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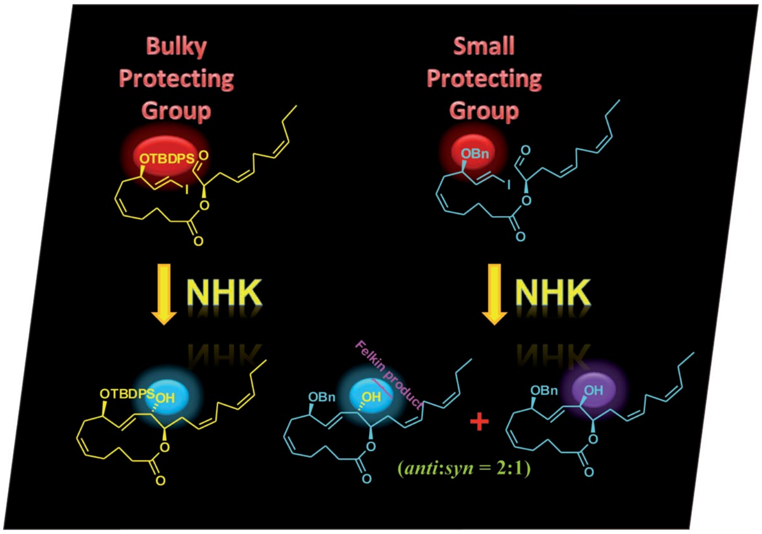
COVER PICTURE

The cover picture shows how a bulky protecting group directs the intramolecular Nozaki–Hiyama–Kishi reaction to afford exclusively one stereoisomer, whereas a small protecting group directs the reaction to afford both *anti* and *syn* isomers in a 2:1 ratio. Details are discussed in the article by D. K. Mohapatra, J. S. Yadav et al. on p. 4775ff.



CONTENTS

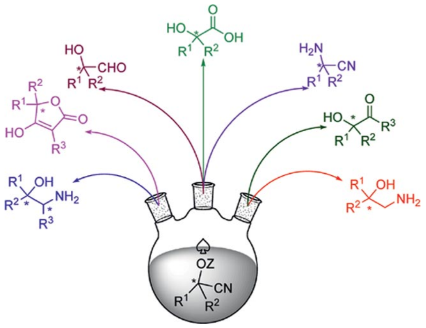
MICROREVIEW

Chiral Cyanohydrins

W. Wang, X. Liu, L. Lin,
X. Feng* 4751–4769

Recent Progress in the Chemically Catalyzed Enantioselective Synthesis of Cyanohydrins

Keywords: Asymmetric catalysis / Cyanides / Aldehydes / Ketones / Cyanohydrins / Enantioselectivity



The catalytic enantioselective cyanation of carbonyl compounds has received growing attention because the resulting enantiomerically pure cyanohydrins can serve as the linchpin for further manipulations. This microreview provides an overview of the current state and our own efforts in the field.

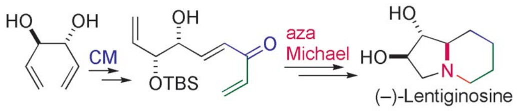
SHORT COMMUNICATION

Natural Product Synthesis

S.-W. Liu, H.-C. Hsu, C.-H. Chang,
H.-H. G. Tsai, D.-R. Hou* 4771–4773

Asymmetric Synthesis of (−)-Lentiginosine by Double Aza-Michael Reaction

Keywords: Aza-Michael reaction / Alkaloids / Asymmetric synthesis / Metathesis



(−)-Lentiginosine was synthesized by diastereoselective double aza-Michael reaction of the key trienone with benzylamine to yield the corresponding 4-oxopiperidine, which was converted into the indolizidine after ozonolysis and reductive amination.

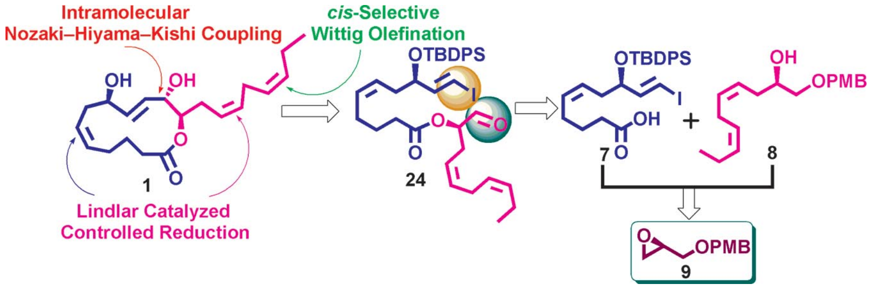
FULL PAPERS

Asymmetric Total Synthesis

D. K. Mohapatra,* P. P. Das,
M. R. Pattanayak, G. Gayatri,
G. N. Sastry, J. S. Yadav* 4775–4784

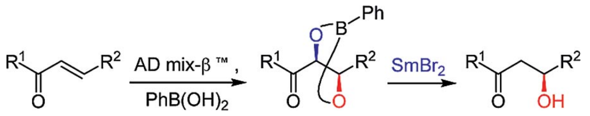
Protecting-Group Directed Stereoselective Intramolecular Nozaki–Hiyama–Kishi Reaction: A Concise and Efficient Total Synthesis of Amphidinolactone A

Keywords: Cytotoxicity / Kinetic resolution / Olefination / Macrocycles / Lactones



A convergent total synthesis of amphidinolactone A was achieved in an overall yield of 22%. The longest linear synthetic sequence involved 13 steps. A stereoselective intramolecular Nozaki–Hiyama–Kishi reaction was used for the construction of the 13-membered lactone ring as the key step.

Dihydroxylation/Monodehydroxylation



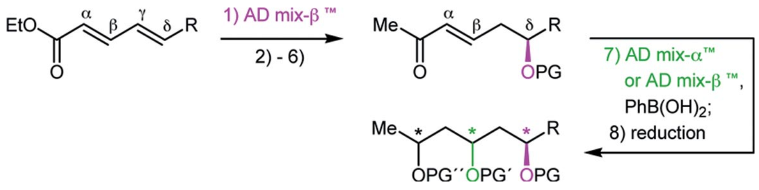
α,β-Unsaturated ketones were subjected to the Muñiz variation of Sharpless' AD mix-β™ procedure. The resulting α,β-dihydroxy ketone phenylboronates (≥97% *ee*) were reduced with Sm^{II} bromide in THF/MeOH. This furnished β-hydroxy ketones at −78 °C and 1,3-diol phenylboronates (58–100% *trans*) at 0 °C.

A. Zörb, R. Brückner* **4785–4801**

Conversion of Conjugated Enones into Enantiomerically Pure β-Hydroxy Ketones or 1,3-Diols – Samarium(II) Bromide Reductions of Protected α,β-Dihydroxy Ketones

Keywords: Asymmetric dihydroxylation / Defunctionalization / Diastereoselectivity / Reduction / Samarium reagents

Dihydroxylation/Monodehydroxylation



Asymmetric dihydroxylation (AD) of conjugated dienoates, carbonate formation, Pd-catalyzed C^{γ}–O bond cleavage, and etherification furnished δ-hydroxy enoates. Conversion into the corresponding ketones and AD under Muñiz conditions gave *B*-ethylboronates. Reduction of the C^{α}–O bond with Sm^{II} gave protected β,δ-dihydroxy ketones, which were elaborated to the four diastereomeric 1,3,5-triol derivatives.

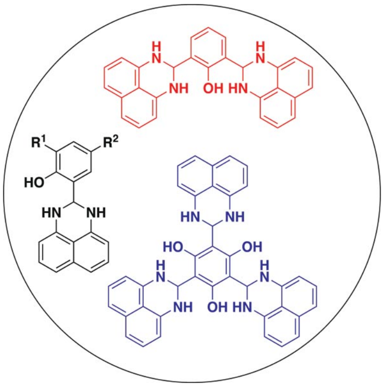
P. Walleser, R. Brückner* **4802–4822**

Stereocontrolled Synthesis of 1,3,5-Triols by an Iteration of Asymmetric Dihydroxylation and Deoxygenation

Keywords: Asymmetric dihydroxylation / Asymmetric synthesis / Deoxygenation / Diastereoselectivity / Samarium reagents / Skipped polyols

Heterocyclic Chemistry

We report on a versatile and generally high yielding preparation method for 2-aryl-substituted 2,3-dihydro-1*H*-perimidines derived from a 1,8-diaminonaphthalene scaffold. The method involves salicylaldehydes as reagents with various functional groups that allow for post-modification. The method proved also to be successful for various multi-perimidinal structures.

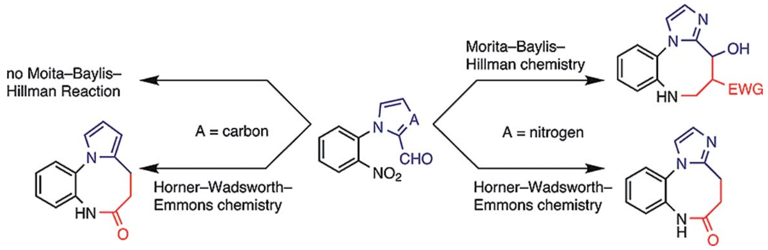


M. M. Belmonte, E. C. Escudero-Adán, J. Benet-Buchholz, R. M. Haak, A. W. Kleij* **4823–4831**

Facile Synthesis of Substituted Mono-, Di-, Tri- and Tetra-2-aryl-2,3-dihydro-1*H*-perimidines

Keywords: Nitrogen heterocycles / Perimidines / Zinc catalysis

Heterocyclic Chemistry



Expeditious strategies for obtaining fused benzodiazocines and fused benzodiazocinones via Morita–Baylis–Hillman and Horner–Wadsworth–Emmons reactions, respectively, have been developed.

A. Mishra, S. Batra* **4832–4840**

Expeditious Synthesis of Imidazole- and Pyrrole-Fused Benzodiazocines

Keywords: Nitrogen heterocycles / Reductive cyclization

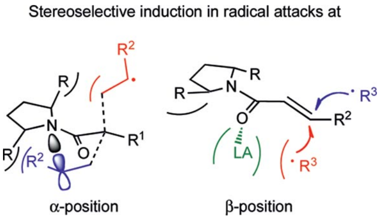
CONTENTS

Asymmetric Radical Reactions

M. K. Georgieva, F. J. S. Duarte, S. M. Bakalova, A. G. Santos* **4841–4850**

2,5-Disubstituted Pyrrolidines as Chiral Auxiliaries in Radical Reactions: A Theoretical Approach

Keywords: Radical reactions / Chiral auxiliaries / Transition states / Ab initio calculations / Lewis acid catalysis



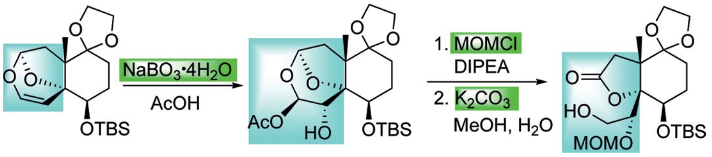
Radical additions to amides with stereocontrol by C_2-symmetric chiral auxiliaries have been studied by theoretical methods, and the factors that affect the selectivity of the additions at the α and β-positions have been clarified. Rationalized structural modifications as well as the use of achiral Lewis acids are proposed to maximize the selectivity of addition.

Stereodefined Ring Systems

Z. Elkhayat, I. Safir, Z. Gandara, P. Retailleau, S. Arseniyadis* ... **4851–4860**

Efficient Construction of Highly Substituted and Stereodefined *cis*-Fused Lactones

Keywords: Epoxidation / Domino reactions / Lactones / Terpenoids / Fused-ring systems



A serial epoxidation/ring-opening sequence sets the stage for an intramolecular Cannizzaro-type oxidoreduction, which leads to stereodefined bis-angularly substituted fused lactones.

3-Benzazepines

V. A. Peshkov, O. P. Pereshivko, P. A. Donets, V. P. Mehta, E. V. Van der Eycken* **4861–4867**

Diversity-Oriented Microwave-Assisted Synthesis of the 3-Benzazepine Framework

Keywords: C-C coupling / Cyclization / Nitrogen heterocycles / Medium-ring compounds / Microwave chemistry

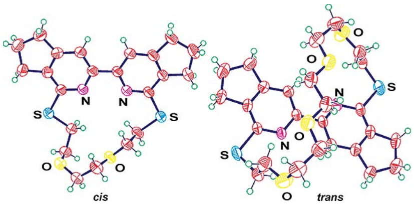
An efficient microwave-assisted protocol for the diversity-oriented two-step synthesis of 3-benzazepines is described.

Biheterocycles Synthesis

J. Ławecka, Z. Karczmarzyk, E. Wolińska, D. Branowska, A. Rykowski* ... **4868–4875**

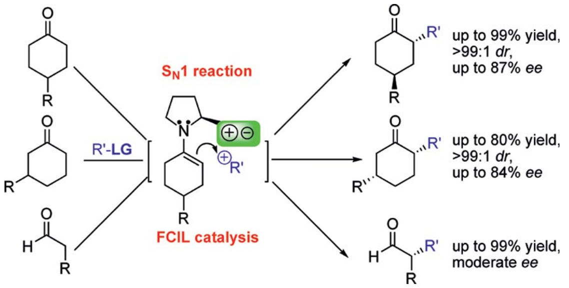
A Convenient Approach to 16-, 19-, and 22-Membered 2,2′-Bipyridine Thiacrown Ethers and Their Conformation Preferences

Keywords: Heterocycles / Cycloaddition / Crown compounds / Structure elucidation / Conformation analysis



Homocoupling of 1,2,4-triazines bisulfides followed by Diels–Alder reaction of the resulting macrocycles with an enamine furnishes annulated 2,2′-bipyridine thiacrown ethers and their corresponding chiral sulfoxides. Their conformation preferences were established by X-ray crystallography and DFT calculations.

Chiral Ionic Liquids



Functionalized chiral ionic liquids were used as catalysts for S$_N$1 α-alkylation of ketones and aldehydes; up to 99% yield, >99:1 *dr* and 87% *ee* were obtained. An efficient desymmetric procedure for 4-substituted cyclohexanones and a kinetic resolution procedure for 3-substituted cyclohexanones were developed.

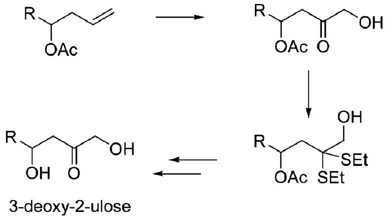
L. Zhang, L. Cui, X. Li, J. Li, S. Luo,*
J.-P. Cheng 4876–4885

Functionalized Chiral Ionic Liquid Catalyzed Asymmetric S$_N$1 α-Alkylation of Ketones and Aldehydes

Keywords: Ionic liquids / Asymmetric catalysis / Alkylation / Carbocations / Nucleophilic substitution

Rare Carbohydrates

The oxidation of terminal olefins derived from chain-elongated carbohydrates with potassium permanganate offers direct access to the structural motif of the 3-deoxy-2-uloses in good yields and selectivities.



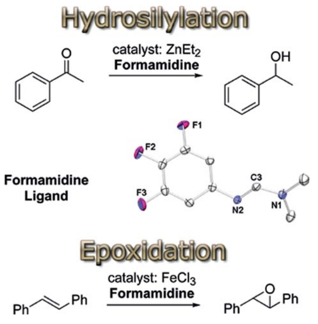
C. Schmölzer, M. Fischer,
W. Schmid* 4886–4892

Permanganate Oxidation Revisited: Synthesis of 3-Deoxy-2-uloses via Indium-Mediated Chain Elongation of Carbohydrates

Keywords: Carbohydrates / Allylation / Oxidation / Indium / Thioketals

Zinc and Iron Catalysis

Versatility of formamidines: In the present study the great abilities of formamidines ligands in reduction as well as oxidation chemistry by means the zinc-catalyzed hydrosilylation of carbonyl compounds and the iron-catalyzed epoxidation of C–C double bonds are figured out.

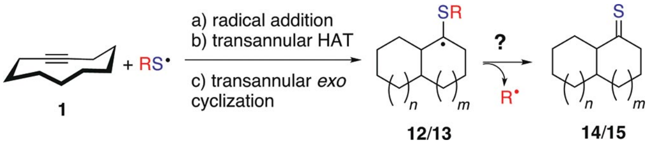


S. Enthaler,* K. Schröder, S. Inoue,
B. Eckhardt, K. Junge, M. Beller,
M. Drieß 4893–4901

Formamidines – Versatile Ligands for Zinc-Catalyzed Hydrosilylation and Iron-Catalyzed Epoxidation Reactions

Keywords: Homogeneous catalysis / Zinc / Iron / Amidine ligands / Hydrosilylation / Epoxidation

Radical Cyclizations



The performance of thiyl radicals RS• in “self-terminating radical cyclisations” was explored. Using the medium-sized cyclodecyne (**1**) as model system, the reactions with PhS•, BnS•, *t*BuS• and AllylS•, respectively, were studied using experimental and computational techniques.

K. J. Tan, J. M. White,
U. Wille* 4902–4911

Self-Terminating Radical Cyclizations: How Are Thiyl Radicals Performing?

Keywords: Radicals / Radical cyclizations / Thiyl radicals / Alkynes / Computational chemistry / Reaction mechanisms

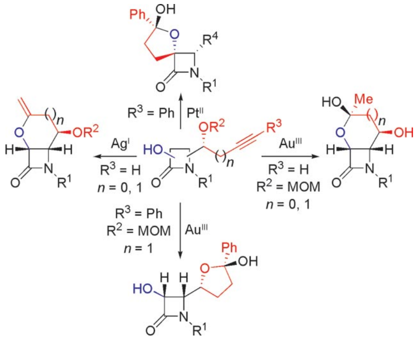
CONTENTS

Alkynol Cyclizations

B. Alcaide,* P. Almendros,*
T. Martínez del Campo,
R. Carrascosa 4912–4919

💻 Metal-Catalyzed Cycloisomerization and Tandem Oxycyclization/Hydroxylation of Alkynols: Synthesis of Nonfused, Spiranic and Fused Oxabicyclic β-Lactams

Keywords: Alkynes / Cyclization / Gold / Lactams / Platinum



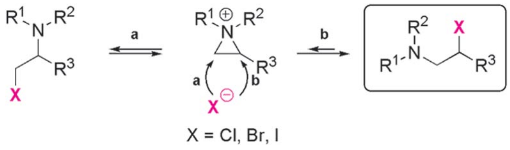
A variety of diversely functionalized nonfused, spiranic and fused oxabicyclic β-lactams can be prepared in good yield through precious metal catalyzed cycloisomerization and tandem oxycyclization/hydroxylation of alkynols. Silver exclusively affords cycloisomerization products, whereas the presence of a catalytic amount of platinum or gold salts favors the formation of tandem oxycyclization/hydroxylation adducts.

Aziridinium Chemistry

M. D'hooghe, S. Catak, S. Stanković,
M. Waroquier, Y. Kim, H.-J. Ha,*
V. Van Speybroeck,*
N. De Kimpe* 4920–4931

💻 Systematic Study of Halide-Induced Ring Opening of 2-Substituted Aziridinium Salts and Theoretical Rationalization of the Reaction Pathways

Keywords: Nitrogen heterocycles / Aziridines / Halides / Regioselectivity / Reaction mechanisms / Density functional calculations



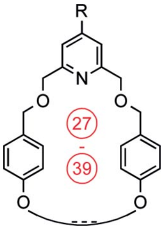
The ring opening of 2-alkyl-substituted aziridinium salts with chloride, bromide and iodide proceeds under thermodynamic control with product stabilities dictating the outcome of the reactions. Fluoride-mediated ring opening, however, proceeds under kinetic control, the reaction outcome being dictated only by steric interactions.

Macrocycles

U. Lüning,* E. Mak, M. Zindler,
B. Hartkopf, R. Herges 4932–4940

27- to 39-Membered Pyridine Macrocycles

Keywords: Combinatorial chemistry / Macrocycles / Metathesis / Nitrogen heterocycles



A set of 27- to 39-membered pyridine macrocycles has been synthesized by Williamson ether synthesis or ring-closing metathesis. In addition to the length, also the nature of the aliphatic chain were varied: saturated and unsaturated.

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* Author to whom correspondence should be addressed.

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