

# Organic & Biomolecular Chemistry

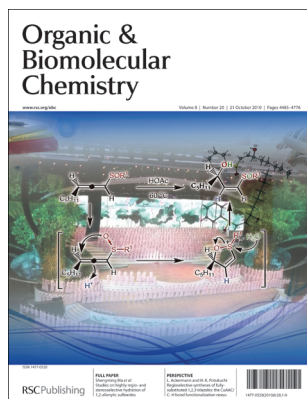
An international journal of synthetic, physical and biomolecular organic chemistry

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## IN THIS ISSUE

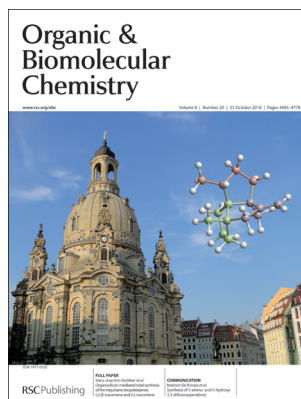
ISSN 1477-0520 CODEN OBCRAK 8(20) 4485–4776 (2010)



### Cover

See Shengming Ma *et al.*, pp. 4554–4561.  
1,2-Allenlyic sulfoxides were hydrated *via* the five-membered intermediate with excellent regio- and stereoselectivity affording synthetically useful stereodefined 2-alkenols.

Image reproduced by permission of Shengming Ma from *Org. Biomol. Chem.*, 2010, **8**, 4554.



### Inside cover

See Hans-Joachim Knölker *et al.*, pp. 4562–4568.  
The element silicon is the connection between the Frauenkirche in Dresden, built of sandstone, and the triquinane framework of the natural product  $\beta$ -isocomene, constructed by a silicon-mediated cycloaddition.

Image reproduced by permission of Hans-Joachim Knölker from *Org. Biomol. Chem.*, 2010, **8**, 4562.

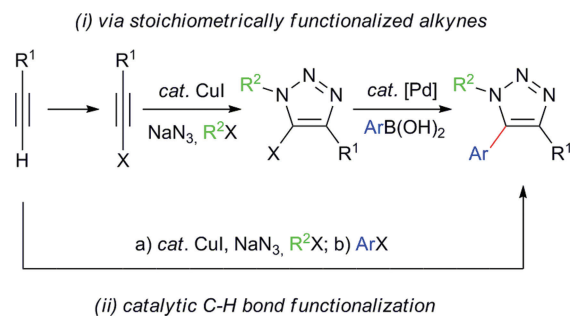
## PERSPECTIVE

4503

### Regioselective syntheses of fully-substituted 1,2,3-triazoles: the CuAAC/C–H bond functionalization nexus

Lutz Ackermann\* and Harish Kumar Potukuchi

Regioselective syntheses of 1,4,5-trisubstituted 1,2,3-triazoles were accomplished by three different strategies, relying on (i) the interception of stoichiometrically formed 5-cuprated-1,2,3-triazoles, (ii) the use of stoichiometrically functionalized alkynes or (iii) catalytic C–H bond functionalizations.



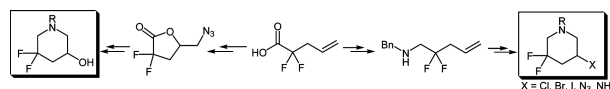
## COMMUNICATIONS

4514

### Synthesis of 5-amino- and 5-hydroxy-3,3-difluoropiperidines

Riccardo Surmont, Guido Verniest, Jan Willem Thuring, Peter ten Holte, Frederik Deroose and Norbert De Kimpe\*

Synthetic routes toward new 5-amino- and 5-hydroxy-3,3-difluoropiperidines involving *N*-halosuccinimide-induced cyclization of 2,2-difluoro-4-pentenylamines and iodolactonization of 2,2-difluoro-4-pentenoic acid are described.



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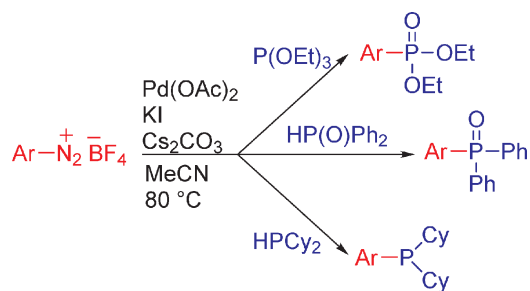
## COMMUNICATIONS

4518

**Arenediazonium tetrafluoroborates in palladium-catalyzed C–P bond-forming reactions. Synthesis of arylphosphonates, -phosphine oxides, and -phosphines**

Roberta Berrino, Sandro Cacchi,\* Giancarlo Fabrizi, Antonella Goggiani and Paolo Stabile

A palladium-catalyzed synthesis of aryl–P derivatives from arenediazonium tetrafluoroborates has been developed that can be performed as a one-pot process from anilines.

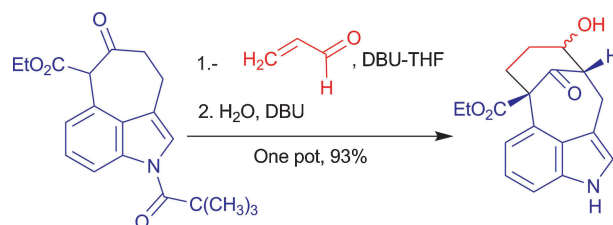


4521

**Concise and very efficient synthesis of the *N*-methylwelwistatin tetracyclic core based on an anionic domino process**

Miriam Ruiz, Pilar López-Alvarado and J. Carlos Menéndez\*

An anionic domino reaction is used to create the tetracyclic core of the alkaloid *N*-methylwelwistatin from Kornfeld's ketone.

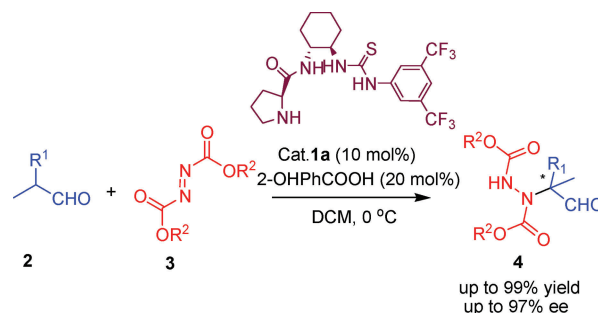


4524

**Effective construction of quaternary stereocenters by highly enantioselective  $\alpha$ -amination of branched aldehydes**

Ji-Ya Fu, Xiao-Ying Xu, Yan-Chun Li, Qing-Chun Huang and Li-Xin Wang\*

Chiral proline amide-thiourea bifunctional catalysts were successfully applied to the highly enantioselective amination of branched aldehydes with azadicarboxylates in excellent yields (up to 99%) and enantioselectivities (up to 97% ee).

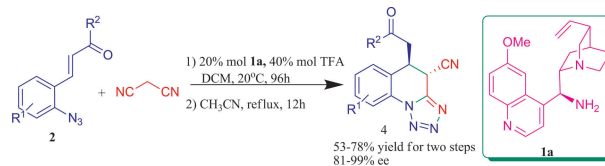


4527

**The organocatalytic two-step synthesis of diversely functionalized tricyclic tetrazoles**

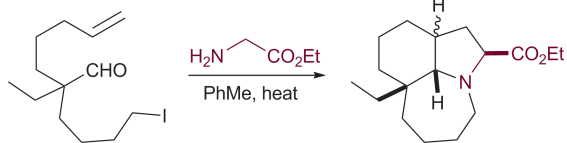
Xiong Huang, Ping Li, Xin-Sheng Li, Dong-Cheng Xu and Jian-Wu Xie\*

A simple method for the synthesis of diversely functionalized tricyclic tetrazoles from functionalized  $\alpha,\beta$ -unsaturated ketones and malononitrile was described.



## COMMUNICATIONS

4530

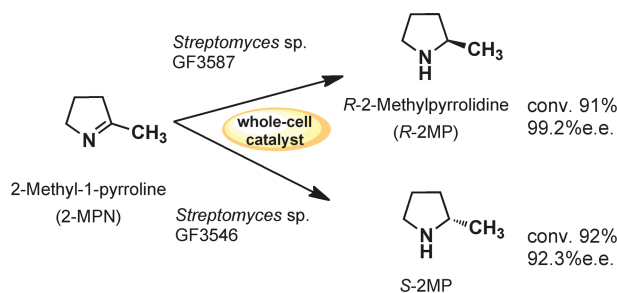


### Synthesis of the core ring system of the stemona alkaloids by cascade condensation, cyclization, intramolecular cycloaddition

Adam. J. M. Burrell, Luke Watson, Nathaniel G. Martin, Niall Oram and Iain Coldham\*

Heating amino-acids or amino-esters with 6-iodohexanals gives azomethine ylides that undergo intramolecular cycloaddition to the tricyclic core of stenine and neostenine

4533

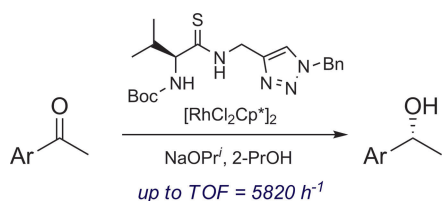


### Asymmetric synthesis of chiral cyclic amine from cyclic imine by bacterial whole-cell catalyst of enantioselective imine reductase

Koichi Mitsukura,\* Mai Suzuki, Kazuhiro Tada, Toyokazu Yoshida and Toru Nagasawa

*Streptomyces* sp. GF3587 and 3546 were found to be imine-reducing strains with high *R*- and *S*-selectivity by screening using 2-methyl-1-pyrroline (2-MPN).

4536

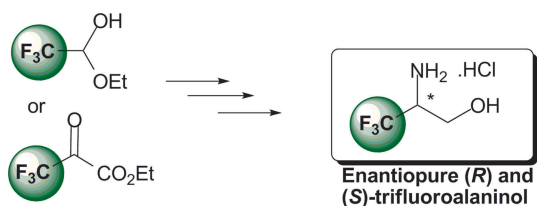


### Asymmetric transfer hydrogenation of ketones catalyzed by rhodium complexes containing amino acid triazole ligands

Fredrik Tinnis and Hans Adolfsson\*

Active and selective catalysts for the asymmetric reduction of ketones were obtained from  $[\text{RhCl}_2\text{Cp}^*]_2$ , and novel *L*-amino acid thioamide ligands functionalized with 1,2,3-triazoles.

4540



### Straightforward synthesis of enantiopure (*R*)- and (*S*)-trifluoroalaninol

Julien Pytkowicz, Olivier Stéphaney, Sinisa Marinkovic, Sébastien Inagaki and Thierry Brigaud\*

Enantiopure (*R*)- and (*S*)-trifluoroalaninol were conveniently synthesized in a few steps from fluoral hemiacetal or ethyl trifluoropyruvate.

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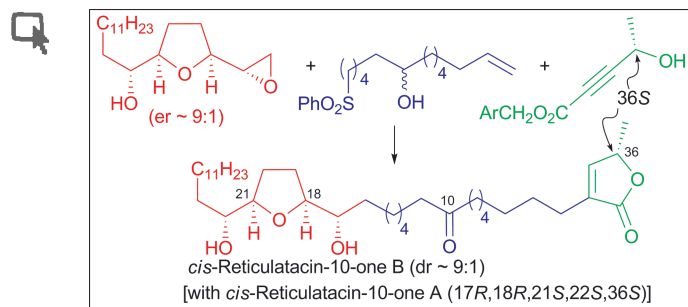
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## COMMUNICATIONS

4543

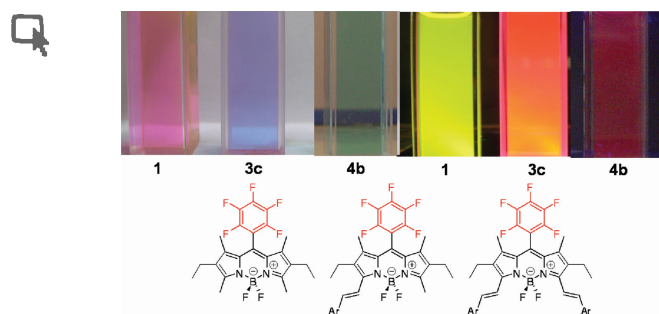
**Total synthesis of *cis*-reticulatacin-10-ones A and B: absolute stereochemical assignment**

Sherif B. Abdel Ghani, Lynda J. Brown, Bruno Figadère and Richard C. D. Brown\*

The natural product *cis*-reticulatacin-10-one, isolated from *Annona muricata* L., was shown to be a mixture of A (17*R*,18*R*,21*S*,22*S*,36*S*) and B (17*S*,18*S*,21*R*,22*R*,36*S*) diastereoisomers by using chiral HPLC to compare the natural isolate with standards prepared by total synthesis.

## PAPERS

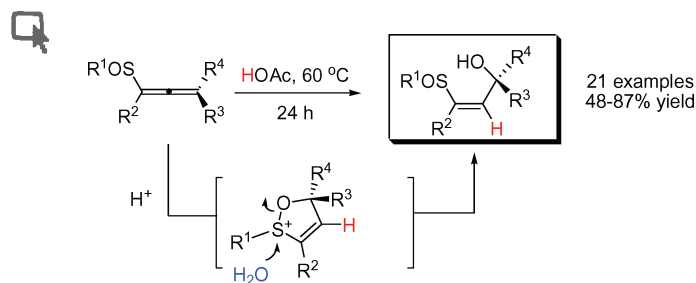
4546

**Rational design of visible and NIR distyryl-BODIPY dyes from a novel fluorinated platform**

Olivier Galangau, Cécile Dumas-Verdes, Rachel Méallet-Renault and Gilles Clavier\*

A new series of red emissive distyryl-BODIPY has been obtained from a novel fluorinated platform with various electron donor and, for the first time, electron acceptor aromatics.

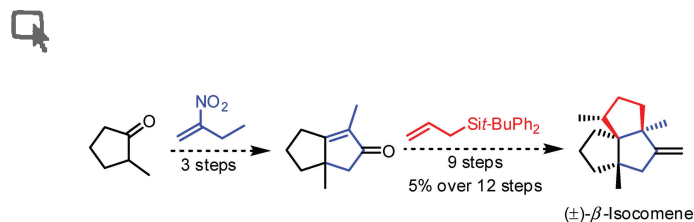
4554

**Studies on highly regio- and stereoselective hydration of 1,2-allenyl sulfoxides**

Zhao Fang, Chao Zhou, Chunling Fu\* and Shengming Ma\*

A highly regio- and stereoselective hydration of 1,2-allenyl sulfoxides with proton as the electrophile affords 3-sulfoxy-2(*Z*)-alkenols *via* a five-membered intermediate.

4562

**Organosilicon-mediated total synthesis of the triquinane sesquiterpenes (±)-β-isocomene and (±)-isocomene**

Arndt W. Schmidt, Thomas Olpp, Elke Baum, Tina Stiffel and Hans-Joachim Knölker\*

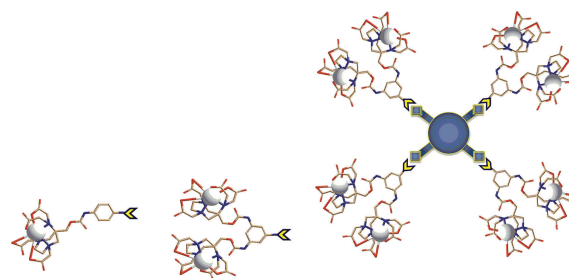
We describe an efficient total synthesis of the sesquiterpenes (±)-β-isocomene and (±)-isocomene using a Lewis acid-promoted [3 + 2] cycloaddition of allyl-*tert*-butyldiphenylsilane as the key-step.

4569

### AAZTA-based bifunctional chelating agents for the synthesis of multimeric/dendrimeric MRI contrast agents

Giuseppe Gugliotta, Mauro Botta and Lorenzo Tei\*

Novel mono- and dimeric bifunctional AAZTA-based chelating ligands were used as versatile modules for the synthesis of octameric Gd(III) complexes as MRI probes.

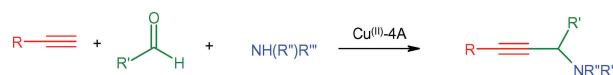


4575

### A simple method for the preparation of propargylamines using molecular sieve modified with copper(II)

Anna Fodor, Árpád Kiss, Nóra Debreczeni, Zoltán Hell\* and Iván Gresits

A new, heterogeneous, 4 Å molecular sieve-supported copper(II) catalyst was developed and was used successfully in the A<sup>3</sup> coupling.

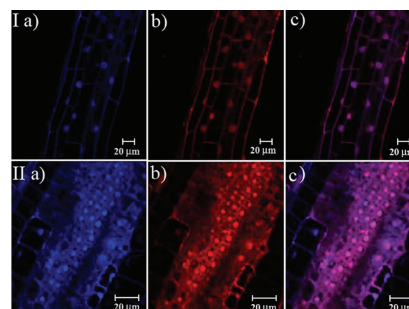


4582

### Two-photon fluorescence imaging of DNA in living plant turbid tissue with carbazole dicationic salt

Yuanhong Zhang, Junjie Wang, Pengfei Jia, Xiaoqiang Yu,\* Heng Liu,\* Xin Liu, Ning Zhao and Baibiao Huang\*

**Fluorescent imaging:** In living plant hypocotyls and roots of *Arabidopsis thaliana*, the imaging depth of 9E-BHVC is higher than that of DAPI.

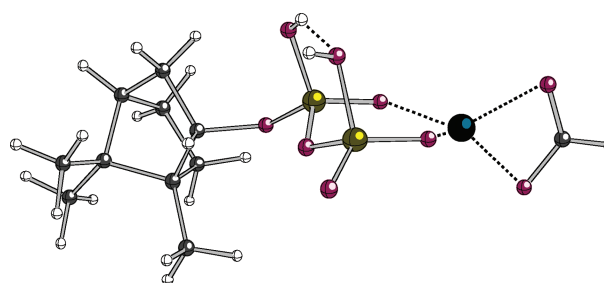


4589

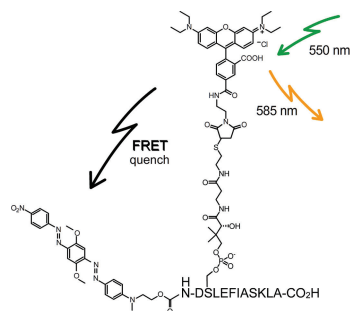
### Quantum chemical dissection of the classic terpinyl/pinyl/bornyl/camphyl cation conundrum—the role of pyrophosphate in manipulating pathways to monoterpenes

Young J. Hong and Dean J. Tantillo\*

Quantum chemical methods are used to reveal details of the conversion of geranyl diphosphate to bornyl diphosphate and several monoterpenes.



4601

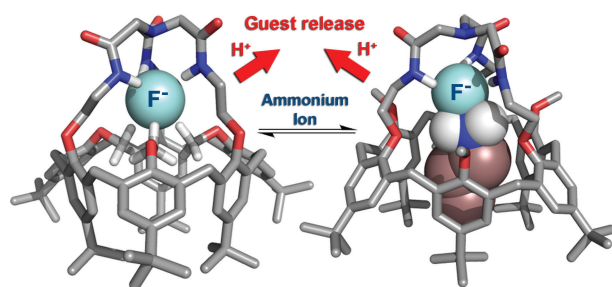


### Preparation of FRET reporters to support chemical probe development

Timothy L. Foley, Adam Yasgar, Christopher J. Garcia, Ajit Jadhav, Anton Simeonov and Michael D. Burkart\*

We describe economical routes for the preparation of rhodamine maleimide and non-emitting quencher probes to enable a high throughput screening campaign that seeks to identify inhibitors of phosphopantetheinyl transferase.

4607

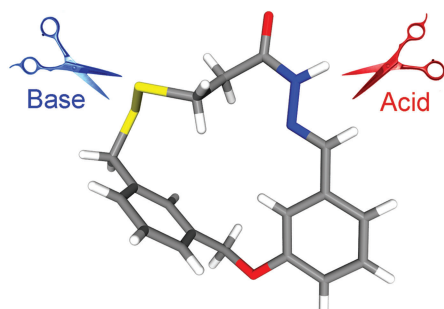


### An allosteric heteroditopic receptor for neutral guests and contact ion pairs with a remarkable selectivity for ammonium fluoride salts

Angélique Lascaux, Stéphane Le Gac, Johan Wouters, Michel Luhmer and Ivan Jabin\*

The syntheses and unique host–guest properties of two novel calix[6]arene-based heteroditopic receptors are presented.

4617

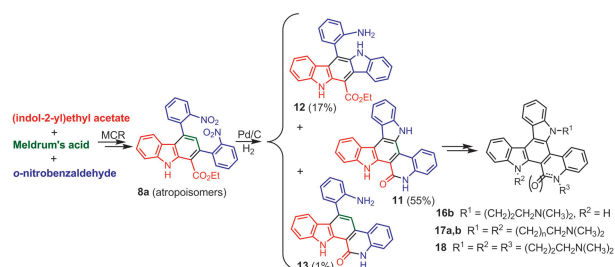


### Synthesis and solid state structure of a hydrazone-disulfide macrocycle and its dynamic covalent ring-opening under acidic and basic conditions

Max von Delius, Edzard M. Geertsema, David A. Leigh\* and Alexandra M. Z. Slawin

A macrocycle that can be selectively ring-opened under thermodynamic control at either a disulfide or a hydrazone linkage is described.

4625



### Synthesis and biological evaluation of new penta- and heptacyclic indolo- and quinolinocarbazole ring systems obtained via Pd<sup>0</sup> catalysed reductive N-heteroannulation

Marie Laronze-Cochard, Fabien Cochard, Etienne Daras, Amélie Lansiaux, Bertrand Brassart, Enguerran Vanquelf, Elise Prost, Jean-Marc Nuzillard, Brigitte Baldeyrou, Jean-François Goosens, Olivier Lozach, Laurent Meijer, Jean-François Riou, Eric Henon\* and Janos Sapi\*

Several biologically active (CNS, cancer) polycyclic carbazoles have been prepared by Pd/C–H<sub>2</sub>-assisted N-heteroannulation, as the key-step.



# Prizes and Awards

## Rewarding Excellence and Dedication

# Organic Chemistry Awards

The Organic Chemistry awards portfolio rewards excellence in both industry and academia, for original research in any aspect of organic chemistry as well as specific areas including organometallic and physical organic chemistry.

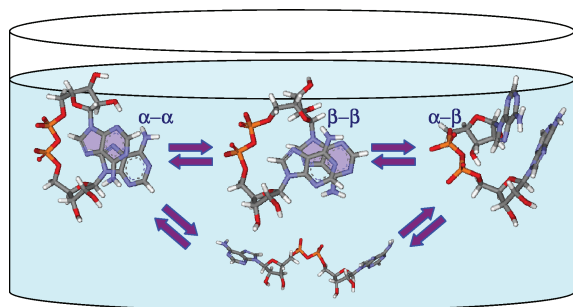
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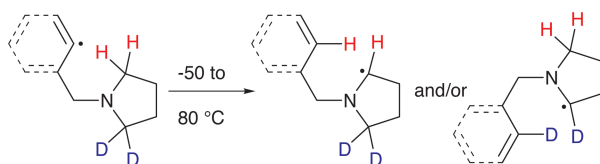


### What is the conformation of physiologically-active dinucleoside polyphosphates in solution? Conformational analysis of free dinucleoside polyphosphates by NMR and molecular dynamics simulations

Noa Stern, Dan Thomas Major, Hugo Emilio Gottlieb, Daniel Weizman and Bilha Fischer\*

Natural dinucleotides at physiological pH exist mostly in a stacked, rather than extended, conformation, in several interconverting stacking modes which do not alter the standard conformation of the nucleotide moieties.

4653

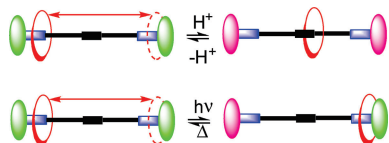


### Synthetic use of the primary kinetic isotope effect in hydrogen atom transfer: generation of $\alpha$ -aminoalkyl radicals

Mark E. Wood,\* Sabine Bissiriou, Christopher Lowe, Andrew M. Norrish, Katell Sénéchal, Kim M. Windeatt, Simon J. Coles and Michael B. Hursthouse

Systematic studies illustrate the extent to which deuterium can be used to prevent intramolecular hydrogen atom transfer in the generation of  $\alpha$ -aminoalkyl radicals in a pyrrolidine ring.

4666

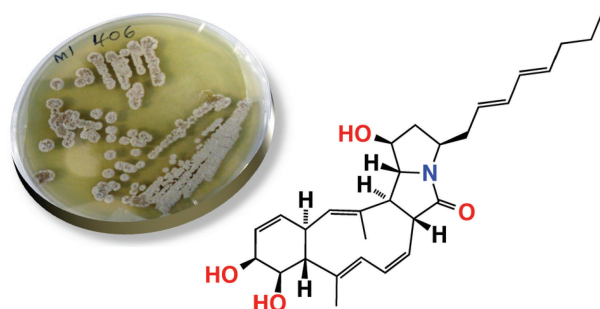


### Controlling Ring Translation of Rotaxanes

Antje Vetter and Werner Abraham\*

Protons and photons are able to stop the wheel translation in acridane rotaxanes by conversion into the corresponding acridinium rotaxanes.

4682



### Heronamides A–C, new polyketide macrolactams from an Australian marine-derived *Streptomyces* sp. A biosynthetic case for synchronized tandem electrocyclization

Ritesh Raju, Andrew M. Piggott, Melissa M. Conte and Robert J. Capon\*

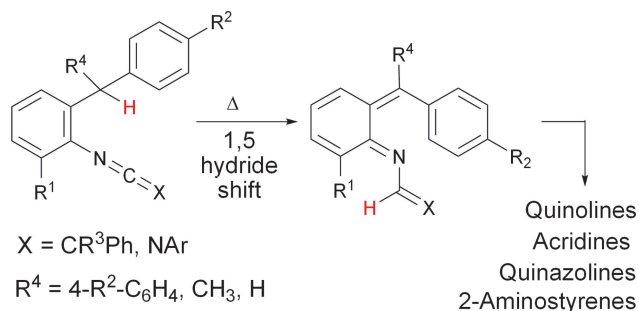
A *Streptomyces* sp. isolated from sediment collected off Heron Island, Australia, afforded three new polyketide macrolactams, heronamides A–C. Heronamide C elicits a dramatic and reversible effect on mammalian cell morphology.

4690

### Domino reactions initiated by intramolecular hydride transfers from tri(di)arylmethane fragments to ketenimine and carbodiimide functions

Mateo Alajarin,\* Baltasar Bonillo, Maria-Mar Ortin, Pilar Sanchez-Andrada, Angel Vidal\* and Raul-Angel Orenes

Ketenimines and carbodiimides bearing tri(di)arylmethane substructures experience tandem [1,5]-H (or Ar) shift/6 $\pi$ -ERC sequences. The H shifts are qualified as hydride transfers.

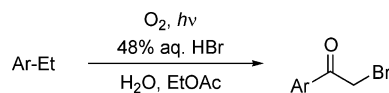


4701

### Direct synthesis of $\alpha$ -bromoketones from alkylarenes by aerobic visible light photooxidation

Norihiro Tada, Kazunori Ban, Shin-ichi Hirashima, Tsuyoshi Miura and Akichika Itoh\*

The direct synthesis of  $\alpha$ -bromoketones from alkylarenes by aerobic photooxidation with hydrobromic acid is reported.

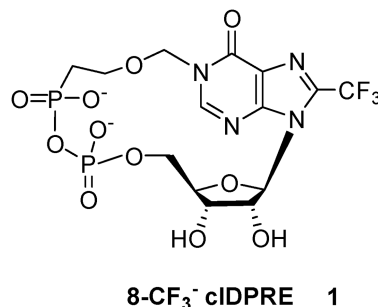


4705

### Trifluoromethylated cyclic-ADP-ribose mimic: synthesis of 8-trifluoromethyl-*N*<sup>1</sup>-[(5'-*O*-phosphorylethoxy)methyl]-5'-*O*-phosphorylinosine-5',5''-cyclic pyrophosphate (8-CF<sub>3</sub>-cIDPRE) and its calcium release activity in T cells

Min Dong, Tanja Kirchberger, Xiangchen Huang, Zhen Jun Yang, Liang Ren Zhang, Andreas H. Guse\* and Li He Zhang\*

A convenient reagent and protection strategy are reported for the synthesis of cell membrane-permeant trifluoromethylated cyclic-ADP-ribose agonist, 8-CF<sub>3</sub>-cIDPRE **1**.

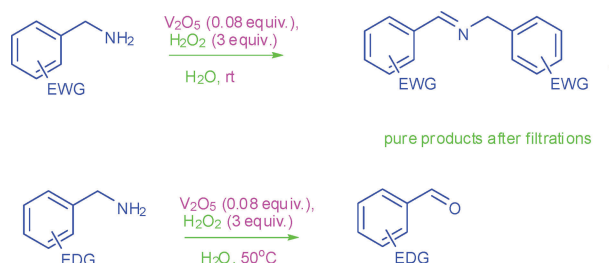


4716

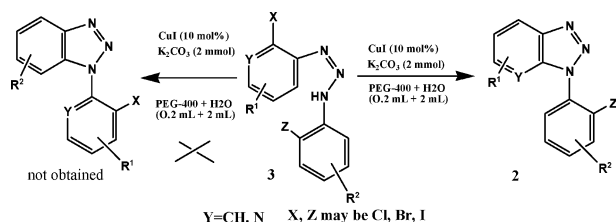
### Convenient and clean synthesis of imines from primary benzylamines

Guobiao Chu and Chunbao Li\*

Clean oxidation of primary benzylamines has been successfully achieved, using H<sub>2</sub>O<sub>2</sub> in water at room temperature catalyzed by V<sub>2</sub>O<sub>5</sub>. The products were obtained in good to quantitative yields.



4720

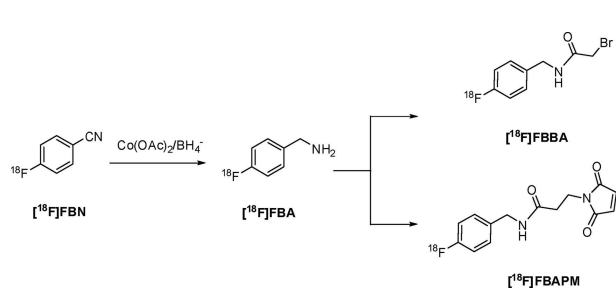


### A ligand-free copper (I) catalysed intramolecular N-arylation of diazoaminobenzenes in PEG-water: an expeditious protocol towards regioselective 1-aryl benzotriazoles

Chhanda Mukhopadhyay,\* Pradip Kumar Tapaswi and Ray J. Butcher

Regiospecific 1-aryl benzo and pyridotriazoles have been synthesized by the application of ligand-free copper(I) catalysed intramolecular N-arylation reaction.

4730

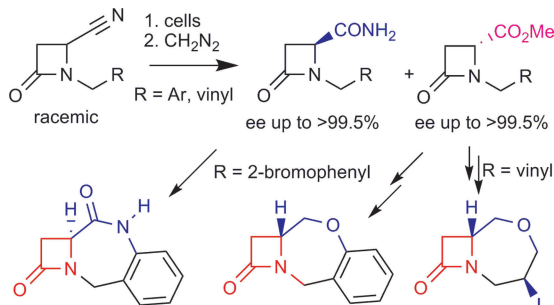


### Synthesis and application of 4-[<sup>18</sup>F]fluorobenzylamine: A versatile building block for the preparation of PET radiotracers

Ingrid Koslowsky, John Mercer and Frank Wuest\*

A novel synthesis of 4-[<sup>18</sup>F]fluorobenzylamine ([<sup>18</sup>F]FBA) by means of transition metal-assisted sodium borohydride reduction of 4-[<sup>18</sup>F]fluorobenzonitrile ([<sup>18</sup>F]FBN) is described.

4736

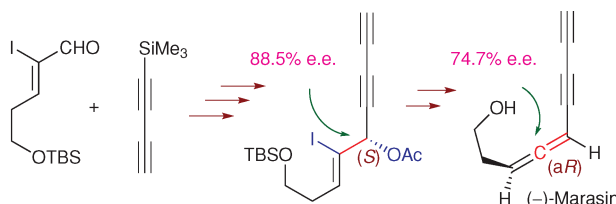


### Highly efficient and enantioselective biotransformations of β-lactam carbonitriles and carboxamides and their synthetic applications

Dong-Hui Leng, De-Xian Wang, Zhi-Tang Huang and Mei-Xiang Wang\*

Biotransformations of nitriles and amides provide a highly efficient and enantioselective approach to enantioenriched β-lactam compounds, which are useful intermediates in the synthesis of fused heterocycles

4744



### An enantioselective total synthesis of natural antibiotic marasin

Yan Zhang and Yikang Wu\*

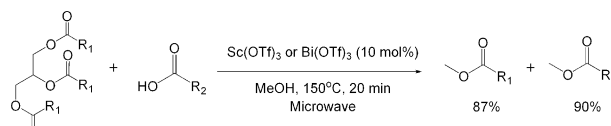
An enantioselective synthesis of the natural antibiotic marasin has been achieved, with the chiral allenic axis derived from a stereogenic center at the allylic position via an *i*-PrMgBr-mediated elimination reaction. Results of constructing the key chiral allene-diene arrangement using different protocols are also reported.

4753

### Efficient conversion of triacylglycerols and fatty acids to biodiesel in a microwave reactor using metal triflate catalysts

Aaron M. Socha and Jason K. Sello\*

The Lewis acidic metals scandium and bismuth triflate catalyze conversion of naturally occurring fatty acids and their glyceryl triesters to methyl esters in > 90% yield upon microwave heating.

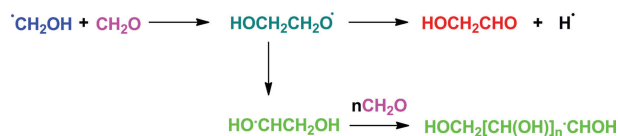


4757

### Radical routes to interstellar glycolaldehyde. The possibility of stereoselectivity in gas-phase polymerization reactions involving $\text{CH}_2\text{O}$ and $\text{CH}_2\text{OH}$

Tianfang Wang and John H. Bowie\*

Reaction of  $\cdot\text{CH}_2\text{OH}$  with  $\text{CH}_2\text{O}$  may form (i)  $\text{HOCH}_2\text{CHO}$  (glycolaldehyde) and  $\text{H}^\cdot$ , and (ii)  $\text{HOCH}_2\cdot\text{CHOH}$ . Reaction between  $\text{HOCH}_2\cdot\text{CHOH}$  and  $\text{CH}_2\text{O}$  may yield polymer  $\text{HOCH}_2[\text{CH}(\text{OH})]_n\cdot\text{CHOH}$ .

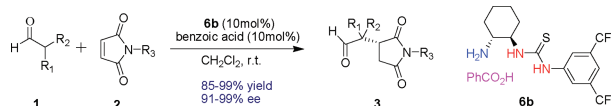


4767

### A highly efficient asymmetric Michael addition of $\alpha,\alpha$ -disubstituted aldehydes to maleimides catalyzed by primary amine thiourea salt

Feng Yu, Zhichao Jin, Huicai Huang, Tingting Ye, Xinmiao Liang\* and Jinxing Ye\*

The Michael addition of  $\alpha,\alpha$ -disubstituted aldehydes to maleimides catalyzed by a simple bifunctional primary amine thiourea catalyst/benzoic acid system was successfully developed to generate quaternary carbon centers in high yields (up to 99%) with excellent enantioselectivities (91–99%).



The Royal Society of Chemistry, Dalton Division

**Dalton Discussion 12**

**Catalytic C–H and C–X Bond Activation**

Durham University, UK

13–15 September 2010

**Monday 13th September**

**Session 1**

**I1 The mechanism of the modified Ullmann reaction**

*Hans de Vries*

**C3 The unexpected role of pyridine-2-carboxylic acid in manganese based oxidation catalysis with pyridin-2-yl based ligands**

*Dirk Pijper, Pattama Saisaha, Johannes W. de Boer, Rob Hoen, Christian Smit, Auke Meetsma, Ronald Hage, Ruben van Summeren, Paul L. Alsters, Ben L. Feringa and Wesley R. Browne*

**Session 2**

**K1 Arylation of unactivated arenes**

*Aiwen Lei, Wei Liu, Chao Liu and Mao Chen*

**C1 A versatile gold synthon for acetylene C–H bond activation**

*George C. Fortman, Albert Poater, Jack W. Levell, Sylvain Gaillard, Alexandra M. Z. Slawin, Ifor D. W. Samuel, Luigi Cavallo and Steven P. Nolan*

**C2 Pd-catalysed regioselective C–H functionalisation of 2-pyrones**

*Michael J. Burns, Robert J. Thatcher, Richard J. K. Taylor and Ian J. S. Fairlamb*

## Tuesday 14 September

### Session 3

- K2**            **Cross coupling reactions of polyfluoroarenes via C–F activation**  
*Alex D. Sun and Jennifer A. Love*
- C5**            **Studies in catalytic C–H amination involving nitrene C–H insertion**  
*Florence Collet, Camille Lescot, Chungen Liang and Philippe Dauban*

### Session 4

- I2**            **Anilide activation of adjacent C–H bonds in the palladium-catalysed Fujiwara–Moritani Reaction**  
*Waqar Rauf, Amber L. Thompson and John M. Brown*
- C7**            **Regioselective functionalization of iminophosphoranes through Pd-mediated C–H bond activation: C–C and C–X bond formation**  
*David Aguilar, Rafael Navarro, Tatiana Soler and Esteban P. Urriolabeitia*
- C8**            **Insights into the intramolecular acetate-mediated formation of ruthenium vinylidene complexes: a ligand-assisted proton shuttle (LAPS) mechanism**  
*David G. Johnson, Jason M. Lynam, John M. Slattery and Christine E. Welby*

### Session 5

- K3**            **LiCl-promoted Pd(II)-catalyzed *ortho* carbonylation of *N,N*-dimethylbenzylamines**  
*Hu Li, Gui-Xin Cai and Zhang-Jie Shi*
- C9**            **Alkyne insertion into cyclometallated pyrazole and imine complexes of iridium, rhodium and ruthenium; relevance to catalytic formation of carbo- and heterocycles**  
*Youcef Boutadla, David L. Davies, Omar Al-Duaij, John Fawcett, Rachel C. Jones and Kuldip Singh*
- C10**          **Molecular mechanism of acid-triggered aryl-halide cross-coupling reaction via reductive elimination in well-defined aryl-Cu(III)-halide species**  
*Alicia Casitas, Albert Poater, Miquel Solà, Shannon S. Stahl, Miquel Costas and Xavi Ribas*

### Session 6

- I3**            **Solvent-free aromatic C–H functionalisation/halogenation reactions**  
*Robin B. Bedford, Jens U. Engelhart, Mairi F. Haddow, Charlotte J. Mitchell and Ruth L. Webster*
- C12**          **Surface catalysed Suzuki–Miyaura cross-coupling by Pd nanoparticles: an operando XAS study**  
*Adam F. Lee, Peter J. Ellis, Ian J. S. Fairlamb and Karen Wilson*
- C13**          **Hydrofluoroarylation of alkynes with fluoroarenes**  
*Kyalo Stephen Kanyiva, Natsuko Kashihara, Yoshiaki Nakao, Tamejiro Hiyama, Masato Ohashib and Sensuke Ogoshi*

**Wednesday 15 September****Session 7**

- K4**                    **Synthesis, structure, and reductive elimination in the series  $\text{Tp}'\text{Rh}(\text{PR}_3)(\text{Ar}^{\text{F}})\text{H}$ ; determination of rhodium–carbon bond energies of fluoroaryl substituents**

*Taro Tanabe, William W. Brennessel, Eric Clot, Odile Eisenstein and William D. Jones*

- C14**                    **Importance of palladium–carbon bond energies in direct arylation of polyfluorinated benzenes**

*Julie Guihaumé, Eric Clot, Odile Eisenstein and Robin N. Perutz*

**Session 8**

- I4**                      **Computational study of ethene hydroarylation at  $[\text{Ir}(\kappa^2\text{-OAc})(\text{PMe}_3)\text{Cp}]^+$**

*David L. Davies, Stuart A. Macgregor and Amalia I. Poblador-Bahamonde*

- C15**                    **DFT study of the mechanism of benzocyclobutene formation by palladium-catalyzed  $\text{C}(\text{sp}^3)\text{-H}$  activation: role of the nature of the base and the phosphine**

*Christos Kefalidis, Olivier Baudoin and Eric Clot*

- C16**                    **Combined experimental and theoretical investigation into C-H activation of cyclic alkanes by  $\text{Cp}'\text{Rh}(\text{CO})_2$  ( $\text{Cp}'=\text{h}5\text{-C}_5\text{Me}_5$  or  $\text{h}5\text{-C}_5\text{H}_5$ )**

*Mike George*