

Organic & Biomolecular Chemistry

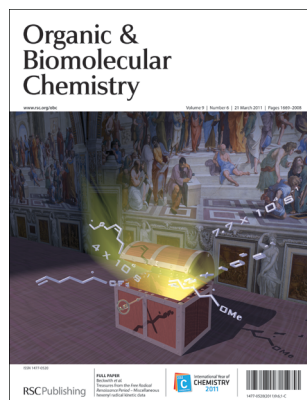
An international journal of synthetic, physical and biomolecular organic chemistry

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See Beckwith *et al.*,
pp. 1736–1743.

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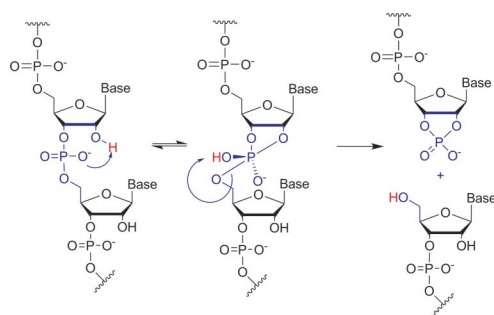
PERSPECTIVES

1687

Cleavage of RNA phosphodiester bonds by small molecular entities: a mechanistic insight

Harri Lönnberg*

Major mechanistic findings concerning the cleavage of RNA phosphodiester bonds by small molecules, ions and complexes are surveyed.

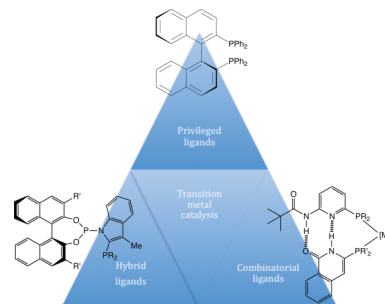


1704

Hybrid bidentate phosphorus ligands in asymmetric catalysis: Privileged ligand approach vs. combinatorial strategies

Jeroen Wassenaar and Joost N. H. Reek*

In this perspective privileged and combinatorial ligand design concepts are discussed, highlighting their differences and complementarities. Special attention is paid to hybrid bidentate ligands that bridge the gap between these strategies.



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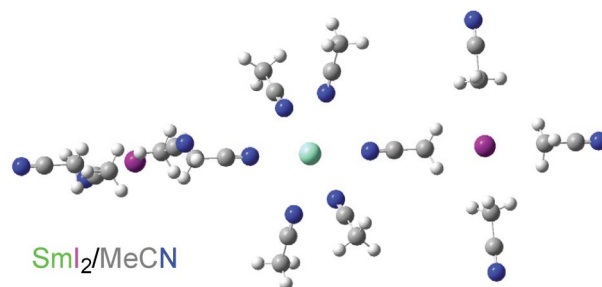
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1714

A convenient pathway to Sm(II)-mediated chemistry in acetonitrile

Todd Maisano, Kevin E. Tempest,
Dhandapani V. Sadasivam and Robert A. Flowers, II*

Atom efficient generation of Sm(OTf)₂ in acetonitrile provides a stable alternative to SmI₂.

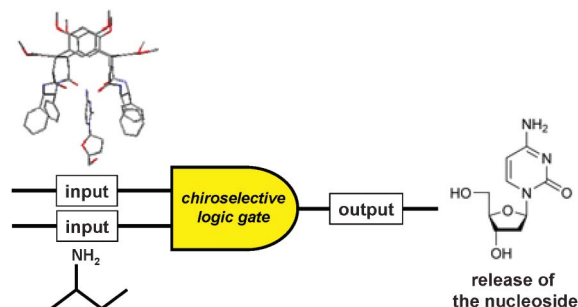


1717

Unprecedented gas-phase chiroselective logic gates

Bruno Botta, Caterina Frascchetti, Ilaria D'Acquarica,
Fabiola Sacco, Jochen Mattay, Matthias C. Letzel and
Maurizio Speranza*

Pyrimidine nucleosides are selectively released from three-body gaseous aggregates depending upon the configuration of the other two components.

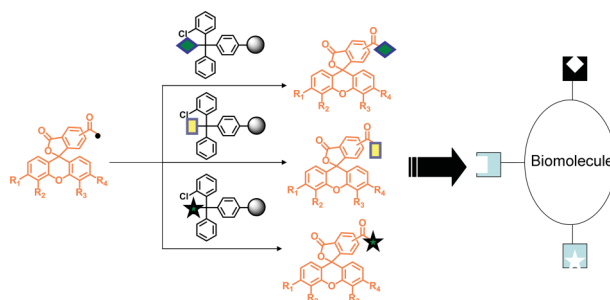


1720

Efficient solid phase strategy for preparation of modified xanthenes dyes for biolabelling

Juan M. Cardenas-Maestre and
Rosario M. Sanchez-Martin*

An easy and quick solid phase approach for the preparation of xanthenes dyes is presented. This method offers the possibility of modifying dyes with different functional groups -nucleophiles, electrophiles and groups capable of reversible reactions- in two simple synthetic steps, allowing them to be used for conjugation and labelling of a myriad of biomolecules, such as proteins.

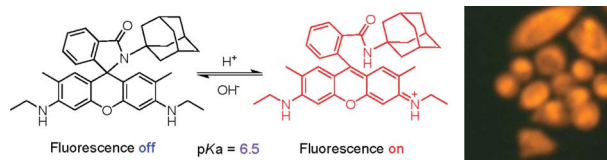


1723

A rational approach to tuning the pK_a values of rhodamines for living cell fluorescence imaging

Lin Yuan, Weiyang Lin* and Yanming Feng

A novel strategy to systematically tune the pK_a values of rhodamines is described.



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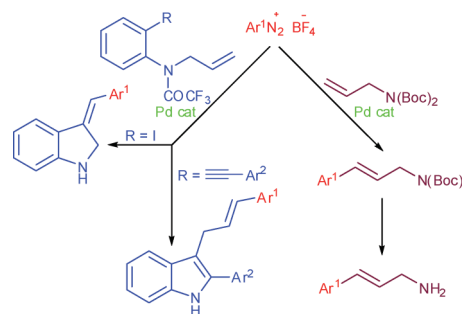
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1727

Heck reaction of arenediazonium salts with *N,N*-diprotected allylamines. Synthesis of cinnamylamines and indoles

Sandro Cacchi,* Giancarlo Fabrizi, Antonella Goggiamani and Alessio Sferazza

The palladium-catalyzed reactions of arenediazonium tetrafluoroborates with *N,N*-diprotected allylamines provide a novel easy approach to cinnamylamines, 2,3-disubstituted indoles, and alkylidene indolines.



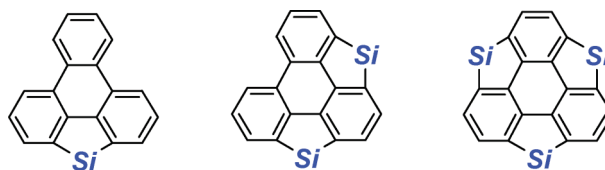
PAPERS

1731

Synthesis, structures and optical properties of trisilasumanene and its related compounds

Tomoharu Tanikawa, Masaichi Saito,* Jing Dong Guo and Shigeru Nagase

Novel trisilasumanenes that have no substituents on the *exo* carbon atoms, silicon analogues of sumanene, were prepared *via* repetitive lithiations of triphenylene followed by introduction of silicon functionalities. The optical properties of these trisilasumanenes and their related compounds were investigated by UV-vis and fluorescence spectroscopy.

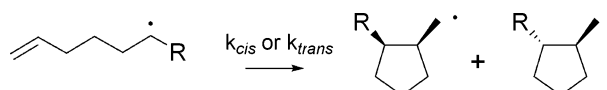


1736

Treasures from the *Free Radical Renaissance Period* – Miscellaneous hexenyl radical kinetic data

Athelstan L. J. Beckwith and Carl H. Schiesser*

Rate constant data and Arrhenius parameters have been determined for a series of substituted hexenyl radicals of differing electronic and steric demand. Rate constants ($k_{cis} + k_{trans}$) were found to lie in the range $0.4\text{--}2.1 \times 10^5 \text{ s}^{-1}$ at 25° . *Cis/trans* and k_c/k_H ratios were found to be solvent dependent.

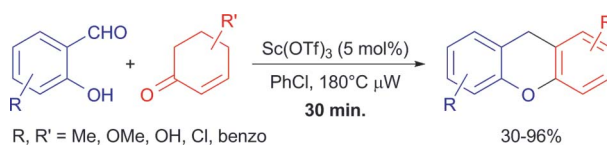


1744

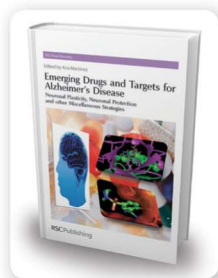
Lewis acid-catalysed one pot synthesis of substituted xanthenes

Esther Böß, Tim Hillringhaus, Jacqueline Nitsch and Martin Klussmann*

Substituted xanthenes can be made from salicylaldehydes and cyclohexenones or tetralones by scandium triflate catalysis under microwave or thermal heating.



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Edited by Ana Martinez | Medicinal Chemistry Institute–CSIC, Spain
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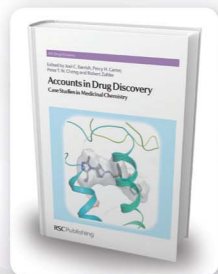
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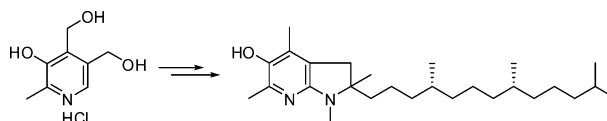
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1749

New synthetic route to N-tocopherol derivatives: synthesis of pyrrolopyridinol analogue of α -tocopherol from pyridoxine

Tae-gyu Nam, Jin-Mo Ku, Hyeung-geun Park, Ned A. Porter* and Byeong-Seon Jeong*

A new synthetic route to pyrrolopyridinol antioxidants from easily accessible pyridoxine was developed which includes phase-transfer catalytic alkylation and intramolecular Cu(I)-catalyzed amination as key steps.

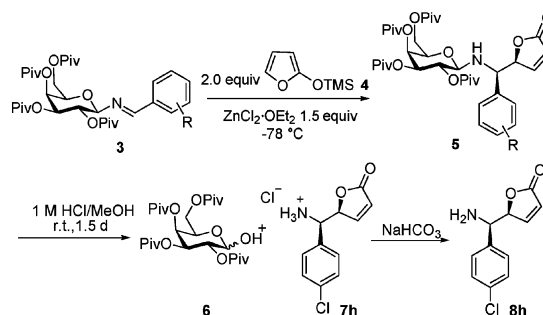


1756

Highly efficient asymmetric vinylogous Mannich reaction induced by *O*-pivaloylated D-galactosylamine as the chiral auxiliary

Jipan Yu, Zhiwei Miao* and Ruyi Chen*

The diastereospecific formation of β -*N*-glycoside-linked α -amino-2(5*H*)-furanone **5** has been achieved with high yield *via* a vinylogous Mannich reaction giving ratios of diastereomers higher than 20:1. This procedure provides rapid access to biologically important γ -butenolide derivatives.

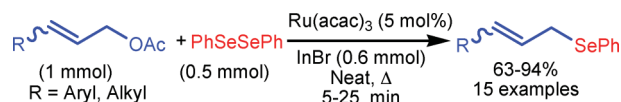


1763

Ruthenium(III)-catalysed phenylselenenylation of allyl acetates by diphenyl diselenide and indium(I) bromide in neat: isolation and identification of intermediate

Amit Saha and Brindaban C. Ranu*

A fast and efficient Ru(acac)₃-catalysed phenylselenenylation of allyl acetates by diphenyl diselenide and indium(I) bromide has been achieved in neat.

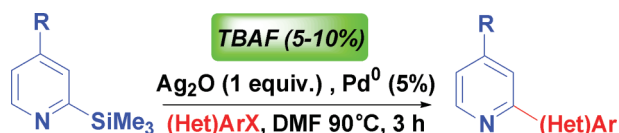


1768

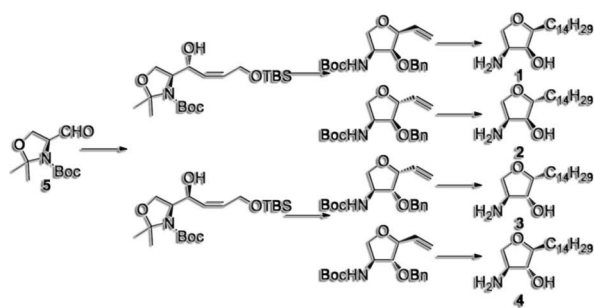
TBAF-Catalysed silver oxide-mediated cross-coupling of functional trimethylsilylpyridines: access to arylpyridines and biheteraryl compounds

Frédéric Louërat, Heather Tye, Spencer Napier, Michael Garrigou, Mark Whittaker and Philippe C. Gros*

Silver oxide and catalytic TBAF efficiently promoted the coupling of functional trimethylsilylpyridines with (hetero)aromatic halides.



1774

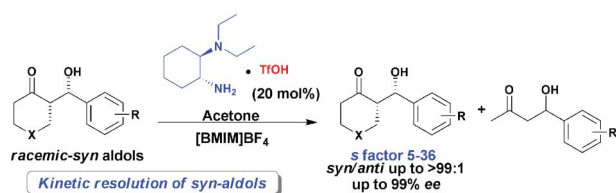


Asymmetric synthesis of Pachastrissamine (Jaspine B) and its diastereomers *via* η^3 -allylpalladium intermediates

Mikko Passiniemi and Ari M. P. Koskinen*

Pachastrissamine **1** and all three of its diastereomers **2**, **3**, **4** were produced in 9 steps starting from commercially available Garner's aldehyde **5**.

1784

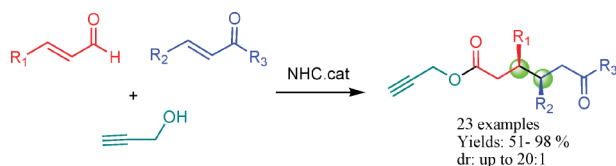


Highly enantioselective synthesis of *syn*-aldols of cyclohexanones *via* chiral primary amine catalyzed asymmetric transfer aldol reactions in ionic liquid

Pengxin Zhou, Sanzhong Luo* and Jin-Pei Cheng*

Chiral primary-tertiary diamine/TfOH was found to catalyze effective kinetic resolution of racemic *syn*-aldols of cyclohexanones in ionic liquid, affording the chiral *syn*-aldols with up to 99 : 1 *syn/anti* and 99% ee.

1791

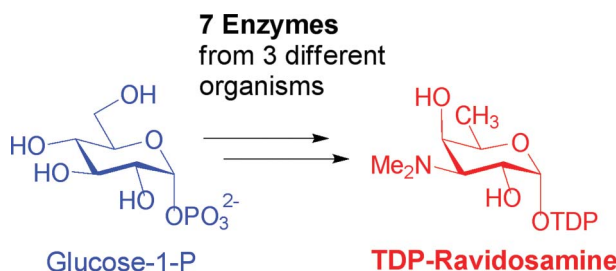


N-Heterocyclic carbene-catalyzed (NHC) three-component domino reactions: highly stereoselective synthesis of functionalized acyclic ϵ -ketoesters

Jianze Ma, You Huang* and Ruyu Chen*

Highly efficient and stereoselective NHC-catalyzed domino reaction: the same catalyst, similar substrates, different pathway.

1799



Characterization of the TDP-D-ravidosamine biosynthetic pathway: one-pot enzymatic synthesis of TDP-D-ravidosamine from thymidine-5-phosphate and glucose-1-phosphate

Madan K. Kharel, Hui Lian and Jürgen Rohr*

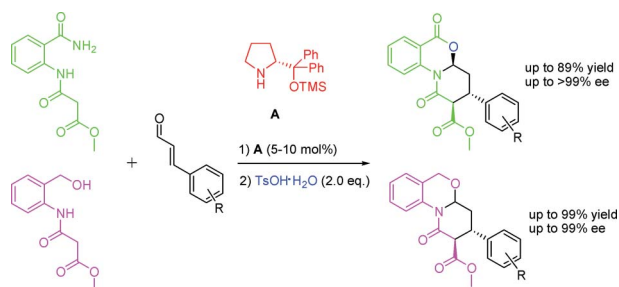
An efficient one-pot enzymatic total synthesis for TDP-D-ravidosamine was developed, verifying the involvement of five *rav* enzymes in its biosynthesis.

1809

A one-pot asymmetric organocatalytic tandem reaction for the synthesis of oxazine derivatives

Zhichao Jin, Feng Yu, Xiao Wang, Huicai Huang, Xiaoyan Luo, Xinmiao Liang and Jinxing Ye*

An easy one-pot tandem reaction catalyzed by a chiral secondary amine for the synthesis of optically active oxazine derivatives has been performed and the corresponding substituted benzo[*d*]pyrido[2,1-*b*][1,3]oxazine derivatives were afforded in generally high yields (up to 99%) and excellent enantioselectivities (up to >99%).

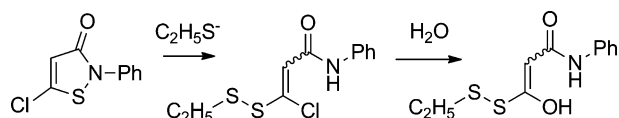


1817

Isothiazolones; thiol-reactive inhibitors of cysteine protease cathepsin B and histone acetyltransferase PCAF

Rosalina Wisastra, Massimo Ghizzoni, Harm Maarsingh, Adriaan J. Minnaard, Hidde J. Haisma and Frank J. Dekker*

Isothiazolones react chemoselectively with thiolates to form disulfides.

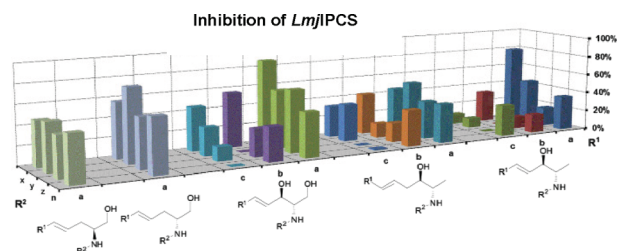


1823

Exploring *Leishmania major* Inositol Phosphorylceramide Synthase (*Lmj*IPCS): Insights into the ceramide binding domain

John G. Mina, Jackie A. Mosely, Hayder Z. Ali, Paul W. Denny* and Patrick G. Steel*

A series of ceramide analogues have been synthesised and evaluated as substrates for the protozoan enzyme inositolphosphoryl ceramide synthase from *Leishmania Major*

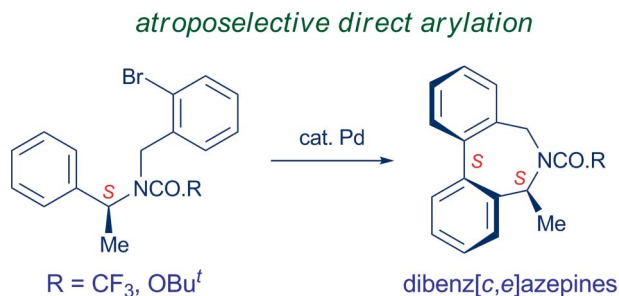


1831

Atroposelective formation of dibenz[*c,e*]azepines via intramolecular direct arylation with centre-axis chirality transfer

Caroline A. Cheetham, Richard S. Massey, Silvain L. Pira, Robin G. Pritchard and Timothy W. Wallace*

5-Substituted 6,7-dihydrodibenz[*c,e*]azepines, a class of secondary amine incorporating a centre-axis chirality relay, are accessible from 1-substituted *N*-(2-bromobenzyl)-1-phenylmethanamines via *N*-acylation and ring-closing intramolecular direct arylation. The ring closure proceeds with high atroposelectivity.



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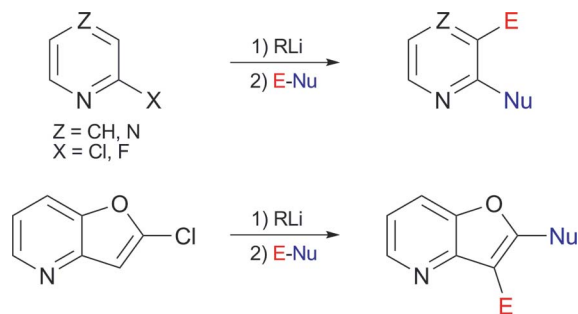
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1839

One-pot double functionalisation of π -deficient heterocyclic lithium reagents

Anthony Chartoire, Corinne Comoy and Yves Fort*

We report an efficient method for the double functionalisation of lithiated halogenopyridines, -pyrazines or -furopyridines through a convenient one-pot electrophilic trapping/nucleophilic substitution sequence.

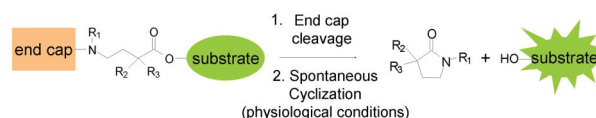


1846

Design, synthesis, and cyclization of 4-aminobutyric acid derivatives: potential candidates as self-immolative spacers

Matthew A. DeWit and Elizabeth R. Gillies*

A series of 4-aminobutyric acid derivatives was synthesized. They were demonstrated to cyclize rapidly in aqueous solution at neutral and mildly acidic pH, thus suggesting their promise as new self-immolative spacers.

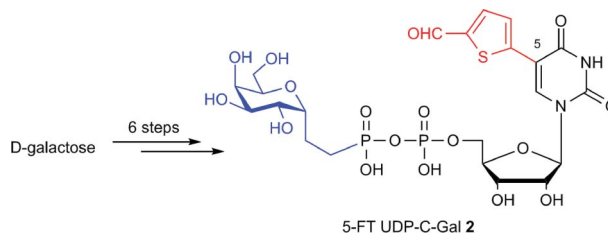


1855

The first C-glycosidic analogue of a novel galactosyltransferase inhibitor

Karine Descroix and Gerd K. Wagner*

The efficient synthesis of a new, base-modified UDP-C-glycoside (compound **2**) with activity against UDP-Gal 4'-epimerase (GalE) is reported.

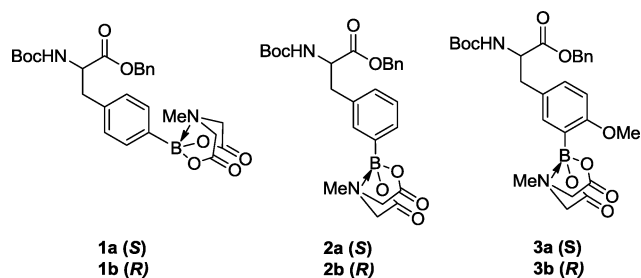


1864

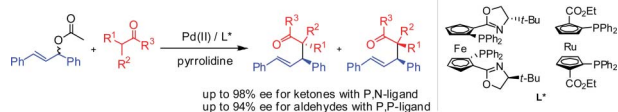
Synthesis and properties of MIDA boronate containing aromatic amino acids: New peptide building blocks

Neil Colgin, Tony Flinn and Steven L. Cobb*

Novel phenylalanine and tyrosine derivatives containing a *N*-methyliminodiacetic acid boronate group have been prepared. This new class of synthetic building blocks has potential applications in both peptide chemistry and natural product synthesis.



1871

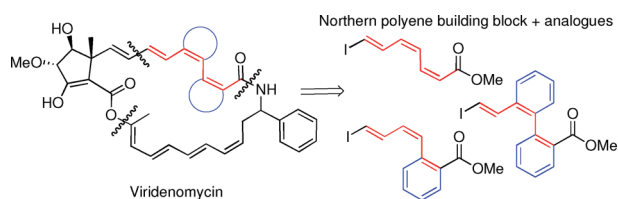


Efficient palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes

Xiaohu Zhao, Delong Liu, Fang Xie, Yangang Liu and Wanbin Zhang*

The first palladium-catalyzed asymmetric allylic alkylation of ketones and aldehydes *via* enamines generated *in situ* as nucleophiles with excellent enantioselectivities and yields is reported.

1876

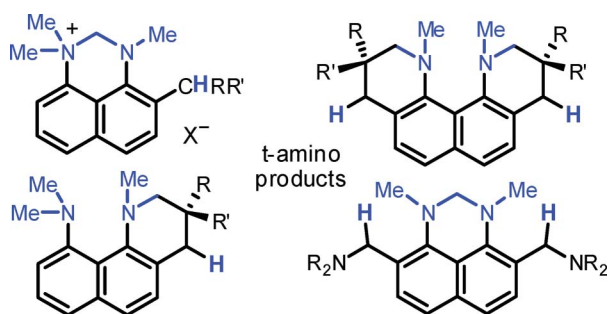


Studies towards the synthesis of the northern polyene of viridenomycin and synthesis of *Z*-double bond analogues

Jonathan P. Knowles, Victoria E. O'Connor and Andrew Whiting*

The development of highly stereoselective coupling methods is reported, which are suitable for the construction of models of the northern hemisphere of viridenomycin, together with arylated analogues.

1887

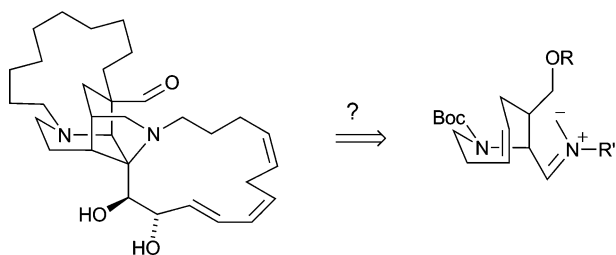


Naphthalene proton sponges as hydride donors: diverse appearances of the *tert*-amino-effect

Alexander F. Pozharskii,* Maria A. Povalyakhina, Alexander V. Degtyarev, Oxana V. Ryabtsova, Valery A. Ozeryanskii, Olga V. Dyablo, Anna V. Tkachuk, Olga N. Kazheva, Anatolii N. Chekhlov and Oleg A. Dyachenko

Hydrogen atoms (bold blue in the image) of *peri*-NMe₂ groups in the naphthalene proton sponge can intramolecularly migrate to an electron-accepting *ortho*-substituent(s) to give benzo[*h*]quinolines, quino[7,8:7',8']quinolines, *ortho*-Mannich bases and so on.

1901



Transannular dipolar cycloaddition as an approach towards the synthesis of the core ring system of the sarain alkaloids

Andrew I. Franklin, David Bensa, Harry Adams and Iain Coldham*

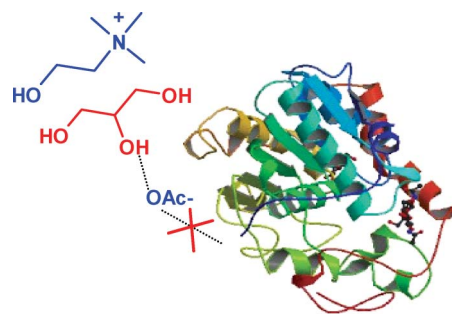
Attempted transannular cycloaddition was unsuccessful towards the core of the sarain alkaloids

1908

New eutectic ionic liquids for lipase activation and enzymatic preparation of biodiesel

Hua Zhao,* Gary A. Baker and Shailetha Holmes

A new eutectic ionic liquid based on choline acetate and glycerol is compatible with lipase B from *Candida antarctica* [structure from PDB ID: 1TCB].



1917

Polymer supported synthesis of novel benzoxazole linked benzimidazoles under microwave conditions: *In vitro* evaluation of VEGFR-3 kinase inhibition activity

Kaushik Chanda, Barnali Maiti, Gorakh S. Yellol, Ming-Hsien Chien, Min-Liang Kuo and Chung-Ming Sun*

Efficient soluble polymer supported synthesis of novel benzoxazole-benzimidazole hybrids using microwave irradiation. The compounds show promising *in vitro* VEGFR-3 kinase inhibition activity.

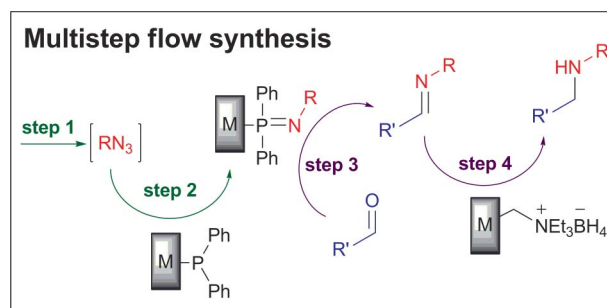


1927

Flow synthesis of organic azides and the multistep synthesis of imines and amines using a new monolithic triphenylphosphine reagent

Catherine J. Smith, Christopher D. Smith, Nikzad Nikbin, Steven V. Ley and Ian R. Baxendale

In situ generated azides are applied to Staudinger aza-Wittig reactions in flow with a new, conveniently formatted monolithic triphenylphosphine reagent.

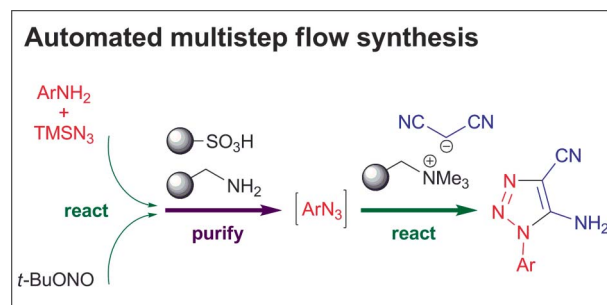


1938

A fully automated, multistep flow synthesis of 5-amino-4-cyano-1,2,3-triazoles

Catherine J. Smith, Nikzad Nikbin, Steven V. Ley, Heiko Lange and Ian R. Baxendale

Aryl azides are generated and purified in flow, then carried on directly to the synthesis of triazole building blocks.



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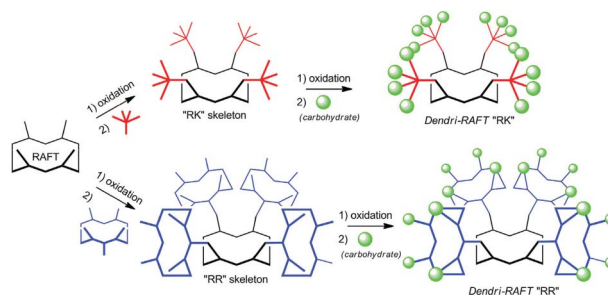


1948

Dendri-RAFTs: a second generation of cyclopeptide-based glycoclusters

Isabelle Bossu, Miroslav Šulc, Karel Křenek, Emilie Dufour, Julian Garcia, Nathalie Berthet, Pascal Dumy, Vladimír Křen* and Olivier Renaudet*

We describe a new series of hexadecavalent glycoclusters, namely “dendri-RAFTs”, differing in their spatial arrangement and glycosidic density.

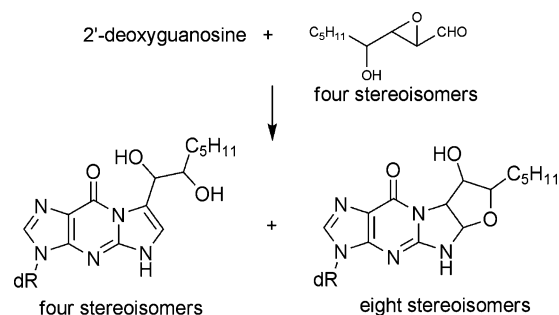


1960

Synthesis of the four stereoisomers of 2,3-epoxy-4-hydroxynonanal and their reactivity with deoxyguanosine

Katya V. Petrova, Donald F. Stec, Markus Voehler and Carmelo J. Rizzo*

Individual stereoisomers of 2,3-epoxy-4-hydroxynonanal (EHN) were synthesized and reacted with deoxyguanosine to afford a 7-(1,2-dihydroxyheptyl)-1, *N*²-etheno-2'-deoxyguanosine and two tetracyclic adducts. The adducts were characterized by NMR, CD, and molecular mechanics calculations.

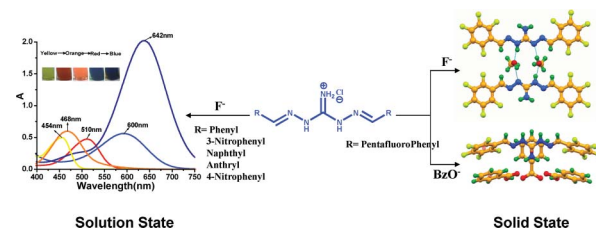


1972

Functionalized guanidinium chloride based colourimetric sensors for fluoride and acetate: single crystal X-ray structural evidence of -NH deprotonation and complexation

Purnandhu Bose, B. Nisar Ahamed and Pradyut Ghosh*

A series of simple guanidinium based receptors acts as a newer type of colourimetric sensor for fluoride in general by deprotonation. Using one of the receptors distinguishable colour changes are observed for F⁻, AcO⁻ and H₂PO₄⁻.

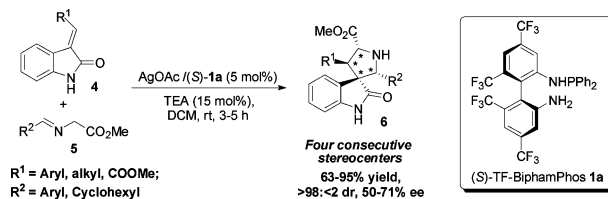


1980

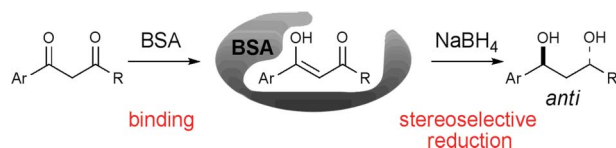
Catalytic asymmetric 1,3-dipolar cycloaddition of *N*-unprotected 2-oxoindolin-3-ylidene derivatives and azomethine ylides for the construction of spirooxindole-pyrrolidines

Tang-Lin Liu, Zhi-Yong Xue, Hai-Yan Tao and Chun-Jiang Wang*

Asymmetric 1,3-dipolar cycloaddition of *N*-unprotected 2-oxoindolin-3-ylidene with azomethine ylides for the construction of spirooxindole-pyrrolidines has been achieved with AgOAc/TF-BiphamPhos complexes for the first time.



1987

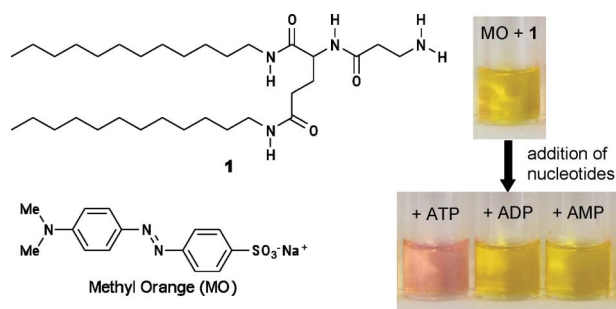


Albumin-directed stereoselective reduction of 1,3-diketones and β -hydroxyketones to *anti* diols

Federico Berti,* Simone Bincoletto, Ivan Donati, Giampaolo Fontanive, Massimo Fregonese and Fabio Benedetti*

Complexation of aromatic 1,3-diketones and hydroxyketones by albumin allows total control of the selectivity in the NaBH₄ reduction giving *anti*-diols.

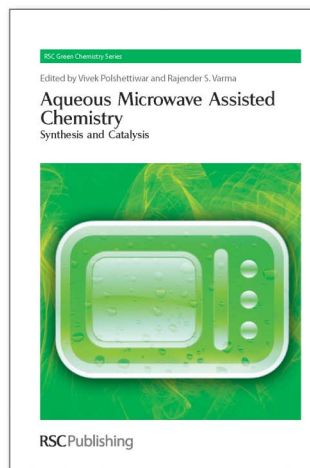
2000



Functionalization of methyl orange using cationic peptide amphiphile: colorimetric discrimination between ATP and ADP at pH 2.0

Naoya Ryu and Hiroshi Hachisako*

A solvatochromic acid–base indicator, methyl orange (MO), was applied to colorimetric discrimination between adenosine 5'-triphosphate (ATP) and the corresponding diphosphate (ADP) in water at pH 2.0 using an L-glutamic acid-derived cationic peptide amphiphile 1.



Aqueous Microwave Assisted Chemistry Synthesis and Catalysis

Edited by Vivek Polshettiwar and Rajender S. Varma

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