



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

K. Tedsree, A. T. Kong, S. C. Tsang*

Formate as a Surface Probe for Ru Nanoparticles in Liquid ^{13}C NMR Spectroscopy

A. Asati, S. Santra, C. Kaittanis, S. Nath, J. M. Perez*

Oxidase Activity of Polymer-Coated Cerium Oxide Nanoparticles

K. M. Gericke, D. I. Chai, N. Bieler, M. Lautens*

The Norbornene Shuttle: Multicomponent Domino Synthesis of Tetrasubstituted Helical Alkenes through Multiple C–H Functionalization

J.-Q. Wang, S. Stegmaier, T. F. Fässler*

$[\text{Co}@\text{Ge}_{10}]^{3-}$: An Intermetallic Cluster with an Archimedean Pentagonal Prismatic Structure

Author Profile

Rustem F. Ismagilov

637

Books

Arrow Pushing in Organic Chemistry

Daniel E. Levy

reviewed by S. A. Snyder — 640

Acid Catalysis in Modern Organic Synthesis

Hisashi Yamamoto, Kazuaki Ishihara

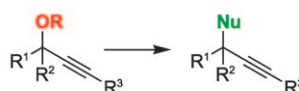
reviewed by D. F. Fischer, R. Peters — 640

Highlights

Catalytic Propargylation

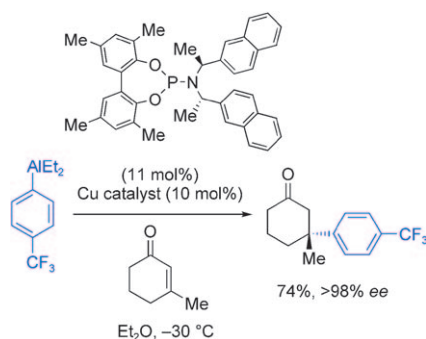
N. Ljungdahl, N. Kann* — 642–644

Transition-Metal-Catalyzed Propargylic Substitution



Keen for a share in the glory: Until recently, the title reaction stood in the shadows, its famous sister, catalytic allylic substitution, in the limelight. Catalytic propargylic substitution has now emerged as an efficient transformation that can be

catalyzed by a variety of transition metals (see picture). Among the recent developments are copper-catalyzed asymmetric propargylic amination reactions. Nu = nucleophile



Choosing the right metal for the job: A broad range of asymmetric conjugate addition reactions are catalyzed efficiently by copper complexes, provided the appropriate organometallic reagent is used. With aluminum reagents, for example, quaternary stereogenic centers with functionalized aryl substituents can be generated with high enantioselectivity (see scheme).

Conjugate Addition

T. Thaler, P. Knochel* — 645–648

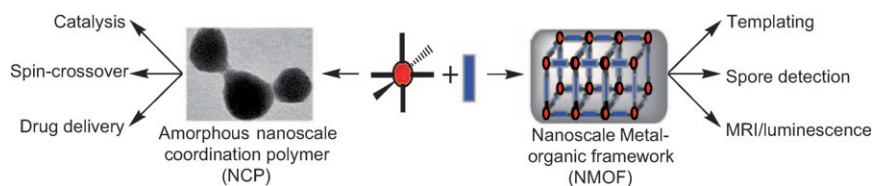
Copper-Catalyzed Asymmetric Michael Addition of Magnesium, Zinc, and Aluminum Organometallic Reagents: Efficient Synthesis of Chiral Molecules

Minireviews

Coordination Polymers

W. Lin,* W. J. Rieter,
K. M. L. Taylor — 650–658

Modular Synthesis of Functional
Nanoscale Coordination Polymers



Next-generation nanomaterials: The coordination-directed assembly of metal ions and organic bridging ligands has afforded bulk-scale functional hybrid materials. Their scaling-down to the nano-regime has led to nanoscale coordination

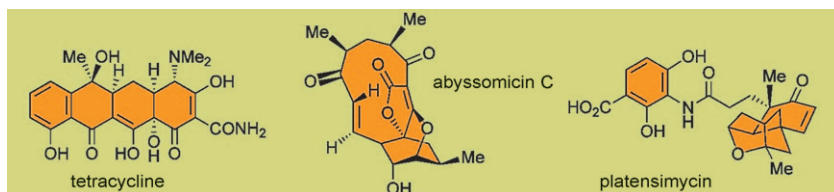
polymers and metal–organic frameworks which have been used in a broad range of applications including catalysis, spin-crossover, templating, biosensing, bio-medical imaging, and anticancer drug delivery.

Reviews

Natural Products

K. C. Nicolaou,* J. S. Chen,
D. J. Edmonds, A. A. Estrada — 660–719

Recent Advances in the Chemistry and
Biology of Naturally Occurring Antibiotics



Exciting developments in the area of antibiotics are discussed in this stimulating review article as the authors present highlights of research carried out since the year 2000, emphasizing the pivotal

role that total synthesis plays in moving the field forward and into new possibilities of drug design. The three compounds are shown as an illustration of the structural diversity of antibiotics.

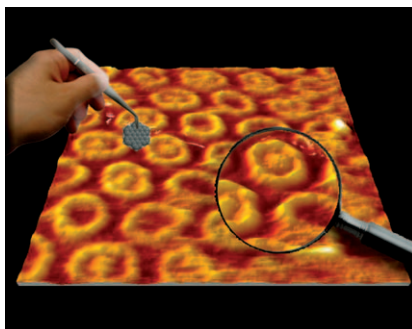
Communications

Host–Guest Systems

B. Schmaltz, A. Rouhanipour, H. J. Räder,
W. Pisula, K. Müllen* — 720–724



Filling the Cavity of Conjugated Carbazole
Macrocycles with Graphene Molecules:
Monolayers Formed by Physisorption
Serve as a Surface for Pulsed Laser
Deposition



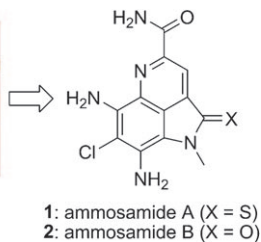
Finding the middle ground: A 1:1 host–guest complex consisting of a hexa-*peri*-hexabenzocoronene molecule sitting in the middle of the free cavity of a giant π -conjugated carbazole macrocycle has been obtained (see STM image). The complex has been prepared by physisorption of a monolayer of macrocycles followed by gas-phase deposition of graphene molecules by pulsed laser deposition.

For the USA and Canada:

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national chemical society prices are available
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From the ocean: Ammosamides A (**1**) and B (**2**) were isolated from a marine-derived *Streptomyces* species collected in the Bahamas. The structures of these chlorinated tricyclic pyrroloquinoline alkaloids were solved using X-ray crystallographic techniques. Ammosamide A (**1**) was shown to contain an unusual thio- γ -lactam ring. Both metabolites show specific nanomolar cytotoxicity against selected cancer cell lines.

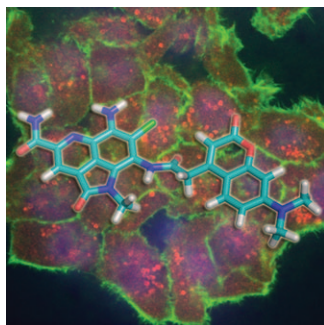
Ammosamides, Biological Chemistry

C. C. Hughes, J. B. MacMillan, S. P. Gaudêncio, P. R. Jensen, W. Fenical* — 725–727

The Ammosamides: Structures of Cell Cycle Modulators from a Marine-Derived *Streptomyces* Species



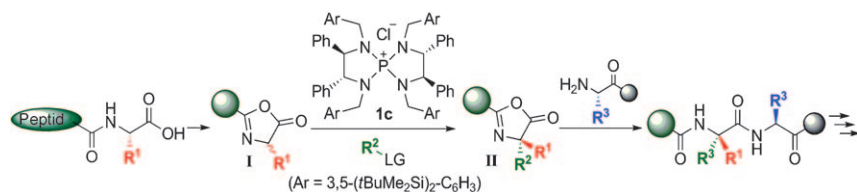
The protein target of the ammosamides, cytotoxic natural products from a marine-derived actinomycete, has been elucidated. An immunoaffinity fluorescent tag was used to construct a fluorescent molecular probe (see structure). First, uptake and localization of the probe in cells was visualized with fluorescence microscopy. The probe was then used to co-immunoprecipitate proteins that bound to the ammosamide core. Myosin was thus identified as a target.



Ammosamides, Chemical Biology

C. C. Hughes, J. B. MacMillan, S. P. Gaudêncio, W. Fenical,* J. J. La Clair* — 728–732

Ammosamides A and B Target Myosin



Dual-purpose activation: Peptide C-terminal azlactones **I** undergo stereoselective alkylation with high efficiency by the use of a newly devised chiral tetraamino-phosphonium salt as a phase-transfer catalyst, and the alkylated azlactone

products **II** can be employed directly for peptide ligation (see scheme, LG = leaving group). In this way, a wide range of chiral quaternary α -amino acid residues can be incorporated at specific sites of a peptide strand.

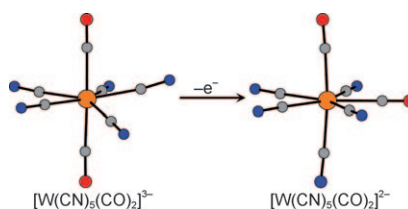
Peptide Modification

D. Uruguchi, Y. Asai, T. Ooi* — 733–737

Site-Directed Asymmetric Quaternization of a Peptide Backbone at a C-Terminal Azlactone



Mixed company: The use of a mixed carbonyl/cyanide ligand set enables stabilization of two new heptacoordinate complexes: $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ and $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$. In the trianionic complex the two carbonyl ligands occupy the axial positions. Remarkably, one-electron oxidation causes loss of this axial symmetry, as shown by X-ray crystallography (see picture, orange W, gray C, blue N, red O), IR, and EPR spectroscopy.



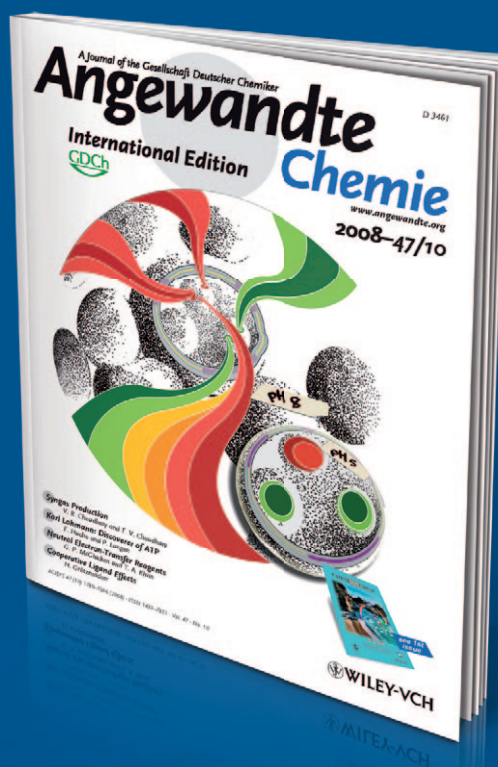
Isomerization

H. I. Karunadasa, J. R. Long* — 738–741

Synthesis and Redox-Induced Structural Isomerization of the Pentagonal Bipyramidal Complexes $[\text{W}(\text{CN})_5(\text{CO})_2]^{3-}$ and $[\text{W}(\text{CN})_5(\text{CO})_2]^{2-}$



Incredibly inexpensive.



Do chemistry journals really cost so much? Perhaps some do, but certainly not *Angewandte Chemie*! In 2008, an entire institution could subscribe through Wiley InterScience* for 5000 € and get access to 52 issues with over 1600 articles and all associated online search options, and for just 5 % more, the printed issues could be included as well. For full members of the German Chemical Society (GDCh), a personal subscription cost not much more than 300 €, and student GDCh members paid less than 150 €, which is just under 3 € per issue - a price that even compares with high-circulation newsstand publications!

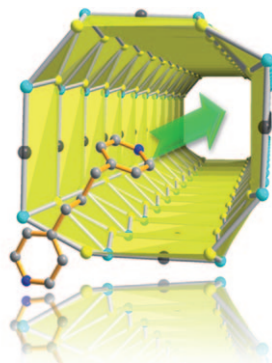
*www.interscience.wiley.com



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Glowing with pride: An activator-free gallium oxalatophosphite is a new class of color conversion phosphors for NUV and blue light-emitting diodes. It is synthesized by using an organic template and an environmentally friendly eutectic solvent in a reaction that shows efficient atom economy. The resulting material has a tubular structure (see picture) and intriguing luminescence properties.

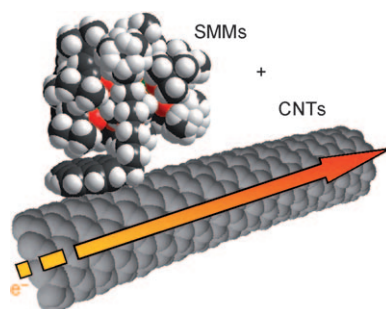
Luminescent Metal Phosphites

P. C. Jhang, Y. C. Yang, Y. C. Lai, W. R. Liu, S. L. Wang* — 742–745

A Fully Integrated Nanotubular Yellow-Green Phosphor from an Environmentally Friendly Eutectic Solvent



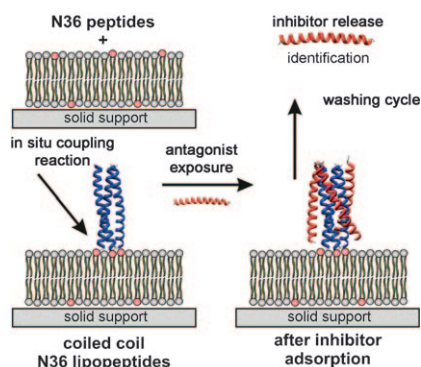
Devices and desires: The self-assembly of single-molecule-magnet (SMM) carbon-nanotube (CNT) hybrids (see picture) in conditions compatible to the creation of electronic devices is described. The process is controlled at the single-molecule level, and the resulting CNT–field-effect transistors display single-SMM sensitivity at room temperature.



Single-Molecule Studies

L. Bogani,* C. Danieli, E. Biavardi, N. Bendiab, A.-L. Barra, E. Dalcanele, W. Wernsdorfer, A. Cornia — 746–750

Single-Molecule-Magnet Carbon-Nanotube Hybrids



A sheep in wolf's clothes? Mimicking the crucial conformational step in viral fusion promises to be an efficient method to detect potential antagonists of retroviral infection (see scheme). Reconstituted lipopeptides derived from the N peptides of the class I virus fusion protein of SIV serve as receptors for potential inhibitors that function like the C peptides of the virus protein.

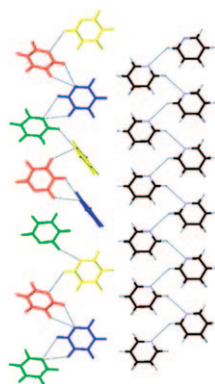
Lipopeptides

S. Schuy, E. Schäfer, N. C. Yoder, S. Hobe, K. Kumar, R. Vogel, A. Janshoff* — 751–754

Coiled-Coil Lipopeptides Mimicking the Prehairpin Intermediate of Glycoprotein gp41



Not so simple: It is normally assumed that deuteration has only a minor effect on the stabilities of crystal structures. This assumption is wrong for pyridine. A low-temperature polymorph exists for [D₃]pyridine, but not for [H₃]pyridine, which adds a further twist to the already unusual structural chemistry of one of the simplest and most familiar laboratory chemicals.



Low-Temperature Polymorphs

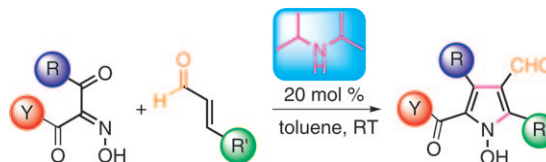
S. Crawford, M. T. Kirchner, D. Bläser, R. Boese,* W. I. F. David, A. Dawson, A. Gehrke, R. M. Ibberson, W. G. Marshall, S. Parsons,* O. Yamamuro — 755–757

Isotopic Polymorphism in Pyridine



Pyrrole Synthesis

B. Tan, Z. Shi, P. J. Chua, Y. Li,
G. Zhong* ————— **758–761**

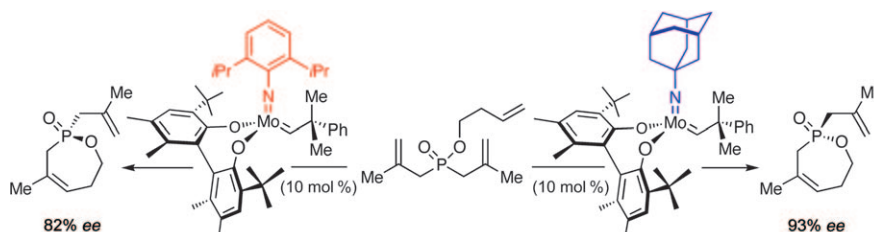


A facile synthesis of *N*-hydroxypyrroles has been developed using readily available α -carbonyl oximes and α,β -unsaturated aldehydes. The domino reaction

proceeds through iminium activation of α,β -unsaturated aldehydes, Michael addition using oximes as *N*-selective nucleophiles, and aldol condensation.

Enantioselective Catalysis

J. S. Harvey, S. J. Malcolmson,
K. S. Dunne, S. J. Meek, A. L. Thompson,
R. R. Schrock, A. H. Hoveyda,*
V. Gouverneur* ————— **762–766**

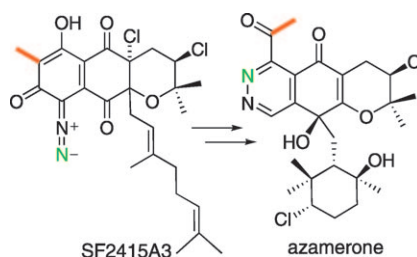


The first catalytic route toward the title compounds by asymmetric ring-closing metathesis is described. A remarkable reversal of enantioselectivity is observed when the achiral imido ligand of the chiral

molybdenum-catalyst is changed (see scheme), thus highlighting the importance of the achiral and the chiral ligands in catalyst design.

Natural Product Synthesis

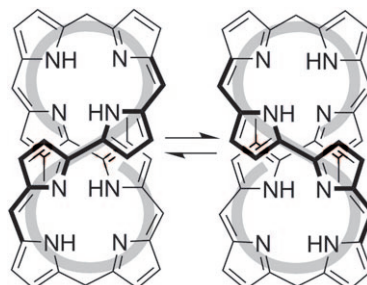
J. M. Winter, A. L. Jansma,
T. M. Handel, B. S. Moore* — **767–770**



All in the family: Knowledge of the biosynthesis of *N–N* containing natural products is limited. Feeding experiments with ^{13}C and ^{15}N -labeled molecules establish that the phthalazinone core of azamerone is derived from the diazo chlorinated meroterpenoid SF2415A3. A biosynthetic mechanism involving an oxidative rearrangement of the aryl diazoketone followed by rearomatization with the dinitrogen group is proposed.

Helical Porphyrinoids

J. Setsune,* A. Tsukajima,
N. Okazaki, J. M. Lintuluoto,
M. Lintuluoto ————— **771–775**



Fixed chirality: The treatment of cyclooctapyrroles (see picture) with a metal source with optically active carboxylate or amine ligands leads to enantioselective metalation to give stereochemically stable helical mononuclear and dinuclear complexes without a chiral auxiliary. The helicity of the dicopper complex was determined by the simulation of the CD spectrum on the basis of X-ray crystallographic data.



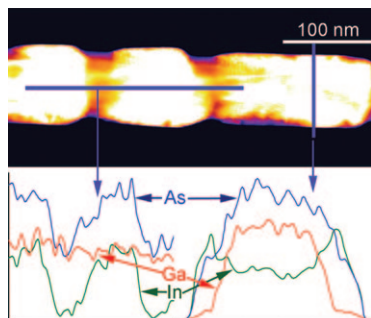
Hydrogen-bond activation by a diol promotes enantioselective Mukaiyama aldol reactions of acyl phosphonates. This mild and general method gives α -hydroxy

phosphonate products having two chiral centers, one tertiary and one quaternary, formed with high diastereo- and enantioselectivity.

Asymmetric Catalysis

V. B. Gondi, K. Hagihara,
V. H. Rawal* 776–779

Diastereoselective and Enantioselective
Synthesis of Tertiary α -Hydroxy
Phosphonates through Hydrogen-Bond
Catalysis

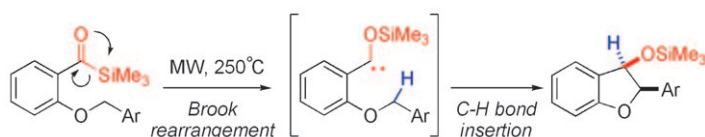


Rings around the wire: Novel hierarchical heterostructures, assembled by radial deposition of InAs on GaAs nanowires with nonplanar side walls, result in the formation of InAs nanorings. The mechanism of formation of such structures, determined by transmission electron microscopy, involves the preferential nucleation of InAs at concave regions of the GaAs surface by capillarity effects.

Nanostructures

M. Paladugu, J. Zou,* Y.-N. Guo,
X. Zhang, H. J. Joyce, Q. Gao, H. H. Tan,
C. Jagadish,* Y. Kim 780–783

Formation of Hierarchical InAs
Nanoring/GaAs Nanowire
Heterostructures



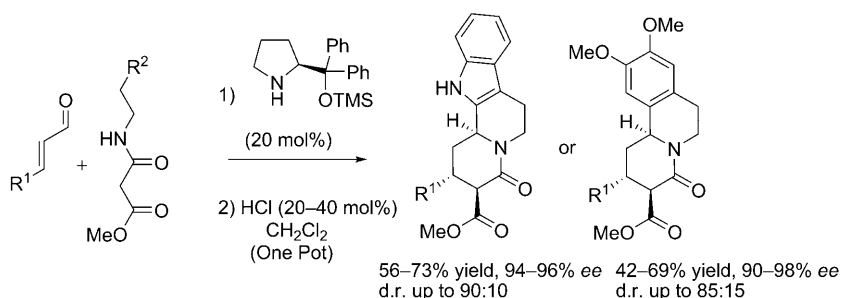
Instant carbenes—that's hot: The thermal 1,2-Brook rearrangement of acylsilanes generates siloxycarbene intermediates that can undergo intramolecular

C–H bond insertion to provide benzofuran derivatives. This metal-free tandem reaction occurs in less than 10 minutes in the microwave.

C–H Functionalization

Z. Shen, V. M. Dong* 784–786

Benzofurans Prepared by C–H Bond
Functionalization with Acylsilanes



One pot + two steps = three stereocenters: A short enantioselective synthesis to access the indolo[2,3-a]quinolizidine and the benzo[a]quinolizidine skeleton has been developed (see scheme; TMS = tri-

methylsilyl, R^1 = aromatic, R^2 = 3-indoyl or 3,4-dimethoxyphenyl). The sequence involves an organocatalytic conjugate addition and subsequent acid-catalyzed cyclization of the acyliminium ion.

Asymmetric Catalysis

J. Franzén,* A. Fisher 787–791

Asymmetric Alkaloid Synthesis: A One-
Pot Organocatalytic Reaction to
Quinolizidine Derivatives

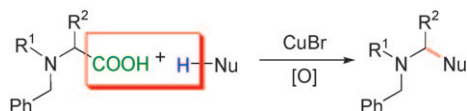


C–C Coupling

H.-P. Bi, L. Zhao, Y.-M. Liang,*
C.-J. Li* **792–795**



The Copper-Catalyzed Decarboxylative Coupling of the sp^3 -Hybridized Carbon Atoms of α -Amino Acids



Joined at the Cs: A novel intermolecular decarboxylative C_{sp^3} – C_{sp^3} , C_{sp^3} – C_{sp^2} , and C_{sp^2} – C_{sp} coupling catalyzed by CuBr and using α -amino acids as starting materials

has been developed (see scheme). Various functionalized nitrogen-containing compounds were obtained by this method.

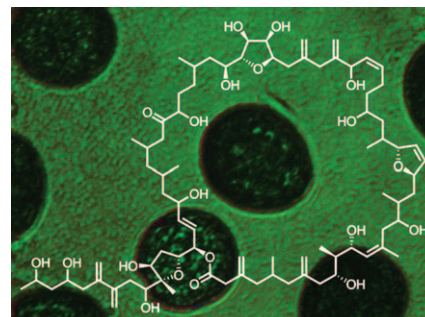
Structure Elucidation

J. G. Napolitano, M. Norte,*
J. M. Padrón, J. J. Fernández,*
A. Hernández Daranas* **796–799**



Belizeanolide, a Cytotoxic Macrolide from the Dinoflagellate *Prorocentrum belizeanum*

An exclusive club: The first member of an unprecedented class of polyunsaturated and polyhydroxylated macrocycle, belizeanolide (see structure), has been isolated from a marine dinoflagellate. The corresponding open form, belizeanolic acid, was also found. Their structures were determined primarily by analysis of NMR spectroscopic data. Both compounds showed significant antiproliferative activities.

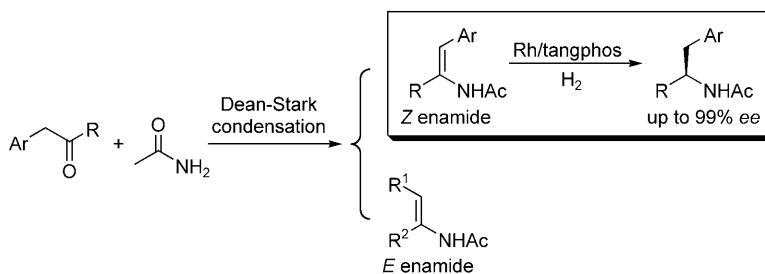


Asymmetric Catalysis

J. Chen, W. Zhang, H. Geng, W. Li, G. Hou,
A. Lei,* X. Zhang* **800–802**



Efficient Synthesis of Chiral β -Aryl-isopropylamines by Using Catalytic Asymmetric Hydrogenation



Direct condensation of β -arylketones with acetamide afforded both *Z* and *E* enamides. The *Z*-configured substrates underwent hydrogenation with excellent enantioselectivity by using the Rh/tang-

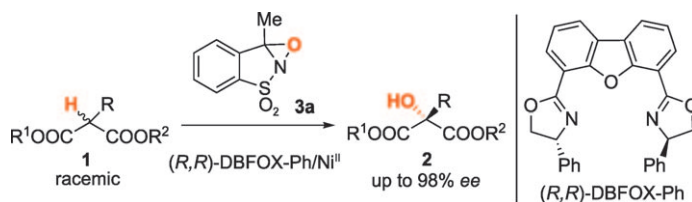
phos catalytic system (see scheme; tangphos = 1,1'-di-*tert*-butyl-[2,2']-diphospholanyl). The product β -arylisopropylamines are important precursors to several drugs.

Hydroxylation

D. S. Reddy, N. Shibata,* J. Nagai,
S. Nakamura, T. Toru **803–806**

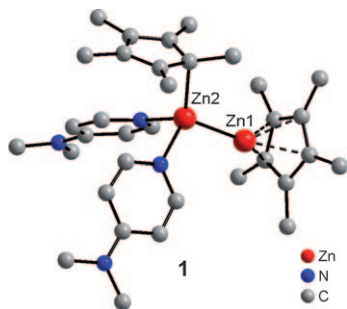


A Dynamic Kinetic Asymmetric Transformation in the α -Hydroxylation of Racemic Malonates and Its Application to Biologically Active Molecules



Sly like a “DBFOX”: The chiral α -hydroxy malonate **2** can be prepared in high yield and with up to 98 % *ee* from racemic malonate **1** through α -hydroxylation using oxaziridine **3** and is catalyzed by the (*R,R*)-

DBFOX-Ph/ Ni^{II} complex (see scheme). Biologically useful molecules have been prepared by using this method and illustrate its efficiency.



Reaction without Zn–Zn rupture:

$[\text{Cp}^*_2\text{Zn}_2]$ reacts with a fourfold excess of the strong Lewis base 4-dimethylaminopyridine (dmap) to unexpectedly form the Lewis acid–base adduct **1**, in which both dmap molecules coordinate in a geminal binding mode to only one zinc atom. $\text{Cp}^* = \text{C}_5\text{Me}_5$.

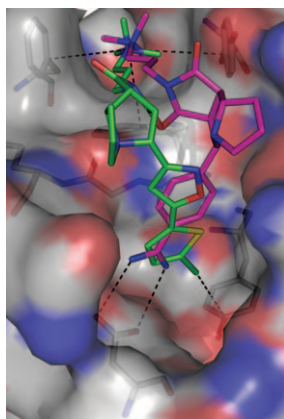
Low-Valent Lewis Acids

D. Schuchmann, U. Westphal, S. Schulz,*
U. Flörke, D. Bläser, R. Boese **807–810**

The Reaction of Dizincocene with
Preservation of the Zn–Zn Bond



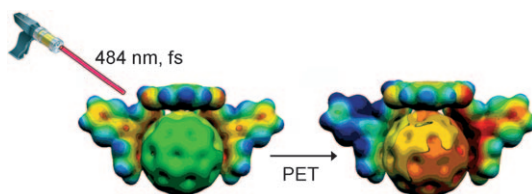
In pocket: A new class of potent inhibitors of factor Xa features a quaternary ammonium ion to fill the aromatic box in the S4 pocket and a 2-chlorothiophenyl group to occupy the S1 pocket (see picture; red O, blue N, yellow S, green Cl). Changing from a primary to a quaternary ammonium ion increases the binding affinity by a factor of 1000. The poor affinity in the former case suggests negligible cation– π interactions between Lys and Trp.



Enzyme Inhibitors

L. M. Salonen, C. Bucher, D. W. Banner,*
W. Haap, J.-L. Mary, J. Benz, O. Kuster,
P. Seiler, W. B. Schweizer,
F. Diederich* **811–814**

Cation– π Interactions at the Active Site of
Factor Xa: Dramatic Enhancement upon
Stepwise N-Alkylation of Ammonium Ions



On the ball: Charge transfer occurs readily in tightly interacting complexes formed from π -extended tetrathiafulvalenes, which act as pincerlike receptors, and C_{60} in a variety of solvents upon photoexcitation (see picture; PET = photoelectron transfer). It should be feasible to construct simple photovoltaic devices from systems based on similar recognition motifs.

tion (see picture; PET = photoelectron transfer). It should be feasible to construct simple photovoltaic devices from systems based on similar recognition motifs.

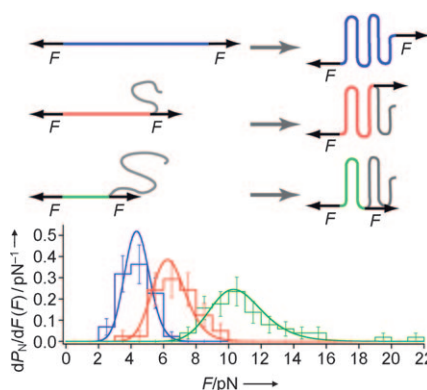
Electron Transfer

S. S. Gayathri, M. Wielopolski,
E. M. Pérez, G. Fernández, L. Sánchez,
R. Viruela, E. Ortí,* D. M. Guldi,*
N. Martín* **815–819**

Discrete Supramolecular Donor–Acceptor
Complexes



The anisotropy of the folding-energy landscape of proteins under force can be tested with cysteine engineering. The shorter the actively contracting polypeptide (see scheme, from blue to green), the higher the force at which the protein folds. The anisotropy of the folding mechanics can be described surprisingly simply with the help of a minimal model, mainly considering the entropic elasticity of the polypeptide.



Protein Folding

M. Schlierf, M. Rief* **820–822**


Surprising Simplicity in the Single-Molecule Folding Mechanics of Proteins



Supporting information is available on www.angewandte.org (see article for access details).



A video clip is available as Supporting Information on www.angewandte.org (see article for access details).



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**Spotlights Angewandte's
Sister Journals** _____ **638–639**

Keywords _____ **824**

Authors _____ **825**

Preview _____ **827**

Corrigendum

High Internal Phase Emulsions Stabilized
Solely by Functionalized Silica Particles

V. O. Ikem, A. Menner,
A. Bismarck* _____ **8277–8279**

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We would like to correct the following statement "*All previous reports on particle-stabilized emulsions deal with emulsions that have internal phase levels below 70 vol%.*" made in the introduction of our recent article. Since the publication of our communication, three papers^[1–3] describing Pickering w/o and o/w emulsions with different internal phase levels and stabilities, which were not referenced in our paper, have been brought to our attention. Arditty et al.^[2] describe silicone oil-in-water Pickering emulsions with up to 90 wt% internal phase and water-in-silicone oil Pickering emulsions having internal phase levels of up to 75 wt% stabilized using as received hydrophilic silica particles and silanized hydrophobic silica particles, respectively. Therefore, we should have stated "*Reports on particle stabilized w/o emulsions deal with emulsions having internal phase levels of up to 75 vol%. However, Arditty et al. reported on the preparation of o/w Pickering-HIPEs with up to 90% internal phase by manual shaking.*" Furthermore, we also stated in our communication that "*Binks and Lumsdon^[1] further stated that particle-stabilized emulsions phase invert between volume fractions of 0.65 and 0.7, which means the major phase becomes the continuous phase.*" This statement is correct for the water-in-oil Pickering emulsions described in Ref. [4], however, Binks and Lumsdon^[1] also provide examples of phase inversion occurring at different oil/water ratios starting from as low as 0.4. We would like to apologize to the authors of papers [1–3] for not acknowledging their research.

[1] B. P. Binks, S. O. Lumsdon, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2959.

[2] S. Arditty, C. P. Whitby, B. P. Binks, V. Schmitt, F. Leal-Calderon, *Eur. Phys. J. E* **2003**, *11*, 273.

[3] B. P. Binks, J. A. Rodrigues, *Langmuir* **2003**, *19*, 4905.

[4] B. P. Binks, S. O. Lumsdon, *Langmuir* **2000**, *16*, 2539.