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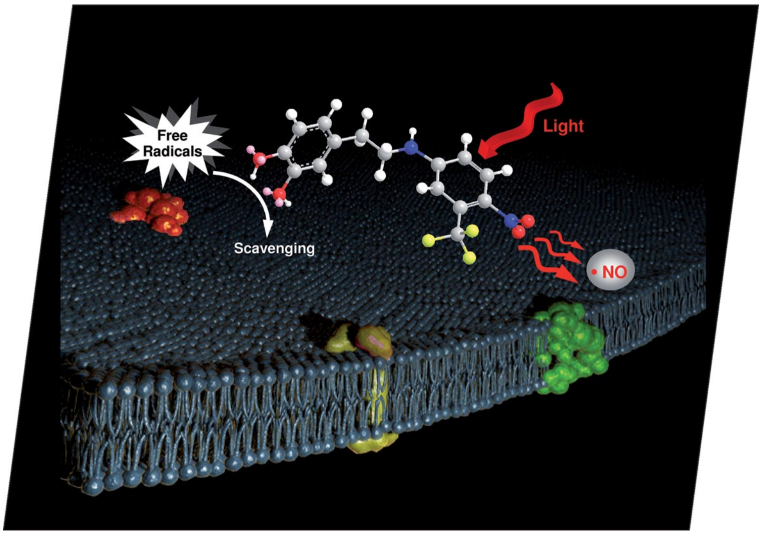
COVER PICTURE

The cover picture shows a novel molecular conjugate that merges radical scavenging properties with the ability to release nitric oxide (NO) under the control of visible light stimuli. This compound consists of a catecholic unit, as an antioxidant centre, that is joined to a nitroaniline derivative, as a suitable NO photodonor, through an alkyl spacer. Suitable choice of the two independent units allows preservation of their single properties once merged into the same molecular skeleton, offering the possibility of joining two functional molecules in a single compound without loss of their effectiveness. Details are discussed in the article by E. Vittorino and S. Sortino on p. 421ff.



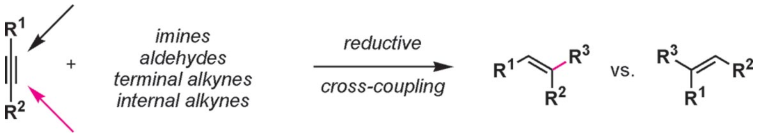
MICROREVIEW

Reductive Cross-Coupling

H. A. Reichard, M. McLaughlin, M. Z. Chen, G. C. Micalizio* 391–409

Regioselective Reductive Cross-Coupling Reactions of Unsymmetrical Alkynes

Keywords: Cross-coupling / Alkynes / Alkenes / Titanium / Synthetic methods / Reduction / Carbometalation



Reductive cross-coupling chemistry is emerging as a powerful strategy for bimolecular C–C bond formation. A central issue in this area of chemistry is controlling site-selectivity (regioselectivity) in the convergent coupling process. Here, we discuss the state-of-the-art with respect to controlling regioselectivity in reductive cross-coupling chemistry of alkynes. The emphasis of this review is on bond construction, not the nature of the metal employed or whether or not the coupling process proceeds in a catalytic manner.

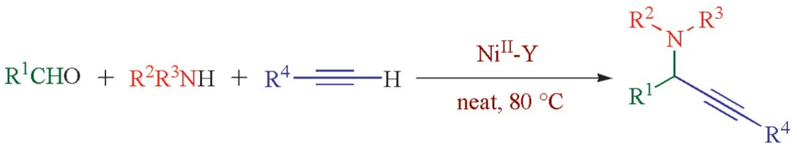
SHORT COMMUNICATIONS

Heterogeneous Catalysis

K. Namitharan, K. Pitchumani* 411–415

Nickel-Catalyzed Solvent-Free Three-Component Coupling of Aldehyde, Alkyne and Amine

Keywords: Nickel / Solvent-free reaction / Multicomponent / Heterogeneous catalysis / Propargylamines



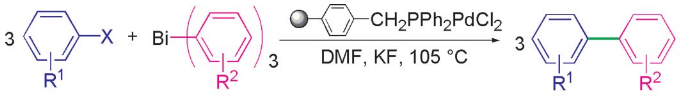
A one-pot three-component solvent-free coupling of aldehyde, alkyne, and amine in the presence of Ni^{2+}-exchanged Y-zeolite as catalyst gives various propargylamines in good to excellent yields. In addition, the catalyst is recycled without any appreciable leaching, and the reaction proceeds under aerobic conditions, thus making this protocol environmentally more acceptable.

Heterogeneous Catalysis

W.-J. Zhou, K.-H. Wang, J.-X. Wang,* D.-F. Huang 416–419

Reusable, Polystyrene-Resin-Supported, Palladium-Catalyzed, Atom-Efficient Cross-Coupling Reaction of Aryl Halides with Triarylbismuths

Keywords: Cross-coupling / Bismuth / Halides / Heterogeneous catalysis / Supported catalysts / Palladium



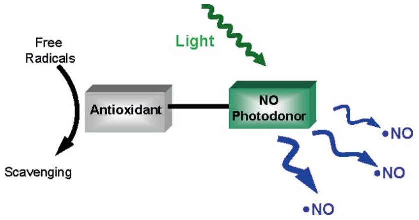
X = I, Br
R^1 = H, 4-Cl, 4-NO$_2$, 3-NO$_2$, 4-CH$_3$, 4-OCH$_3$, 4-CHO, 4-CN, 2-Cl, 3-CH$_3$, 4-COCH$_3$
R^2 = H, 4-Cl, 4-F, 4-CH$_3$, 4-OCH$_3$

Various biaryl compounds were synthesized by an atom-efficient procedure through the cross-coupling reaction of triarylbismuths with aryl halides catalyzed by polystyrene-supported palladium in an open atmosphere.

FULL PAPERS

Bifunctional Antioxidants

We have designed and synthesized, by a very simple procedure, a water-soluble molecular conjugate that combines radical scavenging properties to the delivery of nitric oxide in a way exclusively controlled by visible light external stimuli.

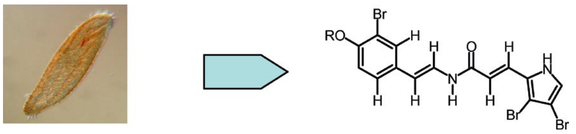


E. Vittorino, S. Sortino* **421–426**

A Phenolic Antioxidant Releasing Nitric Oxide on Demand

Keywords: Photochemistry / Nitric oxide / Phenols / Antioxidants / Radicals

Natural Products Chemistry



Keronopsamides A–C, isolated from a cell culture of the marine ciliate *Pseudokeronopsis riccii* are new pigments based on an unprecedented amide linkage between a basic bromophenol moiety and an alkyl-substituted dibromopyrrole. The relative stabilities of tautomeric forms and rotational conformers have been investigated by NMR techniques and DFT-based computations.

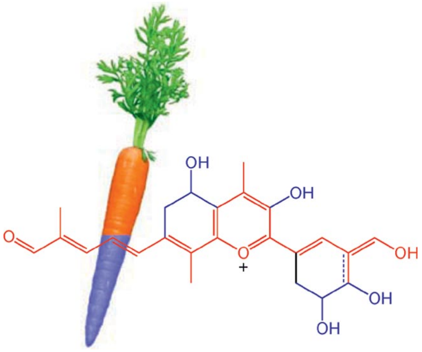
G. Guella,* R. Frassanito, I. Mancini, T. Sandron, L. Modeo, F. Verni, F. Dini, G. Petroni **427–434**

Keronopsamides, a New Class of Pigments from Marine Ciliates

Keywords: Natural products / Marine ciliates / *Pseudokeronopsis riccii* / Cortical granules / Keronopsamides / Dyes/pigments / Structure elucidation

Pyran Polyenes

The straight conjugation of pyran polyenes is obstructed by an oxo barrier, which results in a deviation of the conjugation through *cis* bonds. Nevertheless, pyran carotenoids absorb at longer λ_{max} than the corresponding all-*trans* carotenoids, especially when protonated. These pyranium compounds combine the structural elements of carotenoids and anthocyanidins.



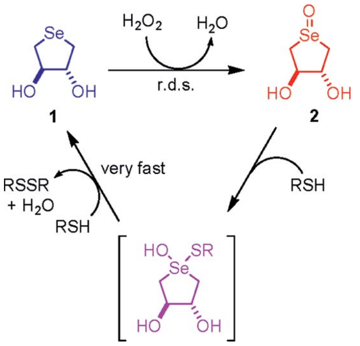
C. L. Øpstad, H.-R. Sliwka,* V. Partali **435–439**

New Colours for Carotenoids – Synthesis of Pyran Polyenes

Keywords: Carotenoids / Chromophores / Aldehydes / Auxochromes

Antioxidant Models

Water-soluble cyclic selenide **1** exhibited higher GPx-like catalytic activities than the linear selenide analog in the reaction of H_2O_2 with mono-, di-, and polythiol substrates. The enhanced catalytic activities can be ascribed to the cyclic structure, which elevates the HOMO energy level of **1** and makes the selenium atom more exposed to the surroundings.



F. Kumakura, B. Mishra, K. I. Priyadarsini, M. Iwaoka* ... **440–445**

A Water-Soluble Cyclic Selenide with Enhanced Glutathione Peroxidase-Like Catalytic Activities

Keywords: Antioxidants / Enzyme models / Peroxides / Protein folding / Selenium

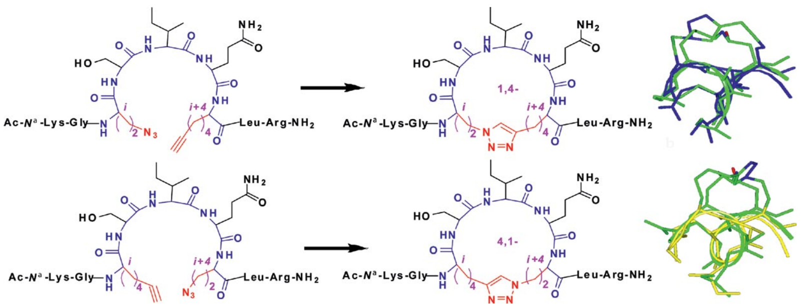
CONTENTS

Click Chemistry

M. Scrima, A. Le Chevalier-Isaad, P. Rovero, A. M. Papini, M. Chorev, A. M. D'Ursi* .... **446−457**

Cu^{I}-Catalyzed Azide−Alkyne Intramolecular *i*-to-(*i*+4) Side-Chain-to-Side-Chain Cycli-zation Promotes the Formation of Helix-Like Secondary Structures

Keywords: Cyclopeptides / Helical structures / Conformation analysis / Click chemistry / Human parathyroid hormone-related protein



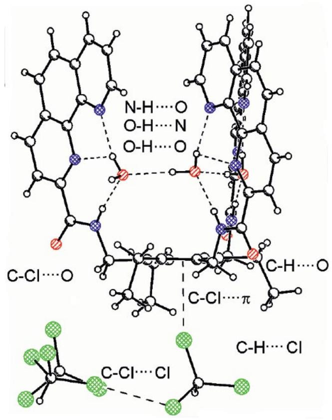
Linear peptides containing ω-azido- and ω-yl-α-amino acid residues in positions *i* and *i*+4 were cyclized by intramolecular azide−alkyne 1,3-dipolar cycloaddition. NMR studies show that the maximum helix stabilizing effect is observed for triazolyl rings flanked by 2 and 4 methylene groups, resulting in the same bridge size, but differing in the orientation of the triazolyl and the reciprocal distribution of CH_2 groups in the bridge.

Hydrogen and Halogen Bonding

M. Mazik,* A. Hartmann, P. G. Jones .... **458−463**

Hydrogen and Halogen Bonding in the Crystal Structure of a 1,3,5-Substituted 2,4,6-Triethylbenzene Consisting of Three Phenanthroline Units

Keywords: Halogen bonds / Hydrogen bonds / Noncovalent interactions / Supramolecular chemistry / Crystal engineering



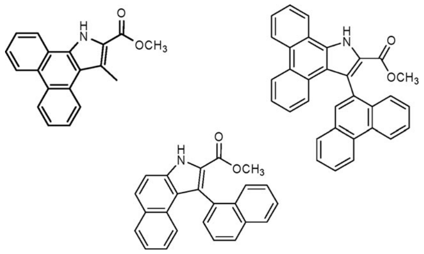
An aggregate consisting of a phenanthroline-based compound, water, and chloroform molecules is stabilized by N−H···O, O−H···N, O−H···O, C−H···O, and C−H···Cl hydrogen bonds as well as C−Cl···O, C−Cl···π, and C−Cl···Cl interactions. Particularly short C−H···O hydrogen bonds are observed in the crystal structure.

Fluorescent Probes

G. Pereira, E. M. S. Castanheira,* P. M. T. Ferreira,* M.-J. R. P. Queiroz .... **464−475**

Synthesis and Photophysical Studies of New Fluorescent Indole Derivatives Obtained from β-Bromodehydroamino Acids − Interaction with Fluoride Anions

Keywords: Suzuki−Miyaura coupling / Metal-assisted cyclization / Indoles / Fluorescent probes / Fluorides / Nitrogen heterocycles / Cyclization



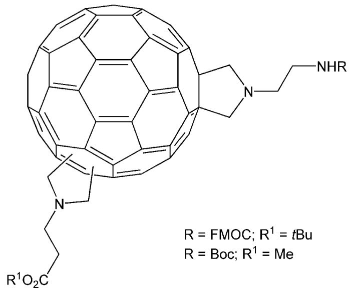
New fluorescent indole derivatives were synthesised from β-bromodehydroamino acid derivatives and aryl boronic acids by using a Suzuki coupling reaction followed by a C−N intramolecular cyclisation reaction. The photophysical properties of the new indole derivatives indicate their potential use as fluorescent probes. The interaction of these compounds with fluoride anion was studied.

Fullerene Chemistry

D. Milic,* M. Prato .... **476−483**

Fullerene Unsymmetrical Bis-Adducts as Models for Novel Peptidomimetics

Keywords: Fullerenes / Cycloaddition / Aminoacids / Heterocycles / Peptidomimetics

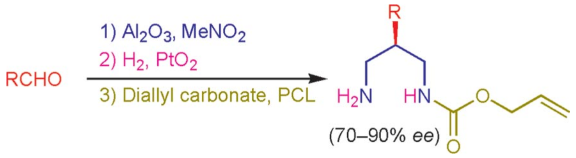


Two classes of unsymmetrical, orthogonally protected bis-fulleropyrrolidinic amino acids have been designed as model compounds for novel fulleropeptidomimetics. The synthesis of NHFmoc/CO_2tBu and NHBoc/CO_2Me fulleropyrrolidinic couples is presented. All the *trans* as well as the *equatorial* (*e*′ and *e*′′) isomers were separated and fully characterized by NMR spectroscopy and mass spectrometry.

Optically Active Heterocycles

**N. Ríos-Lombardía, E. Busto,
V. Gotor-Fernández,*
V. Gotor*** **484–493**

Synthesis of Optically Active Heterocyclic Compounds by Preparation of 1,3-Dinitro Derivatives and Enzymatic Enantioselective Desymmetrization of Prochiral Diamines



A general synthetic methodology for the preparation of novel monocarbamates in good to high enantiomeric excesses (70–90% *ee*) is described. Thus, commercially available aldehydes have been transformed into 1,3-dinitro compounds, which were hydrogenated by using platinum oxide as the catalyst and then enantioselectively desymmetrized by using *Pseudomonas cepacia* lipase as the biocatalyst.

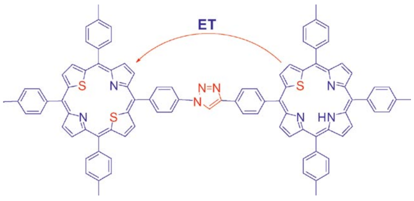
Keywords: Asymmetric catalysis / Hydrogenation / Desymmetrization / Amines / Heterocycles

Clicked Porphyrin Dyads

V. S. Shetti, M. Ravikanth* **494–508**

Synthesis of Triazole-Bridged Unsymmetrical Porphyrin Dyads and Porphyrin–Ferrocene Conjugates

Azidoporphyrins with N_4, N_3S, N_2S_2 and N_2SO cores were synthesized under mild reaction conditions and used for the synthesis of a series of triazole-bridged unsymmetrical porphyrin dyads and porphyrin–ferrocene conjugates.

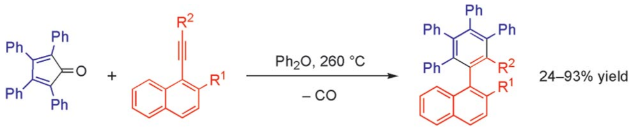


Keywords: Click chemistry / Energy transfer / Electron transfer / Azides / Sandwich complexes / Porphyrinoids

Functionalized Atropisomeric Biaryls

**M. Hapke*, A. Gutnov, N. Weding,
A. Spannenberg, C. Fischer,
C. Benkhäuser-Schunk,
B. Heller** **509–514**

Use of the Diels–Alder Cycloaddition of Tetracyclone and Internal Aryl Acetylenes for the Synthesis of Functionalized Atropisomeric Biaryls



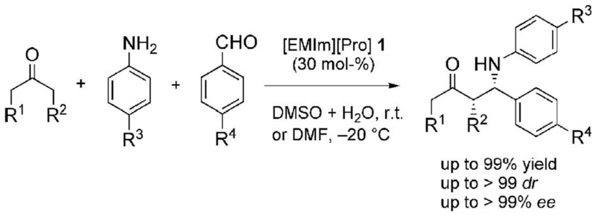
The cycloaddition of tetracyclone and internal aryl acetylenes successfully yielded atropisomeric biaryls in mostly high yields when the acetylenes were carrying electron-accepting substituents. The resolution of the atropisomers via diastereomers was exemplified, leading to the isolation of the enantiomerically pure phosphane oxides and subsequently phosphanes.

Keywords: Atropisomerism / Biaryls / Diels–Alder reaction / Cycloaddition / Alkynes

Asymmetric Catalysis

**X. Zheng, Y.-B. Qian,
Y. Wang*** **515–522**

2-Pyrrolidinecarboxylic Acid Ionic Liquid as a Highly Efficient Organocatalyst for the Asymmetric One-Pot Mannich Reaction



The first direct asymmetric one-pot three-component Mannich reaction using 2-pyrrolidinecarboxylic acid ionic liquid as a catalyst has been developed. The *syn* Mannich adducts were prepared in high yields and with excellent chemo-, regio-, and enantioselectivity either under mild conditions or at a low temperature.

Keywords: Asymmetric synthesis / Ionic liquids / Organocatalysis / Enantioselectivity

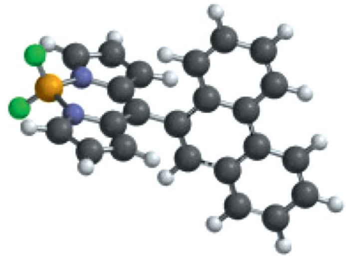
CONTENTS

Molecular Rotors

A. C. Benniston, A. Harriman,*
V. L. Whittle, M. Zelzer 523–530

Molecular Rotors Based on the Boron Dipyrromethene Fluorophore

Keywords: Dyes/pigments / Fluorescence / Viscosity / Sensors / Photophysics



The design elements for an efficacious, molecular-scale fluorescent rotor are illustrated by reference to the comparison of two boron dipyrromethene based dyes bearing *meso* substituents of disparate size. A major issue relates to the distinction between the recognition of viscosity and polarity changes.

Nitrogen Heterocycles

V. Singh, S. Hutait, S. Biswas,
S. Batra* 531–539

Versatility of Substituted 1-Formyl-9*H*-β-carbolines for the Synthesis of New Fused β-Carbolines via Intramolecular 1,3-Dipolar Cycloaddition

Keywords: Nitrogen heterocycles / β-Carbolines / Cycloaddition / Alkylation / Microwave chemistry

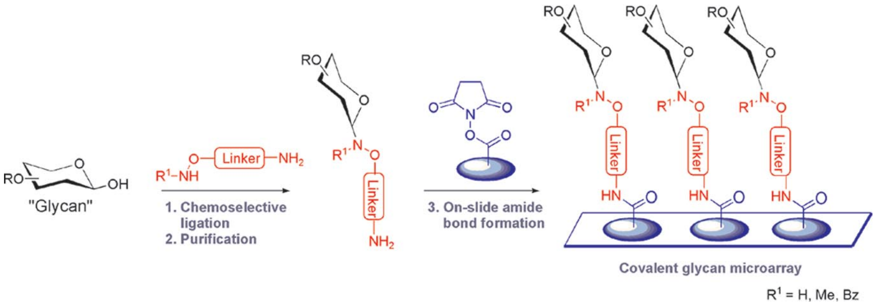
A simple route to the synthesis of several ring-fused β-carbolines through 1-formyl-9*H*-β-carbolines using 1,3-dipolar cycloaddition as the key-step is reported.

Glycochips

E. Cló, O. Blixt,
K. J. Jensen* 540–554

Chemoselective Reagents for Covalent Capture and Display of Glycans in Microarrays

Keywords: Nanobioscience / Glycomics / Microarrays / Lectins / Carbohydrates / Chemoselectivity



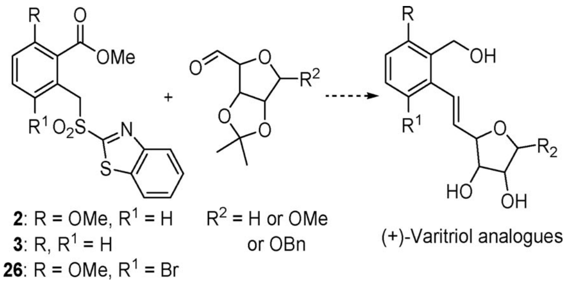
Novel bifunctional linkers with an *N*-substituted aminooxy group for reaction with unprotected carbohydrates in solution allow the easy construction of glycan microarrays with correct display of glycans.

Julia Olefination

A. Senthilmurugan,
I. S. Aidhen* 555–564

Synthesis of (+)-Varitriol Analogues via Novel and Versatile Building Blocks Based on Julia Olefination

Keywords: Natural products / Varitriol analogues / Julia olefination / Sulfones

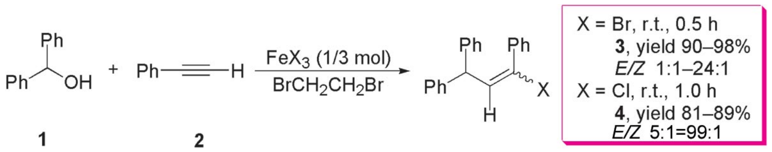


A new strategy for the synthesis of varitriol analogues has been achieved by using Julia olefination as the key step. The convenient synthesis and the high yielding reactivity of the building blocks with a variety of aryl-, alkyl- and carbohydrate-derived aldehydes justify their use in the newly presented methodology.

Fe-Promoted C–C Bond Formation

K. Ren, M. Wang, L. Wang* **565–571**

FeX_3-Promoted Intermolecular Addition of Benzylic Alcohols to Aromatic Alkynes: A Mild and Efficient Strategy for the Synthesis of Alkenyl Halides



A convenient, effective, mild and simple strategy has been developed for the synthesis of alkenyl halides by the intermolecular addition of benzylic alcohols to aromatic alkynes in the presence of iron(III) bromide or chloride. Alkenyl bromides and chlorides were obtained with high regio- and stereoselectivity (*E*/*Z* up to 99:1) in good to excellent yields in 0.5–1 h under mild reaction conditions.

Keywords: Alkenes / Alkynes / Alcohols / Iron / Synthetic methods / Halides

CORRECTION

Keywords: Alkenes / Alkynes / Alcohols / Iron / Synthetic methods / Halides

FeX_3-Promoted Intermolecular Addition of Benzylic Alcohols to Aromatic Alkynes: A Mild and Efficient Strategy for the Synthesis of Alkenyl Halides

K. Ren, M. Wang, L. Wang* **572**

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* Author to whom correspondence should be addressed.

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

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