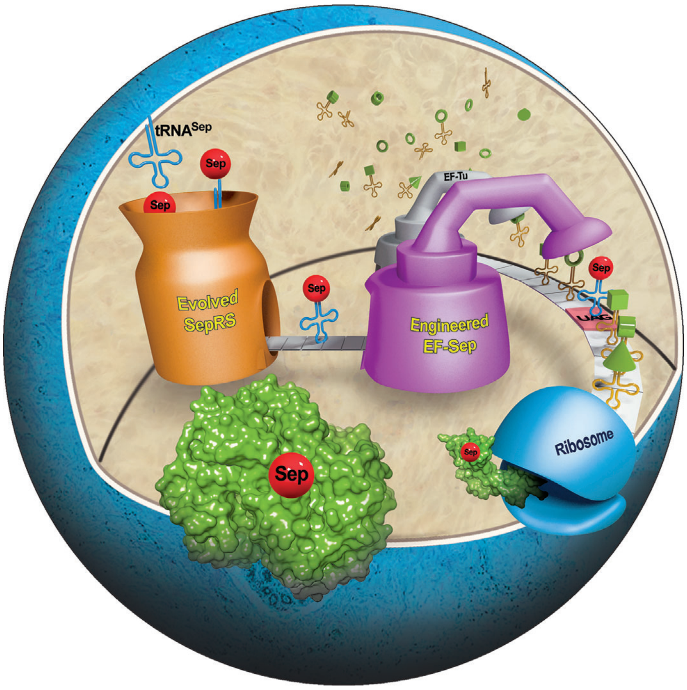
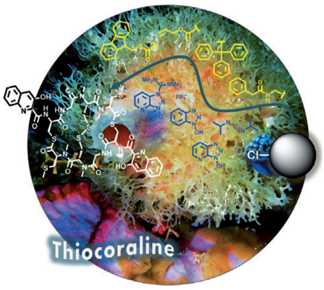
Selective phosphoserine incorporation …

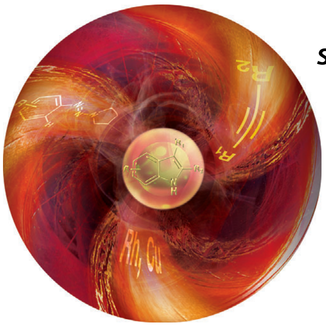


… is described by H.-S. Park et al. in their Communication on page 5771 ff. A general strategy for producing recombinant histones with site-specific serine phosphorylation has been developed by engineering phosphoseryl-tRNA synthethase (SepRS) and elongation factor Tu (EF-Tu). This method should facilitate the study of histone phosphorylation and cross-regulatory mechanisms.

Natural Products

In their Communication on page 5726 ff., J. Tulla-Puche, F. Albericio, et al. describe the solid-phase synthesis of the complex cyclothiodepsipeptide thiocoraline. The applied phenylacetamidomethyl protecting group was cleaved by an immobilized enzyme.



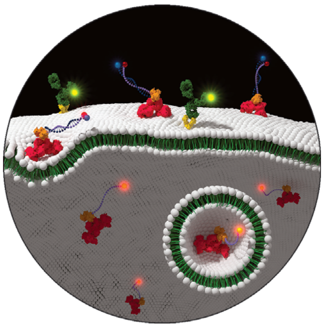


Synthetic Methods

In their Communication on page 5795 ff., Y. Huang et al. describe a general procedure for the synthesis of unprotected indoles. By using a cleavable triazene as the directing group, a C–H annulation with excellent regioselectivity was accomplished.

Cell Internalization

The internalization of proteins and nanoparticles in living cells can be quantified by using a new DNA nanosensor, as described by A. P. R. Johnston and H. Liu on page 5744 ff. This technique enables multicolor assays and studies in primary cells without compromising sensitivity or quantification.



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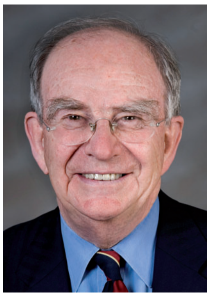
Editorial



"... In Great Britain and most probably also in other countries, a restoration of the proven qualities of intellectual freedom is mandatory. It has contributed so much to the culture, and facilitated the economic growth and the communal well-being, of the nation ..."
Read more in the Editorial by Sir John Meurig Thomas.

J. M. Thomas* ________ **5654–5655**

Intellectual Freedom in Academic Scientific Research under Threat

Service

Spotlight on Angewandte's Sister Journals **5672–5675**

Author Profile

"I chose chemistry as a career because it is so beautiful and yet still mysterious. I decided to be a chemist when I was 10 years old and I have never to this day regretted that rather early decision.
I would not want to use whatever luck I might have for the lottery but rather would like to use it for my work in chemistry ..."
This and more about Hisashi Yamamoto can be found on page 5678.

Hisashi Yamamoto ________ **5678–5679**

News

A. Imberty

I. Alves

D. Laurencin

G. Masson

M. Sliwa

CNRS Silver and Bronze Medals 2013 ________ **5680**

Books

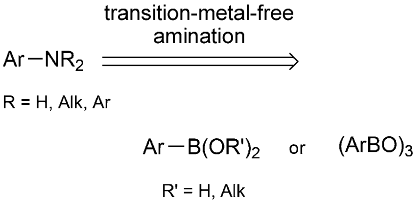
Prize Fight — Morton A. Myers — *reviewed by J. Labinger* ____________ **5681**

Highlights

Synthetic Methods

V. Coeffard, X. Moreau, C. Thomassigny, C. Greck* ____________ **5684 – 5686**

Transition-Metal-Free Amination of Aryl boronic Acids and Their Derivatives



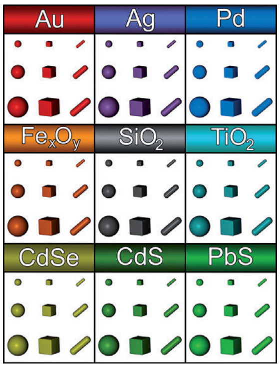
Free rein: Advances in transition-metal-free direct amination of aryl boronic acids and their derivatives have been recently described (see scheme). These reactions are based on the use of hydroxylamine or azide derivatives and offer great potential for further applications.

Essays

Programmable Atom Equivalents

R. J. Macfarlane, M. N. O'Brien, S. H. Petrosko, C. A. Mirkin* ____________ **5688 – 5698**

Nucleic Acid-Modified Nanostructures as Programmable Atom Equivalents: Forging a New "Table of Elements"



A nanoparticle-based analogue to the Periodic Table of the elements, where rather than arranging entries by electronic configuration, they are arranged by nanoscale architectural feature (e.g., composition, size, shape, and surface functionality). Using this table as a guide, the design considerations associated with using nucleic acids to assemble these nanoparticle-based programmable atom equivalents (PAEs) into superlattices is discussed.

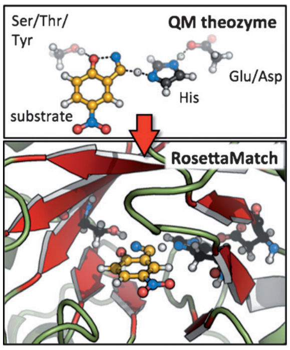
Reviews

Enzyme Design

G. Kiss, N. Çelebi-Ölçüm, R. Moretti, D. Baker, K. N. Houk* ____________ **5700 – 5725**

Computational Enzyme Design

The "inside-out" approach to computer-based enzyme design unites the newest developments in the areas of computational chemistry and biology. This has enabled the design of proteins that catalyze reactions not accelerated in nature. The achievements and limitations of the current technology are highlighted and compared to other methods.



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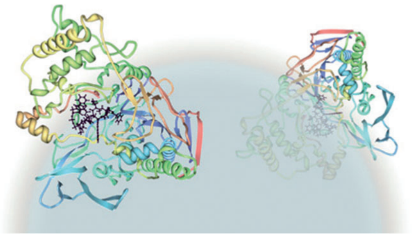
Communications

Natural Products

J. Tulla-Puche,* M. Góngora-Benítez,
N. Bayó-Puxan, A. M. Francesch,
C. Cuevas, F. Albericio* ____ **5726 – 5730**

Enzyme-Labile Protecting Groups for the Synthesis of Natural Products: Solid-Phase Synthesis of Thiocoraline

Frontispiece

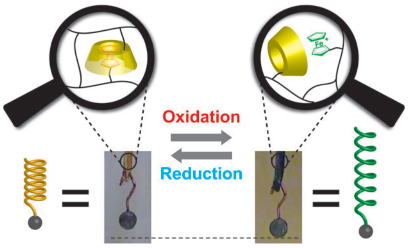


Another (orthogonal) dimension: The solid-phase synthesis of thiocoraline was accomplished for the first time by a combined approach involving chemical and enzymatic methods. One-pot cleavage of the phenylacetamidomethyl protecting group using immobilized penicillin G acylase enzyme (see picture) and disulfide formation are the key steps of the synthetic strategy.

Redox-Responsive Actuators

M. Nakahata, Y. Takashima,
A. Hashidzume, A. Harada* **5731 – 5735**

Redox-Generated Mechanical Motion of a Supramolecular Polymeric Actuator Based on Host–Guest Interactions

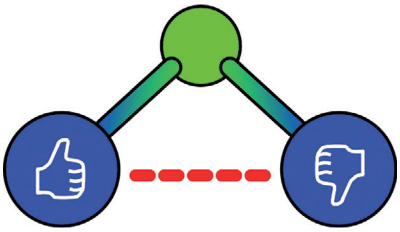


A supramolecular hydrogel is formed by a water-soluble polymer cross-linked with host–guest inclusion complexes between cyclodextrin and ferrocene. Dissociation and re-formation of inclusion complexes by redox stimuli lead to macroscale expansion and contraction of the hydrogel. The gel is utilized as a redox-responsive actuator and the mechanical work done is evaluated.

Biradicals

E. Miliordos, K. Ruedenberg,
S. S. Xantheas* __________ **5736 – 5739**

Unusual Inorganic Biradicals: A Theoretical Analysis

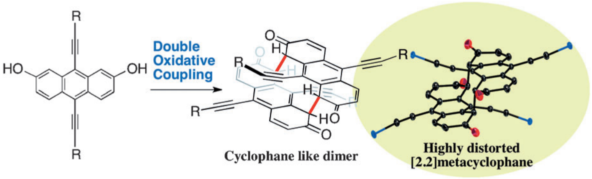


The biradical character β (1 for an ideal biradical) is determined from multi-reference configuration interaction (MRCI) wavefunctions. Triatomics in the series FX_2^+ ($X=O$, S, Se, Te, Po) exhibit unusually high biradical characters for $X=Te$, Po ($0.76<\beta<0.92$), the largest among the homologous 18 valence electron molecules CX_2^{2-}, NX_2^-, X_3, and OX_2. On the same scale, the biradical character of O_3 is just 0.19, whereas that of $C(CH_2)_3$ is 0.97.

Cyclophanes

Y. Koyama, S. Hiroto,*
H. Shinokubo* __________ **5740 – 5743**

Synthesis of Highly Distorted π-Extended [2.2]Metacyclophanes by Intermolecular Double Oxidative Coupling



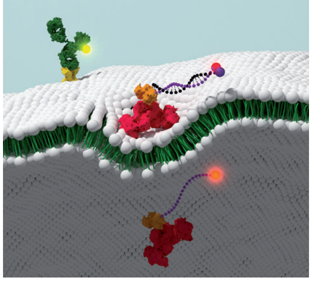
A strained relationship: Oxidation of dihydroxy-substituted acenes provides face-to-face [2.2]metacyclophane-like dimers (see scheme; O red, Si of iPr_3Si groups blue). The products exhibited highly distorted structures caused by steric repulsion. UV/Vis and electrochemical analysis revealed that the HOMO–LUMO gap was decreased upon dimerization.

Internalization Sensor

H. Liu, A. P. R. Johnston* — **5744 – 5748**

A Programmable Sensor to Probe the Internalization of Proteins and Nanoparticles in Live Cells

Back Cover

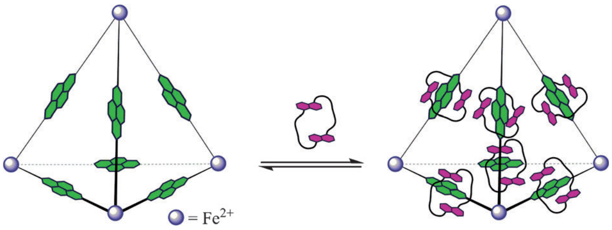


A molecular sensor has been developed to probe the internalization of proteins and nanoparticles into live cells. This simple, high-throughput technique is compatible with cell phenotyping and is independent of the cellular fate of the material.

Complex Catenanes

S. P. Black, A. R. Stefankiewicz,
M. M. J. Smulders, D. Sattler,
C. A. Schalley,* J. R. Nitschke,*
J. K. M. Sanders* — **5749 – 5752**

Generation of a Dynamic System of Three-Dimensional Tetrahedral Polycatenanes

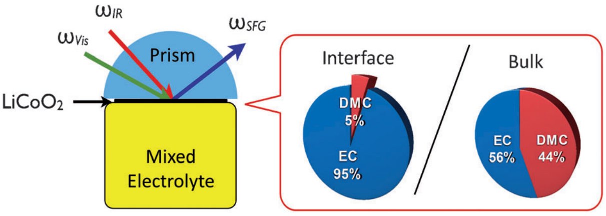


Seven of the best: A dynamic combinatorial library of polycatenated tetrahedra was prepared by complexation between a dynamic Fe_4L_6 tetrahedral cage, constructed from ligands containing an electron-deficient naphthalenediimide core, and an electron-rich aromatic crown ether, 1,5-dinaphtho[38]crown-10. The highest order species in the library is the tetrahedral [7]catenane.

Solvent Adsorption on $LiCoO_2$

L. Yu, H. Liu, Y. Wang, N. Kuwata,
M. Osawa, J. Kawamura,
S. Ye* — **5753 – 5756**

Preferential Adsorption of Solvents on the Cathode Surface of Lithium Ion Batteries

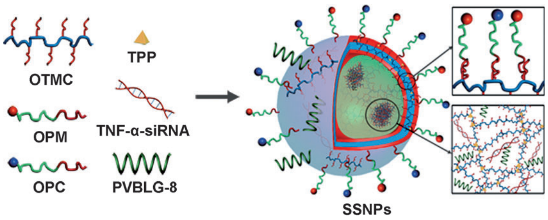


The adsorption structures of solvents on the surface of $LiCoO_2$, which is the most widely used cathode material for Li-ion batteries, in contact with nonaqueous electrolyte solutions of carbonate esters have been characterized by in situ sum frequency generation (SFG) spectroscopy. The cyclic carbonate of ethylene carbonate (EC) is preferentially adsorbed on the $LiCoO_2$ surface, in contrast to linear carbonates, such as dimethyl carbonate (DMC).

Oral Delivery of siRNA

L. Yin, Z. Song, Q. Qu, K. H. Kim,
N. Zheng, C. Yao, I. Chaudhury, H. Tang,
N. P. Gabrielson, F. M. Uckun,
J. Cheng* — **5757 – 5761**

Supramolecular Self-Assembled Nanoparticles Mediate Oral Delivery of Therapeutic TNF-α siRNA against Systemic Inflammation

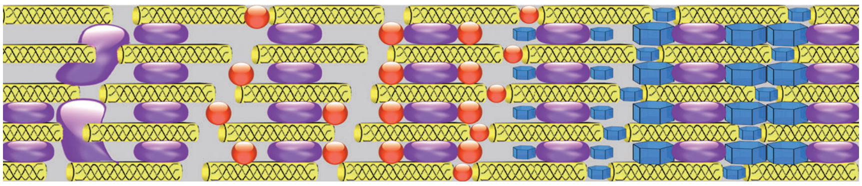


A functional package: Multifunctional supramolecular self-assembled nanoparticles (SSNPs) consist of a set of rationally designed components that collectively facilitate efficient intestinal absorption of siRNA and induce potent TNF-α silencing in macrophages. Single gavage of SSNPs in mice depletes systemic TNF-α production at an siRNA dose as low as 50 μg kg^{-1}, and thus protects mice from lipopolysaccharide-induced hepatic injury.

Biomineralization

L. N. Niu, K. Jiao, H. Ryou, C. K. Y. Yiu, J. H. Chen,* L. Breschi, D. D. Arola, D. H. Pashley, F. R. Tay* ——— **5762 – 5766**

Multiphase Intrafibrillar Mineralization of Collagen



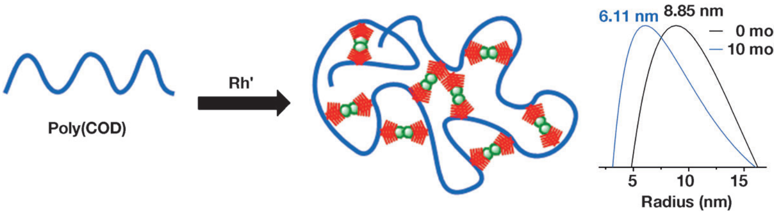
Why waste space? In the first stage of the multiphase biomineralization of collagen, silicic acid precursors (purple) infiltrated the collagen fibril (yellow) and condensed into amorphous silica to give a hierarchical composite. Amorphous calcium phosphate precursors (red) then filled the intrafibrillar spaces of the silicified collagen, where the precipitation and maturation of apatite crystallites (blue) occurred to complete the process.

Organometallic Nanoparticles

S. Mavila, C. E. Diesendruck, S. Linde, L. Amir, R. Shikler, N. G. Lemcoff* ——— **5767 – 5770**

Polycyclooctadiene Complexes of Rhodium(I): Direct Access to Organometallic Nanoparticles

Inside Cover



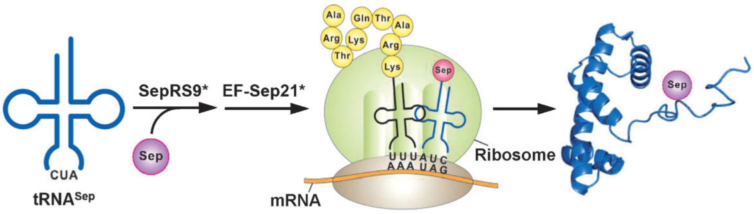
Content matters: The reaction of polycyclooctadiene (Poly(COD)) and $[\{RhCl(C_2H_4)_2\}_2]$ produced well-defined π-bound hybrid polymers, the size of which depended on rhodium content (see picture). The reaction of these polymers with a phosphine aldehyde led to the regeneration of the original polymers, thus proving the accessibility of the metal.

Protein Modifications

S. Lee, S. Oh, A. Yang, J. Kim, D. Söll, D. Lee,* H.-S. Park* ——— **5771 – 5775**

A Facile Strategy for Selective Incorporation of Phosphoserine into Histones

Front Cover



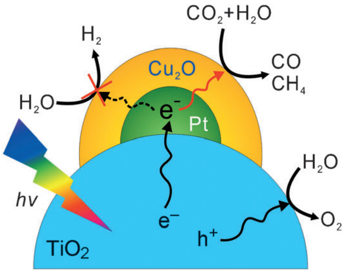
Phosphoserine incorporation: A general strategy for producing recombinant histones with site-specific serine phosphorylation is developed by engineering phosphoseryl-tRNA synthetase (SepRS) and elongation factor Tu (EF-Tu; see picture). Serine-phosphorylated nucleosomes provide direct evidence for crosstalk between phosphorylation and acetylation in histones.

Heterogeneous Catalysis

Q. Zhai, S. Xie, W. Fan, Q. Zhang,* Y. Wang, W. Deng, Y. Wang* **5776 – 5779**

Photocatalytic Conversion of Carbon Dioxide with Water into Methane: Platinum and Copper(I) Oxide Co-catalysts with a Core–Shell Structure

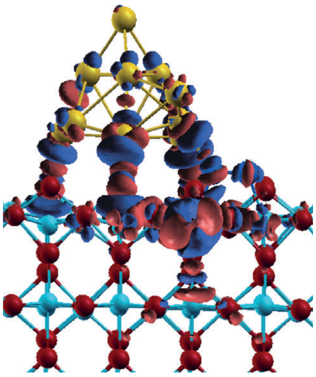
Binary co-catalysts of Pt and Cu_2O with a core–shell structure significantly enhance the photocatalytic reduction of CO_2 with H_2O to CH_4 and CO. The Cu_2O shell provides sites for the preferential activation and conversion of CO_2, whereas the Pt core extracts the photogenerated electrons from TiO_2. The deposition of Cu_2O shell on Pt nanoparticles markedly suppresses the reduction of H_2O to H_2 (see picture).



Selective Alcohol Oxidation

M. Farnesi Camellone,* J. Zhao, L. Jin, Y. Wang,* M. Muhler, D. Marx **5780 – 5784**

Molecular Understanding of Reactivity and Selectivity for Methanol Oxidation at the Au/TiO$_2$ Interface

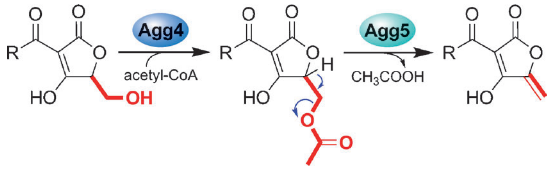


Gold catalysis: Experimental and theoretical data demonstrated consistently that the interfacial sites on a Au/TiO$_2$ catalyst show both high reactivity and selectivity for low-temperature methanol oxidation with O$_2$ to give formaldehyde. The microscopic mechanism of this complex reaction has been unraveled in full molecular detail (see picture, gold cluster on TiO$_2$ surface).

Tetronate Antibiotics

C. Kanchanabanca, W. Tao, H. Hong, Y. Liu, F. Hahn, M. Samborskyy, Z. Deng, Y. Sun,* P. F. Leadlay* **5785 – 5788**

Unusual Acetylation–Elimination in the Formation of Tetronate Antibiotics

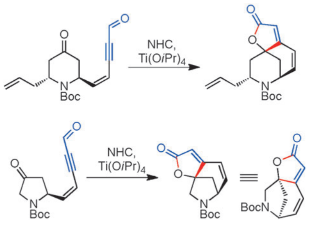


The identity and reactivity of the intermediates in agglomerin biosynthesis were established and the respective roles of the acetyltransferase Agg4 and the eliminating enzyme Agg5 identified (see scheme). It is proposed that enzymes homologous to Agg4 and Agg5 carry out the dehydration steps in all spirotetronate biosynthetic pathways. If this proves correct, it may assist engineering of these pathways.

Cooperative Catalysis

A. M. ElSohly, D. A. Wespe, T. J. Poore, S. A. Snyder* **5789 – 5794**

An Efficient Approach to the Securinega Alkaloids Empowered by Cooperative N-Heterocyclic Carbene/Lewis Acid Catalysis

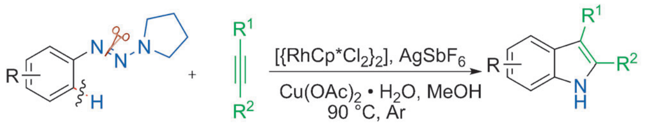


Folding it all together: Most of the syntheses developed for the securinega alkaloid class require lengthy sequences to create their bridging butenolide domains. A novel approach uses N-heterocyclic carbenes (NHCs) and Lewis acids to forge the entire domain in a single step from appropriate precursors, showing that ynal-derived homoenolates can participate as nucleophiles in intramolecular settings (see scheme).

Synthetic Methods

C. Wang, H. Sun, Y. Fang, Y. Huang* **5795 – 5798**

General and Efficient Synthesis of Indoles through Triazene-Directed C–H Annulation



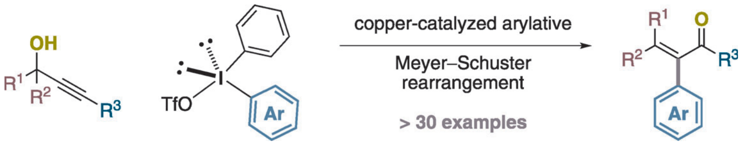
Unprotected indoles are prepared with the title method, which has a wide scope for alkynes. Excellent regioselectivity was accomplished for aryl–alkyl and alkyl–alkyl disubstituted acetylenes. This reaction features an unusual 1,2 rhodium migration and ring-contraction-triggered N–N bond cleavage. It allows rapid conversion of the reaction products into several functional molecules.

Inside Back Cover

Copper Catalysis

B. S. L. Collins, M. G. Suero,
M. J. Gaunt* ———— **5799 – 5802**

Copper-Catalyzed Arylative Meyer–Schuster Rearrangement of Propargylic Alcohols to Complex Enones Using Diaryliodonium Salts

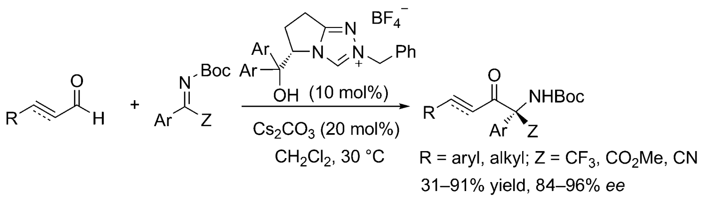


Free choice: A copper-catalyzed arylative Meyer–Schuster rearrangement is described. The reaction is compatible with a range of substituted propargylic alcohols and diaryliodonium salts and delivers complex trisubstituted enone products selectively as the *E* isomers.

Organocatalysis

L.-H. Sun, Z.-Q. Liang, W.-Q. Jia,
S. Ye* ———— **5803 – 5806**

Enantioselective N-Heterocyclic Carbene Catalyzed Aza-Benzoin Reaction of Enals with Activated Ketimines



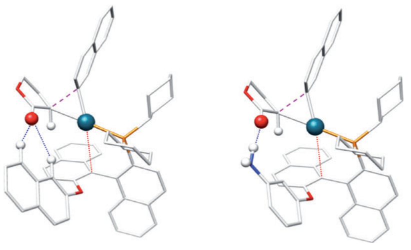
α-Amino ketones, which are versatile building blocks for organic synthesis, were obtained with the title reaction. A free hydroxy group on the NHC catalyst was found to be crucial for the reaction, and the possible competing reaction through a homoenolate or enolate was not observed with this catalyst (see scheme).

Cross-Coupling

Z. Huang, Z. Chen, L. H. Lim,
G. C. P. Quang, H. Hirao,
J. Zhou* ———— **5807 – 5812**

Weak Arene C–H···O Hydrogen Bonding in Palladium-Catalyzed Arylation and Vinylation of Lactones

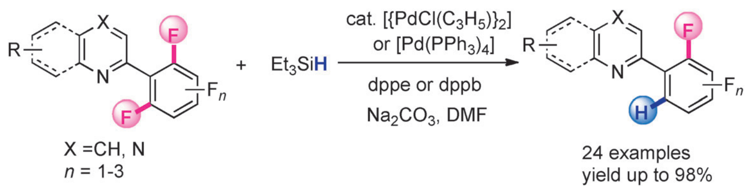
Weak force in action: In the title reaction, the palladium catalyst (see figure, left) uses weak CH···O hydrogen bonding to control the absolute configuration of the new stereocenter. A similar palladium catalyst (right) used conventional NH···O hydrogen bonding to guide stereoselection.



Catalytic C–F Activation

Z. Chen, C.-Y. He, Z. Yin, L. Chen, Y. He,
X. Zhang* ———— **5813 – 5817**

Palladium-Catalyzed *Ortho*-Selective C–F Activation of Polyfluoroarenes with Triethylsilane: A Facile Access to Partially Fluorinated Aromatics

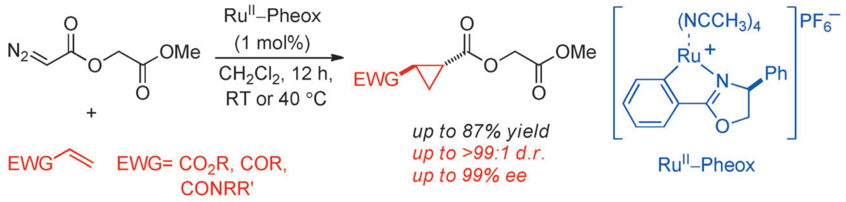


PdF: A simple catalytic system, broad substrate scope, and high versatility provide a useful and facile access to partially fluorinated aromatics (see scheme). Tuning the reaction conditions enables a diverse range of product structures to be prepared.

Heterogeneous Catalysis

S. Chanthamath, S. Takaki, K. Shibatomi, S. Iwasa* ______ **5818 – 5821**

Highly Stereoselective Cyclopropanation of α,β-Unsaturated Carbonyl Compounds with Methyl (Diazoacetoxy)acetate Catalyzed by a Chiral Ruthenium(II) Complex

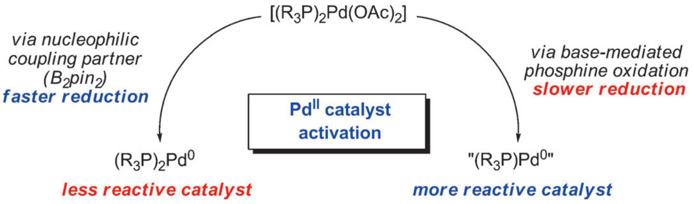


Tantalizing triangles: The title reaction gives bicarbonyl cyclopropane products that can lead to versatile intermediates with high yields and stereoselectivities. This system was also applied to the enantioselective total synthesis of spiro cyclopropane oxindole, an HIV-1 nonnucleoside reverse transcriptase inhibitor.

Catalyst Activation

C. S. Wei,* G. H. M. Davies, O. Soltani, J. Albrecht, Q. Gao, C. Pathirana, Y. Hsiao, S. Tummala, M. D. Eastgate **5822 – 5826**

The Impact of Palladium(II) Reduction Pathways on the Structure and Activity of Palladium(0) Catalysts

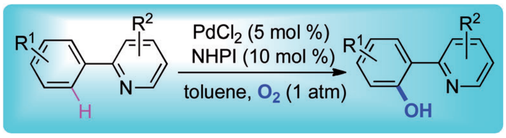


Two roads diverged: The mechanism of in situ Pd^{II} catalyst activation to generate an active $\{L_nPd^0\}$ catalyst from an air-stable Pd^{II} precursor was examined using the standard conditions of a Miyaura borylation reaction. Two pathways for catalyst activation exist under these conditions, producing two structurally and chemically distinct $\{L_nPd^0\}$ complexes (see scheme).

C–H Activation

Y. Yan, P. Feng, Q.-Z. Zheng, Y.-F. Liang, J.-F. Lu, Y. Cui, N. Jiao* ____ **5827 – 5831**

$PdCl_2$ and *N*-Hydroxyphthalimide Co-catalyzed C_{sp^2}–H Hydroxylation by Dioxygen Activation

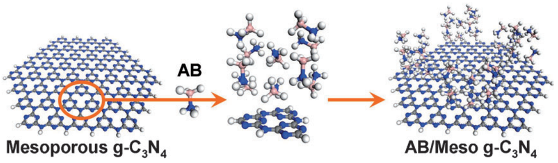


Rad transition: The combination of transition-metal-catalyzed C–H activation and a NHPI-initiated radical process is essential for the title transformation. The neutral conditions and the ideal oxidant, molecular oxygen, make this hydroxylation environmentally friendly and practical. NHPI = *N*-hydroxyphthalimide.

Hydrogen storage

Z. W. Tang, X. W. Chen, H. Chen, L. M. Wu, X. B. Yu* ______ **5832 – 5835**

Metal-Free Catalysis of Ammonia–Borane Dehydrogenation/Regeneration for a Highly Efficient and Facilely Recyclable Hydrogen-Storage Material

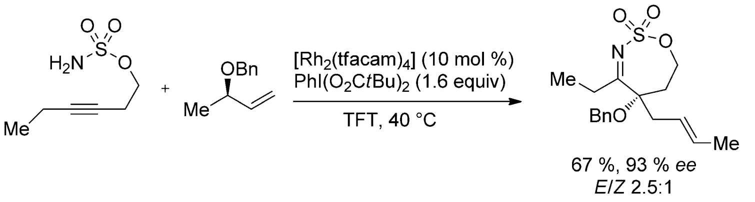


As easy as ABC: Mesoporous graphitic carbon nitride (MGCN; g-C_3N_4) is utilized to support ammonia borane (AB) on the basis of its accessible nanoporous structure and basic properties. A high loading of uniformly dispersed AB nanoparticles into the MGCN is possible giving greatly enhanced H_2 generation from AB, and facile regeneration cycles by a hydrazine hydrogenation process, even at room temperature.

Heterocycles

N. Mace, A. R. Thornton, S. B. Blakey* ________ **5836 – 5839**

Unveiling Latent α-Iminocarbene Reactivity for Intermolecular Cascade Reactions through Alkyne Oxidative Amination



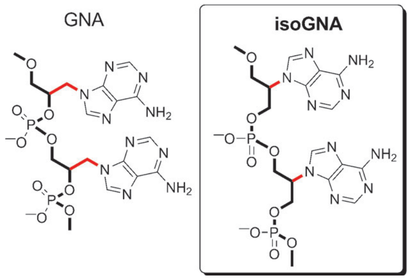
Setting a trap: Described is the development of a metallonitrene-initiated alkyne oxidation cascade with intermolecular trapping of the reactive intermediate with a variety of allyl ethers to provide α-oxyimine products in which new C=N, C–O, and C–C bonds have all been generated (see Scheme; tfacam = trifluoroacetamide).

Modified Nucleic Acids

P. Karri, V. Punna, K. Kim, R. Krishnamurthy* ________ **5840 – 5844**

Base-Pairing Properties of a Structural Isomer of Glycerol Nucleic Acid

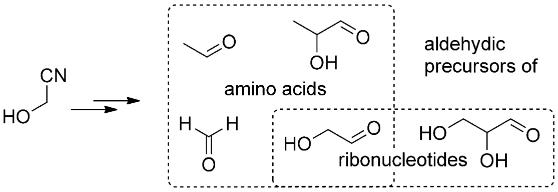
Know your limit! IsoGNA (a structural isomer of GNA) was found—in sharp contrast to GNA—to be highly restricted in its ability to base-pair with itself and other nucleic acids. While homogeneous sequences (e.g. isoGNA(A)$_{16}$) formed duplexes, the heterogeneous sequences showed no base-pairing. This exemplifies the limitations of canonical nucleobases as the recognition elements in simpler, more primitive phosphate backbones.



Prebiotic Systems Chemistry

D. J. Ritson, J. D. Sutherland* ________ **5845 – 5847**

Synthesis of Aldehydic Ribonucleotide and Amino Acid Precursors by Photoredox Chemistry

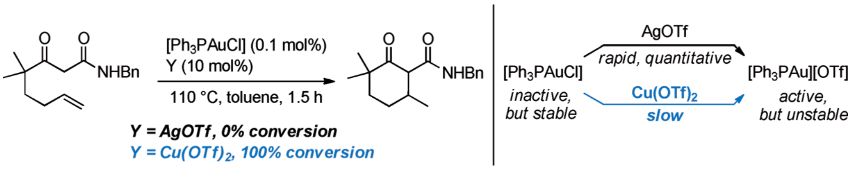


Light work: UV irradiation of a system formed by adding copper(I) cyanide to an aqueous solution of glycolonitrile, sodium phosphate, and hydrogen sulfide efficiently generates aldehyde precursors to the building blocks of RNA and proteins.

Gold Catalysis

A. Guérinot, W. Fang, M. Sircoglou, C. Bour, S. Bezzenine-Lafollée,* V. Gandon* ________ **5848 – 5852**

Copper Salts as Additives in Gold(I)-Catalyzed Reactions



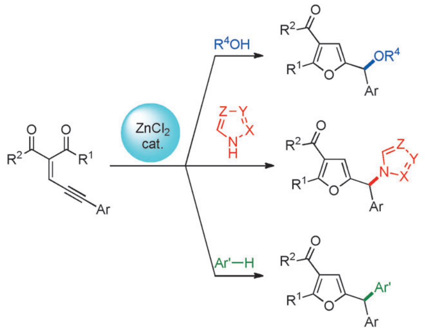
The right combination: Cu^{I} and Cu^{II} salts can advantageously replace silver additives in Au^{I}-catalyzed reactions. On the basis of reactivity studies and NMR experiments, it is believed that anion metathesis between CuY$_n$ (Y = OTf, BF$_4$, PF$_6$, SbF$_6$) and [R$_3$PAuCl] takes place to give [R$_3$PAu]Y. As this process is slow, there is no fast decay of the active species, thus allowing large-scale reactions, even at high temperatures, with low loadings of the gold complex.

Zinc Catalysis

J. González, J. González, C. Pérez-Calleja, L. A. López,* R. Vicente* **5853 – 5857**

Zinc-Catalyzed Synthesis of Functionalized Furans and Triarylmethanes from Enynones and Alcohols or Azoles: Dual X–H Bond Activation by Zinc

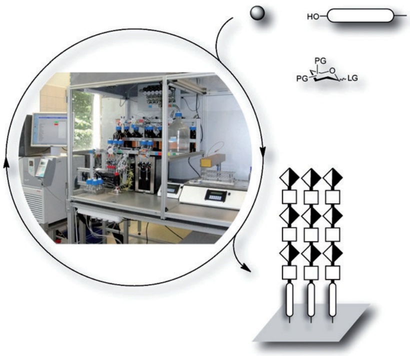
Ba'zinc'ga! A zinc-catalyzed sequence involving a cyclization with a subsequent C–O, C–N, or C–C bond formation enables the preparation of a variety of valuable furfuryl ethers (with alcohols) and unsymmetrically substituted triarylmethane derivatives (with azoles or arenes). $ZnCl_2$ serves as the catalyst.



Carbohydrate Synthesis (1)

S. Eller, M. Collot, J. Yin, H. S. Hahm, P. H. Seeberger* **5858 – 5861**

Automated Solid-Phase Synthesis of Chondroitin Sulfate Glycosaminoglycans

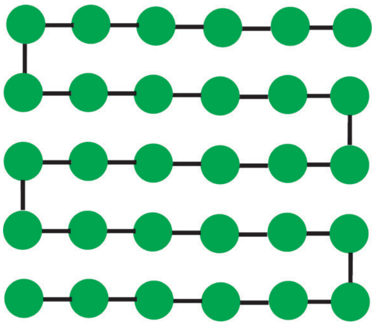


Glycosaminoglycans (GAGs) are important sulfated carbohydrates prevalent in the extracellular matrix. The synthesis of structurally defined GAGs requires laborious procedures, and incorporating defined sulfation patterns is challenging. The automated synthesis of defined sulfated chondroitin hexasaccharides on solid support has been achieved using a photolabile linker that is efficiently cleaved in a continuous-flow photoreactor.

Carbohydrate Synthesis (2)

O. Calin, S. Eller, P. H. Seeberger* **5862 – 5865**

Automated Polysaccharide Synthesis: Assembly of a 30mer Mannoside

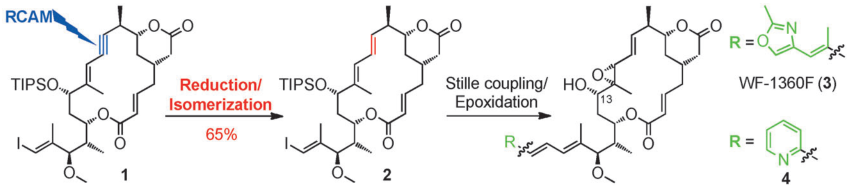


Automated carbohydrate synthesis breaks new grounds: The longest sugar chemically synthesized to date (a 30 mer) has been accessed. Key to the process is the use of a catch–release technique, which labels the saccharide, thus allowing it to be separated later through temporary attachement to magnetic particles.

Total Synthesis

C. M. Neuhaus, M. Liniger, M. Stieger, K.-H. Altmann* **5866 – 5870**

Total Synthesis of the Tubulin Inhibitor WF-1360F Based on Macrocycle Formation through Ring-Closing Alkyne Metathesis

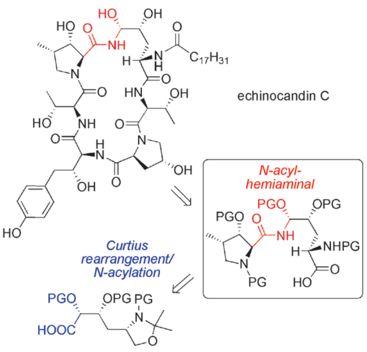


Key steps in this total synthesis of the antimitotic natural product WF-1360F (**3**) include the formation of the macrocycle through ring-closing alkyne metathesis and the subsequent conversion of the ensuing alkyne moiety into an *E*-configured double bond. As illustrated by the synthesis of **4**, the macrocyclic vinyl iodide **2** can also serve as a common precursor for the synthesis of side-chain-modified rhizoxin analogues (see scheme; TIPS = triisopropylsilyl).

Natural Product Synthesis

F. Messik, M. Oberthür* _______ 5871 – 5875

Total Synthesis of the Antifungal Agent Echinocandin C

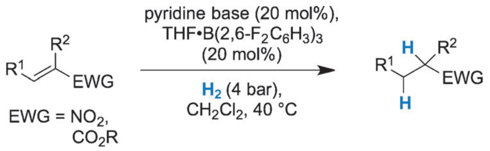


Reliably stable: A dipeptide building block with fully elaborated *N*-acyl hemiaminal proved to be a versatile precursor for echinocandin C, a prototypical member of the echinocandin group of antimycotic drugs. This first total synthesis of an *N*-acyl hemiaminal-containing echinocandin is concise and highly convergent, thereby making additional derivatives easily accessible. PG = protecting group.

Frustrated Lewis Pairs

L. Greb, C.-G. Daniliuc, K. Bergander,
J. Paradies* _______ 5876 – 5879

Functional-Group Tolerance in Frustrated Lewis Pairs: Hydrogenation of Nitroolefins and Acrylates

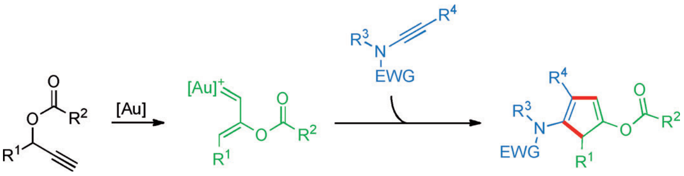


Weak Lewis acid for high nucleophilicity: Hydridoborate derived from B(2,6-$F_2C_6H_3)_3$ shows significant hydride character. Solid-state and solution structure analysis revealed a dihydrogen-bonded aggregate. The new frustrated Lewis pair was applied in the hydrogenation of nitroolefins and acrylates (see scheme; EWG = electron-withdrawing group). The decreased Lewis acidity provides higher reactivity and functional-group tolerance.

Gold Carbenoids

E. Rettenmeier, A. M. Schuster,
M. Rudolph, F. Rominger, C. A. Gade,
A. S. K. Hashmi* _______ 5880 – 5884

Gold Catalysis: Highly Functionalized Cyclopentadienes Prepared by Intermolecular Cyclization of Ynamides and Propargylic Carboxylates



When an ynamide meets a gold carbenoid: Highly electrophilic gold carbenoids available from propargylic esters by means of 1,2-acyloxy migration open up new reaction pathways for ynamide gold chemistry. In this way highly functionalized cyclopentadiene derivatives become accessible (see scheme; EWG = electron-withdrawing group).

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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Angewandte Corrigendum

Indium-Catalyzed Cycloisomerizations of Cyclopropene-3,3-Dicarbonyl Compounds: Efficient Access to Benzo-Fused Heteroaromatics and Heterobiaryls

L. H. Phun, J. Aponte-Guzman, S. France* ______ 3198–3202

Angew. Chem. Int. Ed. **2012**, *51*

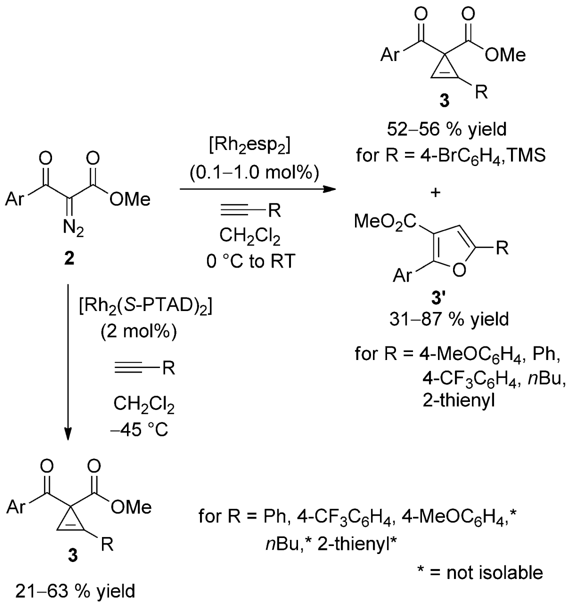
DOI: 10.1002/anie.201107717

Upon further 2D NMR spectroscopic studies, the authors of this Communication discovered that their initial assignment of several cyclopropenes was incorrect. Compounds **3a**, **3b**, and **3d**–**3m** are actually furan derivatives. Under the reported cyclopropenation conditions (with [Rh_2esp_2]), the product is either the furan or the cyclopropene, depending on the nature of the alkyne substituent: with R = 4-$MeOC_6H_4$, Ph, 4-$CF_3C_6H_4$, *n*Bu, and 2-thienyl, the furan **3′** is formed in 32–87% yield, while with R = 4-BrC_6H_4 and TMS, cyclopropenes **3a** and **3n** are formed in 56 and 52% yield, respectively (see the updated Scheme 2).

When the cyclopropenations are performed with [$Rh_2(Oct)_4$] or [Rh_2(*S*-PTAD)$_4$] at −45 °C, in each case the cyclopropenes were formed preferentially. However, cyclopropenes bearing electron-donating groups (4-$MeOC_6H_4$, *n*Bu, CH_2TMS, and 2-thienyl) could not be isolated by flash chromatography. These cyclopropenes can be generated in situ and reacted further.

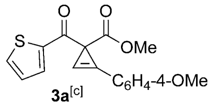
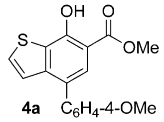
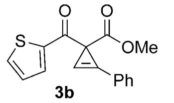
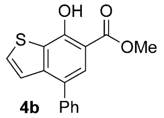
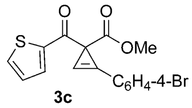
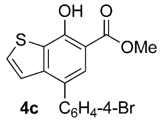
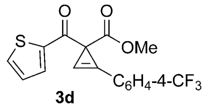
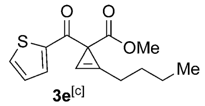
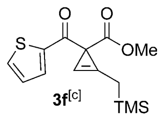
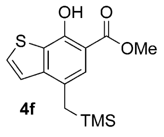
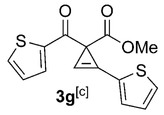
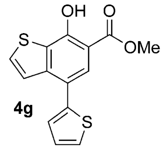
The furan derivatives undergo In(OTf)$_3$-catalyzed ring-opening and reorganization through zwitterionic intermediates to give the observed benzo-fused products. In relation to the hypothesis in the manuscript, the cyclopropene substrates do proceed to the benzo-fused products as reported in the manuscript (see updated Table 1).

The authors apologize for this mistake.



Scheme 2. Rhodium(II)-catalyzed cyclopropenation.

Table 1: In(OTf)$_3$-catalyzed cyclopropene cycloisomerizations.[a]

Entry	3	4	*t* [h]	Yield [%]
1	 **3a**[c]	 **4a**	12	15(86)[d]
2	 **3b**	 **4b**	8	63(86)[d]
3	 **3c**	 **4c**	12	86
4	 **3d**	–	24	–[e]
5	 **3e**[c]	–	24	–[e]
6	 **3f**[c]	 **4f**	7.5	29(68)[d]
7	 **3g**[c]	 **4g**	7	25(83)[d]

[a] Reactions run with cyclopropene (1 equiv) and In(OTf)$_3$ (5 mol%) in CH_2Cl_2 at 25 °C. [b] Yields of product isolated after column chromatography. [c] Not isolated and used crude due to instability. [d] Values in parentheses represent the yields obtained when the furan **3′** was employed under the reaction conditions. [e] No reaction after 24 h.