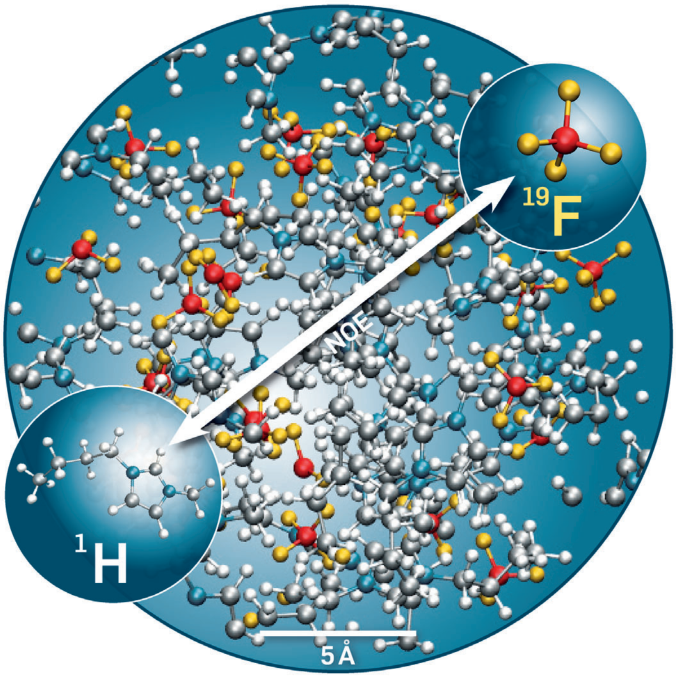
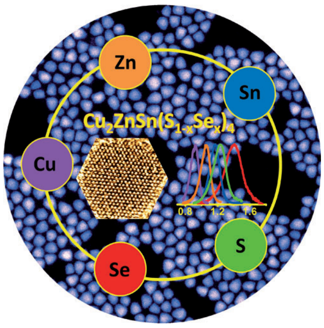
The nuclear Overhauser effect …



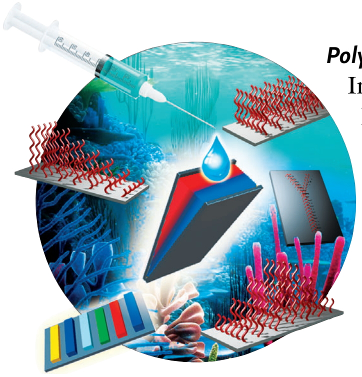
… (NOE) is used for studying the local structures in ionic liquids. In their Communication on page 9242 ff., H. Weingärtner et al. report a new model theory that makes it possible to analyze intermolecular ^{1}H-^{19}F NOE data of 1-butyl-3-methylimidazolium tetrafluoroborate. The arrow in the picture indicates that a H-F NOE at a H–F distance of about 20 Å can be predicted, although it is common knowledge that this effect is only observed for a distance of 5 Å.

Nanocrystals

In their Communication on page 9120 ff., K. M. Ryan et al. report a photoluminescence study of alloyed $Cu_2ZnSn(S_{1-x}Se_x)_4$ wurtzite nanocrystals (10 nm in size) with a varying composition (x = 0–1).



Polymer Brushes



In their Communication on page 9125 ff., W. T. S. Huck, W. Liu, F. Zhou et al. have developed a method to grow polymer brushes in complex gradient patterns. A sandwiched metal substrate achieves this with only a few microliters of growth solution.

Computational Chemistry

In their Communication on page 9275 ff., M. Solà, J. M. Luis et al. show that it is the maximum aromaticity criterion that determines the most suitable hosting cages for the encapsulation of metal clusters in endohedral metallofullerenes.

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Service

Author Profile

"My greatest achievement has been finishing a marathon run in reasonable time.
Guaranteed to make me laugh is Loriot (German humorist). …"
This and more about Stefan Grimme can be found on page 9074.

News

B. List

K. Itami

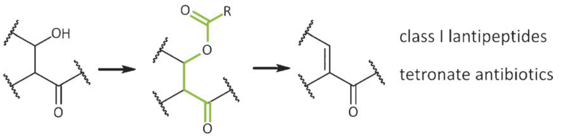
B. L. Feringa

J. Jurczak

Books

Highlights

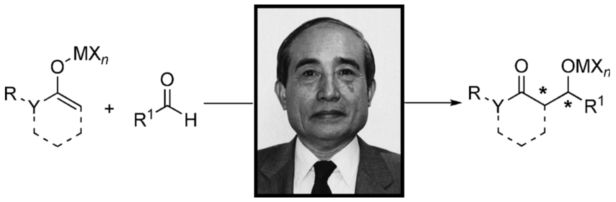
Biosynthesis



Enoyl intermediates are normally obtained through β-elimination of β-hydroxy carbonyl compounds. The OH group is eliminated either directly or is first activated through phosphorylation. Alternative strategies have now been identified: Glutamination or acetylation of a β-hydroxycarbonyl compound followed by β-elimination of an ester was proven to be a key step in the biosynthesis of class I lantipeptide and tetronate antibiotics.

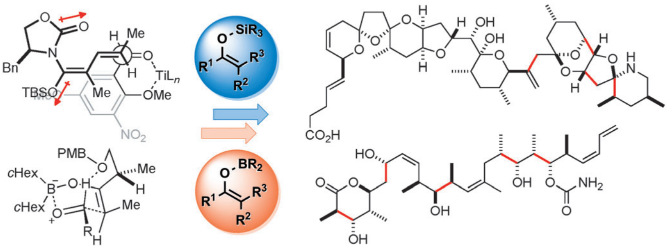
Minireviews

Asymmetric Catalysis



Aldol evergreen: Since the landmark publication of the first directed aldol addition reaction in 1973, the site, diastereo-, and enantioselective reaction has been elevated to the rarefied status of being both a named and a strategy-level reaction. The challenges of merging site, diastereo-, and enantioselectivity with catalysis into a unified reaction manifold have stimulated the development of Lewis base catalyzed aldol addition reactions.

Natural Products



Four decades since Mukaiyama's first reports on the use of silicon and boron enolates in directed aldol reactions, this highly controlled carbon–carbon bond-forming method has been developed into a powerful tool for natural product synthesis. A number of representative total syntheses that demonstrate the impact of the Mukaiyama aldol reaction are described and the underlying mechanistic rationale that determines the stereochemical outcomes is discussed.

For the USA and Canada:
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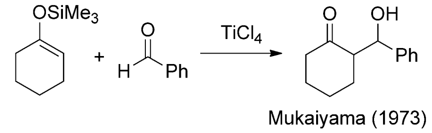
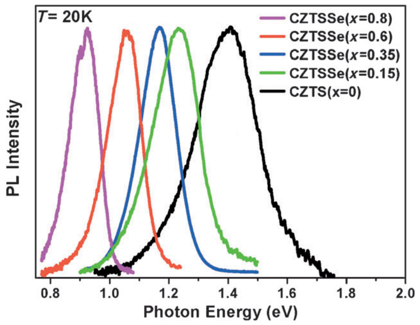


The rest is history: Teruaki Mukaiyama developed three directed cross-aldol reactions, which were mediated by silyl enol ethers, boron enolates, and tin(II) enolates. These reactions had an immense impact on the stereoselective construction of acyclic polyoxygenated carbon frameworks. This Minireview provides a look at the history of the three directed cross-aldol reactions and portrays the early stages of their development.

Mukaiyama Aldol Reaction

Communications

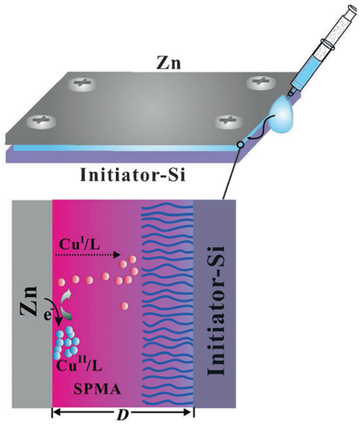
Inorganic nanostructures: Alloyed $Cu_2ZnSn(S_{1-x}Se_x)_4$ wurtzite nanocrystals (10 nm in size) with a varying composition ($x = 0$–1) were synthesized using a colloidal hot injection route. A photoluminescence (PL) emission study of these nanocrystals shows a compositionally tunable band-gap ranging between 0.9–1.4 eV that directly correlates to the sulfur-to-selenium ratio (see picture).



Nanocrystals

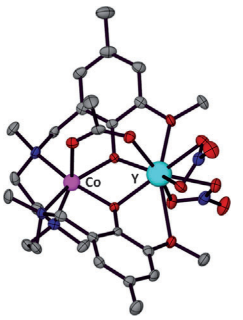
Frontispiece

Brushing up on polymers: A difference in electrochemical potential allows surface-initiated atom-transfer radical polymerization on a sandwiched metal substrate using microliter volumes. Cu^I activators are continuously generated and diffuse to the initiator-modified substrate (see scheme), while Cu^{II} deactivators maintain polymerization. Polymer-brush gradients of SPMA and complex shapes were produced using this method.



Polymer Brushes

Inside Back Cover

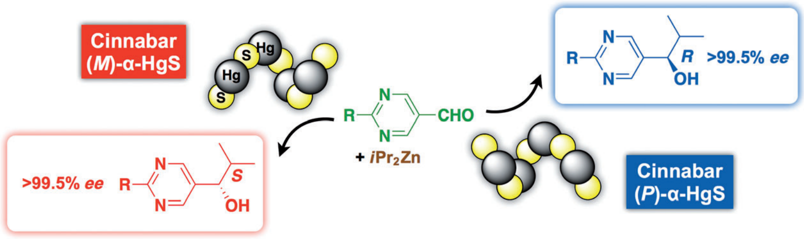


A magnetic Co-production: The complex $[Co(\mu\text{-}L)(\mu\text{-}OAc)Y(NO_3)_2]$ (see structure O red, N blue, C gray), in which the Co^{II} ion exhibits a D value of approximately $+45\ cm^{-1}$, as determined by magnetic and inelastic neutron scattering experiments, exhibits slow magnetic relaxation and single-ion magnet behavior.

Magnetic Properties

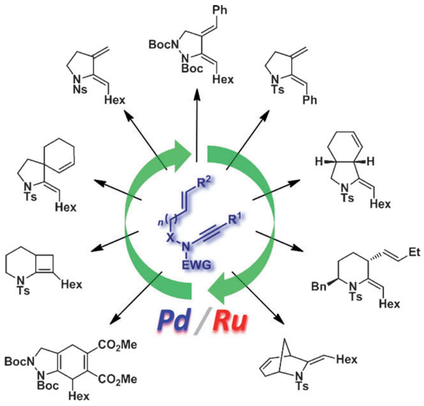

Providing a
healthy mix

Asymmetric Autocatalysis



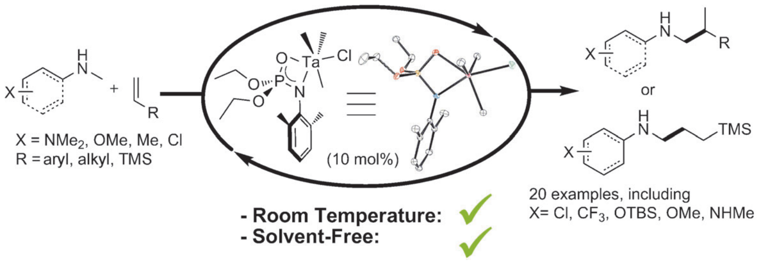
A chiral mineral, cinnabar, served as a chiral source of asymmetric autocatalysis to afford enantioenriched 5-pyrimidyl alkanol. The adsorption structures of related compounds were observed with atomic force microscopy. Enantioselective adsorption of the asymmetric autocatalyst was found in microcrystal formations at the chiral surface of cinnabar.

Heterocycles



I want to ride my azacycle: The title reaction of enynamides affords a wide diversity of azacycles. The reactions are high-yielding, highly stereoselective, and proceed rapidly under mild reaction conditions. Equivalent transformations using enynhydrazides offer new routes to pyrazole and indazole scaffolds. Boc = *tert*-butoxycarbonyl, EWG = electron-withdrawing group, Ns = 4-nitrobenzenesulfonyl, Ts = 4-toluenesulfonyl.

C–H Activation

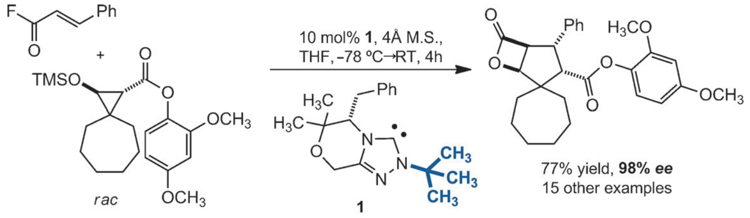


A cooled reaction: Phosphoramidate–$ClTaMe_3$ complexes promote the first example of room-temperature hydroaminoalkylation catalysis. This reaction can be realized under solvent-free conditions and with challenging substrates such as styrenes and dialkyl amines. When using a vinylsilane substrate, for the first time the linear regioisomer is obtained preferentially using a Group 5 metal. TBS = *tert*-butyldimethylsilyl, TMS = trimethylsilyl.

N-Heterocyclic Carbene

L. Candish, C. M. Forsyth,
D. W. Lupton* ______ 9149 – 9152

N-tert-Butyl Triazolylidenes: Catalysts for the Enantioselective (3+2) Annulation of α,β-Unsaturated Acyl Azoliums

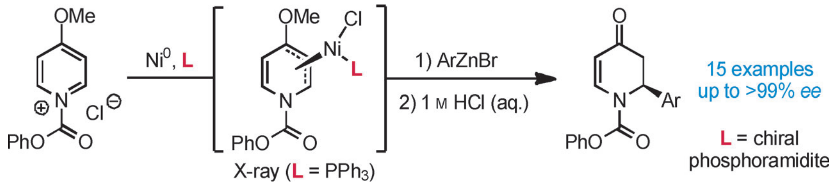


But(yl) not futile: A range of *N-tert*-butyl-substituted triazolylidene N-heterocyclic carbenes have been prepared. Of these, the morpholinone-derived catalyst (**1**) proved best suited to the enantioselective synthesis of cyclopentanes from donor–acceptor cyclopropanes and α,β-unsaturated acyl fluorides. The performance of this catalyst has been correlated to the electronic nature of the catalyst by ^{13}C NMR analysis. M.S. = molecular sieves, TMS = trimethylsilyl.

Cross-Coupling Methods

S. T. Chau, J. P. Lutz, K. Wu,
A. G. Doyle* ______ 9153 – 9156

Nickel-Catalyzed Enantioselective Arylation of Pyridinium Ions: Harnessing an Iminium Ion Activation Mode

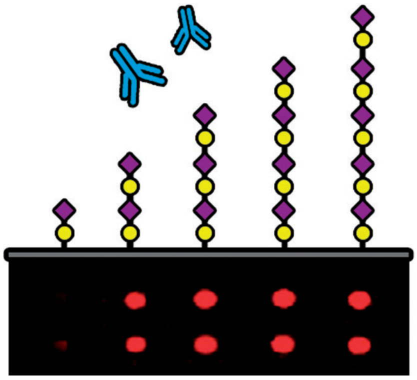


A nickel for your thoughts ... An enantioselective nickel-catalyzed cross-coupling between *N*-acylpyridinium salts and organozinc reagents is reported. The catalytic system, which is comprised of an air-stable Ni^{II} source and a chiral phosphoramidite ligand, affords 2-substituted-2,3-dihydro-4-pyridones with up to > 99 % *ee*.

Carbohydrate Vaccine

C.-H. Wang, S.-T. Li, T.-L. Lin, Y.-Y. Cheng,
T.-H. Sun, J.-T. Wang, T.-J. R. Cheng,
K. K. T. Mong, C.-H. Wong,
C.-Y. Wu* ______ 9157 – 9161

Synthesis of *Neisseria meningitidis* Serogroup W135 Capsular Oligosaccharides for Immunogenicity Comparison and Vaccine Development

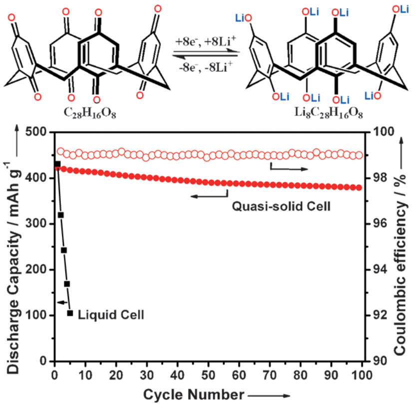


Sweetening the deal: *N. meningitidis* serogroup W135 capsular oligosaccharides were synthesized in lengths from disaccharides to decasaccharides. Sera from mice immunized with these oligosaccharide–protein conjugates were examined by a glycan microarray (see picture) and bactericidal assay for antibody specificity and the ability to kill bacteria.

Lithium batteries

W. Huang, Z. Zhu, L. Wang, S. Wang,
H. Li, Z. Tao, J. Shi, L. Guan,
J. Chen* ______ 9162 – 9166

Quasi-Solid-State Rechargeable Lithium-Ion Batteries with a Calix[4]quinone Cathode and Gel Polymer Electrolyte



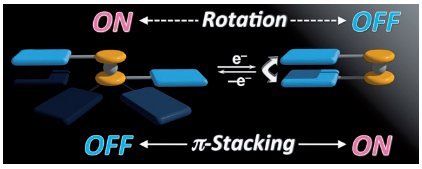
Filled to capacity: Calix[4]quinone (C4Q) has eight available carbonyl groups for binding lithium ions (see picture). It can be exploited to prepare quasi-solid-state rechargeable lithium batteries with a poly(methyl acrylate)/poly(ethylene glycol) based gel polymer electrolyte and a LiClO$_4$/DMSO loading. It shows an initial discharge capacity of 422 mA h g^{-1} and a capacity retention of 379 mA h g^{-1} after 100 cycles.

Molecular Switches

A. Takai, T. Yasuda, T. Ishizuka, T. Kojima, M. Takeuchi* ____ **9167 – 9171**

A Directly Linked Ferrocene–Naphthalenediimide Conjugate: Precise Control of Stacking Structures of π-Systems by Redox Stimuli

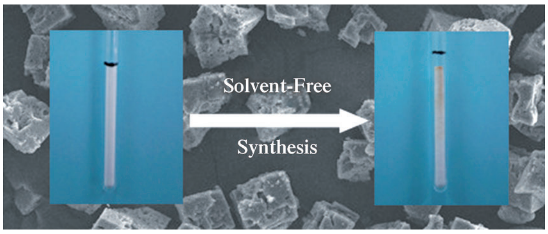
A ferrocene derivative having directly connected naphthalenediimide moieties has been synthesized. The stacking–destacking structures of the naphthalenediimides can be switched in response to redox stimuli by associating with the pivoting motion of ferrocene. The conformation and the electronic structure of naphthalenediimides are elucidated quantitatively in each electron-transfer state. The composite exhibited n-type semiconducting behavior.



Zeolite Synthesis

Y. Jin, Q. Sun, G. Qi, C. Yang, J. Xu, F. Chen, X. Meng,* F. Deng,* F.-S. Xiao* ____ **9172 – 9175**

Solvent-Free Synthesis of Silicoaluminophosphate Zeolites

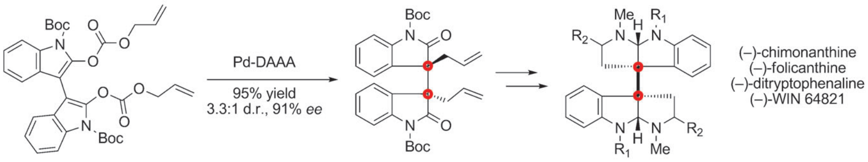


Solvents, who needs them? Silicoaluminophosphate zeolites with various frameworks have been successfully synthesized by a solvent-free route. Catalytic tests for the conversion of methanol to olefins show that thus obtained SAPO-34 (see picture) exhibited catalytic performance comparable to that of zeolites made by the conventional hydrothermal route.

Palladium Catalysis

B. M. Trost,* M. Osipov ____ **9176 – 9181**

Palladium-Catalyzed Asymmetric Construction of Vicinal All-Carbon Quaternary Stereocenters and its Application to the Synthesis of Cyclotryptamine Alkaloids

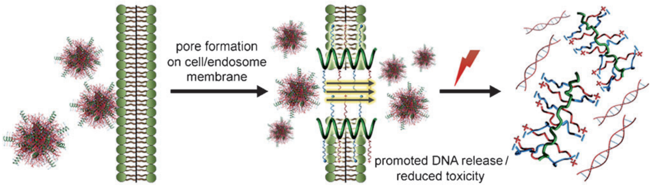


A twofold Pd-DAAA Pd-catalyzed decarboxylative allylic alkylation (see scheme) was used to construct two vicinal all-carbon quaternary stereocenters (marked in red) in a diastereo- and enantioselective fashion. The products of the Pd-DAAA were further elaborated to complete the formal syntheses of cyclotryptamine alkaloids. The twofold Pd-catalyzed transformation proceeds through an initial matched allylation followed by a second mismatched allylation to deliver the desired product.

Gene Delivery

L. Yin, H. Tang, K. H. Kim, N. Zheng, Z. Song, N. P. Gabrielson, H. Lu, J. Cheng* ____ **9182 – 9186**

Light-Responsive Helical Polypeptides Capable of Reducing Toxicity and Unpacking DNA: Toward Nonviral Gene Delivery

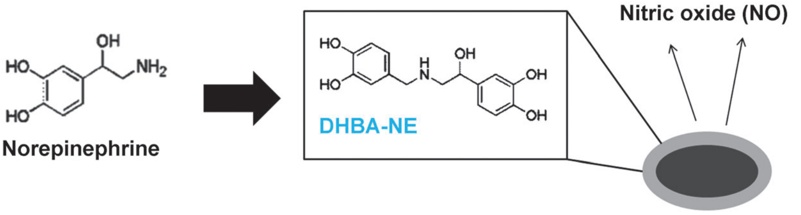


Gene delivery vehicles: Helical, cationic polypeptides with light-responsive domains showed potent membrane activity and promoted efficient cellular internalization of DNA (see picture). After transfection, a light trigger induces protecting-group removal to expose anionic carboxylate groups. The reduced cationic charge and helix distortion of the polypeptides result in enhanced DNA unpacking and reduced material toxicity because of the eliminated membrane activity.

Bio-inspired Chemistry

S. Hong, J. Kim, Y. S. Na, J. Park, S. Kim, K. Singha, G.-I. Im, D.-K. Han, W. J. Kim,* H. Lee* ______ **9187 – 9191**

Poly(norepinephrine): Ultrasmooth Material-Independent Surface Chemistry and Nanodepot for Nitric Oxide



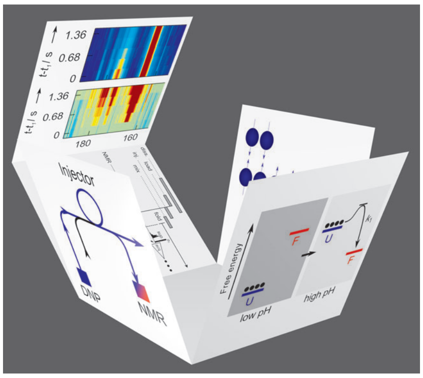
Capture and release: The material-independent surface chemistry of a poly(norepinephrine) (pNE) which exhibits perfect smoothness at the nanometer scale is controlled by 3,4-dihydroxybenzaldehyde-norepinephrine (DHBA-NE) conjugates. The pNE layer containing DHBA-NE serves to store and release small therapeutics such as nitric oxide.

NMR Spectroscopy

H.-Y. Chen, M. Ragavan, C. Hilty* ______ **9192 – 9195**

Protein Folding Studied by Dissolution Dynamic Nuclear Polarization

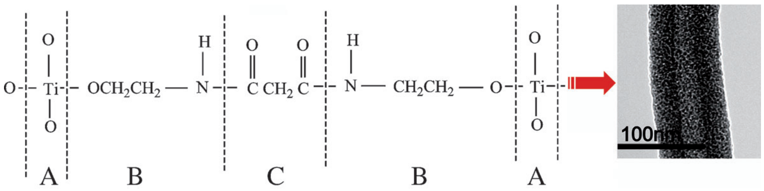
Folding and hyperpolarization: A method is presented for the measurement of protein folding by nuclear magnetic resonance. Denatured polypeptide is hyperpolarized using dissolution dynamic nuclear polarization, yielding a substantial signal enhancement that allows real-time ^{13}C NMR spectroscopy of the refolding process after a rapid pH jump. The resulting spectra indicate global and site-specific changes in the protein.



Photocatalysis

C. Q. Chen, P. Li, G. Z. Wang, Y. Yu, F. F. Duan, C. Y. Chen, W. G. Song, Y. Qin,* M. Knez* ______ **9196 – 9200**

Nanoporous Nitrogen-Doped Titanium Dioxide with Excellent Photocatalytic Activity under Visible Light Irradiation Produced by Molecular Layer Deposition

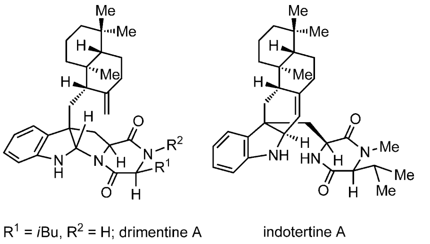


Ultrathin films: A new molecular layer deposition process for the synthesis of nanoporous nitrogen-doped titanium dioxide films is developed. This process is based on a four-step ABCB reaction sequence using $TiCl_4$, ethanolamine, and malonyl chloride as precursors (see picture). The obtained nanoporous N-doped TiO_2 exhibits excellent photocatalytic activity upon irradiation with visible light.

Natural Product Synthesis

Y. Sun, R. Li, W. Zhang, A. Li* ______ **9201 – 9204**

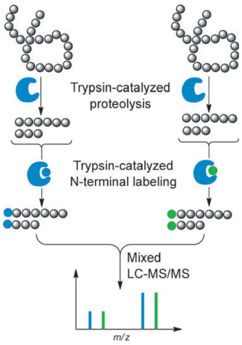
Total Synthesis of Indotertine A and Drimentines A, F, and G



R^1 = *i*Bu, R^2 = H; drimentine A
R^1 = *i*Pr, R^2 = H; drimentine G
R^1 = *i*Pr, R^2 = Me; drimentine F

Oh my darling, Drimentine: The first total synthesis of the pyrroloindoline alkaloids drimentines A, F, and G, and their congener, indotertine A, is reported. An intermolecular radical conjugate addition was key in the synthesis of the drimentine alkaloids, and a biologically inspired iminium–olefin cyclization converted drimentine F into indotertine A.

Two times an enzyme: Trypsin was first used as a protease to catalyze the digestion of proteins and then as a ligase to catalyze the linking of isotopically labeled amino acids to the N termini of tryptic peptides for quantitative proteomics. Reliable and accurate quantification of proteins was demonstrated for model proteins as well as proteome samples.



Isotopic Labeling

Y. Pan, M. Ye,* L. Zhao, K. Cheng,
M. Dong, C. Song, H. Qin, F. Wang,
H. Zou* ________ **9205–9209**

N-Terminal Labeling of Peptides by Trypsin-Catalyzed Ligation for Quantitative Proteomics

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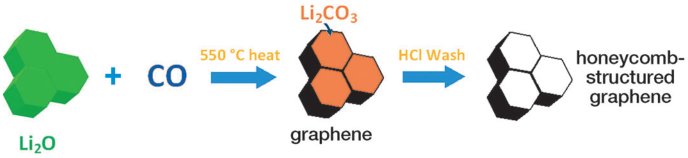


A useful Li: A simple reaction between Li_2O and CO, gives a new type of three-dimensional graphene sheets—honeycomb-structured graphene. A dye-sensitized solar cell (DSSC) with the new graphene counter electrode has an energy conversion efficiency as high as 7.8 %, which is comparable to that of DSSCs with an expensive Pt counter electrode.

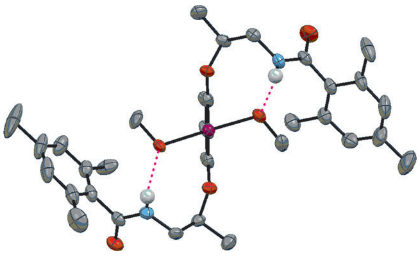
Graphene Materials

H. Wang, K. Sun, F. Tao, D. J. Stacchiola,
Y. H. Hu* ________ **9210–9214**

3D Honeycomb-Like Structured Graphene and Its High Efficiency as a Counter-Electrode Catalyst for Dye-Sensitized Solar Cells

---

Iodine chooses: A conformationally flexible C_2-symmetric organoiodine(III) catalyst for the highly enantioselective catalytic oxidative dearomatization of phenols has been developed. Catalysis is controlled by intramolecular hydrogen-bonding interactions and additional achiral alcohols.



Catalyst Development

M. Uyanik, T. Yasui,
K. Ishihara* ________ **9215–9218**

Hydrogen Bonding and Alcohol Effects in Asymmetric Hypervalent Iodine Catalysis: Enantioselective Oxidative Dearomatization of Phenols

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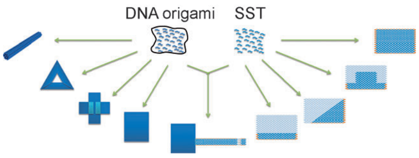
Efficient self-assembly: Self-assembly of DNA nanostructures at room temperature was achieved by incubating the component strands in the presence of a denaturing agent (30–40% formamide). This isothermal method is efficient for assembly of both DNA origami (purple, see scheme) and single-stranded tile (SST, blue) structures, as well as an SST ribbon growing on an origami template.



DNA Nanostructures

Z. Zhang, J. Song, F. Besenbacher,
M. Dong,* K. V. Gothelf* ___ **9219–9223**

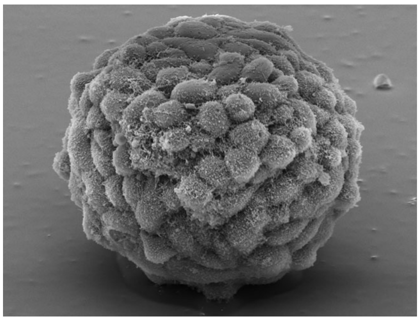
Self-Assembly of DNA Origami and Single-Stranded Tile Structures at Room Temperature

Cell Sorting

C. Siltanen, D.-S. Shin,* J. Sutcliffe,
A. Revzin* ______ **9224 – 9228**

Micropatterned Photodegradable Hydrogels for the Sorting of Microbeads and Cells

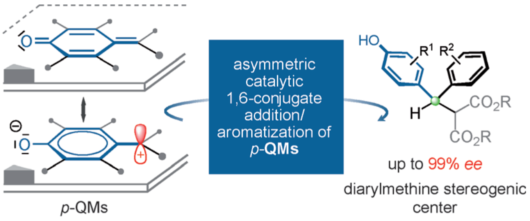
Sorted out: Soft-lithography micropatterning of a photodegradable poly(ethylene glycol) hydrogel was utilized to sort cell-bound microbeads. Biofunctionalized microbeads were patterned, screened for cell binding activity, and isolated from arrays by UV irradiation. The technique is a simple approach for sorting and downstream processing of cultured cells.



Asymmetric Catalysis

W.-D. Chu, L.-F. Zhang, X. Bao,
X.-H. Zhao, C. Zeng, J.-Y. Du, G.-B. Zhang,
F.-X. Wang, X.-Y. Ma,
C.-A. Fan* ______ **9229 – 9233**

Asymmetric Catalytic 1,6-Conjugate Addition/Aromatization of *para*-Quinone Methides: Enantioselective Introduction of Functionalized Diarylmethine Stereogenic Centers

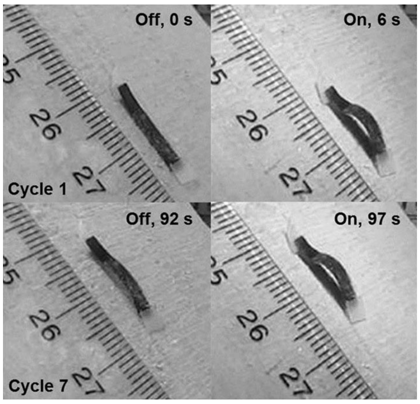


It's just a phase: The title reaction sequence of *para*-quinone methides (*p*-QMs) has been developed with malonates under phase-transfer catalysis. The reaction also offers an alternative route to asymmetric construction of diarylmethine stereocenters in excellent enantioselectivities and high yields.

Soft Robotics

R. R. Kohlmeyer, J. Chen* ______ **9234 – 9237**

Wavelength-Selective, IR Light-Driven Hinges Based on Liquid Crystalline Elastomer Composites



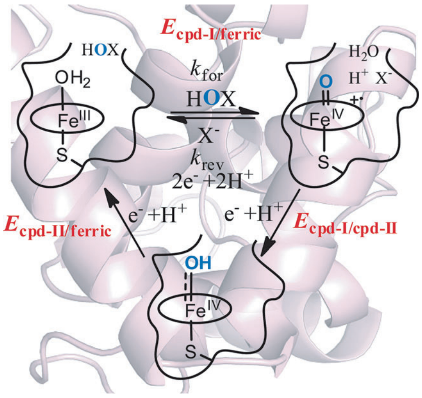
An uphill climb: The title systems show fast, reversible bending with a large strain. Such hinges can power remote-controlled soft robots, including foldable origami structures, Venus flytrap-inspired grippers that can pick up delicate objects, and inchworm walkers that can crawl up a 50° incline (see picture).

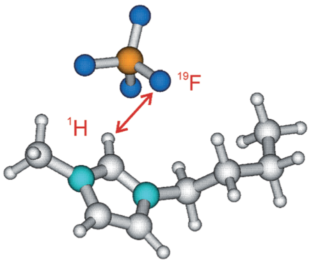
Reactive Intermediates

X. Wang, S. Peter, R. Ullrich, M. Hofrichter,
J. T. Groves* ______ **9238 – 9241**

Driving Force for Oxygen-Atom Transfer by Heme-Thiolate Enzymes

Absolutely: Redox potentials for three redox couples in *Aae*APO-catalyzed reactions have been measured, thus placing these heme-thiolate reactive intermediates on an absolute energy scale for the first time. The importance of the axial thiolate ligand and the basic nature of compound II ferryl oxygen atom are discussed in terms of these redox potentials.

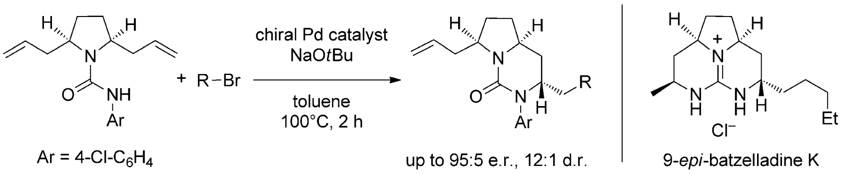




Frequency-dependent NOE: A new model theory was used to analyze the spatial range of the intermolecular nuclear Overhauser effect in ionic liquids. The spatial range undergoes a transition from long-range nature at low frequency to a short-range character at high frequencies. The experimentally accessible cross-relaxation rate involves contributions from both regimes, but the long-range component dominates.

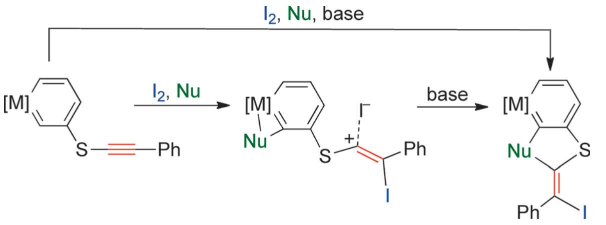
Ionic Liquids

Front Cover



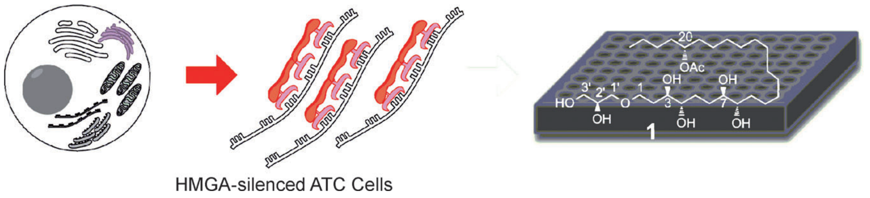
Lost symmetry: Fused bicyclic ureas are enantioselectively obtained through Pd-catalyzed desymmetrizing carboaminations of *meso*-2,5-diallylpyrrolidinyl ureas (see scheme). The reactions generate a C–N and a C–C bond, and afford products with three stereocenters. One of these products was transformed to a tricyclic guanidine and then to 9-*epi*-batzelladine K over several steps.

Asymmetric Catalysis



Caught in the act: Key intermediates in an iodine-mediated electrophilic cyclization reaction was isolated by introducing metallabenzenes as the starting material. The unique structure of the intermediate should be described as the intimate ion pair form, instead of the widely accepted iodonium ion form.

Heterocycles



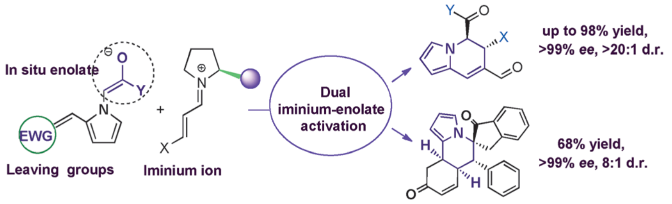
From Antarctic waters: Human anaplastic thyroid carcinoma (ATC) cells which stably express antisense construct against nuclear high-mobility group A (HMGA) proteins were used in a novel phenotypic assay for screening marine natural extracts. The rational search led to the isolation and identification of a novel polyoxygenated linear lipid (**1**) that showed important and selective cytotoxicity against ATC-derived tumor cell lines.

Anticancer Lead Discovery

Asymmetric Synthesis

X. Jiang, B. Tan,
C. F. Barbas III* ______ **9261 – 9265**

Core-Structure-Motivated Design of Iminium–Enolate Organocascade Reactions: Enantioselective Syntheses of 5,6-Dihydroindolizines

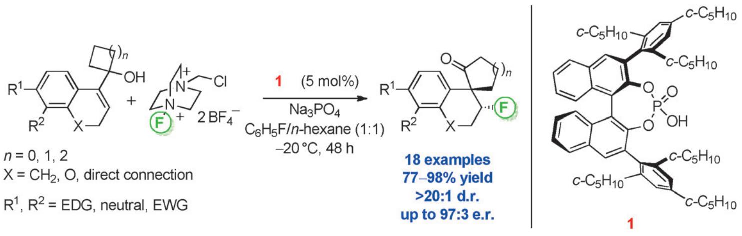


Indolizine skeletons: A highly efficient dual iminium–enolate generation/activation process is introduced as a new platform for the design of organocatalytic intermolecular domino reactions for the direct construction of 5,6-dihydroindolizine derivatives. This process provides ready access to indolizine skeletons with high optically purity from simple starting materials (see picture).

Synthetic Methods

F. Romanov-Michailidis, L. Guénée,
A. Alexakis* ______ **9266 – 9270**

Enantioselective Organocatalytic Fluorination-Induced Wagner–Meerwein Rearrangement

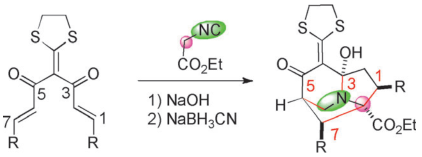


Cracked under strain: Strained allylic cyclobutanols and cyclopropanols readily undergo a ring expansion described by the title rearrangement. This reaction is promoted by catalytic amounts of **1** and displays high tolerance with respect to the substrate scope. The corresponding β-fluoro spiroketone products are isolated in high yields and with excellent stereoselectivities. EDG = electron-donating group, EWG = electron-withdrawing group.

Heterocycles

X. Xu, L. Zhang, X. Liu, L. Pan,*
Q. Liu* ______ **9271 – 9274**

Facile [7C+1C] Annulation as an Efficient Route to Tricyclic Indolizidine Alkaloids



A handle on annulation: The two alkenoyl moieties of the cyclic dithiolane are parallel to each other and enables the [7C+1C] annulation with ethyl isocyanoacetate to occur. As a result, tricyclic indolizidine alkaloids are constructed by a two-step, base-catalyzed [7C+1C] annulation/intramolecular cyclization with subsequent reduction/cyclization.

Computational Chemistry

M. Garcia-Borràs, S. Osuna, M. Swart,
J. M. Luis,* M. Solà* ______ **9275 – 9278**

Maximum Aromaticity as a Guiding Principle for the Most Suitable Hosting Cages in Endohedral Metallofullerenes

Back Cover

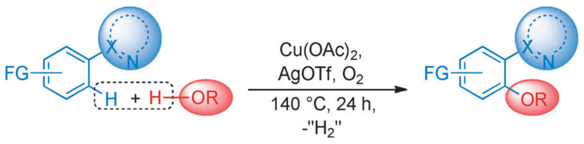
THE MOST “AROMATIC” ONE

Encapsulating! The encapsulation of metal clusters in endohedral metallofullerenes takes place in cages that, in most cases, are far from being the most stable isomer in the corresponding hollow fullerenes. In contrast to previous proposals, new results indicate that it is the maximum aromaticity criterion that determines the most suitable hosting cages.

C–H Activation

S. Bhadra, C. Matheis, D. Katayev, L. J. Gooßen* ______ **9279 – 9283**

Copper-Catalyzed Dehydrogenative Coupling of Arenes with Alcohols

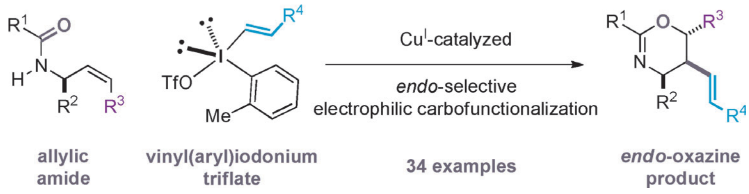


What a couple! Arenes functionalized with donating groups undergo oxidative dehydrogenative coupling with alcohols in the presence of a copper/silver catalyst system. This intermolecular C–H alkoxylation provides a convenient synthetic route to the important class of aryl ethers. The catalyst system also allows the alkoxylation of benzylic C–H groups with formation of benzyl alkyl ethers.

Alkene Difunctionalization

E. Cahard, N. Bremeyer, M. J. Gaunt* ______ **9284 – 9288**

Copper-Catalyzed Intramolecular Electrophilic Carbofunctionalization of Allylic Amides

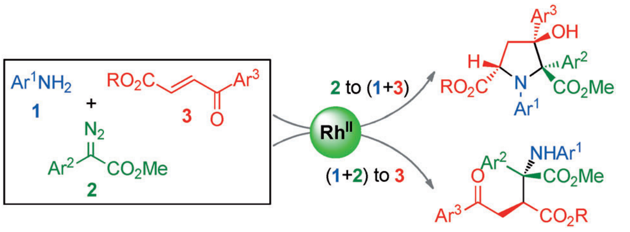


An *endo*-selective copper-catalyzed oxyarylation and oxyvinylation of allylic amides was developed. The products are the six-membered ring oxazines and are formed exclusively as the *anti* isomers. A range of substituted allylic amides and a wide selection of diaryliodonium and vinyl(aryl)iodonium triflates are compatible with this transformation.

Multicomponent Reactions

C. Jing, D. Xing, Y. Qian, T. Shi, Y. Zhao, W. Hu* ______ **9289 – 9292**

Diversity-Oriented Three-Component Reactions of Diazo Compounds with Anilines and 4-Oxo-Enoates

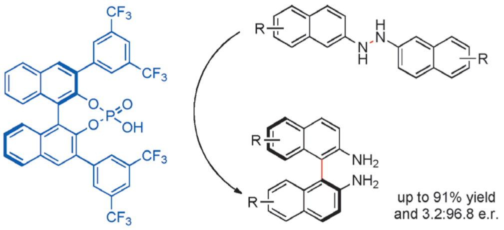


Choosing a path: The title reaction can proceed through two different reaction pathways, and is controlled by the addition sequence of the substrates. Divergent polyfunctional products, pyrrolidines or linear α-amino ester derivatives, are obtained in good yields and high diastereoselectivities.

Organocatalysis

C. K. De, F. Pesciaioli, B. List* ______ **9293 – 9295**

Catalytic Asymmetric Benzidine Rearrangement

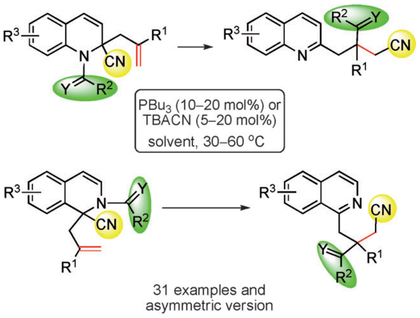


A chiral Brønsted acid catalyzes the asymmetric benzidine rearrangement of *N*,*N*′-dinaphthylhydrazines. Different electronically and structurally diverse axially chiral 2,2′-binaphthyl diamine (BINAM) derivatives are obtained with high enantioselectivity.

Synthetic Methods

J.-M. Chen, G.-F. Zou,
W.-W. Liao* ______ **9296 – 9300**

Metal-Free Intramolecular Carbocyanation of Activated Alkenes: Functionalized Nitriles Bearing β-Quaternary Carbon Centers

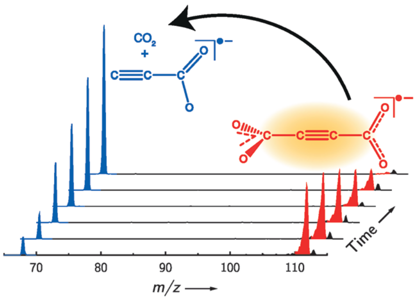


The CN shuffle: The described intramolecular alkenyl- and acylcyanation reaction of activated alkenes proceed by cleavage of a C–N bond. This protocol provides access to functionalized acyclic nitriles with quaternary carbon centers under neutral and mild reaction conditions, demonstrates broad scope, and good functional-group compatibility and versatility. Y = O or CHR^4; R^1,R^4 = electron-withdrawing group; TBACN = tetrabutylammonium cyanide.

Radicals

B. L. J. Poad,* B. B. Kirk,
P. I. Hettiarachchi, A. J. Trevitt,
S. J. Blanksby, T. Clark* ____ **9301 – 9304**

Direct Detection of a Persistent Carbonyloxyl Radical in the Gas Phase



Long lived: Carbonyloxyl radicals ($RCO_2^\bullet$) are reactive intermediates that play key roles in initiating polymerization reactions. This reactivity also makes their direct observation difficult. For the first time a persistent organic $RCO_2^\bullet$ radical is detected in the gas phase, its extraordinary longevity is attributed to the high barrier towards fragmentation owing to the endothermicity of the decarboxylation products.

DOI: 10.1002/anie.201306077

50 Years Ago …

Angewandte Chemie International Edition was first published in 1962, the mother journal first in 1888. In this monthly flashback, we feature some of the articles that appeared 50 years ago. This look back can open our eyes, stimulate discussion, or even raise a smile.

Angewandte Chemie has always published a broad range of Reviews: The first Review (by E. Jucker) was on the chemistry of psychotherapeutic agents, including neuroleptics, antidepressants, and tranquilizers. In other Reviews, F. Drawart and O. Bachmann discussed how radiocarbon-labeled compounds could be separated and detected in the gas phase, O. Glemser outlined the preparation, properties, and structure of cyclic and acyclic sulfur–nitrogen halides, and E. Wiberg et al. discussed the chemistry of metal silyls $M(SiR_3)_n$, where M is Zn, Hg, Al, or Sn, and R is hydrogen or an organic group.

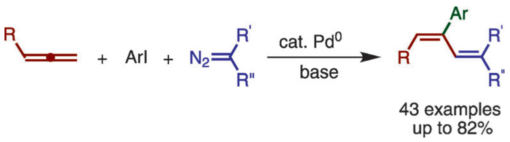
These days Communications are often around four pages long. Fifty years ago, this was enough for the entire Communications section! Three of the Communications were on organotin chemistry: H. Schumann et al. reported on the preparation of organotin phosphides from either organotin halides or lithium triorganyltin species. W. P. Neumann et al. published two Communications, the first on H–D exchange in trialkyltin, germanium, and silicon hydrides, and the second on addition reactions of organotin hydrides onto olefins in the presence of aluminum trialkyl species, which act as a catalyst.

Read more in Issue 9/1963.

Synthetic Methods

Q. Xiao, B. Wang, L. Tian, Y. Yang, J. Ma, Y. Zhang, S. Chen,* J. Wang* ______ **9305–9308**

Palladium-Catalyzed Three-Component Reaction of Allenes, Aryl Iodides, and Diazo Compounds: Approach to 1,3-Dienes

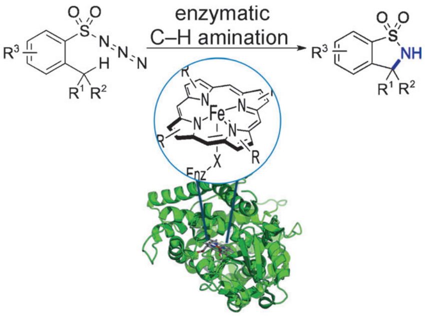


'Diene' to know: The title reaction leads to the formation of 1,3-dienes in high yields (see scheme). The reaction also proceeds with the use of N-tosylhydrazone substrates. Carbopalladation to the allene and palladium carbene migratory insertion are proposed to play the key role in this transformation.

Enzymatic C–H Amination

J. A. McIntosh, P. S. Coelho, C. C. Farwell, Z. J. Wang, J. C. Lewis, T. R. Brown, F. H. Arnold* ______ **9309–9312**

Enantioselective Intramolecular C–H Amination Catalyzed by Engineered Cytochrome P450 Enzymes In Vitro and In Vivo

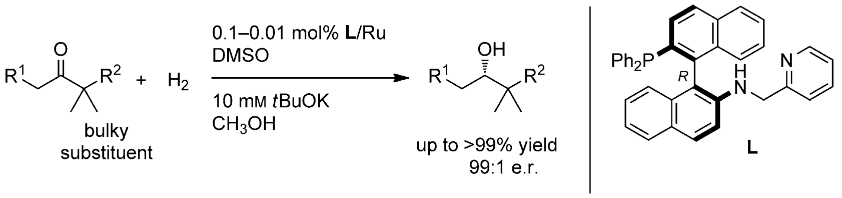


Nitrogen activation: Though P450 enzymes are masters of oxygen activation and insertion into C–H bonds, their ability to use nitrogen for the same purpose has so far not been explored. Engineered variants of cytochrome P450$_{BM3}$ have now been found to catalyze intramolecular C–H aminations in azide substrates. Mutations to two highly conserved residues significantly increased this activity.

Synthetic Methods

T. Yamamura, H. Nakatsuka, S. Tanaka, M. Kitamura* ______ **9313–9315**

Asymmetric Hydrogenation of *tert*-Alkyl Ketones: DMSO Effect in Unification of Stereoisomeric Ruthenium Complexes

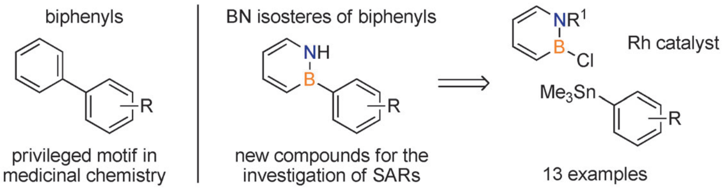


Face off: The ruthenium complexes of a new axially chiral PNN ligand (**L**) are highly efficient in the presence of dimethylsulfoxide (DMSO) for hydrogenation of both functionalized and unfunctionalized *tert*-alkyl ketones. DMSO is thought to narrow down the many possible complex stereoisomers into a single facial **L**/Ru complex, thus enhancing the reactivity, selectivity, and productivity.

BN Heterocycles

G. E. Rudebusch, L. N. Zakharov, S.-Y. Liu* ______ **9316–9319**

Rhodium-Catalyzed Boron Arylation of 1,2-Azaborines

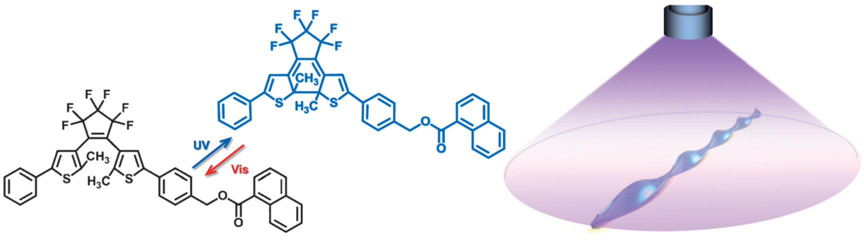


A Sn-phony in B! BN isosteres of biphenyl compounds are prepared through Rh-catalyzed cross-coupling between 2-chloro-1,2-azaborines and arylstannanes (see scheme). The synthetic method should enable investigations of structure–activity relationships (SARs) by expanding the chemical space of the pharmaceutically relevant biphenyl structure through BN/CC isosterism.

Photochromic Actuators

D. Kitagawa, H. Nishi,
S. Kobatake* ———— 9320 – 9322

Photoinduced Twisting of a Photochromic Diarylethene Crystal

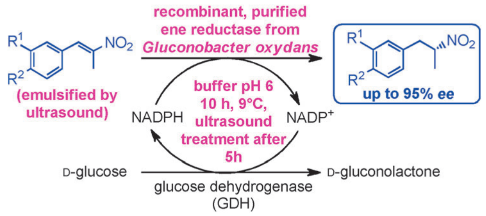


Let’s do the twist! Molecular crystals of a diarylethene derivative exhibit photoreversible twisting upon irradiation with UV and visible light. The left-handed and right-handed helix formation is ascribed to the contraction of the crystal in a diagonal direction, depending on which face is irradiated with UV light.

Asymmetric Catalysis

E. Burda, T. Reß, T. Winkler, C. Giese,
X. Kostrov, T. Huber, W. Hummel,*
H. Gröger* ———— 9323 – 9326

Highly Enantioselective Reduction of α-Methylated Nitroalkenes



Highly selective: The reduction of α-methyl-substituted nitroalkenes succeeds in a highly enantioselective fashion with an ene reductase from *Gluconobacter oxydans*. Under optimized reaction conditions the desired nitroalkanes are formed with enantiomeric excesses of up to 95% in these biotransformations.

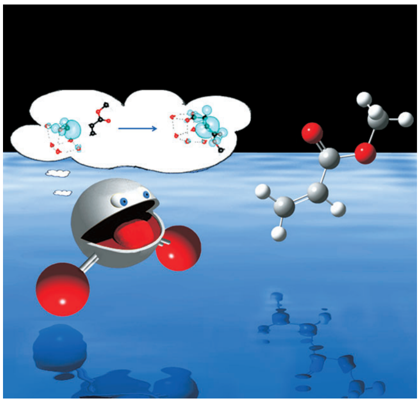
CO_2 Activation

A. Akhgarnusch, R. F. Höckendorf,
Q. Hao, K. P. Jäger, C.-K. Siu,*
M. K. Beyer* ———— 9327 – 9330

Carboxylation of Methyl Acrylate by Carbon Dioxide Radical Anions in Gas-Phase Water Clusters

Inside Cover

The addition of CO_2 to olefins in nanoscale water droplets was studied by mass spectrometry. One electron is enough to turn a CO_2 molecule into its bent, reactive radical anionic form (left in scheme), which is stabilized by a hydration shell. This species reacts with methyl acrylate by radical addition to the carbon–carbon double bond. Without the hydration shell, however, neutral carbon dioxide is released.



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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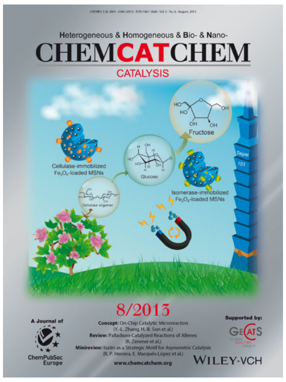
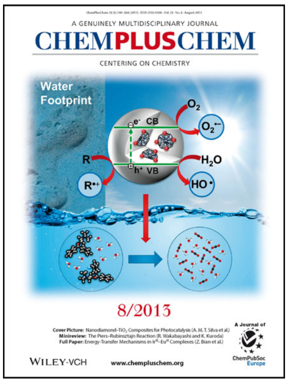
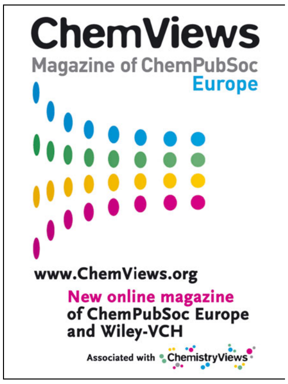
This article is accompanied by a cover picture (front or back cover, and inside or outside).







Abstracts for Communications

From January 2014 onwards, all Communications in *Angewandte Chemie* will contain an abstract as their first paragraph. We therefore request that every new Communication be submitted with such an abstract. When you write the abstract, please keep the following aspects in mind (they can be found in more detail in the Author Guidelines on the journal's homepage in Section 3.1):

In the abstract, the **motivation** for the work, the **methods** applied, the **results**, and the **conclusions** drawn should be presented (maximum 1000 characters). The abstract should contain several keywords to aid finding the paper online, and it should not mention graphical elements, tables, or references within the paper.