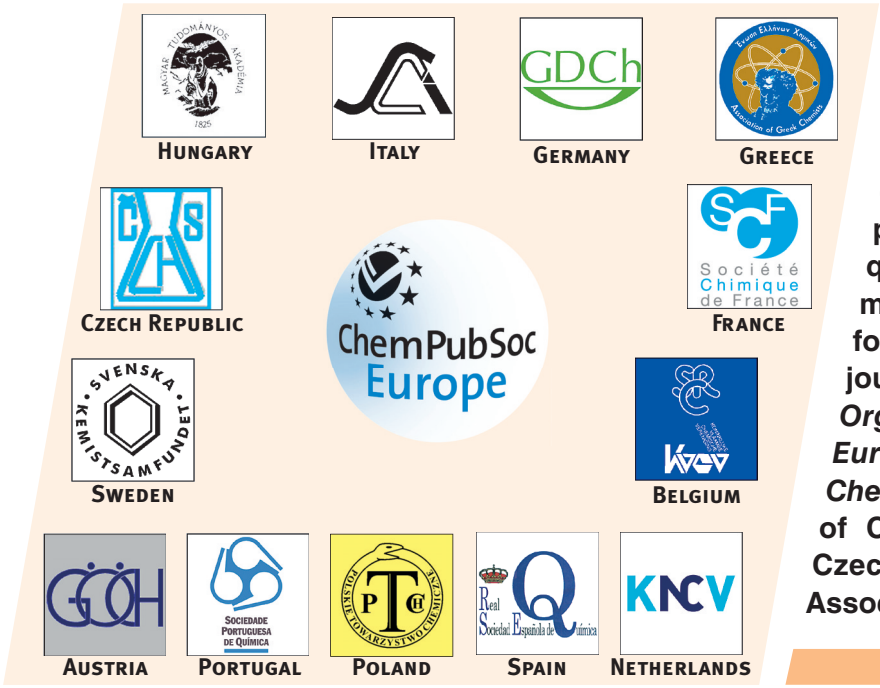
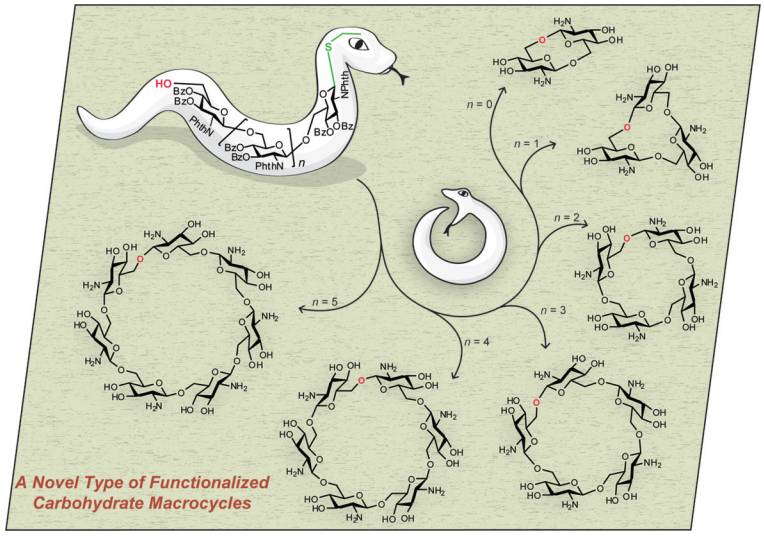


EurJOC is co-owned by 11 societies of ChemPubSoc Europe, a union of European chemical societies for the purpose of publishing high-quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Organic Chemistry* and the *European Journal of Inorganic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem*, *ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem*.

COVER PICTURE

The cover picture shows the synthesis of a novel type of functionalized cyclic oligosaccharides by unusually efficient *head-to-tail* intramolecular glycosylation of corresponding monohydroxy ethylthio glycosides derived from oligo-(1→6)-β-D-glucosamines. Detailed NMR and conformational investigations show that the carbohydrate macrocycles obtained may be regarded as convenient scaffolds for the design of conjugates with defined valency, symmetry and flexibility. The absence of a distinct hydrophobic cavity prevents the possibility of the formation of inclusion complexes as in cyclodextrins. Details are discussed in the article by N. E. Nifantiev et al. on p. 2465 ff.



CONTENTS

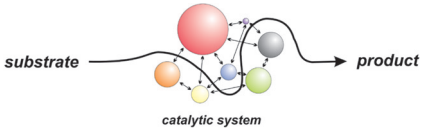
MICROREVIEW

Supramolecular Catalysis

G. Gasparini, M. Dal Molin, L. J. Prins* 2429–2440

Dynamic Approaches towards Catalyst Discovery

Keywords: Catalyst discovery / Dynamic combinatorial chemistry / Supramolecular catalysis / Noncovalent interactions / Molecular recognition



The discovery of a new catalyst is one of the most rewarding events, but also one of the most challenging in terms of energy and time consumption. In this Microreview article the potential of supramolecular chemistry to facilitate catalyst development is discussed.

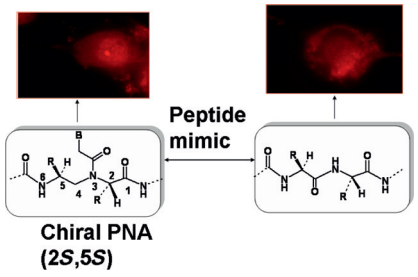
SHORT COMMUNICATIONS

Peptide-Like PNAs

S. Sforza*, T. Tedeschi, A. Calabretta, R. Corradini, C. Camerin, R. Tonelli, A. Pession, R. Marchelli 2441–2444

A Peptide Nucleic Acid Embedding a Pseudopeptide Nuclear Localization Sequence in the Backbone Behaves as a Peptide Mimic

Keywords: Peptide nucleic acids / Peptidomimetics / Amino acids / Cell recognition



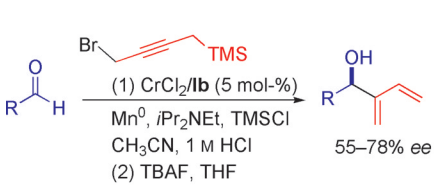
A modified peptide nucleic acid (PNA) containing embedded amino acid side chains in its backbone that mimic a peptide sequence has been designed and synthesized. The modified PNA was tested for its ability to penetrate into nuclei of cancer cells, analogously to the standard peptide nuclear localization signal, demonstrating its behavior as a fully functional peptide mimic.

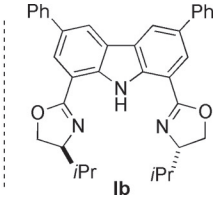
Asymmetric Catalysis

M. Durán-Galván, B. T. Connell* 2445–2448

Asymmetric Synthesis of (1,3-Butadien-2-yl)methanols from Aldehydes via [1-(Silylmethyl)allenyl]methanols

Keywords: Asymmetric catalysis / Chromium / Allenylmethanols / Dienes / Regioselectivity





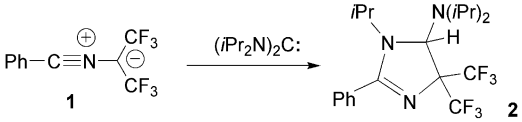
An asymmetric synthesis of (1,3-butadien-2-yl)methanols is described. The method consists of an asymmetric Cr-catalyzed addition of a silylpropargyl bromide to a variety of aldehydes to obtain enantioenriched [1-(silylmethyl)allenyl]methanols, which then undergo desilylation/isomerization to deliver the desired nonracemic (1,3-butadienyl)methanol products.

Carbenes or Zwitterions?

D. Poliakov, I. Shevchenko* 2449–2451

Ambident Reactivity of Bis(Diisopropylamino)carbene

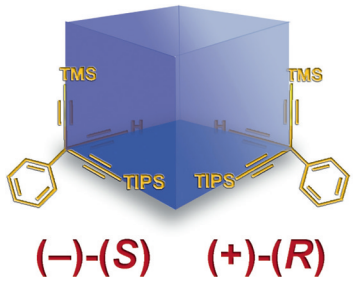
Keywords: Carbenes / Zwitterions / Carbonyl compounds / Deoxygenation / Cyclization



Bis(diisopropylamino)carbene can react with nitrile ylide **1** with the participation of the carbon and nitrogen atoms of the N–C–N unit.

Chiral Methanes

The synthesis and optical resolution of an asymmetrically silyl-protected trialkynyl(phenyl)methane was accomplished. The absolute configuration was unambiguously determined by using VCD spectroscopy and optical rotatory dispersion, in combination with quantum chemical calculations. This building block will be used for the construction of a phenylated expanded cubane.

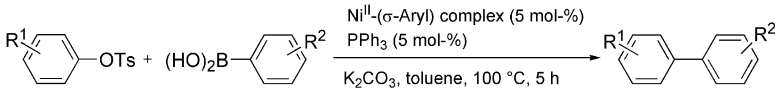


B. Buschhaus, V. Convertino, P. Rivera-Fuentes, J. L. Alonso-Gómez, A. G. Petrovic, F. Diederich* 2452–2456

Optically Active Trialkynyl(phenyl)methane: Synthesis and Determination of Its Absolute Configuration by Vibrational Circular Dichroism (VCD) and Optical Rotatory Dispersion (ORD)

Keywords: Alkynes / Chiral methanes / Chiral resolution / Optical rotatory dispersion / Vibrational circular dichroism

Ni-Catalyzed Suzuki Reactions



A practical, efficient protocol was developed for the Suzuki reaction of aryl tosylates with arylboronic acids. The process was promoted by a nickel-based catalyst system consisting of the easily available Ni^{II}–(σ-aryl) complex and the simple ligand PPh_3 in toluene in the presence of the base K_2CO_3.

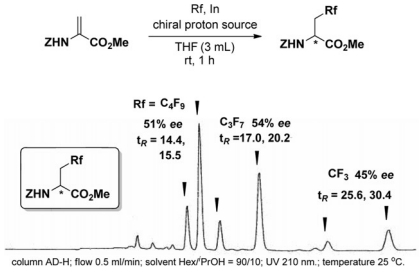
X.-H. Fan, L.-M. Yang* 2457–2460

Ni^{II}–(σ-Aryl) Complex Catalyzed Suzuki Reaction of Aryl Tosylates with Arylboronic Acids

Keywords: Synthetic methods / Cross-coupling / Nickel / Boron / Biaryls

Fluorinated Amino Acids

Direct access to β-perfluoroalkyl α-amino acids by the In-mediated reductive radical addition of perfluoroalkyl iodides to dehydroamino acids followed by asymmetric protonation to give products in up to 58%*ee* is reported. The reaction is further extended to the direct "racemic" mixture synthesis to give enantiopure pairs of different lengths of fluorinated amino acids.



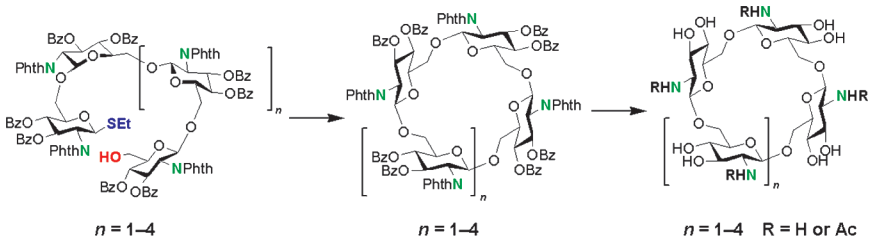
T. Yajima,* T. Tonoi, H. Nagano, Y. Tomita, K. Mikami* 2461–2464

Direct Racemic Mixture Synthesis of Fluorinated Amino Acids by Perfluoroalkyl Radical Addition to Dehydroamino Acids Terminated by Asymmetric Protonation

Keywords: Protonation / Chirality / Amino acids / Radical reactions / Indium

FULL PAPERS

Carbohydrate Macrocycles



Unusually efficient macrocyclization resulted in the formation of a series of novel cyclic oligosaccharides. The preferred coiled conformation of the acyclic precursors could be the main driving force for these intramolecular reactions.

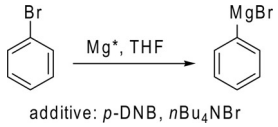
M. L. Gening, D. V. Titov, A. A. Grachev, A. G. Gerbst, O. N. Yudina, A. S. Shashkov, A. O. Chizhov, Y. E. Tsvetkov, N. E. Nifantiev* 2465–2475

Synthesis, NMR, and Conformational Studies of Cyclic Oligo-(1→6)-β-D-Glucosamines

Keywords: Carbohydrates / Oligosaccharides / Conformation analysis / Macrocycles

Grignard Reagents

Several patterns of reactivity are shared by the $S_{RN}1$ and Grignard mechanisms. The formation of phenylmagnesium bromide from bromobenzene and magnesium slurry is inhibited by *p*-dinitrobenzene. Nevertheless, experimental procedures and salt effects suggest a linear rather than a chain mechanism.



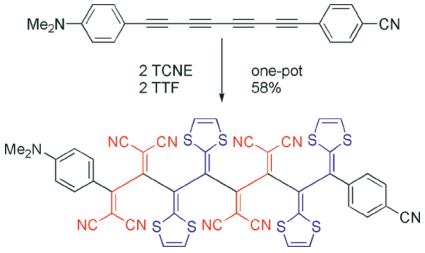
N. Bodineau, J.-M. Mattalia,* H. Hazimeh, K. L. Handoo, V. Timokhin, J.-C. Négrel, M. Chanon 2476–2486

About the Inhibition of Grignard Reagent Formation by *p*-Dinitrobenzene: Comparing the Mechanism of Grignard Reagent Formation and the $S_{RN}1$ Mechanism

Keywords: Grignard reaction / Magnesium / Salt effect / Reaction mechanisms / Electron transfer

Push-Pull Chromophores

Chiral and achiral push-pull chromophores are obtained by cascades of cycloaddition/cycloreversion reactions of tetracyanoethene (TCNE) and tetrathiafulvalene (TTF) with oligoynes. These sequential, one-pot transformations are strictly electronically controlled and provide a new access to [AB]-type oligomers with dendralene-type backbones.



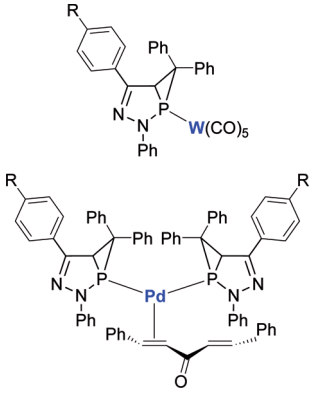
B. B. Frank, M. Kivala, B. Camafort Blanco, B. Breiten, W. B. Schweizer, P. R. Laporta, I. Biaggio, E. Jahnke, R. R. Tykwinski, C. Boudon, J.-P. Gisselbrecht, F. Diederich* 2487–2503

Chiral and Achiral Charge-Transfer Chromophores with a Dendralene-Type Backbone by Electronically Controlled Cycloaddition/Cycloreversion Cascades

Keywords: Alkynes / Charge transfer / Chirality / Conjugation / Cycloaddition / Cascade reactions

Phosphirane Complexes

Not yet well developed is the coordination chemistry of phosphiranes. Bicyclic phosphirano[1,2-*c*][1,2,3]diazaphospholes have now been found to form thermally quite stable $W(CO)_5$ complexes. With these ligands the first (phosphirane)palladium(0) complexes have been prepared and characterized structurally. These complexes can act as pre-catalysts in the Suzuki biaryl synthesis from 4-bromotoluene and $PhB(OH)_2$.



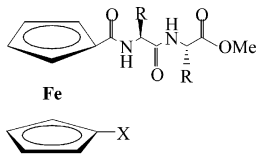
S. Maurer, C. Burkhart, G. Maas* 2504–2511

Phosphiranes as Ligands: Tungsten(0) and Palladium(0) Complexes of Phosphirano[1,2-*c*][1,2,3]diazaphospholes

Keywords: Complexes / Palladium / Phosphiranes / Phosphorus heterocycles / Tungsten

Ferrocene Conjugates

It was shown that for ferrocene-containing dipeptides a self-assembly processes prevails in the solid state. Spectroscopic studies in solution demonstrate the domination of IHBd NH_{AA2}, forming intra- and interchain conformers. The interchain HB in **6** induced (*P*)-helical ferrocene chirality, reflected in a positive Cotton effect. DFT calculations corroborate the experimental data.



3, X = R = H
4, X = H, R = Me
5, X = Ac, R = H
6, X = Ac, R = Me

J. Lapić, S. Djaković, I. Kodrin, Z. Mihalić, M. Cetina,* V. Rapić* 2512–2524

Preparation and Conformation Analysis of *N*-(Ferrocenoyl)dipeptide Esters and Their 1′-Acetyl Derivatives

Keywords: Bioorganometallic chemistry / Conformation analysis / Ferrocene / Peptides / Hydrogen bonds / Pi interactions / Density functional calculations

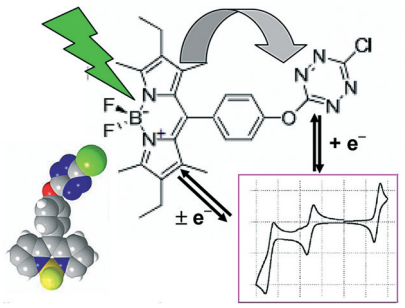
CONTENTS

New BODIPY-Tetrazine Dyads

C. Dumas-Verdes, F. Miomandre,*
E. Lépicier, O. Galangau, T. T. Vu,
G. Clavier, R. Méallet-Renault,
P. Audebert* 2525–2535

BODIPY-Tetrazine Multichromophoric Derivatives

Keywords: Heterocycles / Dyes/Pigments / Fluorescence / Electrochemistry / Density functional calculations / Chromophores



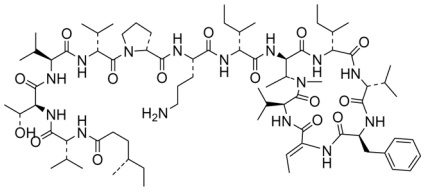
The photophysical, electrochemical and spectroelectrochemical properties of new BODIPY-tetrazine dyads have been investigated. As expected, these dyes have very low fluorescence yields due mainly to intramolecular energy transfer between the BODIPY chromophore and the tetrazine moiety.

Cyclodepsipeptide Antitumor Drug

I. Izzo,* G. A. Acosta,
J. Tulla-Puche, T. Cupido,
M. J. Martin-Lopez, C. Cuevas,
F. Albericio* 2536–2543

Solid-Phase Synthesis of Aza-Kahalalide F Analogues: (2*R*,3*R*)-2-Amino-3-azidobutanoic Acid as Precursor of the Aza-Threonine

Keywords: Peptides / Depsipeptides / Solid-phase synthesis / Natural products / Antitumor agents / Azides



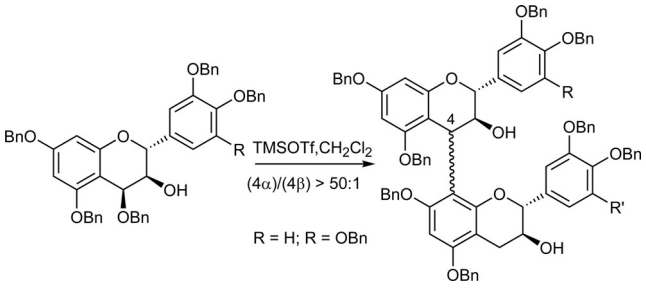
The solid-phase synthesis of six novel analogues of Kahalalide F, a potent cytotoxic natural product currently undergoing Phase II clinical trials, is reported.

Flavanoid Synthesis

K. Krohn,* I. Ahmed, M. John,
M. C. Letzel, D. Kuck 2544–2554

Stereoselective Synthesis of Benzylated Prodelphinidins and Their Diastereomers with Use of the Mitsunobu Reaction in the Preparation of Their Gallocatechin Precursors

Keywords: Natural products / Phytochemistry / Polyphenols / Flavanoids / C-C coupling



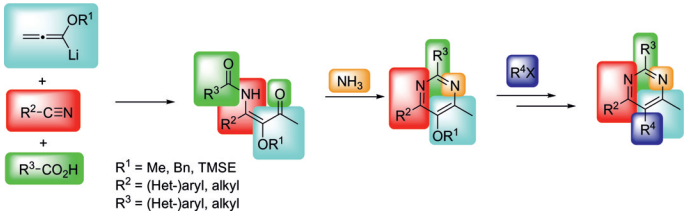
Benzylated gallocatechins have been coupled for the first time to the prodelphinidins, to afford the benzylated catechin-(4α→8)-gallocatechin (**13**), gallocatechin-(4α→8)-catechin (**14**), and gallocatechin-(4α→8)-gallocatechin (**15**). Their ESI(+)-CID mass spectra exhibited regioselective retro-Diels–Alder (RDA) reactions and unusual sequential losses of pairs of C_7H_7· radicals.

Heterocyclic Chemistry

T. Lechel, H.-U. Reissig* 2555–2564

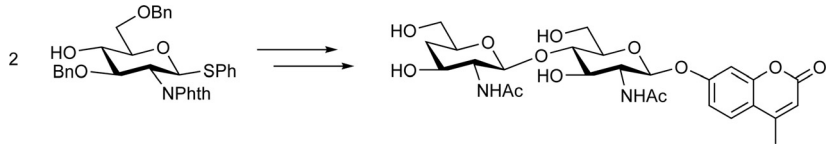
New 5-Alkoxypyrimidine Derivatives from β-Alkoxy β-Keto Enamides and Ammonium Salts

Keywords: Nitrogen heterocycles / Allenes / Enamides / Palladium / Pyrimidines



A series of highly substituted β-alkoxy β-keto enamides were prepared by a three-component reaction of lithiated alkoxyallenes, nitriles and carboxylic acids. Apt conditions were developed for their conversion into 5-alkoxypyrimidines. The substitution pattern at C-2 and C-4 of the pyrimidine core has been modified strongly. Subsequent transformations at C-5 to pyrimidin-5-yl nonaflates allowed Pd-catalyzed coupling reactions. 6-CH_3 could easily be converted into other functional groups.

Fluorogenic Substrates



The increased awareness of the involvement of chitinase in several human diseases has led to an increased demand of (4′-deoxychitobiosyl)-4-methylumbelliferone. A flexible and scalable route of synthesis is presented for the construction of this diagnostic probe.

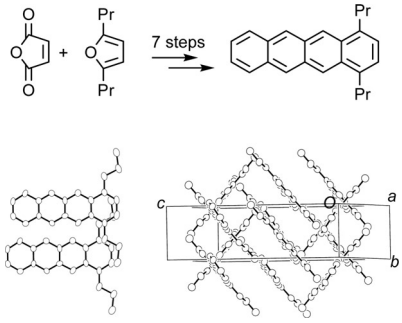
J. Dinkelaar, B. A. Duivenvoorden, T. Wennekes, H. S. Overkleeft, R. G. Boot, J. M. F. G. Aerts, J. D. C. Codée,* G. A. van der Marel* 2565–2570

A Preparative Synthesis of Human Chitinase Fluorogenic Substrate (4′-Deoxychitobiosyl)-4-methylumbelliferone

Keywords: Glycosylation / Chromophores / Fluorescence / Diagnostic tools

Oligoacenes

We have prepared a low-symmetry structure of 1,4-dipropyltetracene as a soluble orange solid. The optical properties both in solution and in the solid state were surveyed. The absorption and fluorescence spectra in the solid state were affected by molecular packing.



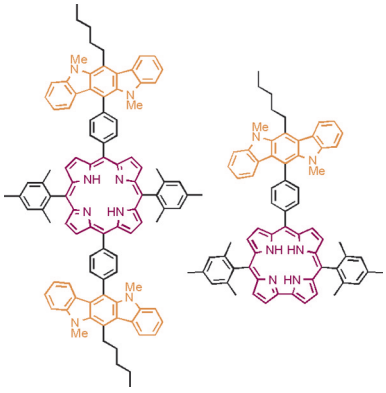
C. Kitamura,* C. Matsumoto, A. Yoneda, T. Kobayashi, H. Naito, T. Komatsu 2571–2575

Synthesis, Optical Properties, and Crystal Structure of 1,4-Dipropyltetracene

Keywords: Polycycles / Arenes / Cycloaddition / Structure elucidation / Optical properties

Porphyrinoids

The synthesis and photophysical study of *meso*-indolo[3,2-*b*]carbazolyl-substituted porphyrinoids are reported. The combination of a luminescent porphyrin or corrole core moiety with appended energy and charge-transporting indolocarbazole substituents affords interesting photophysical probes and provides novel prospects in the area of semiconducting organic materials.

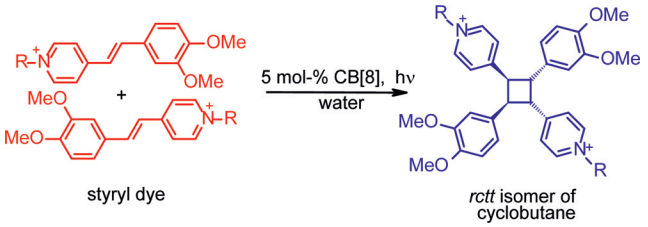


W. Maes,* T. H. Ngo, G. Rong, A. S. Starukhin, M. M. Kruk,* W. Dehaen* 2576–2586

meso-Indolo[3,2-*b*]carbazolyl-Substituted Porphyrinoids: Synthesis, Characterization and Effect of the Number of Indolocarbazole Moieties on the Photophysical Properties

Keywords: Porphyrinoids / Nitrogen heterocycles / Photophysical properties / Luminescence / Molecular electronics / Excitation energy deactivation

Molecular Assembler



Styryl dyes form *syn*-head-to-tail dimeric pairs in the solid state and within the cucurbit[8]uril cavity in water. These dimeric pairs are strongly pre-organized for accomplishing stereospecific [2+2]-photocycloaddition reactions to give *rctt*-cyclobutane derivatives.

S. P. Gromov,* A. I. Vedernikov, L. G. Kuz'mina, D. V. Kondratuk, S. K. Sazonov, Yu. A. Strelenko, M. V. Alfimov, J. A. K. Howard 2587–2599

Photocontrolled Molecular Assembler Based on Cucurbit[8]uril: [2+2]-Autophotocycloaddition of Styryl Dyes in the Solid State and in Water

Keywords: Cavitands / Cycloaddition / Dyes/Pigments / Host–guest systems / Molecular devices / Photochemistry

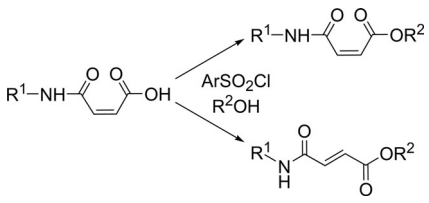
CONTENTS

Esterification of Maleamic Acids

A. Sánchez, E. Pedroso, A. Grandas* 2600–2606

Esterification of Maleamic Acids without Double Bond Isomerization

Keywords: Isomerization / Carboxylic acids / Acylation / Maleamates



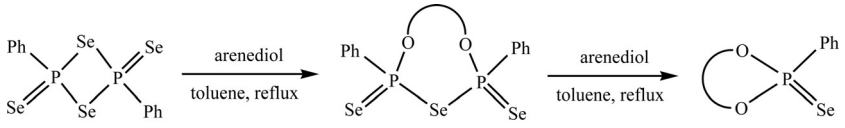
The stereochemical outcomes and yields of arylsulfonyl-chloride-mediated esterifications of maleamic acids are very sensitive to reaction conditions. Maleamates (*Z* isomers) or fumaramates (*E* isomers) can be obtained depending on the excesses of activating agent and alcohol, the substituents on the aromatic ring (methyl or isopropyl) and the solvent (2-picoline or pyridine).

Organoselenium Heterocycles

G. Hua, A. L. Fuller, A. M. Z. Slawin, J. D. Woollins* 2607–2615

Novel Five- to Ten-Membered Organoselenium Heterocycles from the Selenation of Aromatic Diols

Keywords: Main group elements / Heterocycles / Phosphorus / Selenium / Organoselenium compounds



Woollins reagent

C_6H_4 1,2-isomer; naphthacene-2,3-diyl; 1,1'-methylenebis(2-naphthyl); 2,2'-methylenebis(4-chlorophenylene)

A series of new five- to ten-membered organoselenium heterocycles can be readily prepared by the selenation of aromatic diols to give large ring diphosphorus species which undergo ring contraction and elimination of H_2Se to give the corresponding small ring monophosphorus species by reaction with a second equivalent of aromatic diol.

* Author to whom correspondence should be addressed.

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

If not otherwise indicated in the article, papers in issue 12 were published online on April 6, 2010

