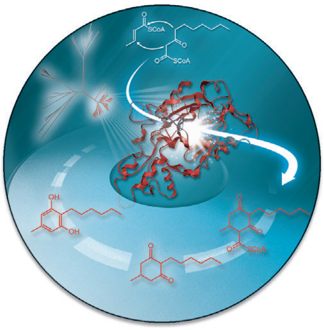
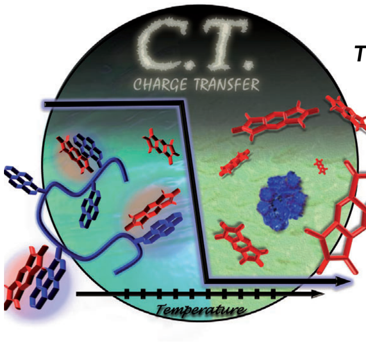
When DNA is encapsulated …

… in a silica sphere, the encoded information can be protected for storage and distribution, much in the way a bottle protects the message inside from the rough sea. As R. N. Grass et al. describe in their Communication on page 4269 ff., a silica layer only 10 nm thick is sufficient to protect DNA from high temperatures and aggressive radical conditions. The glass can be broken by reaction with HF and the information recovered for biochemical analysis.

Biosynthesis
A new class of ketosynthases (DarB) involved in the biosynthesis of 1,3-cyclohexanediones and dialkylresorcinols has been identified by H. B. Bode and co-workers, as reported in their Communication on page 4108 ff.. Picture: Tim Schöner.





Thermoresponsive Polymers
In their Communication on page 4174 ff., K. Sada et al. present facile control of lower critical solution temperature behavior of an organic polymer by manipulating charge-transfer interactions between the polymer and an effector..

Homogeneous Catalysis
B. Åkermark and co-workers present in their Communication on page 4189 ff., a previously undiscovered deactivation pathway for ruthenium-based water oxidation catalysts.

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Service

Author Profile

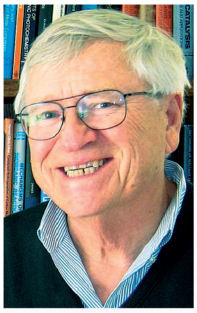
"My favorite saying is ‚Just do it'
When I was eighteen I wanted to be a detective ..."
This and more about Jaephil Cho can be found on page 4066.

News

N. S. Goroff

I. Ojima

E. M. Carreira



P. C. Ford

S. Granick

S. I. Stupp

W. E. Moerner

S. M. Kauzlarich

D. L. Boger

A. T. Bell

P. J. Stang

Books

Asymmetric Organocatalysis Benjamin List, Keiji Maruoka *reviewed by P. I. Dalko* ______ **4069**

Essays

Medicinal Chemistry

S. Laufer,* U. Holzgrabe,
D. Steinhilber ______ **4072 – 4076**

Drug Discovery: A Modern Decathlon

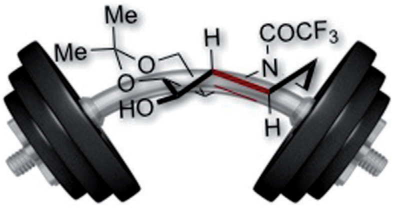
The increasing costs as well as the lack of innovation potency in the development of new drugs have led to a discussion of the possible contribution of the German university landscape, especially pharmaceutical sciences. Successful examples are already apparent in the US.

Minireviews

Total Synthesis

M. R. Wilson, R. E. Taylor* ______ **4078 – 4087**

Strained Alkenes in Natural Product Synthesis



No strain, no gain: The high reactivity of strained alkenes facilitates complex synthetic transformations in a mild and atom-economical fashion. Recent developments in the synthesis and handling of distorted alkenes have led to the use of these highly reactive molecules as critical intermediates in natural product synthesis. The ability of strained alkenes to drive otherwise unfavorable reactions is demonstrated in a number of these examples.

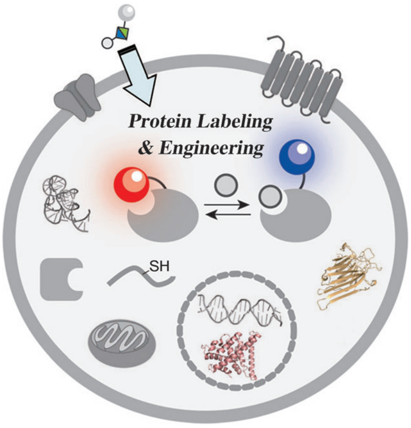
Reviews

Protein Modification

Y. Takaoka, A. Ojida,
I. Hamachi* ______ **4088 – 4106**

Protein Organic Chemistry and Applications for Labeling and Engineering in Live-Cell Systems

Labels of the reconstruction: Chemical modification of proteins with synthetic probes is a powerful means of elucidating protein functions in live cells and of influencing these functions. New reactions that can be successfully applied in living systems represent a worthy challenge to organic chemistry, especially as the labeling and manipulation of endogenous proteins in their natural habitats is currently at an early stage.



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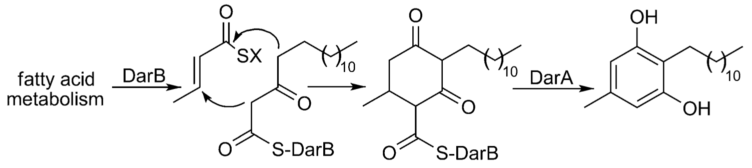
Communications

Biosynthesis

S. W. Fuchs, K. A. J. Bozhüyük,
D. Kresovic, F. Grundmann, V. Dill,
A. O. Brachmann, N. R. Waterfield,
H. B. Bode* ——— 4108 – 4112

Formation of 1,3-Cyclohexanediones and Resorcinols Catalyzed by a Widely Occuring Ketosynthase



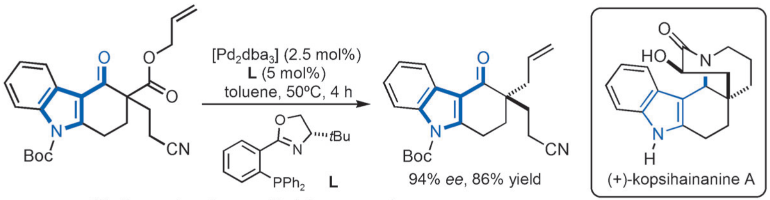
Overlooked, but widespread! A new class of ketosynthases (DarB) involved in the biosynthesis of 1,3-cyclohexanediones and dialkylresorcinols has been identified and characterized in detail. The presence of homologues in 89 different bacteria, including several pathogens, reveals that DarB as well as the corresponding natural products might be widespread, thus presenting a new but so far overlooked pathway to natural products.

Frontispiece

Stereoselective Catalysis

C. J. Gartshore,
D. W. Lupton* ——— 4113 – 4116

Enantioselective Palladium-Catalyzed Decarboxylative Allylation of Carbazolones and Indolones: Formal Synthesis of (+)-Kopsihainanine A



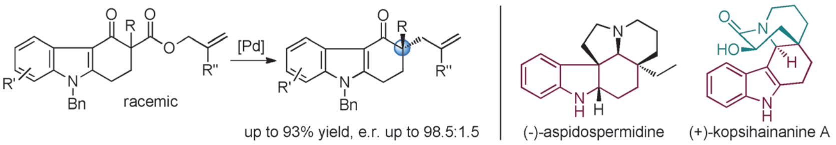
- 17 other carbazolone and indolone examples
- 80–94% *ee*, 72–98% yield

Adding value: A four-step synthesis of enantioenriched carbazolone and indolone derivatives has been developed using an enantioselective Pd-catalyzed decarboxylative allylation. The scope of this reaction is broad, and the materials are suited for natural product synthesis, shown with the completion of a formal synthesis of (+)-kopsihainanine (see scheme).

Alkaloid Synthesis

Z. Li, S. Zhang, S. Wu, X. Shen, L. Zou,
F. Wang, X. Li, F. Peng, H. Zhang,
Z. Shao* ——— 4117 – 4121

Enantioselective Palladium-Catalyzed Decarboxylative Allylation of Carbazolones: Total Synthesis of (−)-Aspidospermidine and (+)-Kopsihainanine A

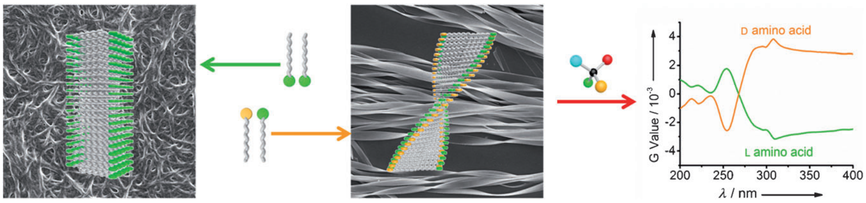


Functionalized chiral carbazolones with α-quaternary carbon centers are formed through the ligand-controlled Pd-catalyzed enantioselective decarboxylative allylic alkylation of carbazolones (see scheme). This catalytic asymmetric reaction was employed as the key step in the total synthesis of aspidospermidine and (+)-kopsihainanine A.

Supramolecular Chirality

H. Cao, X. F. Zhu,
M. H. Liu* ——— 4122 – 4126

Self-Assembly of Racemic Alanine Derivatives: Unexpected Chiral Twist and Enhanced Capacity for the Discrimination of Chiral Species

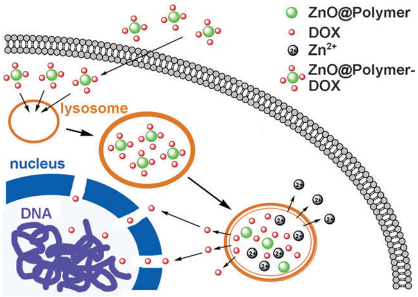


Twisted ribbons were formed by the self-assembly of racemic alanine derivatives (middle picture), whereas only flat nanostructures were obtained from the individual enantiomers (left). The twist was sensitive to a slight enantiomeric excess and showed remarkable macroscopic chirality. Moreover, it could discriminate various amino acid derivatives (right) and even enabled the determination of the *ee* value of a mixed system.

Drug Delivery

Z.-Y. Zhang, Y.-D. Xu, Y.-Y. Ma, L.-L. Qiu, Y. Wang, J.-L. Kong,* H.-M. Xiong* ———— **4127 – 4131**

Biodegradable ZnO@polymer Core–Shell Nanocarriers: pH-Triggered Release of Doxorubicin In Vitro

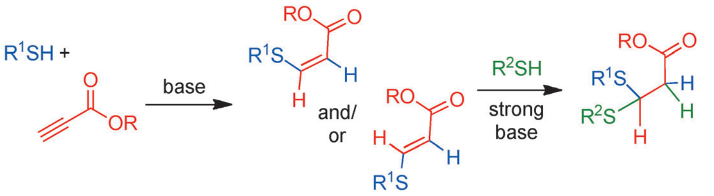


Luminescent ZnO@polymer core–shell nanoparticles were synthesized and loaded with doxorubicin (DOX) for the treatment of human brain cancer cells. Analyses by confocal laser scanning microscopy proved that the ZnO@polymer–DOX nanocomposites were decomposed at lysosomes to release DOX molecules, which penetrated into the nucleus and finally killed the cells (see picture).

Click Chemistry

V. X. Truong, A. P. Dove* ———— **4132 – 4136**

Organocatalytic, Regioselective Nucleophilic “Click” Addition of Thiols to Propiolic Acid Esters for Polymer–Polymer Coupling

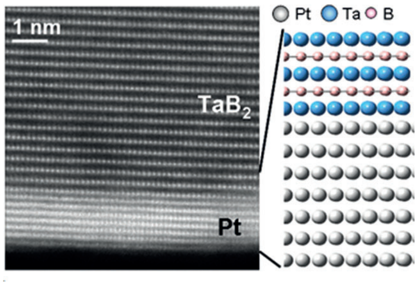


Discerning Tastes: The regioselectivity of the nucleophilic addition of thiols to electron-deficient alkynes is controlled by the choice of the solvent (i.e. the polarity of the reaction mixture) and the catalyst. Both thioalkenes and dithianes can be prepared in a rapid reaction that generates no by-products (see scheme). In turn the utility of this reaction is shown for efficient end-group modification of polymers.

Thin-Film Electrodes

E. Toyoda,* R. Jinnouchi, T. Ohsuna, T. Hatanaka, T. Aizawa, S. Otani, Y. Kido, Y. Morimoto ———— **4137 – 4140**

Catalytic Activity of Pt/TaB$_2$(0001) for the Oxygen Reduction Reaction

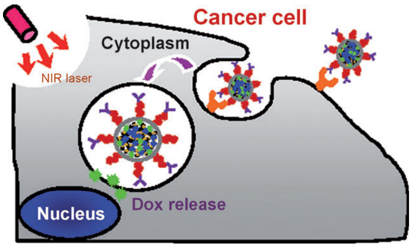


A great film with special effects: An epitaxial Pt thin film with a thickness of 1.5 nm on a TaB$_2$(0001) substrate (see high-angle annular dark-field STEM image) was tested as an electrocatalyst for the oxygen reduction reaction. Its specific activity was twice that observed for polycrystalline Pt or Pt(111). Analysis and DFT calculations showed that the Pt layer is alloyed with Ta, the electronic effect of which on Pt leads to the enhanced activity.

Cancer Nanotechnology

J.-O. You, P. Guo, D. T. Auguste* ———— **4141 – 4146**

A Drug-Delivery Vehicle Combining the Targeting and Thermal Ablation of HER2+ Breast-Cancer Cells with Triggered Drug Release

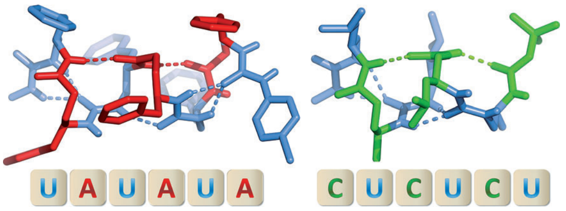


Covering all three bases: Drug-delivery vehicles that encapsulate doxorubicin (Dox) within a pH-sensitive matrix embedded with gold nanoparticles were synthesized with Herceptin–poly(ethylene glycol) conjugates on the surface for the specific binding of cancer cells (see picture; NIR = near infrared). Cell targeting was combined with enhanced cytotoxicity through triggered drug release (at pH 5–6) and thermal ablation (a photothermal effect).

Peptidomimetics

N. Pendem, Y. R. Nelli, C. Douat,
L. Fischer, M. Laguerre, E. Ennifar,
B. Kauffmann,
G. Guichard* ____________ **4147 – 4151**

Controlling Helix Formation in the γ-Peptide Superfamily: Heterogeneous Foldamers with Urea/Amide and Urea/Carbamate Backbones

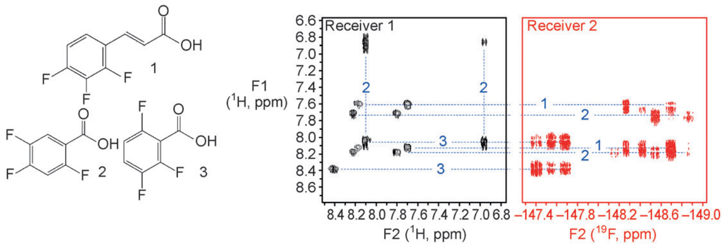


One fold to rule them all: New heterogeneous aliphatic backbone foldamers belonging to the γ-peptide superfamily and containing various combinations of urea/amide (U/A) and urea/carbamate (U/C) units are reported. Structural studies at atomic resolution reveal hydrogen-bonded helical structures akin to that formed by cognate U_n homo-oligomers.

NMR Spectroscopy

K. J. Donovan, E. Kupče,
L. Frydman* ____________ **4152 – 4155**

Multiple Parallel 2D NMR Acquisitions in a Single Scan

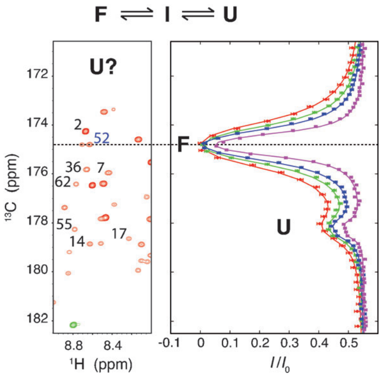


Faster than ultrafast: A new sequence combining "ultrafast" single-shot 2D NMR and parallel receiving technologies is presented. The potential of the resulting parallel ultrafast 2D spectroscopy (PUFSY) NMR experiments is shown by simultaneously collecting homo- and heteronuclear correlation information for ^{1}H–^{19}F systems (see picture) and a ^{1}H–^{31}P system.

Protein Dynamics

P. Vallurupalli,* L. E. Kay* __ **4156 – 4159**

Probing Slow Chemical Exchange at Carbonyl Sites in Proteins by Chemical Exchange Saturation Transfer NMR Spectroscopy

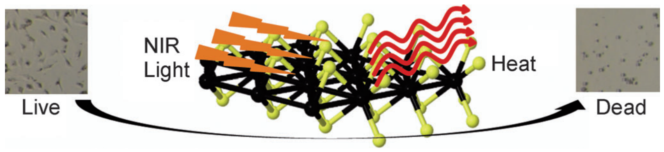


Seeing the invisible: A ^{13}CO NMR chemical exchange saturation transfer (CEST) experiment for the study of "invisible" excited protein states with lifetimes on the order of 5–50 ms has been developed. The ^{13}CO chemical shifts together with those obtained from fits of ^{15}N CEST profiles establish that the A39G FF domain folds via a similar compact intermediate (I) as the wild-type protein (F and U = native and unfolded states).

Organic–Inorganic Hybrid Composites

S. S. Chou,* B. Kaehr,* J. Kim, B. M. Foley,
M. De, P. E. Hopkins, J. Huang,
C. J. Brinker, V. P. Dravid __ **4160 – 4164**

Chemically Exfoliated MoS_2 as Near-Infrared Photothermal Agents

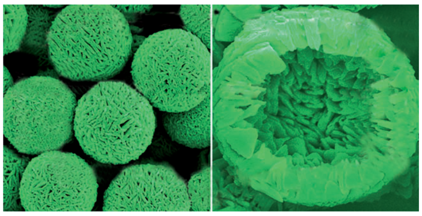


Two-dimensional bio-dynamite: Chemically exfoliated MoS_2 (ceMoS_2), a water-dispersible sheet-like material, is an efficient near-infrared (NIR) photothermal transducer. The superior bio-supramolecular properties of ceMoS_2 and the ability of this material to destroy biomolecular targets through near-infrared (NIR) photothermal transduction were studied (see picture).

Hierarchical Microstructures

B. Wang, H. B. Wu, L. Zhang, X. W. Lou* **4165 – 4168**

Self-Supported Construction of Uniform Fe_3O_4 Hollow Microspheres from Nanoplate Building Blocks



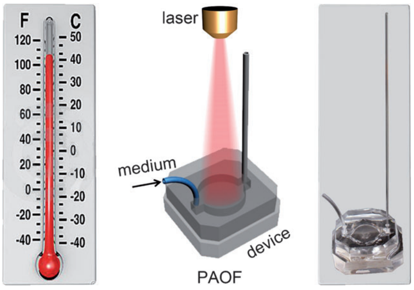
As alike as two peas in a pod: Hollow iron-containing microspheres composed of nanoplate-like building blocks were synthesized by a straightforward strategy and readily converted into magnetic Fe_3O_4 hollow microspheres (see images) without noticeable structural deformation. These Fe_3O_4 microspheres exhibited high reversible capacity and excellent cycling performance when evaluated as an anode material for lithium-ion batteries.

Optofluidics

J. Zeng, D. Goldfeld, Y. Xia* **4169 – 4173**

A Plasmon-Assisted Optofluidic (PAOF) System for Measuring the Photothermal Conversion Efficiencies of Gold Nanostructures and Controlling an Electrical Switch

“Photothermometer”: A PAOF system was constructed using a diode laser as the energy source, an aqueous suspension of plasmonic nanostructures as the photothermal transducer, and a glass capillary for measuring the volumetric expansion of the suspension (see picture). The suspension could be driven to move up the capillary by more than 30 mm and be used to control the operation of an electrical switch.

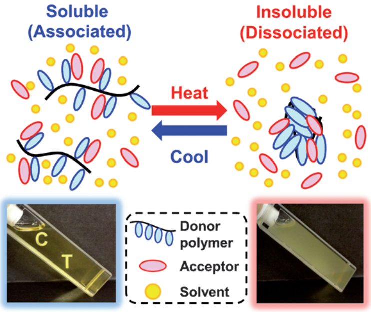


Thermoresponsive Polymers

S. Amemori, K. Kokado, K. Sada* **4174 – 4178**

Polymer Phase-Transition Behavior Driven by a Charge-Transfer Interaction

Cool down and get it together! The lower critical solution temperature (LCST) behavior of a polymer containing pyrene units was controlled by a charge-transfer (CT) interaction with an electron-accepting effector (see picture). The appearance of CT bands enabled quantitative evaluation of the thermodynamics of the association.



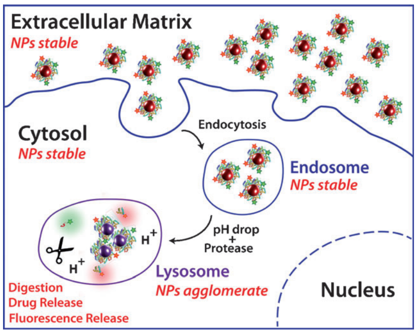
Inside Back Cover

Enzymatic Drug Release

M. Chanana,* P. Rivera_Gil, M. A. Correa-Duarte, L. M. Liz-Marzán, W. J. Parak* **4179 – 4183**

Physicochemical Properties of Protein-Coated Gold Nanoparticles in Biological Fluids and Cells before and after Proteolytic Digestion

What’s going on in there?! Little is known about the fate of nanoparticles (NPs) after their internalization by cells and organisms. Protein-coated gold NPs were used to study the physicochemical properties of NPs in extra- and intracellular fluids. These potential vehicles for enzymatic drug delivery were highly stable at pH 7.4 in the presence of salts and free proteins, but agglomerated reversibly under acidic conditions (see picture).

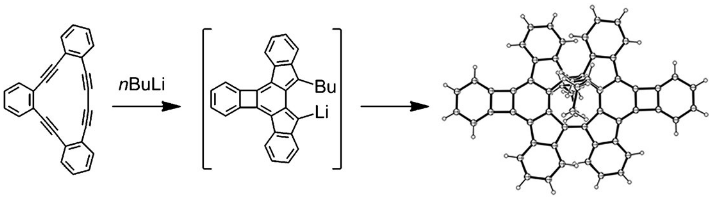


Polycycles

S. Nobusue, A. Shimizu, K. Hori, I. Hisaki, M. Miyata, Y. Tobe* ______ **4184 – 4188**

Oxidative Cyclodimerization After Tandem Cyclization of Dehydrobenzo[14]-annulenes Induced by Alkyllithium

Inside Cover



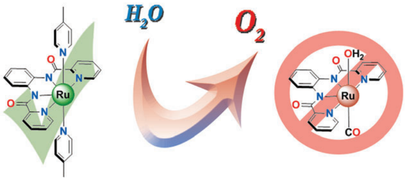
After eight: Reactions of dehydrobenzo-[14]annulenes induced by the addition of *n*-butyllithium led to the discovery of an unprecedented oxidative cyclodimerization, which forms eight-membered ring products in up to 30% yield. The product contains two indeno[2,1-*a*]fluorene components connected by a single and a double bond, which result from three transannular bond formations.

Oxidation of Water

M. D. Kärkäs, T. Åkermark, H. Chen, J. Sun, B. Åkermark* ______ **4189 – 4193**

A Tailor-Made Molecular Ruthenium Catalyst for the Oxidation of Water and Its Deactivation through Poisoning by Carbon Monoxide

Back Cover



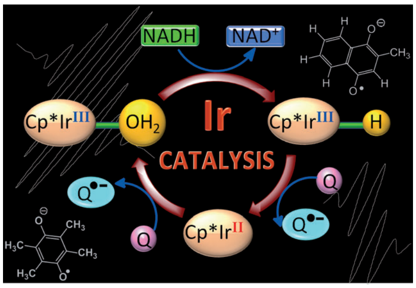
No CO-operation: Two single-site ruthenium complexes, based on a tetradentate ligand, despite structural similarities, display a remarkable difference in their catalytic and chemical behavior (see picture). The fact that the CO-containing complex is formed in the catalytic oxidation of water suggests a novel pathway for the deactivation of ruthenium-based catalysts.

Quinone Reduction

Z. Liu, R. J. Deeth, J. S. Butler, A. Habtemariam, M. E. Newton, P. J. Sadler* ______ **4194 – 4197**

Reduction of Quinones by NADH Catalyzed by Organoiridium Complexes

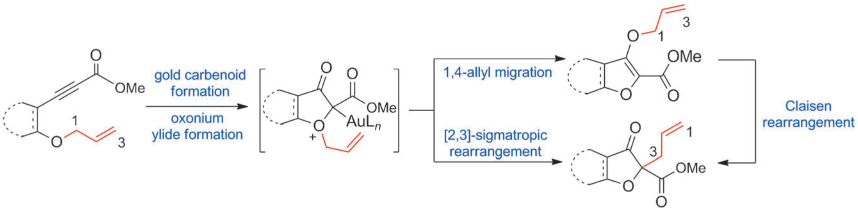
One electron at a time: Half-sandwich organometallic cyclopentadienyl–Ir^{III} complexes containing N,N-chelated ligands can catalyze the reduction of quinones (Q), such as vitamin K_3, to semiquinones ($Q^{\bullet-}$) by coenzyme NADH (see picture). DFT calculations suggest that the mechanism involves hydride transfer followed by two one-electron transfers and the unusual Ir^{II} oxidation state as a key transient intermediate.



Rearrangements

J. Fu, H. Shang, Z. Wang, L. Chang, W. Shao, Z. Yang,* Y. Tang* **4198 – 4202**

Gold-Catalyzed Rearrangement of Allylic Oxonium Ylides: Efficient Synthesis of Highly Functionalized Dihydrofuran-3-ones

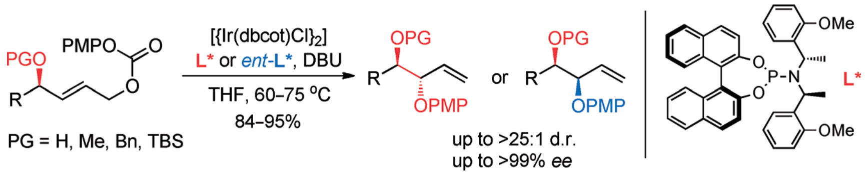


"Diazo" not needed: The title reaction results in the rearrangement of oxonium ylides, which were prepared from readily available homopropargylic allylic ethers instead of diazo compounds, through two different mechanisms: a concerted 2,3-sigmatropic rearrangement, or a stepwise 1,4-allyl migration followed by a Claisen rearrangement (see scheme).

Asymmetric Catalysis

D. Kim, J. S. Lee, S. B. Kong,
H. Han* ______________ 4203 – 4206

Cross-Metathesis/Iridium(I)-Catalyzed Allylic Etherification Strategy: (Iterative) Catalytic Asymmetric Synthesis of *syn*- and *anti*-1,2-Diols

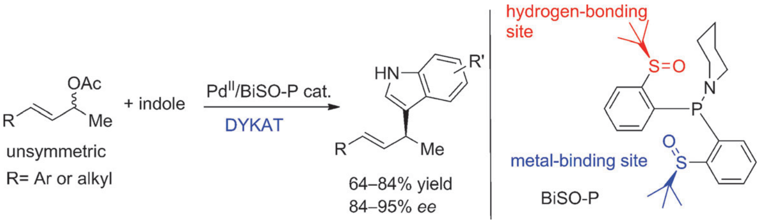


Protection optional: The title reaction strategy is used to prepare 1,2-diols with complete control of their absolute and relative stereochemistry. The method tolerates free and Me-/Bn-/TBS-protected alcohol functionalities, and its diastereoselectivity is controlled by the stereochemistry of the ligands/catalysts used. Protected 1,2,3,4-tetraols are synthesized by iterative applications of the strategy.

Asymmetric Catalysis

L. Du, P. Cao, J. W. Xing, Y. Z. Lou,
L. Y. Jiang, L. C. Li, J. Liao* _ 4207 – 4211

Hydrogen-Bond-Promoted Palladium Catalysis: Allylic Alkylation of Indoles with Unsymmetrical 1,3-Disubstituted Allyl Acetates Using Chiral Bis(sulfoxide) Phosphine Ligands

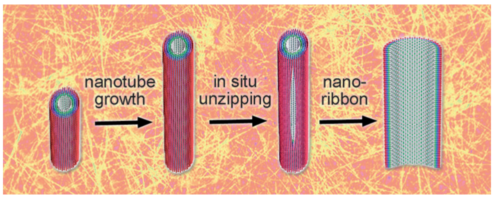


A DYKAT die hard: A new class of chiral BiSO-P ligands were effective for an unprecedented palladium-catalyzed asymmetric allylic alkylation of indoles with the racemic title acetates through a dynamic kinetic asymmetric transformation (DYKAT). The hydrogen bond formed between the sulfinyl group of the ligand and NH of indole plays an important role in the reaction.

Nanoribbons

L. Li, L. H. Li,* Y. Chen,* X. J. Dai,
P. R. Lamb, B.-M. Cheng, M.-Y. Lin,
X. Liu ______________ 4212 – 4216

High-Quality Boron Nitride Nanoribbons: Unzipping during Nanotube Synthesis

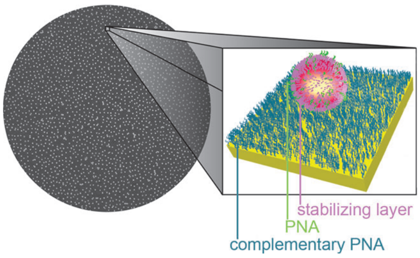


Zipper examined: High-quality boron nitride nanoribbons (BNNRs) can be produced directly during nanotube synthesis without post-treatment. These BNNRs are typically several micrometers long and tens of nanometers wide. Near-edge X-ray absorption fine structure investigations indicated that the BNNRs are of high chemical purity and crystallinity.

Gold Nanoparticles

P. Anstaett, Y. Zheng, T. Thai,
A. M. Funston, U. Bach,*
G. Gasser* ______________ 4217 – 4220

Synthesis of Stable Peptide Nucleic Acid-Modified Gold Nanoparticles and their Assembly onto Gold Surfaces

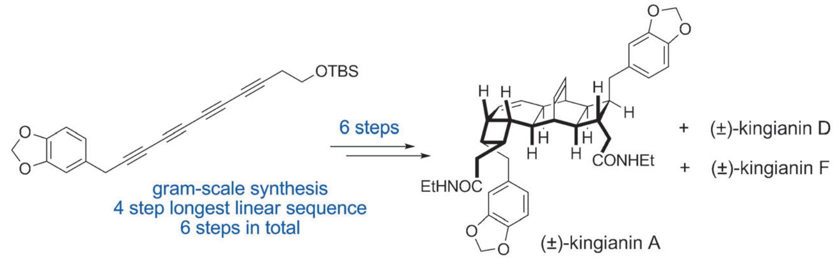


PNA does it better: Peptide nucleic acid (PNA) oligomers were attached to gold nanoparticles (AuNPs) through a variety of mono- and trithiol linkers. These functionalized particles had sufficient stability for sequence-specific self-assembly onto gold surfaces (see figure) in the absence of ions or surfactants. The nanoparticle surface densities obtained were superior to comparable DNA-modified AuNPs.

Biomimetic Synthesis

S. L. Drew, A. L. Lawrence,*
M. S. Sherburn* ________ **4221 – 4224**

Total Synthesis of Kingianins A, D, and F

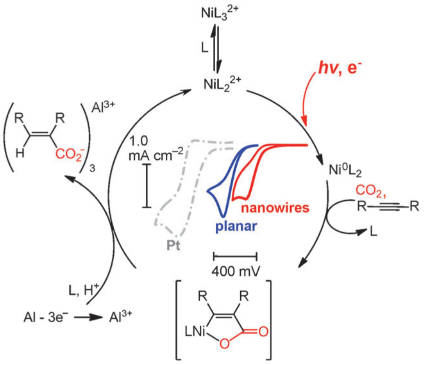


A synthesis fit for a king: The total synthesis of (±)-kingianins A, D, and F has been achieved in ten steps. Key features include the gram-scale synthesis and partial reduction of a conjugated tetrayne to a (*Z*,*Z*,*Z*,*Z*)-tetraene, the domino 8π–6π electrocyclic ring closure of a (*Z*,*Z*,*Z*,*Z*)-tetraene, and the radical-cation-catalyzed formal Diels–Alder dimerization of functionalized bicyclo[4.2.0]octadiene precursors.

Photosynthesis

R. Liu, C. Stephani, J. J. Han, K. L. Tan,*
D. Wang* ________ **4225 – 4228**

Silicon Nanowires Show Improved Performance as Photocathode for Catalyzed Carbon Dioxide Photofixation

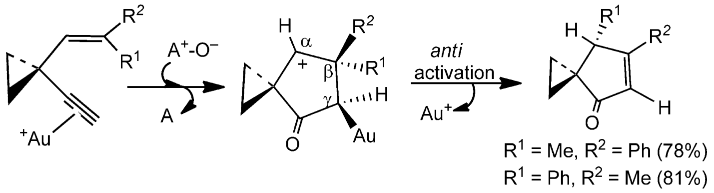


Wired: With silicon as a photocathode and [Ni(bpy)$_2$] as a catalyst, visible light-powered CO_2 photofixation is made possible (see picture). Owing to their multifaceted surfaces, silicon nanowires show a significantly better performance compared to planar Si. The shape of a nanowire is indeed an appealing materials choice for high-efficiency, low-cost solar energy conversion applications.

Rearrangement

S. Ghorpade, M.-D. Su,*
R.-S. Liu* ________ **4229 – 4234**

Gold-Catalyzed Oxidative Cyclizations on 1,4-Enynes: Evidence for a γ-Substituent Effect on Wagner–Meerwein Rearrangements

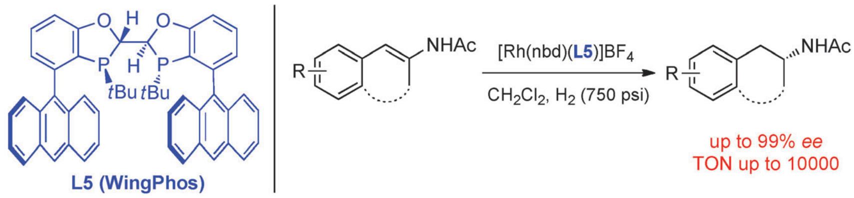


Gold-catalyzed oxidative cyclizations of 1,4-enynes were used to study the γ-effect on the Wagner–Meerwein rearrangement. Both experimental and theoretical work disclose that a gold substituent in the γ-position can direct a stereospecific 1,2-shift of the *anti*-β-substituent regardless of its intrinsic properties.

Homogeneous Catalysis

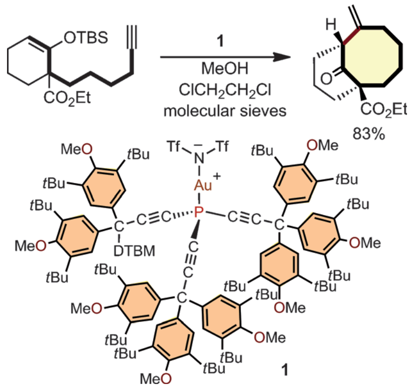
G. Liu, X. Liu, Z. Cai, G. Jiao, G. Xu,
W. Tang* ________ **4235 – 4238**

Design of Phosphorus Ligands with Deep Chiral Pockets: Practical Synthesis of Chiral β-Arylamines by Asymmetric Hydrogenation



WingPhos, a C_2-symmetric bisphosphorus ligand with a deep and well-defined chiral pocket was developed. It has shown high efficiency in the rhodium-catalyzed asymmetric hydrogenation of (*E*)-β-aryl-*N*-acetyl enamides, cyclic β-aryl enamides, and heterocyclic β-aryl enamides. A series of chiral β-arylisopropylamines, 2-aminotetralines, and 3-aminochromans can be synthesized with excellent *ee* values (nbd = 3,5-norbornadiene; TON = turnover number).

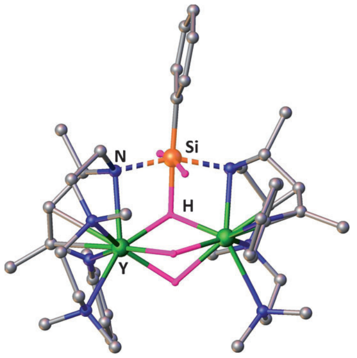
Semihollow triethynylphosphanes were synthesized and employed as ligands in the gold-catalyzed 8-*exo*-dig cyclization of acetylene-tethered silyl enol ethers to obtain eight-membered-ring carbocycles (see scheme). The gold–phosphane catalysts promoted either the annulation toward bicyclic structures or the cyclization of acyclic molecules to form nonfused carbocycles. Tf = Trifluoromethylsulfonyl.



Cyclization

T. Iwai, H. Okochi, H. Ito, M. Sawamura* ________ **4239 – 4242**

Construction of Eight-Membered Carbocycles through Gold Catalysis with Acetylene-Tethered Silyl Enol Ethers

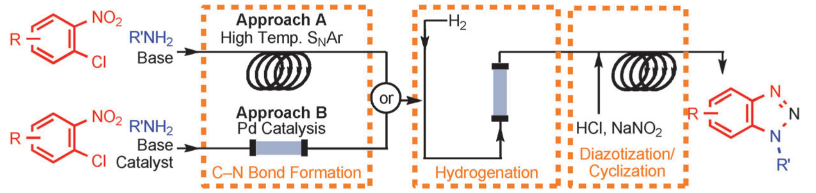


A structural model for the transition state of the σ-bond metathesis between Si—H and M—E bonds (M: d^0 transition metal) was obtained through the formation of an yttrium hydride–silane complex (see picture). The silane moiety can be either retained or released during the reactions of the complex with other substrates.

Transition States

J. L. Zhou, J. X. Chu, Y. Y. Zhang, G. Yang, X. B. Leng, Y. F. Chen* ____ **4243 – 4246**

An Yttrium Hydride–Silane Complex as a Structural Model for a σ-Bond Metathesis Transition State

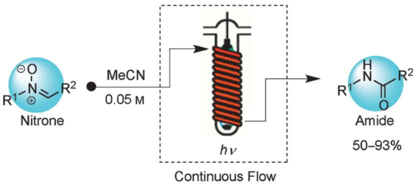


Two approaches have been developed for the regiospecific continuous-flow synthesis of 1-substituted benzotriazoles. They begin with either an S_NAr reaction at high temperature or Pd catalysis and involve consecutive multiphase processes, allowing the multistep synthesis of benzotriazoles to take place in an efficient manner (see picture).

Synthetic Methods

M. Chen, S. L. Buchwald* __ **4247 – 4250**

Continuous-Flow Synthesis of 1-Substituted Benzotriazoles from Chloronitrobenzenes and Amines in a C—N Bond Formation/Hydrogenation/ Diazotization/Cyclization Sequence



Go with the flow: A general approach for amide bond formation by way of a continuous-flow photochemical rearrangement of nitrones was described (see scheme). Simple aryl-alkyl amide bonds as well as complex peptide bonds were constructed efficiently with a residence time less than 20 minutes. A tetrapeptide was synthesized in this way and the method could be applied to peptide fragment coupling.

Synthetic Peptides

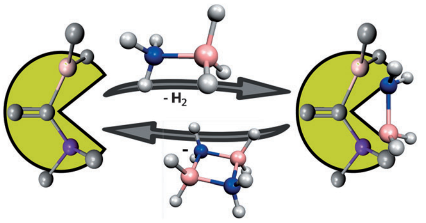
Y. Zhang, M. L. Blackman, A. B. Leduc, T. F. Jamison* ________ **4251 – 4255**

Peptide Fragment Coupling Using a Continuous-Flow Photochemical Rearrangement of Nitrones

Frustrated Lewis Pairs

C. Appelt, J. C. Slootweg,*
K. Lammertsma, W. Uhl* ___ **4256 – 4259**

Reaction of a P/Al-Based Frustrated Lewis Pair with Ammonia, Borane, and Amine–Boranes: Adduct Formation and Catalytic Dehydrogenation



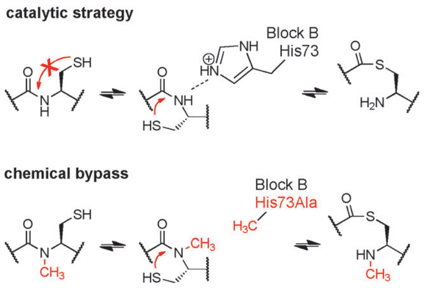
Open wide! The geminal P/Al-based frustrated Lewis pair $(Mes_2P)(tBu_2Al)C{=}C(H)Ph$ forms stable Lewis adducts with BH_3 and NH_3. This compound facilitates the dehydrocoupling of the ammonia–borane adduct by unusual N–H bond activation and elimination of dihydrogen at the boron center, and it is a very active main-group-based FLP catalyst for the dehydrogenation of amine–borane $H_3B{\cdot}NMe_2H$. Mes = mesityl.

Protein Chemistry

J. Binschik, H. D. Mootz* ___ **4260 – 4264**

Chemical Bypass of Intein-Catalyzed N–S Acyl Shift in Protein Splicing

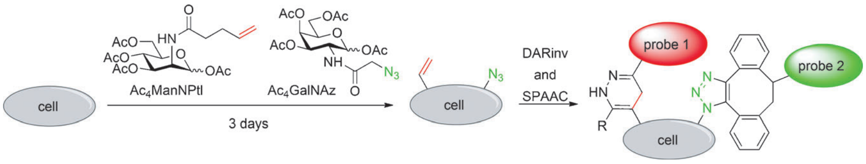
Spliced: An *N*-methyl group was introduced at the scissile peptide bond in a semisynthetic intein precursor. With the chemical modification, thioester formation and protein splicing was observed in the absence of the otherwise critical block B histidine. This finding shows the role of the histidine in ground-state destabilization and rules out other previously proposed roles for this residue in the protein splicing pathway.



Chemical Glycobiology

A. Niederwieser, A.-K. Späte,
L. D. Nguyen, C. Jüngst, W. Reutter,
V. Wittmann* ___ **4265 – 4268**

Two-Color Glycan Labeling of Live Cells by a Combination of Diels–Alder and Click Chemistry



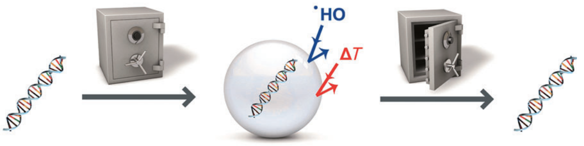
One is not enough: Terminal alkenes are used as chemical reporters and ligation partners for 1,2,4,5-tetrazines in a Diels–Alder reaction with inverse electron demand (DARinv). Combination with strain-promoted azide–alkyne cycloaddition (SPAAC) allows the visualization of two different glycan structures in one experiment.

Stable DNA

D. Paunescu, R. Fuhrer,
R. N. Grass* ___ **4269 – 4272**

Protection and Deprotection of DNA—High-Temperature Stability of Nucleic Acid Barcodes for Polymer Labeling

Front Cover



Tough to remove this label! When protected within a silica sphere, DNA can withstand high temperatures (up to 200 °C) and aggressive radical conditions. Following deprotection with HF, the DNA can be analyzed by standard biochemical methods. This DNA protection/deprotection scheme is compatible with standard polymer processing and can be used for labeling material of nonbiological origin.

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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