



















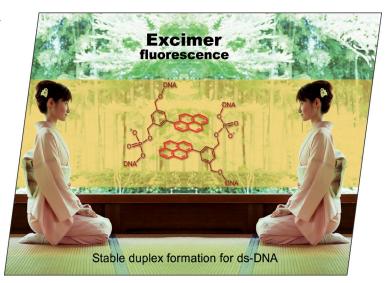






COVER PICTURE

The cover picture shows a DNA duplex containing a biaryl unit, which is made up of benzene and pyrene moieties; an excimer is formed between the biaryl units, which results in the formation of a duplex. In the article by Y. Ueno et al. on p. 4763ff the synthesis of the monomer units and oligonucleotides containing the biaryl units and the thermal stabilities of the duplexes, as well as their absorption and fluorescence properties, are discussed. The authors would like to thank Yoichiro Kato for his help in designing the cover picture.



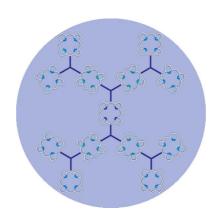
MICROREVIEW

Porphyrin Dendrimers

W. Maes, W. Dehaen* 4719-4752

Synthetic Aspects of Porphyrin Dendrimers

Keywords: Dendrimers / Porphyrins / Synthetic methods / Biomimetic synthesis / Artificial photosynthesis



Porphyrins have been abundantly used as structural components of dendrimers, located variously at the interior cores, within the branching dendrons, at the exterior surfaces, or spread throughout complete dendritic frameworks. A comprehensive overview of the currently available structural diversity of porphyrin-containing dendrimers and the synthetic approaches applied to them is provided.

SHORT COMMUNICATIONS

Iron/Copper Cocatalysis

X.-F. Wu, C. Darcel* 4753-4756



Ligand-Free Iron/Copper-Cocatalyzed Amination of Aryl Iodides

Keywords: Homogeneous catalysis / Iron / Copper / Amination / Green chemistry

(10 mol-%)

An efficient, mild, and simple protocol for the direct amination of aryl iodides was accomplished by using a ligand-free, Fe₂O₃/CuI cocatalytic system in the presence of aqueous ammonia (5 equiv.) in ethanol at 90 °C under aerobic conditions.

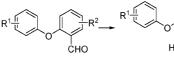
Arylxanthene Synthesis

S. K. Das, R. Singh, G. Panda* 4757-4761



A New Synthetic Route to Unsymmetrical 9-Arylxanthenes

Keywords: Fused-ring systems / Oxygen heterocycles / Arenes / Synthetic methods



90 °C, 16 h

A facile and general three-step synthetic route towards unsymmetrical 9-arylxanthenes was developed. The reaction sequence involves nucleophilic substitution of 2-fluorobenzaldehydes with arenoxides,

Grignard reaction of the resulting 2-arenoxybenzaldehydes with arylmagnesium

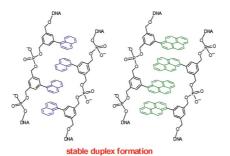
enoxybenzaldehydes with arylmagnesium bromides, followed by FeCl₃-catalyzed intramolecular diarylmethylation of the resulting carbinols.



FULL PAPERS

RNA Molecular Beacons

Oligonucleotides containing biaryl units composed of naphthalene and pyrene moieties were synthesized, and their properties were studied. It was revealed that incorporation of the biaryl units into the duplex structures enhanced their thermal and thermodynamic stabilities. Furthermore, biaryl units containing a pyrene moiety formed an excimer in the duplex.

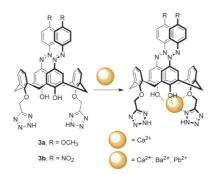


Synthesis and Properties of Oligonucleotides Containing Novel Fluorescent Biaryl Units

Keywords: Biaryls / DNA / RNA recognition / Oligonucleotides / Fluorescent probes

Host-Guest Chemistry

Calix[4]arene **3a** was a highly chromogenic sensor to Ca^{2+} , whereas **3b** showed color changes toward Ca^{2+} , Pb^{2+} , and Ba^{2+} (with decreasing K_a). These lower-rim oxymethyltetrazole-modified azocalix[4]arenes were synthesized by an (n-butyl) $_2$ SnO-mediated 1,3-dipolar cycloaddition of the corresponding oxyacetonitrile with TMSN $_3$.

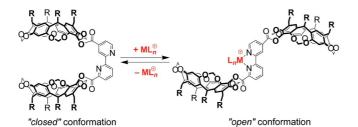


Y.-J. Chen, W.-S. Chung* 4770-4776

Tetrazoles and *para*-Substituted Phenylazo-Coupled Calix[4]arenes as Highly Sensitive Chromogenic Sensors for Ca²⁺

Keywords: Cycloaddition / Inclusion compounds / Nitrogen heterocycles / Calixarenes / Ionophores

Conformational Switching



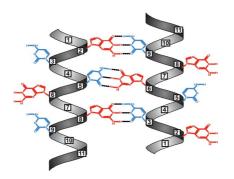
Four new 2,2'-bipyridines that carry resorcinarene moieties were prepared in a highly convergent manner. Upon coordination to suitable transition metal ions or their complexes, these compounds undergo confor-

mational changes from "open" to "closed" forms or vice versa. Rhenium and monomeric copper(I) complexes proved to be strong effectors for this switching.

Towards Allosteric Receptors – Synthesis of Resorcinarene-Functionalized 2,2'-Bi-pyridines and Their Metal Complexes

Keywords: Macrocycles / Calixarenes / Nitrogen heterocycles / Supramolecular chemistry / Allosteric receptors

The decoration of β -peptide 14-helices with nucleobases allows 3D organization of helical secondary structures. Functionalization of two helical faces allows the generation of hydrogen-bonded helix-aggregation of exceptional stability.



Aggregation of β -Peptides

R. Srivastava, A. Kumar Ray, U. Diederichsen* 4793–4800

Higher Aggregation of β -Peptide Networks Controlled by Nucleobase Pairing

Keywords: Aggregation / Peptides / Nucleobases / Helical structures / Structure elucidation / Self-assembly

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DNA Binders

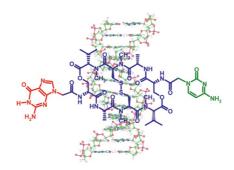
A. Kumar Ray,

U. Diederichsen* 4801-4809



Syntheses of Triostin A Antibiotic and Nucleobase-Functionalized Analogs as New DNA Binders

Keywords: Amino acids / Cyclic depsipeptide / DNA recognition / Nucleobases / Triostin A



Triostin A binds to DNA through bisintercalation while its nucleobase analogs can bind in additional modes due to the presence of hydrogen-bonding acceptor/donor sites. Stepwise solution-phase synthesis following an orthogonal approach furnished the natural product triostin A and its analogs.

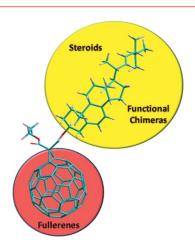
Steroid-Fullerene Hybrids

J. Coro, H. Rodríguez, D. G. Rivera, M. Suárez,* D. Molero, M. Á. Herranz, R. Martínez-Álvarez, S. Filippone,



Functional Chimeras: New Bingel-Hirsch-Type Steroid-Fullerene Hybrids

Keywords: Fullerenes / Steroids / Cycloaddition / Peroxides



Bingel—Hirsch cyclopropanations between C_{60} and malonates bearing different steroid moieties afford new hybrid functionalized chimeras. The diene system present in ergosterol undergoes a subsequent [4+2] cycloaddition with molecular oxygen as a result of the sensitizing ability of the fullerene unit, thus yielding an unexpected endoperoxide.

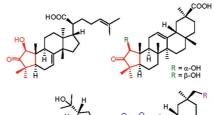
Natural Products

X.-F. He, X.-N. Wang, S. Yin, L. Dong, J.-M. Yue* 4818–4824



Ring A Modified Novel Triterpenoids from *Dysoxylum hainanense*

Keywords: Terpenoids / Structural elucidation / Biological activity / Biosynthesis



The twigs and leaves of *Dysoxylum hain-anense* metabolized six ring A modified novel triterpenoids, dysoxyhainic acids A–E and dysoxyhainol. The structures of these triterpenoids were elucidated. Dysoxyhainic acid A featured an unprecedented 2-nor-1,3- cyclotirucallane skeleton. Two of them exhibited moderate antibacterial activity against Gram-positive bacteria.

Hydroxyproline Calix[4]resorcinarenes

K. A. Hagan, C. M. O'Farrell, T. J. Wenzel* 4825–4832

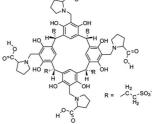


Water-Soluble Calix[4]resorcinarenes with Hydroxyproline Groups as Chiral NMR Solvating Agents for Phenyl- and Pyridyl-Containing Compounds

Keywords: NMR spectroscopy / Chiral resolution / Host-guest systems / Inclusion compounds / Cavitands / Enantioselectivity



Water-soluble sulfonated calix[4]resorcinarenes with *cis-*4-hydroxy-D- and -L-proline, *trans-*4-hydroxy-L-proline and *trans-*3-hydroxy-L-proline substituent groups are generally more effective chiral NMR sol-



vating agents than the corresponding L-proline derivative. Enantiomeric discrimination in the ¹H NMR spectra is large enough to facilitate the analysis of enantiomeric purity.



Asymmetric Catalysis

 R^1 , $R^2 = iPr$, tBu, Ph, Bn

Novel tridentate ligands possessing oxazoline and thiazoline rings were prepared in a high-yielding, convergent synthesis. One of the six ligands prepared was analyzed by X-ray crystallography and all six were applied to the zinc-catalyzed Friedel-Crafts alkylation of indole. Quantitative yields and enantiomeric excesses of up to 76 % were obtained.

New Thiazoline-Oxazoline Ligands and Their Application in the Asymmetric Friedel-Crafts Reaction



Keywords: Asymmetric synthesis / Enantioselectivity / Synthetic methods / Tridentate ligands / Zinc

Sugar-Functionalized Pt Complexes

J. Möker, J. Thiem* 4842-4847

Synthesis of Novel *gluco-* and *galacto-*Functionalized Platinum Complexes

Keywords: Antitumor agents / Carbohydrates / Platinum / Sugar ethers / Sugar-functionalized complexes

According to well-known cytostatics, syntheses of carbohydrate-functionalized platinum complexes were developed. Starting with glucose and galactose, selective protection led to monohydroxy derivatives that

could be etherified by ω -halo ethers. Further Finkelstein reaction and malonate synthesis gave precursor glycoconjugates which could be facily transformed into their diamino platinum complexes.

Asymmetric Catalysis

D.-Z. Xu, S. Shi, Y. Wang* ... 4848-4853

Simple Chiral Pyrrolidine-Pyridine-Based Catalysts for Highly Enantioselective Michael Addition to Nitro Olefins

Keywords: Asymmetric catalysis / Michael addition / Alkenes / Organocatalysis / Pyrrolidine / Catalyst design

Simple chiral pyrrolidine—pyridine-based catalysts, available from commercially available starting materials, have been evaluated as catalysts for use in Michael addition reactions with nitro olefins. An ex-

ceptionally broad range of ketones (cyclic/acyclic/aromatic), an aldehyde, and a variety of nitro olefins are tolerated in this system.

Anion Recognition

Less is more. 2-Carbamoyl-7-ureido-substituted indoles are good anion receptors possessing four H-donor units. Removal of the 2-carbamoyl hydrogen-bond donor site re-

sults in enhanced binding affinities due to an enforced unfavoured conformational change at the amide of the "bigger" receptor. The Halide Binding Behavior of 2-Carbamoyl-7-ureido-1*H*-indoles: Conformational Aspects

Keywords: Host—guest systems / Anion recognition / Nitrogen heterocycles / NMR spectroscopy / Conformational analysis

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N-Heterocyclic Chemistry

A. Ribeiro, M. A. Carvalho,* M. F. Proença 4867-4872

A Mild Approach to the Synthesis of 4-Amino-8-(arylamino)pyrimido[5,4-d]pyrimidine 3-Oxides

Keywords: Nitrogen heterocycles / Nitrones / Purines / Pyrimido[5,4-d]pyrimidines / Rearrangment / Cleavage reactions

This work describes the chemospecific conversion of the hydrochloride of pyrimido-[5,4-d]pyrimidin-4(3H)-one O-benzyloximes to pyrimido[5,4-d]pyrimidine 3-oxides and to a product generated by Dimroth rearrangement.

Tocopherol Chemistry

A. Patel, S. Böhmdorfer, A. Hofinger, T. Netscher, T. Rosenau* 4873-4881

Bromination of Non-α-Tocopherols: A Comparative Synthetic, Kinetic and Computational Study

Keywords: Vitamin E / Tocopherols / Halogenation / Electrophilic substitution / Reactive intermediates / Kinetics / o-Quinone methide

Bromination mechanisms and products for all four tocopherols are compared.

1) HOOCCH(R1)N(R2)COCF3

Napthoquinone Functionalization

J. Deblander, S. Van Aeken, J. Jacobs,

K. Abbaspour Tehrani* 4882-4892

2) (CH₂O)_n, HBr N. De Kimpe, 3) KOH aq. 4) air oxidation A New Synthesis of Benzo[f]isoindole-4,9diones by Radical Alkylation and Bromo- $R^1 = H, Me, Bn; R^2 = H$ $R^1, R^2 = (CH_2)_3$

methylation of 1,4-Naphthoquinones

Keywords: Quinones / Radical reactions / Nitrogen heterocycles / Alkylation / Bromine

A simple radical decarboxylation procedure has been applied to α-amino acids to functionalize 1,4-naphthoquinones under Kochi-Anderson conditions. The alkylated naphthoquinones were converted after bromomethylation and N-deprotection into substituted benzo[f]isoindole-4,9-diones.

Supporting information on the WWW (see article for access details).

If not otherwise indicated in the article, papers in issue 27 were published online on September 1, 2009

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