

Organic & Biomolecular Chemistry

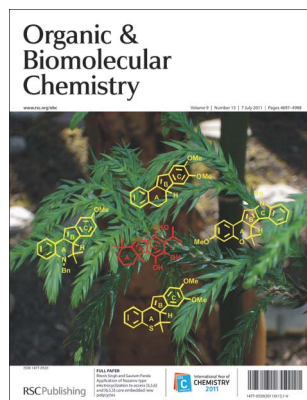
An international journal of synthetic, physical and biomolecular organic chemistry

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IN THIS ISSUE

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Cover

See Ritesh Singh and Gautam Panda, pp. 4782–4790.

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EMERGING AREA

4714

Dioxazaborocanes: old adducts, new tricks

H el ene Bonin,* Thomas Delacroix and Emmanuel Gras*

Dioxazaborocanes represent a class of boronic derivatives featuring an interesting dative bond. As exemplified in this report, they have exhibited attractive reactivities in various reactions commonly used in organic synthesis such as cycloaddition, cross-coupling reactions.



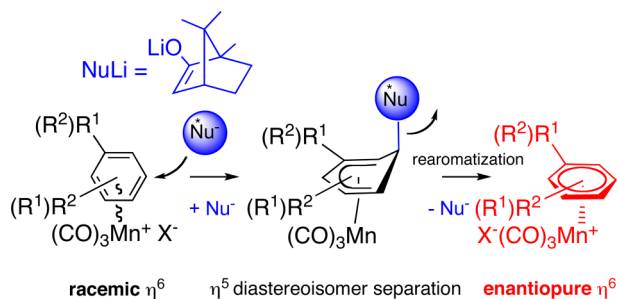
PERSPECTIVE

4725

Planar chiral (η^5 -cyclohexadienyl)- and (η^6 -arene)-tricarbonylmanganese complexes: synthetic routes and application

Francoise Rose-Munch and Eric Rose

Resolution of polysubstituted [$(\eta^6$ -arene) $Mn(CO)_3$] $^+$ complexes by an efficient round trip of (D)-(+)-camphor enolate.



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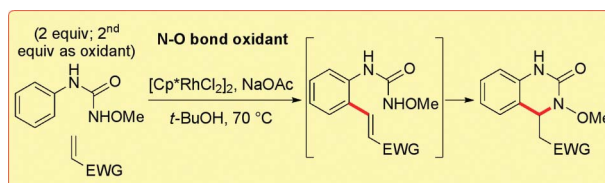
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4736

Investigating *N*-methoxy-*N'*-aryl ureas in oxidative C–H olefination reactions: an unexpected oxidation behaviour

Jens Willwacher, Souvik Rakshit and Frank Glorius*

We report a urea derived directing group (and oxidant) for mild and highly selective oxidative C–H bond olefination.

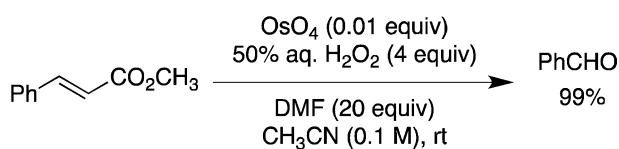


4741

Catalytic oxidative cleavage of olefins promoted by osmium tetroxide and hydrogen peroxide

Stewart R. Hart, Daniel C. Whitehead, Benjamin R. Travis and Babak Borhan*

Suitable conditions for oxidative cleavage of olefins with catalytic OsO_4 and H_2O_2 as the terminal oxidant are disclosed.

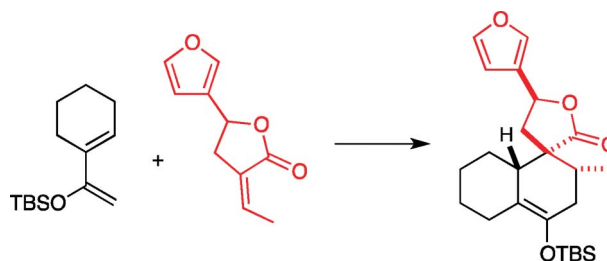


4745

The clerodane ring system: investigating the viability of a direct Diels–Alder approach

Andrew T. Merritt, Rebecca H. Pouwer, David J. Williams, Craig M. Williams* and Steven V. Ley*

A direct Diels–Alder approach to the clerodane system has been investigated highlighting the inherent difficulties associated with this otherwise obvious strategy.

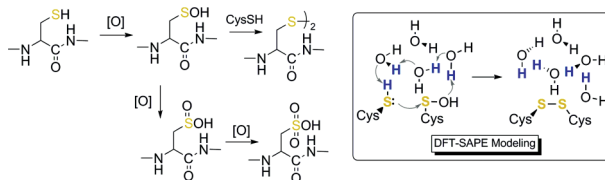


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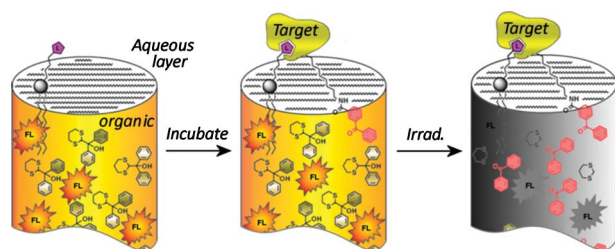
Transition states for cysteine redox processes modeled by DFT and solvent-assisted proton exchange

Craig A. Bayse*

Solvent-assisted proton exchange DFT models of cysteine oxidation and S–S bond formation provide activation barriers consistent with the kinetics of these processes central to biochemical signalling.



4752

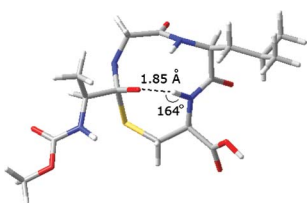


Photochemically amplified detection of molecular recognition events: an ultra-sensitive fluorescence turn-off binding assay

Tiffany P. Gustafson, Greg A. Metzel and Andrei G. Kutateladze*

Photoamplified fluorescence quenching methodology based on massive photo-unmasking of a dual function sensitizer–quencher is developed for ultra-sensitive detection of binding.

4756

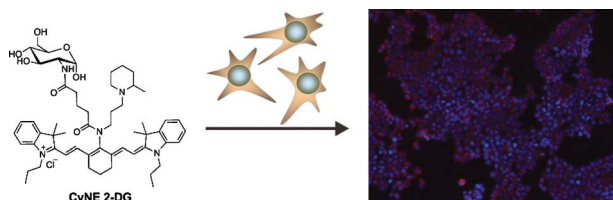


Alternating chemical ligation reactivity of S-acyl peptides explained with theory and computations

Alexander A. Oliferenko and Alan R. Katritzky*

Conformational preorganization and intramolecular hydrogen bonding explains a previously discovered alternating reactivity of S-acyl peptides in internal chemical ligation reactions.

4760

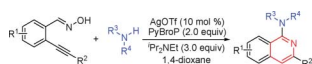


Synthesis and characterization of a cell-permeable near-infrared fluorescent deoxyglucose analogue for cancer cell imaging

Marc Vendrell, Animesh Samanta, Seong-Wook Yun and Young-Tae Chang*

We report a novel NIR fluorescent deoxyglucose analogue (CyNE 2-DG) with good cell permeability and validated its application for cancer cell imaging.

4763



An efficient route to 1-aminoisoquinolines via AgOTf-catalyzed reaction of 2-alkynylbenzaldoxime with amine

Danqing Zheng, Zhiyuan Chen, Jianping Liu* and Jie Wu*

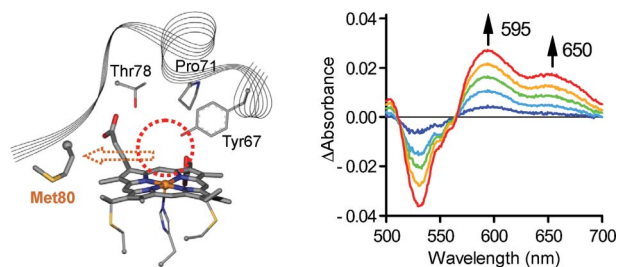
2-Alkynylbenzaldoxime reacts with amine catalyzed by silver triflate leading to 1-aminoisoquinolines in good yield with good functional group tolerance.

4766

Peroxidase activity enhancement of horse cytochrome *c* by dimerization

Zhonghua Wang, Takashi Matsuo, Satoshi Nagao and Shun Hirota*

Peroxidase activity enhancement and Compound I formation were detected in the domain-swapped cytochrome *c* dimer due to the opened ligand-binding site at the heme pocket by dissociation of Met80 from the heme iron.

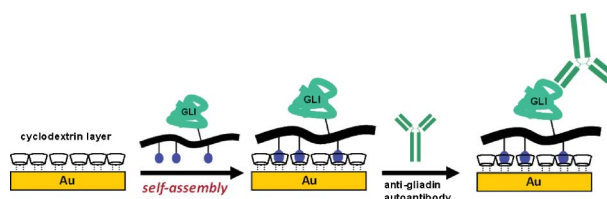


4770

Amperometric detection of antibodies in serum: performance of self-assembled cyclodextrin/cellulose polymer interfaces as antigen carriers

Mayreli Ortiz, Alex Fragoso* and Ciara K. O'Sullivan*

A bifunctionalised carboxymethyl-cellulose polymer bearing adamantane units and an antigenic fragment forms a highly stable interfacial complex with a cyclodextrin-modified surface, allowing the highly sensitive amperometric detection of autoantibodies.

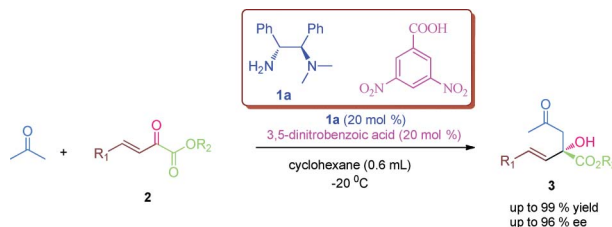


4774

Highly enantioselective aldol reaction of acetone with β,γ -unsaturated α -keto esters promoted by simple chiral primary-tertiary diamine catalysts

Lin Peng, Liang-Liang Wang, Jian-Fei Bai, Li-Na Jia, Yun-Long Guo, Xi-Ya Luo, Fei-Ying Wang, Xiao-Ying Xu* and Li-Xin Wang*

A series of primary-tertiary diamine catalysts were successfully applied to promote the enantioselective aldol reaction of acetone with β,γ -unsaturated α -keto esters in excellent yields (up to 99%) and enantioselectivities (up to 96% ee).

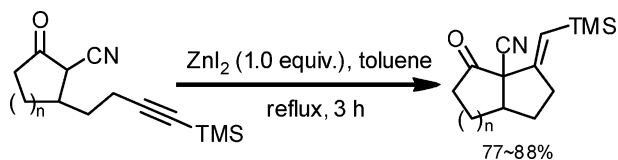


4778

Conia-ene annulation of the α -cyano β -TMS-capped alkynyl cycloalkanone system and its synthetic application

Chih-Lung Chin, Cheng-Feng Liao, Hsing-Jang Liu, Ying-Chieh Wong, Ming-Tsang Hsieh, Prashanth K. Amancha, Chun-Ping Chang and Kak-Shan Shia*

Under catalysis with ZnI_2 , an effective annulation process of ω -silylacetylenic α -cyano ketones has been developed, leading to construction of various bicyclic frameworks characterized with a TMS-containing methylenecyclopentane ring in moderate to high yields.





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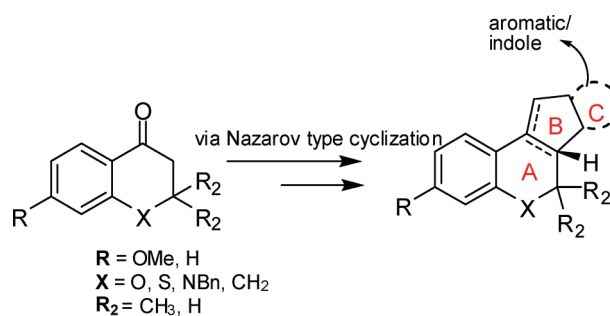
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4782

Application of Nazarov type electrocyclization to access [6,5,6] and [6,5,5] core embedded new polycycles: an easy entry to tetrahydrofluorene scaffolds related to Taiwaniaquinoids and C-nor-D homosteroids

Ritesh Singh and Gautam Panda*

An expedient approach to heteroatom-impregnated tetrahydrofluorene [6,5,6]ABC tricyclic core embedded new polycycles has been achieved via Nazarov type electrocyclization using 2 mol% Sc(OTf)₃.

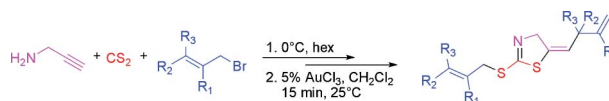


4791

Gold(III) chloride catalysed synthesis of 5-alkylidene-dihydrothiazoles

Thomas S. A. Heugebaert, Leander P. D. Vervaecke and Christian V. Stevens*

A two-step synthesis of dihydrothiazoles from easily available, cheap starting materials is presented. First, the previously unknown *N*-propargylic dithiocarboimidates are produced in good yields. The subsequent gold catalysed ring closure is fast and efficient, leading to dihydrothiazoles through a cascade of 5-*exo*-dig cyclisation and 1,3-alkyl migration.

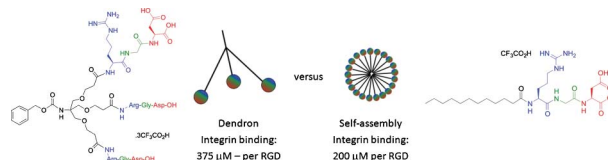


4795

Comparing dendritic and self-assembly strategies to multivalency—RGD peptide—integrin interactions

Daniel J. Welsh and David K. Smith*

Covalent and non-covalent approaches for the organisation of multivalent ligand arrays are compared, and it is demonstrated that self-assembly can be a simple strategy for the organisation of ligand arrays—comparable with a dendritic approach.

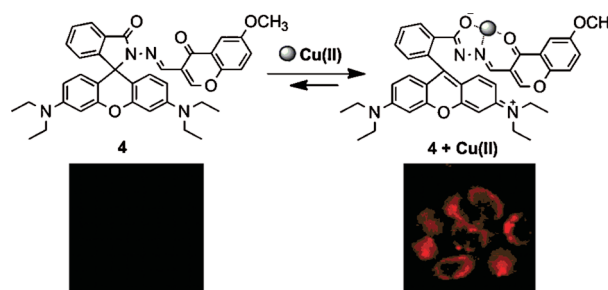


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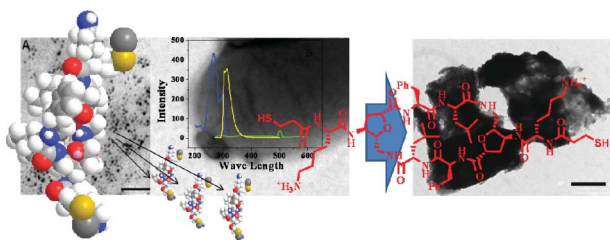
Synthesis, crystal structure and living cell imaging of a Cu²⁺-specific molecular probe

Wei-Yong Liu, Hai-Ying Li, Bao-Xiang Zhao* and Jun-Ying Miao*

A rhodamine chromene-based “turn-on” fluorescence probe can monitor the intracellular Cu²⁺ level in living HeLa cells with high sensitivity and selectivity.



4806

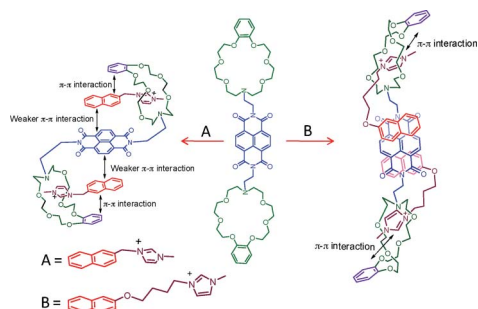


Towards the synthesis of sugar amino acid containing antimicrobial noncytotoxic CAP conjugates with gold nanoparticles and a mechanistic study of cell disruption

Sudip Pal, Kalyan Mitra, Sarfuddin Azmi, Jimut Kanti Ghosh and Tushar Kanti Chakraborty*

Attachment of cyclic cationic peptides containing sugar amino acids to AuNP did not alter their antimicrobial activities, but significantly decreased cytotoxicities.

4811

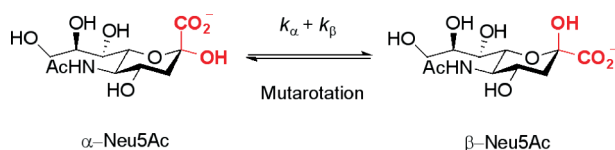


Studies on [3]pseudorotaxane formation from a bis-azacrown derivative as host and imidazolium ion-derivatives as guest

Amal Kumar Mandal, Moorthy Suresh and Amitava Das*

A new host molecule, having two azacrown derivatives bridged by luminescent naphthalene diimide functionality, is found to form a [3]pseudorotaxane derivative with imidazolium ion-based guest molecules in non-polar solvents through hydrogen-bonded adduct formation.

4818

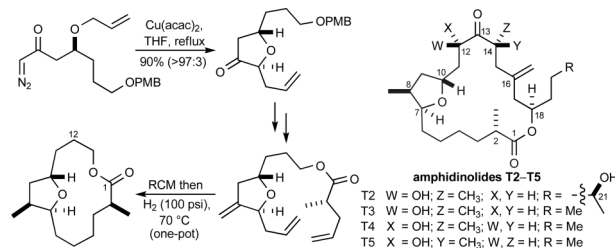


A mechanistic study of sialic acid mutarotation: Implications for mutarotase enzymes

Jefferson Chan, Gurtej Sandhu and Andrew J. Bennet*

Detailed pH- and pD-rate profiles for the mutarotation of sialic acid show that this reaction occurs *via* four different pathways.

4823



Concise synthesis of the C-1-C-12 fragment of amphidinolides T1-T5

J. Stephen Clark,* Flavien Labre and Lynne H. Thomas

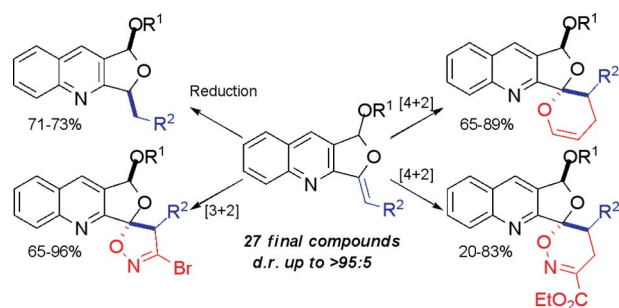
The C-1-C-12 segment found in amphidinolides T1-T5 has been synthesised in an efficient and diastereoselective manner.

4831

Synthesis and reactivity of furoquinolines bearing an external methylene-bond: access to reduced and spirocyclic structures

Xavier Bantreil, Carine Vaxelaire, Thomas Godet, Evelyne Parker, Carole Sauer and Philippe Belmont*

Silver-catalysis led to furoquinolines, and their external methylene-bond was efficiently reduced or reacted to form spirocyclic compounds.

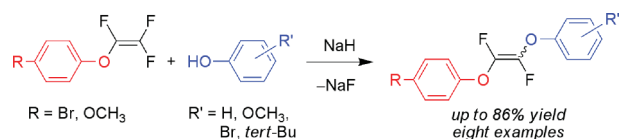


4842

Synthesis of internal fluorinated alkenes *via facile* aryloxylation of substituted phenols with aryl trifluorovinyl ethers

Justin D. Moody, Don VanDerveer, Dennis W. Smith Jr. and Scott T. Iacono*

A versatile transformation *via facile* nucleophilic addition of substituted phenols to aryl trifluorovinylethers affords selective fluorinated alkene substitution.

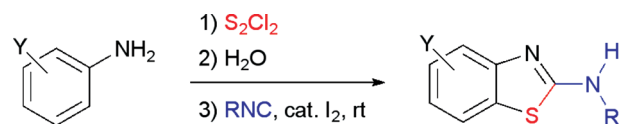


4850

A straightforward synthesis of 2-aminobenzothiazoles from Herz compounds

Ana G. Neo, Rosa M. Carrillo and Carlos F. Marcos*

Herz reaction revisited: 2-aminobenzothiazoles are easily obtained by insertion of isocyanides into 1,2,3-benzodithiazole 2-oxides.

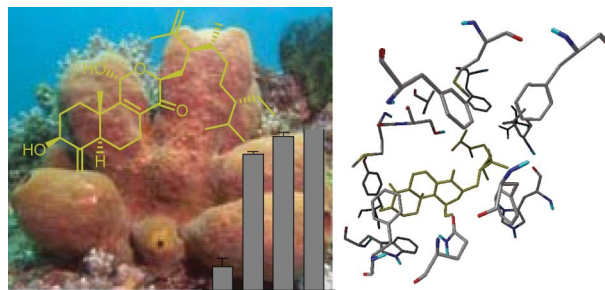


4856

Towards new ligands of nuclear receptors. Discovery of malaitasterol A, an unique bis-secosterol from marine sponge *Theonella swinhoei*

Simona De Marino, Valentina Sepe, Maria Valeria D'Auria, Giuseppe Bifulco, Barbara Renga, Sylvain Petek, Stefano Fiorucci and Angela Zampella*

Malaitasterol A, an unprecedented bis-secosterol, was isolated from a Solomon collection of *Theonella swinhoei*. Malaitasterol A is a potent agonist of pregnane-X-receptor and its putative binding mode to PXR has been obtained through docking calculations.



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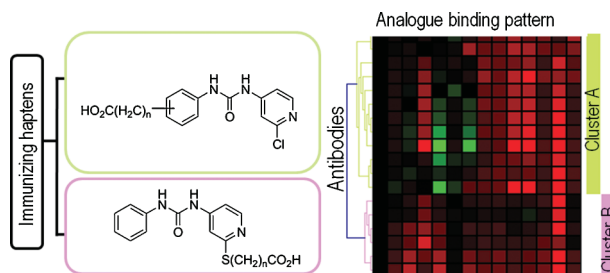
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4863

Forchlorfenuron-mimicking haptens: from immunogen design to antibody characterization by hierarchical clustering analysis

Celia Suárez-Pantaleón, Josep V. Mercader, Consuelo Agulló, Antonio Abad-Somovilla and Antonio Abad-Fuentes*

Functionalized forchlorfenuron haptens were synthesized, antibodies prepared, and hierarchical clustering analysis was applied to antigen-binding characterization in order to correlate immunogen structure and specificity.

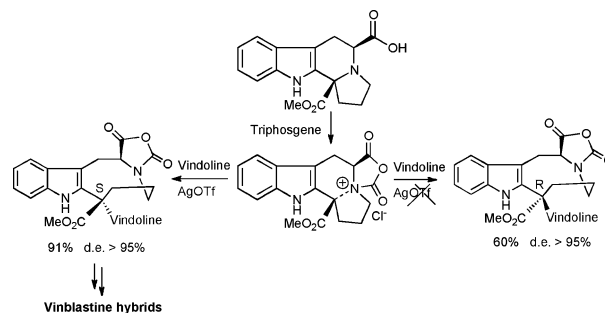


4873

Elaboration of vinblastine hybrids using a reactive *in situ* generated *N*-carboxyanhydride

Claire Rannoux, Fanny Roussi,* Marie-Thérèse Martin and Françoise Guéritte

Vinblastine hybrids were elaborated in a few steps *via* a diastereoselective fragmentation–insertion reaction mediated by an internal *N*-carboxyanhydride.

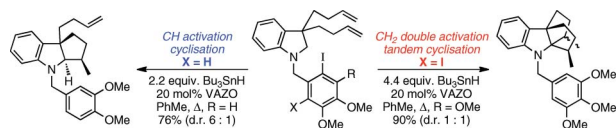


4882

CH activation and CH₂ double activation of indolines by radical translocation: Understanding the chemistry of the indolyl radical

David C. Harrowven,* Kerri J. Stenning, Sally Whiting, Toby Thompson and Robert Walton

CH activation and CH₂ double activation of indolines at C2 may be achieved efficiently through radical translocation. The fate of the C2 indolyl radical is dictated by the substitution at C3.

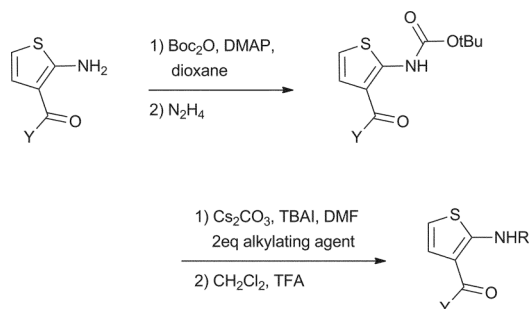


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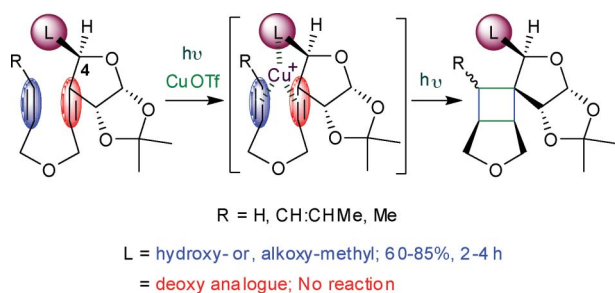
New methodology for the *N*-alkylation of 2-amino-3-acylthiophenes

Luigi Aurelio, Bernard L. Flynn and Peter J. Scammells*

The synthesis of 2-alkyl-3-acylaminothiophenes under mild conditions in which the corresponding 2-carbamoylamino and 2-acylamino-3-acylthiophenes are prepared and treated with an alkylating agent, caesium carbonate, and tetrabutylammonium iodide in DMF is reported.



4903

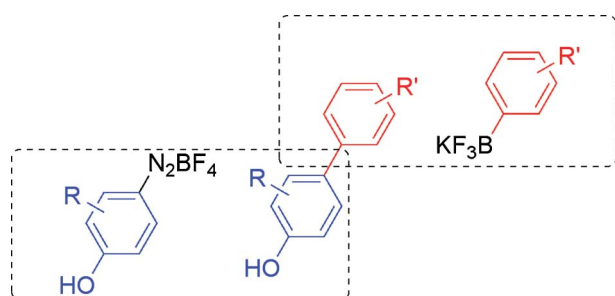


Unprecedented influence of remote substituents on reactivity and stereoselectivity in Cu(I)-catalysed [2 + 2] photocycloaddition. An approach towards the synthesis of tricycloclavulone

Sujit Mondal, Ram Naresh Yadav and Subrata Ghosh*

Hydroxy alkyl substituents at C₄ facilitate Cu(I)-catalysed [2 + 2] photocycloaddition of dienes embedded in a furano sugar while a C₄-deoxy substituent inhibits cycloaddition.

4914

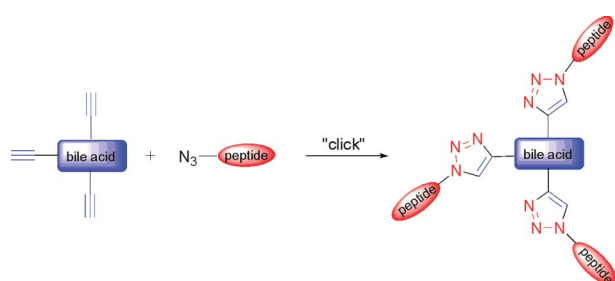


Suzuki–Miyaura cross coupling reactions with Phenoldiazonium salts

Bernd Schmidt* and Frank Hölter

Unprotected phenol diazonium salts are versatile building blocks for the Pd-catalyzed synthesis of 4-hydroxybiaryls.

4921

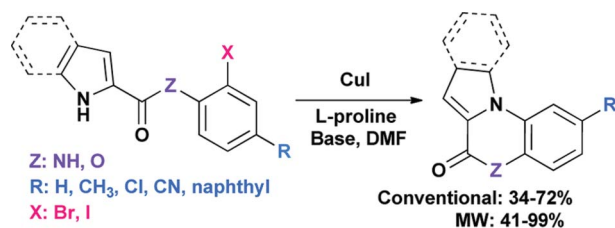


Design and synthesis of bile acid–peptide conjugates linked via triazole moiety

Nadezhda V. Sokolova, Gennadij V. Latyshev, Nikolay V. Lukashev and Valentine G. Nenajdenko*

Novel bile acid–peptide conjugates linked *via* a 1,2,3-triazole moiety based on cholic, deoxycholic and lithocholic acid derivatives were synthesized using Cu(I)-catalyzed 1,3-dipolar cycloaddition (“click” reaction).

4927



Synthesis of pyrrole and indole quinoxalinone and oxazinone derivatives by intramolecular copper-catalyzed reactions

Victoria A. Vaillard, Roberto A. Rossi* and Sandra E. Martín*

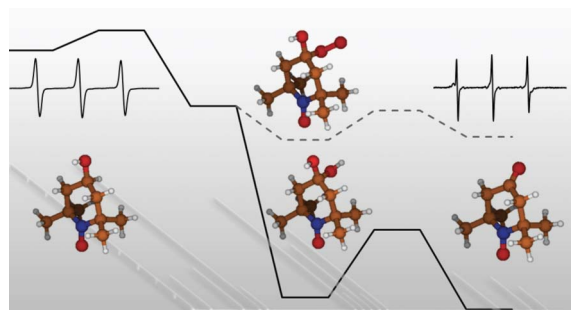
N-Arylation of pyrrole and indole carboxamides and carboxylates by intramolecular Cu-catalyzed reactions to synthesize quinoxalinone and oxazinone.

4936

Oxidation of 4-substituted TEMPO derivatives reveals modifications at the 1- and 4-positions

David L. Marshall, Meganne L. Christian, Ganna Gryn'ova, Michelle L. Coote, Philip J. Barker and Stephen J. Blanksby*

Synergistic ESR and ESI-MS analyses reveal modification of TEMPO derivatives at the 1- and 4-positions upon exposure to hydroxyl radicals.

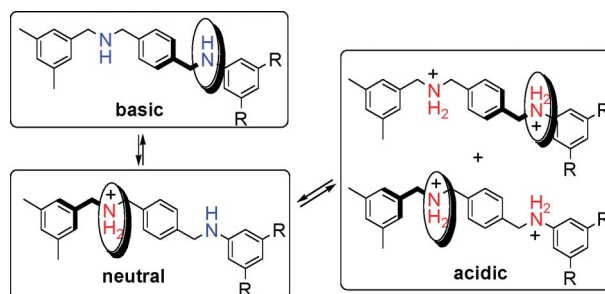


4948

Three-state molecular shuttles operated using acid/base stimuli with distinct outputs

Yuji Tokunaga,* Masanori Kawabata and Naoki Matsubara

The acid/base-mediated three-state translational isomerization of two [2]rotaxanes, containing two different amine centers as binding sites for dibenzo[24]crown-8.

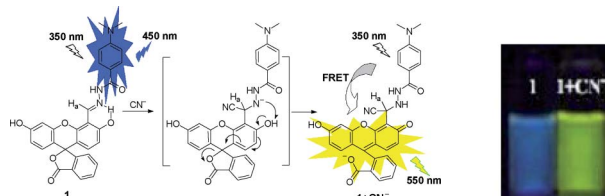


4954

A ratiometric fluorescent probe for cyanide based on FRET

Xin Lv, Jing Liu, Yunlong Liu, Yun Zhao, Maliang Chen, Pi Wang and Wei Guo*

On the basis of FRET from 4-(*N,N*-dimethylamino)benzamide to fluorescein monoanion, a new ratiometric fluorescence probe bearing a hydrazone binding unit was developed for highly selective and sensitive detection of CN^- in aqueous solution.

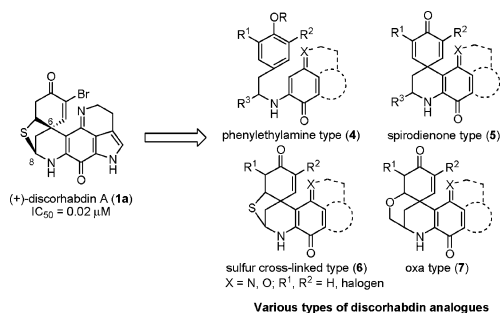


4959

The synthetic and biological studies of discorhabdins and related compounds

Yasufumi Wada, Yu Harayama, Daigo Kamimura, Masako Yoshida, Tomoyuki Shibata, Kousaku Fujiwara, Koji Morimoto, Hiromichi Fujioka* and Yasuyuki Kita*

Various types of discorhabdins and related analogues were synthesized and examination of biological activities of these compounds was achieved.



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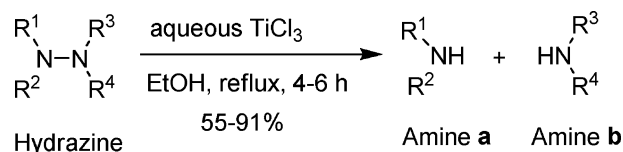
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4977

Reduction of hydrazines to amines with aqueous solution of titanium(III) trichloride

Yan Zhang, Qiang Tang and Meiming Luo*

The N–N bonds in hydrazines are readily cleaved by aqueous titanium(III) trichloride with good functional group tolerance within a broad pH range, affording amines in good yields.



4983

Ready synthesis of free *N-H* 2-arylindoles via the copper-catalyzed amination of 2-bromo-arylacetylenes with aqueous ammonia and sequential intramolecular cyclization

Huifeng Wang, Yaming Li,* Linlin Jiang, Rong Zhang, Kun Jin, Defeng Zhao and Chunying Duan*

The atom economical and low cost synthesis of free *N-H* 2-arylindoles via the copper(II)-catalyzed amination of 2-bromo-arylacetylenes with aqueous ammonia and sequential intramolecular cyclization.



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