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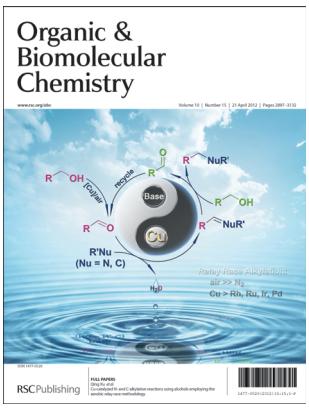
ISSN 1477-0520 CODEN OBCRAK 10(15) 2897–3132 (2012)



Cover
See Qing Xu *et al.*, pp. 2966–2972 and 2973–2978.

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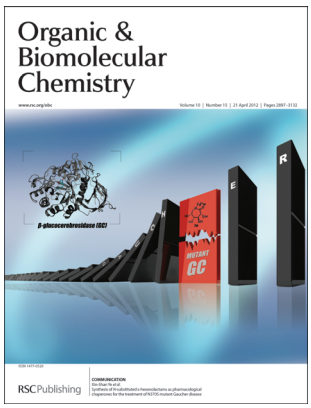


Inside cover
See Guan-Nan Wang *et al.*, pp. 2923–2927.

Image reproduced by permission of Xin-Shan Ye from *Org. Biomol. Chem.*, 2012, **10**, 2923.

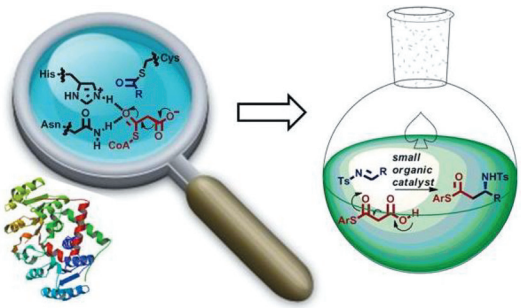
PERSPECTIVE

2911

Bioinspired organocatalytic asymmetric reactions

Luca Bernardi,* Mariafrancesca Fochi, Mauro Comes Franchini and Alfredo Ricci*

There is currently much excitement surrounding the potential of organocatalysis for mimicking the design and construction principles used by Nature. Here we discuss the present state of art outlining various bioinspired approaches, mostly based on hydrogen-bond directed organocatalysis, towards the development of synthetic catalysts that mimic the characteristics of enzymes and their applications to name reactions in organic chemistry.



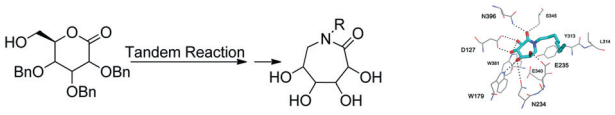
COMMUNICATIONS

2923

Synthesis of *N*-substituted ε-hexonolactams as pharmacological chaperones for the treatment of N370S mutant Gaucher disease

Guan-Nan Wang, Gabriele Twigg, Terry D. Butters, Siwei Zhang, Liangren Zhang, Li-He Zhang and Xin-Shan Ye*

A series of novel *N*-substituted ε-hexonolactams were prepared efficiently using a tandem ring-expansion reaction as the key step. Some synthetic compounds showed better enhancements to N370S mutant β-glucocerebrosidase activity than NB-DNJ and NN-DNJ.



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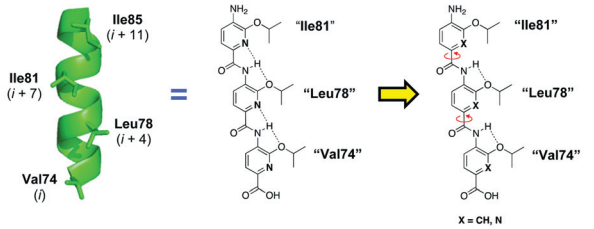
2928

Relaxation of the rigid backbone of an oligoamide-foldamer-based α-helix mimetic: identification of potent Bcl-x_L inhibitors

Jeremy L. Yap, Xiaobo Cao, Kenno Vanommeslaeghe, Kwan-Young Jung, Chander Peddaboina, Paul T. Wilder, Anjan Nan, Alexander D. MacKerell, Jr, W. Roy Smythe and Steven Fletcher*

An SAR analysis of the rigid backbone of an oligopicolinamide α-helix mimetic led to the discovery of more flexible and more potent antagonists of the Bak–Bcl-x_L protein–protein interaction.

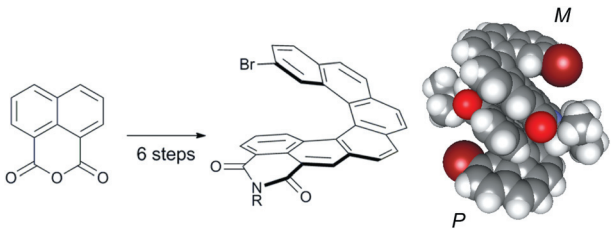


2934

Synthesis and characterization of 1,8-naphthalimide with [6]helicene skeleton

Toshitaka Kogiso, Kosuke Yamamoto, Hiroshi Suemune* and Kazuteru Usui*

The synthesis of a 1,8-naphthalimide with [6]helicene scaffold was achieved by oxidative photocyclization as the key step.

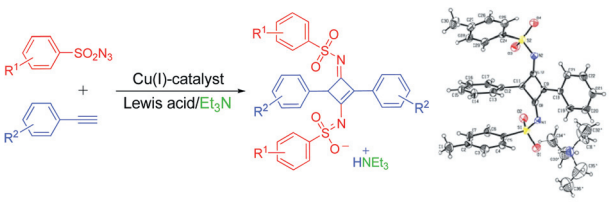


2937

Cascade synthesis of bis-*N*-sulfonylcyclobutenes *via* Cu(I)/Lewis acid-catalyzed (3 + 2)/(2 + 2) cycloadditions: observation of aggregation-induced emission enhancement from restricted C=N photoisomerization

Kayambu Namitharan and Kasi Pitchumani*

An electrophile/Lewis acid triggered (2 + 2) cycloaddition of *N*-sulfonylketenimines generated *in situ* from copper(I) catalyzed (3 + 2) cycloaddition of sulfonyl azides and alkynes to highly emissive bis-*N*-sulfonylcyclobutenes is described.

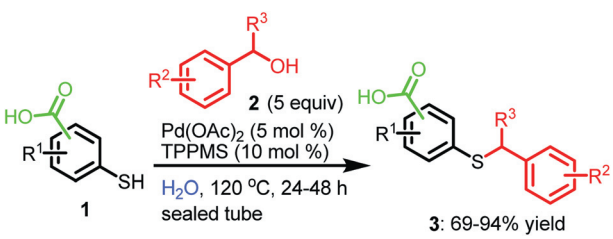


2942

Palladium-catalyzed *S*-benzylation of unprotected mercaptobenzoic acid with benzyl alcohols in water

Hidemasa Hikawa* and Yuusaku Yokoyama*

Palladium-catalyzed *S*-benzylation of unprotected mercaptobenzoic acids with benzyl alcohols gave only *S*-benzylated mercaptobenzoic acids in good yields. Water may play an important role in the smooth generation of the (η^3-benzyl) palladium species by activation of the hydroxyl group of the benzyl alcohol.



BOSS XIII

13th Belgian Organic Synthesis Symposium

July 15>20, 2012, K.U.Leuven, Belgium

Symposium Programme:

- **One-day course** by the recipient of the **Tetrahedron Chair in Organic Synthesis**
  Prof. Ben FERINGA (University of Groningen, The Netherlands)
- **16 plenary lectures**
  Prof. Matthias BELLER (University of Rostock, Germany)
  Prof. Dale L. BOGER (The Scripps Research Institute, USA)
  Prof. Jan-Erling BÄCKVALL (Stockholm University, Sweden)
  Prof. Karl GADEMANN (University of Basel, Switzerland)
  Prof. Frank GLORIUS (University of Münster, Germany)
  Prof. Véronique GOUVERNEUR (University of Oxford, UK)
  Prof. Shu KOBAYASHI (University of Tokyo, Japan)
  Prof. Michael J. KRISCHE (University of Texas, USA)
  Dr Emmanuel LACÔTE (ICSN-CNRS, France)
  Prof. István MARKÓ (Université catholique de Louvain, Belgium)
  Prof. Gary A. MOLANDER (Penn Chemistry, University of Pennsylvania, USA)
  Prof. Klaus MÜLLER (F. Hoffmann-la Roche Ltd, Switzerland)
  Prof. Tobias RITTER (Harvard University, USA)
  Prof. Scott SNYDER (Columbia University, USA)
  Prof. Paul A. WENDER (Stanford University, USA)
  Prof. Ming Hua XU (Shanghai Institute of Materia Medica, China)
- **Lecture** delivered by the recipient of the Janssen Pharmaceutica Prize for Creativity in Organic Synthesis
- **Poster sessions**
- **Exhibition**
- **Social activities**

Janssen Pharmaceutica Prize for Creativity in Organic Synthesis

Call for nominations

The Janssen Pharmaceutica Prize for Creativity in Organic Synthesis is awarded on a biannual basis, on the occasion of the BOSS, to a chemist under the age of 50 who has made a significant contribution to the field of organic synthesis in the broadest sense.

The Prize consists of a trophy, a citation and € 20.000. The laureate of the Prize is expected to deliver a lecture at the BOSS XIII.

All details for the submission of a nomination are available via the symposium website:

www.BOSS13.org

Deadline for nominations

December 31, 2011

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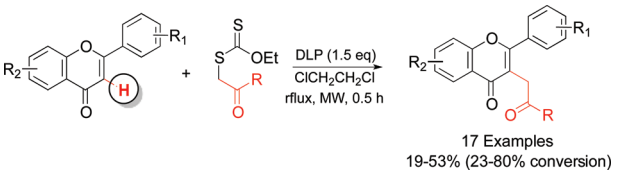
2946

Microwave-assisted C-3 selective oxidative radical alkylation of flavones

Marco V. Mijangos, Joaquin González-Marrero,* Luis D. Miranda,* Paulette Vincent-Ruz, Armando Lujan-Montelongo, Diana Olivera-Díaz, Elhiu Bautista, Alfredo Ortega, María de la Luz Campos-González and Rocio Gamez-Montaño

Flavones were directly alkylated at the C-3 position in moderate yields using a xanthate-based oxidative radical addition procedure.

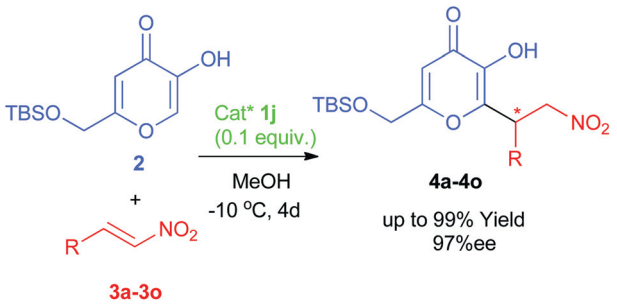


2950

Organocatalytic enantioselective Michael addition of a kojic acid derivative to nitro olefins

Jiyu Wang, Qing Zhang, Hui Zhang, Yujun Feng, Weicheng Yuan and Xiaomei Zhang*

Organocatalytic enantioselective Michael addition of a kojic acid derivative to nitro olefins provided good yields and good enantioselectivities.

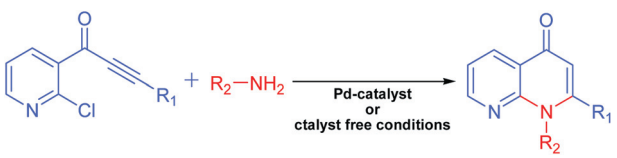


2955

Efficient [5 + 1]-strategy for the assembly of 1,8-naphthyridin-4(1*H*)-ones by domino amination/conjugate addition reactions of 1-(2-chloropyridin-3-yl) prop-2-yn-1-ones with amines

Viktor O. Iaroshenko,* Ingo Knepper, Muhammad Zahid, Rene Kuzora, Sergii Dudkin, Alexander Villinger and Peter Langer*

A facile synthetic approach for the synthesis of 1,8-naphthyridine-4(1*H*)-one derivatives *via* a catalyst free and Pd-supported tandem amination sequence is developed and described.

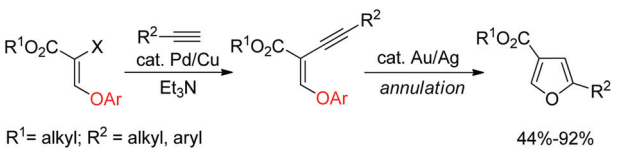


2960

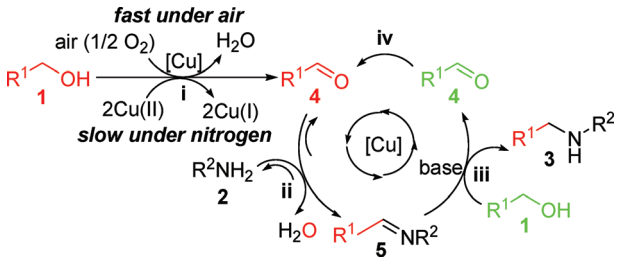
Gold-catalyzed efficient synthesis of 2,4-disubstituted furans from aryloxy-enynes

Ende Li, Wenjun Yao, Xin Xie, Chengyu Wang, Yushang Shao and Yanzhong Li*

(*E*)-1-Aryloxy-1-en-3-ynes are efficiently prepared by the Sonogashira coupling reaction using 2-bromo-3-aryloxypropenoates and terminal alkynes. The resulting (*E*)-1-aryloxy-1-en-3-ynes are successfully applied to the synthesis of 2,4-disubstituted furans through an Au/Ag-catalyzed annulation reaction.



2966

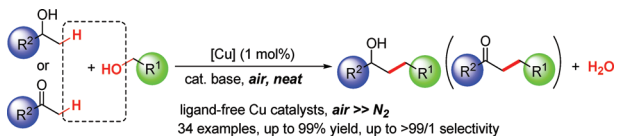


Copper-catalyzed *N*-alkylation of amides and amines with alcohols employing the aerobic relay race methodology

Qiang Li, Songjian Fan, Qing Sun, Haiwen Tian, Xiaochun Yu and Qing Xu*

By employing aerobic oxidative activation of the alcohols, we developed a greener and more advantageous Cu-catalyzed *N*-alkylation reaction of amides and amines with alcohols and propose a more rational mechanism for the reaction.

2973

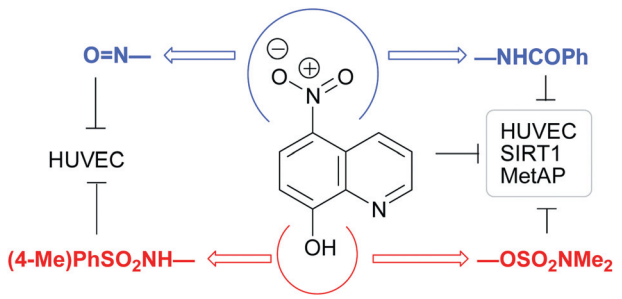


Copper-catalyzed *C*-alkylation of secondary alcohols and methyl ketones with alcohols employing the aerobic relay race methodology

Shiheng Liao, Kangkang Yu, Qiang Li, Haiwen Tian, Zhengping Zhang, Xiaochun Yu and Qing Xu*

By employing aerobic oxidative activation of the alcohols, copper is a superior catalyst in *C*-alkylation reactions of secondary alcohols and methyl ketones with alcohols that most likely proceed *via* a new process rather than the conventional borrowing hydrogen-type mechanisms.

2979

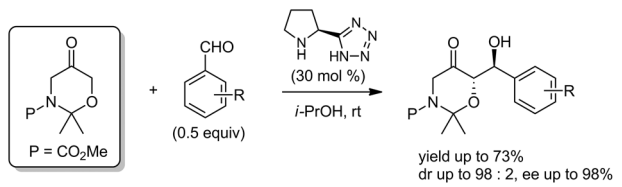


Substituted oxines inhibit endothelial cell proliferation and angiogenesis

Shridhar Bhat, Joong Sup Shim, Feiran Zhang, Curtis Robert Chong and Jun O. Liu*

Structure–activity relationship study of nitroxoline, an antibacterial rediscovered for its anti-angiogenic activity, offered many surprises where minor modifications yielded oxine derivatives with sub-micromolar potency against human umbilical vein endothelial cells (HUVEC), but with entirely different as yet unknown mechanisms.

2993



Aminohydroxyacetone synthons: versatile intermediates for the organocatalytic asymmetric aldol reaction

Yoshiyuki Komatsu, Riki Watanabe, Hideaki Ikishima, Keiji Nakano, Yoshiyasu Ichikawa and Hiyoshizo Kotsuki*

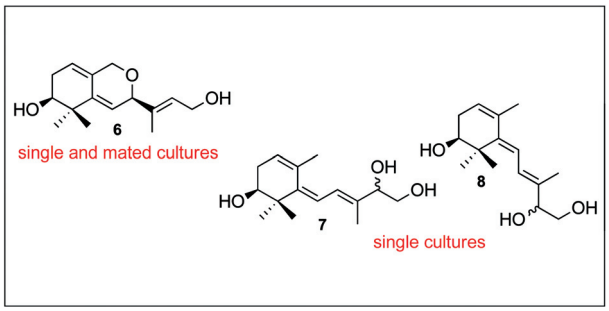
A practical method for the synthesis of 1,3-aminohydroxyacetone synthons was developed, and their utility in the organocatalytic asymmetric aldol reaction was demonstrated in a short synthesis of aza-sugars.

3002

Apocarotenoids in the sexual interaction of *Phycomyces blakesleeanus*

Silvia Polaino, Jose A. Gonzalez-Delgado, Pilar Arteaga, M. Mar Herrador, Alejandro F. Barrero* and Enrique Cerdá-Olmedo*

New 15-C apocarotenoids in *Phycomyces blakesleeanus*.

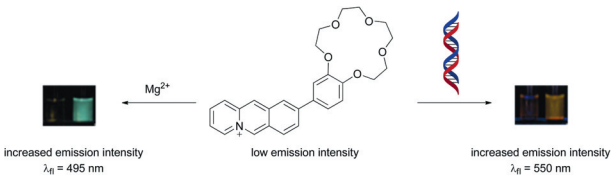


3010

Fluorimetric detection of Mg^{2+} and DNA with 9-(alkoxyphenyl)benzo[*b*]quinolizinium derivatives

Maoqun Tian, Heiko Ihmels* and Shite Ye

A benzo[*b*]quinolizinium-benzo-15-crown-5 ether conjugate is presented that enables the fluorimetric detection of Mg^{2+} and DNA by a significant light-up effect, along with an analyte-specific change of the emission wavelength. Photophysical studies revealed the impact of the *meta*-alkoxy group on the light-up effect.

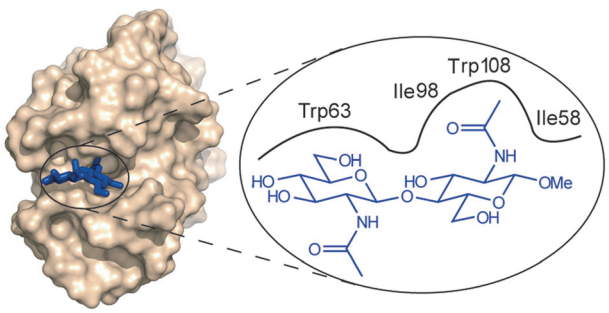


3019

Combining weak affinity chromatography, NMR spectroscopy and molecular simulations in carbohydrate–lysozyme interaction studies

Jens Landström, Maria Bergström, Christoffer Hamark, Sten Ohlson and Göran Widmalm*

Binding sites and ligand conformations were deduced for protein-carbohydrate complexes which showed intermolecular hydrogen bonding and CH/π-interactions.

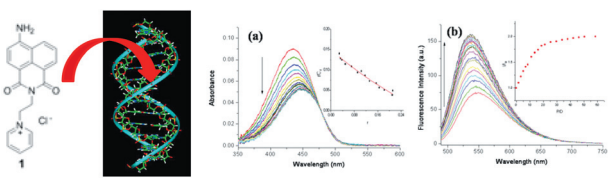


3033

Synthesis and photophysical evaluation of a pyridinium 4-amino-1,8-naphthalimide derivative that upon intercalation displays preference for AT-rich double-stranded DNA

Swagata Banerjee, Jonathan A. Kitchen, Thorfinnur Gunnlaugsson* and John M. Kelly*

The fluorescence of **1** was enhanced and blue-shifted in its 1 : 1 complex with 5′-AMP while it is partially quenched and red-shifted in its complex with 5′-GMP. We also show that **1** intercalates and has strong preference for A–T rich sequences in natural DNA.



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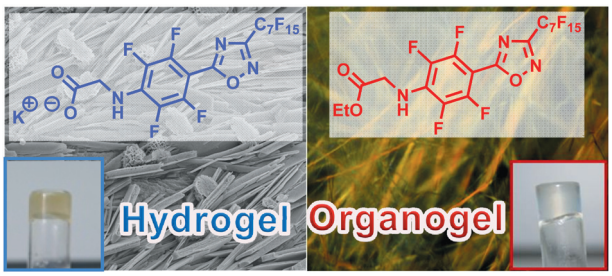
3044

Synthesis of fluorinated oxadiazoles with gelation and oxygen storage ability

Antonio Palumbo Piccionello,* Annalisa Guarcello, Alessandro Calabrese, Ivana Pibiri, Andrea Pace and Silvestre Buscemi

New fluorinated 1,2,4-oxadiazoles were synthesized and characterized as LMWGs. Fluorine content is crucial for the non-covalent interactions involved in the gelation process.

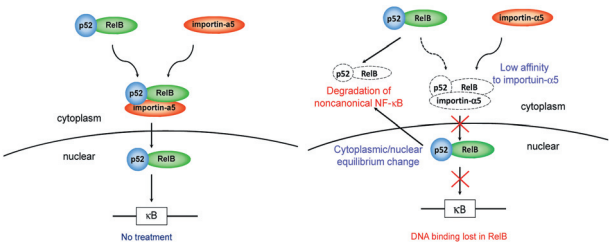


3053

Involvement of DNA binding domain in the cellular stability and importin affinity of NF-κB component RelB

Masatoshi Takeiri, Kana Horie, Daisuke Takahashi, Mariko Watanabe, Ryoichi Horie, Siro Simizu and Kazuo Umezawa*

DNA binding activity of RelB regulates noncanonical NF-κB stability and intracellular localization.

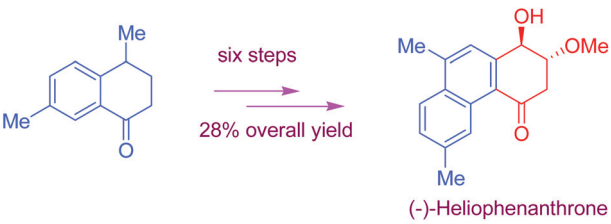


3060

Heteroatom-directed Wacker oxidations. A protection-free synthesis of (−)-heliophenanthrone

Parag Mukherjee and Tarun K. Sarkar*

The first enantioselective synthesis of (−)-heliophenanthrone has been achieved utilizing ring-closing olefin metathesis and Wacker oxidation as key step.

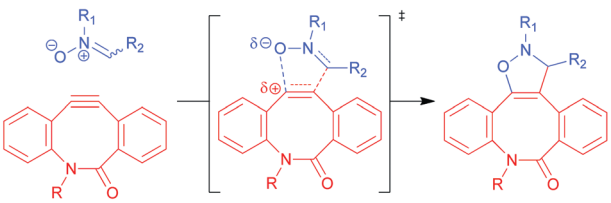


3066

Kinetics studies of rapid strain-promoted [3 + 2]-cycloadditions of nitrones with biaryl-aza-cyclooctynone

Craig S. McKay, Mariya Chigrinova, Jessie A. Blake and John Paul Pezacki*

Strain-promoted cycloadditions of cyclic nitrones with biaryl-aza-cyclooctynone (BARAC) display a 47-fold rate enhancement relative to the reaction of BARAC with benzyl azide. A Hammett plot for the reactions showed a rho value of 0.25, indicating that the reaction is not sensitive to substituents and should have broad applicability.



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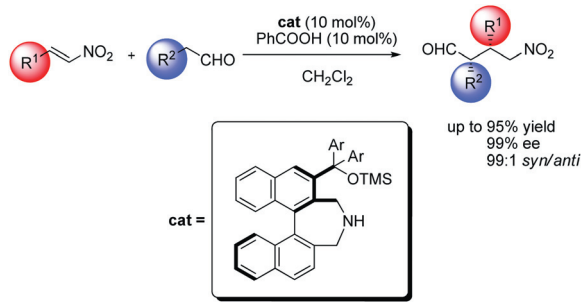
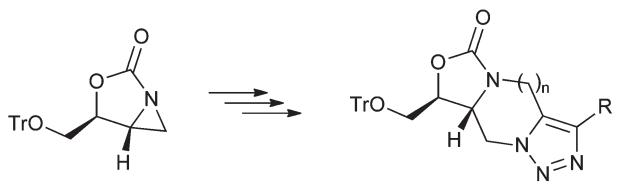


A new synthetic route for axially chiral secondary amines with binaphthyl backbone and their applications in asymmetric Michael reaction of aldehydes to nitroalkenes

Da-Cheng Liang, Ren-Shi Luo, Li-Hua Yin, Albert S. C. Chan and Gui Lu*

Practical synthesis of binaphthyl-based secondary amine organocatalysts and their applications in asymmetric Michael reaction.

3080

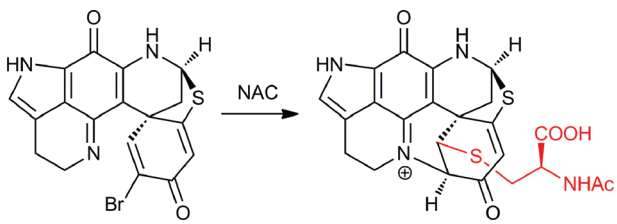


Fused ring aziridines as a facile entry into triazole fused tricyclic and bicyclic heterocycles

Fang Fang, Megan Vogel, Jennifer V. Hines and Stephen C. Bergmeier*

A series of 6–12-membered rings containing both the oxazolidinone and triazole rings have been prepared as conformationally restrained analogs of RNA-binding oxazolidinones. A fused-ring aziridine was the key starting material for the synthesis of these molecules.

3092

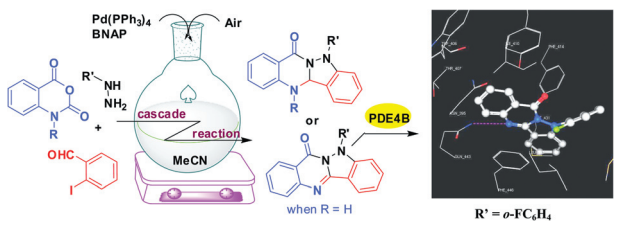


Investigation of the electrophilic reactivity of the cytotoxic marine alkaloid discorhabdin B

Cary F. C. Lam, Tanja Grkovic, A. Norrie Pearce and Brent R. Copp*

The cytotoxic marine alkaloid discorhabdin B reacts with biomimetic sulphur nucleophiles *via* an orchestrated combination of electrophilic C-1 and nucleophilic N-18.

3098



A new cascade reaction: concurrent construction of six and five membered rings leading to novel fused quinazolinones

K. Siva Kumar, P. Mahesh Kumar, V. Sreenivasa Rao, Ahamed A. Jafar, Chandana Lakshmi T. Meda, R. Kapavarapu, Kishore V. L. Parsa and Manojit Pal*

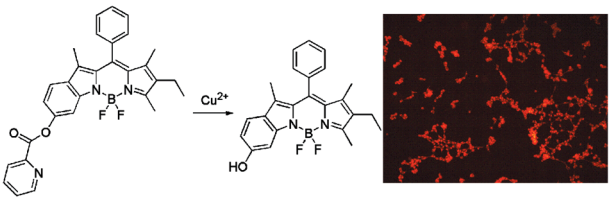
Concurrent construction of six and five membered fused *N*-heterocyclic rings has been achieved *via* a new cascade reaction.

3104

Borondipyrromethene-derived Cu^{2+} sensing chemodosimeter for fast and selective detection

Chunchang Zhao,* Peng Feng, Jian Cao, Xuzhe Wang, Yang Yang, Yulin Zhang, Jinxing Zhang and Yanfen Zhang

A borondipyrromethene-derived fluorescence turn-on probe with fast response and high selectivity towards Cu^{2+} was synthesized to image Cu^{2+} in living cells.

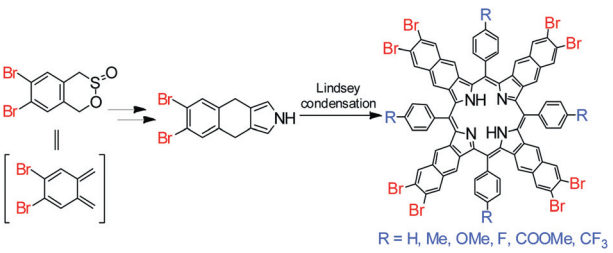


3110

Novel syntheses and properties of *meso*-tetraaryl-octabromo-tetranaphtho[2,3]porphyrins (Ar_4Br_8TNPs)

Xiu-Zhao Jiang, Chen-Xin Cai,* Jin-Tao Liu* and Hidemitsu Uno

The synthesis of a series of novel *meso*-tetraaryl-octabromo-tetranaphtho[2,3]porphyrins (Ar_4Br_8TNPs), properties of these bromoporphyrins and chemical transformation *via* Pd-catalyzed Suzuki coupling reaction are presented.

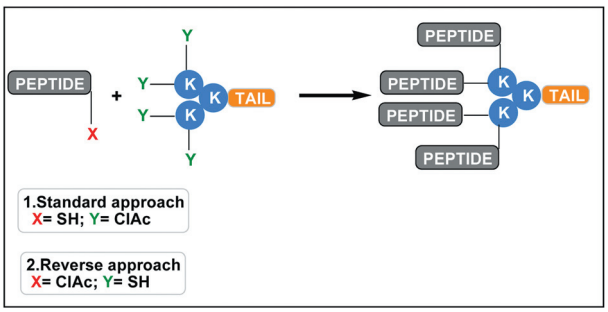


3116

Reverse thioether ligation route to multimeric peptide antigens

Marta Monsó, Wioleta Kowalczyk, David Andreu* and Beatriz G. de la Torre*

Switching the electrophile–nucleophile partner roles in the thioether-based synthesis of dendrimer antigenic peptides has clear advantages, including solid-phase applications.

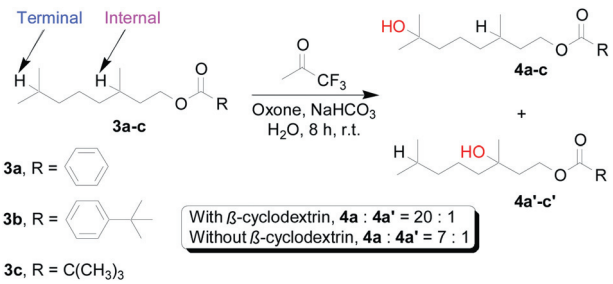


3122

Selective oxidation of unactivated C–H bonds by supramolecular control

Yat-Sing Fung, Siu-Cheong Yan and Man-Kin Wong*

Site-selective oxidation of the terminal over the internal tertiary C–H bond of 3,7-dimethyloctyl esters **3a–c** was achieved by supramolecular control using β-cyclodextrin.



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