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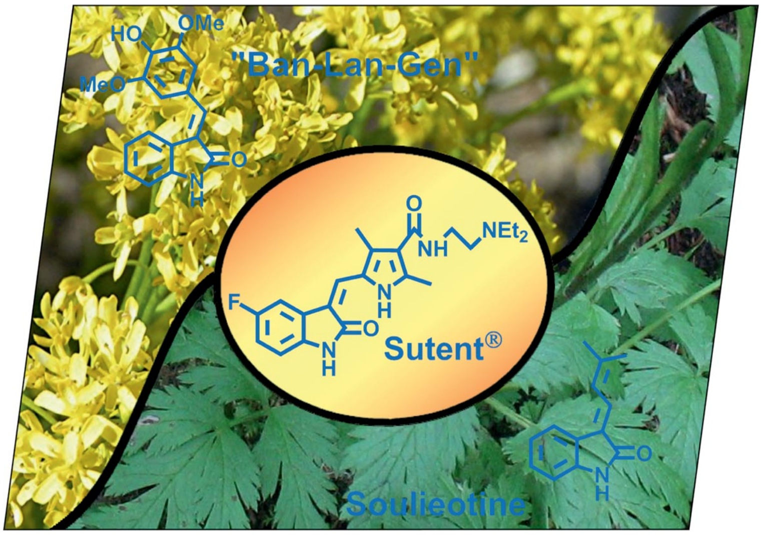
COVER PICTURE

The cover picture shows the structure of Sutent® superimposed upon the plants *Isatis indigotica* (used to prepare the widely used traditional Chinese medicine "Ban-Lan-Gen") and *Souliea vaginata* (the source of Soulieotine). Natural products possessing the 3-alkenyl-oxindole core are presented in the Microreview by A. Millemaggi and R. J. K. Taylor on p. 4527ff. We thank Adam Gooch for his assistance with the cover graphic. The cover photographs are used with permission, and we are grateful to the following sources: *Isatis indigotica*: Creative Commons Copyright, Pethan, 2005. *Souliea vaginata*: Copyright 2007 by D. E. Boufford [photograph from the "Biodiversity of the Hengduan Mountains" website (http://hengduan.huh.harvard.edu/fieldnotes, 19-04-2010)].



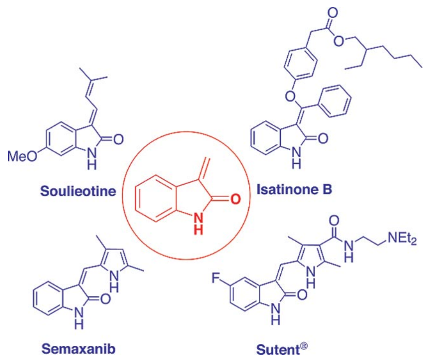
MICROREVIEW

Biologically Active Oxindoles

A. Millemaggi,
R. J. K. Taylor* 4527–4547

3-Alkenyl-oxindoles: Natural Products, Pharmaceuticals, and Recent Synthetic Advances in Tandem/Telescoped Approaches

Keywords: Nitrogen heterocycles / Natural products / Antitumor agents / Domino reactions / Telescoped reactions



The structures and biological activities of naturally occurring and man-made 3-alkenyl-oxindoles are reviewed and recently developed tandem/telescoped synthetic routes are described.

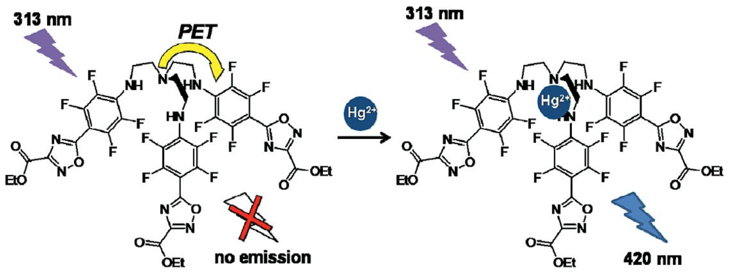
SHORT COMMUNICATIONS

Fluorescent Sensors

I. Pibiri, A. Palumbo Piccionello,*
A. Calabrese, S. Buscemi, N. Vivona,
A. Pace 4549–4553

Fluorescent Hg^{2+} Sensors: Synthesis and Evaluation of a Tren-Based Starburst Molecule Containing Fluorinated 1,2,4-Oxadiazoles

Keywords: 1,2,4-Oxadiazoles / Sensors / Electron transfer / Fluorinated ligands / Mercury



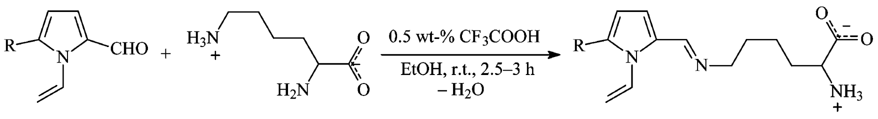
A tripodal tren-based sensor containing oxadiazole fluorophores and fluoroarylated moieties was designed as a new scaffold for cation recognition. Metal coordination induces quenching of PET from the nitrogen atom to the fluorophores and produces an off-on signal response. Selective Hg^{2+} sensing was evidenced in organic and mixed aqueous/organic solvents.

Unnatural Amino Acids

A. V. Ivanov, I. A. Ushakov,
K. B. Petrushenko, A. I. Mikhaleva,
B. A. Trofimov* 4554–4558

Chemo-, Regio- and Stereospecific Synthesis of Unnatural, Fluorescent Amino Acids by Condensation of L-Lysine and 1-Vinylpyrrole-2-carbaldehydes

Keywords: Amino acids / Aldehydes / Nitrogen heterocycles / Schiff bases / Fluorescence

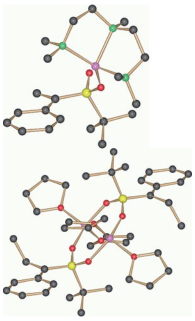


Novel unnatural optically active amino acids bearing the pyrrole moiety have been synthesized under mild conditions in up to 90% yields by chemo-, regio- and stereospecific condensation of 1-vinylpyrrole-2-carbaldehydes with L-lysine involving the ε-amino group only to afford products of exclusively (*E*) configuration. The amino acids synthesized fluoresce in the UV/Vis region.

FULL PAPERS

Chiral α-Sulfonyl Carbanions

DNMR and ab initio calculations show α-*tert*-butylsulfonyl carbanions have an enantiomerization barrier that should be sufficiently high to allow their enantioselective synthesis at low temperatures. Analysis of the racemic lithium α-*tert*-butyl-sulfonyl carbanion salts revealed the existence of monomeric and dimeric CIPs devoid of a Li⋯C bond, which were converted upon action of HMPA into SIPs.



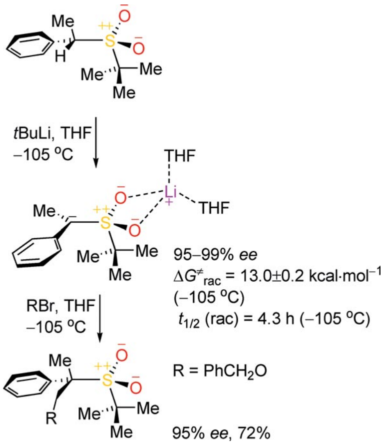
R. Scholz, G. Hellmann, S. Rohs, G. Raabe, J. Runsink, D. Özdemir, O. Luche, T. Heß, A. W. Giesen, J. Atodiresei, H. J. Lindner, H.-J. Gais* 4559–4587

Experimental and Theoretical Investigation of the Enantiomerization of Lithium α-*tert*-Butylsulfonyl Carbanion Salts and the Determination of Their Structures in Solution and in the Crystal

Keywords: Carbanions / Chirality / Enantiomerization / Ab initio calculations / Cryoscopy

Chiral α-Sulfonyl Carbanions

Deprotonation of chiral *S*-*tert*-butyl sulfones with *t*BuLi gives enantiomerically highly enriched lithium α-*tert*-butylsulfonyl carbanion salts that are configurationally stable at −105 °C in the timescale of their synthesis and reactions with electrophiles. They react at low temperatures with electrophiles with high enantioselectivity.

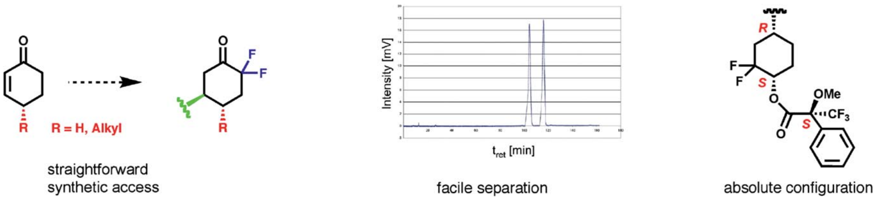


R. Scholz, G. Hellmann, S. Rohs, D. Özdemir, G. Raabe, C. Vermeeren, H.-J. Gais* 4588–4616

Enantioselective Synthesis, Configurational Stability, and Reactivity of Lithium α-*tert*-Butylsulfonyl Carbanion Salts

Keywords: Chirality / Carbanions / Racemization / Enantioselectivity / Alkylation

Organofluorine Building Blocks



straightforward synthetic access

facile separation

absolute configuration

Enantiomerically pure as well as highly decorated α,α-difluorohexanones were synthesized and successfully tested as inhibitors of the malarial aspartic proteases, the plasmepsins. Optically active ligands were obtained by separation of diastereoisomeric Mosher ester precursors, and subsequent analysis allowed the assignment of the absolute configuration.

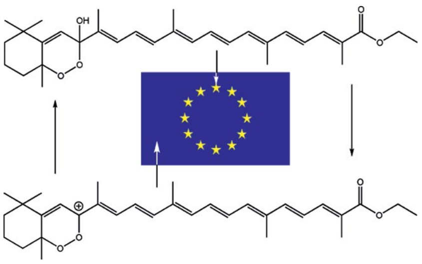
C. Fäh, R. Mathys, L. A. Hardegger, S. Meyer, D. Bur, F. Diederich* 4617–4629

Enantiomerically Pure and Highly Substituted Alicyclic α,α-Difluoro Ketones: Potential Inhibitors for Malarial Aspartic Proteases, the Plasmepsins

Keywords: Medicinal chemistry / Malaria / Inhibitors / Novel building blocks / Difluoro ketones / Chiral resolution

Peroxide Polyenes

A new "European" carotenoid oxide. The orange food colorant carotenoid E160f ("C30-ester") forms a blue carotenoid with FeCl$_3$ in air. In the presence of water, this blue carotenoid is converted into a yellow compound that changes back to blue with traces of acid, and so forth. Thus, these new interconverting carotenoids display the colors of the European flag.



H. Li, E. Rebmann, C. L. Øpstad, R. Schmid, H.-R. Sliwka,* V. Partali 4630–4636

Synthesis of a Highly Unsaturated, Stable Hydroxy Peroxide: A Yellow ⇆ Blue Color-Changing Carotenoid Oxidation Product with Leuco Dye Properties

Keywords: Dyes / Carotenoids / Peroxides / Radical ions / Reactive intermediates

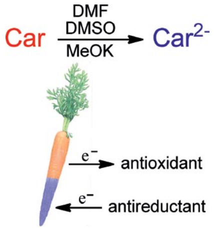
CONTENTS

Antireductants

C. L. Øpstad, H.-R. Sliwka,*
V. Partali 4637–4641

Facile Electron Uptake by Carotenoids Under Mild, Non-Radiative Conditions: Formation of Carotenoid Anions

Keywords: Dyes / Carotenoids / Antioxidants / Electron transfer / Anions / Aldehydes



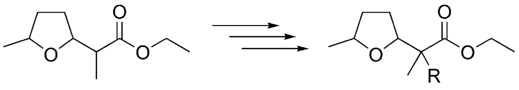
Carotenoids (Car) may just as well be antireductants as they are antioxidants. Exceptional antireductant properties of carotenoids have been predicted by DF calculations. Indeed, dioxocarotenoids in alkaline DMSO or DMF easily take up electrons under ambient conditions and form stable, blue carotenoid dianions.

Lipophilic Nonactin Analogues

F. Loiseau, I. Kholod,
R. Neier* 4642–4661

Thione Esters as Substrates for the Stereoselective Alkylation of Model Compounds of Nonactic Acids

Keywords: Heterocycles / Diastereoselectivity / Retro reactions / Alkylation



13 R = aliphatic chain 37

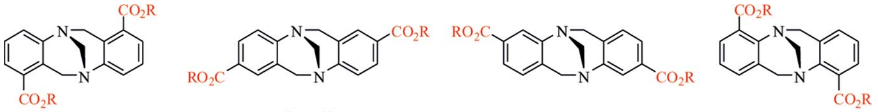
Introducing hydrophobic chains into nonactin would allow the lifetime of the macrolide in the semipermeable membrane of ammonium ion selective electrodes to be increased. We have studied three different routes. The route using thione esters as substrates for the alkylation gave the most satisfactory results. Ring-opening of the tetrahydrofuran and scrambling of the configuration could be avoided.

Tröger's Base Chemistry

M. D. H. Bhuiyan, K.-X. Zhu, P. Jensen,
A. C. Try* 4662–4670

Synthesis of Symmetric Diester-Functionalised Tröger's Base Analogues

Keywords: Tröger's base / Chirality / Aromatic substitution



Type I Type II Type III Type IV

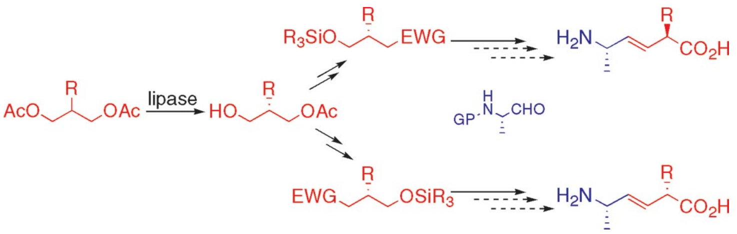
Over 20 aminobenzoates were used to prepare symmetrically substituted diester Tröger's base analogues, bearing esters at the 1,7-, 2,8-, 3,9- and 4,10-positions of the framework.

Peptidyl Olefins

S. Mirilashvili, N. Chasid-Rubinstein,
A. Albeck* 4671–4686

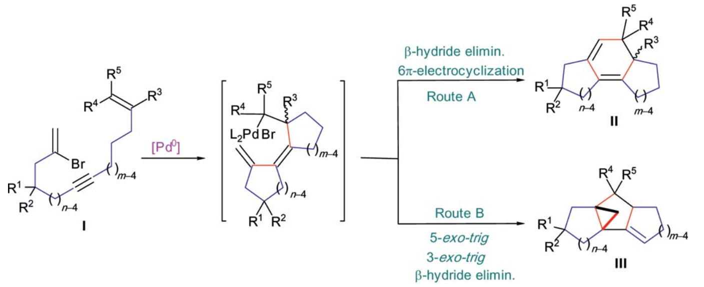
Optically Active N- and C-Terminal Building Blocks for the Synthesis of Peptidyl Olefin Peptidomimetics

Keywords: Asymmetric synthesis / Enzymes / Olefination / Stereocontrol / Peptidomimetics



A chemoenzymatic approach to C-terminal building blocks for the synthesis of peptidyl olefins is described. Lipase-catalyzed hydrolysis of prochiral diesters introduced optical activity. The sequence of the subsequent chemical reactions, either protection–hydrolysis–functionalization or functionalization–hydrolysis–protection, determined the absolute stereochemistry of the product.

Pd-Catalyzed Oligocyclizations



When 2-bromoalka-1,$(n+m+1)$-dien-$(n+1)$-ynes (**I**) were subjected to a palladium precatalyst system typically employed for Heck reactions, two palladium-catalyzed oligocyclization modes either involving a 6π-electrocyclization or a 5-*exo-trig* carbopalladation (route A and B) were observed to give tricyclic or tetracyclic systems such as **II** and **III**, respectively. The preferred mode of the oligocyclization is determined by the tether lengths linking the multiple bonds.

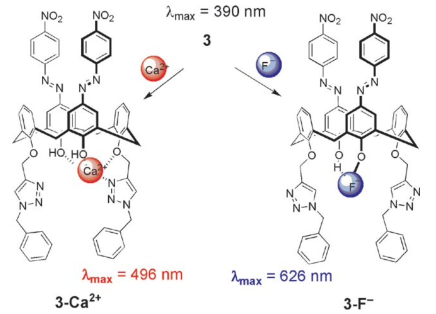
S. Schweizer, W. M. Tokan, P. J. Parsons, A. de Meijere* 4687–4799

Palladium-Catalyzed Oligocyclizations of 2-Bromoalka-1,$(n+m+1)$-dien-$(n+1)$-ynes – Influence of Tether Lengths and Substituents on the Outcome of the Reaction (Part II)

Keywords: Homogenous catalysis / Domino reactions / Palladium catalysis / Carbo-oligocyclization / Dienyne

Supramolecular Ionophores

Azocalix[4]arene **3**, containing both triazoles and hydroxy azophenols as cation and anion binding sites and the azophenol moiety as a coloration unit, was designed and synthesized. A distinct colour change was found for compound **3** in the presence of metal ions (Ca^{2+}, Pb^{2+} and Ba^{2+}) or anions (F^-, AcO^- and $H_2PO_4^-$), which can be detected by the naked eye and has been used to construct a combinational logic circuit at the molecular level.

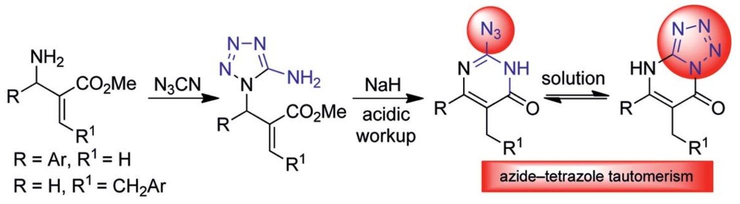


K.-C. Chang, I.-H. Su, Y.-Y. Wang, W.-S. Chung* 4700–4704

A Bifunctional Chromogenic Calix[4]arene Chemosensor for Both Cations and Anions: A Potential Ca^{2+} and F^- Switched INHIBIT Logic Gate with a YES Logic Function

Keywords: Calixarenes / Chromogenic sensors / Logic gates / Host–guest systems / Click chemistry

Tetrazoles



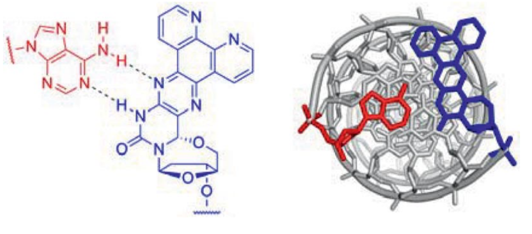
Substituted 5-aminotetrazoles obtained from primary allylamines derived from Morita–Baylis–Hillman chemistry undergo base-promoted intramolecular cyclization to afford 2-azidopyrimidin-4(3*H*)-ones instead of the expected tetrazolo[1,5-*a*]pyrimidin-5(4*H*)-ones. In methanolic solution, the azido derivatives underwent azide–tetrazole tautomerism to afford the desired tetrazolo[1,5-*a*]pyrimidin-7(4*H*)-ones.

S. Nag, S. Bhowmik, H. M. Gauniyal, S. Batra* 4705–4712

Application of Primary Allylamines from Morita–Baylis–Hillman Adducts: Cyanogen Azide Mediated Synthesis of Substituted 5-Aminotetrazoles and Their Attempted Transformation into Tetrazolo[1,5-*a*]pyrimidinones

Keywords: Allylic compounds / Amines / Azides / Tautomerism / Nitrogen heterocycles

Metal-Chelating Nucleosides



A nucleoside containing a 5′-6 ether linkage and a 1,10-phenanthroline ligand moiety was incorporated into DNA. Thermal denaturation studies showed that the nucleoside has base-pairing properties similar to T (left). Modeling indicated that the nucleoside is readily accommodated in the helix (right).

K. Gislason, S. T. Sigurdsson* 4713–4718

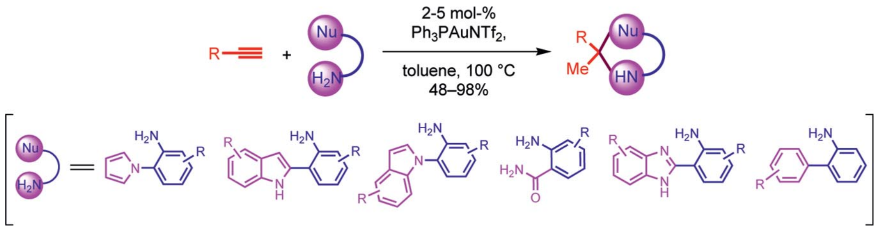
Synthesis of a 5′-6-Locked, 1,10-Phenanthroline-Containing Nucleoside and Its Incorporation into DNA

Keywords: Polypyridines / Stacking interactions / Rigid chelators / 5′-Overhang / Ligand design

CONTENTS

Hydroamination and Hydroarylation

Keywords: Alkynes / Gold catalysts / Nucleophiles / Cyclization / Heterocycles



An efficient Ph$_3$PAuNTf$_2$-catalyzed direct double hydroamination and hydroamination/hydroarylation of terminal alkynes has been developed. A significant rate enhancement was observed when the reactions were conducted under microwave conditions.

CORRECTION

Keywords: Alkynes / Cross-coupling / Iron / Grignard reagents / Homogeneous catalysis

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* Author to whom correspondence should be addressed.

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