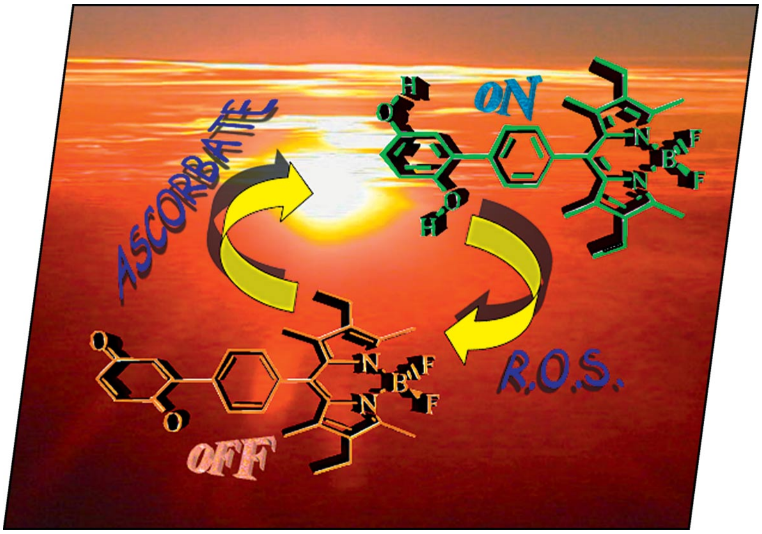
COVER PICTURE

The cover picture shows the chemically induced reversible cycling of a BODIPY-based dyad from the dark quinone state to the highly emissive hydroquinone form. The change in luminescence intensity can be readily seen by the eye. The phenylene spacer between the BODIPY and the redox-active units is essential to the operation of the molecular dyads. Without this group, the fluorescence from the BODIPY group is quenched in both the quinone and hydroquinone forms. The reason for the difference in behaviour is discussed in the article by A. C. Benniston et al. on p. 2705ff, along with the full details of the synthesis, structural, and sensing capabilities of the molecular systems. The authors thank the EPSRC for financial support of the work.



CONTENTS

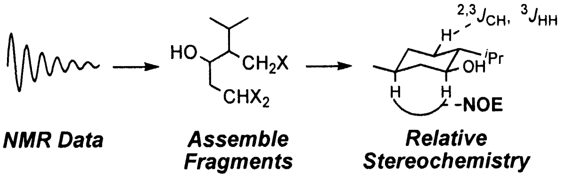
MICROREVIEW

NMR Spectroscopy

E. E. Kwan,* S. G. Huang 2671–2688

Structural Elucidation with NMR Spectroscopy: Practical Strategies for Organic Chemists

Keywords: NMR spectroscopy / Configuration determination / Structure elucidation



NMR spectroscopic methods for structural elucidation in organic chemistry are reviewed. Detailed procedures and recommended experimental parameters are provided for commonly encountered scenarios. The step-by-step analyses of menthol and salvinorin A are provided to illustrate these strategies.

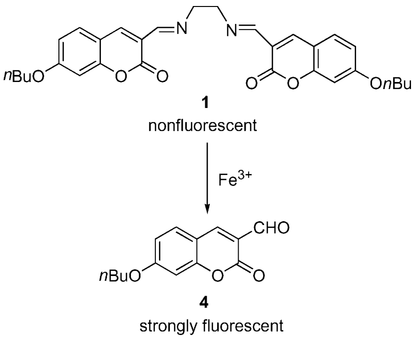
SHORT COMMUNICATIONS

Fe^{3+}-Amplified Probes

W. Lin,* L. Yuan, J. Feng, X. Cao 2689–2692

A Fluorescence-Enhanced Chemodosimeter for Fe^{3+} Based on Hydrolysis of Bis(coumarinyl) Schiff Base

Keywords: Probes / Iron / Fluorescence / Schiff bases



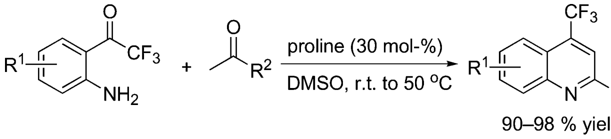
Bis(coumarinyl) Schiff base **1** was developed as a fluorescence turn-on chemodosimeter for Fe^{3+}. It displays a large fluorescence enhancement upon addition of Fe^{3+}. Furthermore, **1** was also highly selective to Fe^{3+} over other metal ions.

Friedlander Annulation

B. Jiang,* J.-j. Dong, Y. Jin, X.-l. Du, M. Xu 2693–2696

The First Proline-Catalyzed Friedlander Annulation: Regioselective Synthesis of 2-Substituted Quinoline Derivatives

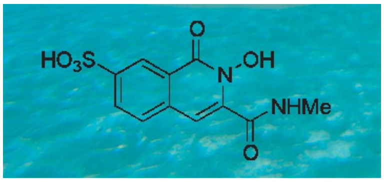
Keywords: Aldol reactions / Quinoline / Cyclization / Proline



The first proline-catalyzed Friedlander annulation for the synthesis of 2-substituted 4-trifluoromethyl quinoline derivatives is described. Excellent regioselectivity as well as good yields are shown in a variety of cases, and a tandem aldol-cyclization pathway might be involved.

Cyclic Hydroxamic Acid Ligands

A sulfonated 2-hydroxyisoquinolin-1-one (1,2-HOIQO) ligand provides a general synthetic route to a new class of aromatic cyclic hydroxamic acids that are extremely water-soluble. The readily functionalized ligand is prepared by amide coupling using a key carboxylic acid intermediate. The reaction sequence is optimized to allow for easy handling and purification by standard methods, which is often impossible for sulfonic acid species.



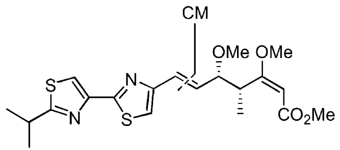
M. Seitz, K. N. Raymond* **2697–2700**

Efficient Route to Highly Water-Soluble Aromatic Cyclic Hydroxamic Acid Ligands

Keywords: O ligands / Ligand design / Aromatic substitution / Heterocycles

Cystothiazole A

Myxobacteria are a great source of biologically active secondary metabolites. Among them the β-methoxyacrylate antibiotic cystothiazole A has attracted particular attention as it exhibits potent antifungal and cytotoxic activity. Herein we present a novel cross-metathesis-based approach towards its total synthesis.



Cystothiazole A

J. Gebauer, S. Arseniyadis,
J. Cossy* **2701–2704**

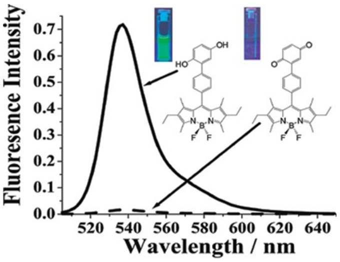
Total Synthesis of Cystothiazole A by Microwave-Assisted Olefin Cross-Metathesis

Keywords: Cystothiazoles / Antibiotics / Myxobacteria / Cross-metathesis / Microwave-assisted synthesis

FULL PAPERS

Sensors

The properties of a series of boron dipyrromethene (BODIPY) dyads, incorporating redox-active units appended at the *meso* position, are described. One such quinone-based dyad shows excellent on/off luminescence switching under external chemical or electrochemical stimulus. The potential uses of this system for detection of reactive oxygen species are discussed.



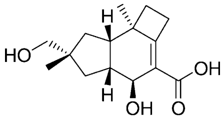
A. C. Benniston,* G. Copley,
K. J. Elliott, R. W. Harrington,
W. Clegg **2705–2713**

Redox-Controlled Fluorescence Modulation in a BODIPY-Quinone Dyad

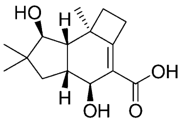
Keywords: BODIPY / Fluorescence / Molecular devices / Redox chemistry / Sensors

Total Synthesis

Their strong activities against some *Mannheimia haemolytica* strains qualified the recently patented pasteurestins A (**1**) and B (**2**) as potential lead structures for new veterinary antibiotics. However, neither the absolute nor the relative configurations were determined from the isolated products. We thus completed total syntheses of **1** and **2** and clarified their structures and their biological profiles. Key steps in both syntheses were two [2+2+2] $CpCo(CO)_2$-mediated Vollhardt cyclotrimerizations.



1



2

M. Kögl, L. Brecker, R. Warrass,
J. Mulzer* **2714–2730**

Novel Protoilludane Lead Structure for Veterinary Antibiotics: Total Synthesis of Pasteurestins A and B and Assignment of Their Configurations

Keywords: Total synthesis / Cyclotrimerization / Antibiotics / Reformatsky reaction / Configurational assignment

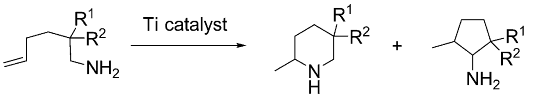
CONTENTS

Hydroamination

C. Müller, W. Saak, S. Doye* 2731–2739

Neutral Group-IV Metal Catalysts for the Intramolecular Hydroamination of Alkenes

Keywords: Alkenes / Amines / Group-IV metals / Hydroamination / Homogeneous catalysis



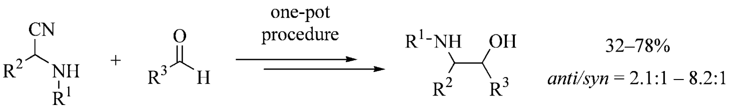
A detailed comparison of the group-IV metal catalysts $Ti(NMe_2)_4$, Ind_2TiMe_2, Ind_2ZrMe_2 and Ind_2HfMe_2 in the hydroamination/cyclization of 1-amino-4-pentenes and 1-amino-5-hexenes suggests that variation of the metal, the ligands present at the metal centres involved, as well as the ring size of the product can result in significant mechanistic changes.

Vicinal Amino Alcohols

C. Kison, T. Opatz* 2740–2745

One-Pot Synthesis of Trisubstituted 1,2-Amino Alcohols from Deprotonated α-Amino Nitriles

Keywords: Amino alcohols / Umpolung / Amino nitriles / Reduction



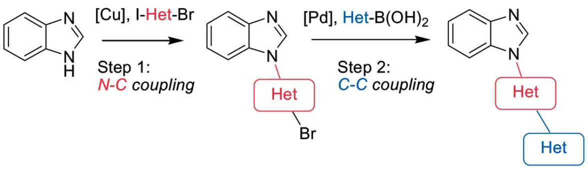
The 1,2-addition of deprotonated α-amino nitriles to aldehydes and subsequent reductive decyanation of the intermediates with BH_3–THF predominantly furnishes *anti*-configured 1,2-amino alcohols in moderate-to-good yields. The reaction sequence allows the synthesis of trisubstituted vicinal amino alcohols from two aldehydes and a primary amine.

Functionalized Heterocycles

J. S. Siddle, A. S. Batsanov, M. R. Bryce* 2746–2750

Sequential Metal-Catalyzed *N*-Heteroarylation and C–C Cross-Coupling Reactions: An Expedient Route to Tris(hetero)aryl Systems

Keywords: N-Heterocycles / Benzimidazole / Benzimidazolone / Imidazole / *N*-Arylation / Cross-coupling



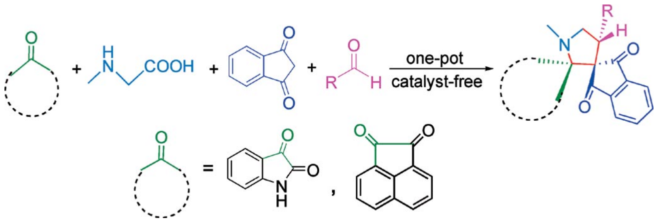
An expedient route to tris(hetero)aryl scaffolds comprising two or three N-heterocyclic rings has been established by sequential copper-catalyzed *N*-heteroarylation of benzimidazole, 1-methylbenzimidazolone, imidazole and pyrrole, followed by palladium-catalyzed Suzuki–Miyaura methodology. Both steps can be accomplished in one pot.

Improved Huisgen Synthesis

M. Li,* W.-L. Yang, L.-R. Wen, F.-Q. Li 2751–2758

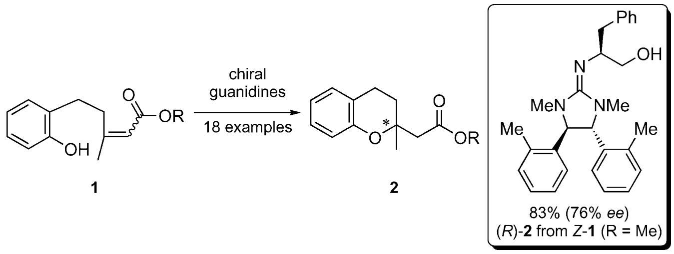
A First Resource-Efficient and Highly Flexible Procedure for a Four-Component Synthesis of Dispiropyrrolidines

Keywords: Azo Compounds / Ylides / Multicomponent reactions / Knoevenagel condensation / Cycloaddition / Spiro compounds



Two series of dispiropyrrolidine derivatives were synthesized by a tandem Knoevenagel–1,3-dipolar cycloaddition reaction sequence of four components in one-pot without any catalyst, which allowed the dipole azomethine ylide and the dipolarophile to be generated in situ.

Asymmetric Organocatalysts



The guanidine-catalyzed 6-*exo*-*trig*-type intramolecular asymmetric oxa-Michael addition of α,β-unsaturated esters with a 2-hydroxyaryl moiety at the C-5 carbon has been examined for the construction of chromane skeletons with a quaternary carbon chiral center.

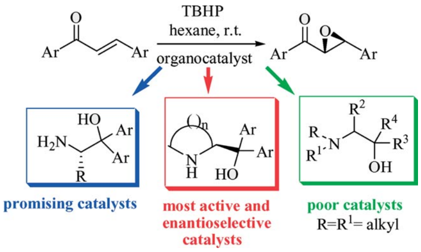
N. Saito, A. Ryoda, W. Nakanishi, T. Kumamoto, T. Ishikawa* ... 2759–2766

Guanidine-Catalyzed Asymmetric Synthesis of 2,2-Disubstituted Chromane Skeletons by Intramolecular Oxa-Michael Addition

Keywords: Asymmetric synthesis / Organocatalysis / Chromane / Guanidine / Michael addition

Organocatalysis

A study on the asymmetric epoxidation of *trans*-chalcones promoted by easily accessible primary, secondary, and tertiary β-amino alcohols and *tert*-butyl hydroperoxide is presented.



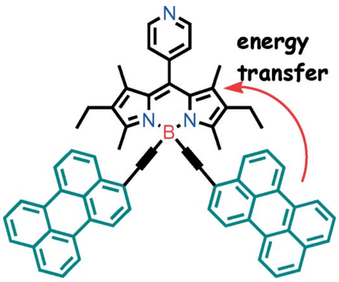
A. Russo, A. Lattanzi* 2767–2773

Asymmetric Epoxidation of *trans*-Chalcones Organocatalyzed by β-Amino Alcohols

Keywords: Asymmetric synthesis / Epoxidation / Organocatalysis / Amino alcohols

Fluorescent Sensor

Rapid electronic energy transfer occurs from the appended perylene units to the BODIPY-based dye, which itself is equipped with an ancillary binding unit. Cations can coordinate to the pyridine N atom and thereby switch on an intramolecular charge-transfer process. On cation binding, fluorescence from perylene increases and that from BODIPY decreases.



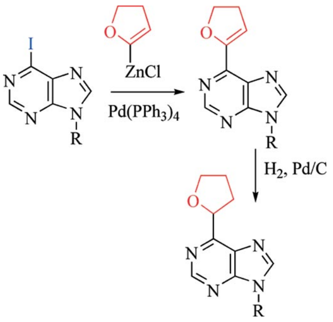
M. A. H. Alamiry, A. Harriman,* L. J. Mallon, G. Ulrich, R. Ziessel* 2774–2782

Energy- and Charge-Transfer Processes in a Perylene–BODIPY–Pyridine Tripartite Array

Keywords: Energy transfer / Perylene / Fluorescence / Chemical sensor / Boron dipyrromethene dye

Purines

A novel organozinc reagent, (4,5-dihydrofuran-2-yl)zinc chloride, undergoes Pd-catalyzed cross-coupling reactions with 6-iodopurines to give 6-(4,5-dihydrofuran-2-yl)purines in high yields. Their catalytic hydrogenation gives 6-(tetrahydrofuran-2-yl)purines. These compounds are saturated analogues of cytostatic and antiviral 6-hetarylpurine nucleosides.



V. Bambuch, R. Pohl, M. Hocek* 2783–2788

Synthesis of 6-(4,5-Dihydrofuran-2-yl)- and 6-(Tetrahydrofuran-2-yl)purine Bases and Nucleosides

Keywords: Purines / Nucleosides / Cross-coupling / Zinc / Hydrogenation

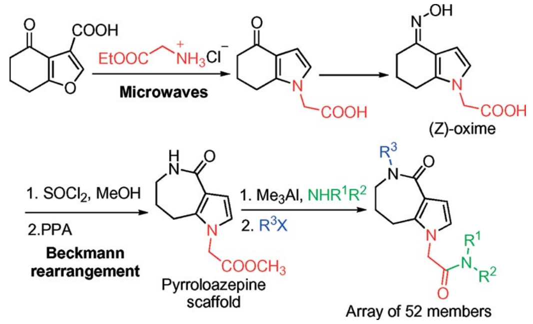
CONTENTS

Combinatorial Synthesis

L. Piras, E. Genesio, C. Ghiron,
M. Taddei* 2789–2800

Scaffold Preparation and Parallel Synthesis of Arrays of 5,6,7,8-Tetrahydropyrroloazepinones in the Solution Phase

Keywords: Combinatorial chemistry / Heterocycles / Microwaves / Ring expansion / Amidation



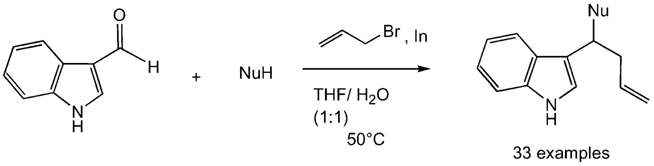
The microwave-assisted cyclocondensation of tetrahydrobenzofuran in the presence of glycine gives 4-oxotetrahydroindole, which can be transformed into the corresponding (*Z*)-oxime. Beckmann rearrangement of the oxime in the presence of polyphosphoric acid produces a pyrrolo-azepine scaffold. Trimethylaluminium-mediated amidation and *N*-alkylation furnishes an array of 52 (pyrrolo-azepinyl)acetamides.

Functionalized Indoles

F. Colombo, G. Cravotto, G. Palmisano,*
A. Penoni, M. Sisti 2801–2807

Three-Component Indium-Mediated Domino Allylation of 1*H*-Indole-3-carbaldehyde with Electron-Rich (Hetero)arenes: Highly Efficient Access to Variously Functionalized Indolylbutenes

Keywords: Indium / Domino reactions / Aldehydes / Allylation / Heterocycles / Nitrogen heterocycles



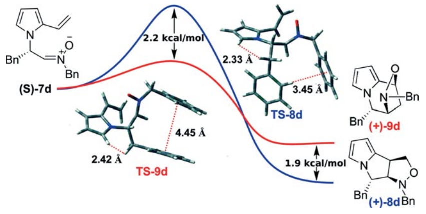
A three-component reaction involving allylindation of 3-carbaldehyde in the presence of C and N nucleophiles under mild conditions and in aqueous media to generate a library of variously functionalized indolylbutenes is reported.

Intramolecular Nitrone Cycloaddition

E. Borsini, G. Broggini,* A. Contini,*
G. Zecchi 2808–2816

Synthesis of Enantiopure Highly Functionalized Pyrrolizines and Indolizines from Natural α-Amino Acids: An Experimental and Theoretical Investigation

Keywords: Cycloaddition / Nitrones / Regioselectivity / Density functional calculations / Pi interactions



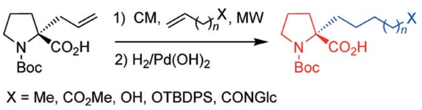
Enantiopure 2,3-dihydro-1*H*-pyrrolizines and 5,6,7,8-tetrahydroindolizines have been synthesized starting from L-α-amino acids and an intramolecular cycloaddition reaction is the key step. A theoretical investigation at the HCTH/6-311+G(d,p)//HCTH/6-31+G(d) level of theory was performed with the aim of rationalizing the effects of substituents on the regiochemistry of the cycloaddition reaction.

Cyclic Quaternary α-Amino Acids

M. Lumini, F. M. Cordero,* F. Pisaneschi,
A. Brandi 2817–2824

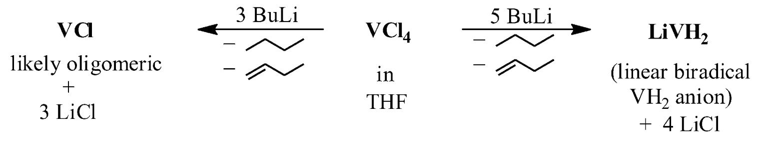
Straightforward Synthesis of α-Substituted Prolines by Cross-Metathesis

Keywords: Amino acids / Nitrogen heterocycles / Cross-coupling / Metathesis / Microwave



A new application of cross-metathesis (CM) to the synthesis of valuable cyclic quaternary α-amino acids decorated with lipophilic and functionalized side chains is described. The method is wide in scope and allows the introduction of variously functionalized side chains on the 2-position of proline starting with *N*-Boc-2-allylproline.

Subvalent Vanadium Salts



The subvalent vanadium reagents, vanadium(I) chloride and lithium vanadium(I) dihydride, have been prepared from VCl_3 or VCl_4 by alkylative reduction with *n*-butyllithium and characterized by gasometric protolysis, infrared and EPR spectral analysis and by reaction with selective organic substrates. The $LiVH_2$ has a biradical anion of an H−V−H linear array.

J. J. Eisch,* P. O. Fregene,
D. C. Doetschman .... 2825−2835

Vanadium(I) Chloride and Lithium Vanadium(I) Dihydride as Epimetallating Reagents for Unsaturated Organic Substrates: Constitution and Mode of Reaction

Keywords: Epimetallation / EPR spectroscopy of VH_2^- / Vanadium(I) chloride / Lithium vanadium(I) dihydride / Organic radical intermediates