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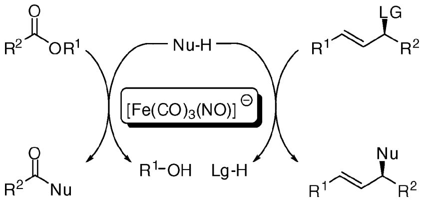
MICROREVIEW

Iron Catalysis

B. Plietker,* A. Dieskau 775–787

The Reincarnation of the Hieber Anion $[Fe(CO)_3(NO)]^-$ – a New Venue in Nucleophilic Metal Catalysis

Keywords: Iron / Subvalent compounds / Sustainable catalysis / Carbonyl ligands / Ferrate



Nowadays demand for selective, energy-efficient, and sustainable chemical transformations has spurred an increasing interest in the development of "sustainable metal catalysis". This expression defines a type of catalytic transformation in which non-toxic, readily available and inexpensive, stable metal complexes are used for catalysis. In the present Microreview the story of the reincarnation of an almost forgotten metal complex species, that celebrates its 50th birthday this year, will be told, the $[Fe(CO)_3(NO)]^-$ anion.

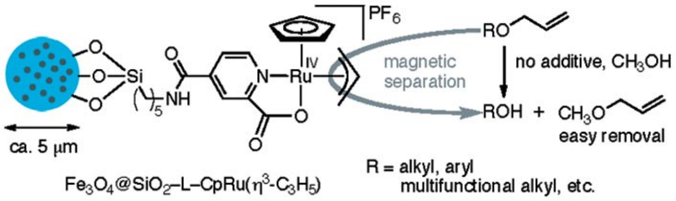
SHORT COMMUNICATIONS

Heterogeneous Deallylation Catalyst

T. Hirakawa, S. Tanaka, N. Usuki,
H. Kanzaki, M. Kishimoto,
M. Kitamura* 789–792

A Magnetically Separable Heterogeneous Deallylation Catalyst: $[CpRu(\eta^3\text{-}C_3H_5)(2\text{-pyridinecarboxylato})]PF_6$ Complex Supported on a Ferromagnetic Microsize Particle $Fe_3O_4@SiO_2$

Keywords: Sustainable chemistry / Supported catalysts / Ruthenium / Protecting groups / Magnetic particles / π-Allyl complexes



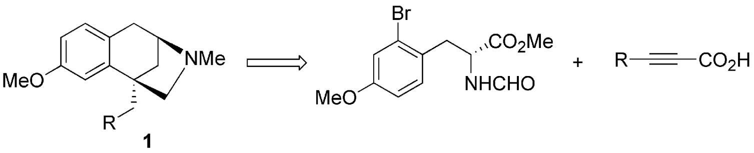
The new heterogeneous deallylation catalyst $Fe_3O_4@SiO_2\text{–L–}CpRu(\eta^3\text{-}C_3H_5)$ was prepared. It displays high saturation magnetization, weak coercive forces, and high dispersibility, and its utility was demonstrated by the deprotection of carboxylic acids, phosphoric acids, and alcohols in the synthesis of dipeptides and a triribonucleotide 3–5 U.

Alkaloid Synthesis

P. A. Donets, J. L. Goeman,
J. Van der Eycken, K. Robeyns,
L. Van Meervelt,
E. V. Van der Eycken* 793–796

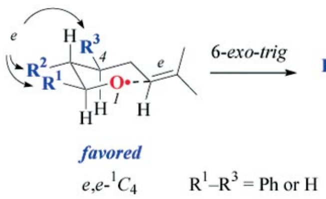
An Asymmetric Approach towards (–)-Aphanorphine and Its Analogues

Keywords: Alkaloids / Asymmetric catalysis / Heck reaction / Radical reactions / Cyclization



The synthesis of compounds **1** was developed on the basis of steps involving asymmetric hydrogenation, reductive Heck cyclization and intramolecular radical cyclization.

Oxyl Radical Cyclizations



Phenyl-substituted 6-methylhept-5-en-1-oxyl radicals undergo irreversible 6-*exo-trig* ring closure reactions affording 2,6-*cis*-, 2,5-*trans*-, and 2,4-*cis*-configured tetrahydropyrans as major cyclization products.

N. Schneiders, T. Gottwald, J. Hartung* .... 797−800

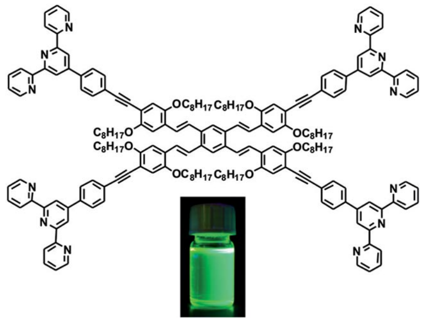
On the Stereoselectivity of Alkenoxyl Radical 6-*exo-trig* Cyclizations

Keywords: Radical reactions / Alkoxyl radical / Carbon radical / Bromination / Cyclization / Stereoselective synthesis / Stereochemical analysis

FULL PAPERS

π-Conjugated Terpyridines

π-Conjugated oligo(terpyridine)s have been synthesized and characterized as new supramolecular templates for potential OLED applications. The photophysical properties of the materials in solution and in the solid state reveal strong influences both of the numbers of terpyridine moieties attached to the central phenyl cores and of the geometries of the compounds.

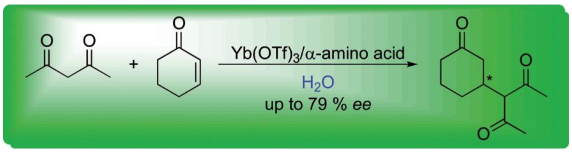


A. Winter, C. Friebe, M. D. Hager, U. S. Schubert* .... 801−809

Synthesis of Rigid π-Conjugated Mono-, Bis-, Tris-, and Tetrakis(terpyridine)s: Influence of the Degree and Pattern of Substitution on the Photophysical Properties

Keywords: Absorption / Fluorescence / Supramolecular chemistry / Terpyridines / Wittig reactions

Lewis Acid Catalysis in Water



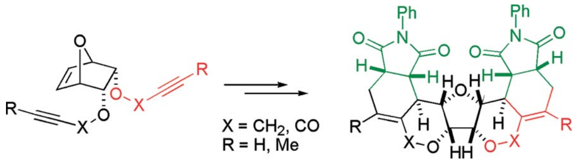
Asymmetric Michael additions in water catalysed with ytterbium triflate/α-amino acids has been studied from a mechanistic perspective. High yielding reactions with up to 79% *ee* has been achieved together with increased knowledge concerning the mechanism.

K. Aplander, R. Ding, M. Krasavin, U. M. Lindström,* J. Wennerberg* .... 810−821

Asymmetric Lewis Acid Catalysis in Water: α-Amino Acids as Effective Ligands in Aqueous Biphasic Catalytic Michael Additions

Keywords: Homogeneous catalysis / Asymmetric catalysis / Water-tolerant Lewis acids / Michael addition / Recyclable catalyst / Reaction mechanisms / Amino acids

Metathesis Reactions



Densely functionalized polycyclic compounds can be obtained from 7-oxanorbornene derivatives functionalized with alkyne appendages by metathesis reactions that are followed by Diels−Alder rections.

A. Aljarilla, M. C. Murcia, A. G. Csákÿ, J. Plumet* .... 822−832

A Convenient Approach to Polycyclic Derivatives with a *cis*-Fused 2,6-Dioxabicyclo[4.3.0]nonane System by the Sequence Ring-Opening/Intramolecular Ring-Closing Enyne Metathesis/Diels−Alder Reaction

Keywords: Metathesis / Cycloaddition / Diels−Alder reaction / Ruthenium / Polycycles

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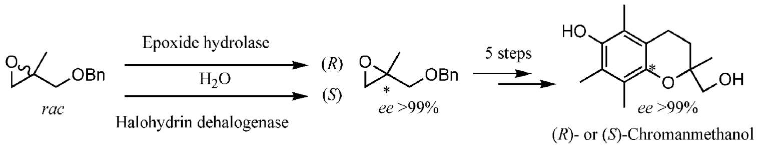
Biotransformations

M. Fuchs, Y. Simeo, B. T. Ueberbacher, B. Mautner, T. Netscher, K. Faber* 833–840

Enantiocomplementary Chemoenzymatic Asymmetric Synthesis of (*R*)- and (*S*)-Chromanemethanol

Keywords: Vitamins / Tocopherol / Biocatalysis / Enantioselectivity / Asymmetric synthesis / Enzymes / Chiral resolution



Both enantiomers of chromanemethanol have been synthesised in >99% *ee* by a chemoenzymatic protocol based on the biocatalytic resolution of a *rac*-oxirane catalysed by an epoxide hydrolase and a halohydrin dehalogenase that display opposite enantiopreferences.

Chiral Recognition

G.-Y. Qing,* T.-L. Sun, F. Wang, Y.-B. He, X. Yang 841–849

Chromogenic Chemosensors for *N*-Acetylaspartate Based on Chiral Ferrocene-Bearing Thiourea Derivatives

Keywords: Receptors / Sensors / Chiral anion detection / Ferrocene / Chromogenic receptor / Enantioselectivity / Thiourea

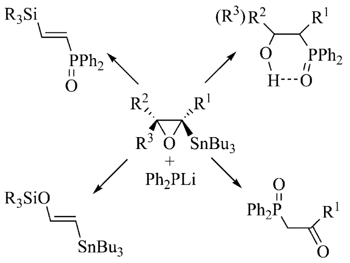
Chiral ferrocene-containing thiourea derivatives **5a** and **6a** exhibit excellent chiral recognition abilities towards *N*-acetylaspartate. The differences in solution colour can be observed by the naked eye.

Stannyloxirane Ring-Opening

A. M. González-Nogal,* P. Cuadrado, M. A. Sarmentero 850–859

Regio- and Stereospecific Cleavage of Stannyloxiranes with Lithium Diphenylphosphide

Keywords: Stannanes / Cleavage reactions / Phosphorylation / Phosphane oxides / Silyl enol ethers



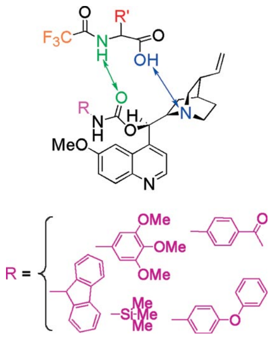
Versatile small synthons of great interest in organic chemistry are obtained from regio- and stereospecific cleavage reactions of stannyl- and silyl-stannyloxiranes with lithium diphenylphosphide. The factors governing α- or β-opening are also discussed.

Quinine Carbamates

G. Uccello-Barretta,* L. Vanni, F. Balzano 860–869

NMR Enantiodiscrimination Phenomena by Quinine C^9-Carbamates

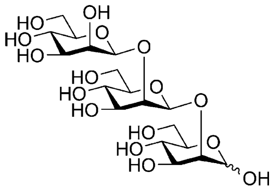
Keywords: Chirality / Chiral recognition / Chiral auxiliaries / Enantiomeric purity / NMR spectroscopy



The molecular basis of enantiodiscrimination phenomena by C^9-carbamates of quinine has been determined by NMR spectroscopy.

Linked Oligomannosides

The stereoselective synthesis and complete NMR spectroscopic characterization of several β-(1→2)-linked oligomannosides, including fully deprotected mannobiose and mannotriose and with additional modifications to the oligosaccharide core, is described.



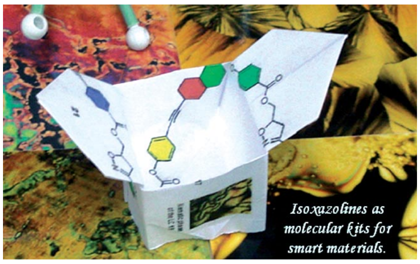
M. Poláková, M. U. Roslund, F. S. Ekholm, T. Saloranta, R. Leino* 870–888

Synthesis of β-(1→2)-Linked Oligomannosides

Keywords: Carbohydrates / Asymmetric synthesis / Glycosylation / Oligosaccharides / NMR spectroscopy

Liquid Crystals

Convenient and practical routes to the synthesis of molecular kits for liquid-crystalline materials based on isoxazolines are described. The synthetic procedure features a 1,3-dipolar [3+2] cycloaddition and a Sonogashira coupling reaction. The final compounds display nematic and smectic liquid-crystalline properties.



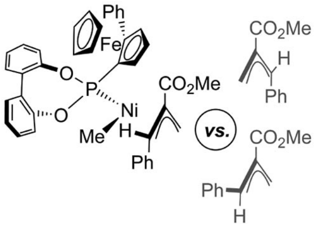
A. Tavares, P. H. Schneider, A. A. Merlo* 889–897

3,5-Disubstituted Isoxazolines as Potential Molecular Kits for Liquid-Crystalline Materials

Keywords: Heterocycles / Cycloaddition / Coupling reactions / Liquid crystals

Nickel-π-Allyls

DFT calculation of the relative energies of the putative non exchanging π-allyl complexes in Ni-Ferrophite-catalysed $AlMe_3$ addition to substituted allylic halides correlates with the observed stereochemical outcome.

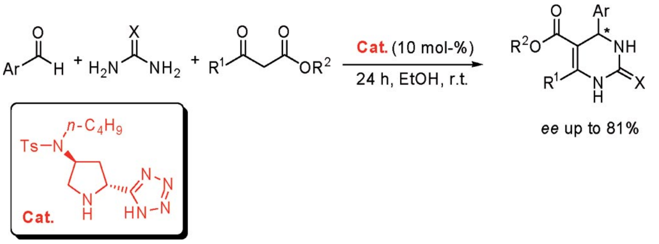


A. Novak, M. J. Calhorda, P. J. Costa, S. Woodward* 898–903

Mapping the Mechanism of Nickel-Ferrophite Catalysed Methylation of Baylis–Hillman-Derived S_N2' Electrophiles

Keywords: Nickel / Aluminum / P ligands / Asymmetric catalysis / Alkylation / Density functional calculations

Organocatalysis



A series of chiral substituted 5-(pyrrolidin-2-yl)tetrazoles have been synthesized and evaluated as organocatalysts for the asymmetric Biginelli reaction to provide 3,4-dihydropyrimidin-2(1*H*)-one (DHPM) derivatives in good yields and moderate enantioselectivities.

Y.-Y. Wu, Z. Chai, X.-Y. Liu, G. Zhao,* S.-W. Wang* 904–911

Synthesis of Substituted 5-(Pyrrolidin-2-yl)tetrazoles and Their Application in the Asymmetric Biginelli Reaction

Keywords: Enantioselectivity / Asymmetric catalysis / Organocatalysis / Biginelli reaction / Tetrazoles

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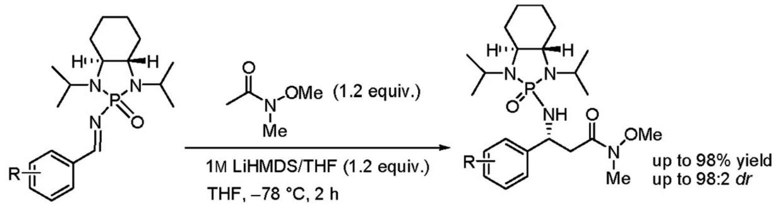
Chiral *N*-Phosphonyl Imines

P. Kaur, T. Nguyen, G. Li 912–916

Chiral *N*-Phosphonylimine Chemistry: Asymmetric Synthesis of *N*-Phosphonyl β-Amino Weinreb Amides

Keywords: Asymmetric synthesis / Phosphorus / Amides / Chiral auxiliaries



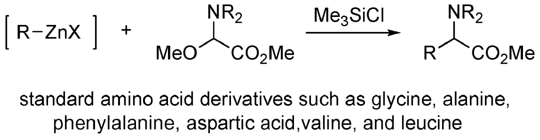
Weinreb amide derived lithium enolate (lithium enolate of *N*-methoxy-*N*-methylacetamide) was found to react with chiral *N*-phosphonyl imines to give chiral *N*-phosphonyl β-amino Weinreb amides in excellent diastereoselectivity (up to *dr* = 99:1) and chemical yields (92 to 98%).

Amino Acid Synthesis

N. Sakai,* J. Asano, Y. Kawada, T. Konakahara 917–922

Facile Approach to Natural or Non-Natural Amino Acid Derivatives: Me_3SiCl-Promoted Coupling Reaction of Organozinc Compounds with N,O-Acetals

Keywords: Amino acids / Acetals / Zinc / Arylation / Alkylation



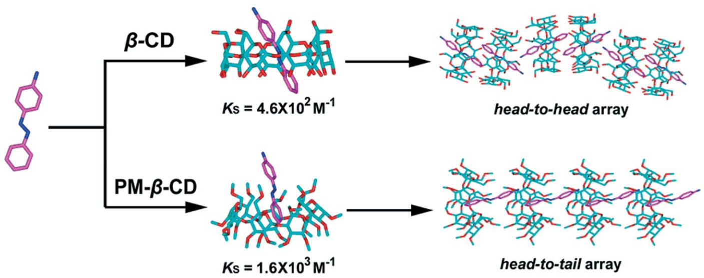
Described herein is a Me_3SiCl-promoted coupling reaction of organozinc compounds with N,O-acetals as a glycine cation equivalent, which led to the preparation of a variety of standard amino acid derivatives, such as glycine, alanine, phenylalanine, aspartic acid, valine, and leucine.

Supramolecular Chemistry

J. Shi, D.-S. Guo, F. Ding, Y. Liu* 923–931

Unique Regioselective Binding of Permethylated β-Cyclodextrin with Azobenzene Derivatives

Keywords: Host–guest systems / Cyclodextrins / Inclusion compounds / Thermodynamics



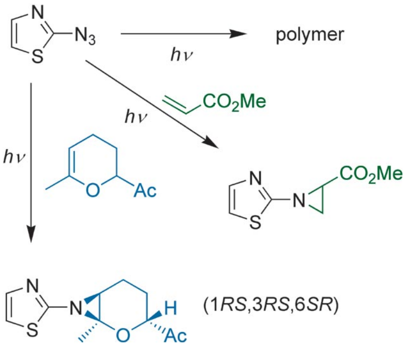
The complexation of permethylated β-cyclodextrin (PM-β-CD) with 4-hydroxyazobenzene and 4-aminoazobenzene presents not only different binding geometries with azobenzene guests but also different spatial arrangements. Furthermore, the binding abilities and thermodynamics of β-cyclodextrin and PM-β-CD upon complexation with azobenzene derivatives were discussed.

Photochemistry of Thiazoles

M. D'Auria, R. Racioppi,* L. Viggiani, P. Zanirato 932–937

Photochemical Reactivity of 2-Azido-1,3-thiazole and 2-Azido-1,3-benzothiazole: A Procedure for the Aziridination of Enol Ethers

Keywords: Photochemistry / Sulfur heterocycles / Nitrogen heterocycles / Enols



Photolysis of 2-azido-1,3-thiazole and 2-azido-1,3-benzothiazole, which give rise to intermediate nitrenes, are studied. In the first case, the reaction is valuable for the aziridination of double bonds of methyl acrylate and various enol ethers.

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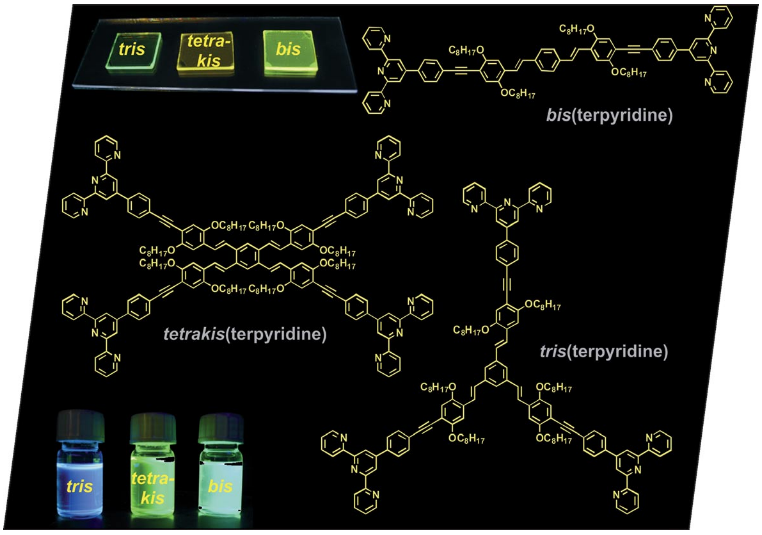
A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

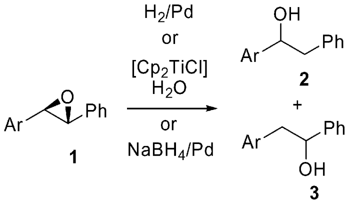
COVER PICTURE

The cover picture shows the bright photoluminescence properties of oligo(terpyridine) derivatives in dilute solution and in thin solid films. The photophysical properties of the materials depend on the number of π-conjugated terpyridine moieties attached to the central phenyl core as well as on the substitution pattern. Details are discussed in the article by U. S. Schubert et al. on p. 801ff.



Epoxide Ring-Opening

Non-symmetrical *trans*-2,3-diaryloxiranes have been regioselectively opened by catalytic hydrogenation over Pd/C, $NaBH_4$/Pd and $[Cp_2TiCl]/H_2O$. The mechanism of the ring-opening reaction was dependent on the ring-opening reaction was dependent on the hydrogenation system applied. Starting from enantioenriched epoxides, no loss of optical purity was observed in the alcohols formed.



N. Di Blasio, M. T. Lopardo, P. Lupattelli* .... **938−944**

1,2-Diarylethanols by Alternative Regioselective Reductive Ring-Opening of 2,3-Diaryloxiranes

Keywords: Epoxides / Ring-opening reactions / Reduction / Alcohols / Enantioselectivity / Regioselectivity

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* Author to whom correspondence should be addressed.

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