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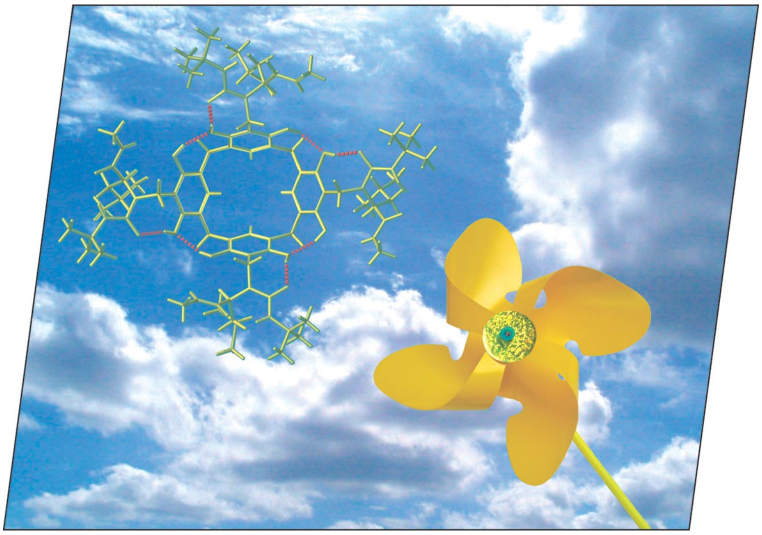
EUChemSoc

The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the X-ray structure of C_4-symmetric, chiral resorcinarene substituted with L-leucine at the upper rim. The molecule is held in the inherently chiral conformation (resembling a chiral C_4-symmetric propeller) by means of twelve intramolecular hydrogen bonds. The seams of hydrogen bonds can be directed in one particular direction because of diastereomeric preferences. The determination of the direction of the hydrogen-bonding seam and the correlation with CD spectra is discussed in the article by A. Szumna et al. on p. 3069ff.



CONTENTS

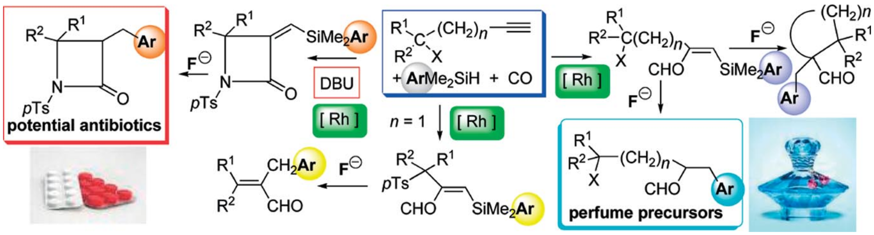
MICROREVIEW

Polyfunctionalised Molecules

L. A. Aronica, A. M. Caporusso, P. Salvadori* **3039–3060**

Synthesis and Reactivity of Silylformylation Products Derived from Alkynes

Keywords: Alkynes / Silanes / Carbonylation / Rearrangement / Aldehydes / Lactams



The silylformylation reaction allows to add a silyl and a formyl moiety to C≡C bonds to afford β-silylalkenals and α-silylmethylene β-lactams. The arylsilyl functionality can be used as carrier for the aryl group which can migrate from Si to C when a fluoride source is present, affording different polyfunctionalised molecules.

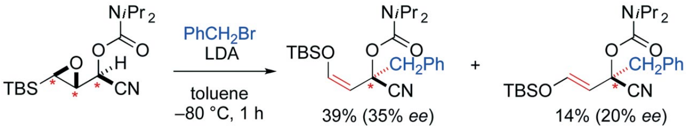
SHORT COMMUNICATIONS

Chiral Carbanions

M. Sasaki, E. Kawanishi, Y. Shirakawa, M. Kawahata, H. Masu, K. Yamaguchi, K. Takeda* **3061–3064**

Chirality Transfer from Epoxide to Carbanion: Base-Induced Alkylation of *O*-Carbamoyl Cyanohydrins of β-Silyl-α,β-epoxy Aldehyde

Keywords: Chirality / Carbanions / Rearrangement / Asymmetric synthesis / Alkylation



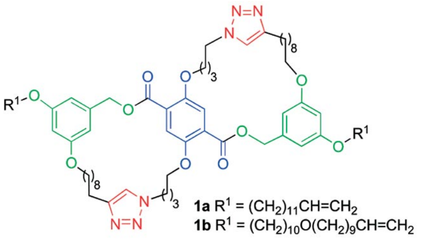
Enantioselective C–C bond formation at an α-position of a nitrile group with an external electrophile can be realized, although in modest *ee*, with the aid of the concerted process of an epoxysilane rearrangement and a carbamoyl group.

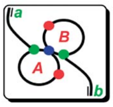
Molecular Knots

E. E. Fenlon,* B. R. Ito **3065–3068**

The Thread & Cut Method: Syntheses of Molecular Knot Precursors

Keywords: Chemical Topology / Chirality / Macrocycles / Molecular knots / Synthesis design

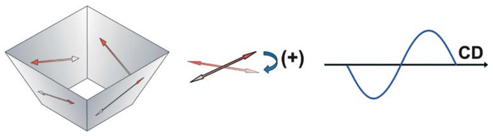




A novel approach to molecular knots is described. This method may allow access to smaller and more complex knots. Two bismacrocyclic knot precursors (**1a** and **1b**) are efficiently prepared through convergent six-step syntheses with overall yields of 9.6% and 8.7%, respectively.

FULL PAPERS

Inherent Chirality



The C_4-symmetric chiral seam of hydrogen bonds in amino acid substituted resorcin[4]arenes is stable enough to determine its direction and to correlate with the Cotton effects observed for the inherently chiral resorcin[4]arene skeleton.

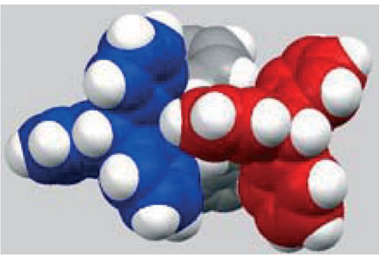
B. Kuberski, M. Pecul, A. Szumna* .... 3069−3078

A Chiral “Frozen” Hydrogen Bonding in C_4-Symmetric Inherently Chiral Resorcin[4]arenes: NMR, X-ray, Circular Dichroism, and Theoretical Study

Keywords: Calixarenes / Amino acids / Atropisomerism / Conformation analysis / Receptors

Triptycenes

Oxidative homocoupling of lithiated 2-substituted indenes furnishes *racemic* dimers, while radical reaction leads to a mixture of *racemic* and *meso* diastereomers. Internal rotation in these dimers was studied by NMR and molecular modelling.

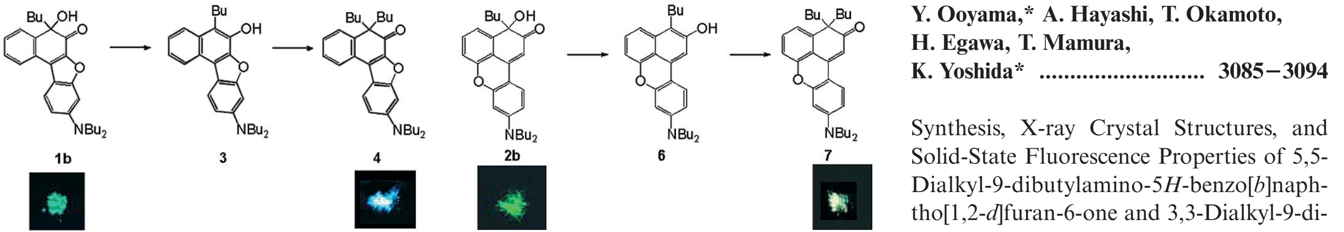


K. Nikitin,* H. Müller-Bunz, Y. Ortin, W. Risse, M. J. McGlinchey* ... 3079−3084

Twin Triptycyl Spinning Tops: A Simple Case of Molecular Gearing with Dynamic C_2 Symmetry

Keywords: C−C coupling / Molecular modelling / Oxidation / Radical reactions

Solid-State Fluorescent Dyes



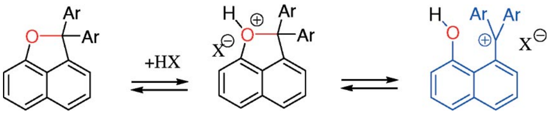
Dramatic dialkyl substituent effects on the solid-state photophysical properties of heterocyclic fluorophores 5,5-dibutyl-9-dibutylamino-5*H*-benzo[*b*]naphtho[1,2-*d*]furan-6-one (**4**) and 3,3-dibutyl-9-dibutylamino-3*H*-benzo[*kl*]xanthen-2-one (**7**) have been discussed on the basis of the X-ray crystal structures.

Y. Ooyama,* A. Hayashi, T. Okamoto, H. Egawa, T. Mamura, K. Yoshida* .... 3085−3094

Synthesis, X-ray Crystal Structures, and Solid-State Fluorescence Properties of 5,5-Dialkyl-9-dibutylamino-5*H*-benzo[*b*]naphtho[1,2-*d*]furan-6-one and 3,3-Dialkyl-9-dibutylamino-3*H*-benzo[*kl*]xanthen-2-one

Keywords: Crystal structure / Dyes/pigments / Fluorescence / Oxygen heterocycles / Substituent effects

Triarylmethyl Cations



The reversibility of the ring-closing reaction has been studied for some 1,8-difunctionalized naphthalenes, including carbocyclic as well as O- and N-heterocyclic model compounds. A naphthofuran bearing a triarylmethyl moiety seemed to act as an indicator under strongly acidic conditions.

G. Dyker,* M. Hagel, G. Henkel, M. Köckerling .... 3095−3101

Naphthyl-Substituted Carbocations: From *peri* Interaction to Cyclization

Keywords: Carbocations / Cyclization / Triarylmethyl cations / *peri* interactions / Ring strain / *para*-Quinonoid compounds

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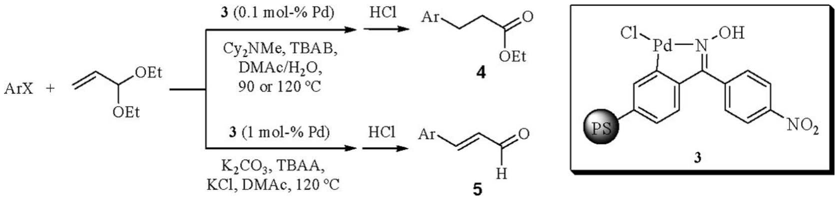
Acrolein Ethyl Acetal Heck Reaction

E. Alacid, C. Nájera* 3102–3106

Acrolein Diethyl Acetal: A Three-Carbon Homologating Reagent for the Synthesis of β-Arylpropanoates and Cinnamaldehydes by Heck Reaction Catalyzed by a Kaiser Oxime Resin Derived Palladacycle

Keywords: Heck reaction / Palladacycles / Aldehydes / Esters / Polymers



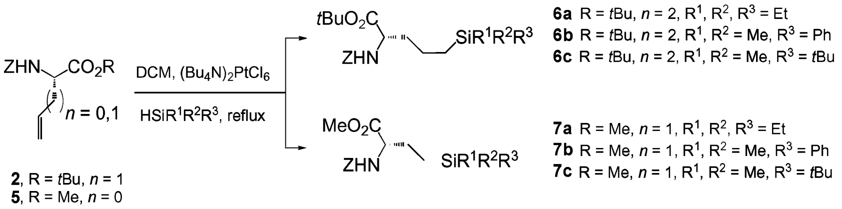
A polymer palladacycle derived from Kaiser oxime resin was applied as a reusable catalyst in the chemoselective Heck reaction of acrolein diethyl acetal with aryl halides under ligand-free conditions to afford ethyl 3-arylpropanoates (Heck conditions) or cinnamaldehydes (Cacchi conditions).

Nonnatural Amino Acid Synthesis

D. Marchand, J. Martinez,
F. Cavelier* 3107–3112

Straightforward Synthesis of Chiral Silylated Amino Acids through Hydrosilylation

Keywords: Amino acids / Hydrosilylation / Peptides / Peptide analogues



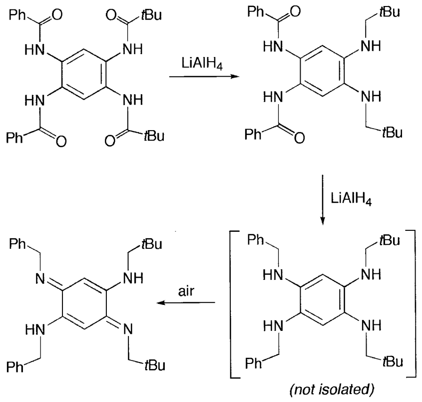
The hydrosilylation of unsaturated amino acids was optimised to obtain silylated amino acids. The platinum $(Bu_4N)_2PtCl_6$ complex was identified as the best catalyst. Seven silicon-containing α-amino acids were prepared in an enantiomerically pure form under mild conditions in good yields with orthogonal protections for versatile use in peptide synthesis.

Chemoselectivity

C. Seillan, P. Braunstein,
O. Siri* 3113–3117

Selective Reduction of Carbonyl Amides: Toward the First Unsymmetrical Bischelating *N*-Substituted 1,2-Diamino-4,5-diamidobenzene

Keywords: Reduction / N ligands / Amides



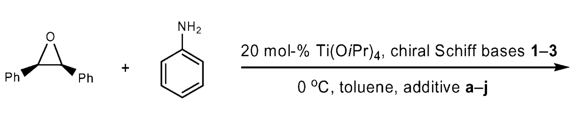
The chemoselective reduction of carbonyl amides affords an unprecedented *N*-substituted 1,2-diamino-4,5-diamidobenzene and/or the first member of a new family of 12π-electron quinonediimines.

Enantioselective Epoxide Opening

R. I. Kureshy,* K. J. Prathap, S. Agrawal,
N. H. Khan, S. H. R. Abdi,
R. V. Jasra 3118–3128

Highly Enantioselective Syntheses of Chiral β-Amino Alcohols in the Presence of Chiral Ti^{IV} Schiff Base Complexes as Catalysts

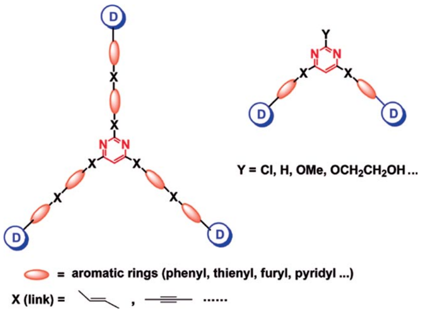
Keywords: Enantioselectivity / Titanium complexes / Schiff bases / Chiral β-amino alcohols / *meso*-Epoxides / Anilines



Chiral Ti^{IV} Schiff base complexes catalyze the enantioselective ring opening reactions of *meso*-stilbene oxide, cyclohexene oxide, cyclooctene oxide and *cis*-butene oxide with anilines in the presence of several additives at 0 °C. Excellent yields (>99%) of chiral β-amino alcohols were achieved with high enantioselectivity (*ee*, >99%) in 10 h when chiral imines were used as additives.

Light-Emitting Materials

We report the synthesis, geometry and electronic and optical properties of various star- and banana-shaped oligomers with a pyrimidine unit as the central core Some of the oligomers synthesised are highly fluorescent and present interesting solvatochromic properties and pH sensibility.



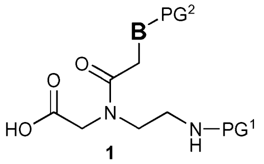
S. Achelle, Y. Ramondenc, F. Marsais, N. Plé* 3129–3140

Star- and Banana-Shaped Oligomers with a Pyrimidine Core: Synthesis and Light-Emitting Properties

Keywords: Pyrimidines / Cross-coupling / Conjugation / Solvatochromism / Fluorescence

Fmoc Orthogonal Synthesis

We present a thorough investigation of six types of protecting groups for the terminal nitrogen atom and five protecting groups on the nucleobases of peptide nucleic acids for fully orthogonal synthesis with Fmoc.



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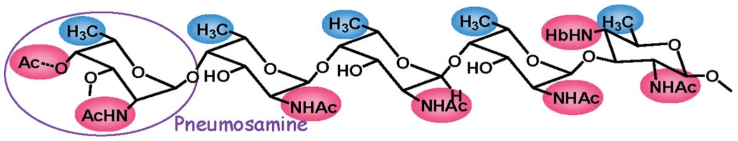
PG^1 = Alloc, Teoc, 4-N_3Cbz, Fmoc, 4-OTBSCbz, Azoc
PG^2 = Cl-Bhoc, F-Bhoc, 4-OMeCbz, Teoc, Boc

S. Pothukanuri, Z. Pianowski, N. Winssinger* 3141–3148

Expanding the Scope and Orthogonality of PNA Synthesis

Keywords: Peptides / Nucleic acids / Combinatorial chemistry / Protecting groups

Lipopolysaccharides



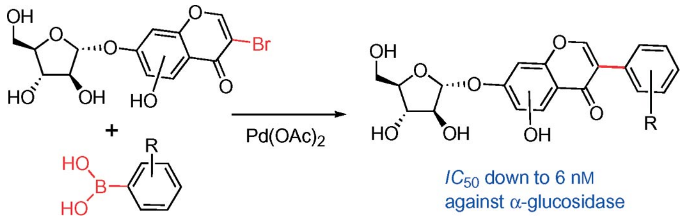
A new O-chain polysaccharide obtained from the lipopolysaccharide isolated from the pathogen *Plesiomonas shigelloides* 302–73 (serotype O1) was characterised by 2D-NMR and MALDI-TOF MS. It is composed of a pentasaccharidic repeating unit containing five N-acylated deoxyamino sugars, of which one is an uncommon pneumosamine.

G. Pieretti, M. M. Corsaro,* R. Lanzetta, M. Parrilli, R. Canals, S. Merino, J. M. Tomás 3149–3155

Structural Studies of the O-Chain Polysaccharide from *Plesiomonas shigelloides* Strain 302–73 (Serotype O1)

Keywords: Lipopolysaccharide / NMR spectroscopy / Pneumosamine / Structure elucidation

Isoflavone Glycosides



Suzuki–Miyaura coupling leads to a variety of isoflavone 7-*O*-α-D-arabinofuranosides, which show α-glucosidase inhibitory activities with IC_{50} values down to 6 nM.

G. Wei, B. Yu* 3156–3163

Isoflavone Glycosides: Synthesis and Evaluation as α-Glucosidase Inhibitors

Keywords: Inhibitors / Glycosides / Suzuki–Miyaura coupling / C–C coupling / Glycosylation

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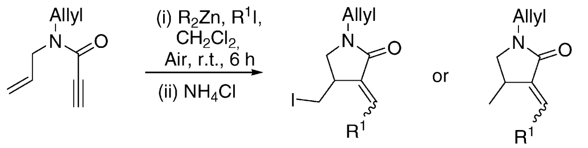
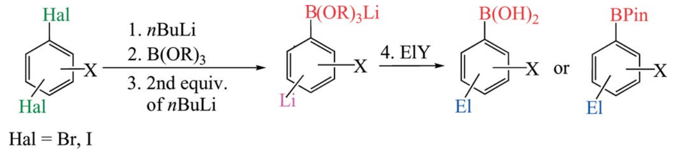
Radical Reactions



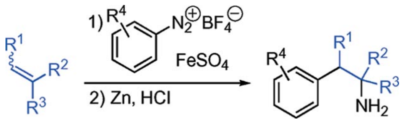
Alkylative cycloisomerization of *N*,*N*-diallylpropiolamide into α-alkylidene-γ-lactams was mediated by dialkylzinc reagents in aerobic medium. In the presence of an alkyl iodide, final oxidation by iodine-atom transfer predominates over reductive zincation. The dialkylzinc-mediated radical process tolerates the presence of the acidic terminal alkyne.

Lithiated Boron "ate" Complexes



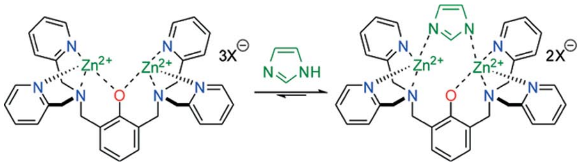
A simple approach to substituted arylboronic acids by bimetallic boron–lithium intermediates is reported.

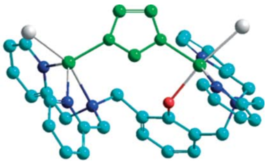
Carbodiazenylation



Radical carbodiazenylation reactions starting from arenediazonium salts offer cost-effective, convenient and efficient access to carboamination products of non-activated olefins.

Imidazole Receptors



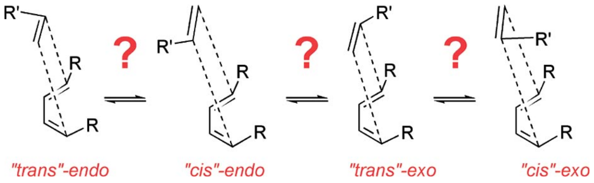


Imidazole chelation with phenol-bridged binuclear zinc–bis(2-picolyl)amine (Dpa) chelates displaces the phenol bridge between the zinc ions. A significant imidazole affinity of the Dpa chelates has been discovered and is supported by NMR and computational studies

Selectivity in Diels–Alder Reactions

S. Baki, J. Maddaluno, A. Derdour, P. Chaquin* 3200–3208

Diels–Alder Reactions of Symmetrically 1,4-Disubstituted Dienes: Theoretical Study on the Influence of the Configuration of the Double Bonds on the Regio- and Endoselectivity



The origin of the regio- and endoselectivities exhibited by symmetrically (*E*,*Z*)-1,4-disubstituted dienes in Diels-Alder reactions is discussed. Classical sources of selectivities such as frontier orbital interactions cannot account for the predicted results, but steric and electrostatic factors were found to be of prime importance. The prediction of selectivities remains difficult.

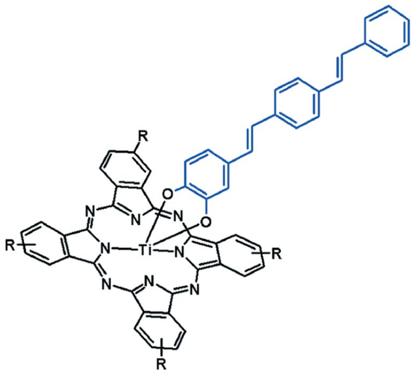
Keywords: Cycloaddition / Diels–Alder reaction / Regioselectivity / Density functional calculations

Titanium(IV) Phthalocyanines

A. Lyubimtsev, M. N. Misir, M. Calvete, M. Hanack* 3209–3214

Titanium Phthalocyanines with Axial Phenylenevinylenes

Soluble, peripherally substituted titanium(IV) phthalocyanines with axial polyphenylenevinylenes (PVs) have been synthesized. They are stable in solution, for example, in dichloromethane, in the dark. Their stability in solution in sunlight depends on the peripheral substituents and on the chain length of the axial PVs.



Keywords: Titanium / Phthalocyanines / Axial substitution / Phenylenvinylene

* Author to whom correspondence should be addressed.

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