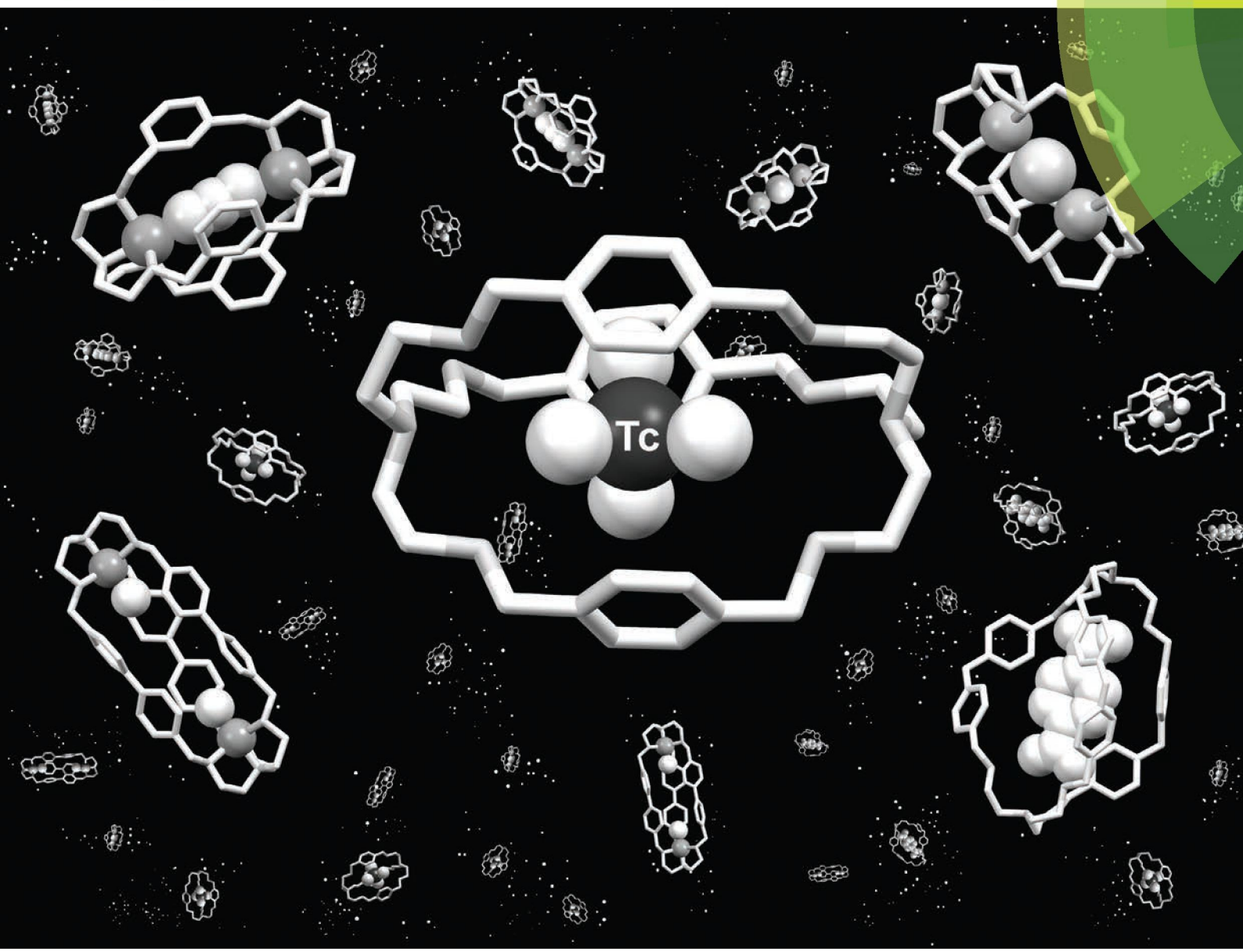
Volume 13 | Number 12 | 28 March 2015 | Pages 3495–3832

Organic & Biomolecular Chemistry

www.rsc.org/obc



ISSN 1477-0520

ROYAL SOCIETY OF CHEMISTRY

REVIEW ARTICLE

Luigi Fabbrizzi *et al.*

Bistren cryptands and cryptates: versatile receptors for anion inclusion and recognition in water

Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

www.rsc.org/obc

The Royal Society of Chemistry is the world's leading chemistry community. Through our high impact journals and publications we connect the world with the chemical sciences and invest the profits back into the chemistry community.

IN THIS ISSUE

ISSN 1477-0520 CODEN OBCRAK 13(12) 3495–3832 (2015)

Cover
See Luigi Fabbrizzi *et al.*, pp. 3510–3524.

Image reproduced by permission of Luigi Fabbrizzi from *Org. Biomol. Chem.*, 2015, **13**, 3510.

Inside cover
See Vijay Luxami, Kamaldeep Paul *et al.*, pp. 3525–3555.

Image reproduced by permission of Vijay Luxami and Kamaldeep Paul from *Org. Biomol. Chem.*, 2015, **13**, 3525.

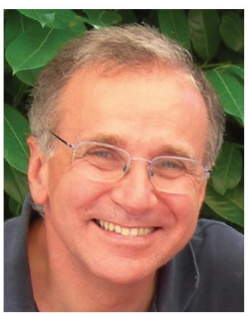
EDITORIAL

3508

Editorial: Recognition and reactivity at interfaces

Paolo Scrimin

Showcasing a collection of cutting edge contributions on the topic of Recognition and Reactivity at Interfaces.



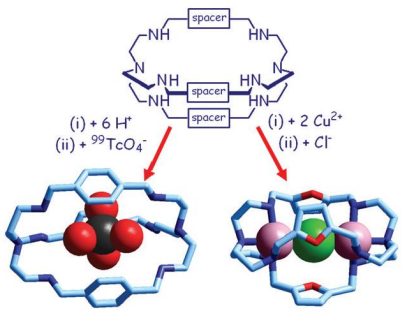
REVIEWS

3510

Bistren cryptands and cryptates: versatile receptors for anion inclusion and recognition in water

Giuseppe Alibrandi, Valeria Amendola, Greta Bergamaschi, Luigi Fabbrizzi* and Maurizio Licchelli

Bistren cryptands can act as selective anion receptors in water in two distinct versions: as hexaprotonated cages and as dicopper(II) cryptates. Both classes of receptors exert geometrical selectivity, but dimetallic cryptates establish the strongest interactions with the anion.



Organic & Biomolecular Chemistry (print: ISSN 1477-0520; electronic: ISSN 1477-0539) is published 48 times a year by the Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK CB4 0WF.

All orders, with cheques made payable to the Royal Society of Chemistry, should be sent to RSC Order Department, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 0WF, UK
Tel +44 (0)1223 432398; E-mail orders@rsc.org

2015 Annual (print+electronic) subscription price: £4572; US$8534. 2015 Annual (electronic) subscription price: £4343; US$8107 Customers in Canada will be subject to a surcharge to cover GST. Customers in the EU subscribing to the electronic version only will be charged VAT. If you take an institutional subscription to any RSC journal you are entitled to free, site-wide web access to that journal. You can arrange access via Internet Protocol (IP) address at **www.rsc.org/ip**. Customers should make payments by cheque in sterling payable on a UK clearing bank or in US dollars payable on a US clearing bank.

Organic & Biomolecular Chemistry

An international journal of synthetic, physical and biomolecular organic chemistry

www.rsc.org/obc

Organic & Biomolecular Chemistry brings together molecular design, synthesis, structure, function and reactivity in one journal. Broad in scope, it publishes research and reviews on topics across organic synthesis, physical organic chemistry, supramolecular chemistry and chemical biology.

Editorial board

Advisory board

Information for authors

Full details on how to submit material for publication in Organic & Biomolecular Chemistry are given in the Instructions for Authors (available from http://www.rsc.org/authors). Submissions should be made via the journal's homepage: http://www.rsc.org/obc.

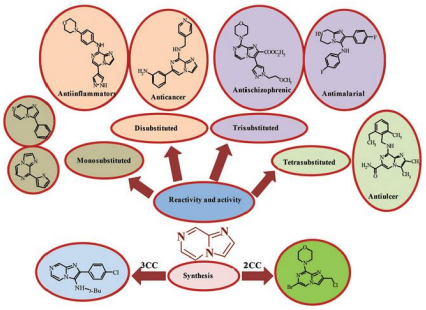
REVIEWS

3525

Recent advances in development of imidazo[1,2-*a*]pyrazines: synthesis, reactivity and their biological applications

Richa Goel, Vijay Luxami* and Kamaldeep Paul*

The synthesis, reactivity and multifarious biological activities at the different positions of imidazo[1,2-*a*]pyrazines are concisely discussed in this review.



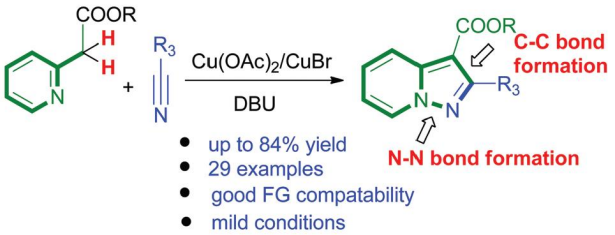
COMMUNICATIONS

3556

Copper-mediated synthesis of pyrazolo[1,5-*a*]pyridines through oxidative linkage of C–C/N–N bonds

Darapaneni Chandra Mohan, Chitrakar Ravi, Sadu Nageswara Rao and Subbarayappa Adimurthy*

Copper-mediated synthesis of pyrazolo[1,5-*a*]pyridine-3-carboxylates through oxidative linkage of C–C and N–N bonds under mild reaction conditions with broad substrate scope is described.

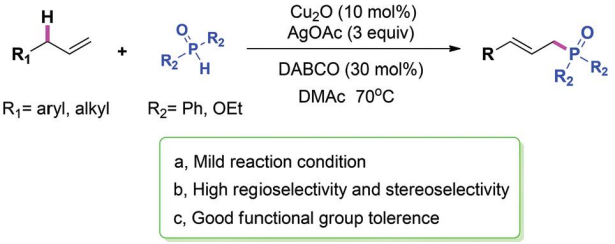


3561

Copper-catalyzed allylic C–H phosphonation

Bin Yang, Hong-Yu Zhang and Shang-Dong Yang*

A novel copper-catalyzed allylic C–H phosphonation reaction has been developed under mild reaction conditions.

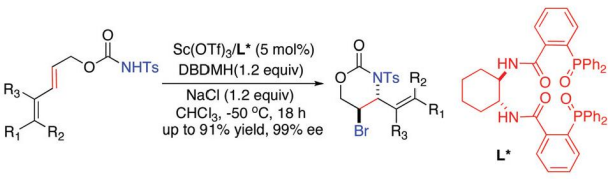


3566

Enantioselective 6-*endo* bromoaminocyclization of 2,4-dienyl *N*-tosylcarbamates catalyzed by a chiral phosphine oxide-Sc(OTf)$_3$ complex. A dramatic additive effect

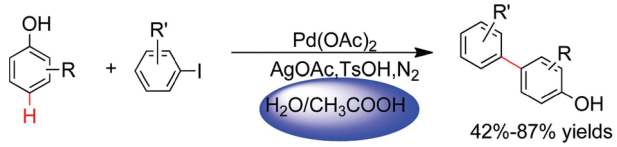
Hu Huang, Hongjie Pan, Yudong Cai, Mao Liu, Hua Tian and Yian Shi*

This paper describes an effective enantioselective 6-*endo* bromoaminocyclization of 2,4-dienyl *N*-tosylcarbamates catalyzed by a chiral phosphine oxide-Sc(OTf)$_3$ complex with a dramatic additive effect.



COMMUNICATIONS

3571

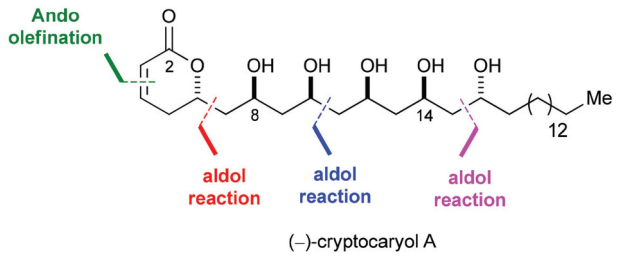


Palladium-catalyzed direct arylation of phenols with aryl iodides

Rongrong Long, Xufei Yan, Zhiqing Wu, Zhengkai Li, Haifeng Xiang and Xiangge Zhou*

An efficient protocol of palladium-catalyzed direct *para*-arylation of unfunctionalized phenols with aryl iodides under mild conditions was reported.

3575

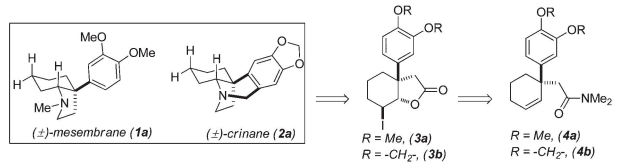


The total synthesis of (–)-cryptocaryol A

L. C. Dias,* P. K. Kuroishi and E. C. de Lucca Jr.

A stereoselective total synthesis of (–)-cryptocaryol A (**1**) is described. Key features of the 17-step route include the use of three boron-mediated aldol reaction–reduction sequences to control all stereocenters and an Ando modification of the Horner–Wadsworth–Emmons olefination that permitted the installation of the *Z* double bond of the α-pyrone ring.

3585

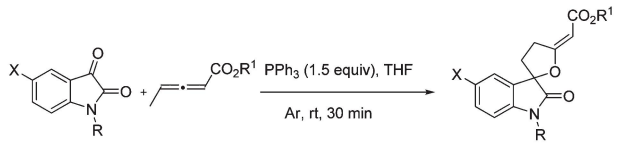


Concise total syntheses of (±)-mesembrane and (±)-crinane

Mrinal Kanti Das, Subhadip De, Shubhashish and Alakesh Bisai*

A unified approach to the Amaryllidaceae alkaloids having a *cis*-3a-aryloctahydroindole scaffold is developed *via* a key Eschenmoser–Claisen rearrangement of all-carbon quaternary stereocenters present in these alkaloids. Utilizing this strategy, a concise total synthesis of (±)-mesembrane and (±)-crinane is achieved.

3589



Phosphine-mediated reaction of 3-methyl allenoate and isatins: a protocol for the synthesis of spirofuran oxindoles

Anu Jose, A. J. Jayakrishnan, K. C. Seetha Lakshmi, Sunil Varughese and Vijay Nair*

A facile synthesis of spirofuran oxindoles *via* phosphine-mediated reaction of 3-alkyl allenoate with isatins is presented.

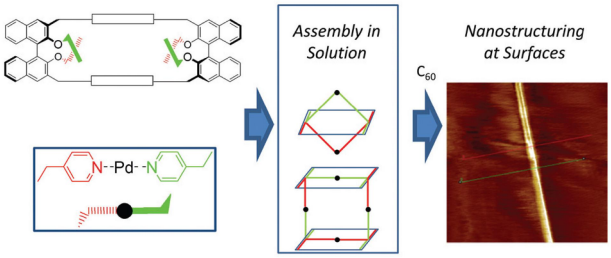
PAPERS

3593

Chiral nanostructuring of multivalent macrocycles in solution and on surfaces

Marco Caricato, Arnaud Delforge, Davide Bonifazi, Daniele Dondi, Andrea Mazzanti and Dario Pasini*

A chiral, multivalent macrocycle assembles upon metal–pyridine coordination into ordered nanostructures in solution and on surfaces.

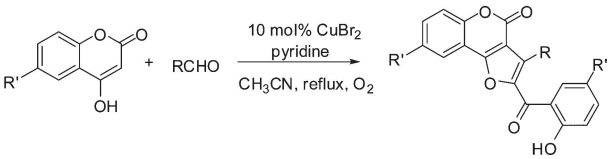


3602

Copper(II) bromide-catalyzed intramolecular decarboxylative functionalization to form a C(sp^3)–O bond for the synthesis of furo[3,2-*c*]coumarins

W. L. Zhang, S. N. Yue, Y. M. Shen, H. Y. Hu, Q.-H. Meng, H. Wu* and Y. Liu*

Copper(II) bromide-catalyzed intramolecular decarboxylative functionalization to form a C(sp^3)–O bond has been developed.

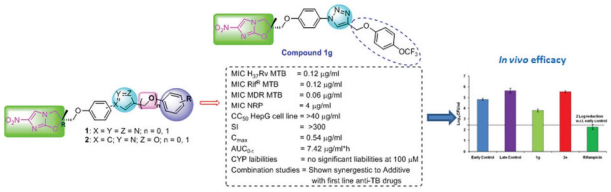


3610

Synthesis of new generation triazolyl- and isoxazolyl-containing 6-nitro-2,3-dihydroimidazooxazoles as anti-TB agents: *in vitro*, structure–activity relationship, pharmacokinetics and *in vivo* evaluation

G. Munagala, K. R. Yempalla, S. Singh, S. Sharma, N. P. Kalia, V. S. Rajput, S. Kumar, S. D. Sawant, I. A. Khan,* R. A. Vishwakarma* and P. P. Singh*

Promising nitroimidazoloxazole scaffold gives another novel triazolyl-containing 6-nitro-2,3-dihydroimidazooxazole as anti-TB lead.

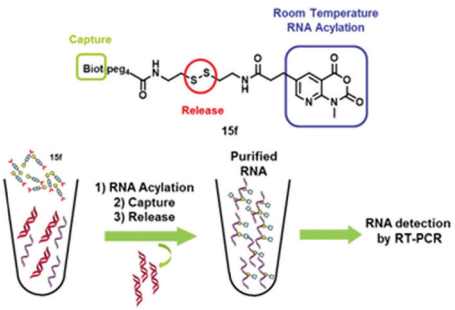


3625

A biotin-conjugated pyridine-based isatoic anhydride, a selective room temperature RNA-acylating agent for the nucleic acid separation

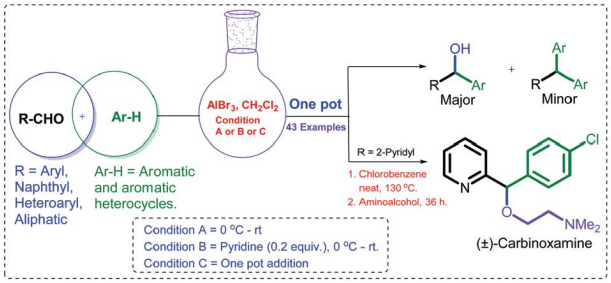
S. Ursuegui, R. Yougnia, S. Moutin, A. Burr, C. Fossey, T. Cailly, A. Laayoun, A. Laurent* and F. Fabis*

A biotin-conjugated pyridine based isatoic anhydride has been designed and evaluated for nucleic acid separation after RNA 2′-OH acylation at room temperature.



PAPERS

3633

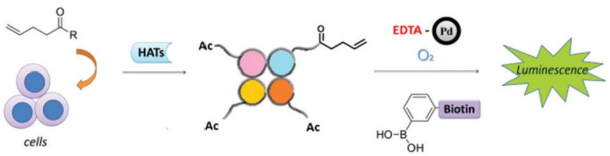


The cooperative effect of Lewis pairs in the Friedel–Crafts hydroxyalkylation reaction: a simple and effective route for the synthesis of (±)-carbinoxamine

Harikrishnan Adhikesavan, Sanjeevi Jayakumar and Ramanathan Chinnasamy Ramaraj*

Lewis acid (with or without a Lewis base) enhances the electrophilicity of aldehydes to react with aromatic π-nucleophiles and generate carbinols.

3648

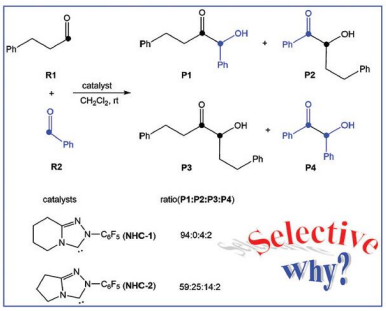


Metabolic alkene labeling and *in vitro* detection of histone acylation *via* the aqueous oxidative Heck reaction

Maria E. Ourailidou, Paul Dockerty, Martin Witte, Gerrit J. Poelarends and Frank J. Dekker*

EDTA-Pd(II) as a novel catalyst for protein labeling *via* the aqueous oxidative Heck reaction.

3654

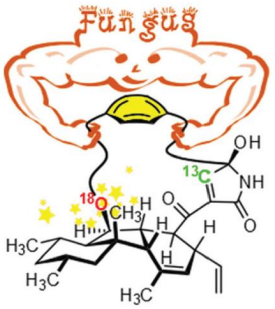


Theoretical investigation on the chemoselective N-heterocyclic carbene-catalyzed cross-benzoin reactions

Tao Liu, Shu-Min Han, Ling-Li Han, Lu Wang, Xiang-Yang Cui, Chong-Yang Du and Siwei Bi*

A density functional theory study was performed to understand the detailed mechanisms of the cross-benzoin reactions catalyzed by N-heterocyclic carbene (NHC) species.

3662



Direct biosynthetic cyclization of a distorted paracyclophane highlighted by double isotopic labelling of L-tyrosine

Alexandre Ear, Séverine Amand, Florent Blanchard, Alain Blond, Lionel Dubost, Didier Buisson* and Bastien Nay*

The biosynthesis of pyrrocidines was investigated using a double (^{18}O,^{13}C) labelling of L-tyrosine. It shows that the phenolic ^{18}O is incorporated during aryl ether bond formation.

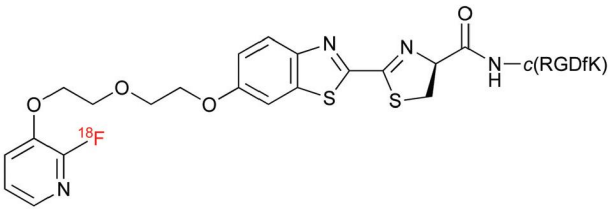
PAPERS

3667

A novel 2-cyanobenzothiazole-based ^{18}F prosthetic group for conjugation to 1,2-aminothiol-bearing targeting vectors

James A. H. Inkster, Didier J. Colin and Yann Seimbille*

[^{18}F]FPyPEGCBT is a new ^{18}F labelling agent which contains a 2-substituted pyridine for incorporation of [^{18}F]F$^-$ and a 2-cyanobenzothiazole moiety for chemo-selective conjugation to 1,2-aminothiol-bearing biomolecules.

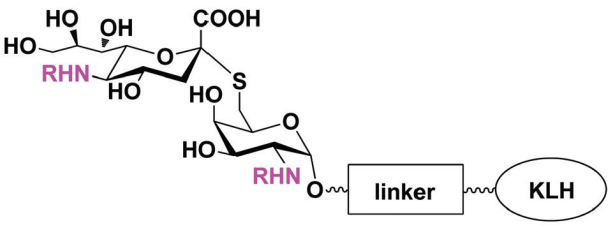


3677

Synthetic and immunological studies of *N*-acyl modified *S*-linked STn derivatives as anticancer vaccine candidates

Chang-Xin Huo, Xiu-Jing Zheng, An Xiao, Chang-Cheng Liu, Shuang Sun, Zhuo Lv and Xin-Shan Ye*

N-Modified *S*-linked STn glycoconjugates significantly stimulated the production of IgG antibodies capable of recognizing the naturally occurring STn antigen.



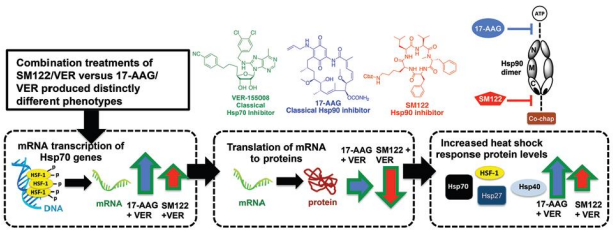
Modified glycoconjugates for vaccine development

3691

Combining an Hsp70 inhibitor with either an N- or C-terminal Hsp90 inhibitor produces mechanistically distinct phenotypes

Y. Wang and S. R. McAlpine*

Blocking the function of both heat shock protein 90 and 70 (Hsp90 and Hsp70) simultaneously limits these chaperones' cytoprotective effects on cancer cells.

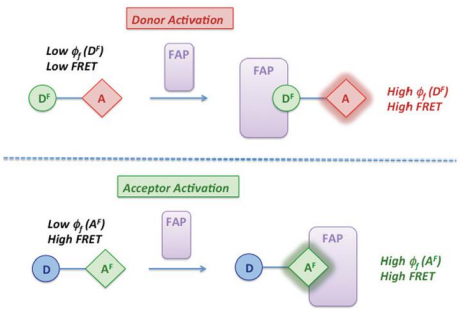


3699

Bichromophoric dyes for wavelength shifting of dye-protein fluoromodules

Ha H. Pham, Christopher Szent-Gyorgyi, Wendy L. Brotherton, Brigitte F. Schmidt, Kimberly J. Zanotti, Alan S. Waggoner and Bruce A. Armitage*

Dye-protein fluoromodules consist of fluorogenic dyes and single chain antibody fragments that form brightly fluorescent noncovalent complexes.



PAPERS

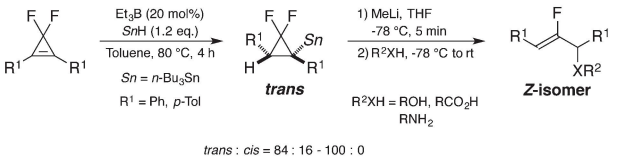
3711

$NiSO_4$-catalyzed C–H activation/C–S cross-coupling of 1,2,3-triazole *N*-oxides with thiols

Jiayi Zhu, Yu Chen, Feng Lin, Baoshuang Wang, Zhengwang Chen* and Liangxian Liu*

An efficient nickel-catalyzed protocol for C–S cross-coupling through the direct functionalization of 2-aryl-1,2,3-triazole *N*-oxide C–H bonds with aryl or alkyl thiols, or diphenyl disulfide has been developed.

3721

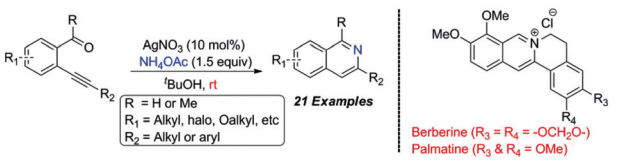


An efficient approach to *gem*-difluorocyclopropylstannanes *via* highly regio- and stereoselective hydrostannylation of *gem*-difluorocyclopropenes and their unique ring-opening reaction to afford β-fluoroallylic alcohols

T. Nihei, T. Hoshino and T. Konno*

gem-Difluorocyclopropylstannanes, prepared *via* the hydrostannylation of *gem*-difluorocyclopropenes, were treated with MeLi and then quenching agents, to give (*Z*)-β-fluoroallyllic alcohols, ethers, esters, and amides.

3732

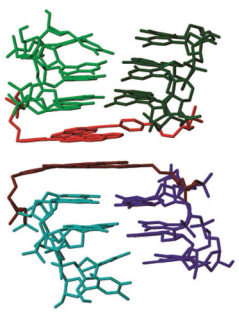


A room-temperature protocol to access isoquinolines through Ag(I) catalysed annulation of *o*-(1-alkynyl)arylaldehydes and ketones with NH_4OAc: elaboration to berberine and palmatine

Virsinha Reddy, Abhijeet S. Jadhav and Ramasamy Vijaya Anand*

A silver catalysed protocol for the synthesis of a wide range of isoquinolines from *o*-(1-alkynyl)arylaldehydes has been developed under mild conditions and elaborated to the synthesis of berberine and palmatine.

3742



Interdependence of pyrene interactions and tetramolecular G4-DNA assembly

Osman Doluca, Jamie M. Withers, Trevor S. Loo, Patrick J. B. Edwards, Carlos González and Vyacheslav V. Filichev*

Our results demonstrate the expanded capabilities of G-quadruplex DNAs for directed chromophore arrangements and show new perspectives in the design of G-quadruplexes governed by non-guanine moieties.

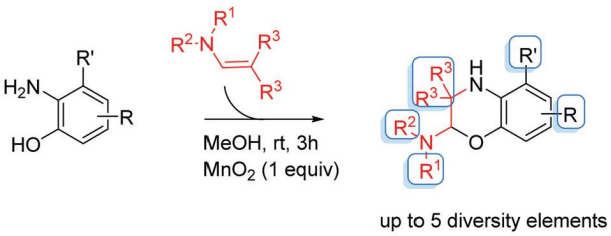
PAPERS

3749

Regiospecific synthesis of neuroprotective 1,4-benzoxazine derivatives through a tandem oxidation–Diels–Alder reaction

Khac Minh Huy Nguyen, Leslie Schwendimann, Pierre Gressens and Martine Largeron*

Highly functionalized 1,4-benzoxazine derivatives have been synthesized at room temperature, with complete regiochemical control, through a tandem oxidation–Diels–Alder reaction.

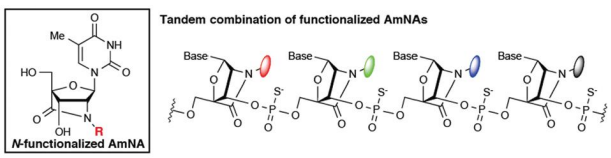


3757

Amido-bridged nucleic acids with small hydrophobic residues enhance hepatic tropism of antisense oligonucleotides *in vivo*

Tsuyoshi Yamamoto, Aiko Yahara, Reiko Waki, Hidenori Yasuhara, Fumito Wada, Mariko Harada-Shiba and Satoshi Obika*

High scalability of a novel bicyclic nucleoside building block, amido-bridged nucleic acid (AmNA), to diversify pharmacokinetic properties of therapeutic antisense oligonucleotides is described.

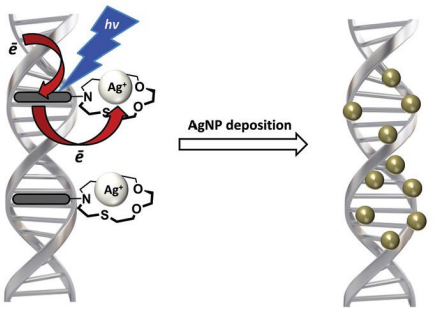


3766

Photoinduced formation of stable Ag-nanoparticles from a ternary ligand-DNA-Ag^+ complex

Daria V. Berdnikova, Heiko Ihmels,* Holger Schönherr, Marc Steuber and Daniel Wesner

The irradiation of a ternary complex between an intercalator crown-ether conjugate, double-stranded DNA, and Ag^+ ions leads to the formation of stable Ag nanoparticles.

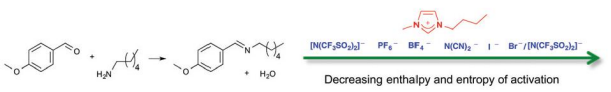


3771

Developing principles for predicting ionic liquid effects on reaction outcome. The importance of the anion in controlling microscopic interactions

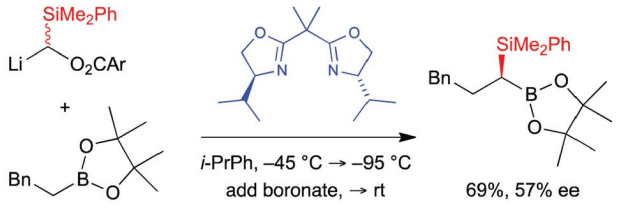
Sinead T. Keaveney, Ronald S. Haines and Jason B. Harper*

Predictable changes in the rate constant of a condensation reaction were seen as the solvent composition was varied. The cation–nucleophile interaction could be controlled in a predictable manner; activation parameters varied linearly with the H-bond acceptor ability of the anions used.



PAPERS

3781



• 3 examples of α-silylalkylboronate synthesis: 35-69%, 9-57% ee
• 9 examples of α-phenylalkylboronate synthesis: 35-83%, 70-96% ee

Enantioselective synthesis of α-phenyl- and α-(dimethylphenylsilyl)alkylboronic esters by ligand mediated stereoinductive reagent-controlled homologation using configurationally labile carbenoids

Adam L. Barsamian, Zhenhua Wu and Paul R. Blakemore*

Enantioselective chain extension of boronic esters with configurationally labile racemic carbenoids is achieved in the presence of scalemic bisoxazoline ligands.

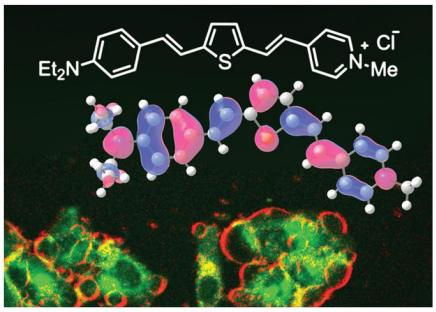
3787

Gold-catalyzed allene cycloisomerization for pyrrole synthesis: towards highly fluorinated BODIPY dyes

Linda Lempke, Tobias Fischer, Jérémy Bell, Werner Kraus, Knut Rurack* and Norbert Krause*

A novel synthetic strategy toward highly fluorinated BODIPY dyes with exceptional photostabilities relying on sustainable gold catalysis has been developed.

3792

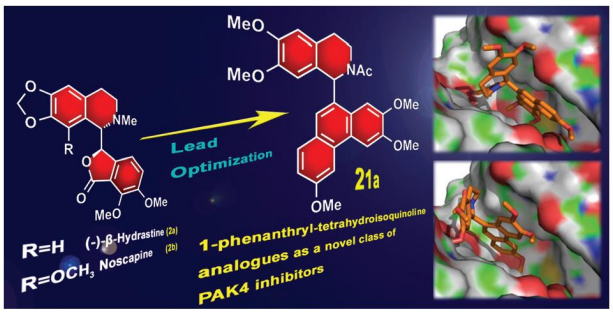


Thiophene-based dyes for probing membranes

Ismael López-Duarte, Phoom Chairatana, Yilei Wu, Javier Pérez-Moreno, Philip M. Bennett, James E. Reeve, Igor Boczarow, Wojciech Kaluza, Neveen A. Hosny, Samuel D. Stranks, Robin J. Nicholas, Koen Clays,* Marina K. Kuimova* and Harry L. Anderson*

We report the synthesis of four new cationic push–pull membrane probes based on a thiophene core and evaluate their photobiological properties.

3803



Design, synthesis and biological evaluation of 1-phenanthryl-tetrahydroisoquinoline derivatives as novel p21-activated kinase 4 (PAK4) inhibitors

Shuai Song, Xiaodong Li, Jing Guo, Chenzhou Hao, Yan Feng, Bingyu Guo, Tongchao Liu, Qiaoling Zhang, Zhen Zhang, Ruijuan Li, Jian Wang, Bin Lin, Feng Li,* Dongmei Zhao* and Maosheng Cheng*

Following the screening of an in-house natural product database, 1-phenanthryltetrahydroisoquinoline analogues were synthesized as novel PAK4 inhibitors.

3819

Synthesis of 3-aminoBODIPY dyes *via* copper-catalyzed vicarious nucleophilic substitution of 2-halogeno derivatives

Julian G. Knight,* Rua B. Alnoman and Paul G. Waddell

Copper catalysed vicarious nucleophilic substitution of 2-halogeno BODIPYs with alkyl amines, anilines and an amide produces the corresponding 3-aminoBODIPY derivatives.