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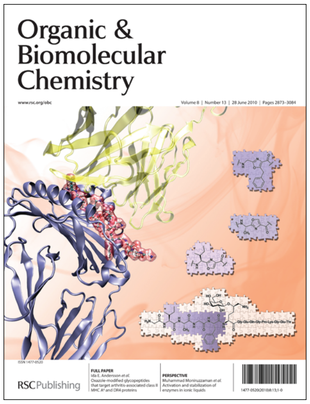
ISSN 1477-0520 CODEN OBCRAK 8(13) 2873–3084 (2010)



Cover
See Andersson *et al.*,
pp. 2931–2940.
Oxazole-modified glycopeptides that probe interactions with class II MHC proteins and T-cell receptors associated with autoimmune arthritis.

Image reproduced by permission of Mattias Hedenström and Ida Andersson from *Org. Biomol. Chem.*, 2010, **8**, 2931.

Inside cover
See Wang *et al.*,
pp. 2923–2925.
New aminonaphthalimide imidazolium podands as luminescence chemosensors were prepared for selectively sensing nucleoside polyphosphates ADP and ATP in living cells.

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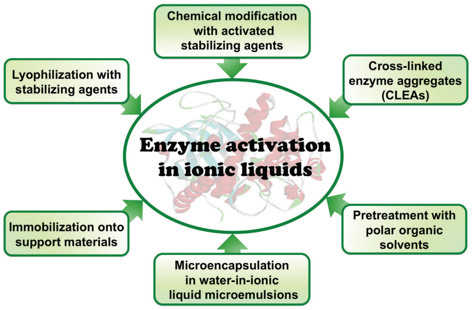
PERSPECTIVES

2887

Activation and stabilization of enzymes in ionic liquids

Muhammad Moniruzzaman, Noriho Kamiya and Masahiro Goto*

Ionic liquids are being increasingly exploited as potential "green" solvents for biocatalytic processes. This perspective summarizes a number of diverse strategies being used successfully for activation and stabilization of enzymes in ionic liquids.

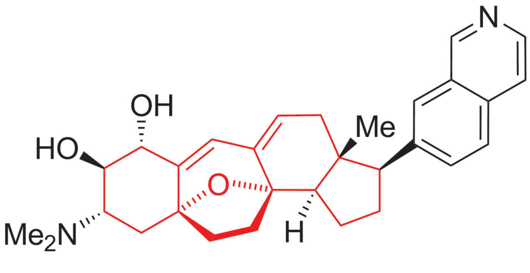


2900

Chemistry of the cortistatins–a novel class of *anti*-angiogenic agents

David Yu-Kai Chen* and Chih-Chung Tseng

This article provides a comprehensive overview of the synthetic studies of the cortistatin family of *anti*-angiogenic agents. In particular, the synthetic strategies employed in the construction of the oxo-bridged pentacyclic core of the cortistatins are illustrated.



Cortistatin A

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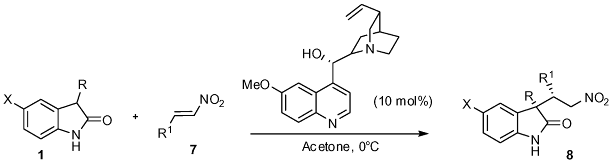
2912

Organocatalytic Michael addition of unprotected 3-substituted oxindoles to nitroolefins

Miao Ding, Feng Zhou, Zi-Qing Qian and Jian Zhou*

Quinidine was found to catalyze the Michael addition of unprotected 3-substituted oxindoles to nitroolefins in excellent yield and moderate to good diastereoselectivity. Bifunctional quinidine derived thiourea catalyst could catalyze this reaction to afford the major diastereomer in 85% ee.



R and R^1: aryl or alkyl groups

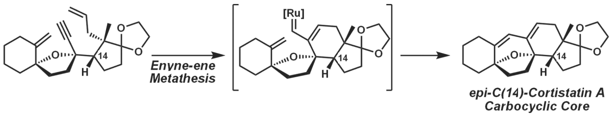
14 examples, 61-96% yield, 1.6/1.0-5.0/1.0 dr

2915

Efforts toward rapid construction of the cortistatin A carbocyclic core *via* enyne-ene metathesis

Corinne Baumgartner, Sandy Ma, Qi Liu and
Brian M. Stoltz*

Our efforts toward the construction of the cortistatin A carbocyclic core *via* an enyne-ene metathesis are disclosed. Interestingly, an attempted S_N2 inversion of a secondary mesylate in our five-membered D-ring piece gave a product with retention of stereochemistry.

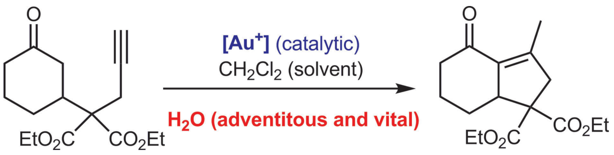


2918

Gold-catalysed room-temperature cycloisomerisation of alkynes and unactivated enolisable ketones

Paul W. Davies* and Christelle Detty-Mambo

The cycloisomerisation of simple keto-alkynes proceeds at room temperature under the mild conditions of gold catalysis. Bicyclic fused and spiro compounds can be obtained by overall 5-*exo* and 6-*exo* carbon–carbon bond-forming cyclisations.

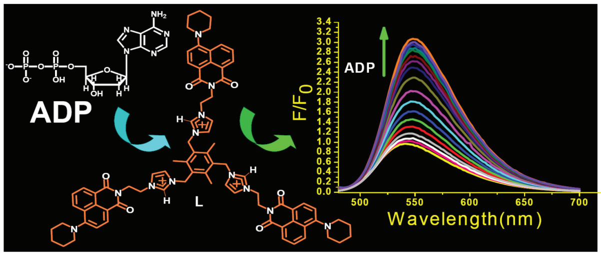


2923

Aminonaphthalimide-based imidazolium podands for turn-on fluorescence sensing of nucleoside polyphosphates

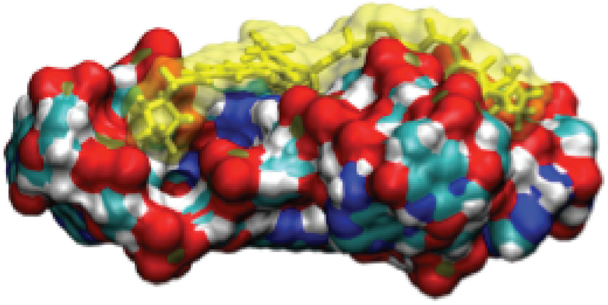
Dehui Wang, Xiaolin Zhang, Cheng He and
Chunying Duan*

New aminonaphthalimide imidazolium podands as luminescence chemosensors were prepared for selectively sensing nucleoside polyphosphates ADP and ATP in living cells.



COMMUNICATIONS

2926



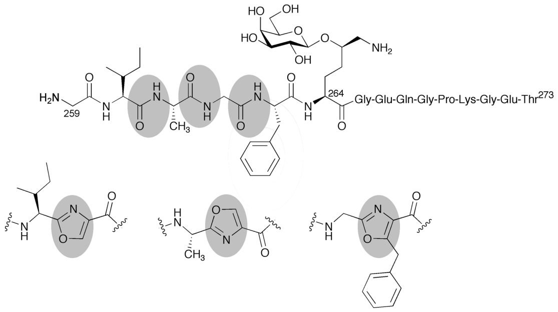
A click chemistry approach to C_3 symmetric, G-quadruplex stabilising ligands

John E. Moses,* Dougal J. Ritson, Fengzhi Zhang, Caterina Maria Lombardo, Shozeb Haider, Neil Oldham and Stephen Neidle*

A structure-based design and syntheses of a series of tris-triazole G-quadruplex binding ligands was achieved. These novel compounds display excellent selectivity for quadruplex DNA over duplex DNA.

PAPERS

2931

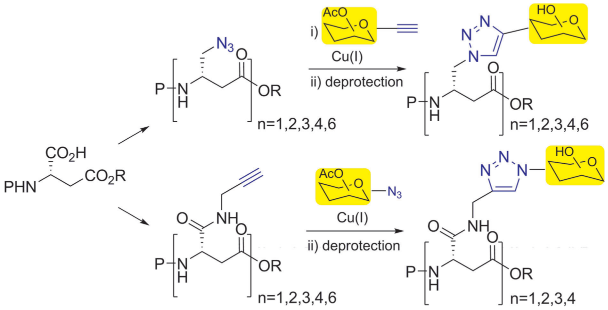


Oxazole-modified glycopeptides that target arthritis-associated class II MHC A^q and DR4 proteins

Ida E. Andersson, Tsvetelina Batsalova, Balik Dzhambazov, Lotta Edvinsson, Rikard Holmdahl, Jan Kihlberg* and Anna Linusson*

Oxazole-modified glycopeptides have been synthesized and evaluated for binding to arthritis-associated class II MHC A^q and DR4 proteins, as well as for their ability to stimulate autoimmune T-cell hybridomas.

2941

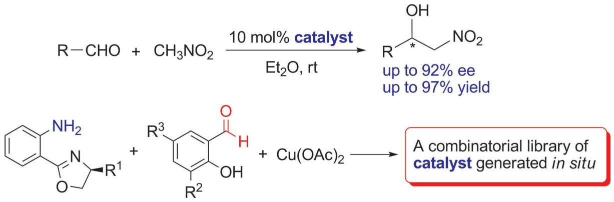


Click glycoconjugation of per-azido- and alkynyl-functionalized β-peptides built from aspartic acid

Marielle Barra, Olivier Roy, Mounir Traïkia and Claude Taillefumier*

Azide- and alkynyl-containing homo-β^3-peptides were synthesised from aspartic acid. Their subsequent conjugation with monosaccharides was efficiently achieved by copper-mediated cycloadditions leading to two novel families of glycoclusters. These compounds represent ideal tools to explore carbohydrate-mediated multivalent interactions.

2956



Efficient *in situ* three-component formation of chiral oxazoline-Schiff base copper(II) complexes: towards combinatorial library of chiral catalysts for asymmetric Henry reaction

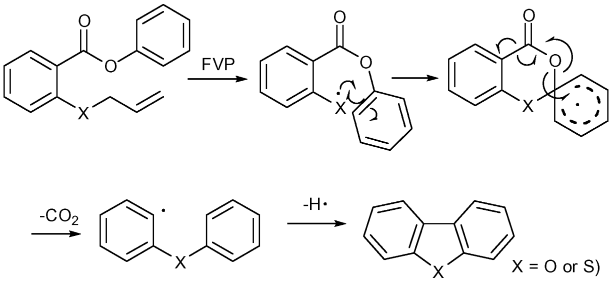
Wen Yang, Han Liu and Da-Ming Du*

A combinatorial *in situ* three-component chiral oxazoline-Schiff base copper(II) complex catalyst formation method was developed. This modular library of complex catalysts was evaluated in an asymmetric Henry reaction. Good yields and up to 92% ee were obtained.

2961

Formation of dibenzofurans by flash vacuum pyrolysis of aryl 2-(allyloxy)benzoates and related reactions

Michael Black, J. I. G. Cadogan* and Hamish McNab*

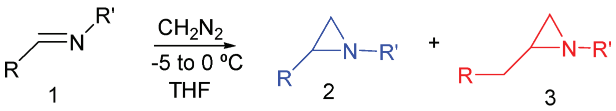


Flash vacuum pyrolysis of aryl 2-(allyloxy)benzoates and of the corresponding aryl 2-(allylthio)benzoates at 650 °C, gives dibenzofurans and dibenzothiophenes, respectively. The scope and mechanism of this reaction are studied in detail.

2968

Catalyst-free aziridination and unexpected homologation of aziridines from imines

Paula Sério Branco,* Vivek Prabhakar Raje,*
Jorge Dourado and Joana Gordo

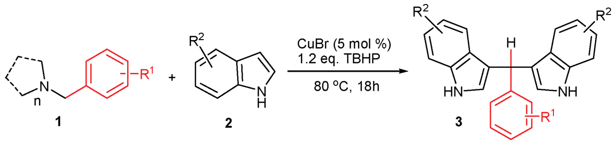


A mild, very simple and rapid procedure for the preparation of *N*-sulfonyl-2-substituted aziridines, involving an aziridination or unexpected homologation–aziridination reaction of *N*-sulfonylimines using diazomethane as the carbene source.

2975

CuBr-catalyzed selective oxidation of *N*-azomethine: highly efficient synthesis of methine-bridged bis-indole compounds

Jianguo Yang,* Zhijing Wang, Fuyou Pan, Yongmin Li and Weiliang Bao*

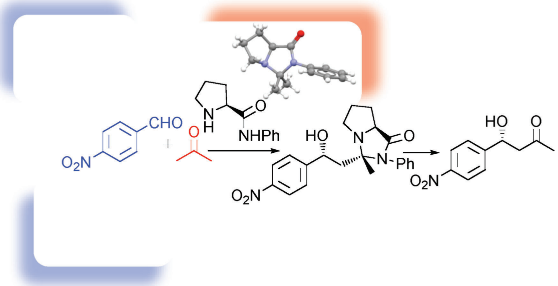


An efficient CuBr catalyzed cleavage of C–N bonds in the oxidative cross-dehydrogenative-coupling of *N*-benzyl amines with indoles mediated by *tert*-butyl hydroperoxide was reported. A series of methine-bridged bis-indole derivatives were successfully synthesized.

2979

Imidazolidinone intermediates in prolinamide-catalyzed aldol reactions

Ángel L. Fuentes de Arriba, Luis Simón, César Raposo, Victoria Alcázar, Francisca Sanz, Francisco M. Muñiz and Joaquín R. Morán*



The aldol reaction catalyzed by aromatic prolinamides has been studied in depth and several imidazolidinone intermediates detected and fully characterized. Their evolution and influence on the course of the reaction is also investigated.

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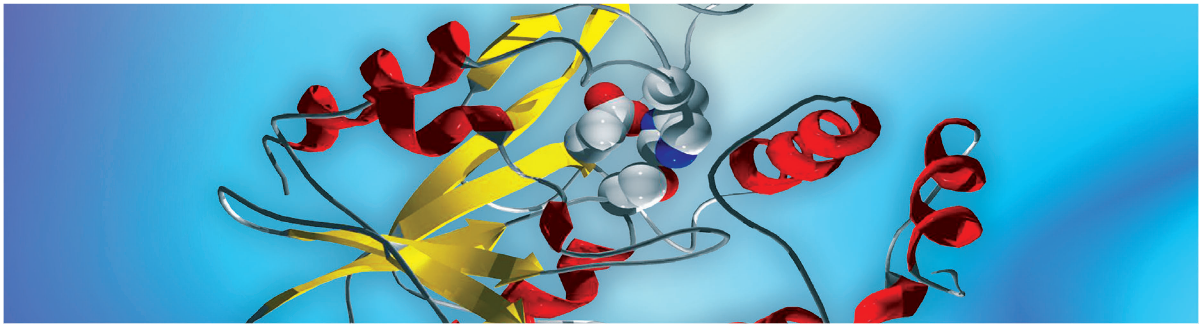
Directing Biosynthesis 2010: Discovery, Evolution, Function

15 - 17 September 2010, Durham University, UK
www.rsc.org/biosynth10



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Following the 2006 edition of the RSC's Directing Biosynthesis meeting, the subject area has broadened and matured, and the area of understanding and directing biosynthesis has become highly topical.

Directing Biosynthesis 2010 will feature the best of the worlds of terpene, alkaloid, non-ribosomal peptide and polyketide biosynthesis, with a focus on understanding and redirecting pathways in a wide variety of organisms.

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- Biosynthesis and enzymology
- Structural biology/directed evolution
- Pathway engineering, semi-synthetic products and synthetic biology

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Jon Clardy *Harvard Medical School, USA*
Seiichi Matsuda *Rice University, USA*
Joseph Noel *The Salk Institute for Biological Studies, USA*
Ben Shen *University of Wisconsin-Madison, USA*
Jon Thorson *University of Wisconsin-Madison, USA*
Sheryl Tsai *University of California, Irvine, USA*
Wilfred van der Donk *University of Illinois-Urbana/Champaign, USA*

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The following speakers have been invited to deliver lectures as members of the Natural Product Reports editorial board:

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Bradley Moore *University of California, San Diego, USA*
Kira Weissman *University of Saarland, Germany*

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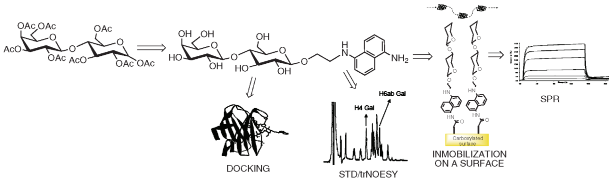
2986

Binding studies of adhesion/growth-regulatory galectins with glycoconjugates monitored by surface plasmon resonance and NMR spectroscopy

F. Javier Muñoz, J. Ignacio Santos, Ana Ardá, Sabine André,
Hans-Joachim Gabius, José V. Sinisterra,
Jesús Jiménez-Barbero and María J. Hernáiz*

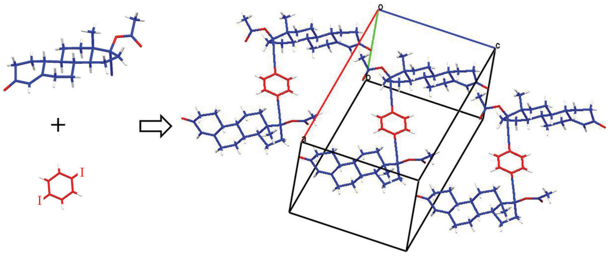


A fluorescent glycan, which can be easily immobilized on a surface, has been prepared. By using SPR, STD/trNOESY and docking measurements, it was possible to analyze galectin–glycan interactions in a sensitive, systematic, reliable and quantitative manner.

2993

Synthesis and solid state characterization of molecular rotors with steroidal stators: ethisterone and norethisterone

Braulio Rodríguez-Molina, Arturo Pozos, Ricardo Cruz,
Margarita Romero, Blas Flores, Noberto Farfán,
Rosa Santillan* and Miguel A. Garcia-Garibay*

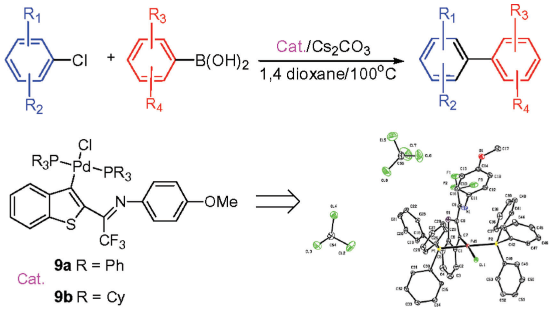


Illustrated here with ethistherone and norethisterone, 19-ethynyl-substituted steroids provide a promising and readily available platform for the one-step synthesis of molecular rotors with 1,4-phenylene groups acting as rotating units.

3001

New cyclopalladated benzothiophenes: a catalyst precursor for the Suzuki coupling of deactivated aryl chlorides

Madavu Salian Subhas, Shailesh S. Racharlawar, B. Sridhar,
P. Kavin Kennady, Pravin R. Likhar,*
Mannepalli Lakshmi Kantam and Suresh K. Bhargava

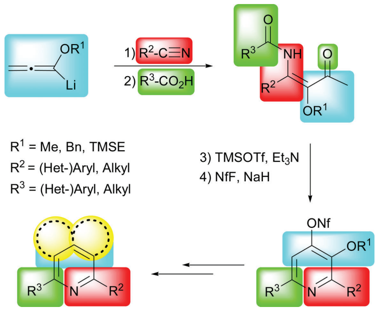


Treating benzothiophene-based palladacycles with excess phosphine ligand selectively afforded trans-bis(phosphine) palladium complexes in good yields. An acyclic palladium complex was tested as catalyst in the Suzuki coupling of sterically hindered aryl chlorides and boronic acids. The palladacycles were also tested for anticancer activity.

3007

A three-component synthesis of β-alkoxy-β-keto-enamides—flexible precursors for 4-hydroxypyridine derivatives and their palladium-catalysed reactions

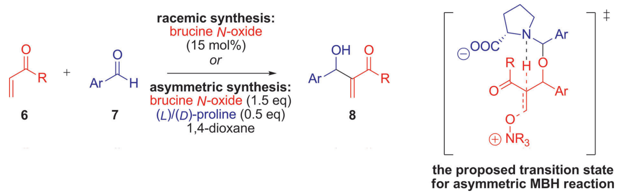
Tilman Lechel, Jyotirmayee Dash, Christian Eidamshaus,
Irene Brüdgam, Dieter Lentz and Hans-Ulrich Reissig*



Starting from lithiated alkoxyallenes a flexible three-component synthesis led to β-alkoxy-β-ketoenamide derivatives in good yields. Cyclisation and conversion into 4-pyridyl nonaflates allowed various palladium-catalysed reactions. Subsequent cyclisations led to furopyridine and benzoisoquinoline derivatives.

PAPERS

3015

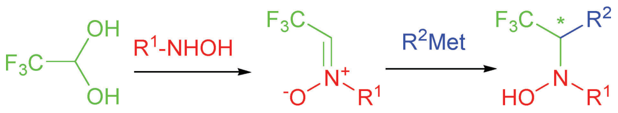


Brucine *N*-oxide-catalyzed Morita–Baylis–Hillman reaction of vinyl ketones: a mechanistic implication of dual catalyst system with proline

Kyungsoo Oh,* Jian-Yuan Li and Jinhyang Ryu

The asymmetric Morita–Baylis–Hillman reaction of vinyl ketones with electron-deficient aromatic aldehydes was catalyzed by proline in the presence of co-catalyst, brucine *N*-oxide.

3025

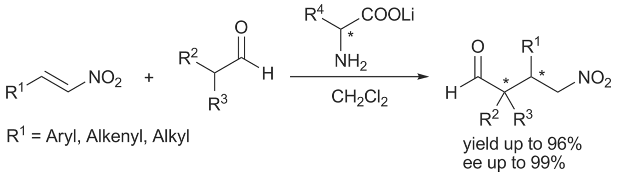


Trifluoromethyl nitrones: from fluoral to optically active hydroxylamines

Thierry Milcent, Nathan Hinks, Danièle Bonnet-Delpon and Benoit Crousse*

We present the nucleophilic diastereoselective additions of organometallic reagents to trifluoromethyl nitrones, affording the corresponding optically active trifluoroethyl hydroxylamines in good yields.

3031

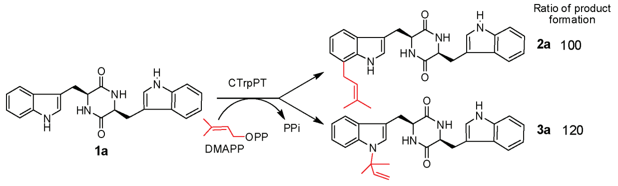


Asymmetric Michael addition of aldehydes to nitroalkenes using a primary amino acid lithium salt

Masanori Yoshida,* Atsushi Sato and Shoji Hara

Enantioselective Michael addition of aldehydes to nitroalkenes catalysed by L-phenylalanine lithium salt gave γ-nitroaldehydes in good yields with high enantioselectivity.

3037



Simultaneous C7- and N1-prenylation of cyclo-L-Trp-L-Trp catalyzed by a prenyltransferase from *Aspergillus oryzae*

Hui-Xi Zou, Xiu-Lan Xie, Uwe Linne, Xiao-Dong Zheng and Shu-Ming Li*

A recombinant prenyltransferase His$_6$-CTrpPT from *Aspergillus oryzae* catalyzes simultaneously the regular C7- and reverse N1-prenylation of tryptophan-containing cyclic dipeptides, as demonstrated by using cyclo-L-Trp-L-Trp.

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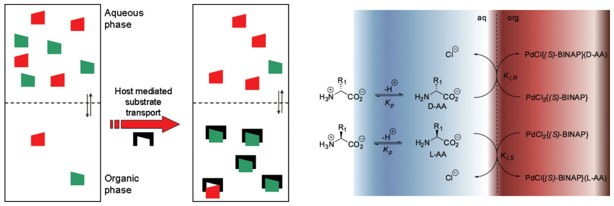
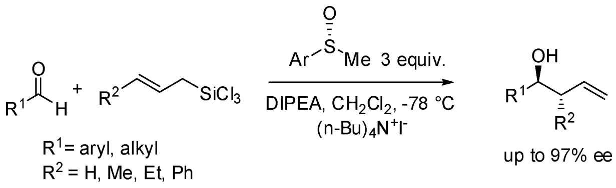


Chiral separation of substituted phenylalanine analogues using chiral palladium phosphine complexes with enantioselective liquid–liquid extraction

Bastiaan J. V. Verkuijl, Boelo Schuur, Adriaan J. Minnaard,* Johannes G. de Vries* and Ben L. Feringa*

Chiral palladium phosphine complexes have been employed in the chiral separation of amino acids and phenylalanine analogues in particular.

3055



Chiral sulfoxides as activators of allyl trichlorosilanes in the stereoselective allylation of aldehydes

Vincenzo De Sio, Antonio Massa* and Arrigo Scettri*

Chiral aryl methyl sulfoxides proved to be efficient activators in the asymmetric allylation of aldehydes with allyl trichlorosilanes. High enantioselectivity was found in the case of electron-poor aldehydes. The high levels of diastereoselectivity and the detection of nonlinear effects have allowed the elucidation of some mechanistic aspects of the reaction.

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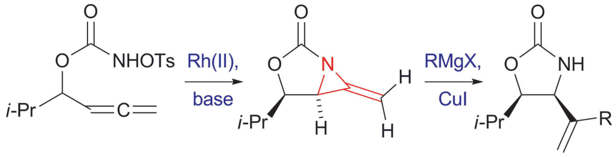
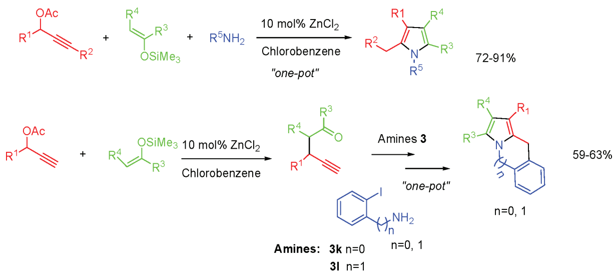


Structure and reactivity of bicyclic methylene aziridines prepared by intramolecular aziridination of allenes

Jeremy Robertson,* George C. Feast, Louise V. White, Victoria A. Steadman (née Doughty) and Timothy D. W. Claridge

The Rh(II)-catalyzed intramolecular aziridination of allenyl-substituted *N*-tosyloxycarbamates leads to bicyclic methylene aziridines that undergo formal S_NV ring-opening with organocuprates.

3064



One-pot highly efficient synthesis of substituted pyrroles and *N*-bridgehead pyrroles by zinc-catalyzed multicomponent reaction

Xiao-tao Liu, Lu Hao, Min Lin, Li Chen and Zhuang-ping Zhan*

A convenient zinc-catalyzed multicomponent process has been developed for the synthesis of substituted pyrroles. The protocol developed has been extended to the synthesis of *N*-bridgehead pyrroles containing polycyclic fragments.

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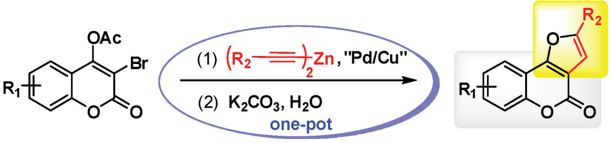
3073

One-pot synthesis of furocoumarins *via* sequential Pd/Cu-catalyzed alkynylation and intramolecular hydroalkoxylation

Lei Chen, Yi Li and Ming-Hua Xu*

A novel and rapid assembly of an interesting class of furocoumarins-4*H*-furo[3,2-*c*]chromen-4-ones has been successfully achieved using one-pot sequential coupling/cyclization strategy with easily available starting materials 3-bromo-4-acetoxycoumarins and terminal alkynes.

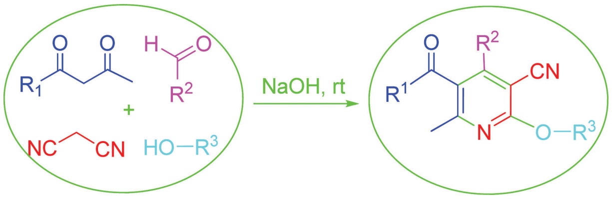


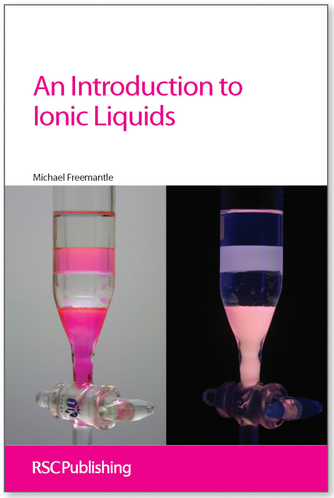
3078

Efficient one-pot synthesis of substituted pyridines through multicomponent reaction

Xin Xin, Yan Wang, Santosh Kumar, Xu Liu, Yingjie Lin and Dewen Dong*

A facile and convenient synthesis of substituted pyridines has been developed *via* a one-pot multicomponent reaction of commercially available 1,3-dicarbonyl compounds, malononitrile, aromatic aldehydes and alcohol in the presence of NaOH under mild conditions.





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Michael Freemantle

This is the first single-author book on ionic liquids and the first introductory book on the topic. An Introduction to Ionic Liquids is written in a clear, concise and consistent way and provides a useful introduction to ionic liquids for those readers who are not familiar with the topic. It is also wide ranging, embracing every aspect of the chemistry and applications of ionic liquids. The book draws extensively on the primary scientific literature to provide numerous examples of research on ionic liquids. These examples will enable the reader to become familiar with the key developments in ionic liquids chemistry over recent years.

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