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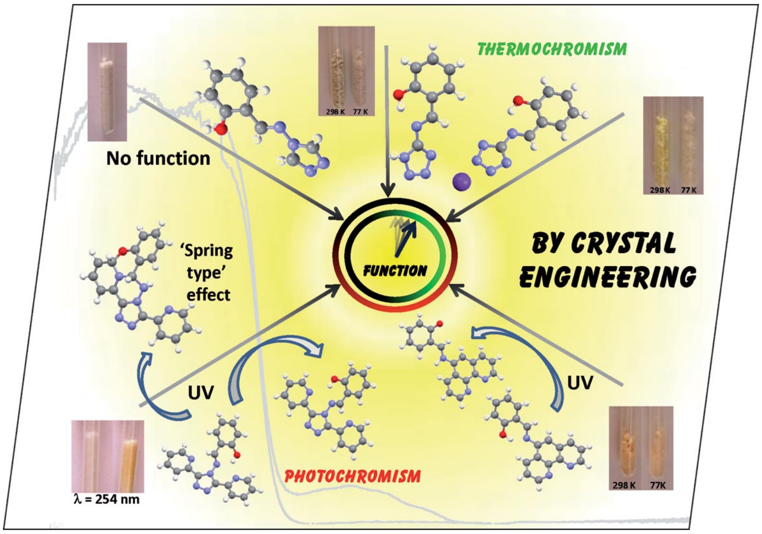
COVER PICTURE

The cover picture shows a panel of functional *N*-salicylidene derivatives that can be rationally designed and assembled by crystal engineering. The amplitude of their thermochromism and/or photochromism can be finely tuned as shown by the central needle. This study is supported by a multidisciplinary approach (syntheses, physical and structural studies, calculations). Details are discussed in the article by Y. Garcia et al. on p. 621ff.



CONTENTS

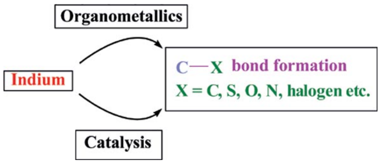
MICROREVIEW

Organoindium Reagents

J. S. Yadav,* A. Antony, J. George,
B. V. Subba Reddy* **591–605**

Recent Developments in Indium Metal and Its Salts in Organic Synthesis

Keywords: Indium / Organoindium reagents / Chiral indium complexes / Chirality / Reaction mechanisms / Synthetic methods



Indium chemistry is of great importance because of the huge potential of indium metal for induction of chirality through the use of chiral indium complexes, for the introduction of organic moieties through organoindium reagents, and for highly efficient reaction catalysis. A brief survey of recently reported reactions is illustrated with selected examples.

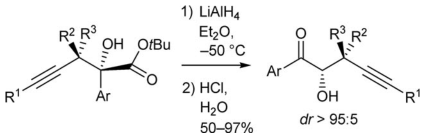
SHORT COMMUNICATIONS

Stereoselective Rearrangement

T. Hameury, V. Bellosta,* J. Guillemont,
L. Van Hijfte, J. Cossy* **607–610**

Reduction of Alkynyl α-Hydroxy Esters: Stereoselective α-Ketol Rearrangement

Keywords: Rearrangement / Hydrides / Diastereoselectivity / α-Ketol



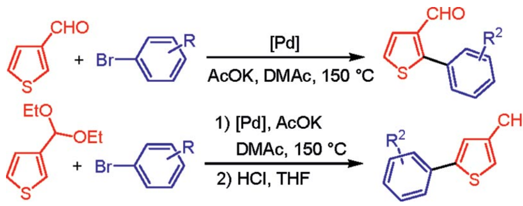
α-Hydroxy ketones can be obtained by α-ketol rearrangement of alkynyl α-hydroxy esters. This rearrangement induced by $LiAlH_4$/acid treatment proceeds stereoselectively through an α-hydroxy aldehyde intermediate which rearranges spontaneously under acidic conditions.

Direct Arylation

J. J. Dong, H. Doucet* **611–615**

Palladium-Catalyzed C2 or C5 Direct Arylation of 3-Formylthiophene Derivatives with Aryl Bromides

Keywords: Arylation / Homogeneous catalysis / C–H activation / Sulfur heterocycles / Palladium



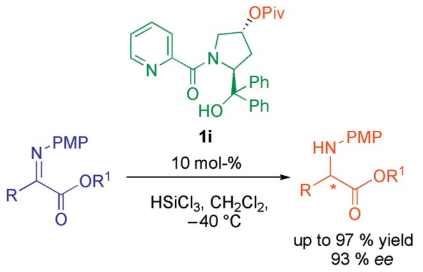
The palladium-catalyzed direct arylation of 3-formylthiopene led to 2-arylated thiophenes with regioselectivities of 76–86%, whereas the arylation of 3-formylthiophene diethyl acetal gave 5-arylated thiophenes with regioselectivities of 64–88%.

Organocatalytic Hydrosilylation

Z.-Y. Xue, Y. Jiang, W.-C. Yuan,
X.-M. Zhang* **616–619**

The First Highly Enantioselective Lewis Base Organocatalyzed Hydrosilylation of α-Imino Esters

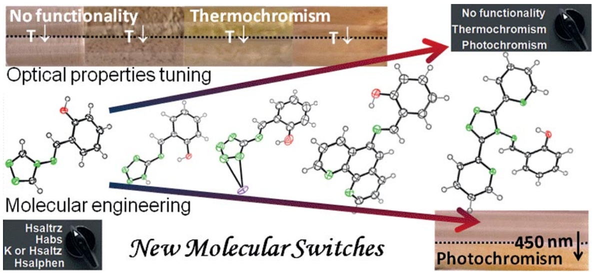
Keywords: Amino acids / Enantioselectivity / Hydrosilylation / Lewis bases / Organocatalysis



Highly enantioselective hydrosilylation of α-imino esters with trichlorosilane promoted by a novel chiral Lewis base **1i** proceeded smoothly to provide various chiral α-amino acid derivatives with good yields (up to 97%) and high enantioselectivities (up to 93% *ee*) at −40 °C in CH_2Cl_2.

FULL PAPERS

Solid-State Molecular Switches



Supramolecular engineering concepts allow fine-tuning of the optical properties of a novel family of salicylidene aniline derivative molecular switches with specific properties (nonfunctional, thermochromism, and photochromism). Such results are supported by a detailed optical and theoretical study.

F. Robert, A. D. Naik, F. Hidara, B. Tinant, R. Robiette, J. Wouters, Y. Garcia* 621–637

Engineering Solid-State Molecular Switches: *N*-Salicylidene N-Heterocycle Derivatives

Keywords: Molecular devices / Thermochromism / Photochromism / Crystal engineering

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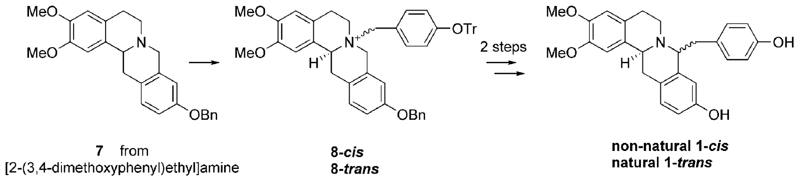
Diastereoselective Total Synthesis



The total synthesis of natural *trans*-8-(arylmethyl)berbine and its non-natural *cis* C-8 epimer, was attained by a synthetic route that makes use of the diastereoselective Stevens rearrangement as the key step.

M. Valpuesta,* M. Ariza, A. Diaz, G. Torres, R. Suau 638–645

Total Synthesis of New 8-(Arylmethyl)-berbines

Keywords: Alkaloids / Rearrangement / Diastereoselectivity / Total synthesis / Natural products

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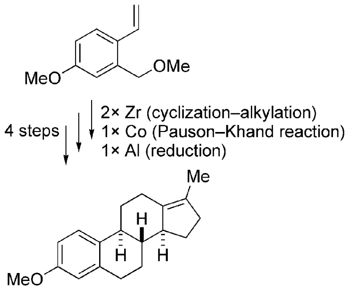
Estrone Synthesis

The synthesis of an estrone intermediate was carried out in four steps from a simple styrene derivative. The crucial reaction sequence for the steroid skeleton construction relied on Zr-mediated cyclization/propargylation followed by Co-mediated Pauson–Khand reaction. The synthesis was finalized by the reduction of the conjugated cycloenone.



R. Betík, P. Herrmann, M. Kotora* 646–655

Synthesis of an (±)-Estrone Precursor: The Scope of Zr- and Co-Mediated Cycloannulations

Keywords: Zirconium / Cobalt / Cyclization / Carbonylation / Steroids

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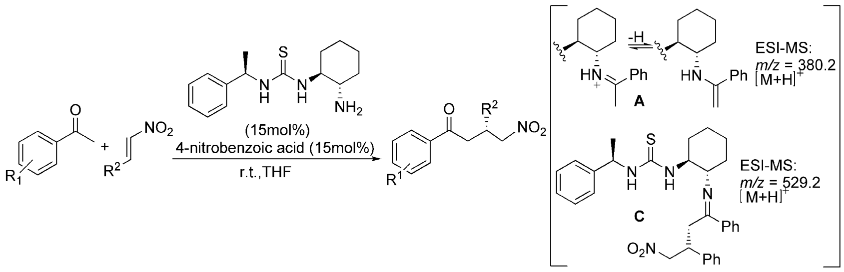
Asymmetric Michael Addition



A simple bifunctional chiral primary amine–thiourea and 4-nitrobenzoic acid were successfully applied to highly enantioselective Michael reactions of aromatic ketones with nitroolefins. A plausible transition pathway has been confirmed. DFT calculations show that the chiral configuration of the catalysts has a remarkable impact on the experimental results.

B.-L. Li, Y.-F. Wang, S.-P. Luo, A.-G. Zhong, Z.-B. Li, X.-H. Du, D.-Q. Xu* 656–662

Enantioselective Michael Addition of Aromatic Ketones to Nitroolefins Catalyzed by Bifunctional Thioureas and Mechanistic Insight

Keywords: Organocatalysis / Asymmetric synthesis / Michael addition / Reaction mechanisms

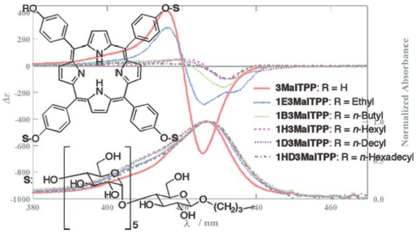
CONTENTS

Porphyrin Aggregation

Y. Mikata,* T. Sawaguchi, T. Kakuchi,* M. Gottschaldt, U. S. Schubert, H. Ohi, S. Yano* 663–671

Control of the Aggregation Properties of Tris(maltohexaose)-Linked Porphyrins with an Alkyl Chain

Keywords: Carbohydrates / Porphyrinoids / Aggregation / Noncovalent interactions / Circular dichroism



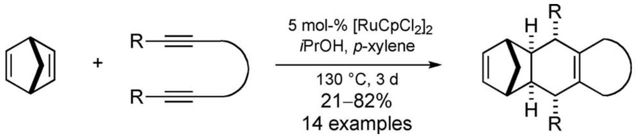
In contrast to the silent CD spectra in DMSO solution, porphyrins with three maltohexaose units and one alkyl chain exhibit a splitting Cotton effect at the Soret band in aqueous solution by aggregation.

Norbornenes

C.-C. Cheng, C.-S. Chang, Y.-L. Hsu, T.-Y. Lee, L.-C. Chang, S.-H. Liu, Y.-T. Wu* 672–679

Ruthenium-Catalyzed Cascade Reactions of Diynes with Norbornadiene – Synthesis of Norbornene Derivatives

Keywords: Norbornadiene / Norbornene / Cascade reaction / Ruthenium / Transfer hydrogenation / Cycloaddition



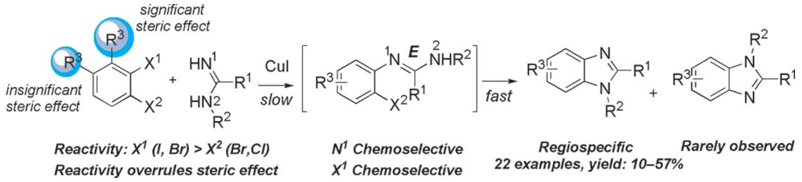
Norbornene derivatives were prepared from norbornadiene and diynes under the catalysis of Ru complexes. This cascade reaction provided high diastereoselectivity. Additionally, one of these cycloadducts was applied in the synthesis of polynorbornenes by the ring-opening metathesis polymerization.

Heterocycle Synthesis

X. Deng,* N. S. Mani 680–686

Reactivity-Controlled Regioselectivity: A Regiospecific Synthesis of 1,2-Disubstituted Benzimidazoles

Keywords: Regioselectivity / Copper catalysis / Amination / Heterocycles



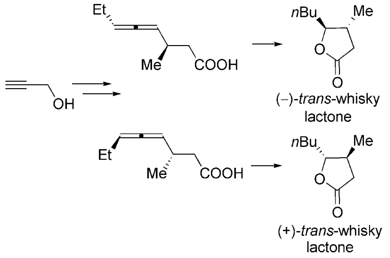
A highly regioselective synthesis leading to 1,2-disubstituted benzimidazoles is developed through the tandem amination reactions between 1,2-differentiated dihaloarenes and *N*-substituted amidines. The regiochemical outcome of this CuI-catalyzed reaction is the result of a combination of N^1/N^2 chemoselectivity on the amidine and reactivity-controlled X^1/X^2 chemoselectivity on the 1,2-dihaloarene.

Total Synthesis

X. Jiang, C. Fu, S. Ma* 687–693

A Concise Synthesis of (–)- and (+)-*trans*-Whisky Lactones

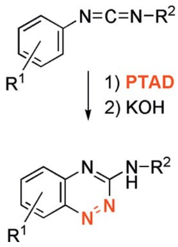
Keywords: Allenes / Lactones / Stereoselectivity / Enantioselectivity



A concise enantioselective multi-step synthetic procedure leading to (–)- and (+)-*trans*-whisky lactones was developed.

Dienophilic Dinitrogen Equivalents

The reaction of *N*-arylcarbodiimides with 4-phenyl-1,2,4-triazoline-3,5-dione (PTAD) affords [4+2] cycloadducts that can then be converted into 3-amino-1,2,4-benzotriazines. In this Diels–Alder/fragmentation sequence, PTAD behaves as a dienophilic synthetic equivalent of dinitrogen. With nonsymmetrical diarylcarbodiimides, highly chemoselective processes can be achieved.



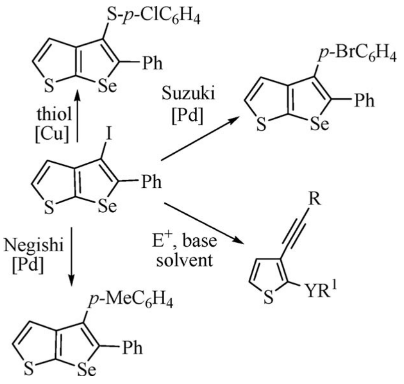
M. Alajarin,* B. Bonillo, M. Marin-Luna, P. Sanchez-Andrada, A. Vidal* ... 694–704

N-Phenyl-1,2,4-triazoline-3,5-dione (PTAD) as a Dienophilic Dinitrogen Equivalent: A Simple Synthesis of 3-Amino-1,2,4-benzotriazines from Arylcarbodiimides

Keywords: Cycloaddition / Nitrogen heterocycles / Synthetic methods / Transition states

Electrophilic Cyclization

The electrophilic cyclization reaction of 3-alkynylthiophenes with different electrophiles proceeded cleanly under mild reaction conditions, giving fused 4-iodoselenophene[2,3-*b*]thiophenes in excellent yields. The obtained chalcogenophenes were readily transformed into more complex products through palladium- or copper-catalyzed cross-coupling reactions.



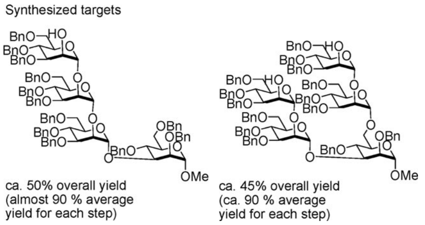
A. L. Stein, J. da Rocha, P. H. Menezes, G. Zeni* 705–710

Synthesis of Fused 4-Iodoselenophene[2,3-*b*]thiophenes by Electrophilic Cyclization of 3-Alkynylthiophenes

Keywords: Fused-ring systems / Sulfur heterocycles / Cyclization / Cross-coupling / Alkynes / Chalcogens

Rapid Oligosaccharide Assembly

Two biologically useful moieties of the gp120 glycan were rapidly assembled in high yields by the iteration of a one-pot sequence of glycosidation/Fmoc removal.

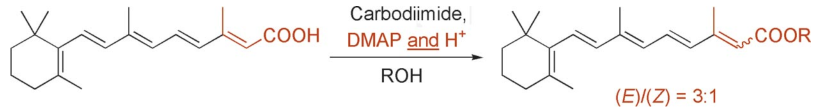


A. Pastore,* M. Adinolfi, A. Iadonisi,* S. Valerio 711–718

One-Pot Catalytic Glycosidation/Fmoc Removal – An Iterable Sequence for Straightforward Assembly of Oligosaccharides Related to HIV gp120

Keywords: Oligosaccharides / Glycosylation / Protecting groups / One-pot synthesis / Fmoc / Synthetic methods

Lipid Synthesis



Acylation of alcohols with all-(*E*)-retinoic acid (ATRA) under carbodiimide activation led to an (*E*)/(*Z*) ratio of 3:1 of the products in the presence of DMAP and a proton source. In their absence, lower yields were obtained, but isomerization was suppressed. Mitsunobu conditions provided the desired esters as single stereoisomers, which was exploited for the synthesis of two ATRA–etherlipid conjugates.

M. S. Christensen, P. J. Pedersen, T. L. Andresen, R. Madsen, M. H. Clausen* 719–724

Isomerization of all-(*E*)-Retinoic Acid Mediated by Carbodiimide Activation – Synthesis of ATRA Ether Lipid Conjugates

Keywords: Phospholipids / Retinoic acid / Acylation / Mitsunobu reaction / Isomerization

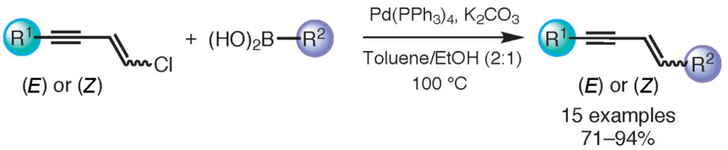
CONTENTS

Chloroenyne Couplings

A. Tikad, A. Hamze, O. Provot, J.-D. Brion, M. Alami* 725–731

Suzuki Coupling Reactions of (*E*)- and (*Z*)-Chloroenynes with Boronic Acids: Versatile Access to Functionalized 1,3-Enynes

Keywords: Cross-coupling / Enynes / Boron / Palladium / C–C coupling



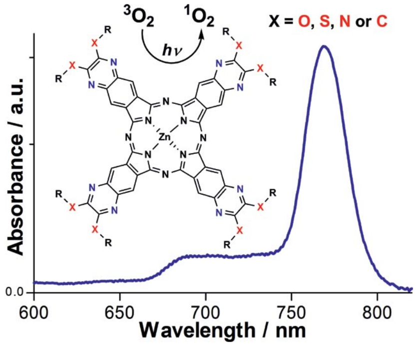
A stereoselective, palladium-catalyzed, cross-coupling reaction between chloroenynes and boronic acids was successfully developed. This procedure is general and provides the desired enynes in high yields. The scope and limitations of this new reaction are described.

Enlarged Phthalocyanines

V. Novakova, P. Zimcik,* M. Miletin, K. Kopecky, Z. Musil 732–739

Tetra[6,7]quinoxalinoporphyrazines: The Effect of an Additional Benzene Ring on Photophysical and Photochemical Properties

Keywords: Absorption / Fluorescence / Nucleophilic substitution / Phthalocyanines / Singlet oxygen



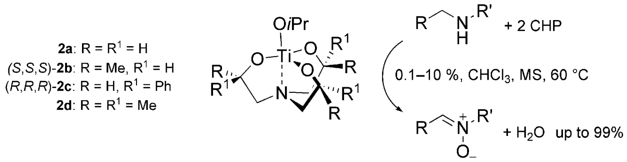
Prepared alkyheteroatom-substituted tetra[6,7]quinoxalinoporphyrazines benefit from an expanded π-system; the absorption of the Q-band is batho- and hyperchromically shifted (730–770 nm in pyridine) in comparison to other porphyrinoid compounds. They showed high singlet oxygen quantum yields ($\Phi_\Delta = 0.50-0.74$) and relatively low fluorescence quantum yields ($\Phi_F < 0.08$).

Catalytic *N*-Oxidation

M. Forcato, M. Mba, W. A. Nugent, G. Licini* 740–748

Effective Oxidation of Secondary Amines to Nitrones with Alkyl Hydroperoxides Catalysed by (Trialkanolaminato)titanium(IV) Complexes

Keywords: Nitrones / Amines / Oxidation / Titanium / Trialkanolamines



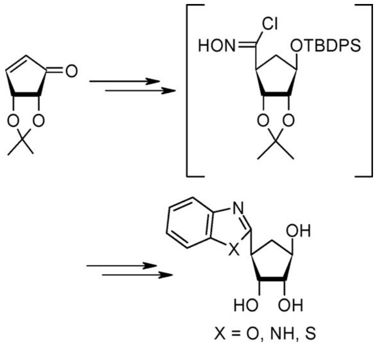
Effective and selective oxidation of secondary amines by alkyl hydroperoxides, in the presence of molecular sieves, can be achieved with C_3 titanium alkoxide catalysts (catalyst loadings down to 0.1 %). Nitrones are isolated in high yields (up to 98 %) under homogeneous conditions and even in the absence of solvent.

Carbocyclic *C*-Nucleosides

U. Pradere, H. Kumamoto, V. Roy, L. A. Agrofoglio* 749–754

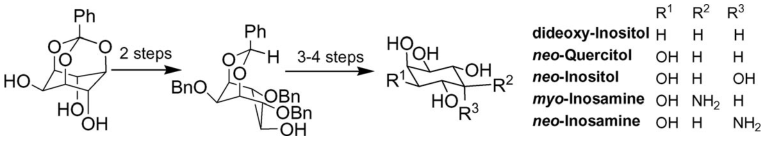
Preparation of Carbocyclic *C*-Nucleosides from α-Chlorooxime Precursor

Keywords: Nucleosides / Heterocycles / Carbocycles / Fused-ring systems / Asymmetric synthesis



The preparation of carbocyclic benzothiazolo, benzoxazolo, and benzimidazolo *C*-nucleosides is described. The key step is the reaction of a *C*-chlorooxime, obtained by *C*-chlorination with the *N*-chlorosuccinimide of a substituted cyclopentane-4-carbohydroximic acid, with different α-amino aromatic compounds. After deprotection, the acidic compounds were obtained in good yields.

Radical Hat-Trick!



An unusual intramolecular hydrogen radical abstraction observed during the deoxygenation of inositol-derived benzylidene acetals via xanthates leads to several functionalized cyclohexanes. These synthetic sequences illustrate the versatility of inositol orthoesters for the preparation of cyclitols and their derivatives.

C. Murali, B. P. Gurale,
M. S. Shashidhar* 755–764

Intramolecular Hydrogen Abstraction in Radicals Derived from Inositol 1,3-Acetals: Efficient Access to Cyclitols 💻

Keywords: Radicals / Radical reactions / Deoxygenation / Cyclitols / Inositol / Inosamine / Xanthate

CORRECTION

Keywords: Cyclization / Indoles / Natural products / Radicals / Synthetic methods

A Concise and Efficient Synthesis of *seco*-Duocarmycin SA

L. F. Tietze,* F. Haunert, T. Feuerstein,
T. Herzig 765

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* Author to whom correspondence should be addressed.

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