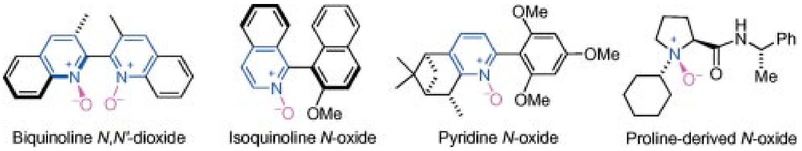
MICROREVIEW

Chiral *N*-Oxides



This Microreview provides an update on the latest development in the application of chiral *N*-oxides derived from tertiary amines and pyridines in asymmetric metal-free and metal-mediated catalysis.

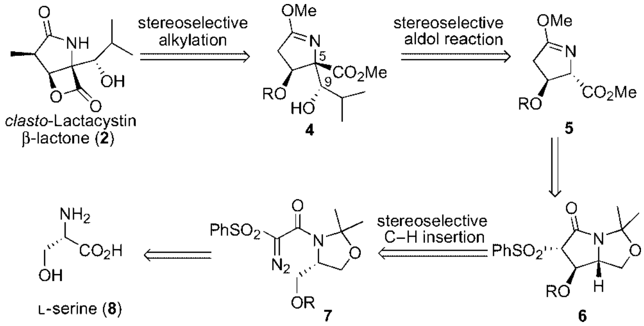
A. V. Malkov,* P. Kočovský* 29–36

Chiral *N*-Oxides in Asymmetric Catalysis

Keywords: Asymmetric catalysis / Homogeneous catalysis / *N*-Oxides / Lewis bases / Organosilicon reagents

SHORT COMMUNICATIONS

Natural Products



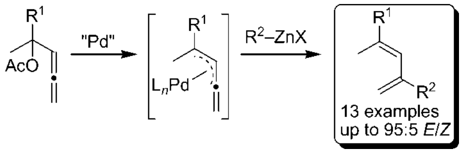
clasto-Lactacystin β-lactone (**2**) was efficiently synthesized from L-serine (**8**), which induced all the stereochemistries selectively. Aldol reaction established the quaternary C(5) and carbinol C(9) centers while C–H insertion resulted in the exclusive synthesis of the γ-lactam **6**.

C. H. Yoon, D. L. Flanigan, K. S. Yoo, K. W. Jung* 37–39

Stereogenic Evolution of *clasto*-Lactacystin β-Lactone from $^{\mathrm{L}}$-Serine

Keywords: Stereoseltive C–H insertion / Rhodium catalysis / γ-Lactam / Aldol reaction / Lactacystin β-lactone

Diene Synthesis



The synthesis of a group of highly substituted dienes by Tsuji–Trost/Negishi-type cross-coupling of allenic acetates is described. High yields, regio- and stereoselectivity are observed using an inexpensive, commercially available catalyst precursor and ligand. It is expected that this method to prepare such dienes will find use in the synthesis of complex biologically relevant molecules.

J. S. Schneekloth, Jr., M. Pucheault, C. M. Crews* 40–43

Construction of Highly Substituted Stereodefined Dienes by Cross-Coupling of α-Allenic Acetates

Keywords: Cross-coupling / Allenes / Alkenes

CONTENTS

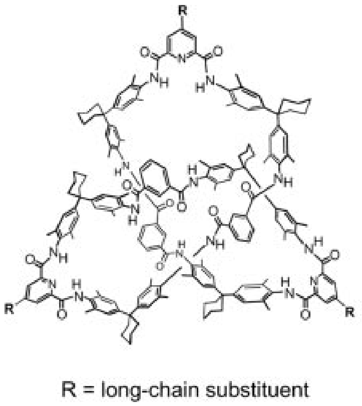
FULL PAPERS

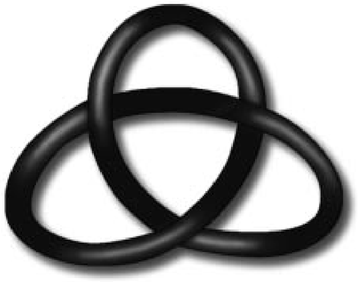
Knots on Surfaces

A. Böhmer, J. Brüggemann, A. Kaufmann, A. Yoneva, S. Müller, W. M. Müller, U. Müller, F. W. Vergeer, L. Chi, L. De Cola, H. Fuchs, X. Chen, T. Kubota, Y. Okamoto, F. Vögtle* 45–52

Long Chain-Substituted and Triply Functionalized Molecular Knots – Synthesis, Topological Chirality and Monolayer Formation

Keywords: Supramolecular chemistry / Template synthesis / Molecular knots / Topological chirality / Enantiomer separation





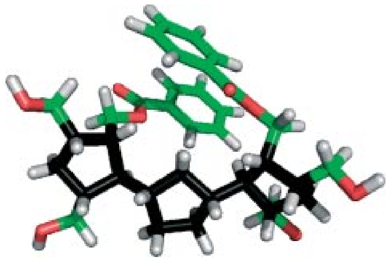
Topological chiral knots armed with solubilizing lipophilic sidearms form Langmuir–Blodgett films allowing AFM studies.

Lipid A Binding Scaffold

P. C. Gareiss, P. B. Palde, R. D. Hubbard, B. L. Miller* 53–61

Conformational and Structural Analysis of a *ter*-Cyclopentane Scaffold for Molecular Recognition

Keywords: Molecular modeling / Molecular recognition / Conformational analysis



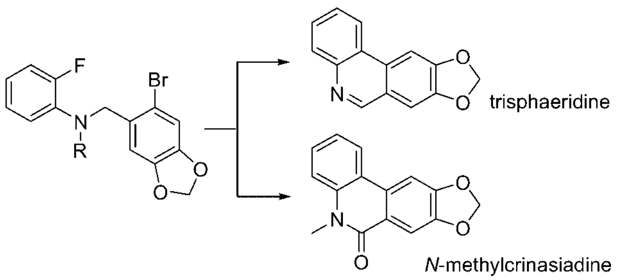
Well-defined oligomers of cycloalkanes comprise a relatively unstudied class of organic compounds, having utility in the development of receptors for biologically relevant molecules such as bacterial Lipid A. The solution phase structure of a *ter*-cyclopentane scaffold was determined by NMR spectroscopy, and the results agree well with molecular modeling simulations.

Benzyne Cyclization

R. Sanz,* Y. Fernández, M. P. Castroviejo, A. Pérez, F. J. Fañanás 62–69

Functionalized Phenanthridine and Dibenzopyranone Derivatives through Benzyne Cyclization – Application to the Total Syntheses of Trisphaeridine and *N*-Methylcrinasiadine

Keywords: Anionic cyclizations / Organolithiums / Nitrogen heterocycles / Oxygen heterocycles / Benzynes / Synthetic methods

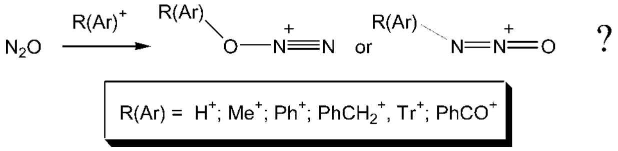


Functionalized benzo[*c*]chromen-6-ones, phenanthridinones, and phenanthridine derivatives have been prepared by anionic cyclization of benzyne-tethered aryllithium intermediates. *Amaryllidaceae* alkaloids trisphaeridine and *N*-methylcrinasiadine have been synthesized by applying this methodology.

Gas-Phase Ion−Molecule Reactions

L. G. Cabrini, M. Benassi, M. N. Eberlin,* T. Okazaki, K. K. Laali* .... 70−77

R(Ar)O−N_2^+ vs. R(Ar)−N_2O^+: Are Alkoxy-(Aryloxy-)diazonium Ions or Alkyl-(Aryl-)*N*-nitroso-onium Ions Formed in the Gas-Phase Reactions of N_2O with H^+, Me^+, Ph^+, $PhCH_2^+$, Tr^+ and $PhCO^+$?



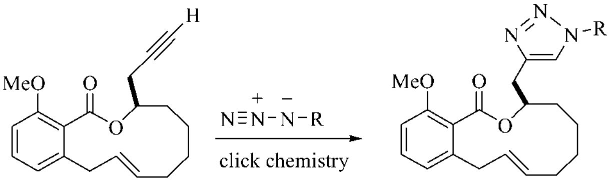
R(Ar)O−N_2^+ versus R(Ar)−N_2O^+: Gas-phase reactions of N_2O with H^+, Me^+, Ph^+, $PhCH_2^+$, Tr^+ (the tropylium ion) and $PhCO^+$ were studied by pentaquadrupole mass spectrometry. Relative energies and geometries of various RO−N_2^+/R−N_2O^+ isomeric pairs were evaluated by MP2 and DFT calculations.

Keywords: Alkoxy-(aryloxy-)diazonium ions / Alkyl-(aryl-)*N*-nitroso-onium ions / Ion molecule reactions / Pentaquadrupole mass spectrometry / Polar cycloadditions / Polar transacetalization

Click Chemistry on Benzolactones

J. Ritschel, F. Sasse, M. E. Maier* .... 78−87

Synthesis of a Benzolactone Collection using Click Chemistry



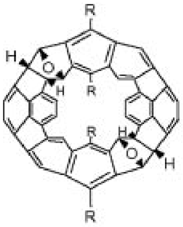
Click chemistry was used to combine a priviledged structure (benzolactone) with other pharmacophores. All benzolactone triazoles showed cytotoxic activity in an L929 mouse fibroblast assay with IC_{50} values in the low micromolar range.

Keywords: Benzolactones / Triazoles / Click chemistry / Azides / 1,3-Dipole / Natural product analogs

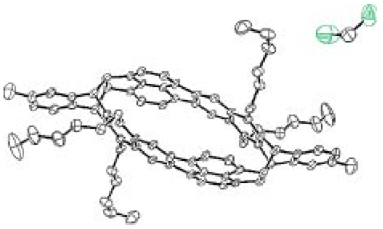
Avoiding Aromaticity

M. Stuparu, D. Lentz, H. Rüegger, A. D. Schlüter* .... 88−100

Exploring the Chemistry of a Double-Stranded Cycle with the Carbon Skeleton of the Belt Region of the C_{84} Fullerene



1



2

Double-stranded compound **1** cannot easily be converted into its fully aromatic analog by dehydration. Under acidic conditions it shows a variety of unusual reactions which include its conversion into the ditoluene adduct **2** of which the single crystal X-ray structure is shown.

Keywords: Aromaticity / Belt-shaped compounds / Cyclarenes / Dehydration / Arenes

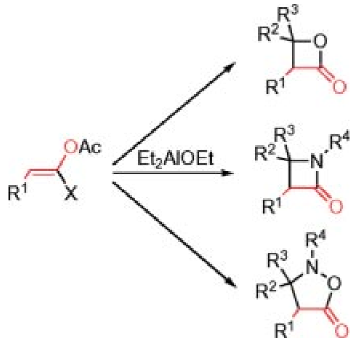
CONTENTS

Heterocycle Synthesis

R. Bejot, S. Anjaiah, J. R. Falck, C. Mioskowski* 101–107

α-Haloenol Acetates: Versatile Reactants for Oxetan-2-one, Azetidin-2-one and Isoxazolidin-5-one Synthesis

Keywords: Aldol reaction / Aluminum / Heterocycles / Lactonization / Tandem reaction



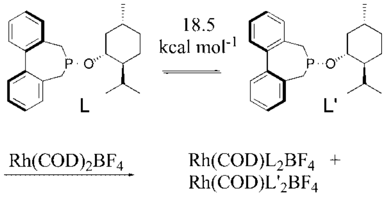
α-Haloenol acetates are investigated as reactants in a diethylaluminum ethoxide mediated tandem aldol–lactonization reaction. The resultant heterocyclic adducts, i.e., oxetan-2-ones, azetidin-2-ones and isoxazolidin-5-ones, are common structural elements in numerous compounds of interest.

Atropisomeric Phosphepines

R. Zalubovskis, E. Fjellander, Z. Szabó, C. Moberg* 108–115

Stereochemical Control of Chirally Flexible Phosphepines

Keywords: Atropisomerism / Phosphepine / Rotational barrier / Rh complex / Hydrogenation



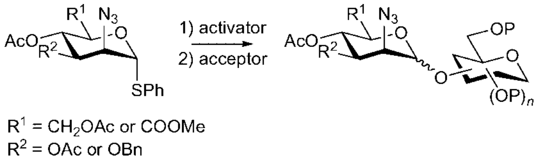
Let's twist again! The barrier to atropisomerization of 6,7-dihydro-5*H*-dibenzo[*c*,*e*]phosphepine was determined to be 18–20 kcal mol^{-1}at 298 K, depending on the group bound to the phosphorus atom. Complexation to Rh^{I} resulted in the formation of only homochiral complexes.

β-Selective Glycosylation

L. J. van den Bos, B. A. Duivenvoorden, M. C. de Koning, D. V. Filippov, H. S. Overkleeft, G. A. van der Marel* 116–124

Study of the Glycosidation Properties of 1-Thiomannosazidopyranosides and 1-Thiomannosaziduronic Acid Esters

Keywords: Carbohydrates / Glycosylation / Thioglycosides / *β*-Mannosamine / Mannuronic acids



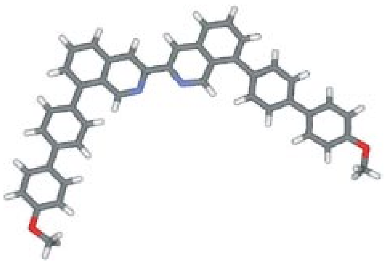
A study on the glycosylation properties of 1-thiomannosazides with a variety of electron-withdrawing substituents in combination with the Ph$_2$SO/Tf$_2$O and NIS/TMSOTf reagent systems is presented. Further, the assembly of a fully protected trisaccharide, corresponding to the repeating unit of the enterobacterial common antigen, using both an orthogonal and a chemoselective coupling strategy, and based on the outcome of our glycosylation studies, is discussed.

Crescent-Shaped Biisoquinolines

F. Durola, D. Hanss, P. Roesel, J.-P. Sauvage,* O. S. Wenger 125–135

A New Family of Biisoquinoline Chelates

Keywords: Biisoquinolines / Chelates / Endotopicity / Steric hindrance / C–C coupling



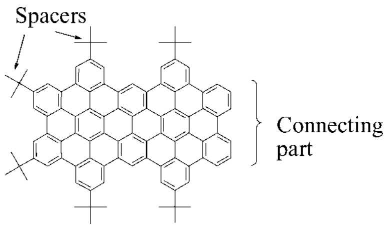
The synthesis of four 8,8′-diaryl-substituted 3,3′-biisoquinolines is reported. These sterically nonhindering endotopic ligands pave the way to molecules with unusual chemical topologies.

Asymmetric Superbenzene

C. Basu, C. Barthes, S. K. Sadhukhan, N. K. Girdhar, A. Gourdon* 136–140

Synthesis of a 2D Lander

Keywords: Molecular devices / Nanotechnology / Arenes / Cycloadditions / Diels–Alder reactions



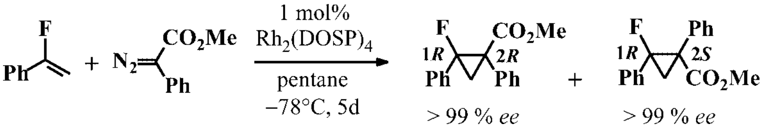
A method for the preparation of an asymmetric superbenzene is presented. The synthesis proceeds through the 12-fold cyclodehydrogenation of a polyaromatic precursor obtained by successive Diels–Alder additions of cyclopentadienones and alkynes.

Asymmetric Cyclopropanation

S. Hruschka, R. Fröhlich, P. Kirsch, G. Haufe* 141–148

Synthesis of New Enantiopure Fluorinated Phenylcyclopropanecarboxylates – Potential Chiral Dopants for Liquid-Crystal Compositions

Keywords: Asymmetric catalysis / Fluorine / Liquid crystals / Chirality / Cyclopropanes



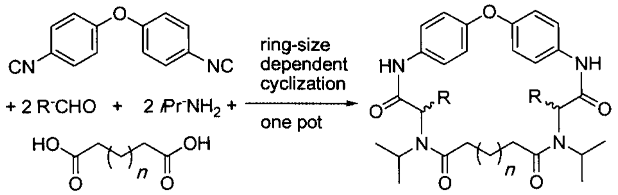
The reaction of α-fluorostyrene with methyl phenyldiazoacetate in the presence of $Rh_2(OAc)_4$ gives a mixture of diastereomeric monofluorinated cyclopropanes. When using chiral rhodium(II) (arylsulfonyl)prolinate catalysts, the products were obtained enantioselectively. The fluorocyclopropane derivatives are of interest as dopants in order to induce chirality in liquid crystal mixtures.

Multiple-Component Macrocyclizations

D. Michalik, A. Schaks, L. A. Wessjohann* 149–157

One-Step Synthesis of Natural Product-Inspired Biaryl Ether-Cyclopeptoid Macrocycles by Double Ugi Multiple-Component Reactions of Bifunctional Building Blocks

Keywords: Multiple component reaction / Biaryl ether / Macrocyclization / Cyclopeptide / Ugi reaction / Peptoid



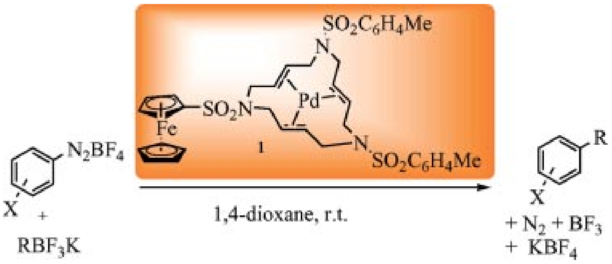
A one-step synthesis of natural product inspired biaryl ether-cyclopeptoid macrocycles by double Ugi multiple-component reactions of bifunctional building blocks is described.

Azamacrocyclic Triolefinic Pd^0 Catalyst

J. Masllorens, I. González, A. Roglans* 158–166

Recoverable Homogeneous Palladium(0) Catalyst for Cross-Coupling Reactions of Arenediazonium Salts with Potassium Organotrifluoroborates: Detection of Catalytic Intermediates by Electrospray Ionization Mass Spectrometry

Keywords: Arenediazonium salts / Potassium organotrifluoroborates / Cross-coupling / Palladium / Mass spectrometry



Air- and moisture-stable palladium(0) complex **1** is an active and recoverable catalyst for Suzuki–Miyaura reactions between arenediazonium salts and potassium organotrifluoroborates. Electrospray Ionization Mass Spectrometry (ESI-MS) studies allow the detection of several catalytic intermediates in the above-mentioned reaction.

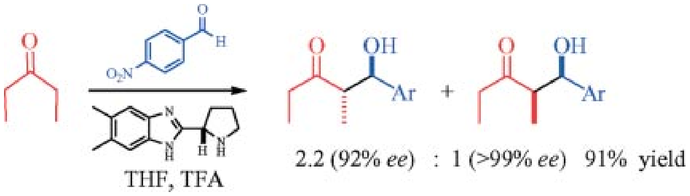
CONTENTS

New Organocatalysts

E. Lacoste, E. Vaique, M. Berlande,
I. Pianet, J.-M. Vincent,*
Y. Landais* 167–177

Benzimidazole-pyrrolidine/H$^+$ (BIP/H$^+$), a Highly Reactive Organocatalyst for Asymmetric Processes

Keywords: Organocatalysis / Aldol reactions / Amination / Robinson annelation / Proline / 1-Silacyclohexan-4-one



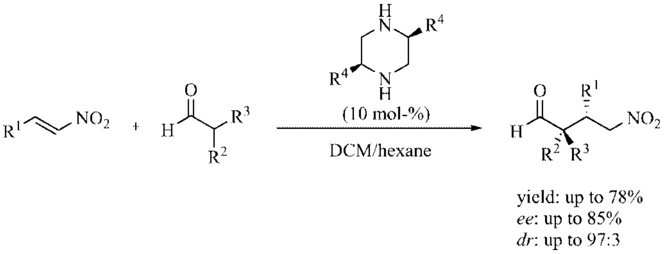
BIP! BIP! A new chiral benzimidazole-pyrrolidine (BIP) has been devised which exhibits excellent activities in various amino-catalyzed processes, leading to products in high yields and enantioselectivities in the presence of an equimolar amount of a Brönsted acid (TFA). A discussion of the role of the Brönsted acid as a co-catalyst is provided along with some applications of this new class of reactive organocatalysts.

Organocatalysis with Piperazine Catalysts

M. T. Barros,*
A. M. Faísca Phillips 178–185

Chiral Piperazines as Efficient Catalysts for the Asymmetric Michael Addition of Aldehydes to Nitroalkenes

Keywords: Asymmetric catalysis / Michael addition / Aldehydes / Nitroalkenes / Piperazines



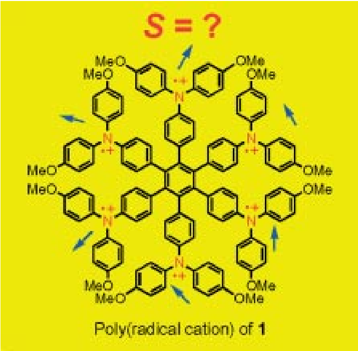
The feasibility of using substoichiometric amounts of piperazine or chiral C_2-symmetric disubstituted piperazines to promote the synthesis of either racemic or chiral γ-formylnitroalkanes from unmodified aldehydes is demonstrated.

Excited High-Spin Poly(radical cation)

Y. Hirao, H. Ishizaki, A. Ito,* T. Kato,*
K. Tanaka 186–190

The Poly(Radical Cation) of a Star-Shaped Oligoarylamine – Detection of Excited High-Spin States

Keywords: Radical ions / Oxidation / Magnetic properties / Redox chemistry / EPR spectroscopy



Intramolecular spin–spin interaction in the highly oxidized species of a star-shaped oligoarylamine, hexakis{4-[bis(*p*-methoxyphenyl)amino]phenyl}benzene (**1**), has been investigated by ESR spectroscopy. It was found that the high-spin states are thermally populated in the highly oxidized species of **1** with increasing temperature.

Bichromophores

S. Gokulnath, V. Prabhuraja, J. Sankar, T. K. Chandrashekar* 191–200

Smaragdyrin–Azobenzene Conjugates: Syntheses, Structure, and Spectral and Electrochemical Properties

The syntheses, characterization, and spectral properties of smaragdyrin–azobenzene conjugates are reported. Electronic absorption and emission spectral studies reveal the presence of a moderate electronic interaction between the azobenzene and smaragdyrin π-systems. The azobenzene is in the (*E*) conformation both in the dipyrromethane and in the smaragdyrin conjugates, as revealed by its single-crystal X-ray structure.

Keywords: Porphyrins / Dipyrromethane / UV/Vis spectroscopy / Isomerization / Electrochemistry

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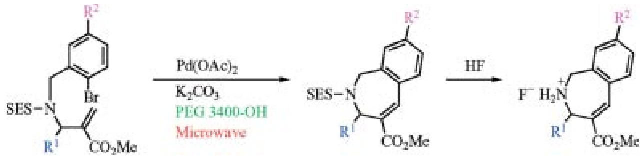
PEG and Microwave in Heck Reactions

V. Declerck, P. Ribière, Y. Nédellec, H. Allouchi, J. Martinez, F. Lamaty* 201–208

A Microwave-Assisted Heck Reaction in Poly(ethylene glycol) for the Synthesis of Benzazepines



A microwave-assisted Heck reaction in poly(ethylene glycol) 3400 was particularly efficient and selective for the formation of trisubstituted olefins. Starting from SES-protected β-amino esters, diverse benzazepines were prepared in excellent yields. Cleavage of the SES group with HF provided the corresponding free-amine benzazepines.

Keywords: Microwaves / Nitrogen heterocycles / Nanoparticles / Palladium / Solvent effects