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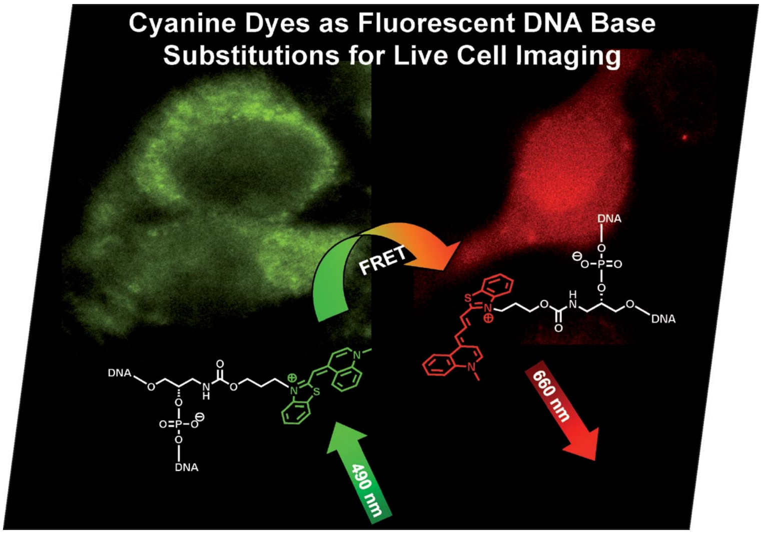
COVER PICTURE

The cover picture shows how thiazole orange and its elongated derivative TO3 can be combined as a fluorescent base pair for imaging nucleic acids inside living cells. Both dyes were incorporated synthetically as DNA base substitutions and are able to display DNA dehybridization by changing color from red to green. Details are discussed in the article by H.-A. Wagenknecht et al. on p. 1239ff.



CONTENTS

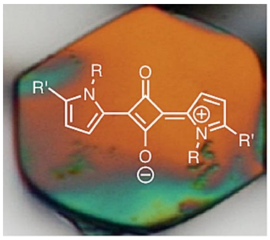
MICROREVIEW

Materials Science

L. Beverina,* P. Salice **1207–1225**

Squaraine Compounds: Tailored Design and Synthesis towards a Variety of Material Science Applications

Keywords: Materials science / Photonics / Photovoltaics / Nonlinear optics / Squaraines



Since their discovery in 1965, squaraine compounds have evolved from insoluble and poorly characterized compounds to highly specialized functional molecules having relevant applications in materials science. We show the main synthetic strategies for squaraine preparation and we discuss most recent results dealing with their exploitation in a variety of relevant technologies.

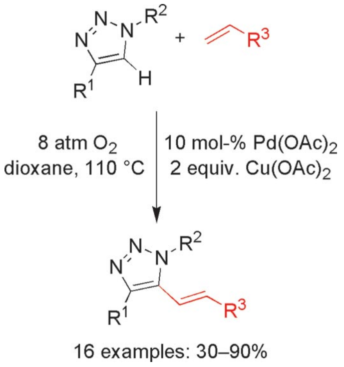
SHORT COMMUNICATIONS

Pd-Catalyzed Alkenylation

H. Jiang*, Z. Feng, A. Wang, X. Liu, Z. Chen **1227–1230**

Palladium-Catalyzed Alkenylation of 1,2,3-Trizoles with Terminal Conjugated Alkenes by Direct C–H Bond Functionalization

Keywords: Palladium / Alkenylation / Nitrogen heterocycles / Alkenes / C–H functionalization



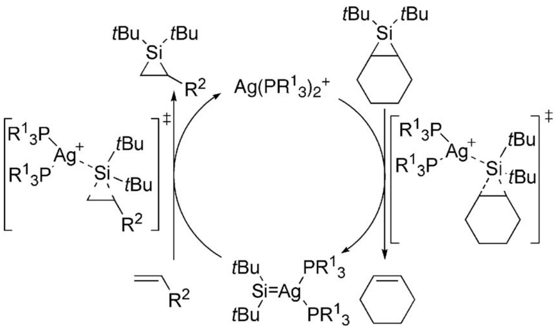
A palladium-catalyzed alkenylation of 1,2,3-triazoles with terminal conjugated alkenes by direct C–H functionalization has been developed in the presence of $Cu(OAc)_2$ and dioxygen. A variety of terminal alkenes can perform the direct oxidative coupling reactions with 1,2,3-triazoles to afford the corresponding alkenylated products in a moderate to good yield.

Transsiliranation Reaction

J. A. Mayoral, S. Rodríguez-Rodríguez, L. Salvatella* **1231–1234**

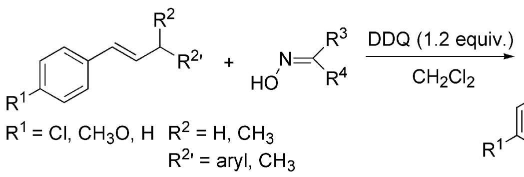
A Theoretical Insight into the Mechanism of the Silver-Catalysed Transsiliranation Reaction

Keywords: Density functional calculations / Reaction mechanisms / Silanes / Silver / Small ring systems



DFT calculations on a silver-catalysed transsiliranation reaction (silylene transfer from a silirane to an alkene) have shown the key role of a silylenesilver ion in the catalytic cycle. Although the triflate-bound species has previously been observed, no significant silylene-transfer activity is predicted for such nonionised structures.

C–H Activation



A concise oxime ether synthesis by a metal-free dehydrogenative cross-coupling reaction between allylic sp^3 C–H bonds and oximes promoted by 2,3-dichloro-5,6-dicyanoquinone (DDQ) is reported. The corresponding oxime ethers are obtained in good yields.

J. Jin, Y. Li, Z.-j. Wang, W.-x. Qian,*
W.-l. Bao* **1235–1238**

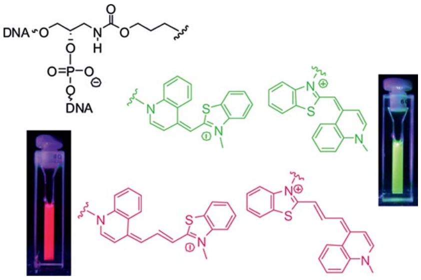
A Concise, Metal-Free Approach to the Synthesis of Oxime Ethers from Cross-Dehydrogenative-Coupling of sp^3 C–H Bonds with Oximes

Keywords: Oxime ethers / C-H activation / Allylic compounds / Cross-coupling / Dehydrogenation

FULL PAPERS

DNA Fluorescence

The optical properties of **TO** and **TO3** were studied in different DNA base environments and with different opposite bases. Both dyes as fluorescent DNA base substitutions show a brightness that is sufficient for bioanalytic and imaging applications. They can be combined to a FRET pair.

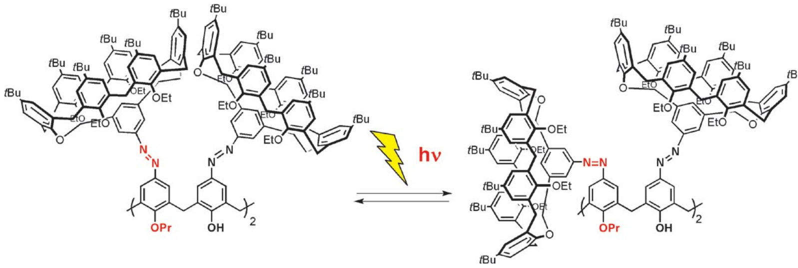


C. Holzhauser, S. Berndl, F. Menacher,
M. Breunig, A. Göpferich,
H.-A. Wagenknecht* **1239–1248**

Synthesis and Optical Properties of Cyanine Dyes as Fluorescent DNA Base Substitutions for Live Cell Imaging

Keywords: Thiazole orange / Nucleic acids / Oligonucleotides / Fluorescence / Energy transfer / Dyes/pigments

Photoisomerization of Azodendrons



Calix[4]- and calix[6]arenes containing azocalix[6]arene groups on the upper rim are described. The kinetics of the *cis*/*trans* isomerization are obtained by either a photoinduced or a thermal process. The global rate constants for this isomerization are approximately two orders of magnitude lower for the thermal process than for the photoinduced process.

H. Galán, G. Hennrich, J. de Mendoza,
P. Prados* **1249–1257**

Synthesis and Photoisomerization of Azocalixarenes with Dendritic Structures

Keywords: Calixarenes / Isomerization / Host–guest systems / Dendrimers / Diazo compounds

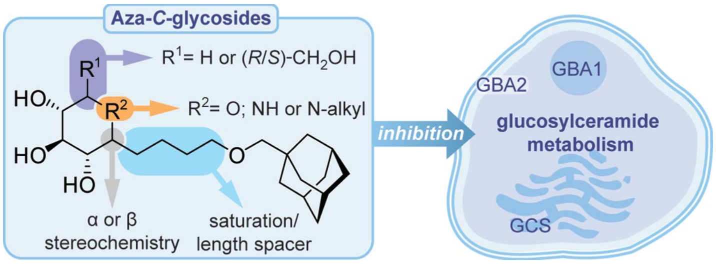
CONTENTS

Iminosugars

T. Wennekes, R. J. B. H. N. van den Berg, T. J. Boltje, W. E. Donker-Koopman, B. Kuijper, G. A. van der Marel, A. Strijland, C. P. Verhagen, J. M. F. G. Aerts,* H. S. Overkleeft* 1258–1283

Synthesis and Evaluation of Lipophilic Aza-C-glycosides as Inhibitors of Glucosylceramide Metabolism

Keywords: Azasugars / Glucosylceramide synthase / Glucocerebrosidase / β-Glucosidase 2 / Structure–activity relationships / Enzymes



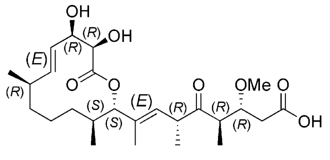
A series of lipophilic β- and α-aza-C-glycosides and its evaluation for inhibitors of three enzymes involved in glucosyl-ceramide metabolism is described. The studies reveal a β-aza-C-glycoside as a selective inhibitor of β-glucosidase 2 and several α-aza-C-glycosides as potent and selective inhibitors of glucocerebrosidase.

Structure Elucidation

R. Jansen, H. Irschik, V. Huch, D. Schummer, H. Steinmetz, M. Bock, T. Schmidt, A. Kirschning,* R. Müller* 1284–1289

Carolacton – A Macrolide Ketocarbonic Acid that Reduces Biofilm Formation by the Caries- and Endocarditis-Associated Bacterium *Streptococcus mutans*

Keywords: Antibiotics / Structure elucidation / Molecular modeling / Natural products



Carolacton

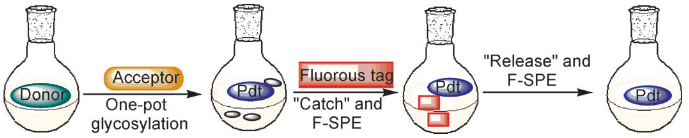
Targeting Biofilms: The structure elucidation of carolacton – the first highly potent compound from myxobacteria that severely reduces the number of viable cells in biofilms – was achieved by a combination of NMR analyses, chemical derivatization, molecular modeling, and X-ray analysis, which allowed confirmation of the absolute configuration of all the stereogenic centers.

Oligosaccharide Assembly

B. Yang, Y. Jing, X. Huang* 1290–1298

Fluorous-Assisted One-Pot Oligosaccharide Synthesis

Keywords: Carbohydrates / Fluorous separation / Hydrazones / Immobilization / One-pot synthesis



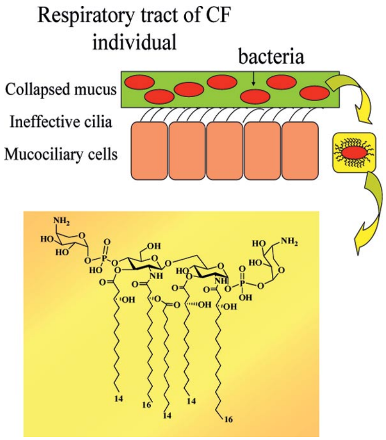
A new "catch" and "release" method for oligosaccharide assembly that combines one-pot synthesis and fluorous solid-phase extraction was developed. A branched trisaccharide and a linear tetrasaccharide were synthesized rapidly in this fashion without the need for any silica gel chromatography.

Lipopolysaccharide Structure

T. Ieranò, A. Silipo, L. Sturiale, D. Garozzo, P. Corris, J. Perry, R. Lanzetta, M. Parrilli, A. De Soyza, A. Molinaro* 1299–1306

Structural Elucidation of a Novel *B. cenocepacia* ET-12 Lipooligosaccharide Isolated from a Cystic Fibrosis Patient after Lung Transplantation

Keywords: Oligosaccharides / *Burkholderia cenocepacia* / Innate immunity / Lung transplantation / Immunology / Inflammation



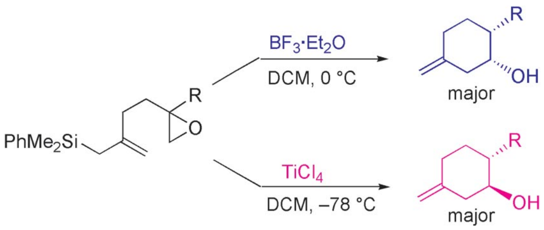
The endotoxin analysed in this work was extracted from a *B. cenocepacia* ET-12 clone recovered after lung transplantation from a cystic fibrosis patient. The lipid A moiety was comprised of a mixture of species carrying one or two 4-amino-4-deoxy-L-arabinose residues. The core oligosaccharide portion was a short saccharidic chain, in which we distinguished the common *Burkholderia* inner-core motif.

Cyclization of (Epoxy–allyl)silanes

F. J. Pulido,* A. Barbero,*
P. Castreño **1307–1313**

Synthesis of 3-Methylenecyclohexan-1-ols by Lewis Acid Catalyzed Cyclization of (Epoxy–allyl)silanes

Keywords: Epoxides / Cyclization / Lewis acids / Lewis acid catalysis / Silanes



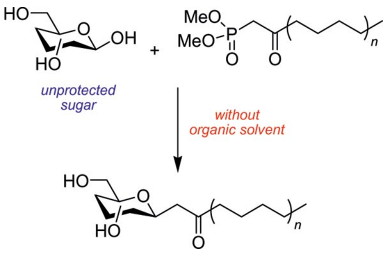
A new tandem isomerization/cyclization process for (epoxy–allyl)silanes is described. The factors governing this process are studied and a mechanism proposed. The stereoselectivity of the reaction shows Lewis acid dependence: thus, cyclization in the presence of $BF_3{\cdot}OEt_2$ leads to *cis*-methylenecyclohexanols, whereas the use of $TiCl_4$ allows the synthesis of *trans*-methylenecyclohexanols.

C-Glycosides

A. Ranoux, L. Lemiègre, M. Benoit,
J.-P. Guégan, T. Benvegnu* ... **1314–1323**

Horner–Wadsworth–Emmons Reaction of Unprotected Sugars in Water or in the Absence of Any Solvent: One-Step Access to *C*-Glycoside Amphiphiles

Keywords: Carbohydrates / *C*-Glycosides / Solvent-free reactions / Surfactants / Green chemistry / Amphiphiles



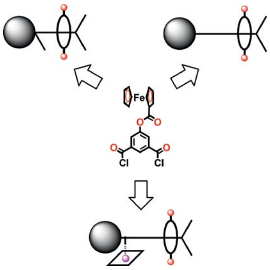
The synthesis of *C*-glycoside amphiphiles under environmentally friendly conditions still represents a real challenge in carbohydrate chemistry. We describe herein the development of organic solvent-free Horner–Wadsworth–Emmons-based reactions that afford an easy conversion of unprotected sugars to the corresponding *C*-glycosides bearing alkyl chains of various lengths.

Highly Functional Rotaxanes

A. Mateo-Alonso,*
M. Prato* **1324–1332**

Synthesis of Fullerene-Stoppered Rotaxanes Bearing Ferrocene Groups on the Macrocycle

Keywords: Rotaxanes / Fullerenes / Porphyrinoids / Ferrocene / Molecular shuttles / Supramolecular chemistry



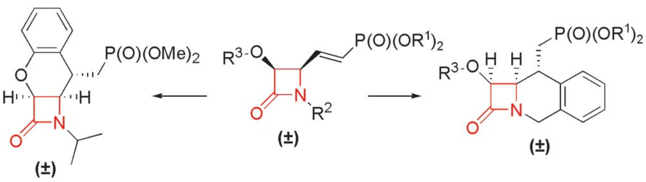
The synthesis, characterisation and behaviour of a family of rotaxanes containing fulleropyrrolidine stoppers and two ferrocene moieties on the macrocycle is reported and discussed in detail.

Benzocarbacephems

S. Van der Jeught, K. G. R. Masschelein,
C. V. Stevens* **1333–1338**

Synthesis of Phosphonobenzocarbacephems by Intramolecular Radical Cyclization of Haloaryl-Substituted β-Lactams

Keywords: Lactams / β-Lactamases / Radical reactions / Cyclization / Benzocarbacephems / Phosphonates



A series of novel benzo-fused tricyclic β-lactams were prepared by starting from epibromohydrin via phosphonoazadienes. The two key reactions in this route are a Staudinger reaction towards the β-lactams followed by radical ring closing, resulting in the envisaged phosphono-substituted tricyclic compounds.

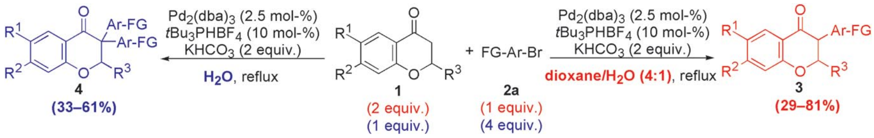
CONTENTS

Pd-Catalyzed Arylation

F. Bellina,* T. Masini,
R. Rossi,* 1339–1344

Palladium-Catalyzed Direct Arylation of 4-Chromanones: Selective Synthesis of Racemic Isoflavanones and 3,3-Diaryl-4-chromanones

Keywords: Direct arylation / Palladium / C–C coupling / Chromanones / Synthetic methods / Isoflavanones



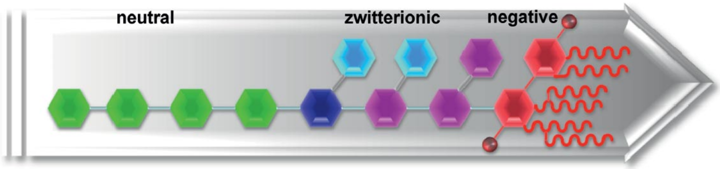
Racemic isoflavanones have been selectively prepared by Pd-catalyzed direct C-3 arylation of 4-chromanones with aryl bromides with the aid of a $Pd_2(dba)_3$/tBu_3PHBF_4 catalyst system in the presence of $KHCO_3$ as the base in a dioxane/water mixture (4:1). This catalyst system has also been used for the synthesis of 3,3-diaryl-4-chromanones through direct arylation of 4-chromanones in water.

Lipooligosaccharide Structure

E. Fregolino, G. Fugazza, E. Galano,
V. Gargiulo, P. Landini, R. Lanzetta,
B. Lindner, L. Pagani, M. Parrilli,
O. Holst,* C. De Castro* 1345–1352

Complete Lipooligosaccharide Structure of the Clinical Isolate *Acinetobacter baumannii*, Strain SMAL

Keywords: Structure elucidation / Mass spectrometry / Glycolipids / NMR spectroscopy



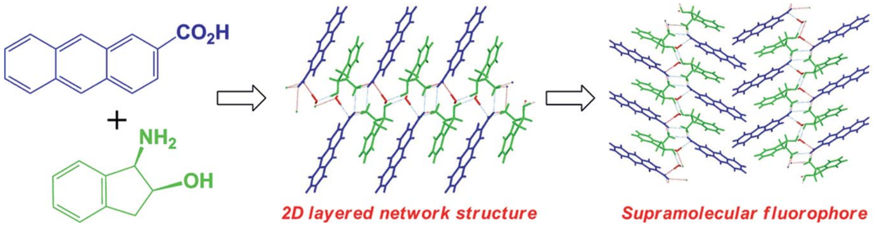
A lipooligosaccharide from *A. baumannii* SMAL possesses an inner core moiety with a zwitterion structure and a heterogeneous mixture of lipid A molecules. The hexa-acylated species is the most abundant, and its acylation pattern together with the types of fatty acids classify this molecule as an agonist Lipid A.

Chiral Supramolecular Fluorophores

Y. Imai,* N. Shiota, T. Kinuta, T. Okuno,
Y. Nakano, T. Harada, T. Sato, M. Fujiki,
R. Kuroda, Y. Matsubara* 1353–1357

A 2D Layered Chiral Supramolecular Organic Fluorophore Composed of 1-Amino-2-indanol and Carboxylic Acid Derivatives

Keywords: Chirality / Crystal engineering / Fluorophores / Supramolecular chemistry / Luminescence



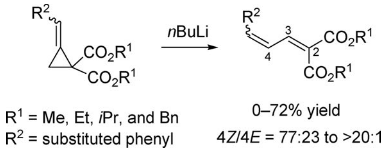
A chiral supramolecular organic fluorophore composed of a 2D layered network structure was developed by combining 1-amino-2-indanol and 2-anthracenecarboxylic acid molecules. This 2D layered chiral supramolecular organic fluorophore exhibits circularly polarized luminescence in the solid state.

Methylenecyclopropane Chemistry

B. Hu, L. Jiang, J. Ren,
Z. Wang* 1358–1363

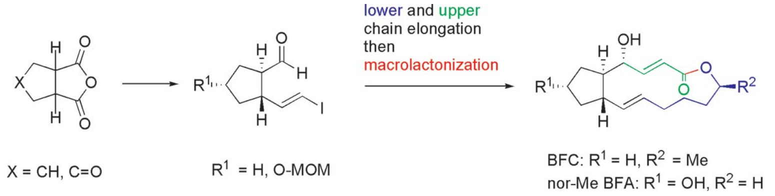
A *n*BuLi-Mediated, Expeditious and Stereoselective Ring-Opening Rearrangement of (Arylmethylene)cyclopropane-1,1-dicarboxylates

Keywords: Small ring systems / Strained molecules / Rearrangement / Ring opening / 1,3-Dienes / Methylenecyclopropane



An *n*BuLi-mediated, expeditious ring-opening rearrangement of (arylmethylene)cyclopropane-1,1-dicarboxylates has been studied. The results are different from those observed for nonactivated methylenecyclopropanes. The stereoselectivities are good, (4*Z*)-1,3-dienes are obtained as the major isomers.

Synthesis of Brefeldin A Analogues



Brefeldin A (BFA) inhibits activation of the G protein Arf1 by its protein effector (GEF) by stabilizing an abortive complex between Arf1-GDP and GEF; this might represent an original tool for cellular pathway inhibition. To study the elements of BFA involved in its binding we prepared three analogues. The formation of the C11–C12 and C3–C4 bonds is unusual in BFA synthesis.

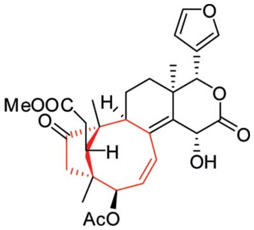
S. Archambaud, F. Legrand, K. Aphecetche-Julienne, S. Collet, A. Guingant,* M. Evain 1364–1380

Total Synthesis of (+)-Brefeldin C, (+)-nor-Me Brefeldin A and (+)-4-*epi*-nor-Me Brefeldin A 💻

Keywords: G protein / Brefeldin A analogues / Desymmetrization / Macrolactonization / Macrocycles / Asymmetric synthesis / Total synthesis

Terpenoids

From the leaves of *Trichilia connaroides*, a new limonoid with an unprecedented bicyclo[5.2.1^{4,10}]decane motif in the nortriterpenoid core, has been isolated. Its structure, including the absolute configuration, was elucidated by spectroscopic analysis and computational methods. Its activity against tumor cell lines and wnt signaling was evaluated. A biosynthetic pathway the limonoid is also proposed.



X. Fang, Y. Di,* Z. Geng, C. Tan, J. Guo, J. Ning, X. Hao* 1381–1387

Trichiliton A, a Novel Limonoid from *Trichilia connaroides* 💻

Keywords: Terpenoids / Natural products / Structure elucidation / Biosynthesis / Reaction mechanisms

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* 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 6 were published online on February 8, 2010