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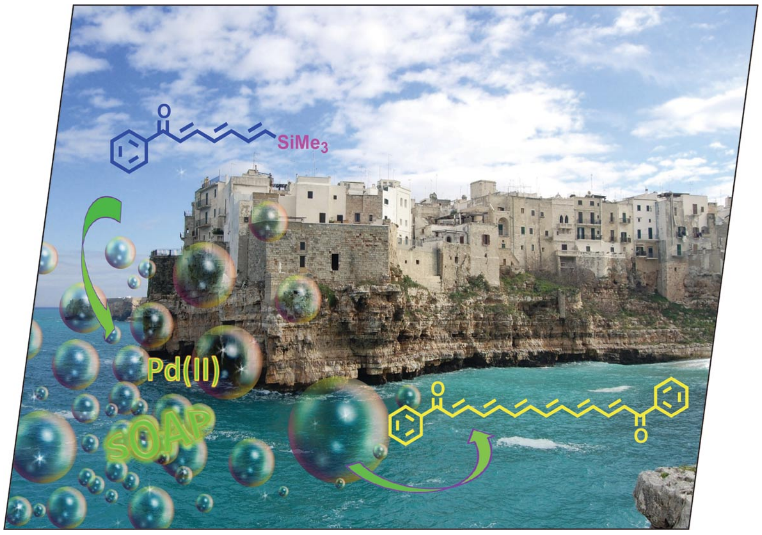
COVER PICTURE

The cover picture shows a Pd-promoted homocoupling reaction of polyenylsilanes carried out in water containing nonionic amphiphiles. The reaction in the "green" aqueous environment affords extended conjugated polyenes with higher yields relative to those obtained when the same process is performed in organic solvents. Details are discussed in the article by G. M. Farinola et al. on p. 2275ff. The background shows a nice view of Polignano a Mare, a lovely small town few miles away from Bari, located on a sea cliff along the Adriatic coast of Puglia.



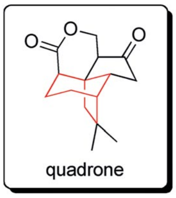
MICROREVIEW

Natural Products

M. Presset, Y. Coquerel,*
J. Rodriguez*........................... 2247–2260

Quadrane Sesquiterpenes: Natural Sources, Biology, and Syntheses

Keywords: Natural products / Sesquiterpenes / Quadrone / Terpenoids / Total synthesis / Structure–activity relationships



18 total or formal syntheses and related work

Quadrane sesquiterpenes are a focused family of potent biologically active natural products featuring a challenging bicyclo[3.2.1]octane core, the most famous representative being (–)-quadrone. Here the data for quadranes reported in the past three decades, including isolation, biogenesis, and biological considerations, are critically analyzed, together with the synthetic efforts in this area.

SHORT COMMUNICATIONS

Chemoselectivity Mapping

N. Bensel, D. Klär, C. Catala,
P. Schneckenburger, F. Hoonakker,
S. Goncalves, A. Wagner* 2261–2264

A Chemometric Approach to Map Reaction Media Chemoselectivity: Example of Selective Debenzylation

Keywords: Chemoselectivity / Hydrogenation / Chemoinformatics / Reactivity

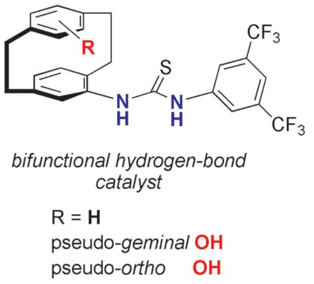
A chemometric process consisting in measuring the reactivity of a tailored set of substrates under standardized and complementary reaction conditions was run to evaluate the possibility of building a coherent database that would give a general overview of the selectivity of a variety of catalysts. This systematic experimental data collection was applied to the hydrogenolysis of *O*-benzyl ether compounds.

Hydrogen-Bond Catalysis

J. F. Schneider, F. C. Falk, R. Fröhlich,
J. Paradies* 2265–2269

Planar-Chiral Thioureas as Hydrogen-Bond Catalysts

Keywords: Thioureas / Hydrogen bonds / Cyclophanes / Organocatalysis / Chirality



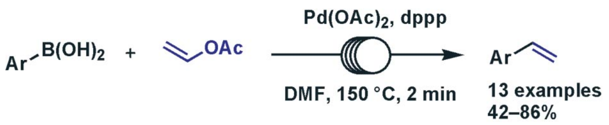
The first planar-chiral thiourea hydrogen-bond catalysts were synthesized from the corresponding [2.2]paracyclophanylamines. Enantiopure bifunctional thioureas operate as hydrogen-bond catalysts and display enhanced activity in comparison to their monofunctionalized derivatives.

Continuous Flow Catalysis

L. R. Odell, J. Lindh, T. Gustafsson,
M. Larhed*.............................. 2270–2274

Continuous Flow Palladium(II)-Catalyzed Oxidative Heck Reactions with Arylboronic Acids

Keywords: Continuous flow / Cross-coupling / Boron / Palladium / Homogeneous catalysis



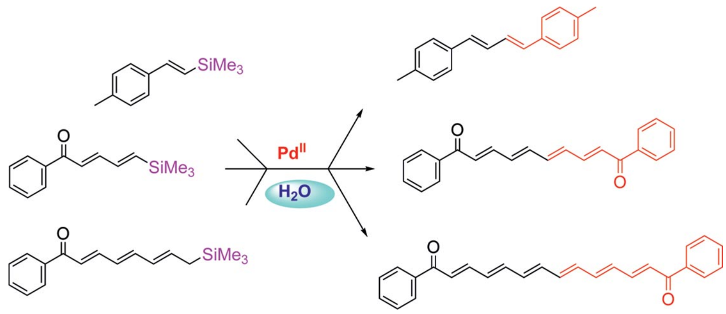
A number of different palladium(II)-catalyzed oxidative Heck reactions were developed by using continuous flow chemistry. The reactions were fast and selective for the coupling of arylboronic acids with both electron-rich and electron-poor olefins. The arylated products were isolated in good to high yields. All reactions were performed by using a commercially available flow reactor.

Coupling of Silanes in Water

S. R. Cicco, G. M. Farinola,* C. Martinelli, F. Naso, M. Tiecco **2275–2279**

Pd-Promoted Homocoupling Reactions of Unsaturated Silanes in Aqueous Micelles

Keywords: Silanes / Palladium / Green chemistry / Surfactants / Micelles



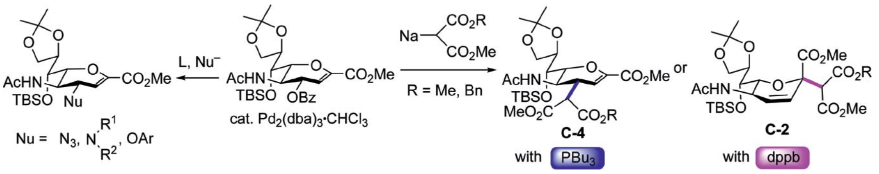
Symmetrically disubstituted *all-E* polyenes are stereoselectively obtained in good yields by palladium-catalyzed homocoupling reactions of unsaturated silanes under micellar conditions. The processes are carried out at room temperature, in water as the only solvent and in the presence of non-ionic surfactants.

Sialic Acids and Palladium

C.-W. Chang, S. Norsikian,* R. Guillot, J.-M. Beau* **2280–2294**

Regio- and Stereocontrolled Palladium-Catalyzed Allylic Substitution on *N*-Acetylneuraminic Acid Derivatives

Keywords: Carbohydrates / Palladium / Regioselectivity / Stereoselective catalysis / Sialic acids



The use of palladium-catalyzed allylic substitution is a regio- and stereoselective solution for the modification of *N*-acetylneuraminic acid at the C-2 or C-4 positions. The regioselectivity in the malonylation reaction is governed by the ligands associated with the allylpalladium complex.

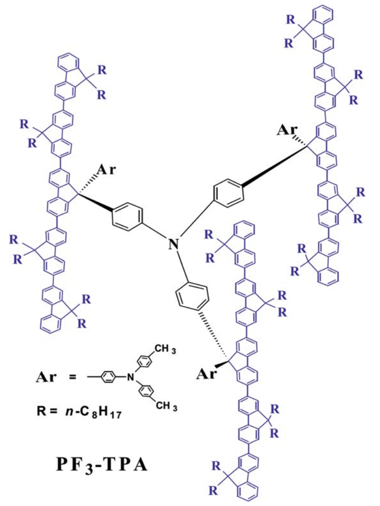
Steric Monodisperse Oligofluorenes

X. Zhang, Y. Quan,* Z. Cui, Q. Chen, J. Ding, J. Lu* **2295–2303**

3D Monodisperse Oligofluorenes with Non-Conjugated Triphenylamine-Based Cores: Synthesis and Optoelectronic Properties

Keywords: Optoelectronic properties / Oligomers / Amines / Fluorescence / Electrochemistry

Two 3D monodisperse oligofluorenes with a non-conjugated triphenylamine core have been synthesized. Three fluorene pentamers were linked by the triphenylamine unit at the 9-position of the central fluorene units. They showed deep-blue fluorescence with high efficiencies. Both oligomers showed a turn-on voltage of 4 V and their luminances reached 1946–1055 cd/m^2 at 7.5–8 V in multi-layer devices.



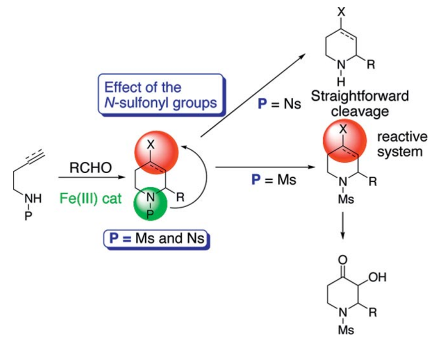
Aza-Prins Cyclization

R. M. Carballo, G. Valdomir, M. Purino, V. S. Martín,* J. I. Padrón* **2304–2313**

Broadening the Synthetic Scope of the Iron(III)-Catalyzed Aza-Prins Cyclization

Keywords: Iron / Homogeneous catalysis / Sulfonamides / Cyclization / Heterocycles

The nature and influence of the *N*-sulfonyl group in aza-Prins cyclization and the reactivity of the six-membered aza-cycle generated has been studied. The *N*-nosyl group can be deprotected keeping intact the functional groups of the aza-cycle. Use of the *N*-mesyl group permitted the derivatization and deprotection of the aza-cycle with a straightforward application in natural product synthesis.



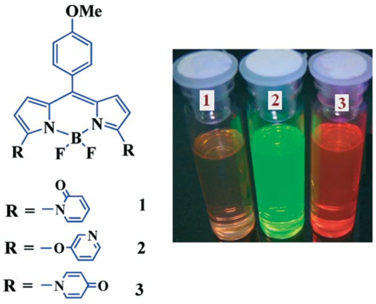
CONTENTS

Fluorescent Probes

T. K. Khan, M. R. Rao, M. Ravikanth* 2314–2323

Synthesis and Photophysical Properties of 3,5-Bis(oxopyridinyl)- and 3,5-Bis(pyridinyloxy)-Substituted Boron-Dipyrromethenes

Keywords: Boron / Nitrogen heterocycles / Dyes/pigments / Fluorescence / Fluorescent probes / Photophysics / Nucleophilic substitution



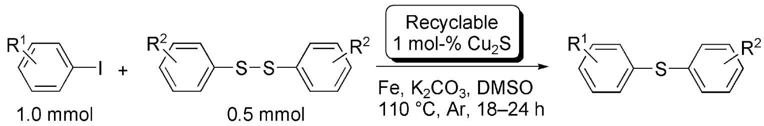
The synthesis of *meso*-aryl and *meso*-furyl boron-dipyrromethenes containing oxopyridinyl and pyridinyloxy substituents at the 3- and 5-positions and their effect on the absorption, electrochemical and fluorescence properties of boron-dipyrromethene dyes are described.

Cross-Coupling Reactions

H. Wang, L. Jiang, T. Chen, Y. Li* 2324–2329

A Highly Efficient, Ligand-Free, and Recyclable Cu_2S-Catalyzed Coupling of Aryl Iodides with Diaryl Disulfides

Keywords: Copper / Cross-coupling / Sulfur / Sustainable chemistry / Heterogeneous catalysis



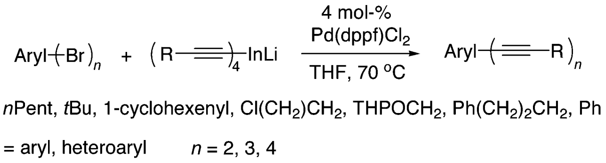
The copper(I) sulfide catalyzed C–S coupling reactions of aryl iodides and diaryl disulfides were conducted in a ligand-free and recyclable system, giving the corresponding aryl sulfides in good to excellent yields.

Multialkynylation with Organoindate

D. Kang, D. Eom, H. Kim, P. H. Lee* 2330–2336

Palladium-Catalyzed Multialkynyl Cross-Coupling Reactions with Tetraalkynylindates

Keywords: Cross-coupling / Indium / Alkynes / Palladium



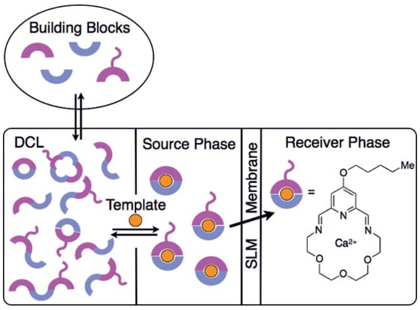
An efficient Pd-catalyzed multialkynyl cross-coupling reaction using in-situ-generated tetraalkynylindates leading to symmetric and unsymmetric multialkynyl aromatic compounds was developed. The four acetylide groups of the tetraalkynylindates can be transferred effectively to a variety of aryl bromides with high atom efficiency.

Dynamic Combinatorial Chemistry

V. Saggiomo, C. Goeschen, R. Herges, R. Quesada, U. Lüning* 2337–2343

Ion Transport Across Membranes Facilitated by a Dynamic Combinatorial Library

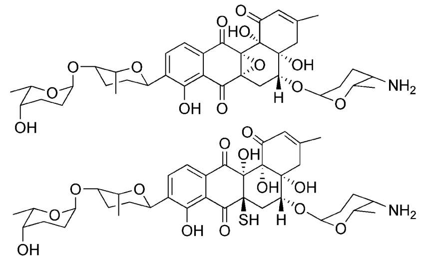
Keywords: Ion transport / Dynamic combinatorial chemistry / Imines / Macrocycles / Membranes / Liposomes



A dynamic combinatorial library has been used to facilitate the transport of Ca^{2+} across a supported liquid membrane. In a dual selection process, the calcium ions first select two matching macrocycles. Then only one of the macrocycles efficiently transports Ca^{2+} due to its better balance between lipo- and hydrophilicity. The first transport experiments with liposomes are presented.

Natural Products

New grecocyclines were detected in the extracts of *Streptomyces* sp. Acta 1362. The grecocyclines contain the 4-epi-α-L-tolyposamine moiety and a free SH group. Fermentation, isolation, structure elucidation, and biological activity of the grecocyclines are described. Experimental data and quantum chemical calculations were used to prove that the amino sugar has the L configuration.

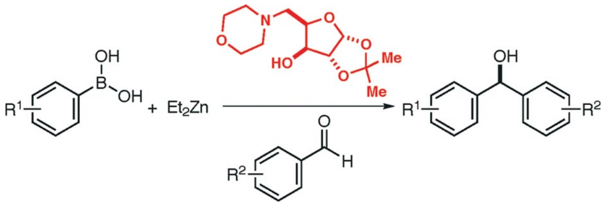


T. Paululat,* A. Kulik, H. Hausmann, A. D. Karagouni, H. Zinecker, J. F. Imhoff, H.-P. Fiedler **2344–2350**

Grecocyclines: New Angucyclines from *Streptomyces* sp. Acta 1362

Keywords: Polyketides / Biological activity / Structure elucidation / Cytotoxicity

Enantioselective Arylation



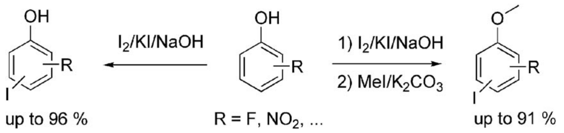
The asymmetric arylation of aldehydes with carbohydrate-based ligands by using boronic acids as the aryl source is described. The chiral diarylmethanol products were obtained in up to 96% *ee*. Semiempirical PM3 calculations were performed to understand the stereochemical outcome of the arylation reaction.

A. D. Wouters, G. H. G. Trossini, H. A. Stefani, D. S. Lüdtke* **2351–2356**

Enantioselective Arylations Catalyzed by Carbohydrate-Based Chiral Amino Alcohols

Keywords: Arylation / Boron / Zinc / Carbohydrates / Asymmetric catalysis

Iodinations



Reliable and efficient iodination: A broad scope of fluorinated phenols and other electron-deficient analogues are iodinated in a practical manner. The method allows selective mono- and multiple-iodination reactions. A telescoped reaction sequence including a subsequent methylation step provides the corresponding anisoles in good to excellent yields.

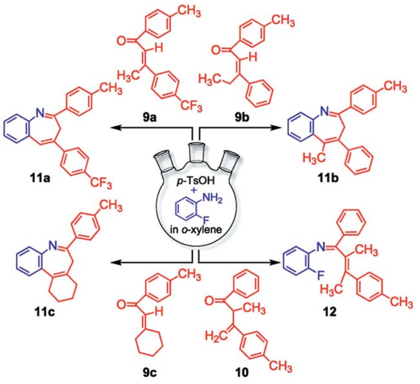
R. Francke, G. Schnakenburg, S. R. Waldvogel* **2357–2362**

Efficient and Reliable Iodination and *O*-Methylation of Fluorinated Phenols

Keywords: Iodination / Phenols / Oxidation / Alkylation / Fluorinated compounds

Heterocyclic Chemistry

Treatment of 2-fluoroaniline with enones **9a–c** gives moderate yields of benzazepines **11a–c**. However, enone **10** gives imine **12**. This will be explained with the aid of DFT calculations, which will also confirm a proposed mechanism. The fluxional behavior of the azepine ring will be probed by NMR spectroscopic experiments.



K. Ramig,* E. M. Greer,* D. J. Szalda, R. Razi, F. Mahir, N. Pokeza, W. Wong, B. Kaplan, J. Lam, A. Mannan, C. Missak, D. Mai, G. Subramaniam, W. F. Berkowitz, P. Prasad, S. Karimi, N. H. Lo, L. V. Kudzma **2363–2371**

Experimental and Theoretical Studies of a One-Flask Synthesis of 3*H*-1-Benzazepines from 2-Haloanilines and α,β-Unsaturated Ketones

Keywords: 1-Benzazepine / DFT calculations / Imine / Intramolecular addition-elimination / Variable-temperature NMR spectroscopy

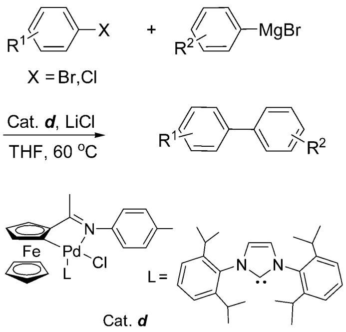
CONTENTS

Unsymmetrical Biaryls

G. Ren, X. Cui, Y. Wu* 2372–2378

Efficient Synthesis of Biaryls through the Kumada Reaction Catalyzed by Carbene Adducts of Cyclopalladated Ferrocenylimine

Keywords: Biaryls / Carbene ligands / Palladium / Ferrocene / Cross-coupling



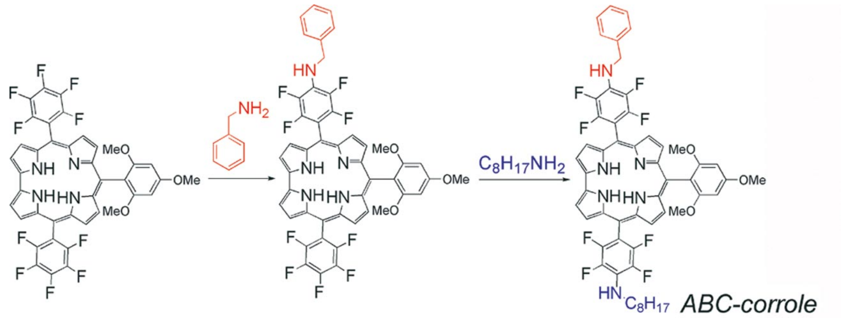
Carbene adducts of cyclopalladated ferrocenylimine were prepared and evaluated in the Kumada reaction. Catalyst complex **d** was highly active for the coupling of *ortho*-substituted aryl chlorides with sterically hindered Grignard reagents and the reaction tolerated various functional groups. Biaryls were efficiently obtained in the presence of 0.5 mol-% catalyst under mild reaction conditions.

Corroles

T. Hori, A. Osuka*.................. 2379–2386

💻 Nucleophilic Substitution Reactions of *meso*-5,10,15-Tris(pentafluorophenyl)corrole; Synthesis of ABC-Type Corrolesand-Corrole-Based Organogels

Keywords: Corroles / Porphyrinoids / Aggregation / Gels / Nucleophilic substitution



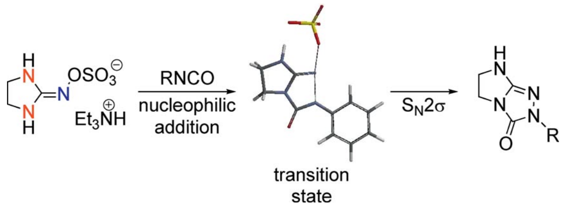
In the nucleophilic substitution reactions of 5,10,15-tris(pentafluorophenyl)corrole with various amines, the *para*-fluorine atoms of the 5- and 15-pentafluorphenyl substituents were found to be more reactive than that of the 10-substituent. This substitution reaction was applied for the synthesis of ABC-type *meso*-aryl-substituted corroles and corrole-based organogels.

Intramolecular Nucleophilic Reactions

J. Sączewski,* M. Gdaniec....... 2387–2394

💻 Synthesis of Heterocycles by Intramolecular Nucleophilic Substitution at an Electron-Deficient sp^2 Nitrogen Atom

Keywords: Nucleophilic addition / Amination / Nucleophilic substitution / Nitrogen heterocycles / Transition states



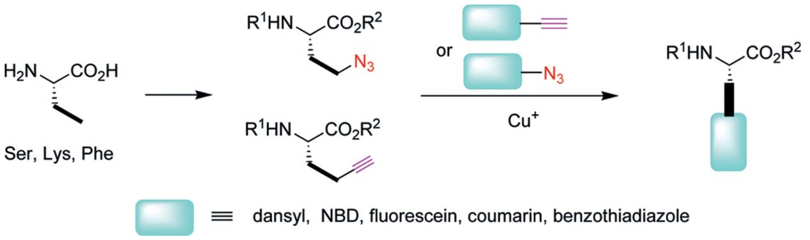
2-Aryl(arylsulfonyl)-6,7-dihydro-2*H*-imidazo[2,1-*c*][1,2,4]triazol-3(5*H*)-ones and 3-arylimino-6,7-dihydroimidazo[2,1-*c*][1,2,4]-thiadiazoles have been synthesized by intramolecular nucleophilic substitution reactions at the sp^2 nitrogen atom of amidate anions. DFT calculations of the stationary points of the N–N and N–S bond formation revealed the in-plane transition states of the $S_N2\sigma$ reactions.

Click Chemistry

**C. Li, E. Henry, N. K. Mani, J. Tang,
J.-C. Brochon, E. Deprez,*
J. Xie*...................................... 2395–2405**

Click Chemistry to Fluorescent Amino Esters: Synthesis and Spectroscopic Studies

Keywords: Amino acids / Click chemistry / Fluorescent probes / Fluorescence / Solvent effects



Fluorescent amino esters can be readily prepared from azido- or alkyne-functionalized amino acids and fluorophores by click chemistry. Benzothiadiazole-substituted amino esters, which exhibit fluorescence in the visible region, display high quantum yields and relatively long lifetimes. The 7-hydroxycoumarin derivative proves to be a suitable pH-sensitive probe for local pH measurement.

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* Author to whom correspondence should be addressed.

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