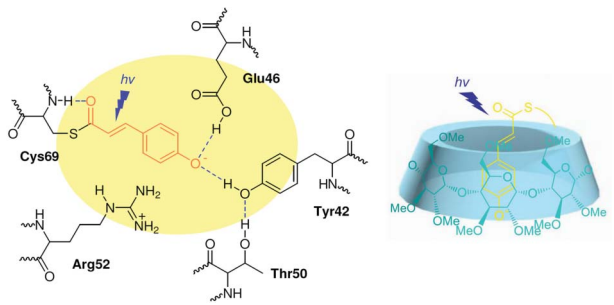
Steering Committee: Katrina Varner, US-EPA, Janet Carter, OSHA, Paul Westerhoff, Arizona State University, Greg Lowry, Carnegie Mellon University, Mark Wiesner, Duke University.

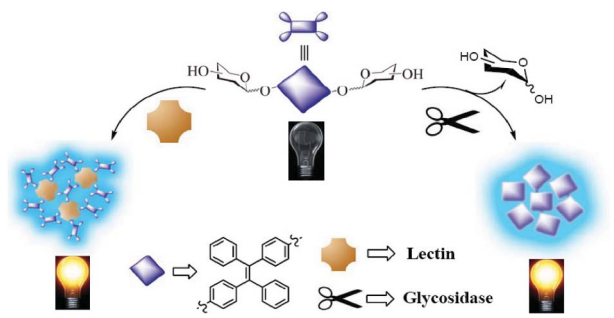
The potential impacts of engineered nanomaterials on human health and the environment have been limited due to insufficient understanding of the risks associated with its development, manipulation and wide-ranging applications. In this inaugural conference, participants will present and discuss cutting edge research on chemical, biological and environmental impacts of engineered nanomaterials. The meeting will feature a wide range of topics, including; synthesis, characterization, exposure, toxicology, metrology, and risk assessment. In addition, the basic mechanisms by which nanoscale materials interact with similar sized particles, larger particles, as well as mixtures will be thoroughly examined. Formal and informal discussions will highlight future directions. Transport, transformation and ultimate fate of these materials in biological and environmental matrices will be explored. The draft program we have assembled is absolutely first-rate, with an international collection of world-leading scientists engaged in research on **Environmental Nanoscience & Technology**.

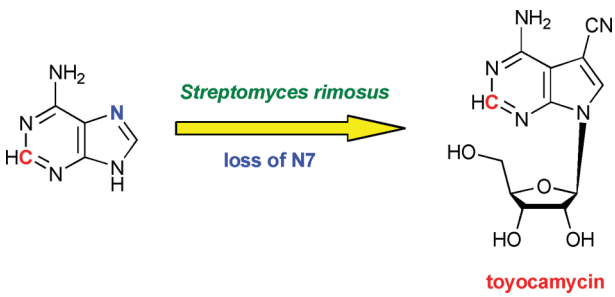
- **Keynote Presentations: Applications of Nanotechnology – Challenges and Opportunities**
  (Mike Roco, NSF / Vicki Colvin, Rice University/Raymond Davis, BASF)
- **Environmental and Biological Implications – Challenges and Opportunities**
  (Iain Gillespie, OECD/ Vicki Stone- Napier University, Edinburgh, UK / Pedro Alvarez, Rice University, David Rejeski, Woodrow Wilson Center, Project on Emerging Nanotechnology)
- **Metrology and Harmonized Methodologies**
  (Vincent Hackley, NIST / Jamie Lead, University of Birmingham, UK / Paul Westeroff, Arizona State University)
- **Environmental Exposures: Fate, Transformation & Ecotoxicology**
  (Vicki Grassian, U. Iowa / Greg Lowry, Carnegie Mellon; Patricia Holden, UC Santa Barbara / Mark Wiesner, Duke University)
- **Exposure Science and Dosimetry**
  (Sally Tinkle, NIEHS/ Yoshida Yasuo, Osaka U., Japan /David Rejeski, Woodrow Wilson Center)
- **Occupational Exposure and Nanomanufacturing Processes**
  (Charles Geraci, NIOSH/ Andrew Maynard, U. Michigan/ Patrick O'Shaughnessry, U. Iowa)
- **Sustainability/Green Nano and Remediation**
  (Tom Theis, U. of Illinois at Chicago / Jim Hutchison, Oregon State University / Fadri Gottschalk, ETH,Switzerland)
- **Nanomedicine**
  (Andrij Holian U. Montana / Andre Nel, UCLA/ Martin Philbert U. Michigan) / Gunter Oberdoster, U. Rochester / Ruth Duncan, Cardiff University, UK
- **Societal Considerations and Future Directions**
  (David Baird, U. South Carolina/ Rosalyn Berne, U. Virginia/ David Guston, ASU)

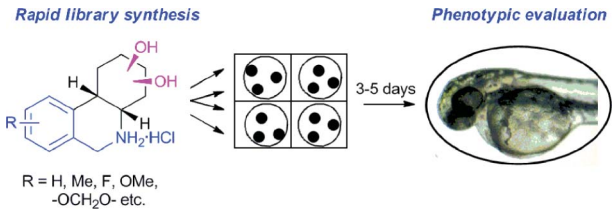
All participants are expected to present a poster. The steering committee is working to provide supplemental funds for students, postdocs and junior faculty to attend the meeting. Please submit an application by **May 8, 2011** at http://www.grc.org/programs.aspx?year=2011&program=environano







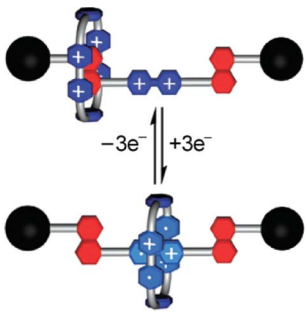




Rapid synthesis and zebrafish evaluation of a phenanthridine-based small molecule library

Lauren R. Donaldson, Stephen Wallace, David Haigh, E. Elizabeth Patton and Alison N. Hulme*

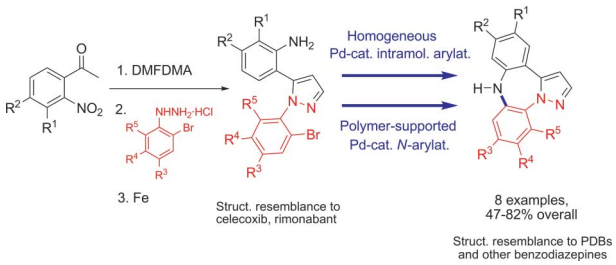
A phenanthridine-based small molecule library was rapidly assembled using Heck methodology; library evaluation identified a novel inhibitor of early-stage zebrafish embryo development.



Degenerate [2]rotaxanes with electrostatic barriers

Hao Li, Yan-Li Zhao, Albert C. Fahrenbach, Soo-Young Kim, Walter F. Paxton and J. Fraser Stoddart*

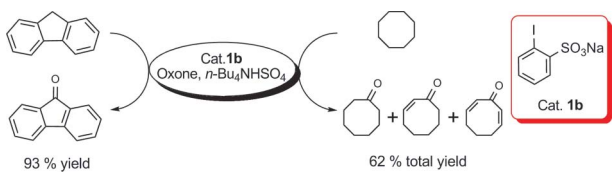
Upon reduction, the one-electron reduced bipyridinium radical cation on the dumbbells of the degenerate [2]rotaxanes serves as an additional recognition site for the two-electron reduced cyclobis(paraquat-*p*-phenylene) diradical cationic rings. The rings in the molecular shuttles can be switched between the three recognition sites – two 1,5-dioxynaphthalene units and one-electron reduced bipyridinium radical cation – under redox control.



An straightforward entry to new pyrazolo-fused dibenzo[1,4]diazepines

Susana Hernández, Isabel Moreno, Raul SanMartin,* María Teresa Herrero and Esther Domínguez*

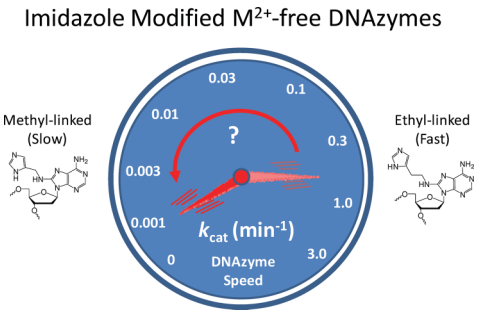
A series of novel pyrazolodibenzo[1,4]diazepines has been synthesized by a sequence involving a tandem sequence amine-exchange/heterocyclization, that gives access to diarylpyrazole intermediates structurally related to rimonabant or celecoxib, followed by a key C_{aryl}–N bond construction, which is conducted in both homogeneous and polymer-supported versions.

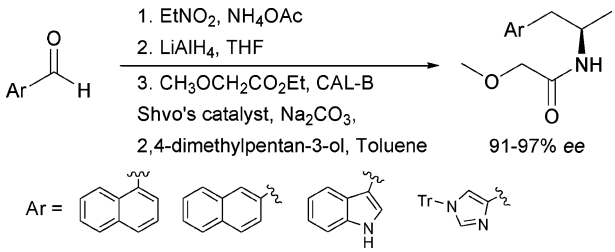


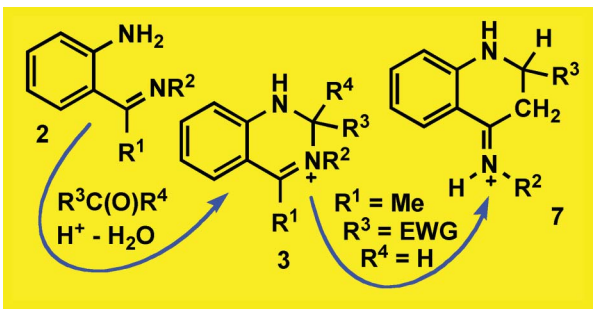
Effective oxidation of benzylic and alkane C–H bonds catalyzed by sodium *o*-iodobenzenesulfonate with Oxone as a terminal oxidant under phase-transfer conditions

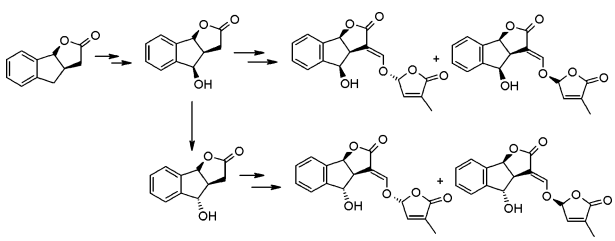
Li-Qian Cui, Kai Liu and Chi Zhang*

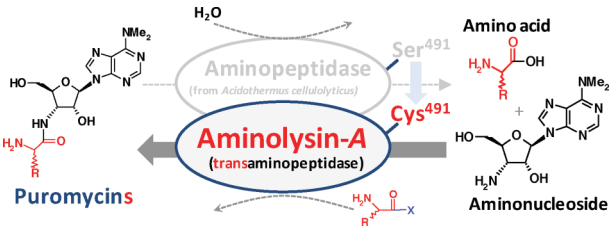
Catalytic oxidation of benzylic and alkane C–H bonds could be efficiently realized using IBS as a catalyst which was generated *in situ* from the oxidation of cat. **1b** by Oxone in the presence of a phase-transfer catalyst tetra-*n*-butylammonium hydrogen sulfate in anhydrous acetonitrile at 60 °C.

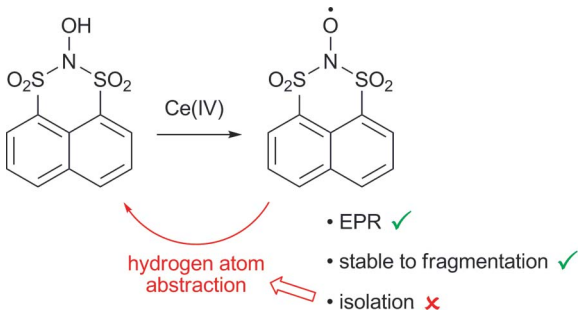


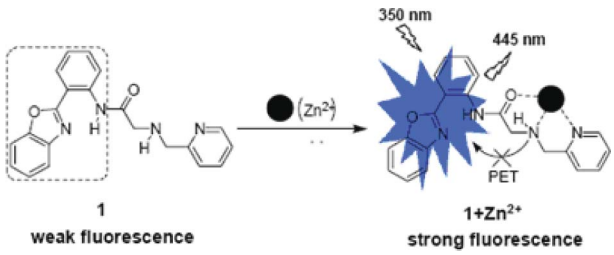


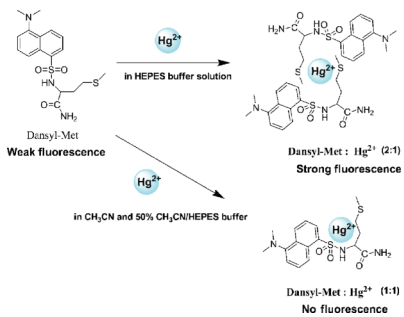












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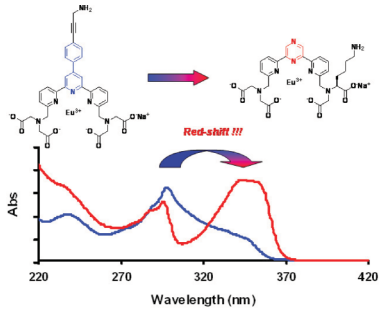
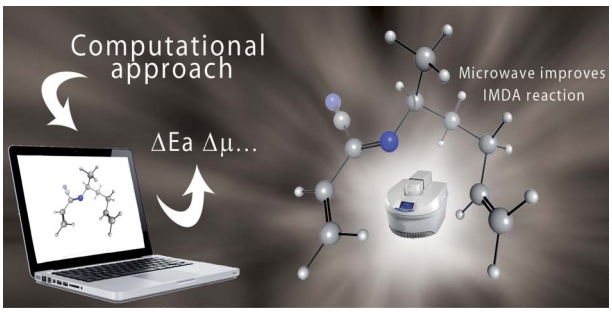


Synthesis and luminescence properties of new red-shifted absorption lanthanide(III) chelates suitable for peptide and protein labelling

Nicolas Maindron, Séverine Poupart, Maxime Hamon, Jean-Baptiste Langlois, Nelly Plé, Ludovic Jean, Anthony Romieu* and Pierre-Yves Renard*

Bis-pyridinylpyrazine-based lanthanide(III) chelates showing a remarkable red-shift on the maximum absorption were synthesised. These new luminescent tags exhibit valuable photo-physical properties in water and are suitable for the labelling of peptides and proteins.

2371

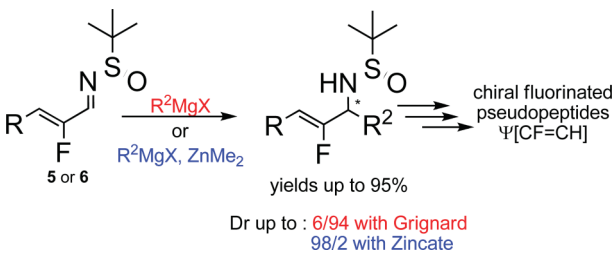


"*In silico*" mechanistic studies as predictive tools in microwave-assisted organic synthesis

A. M. Rodriguez, P. Prieto,* A. de la Hoz and A. Díaz-Ortiz

Computational studies show the energy requirements of reactions, allowing us to determine which processes can be improved under microwave irradiation.

2378

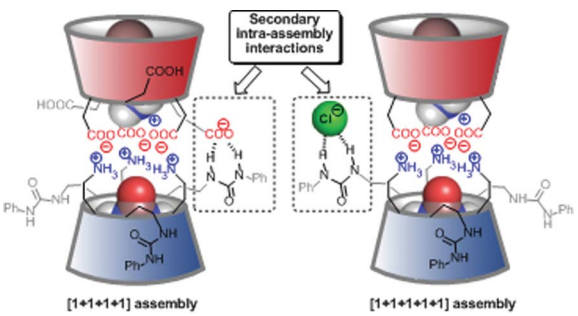


Synthesis of fluorinated pseudopeptides: metal mediated reversal of stereochemistry in diastereoselective addition of organometallic reagents to *N*-(*tert*-butanesulfinyl)-α-fluoroenimines

Camille Pierry, Dominique Cahard, Samuel Couve-Bonnaire and Xavier Pannecoucke*

The synthesis of fluorinated pseudopeptides, featuring a fluoroolefin moiety, was achieved through the stereodivergent addition of organometallic species to chiral *N*-(*tert*-butanesulfinyl)-α-fluoroenimines

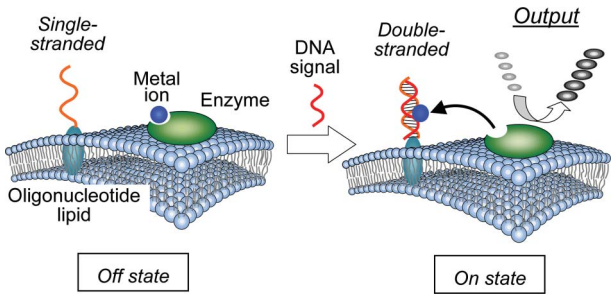
2387

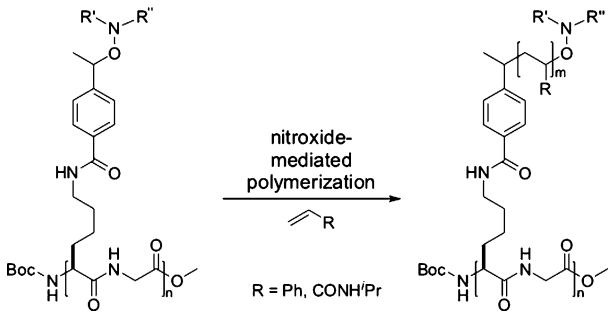


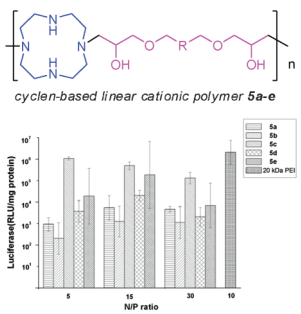
Allosterically driven self-assemblies of interlocked calix[6]arene receptors

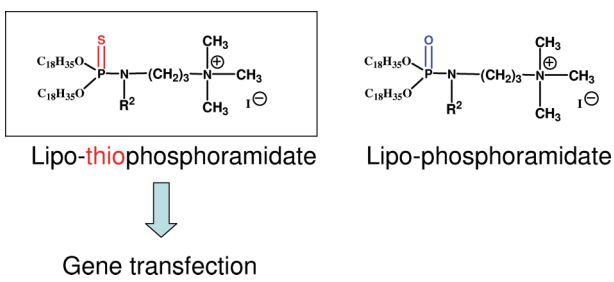
Stéphane Le Gac,* Jean-François Picron, Olivia Reinaud and Ivan Jabin*

Secondary intra-receptor interactions are demonstrated in four and five component assemblies made of complementary calix[6]arene hosts decorated with a dual recognition pattern.







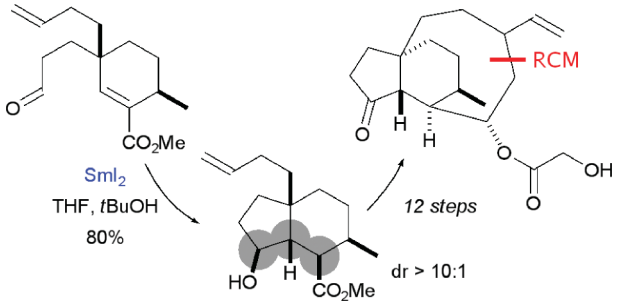


2433

A stereoselective, Sm(II)-mediated approach to decorated *cis*-hydrindanes: synthetic studies on faurinone and pleuromutilin

Thomas J. K. Findley, David Sucunza, Laura C. Miller, Matthew D. Helm, Madeleine Helliwell, David T. Davies and David J. Procter*

A route to *cis*–hydrindanes, featuring SmI_2-mediated cyclisations, has been used in an RCM approach to analogues of the antibacterial pleuromutilin.

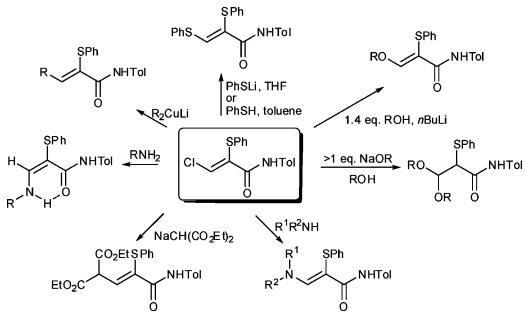


2452

Addition-substitution reactions of 2-thio-3-chloroacrylamides with carbon, nitrogen, oxygen, sulfur and selenium nucleophiles

Marie Kissane, Maureen Murphy, Elisabeth O'Brien, Jay Chopra, Linda Murphy, Stuart G. Collins, Simon E. Lawrence and Anita R. Maguire*

Synthetically versatile conjugate addition of a range of carbon, nitrogen, oxygen, sulfur and selenium nucleophiles to the highly functionalised 2-thio-3-chloroacrylamides is described.

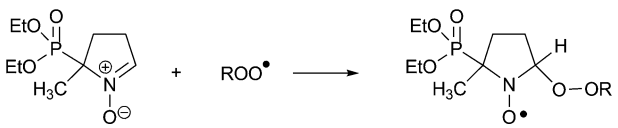


2473

DEPMPO: an efficient tool for the coupled ESR-spin trapping of alkylperoxyl radicals in water

Hakim Karoui,* Florence Chalier, Jean-Pierre Finet and Paul Tordo*

Spin trapping of peroxyl radicals using DEPMPO as the spin trap

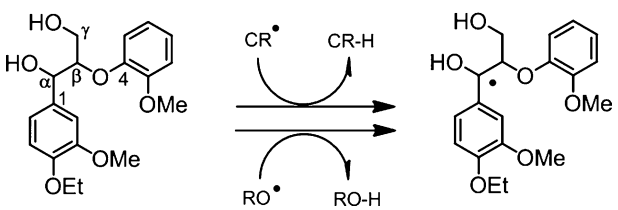


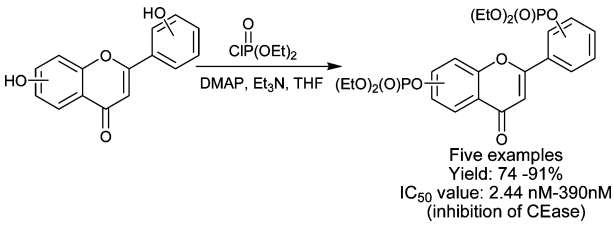
2481

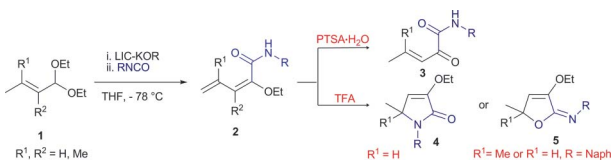
Alkoxyl- and carbon-centered radicals as primary agents for degrading non-phenolic lignin-substructure model compounds

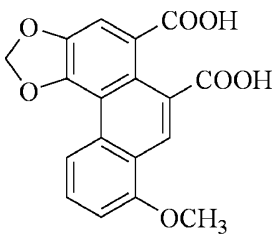
Yasunori Ohashi, Yukiko Uno, Rudianto Amirta, Takahito Watanabe, Yoichi Honda and Takashi Watanabe*

Alkoxyl and carbon-centered radicals are primary agents to abstract hydrogen from non-phenolic lignin substructure model compounds.

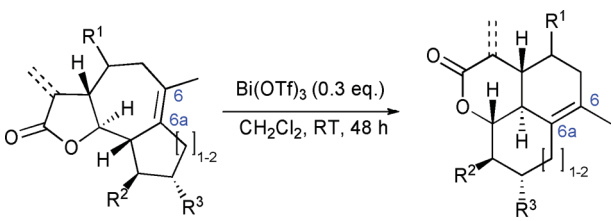


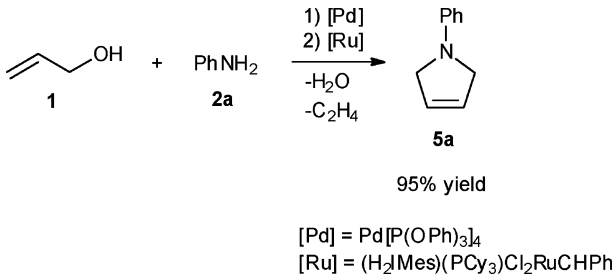






papilistatin





An atom efficient route to *N*-aryl and *N*-alkyl pyrrolines by transition metal catalysis

Supaporn Sawadjoon and Joseph S. M. Samec*

An atom efficient route to pyrroline with only water and ethene as side-products is presented.

