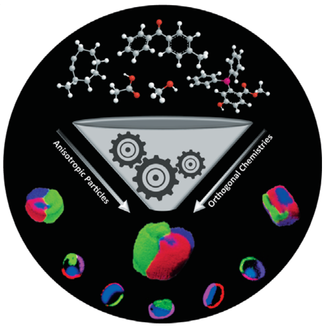
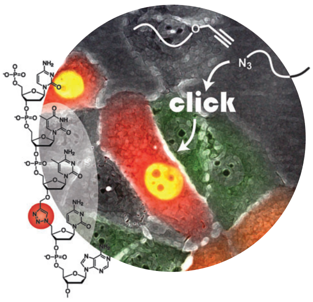
Resveratrol-based natural products …

… can be selectively synthesized by a novel highly modular approach. In their Communication on page 2473 ff., A. Studer and F. Klotter report the use of Pd-catalyzed decarboxylative arylation and an oxidative Heck reaction to introduce structurally important aryl groups to a common building block, which is readily available on a large scale. The modular approach is convincingly documented by the syntheses of quadrangularin A, ampelopsin D, and pallidol.

Microparticles

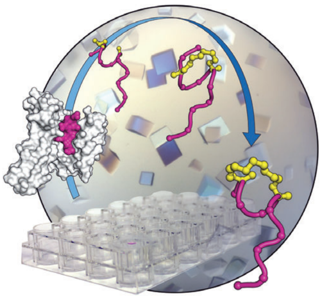
Using electrohydrodynamic co-jetting, microparticles with three different surface patches can be prepared. J. Lahann and co-workers show the bioorthogonal modification of each patch in their Communication on page 2332 ff.





Synthetic Biology

In their Communication on page 2362 ff., A. Tavassoli and co-workers report the correct transcription of click-linked DNA encoding the fluorescent protein mCherry, following microinjection of the click-linked gene into human cells.



PPI Inhibitors

In their Communication on page 2489 ff., T. N. Grossmann and co-workers use target-adapted cross-links to conformationally constrain peptides. The resulting macrocyclic peptides are inhibitors of the protein–protein interaction between the virulence factor ExoS and human protein 14-3-3.

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Service

Author Profile

"My worst nightmare is getting a terrible stomach ache from eating uncooked chicken.
My biggest motivation is to share the joy, success, and sometimes failure of research with my students ..."
This and more about Koji Hirano can be found on page 2276.

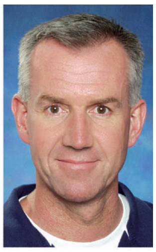
News


B. M. Trost


B. M. Hoffman


C. Toniolo


M. Kelso


C. Jones


S. Perrier


M. J. Crossley


D. W. Lupton


E. W. Meijer


C. A. Mirkin

Books

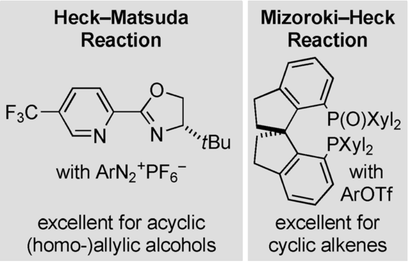
Highlights

Asymmetric Heck Reaction

M. Oestreich* ______ **2282 – 2285**

Breaking News on the Enantioselective Intermolecular Heck Reaction

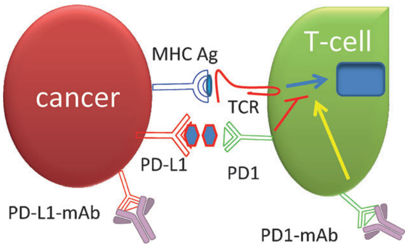
Glowing results with less phosphorus: Tremendous progress has been made recently in asymmetric intermolecular Heck chemistry. Previously unprecedented enantioselective Heck–Matsuda reactions have been accomplished, and mixed phosphine/phosphine oxides have been shown to be superior ligands in enantioselective Mizoroki–Heck reactions. All of this was achieved with chiral ligands containing few or even no phosphorus donors (see scheme).



Cancer Immunotherapy

A. Dömling,* T. A. Holak* _ **2286 – 2288**

Programmed Death-1: Therapeutic Success after More than 100 Years of Cancer Immunotherapy



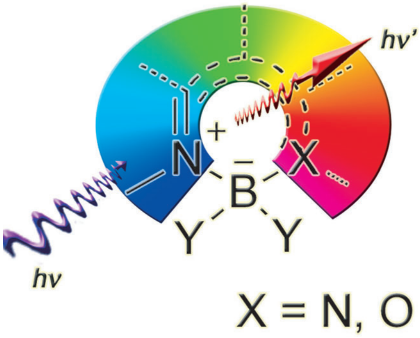
No other cancer therapy target class caused more excitement than the programmed death-1 (PD-1) pathway related. Antibodies against PD-1 and PD-1 ligands represent a therapeutic breakthrough and are the first examples of broadly efficacious and durable cancer immunotherapies. Cancer for the first time seems to have transformed from an often incurable to a "clinically manageable" disease.

Minireviews

Dyes/Pigments

D. Frath, J. Massue,* G. Ulrich,*
R. Ziessel* ______ **2290 – 2310**

Luminescent Materials: Locking π-Conjugated and Heterocyclic Ligands with Boron(III)



Dye by boron: N,N or N,O complexes of boron(III) are easy to prepare and handle, and they display outstanding fluorescence properties in both solution and the solid state. These novel dyes were classified by the number of atoms in the ring systems and by the number of aromatic rings participating in the π conjugation. The optical properties are discussed, and various applications in light-emitting devices as well as probes are anticipated.

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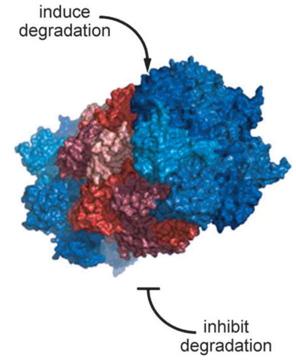
Reviews

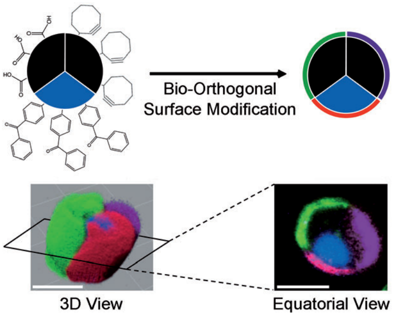
Targeted assault: With two FDA-approved proteasome inhibitors, the ubiquitin proteasome system (UPS) has established itself as a validated metabolic pathway for drug development. Recent advances include the development of inhibitors of alternative targets within the UPS that promise increased specificity, as well as the design of chemical inducers of targeted degradation by the UPS.



Drug Design

Communications

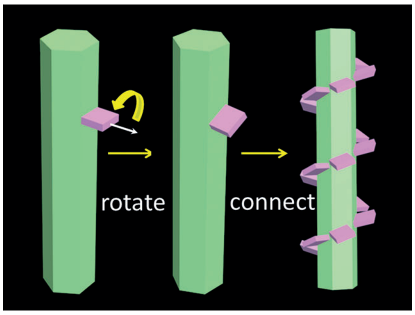
Patchwork family: Three-patch microparticles (see scheme) containing functionalized poly(lactide) derivatives in select compartments were fabricated through the electrohydrodynamic (EHD) co-jetting process. The microparticles were characterized by Raman confocal microspectroscopy and the bio-orthogonal surface modification of each patch was demonstrated.



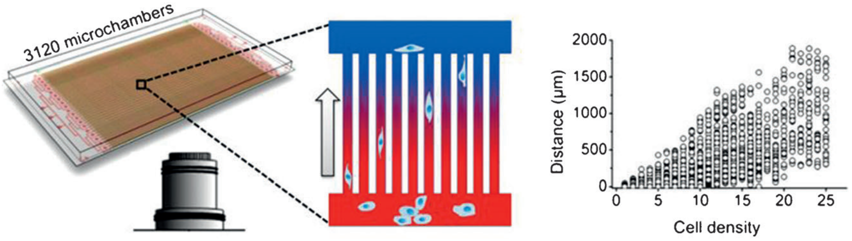
Bioactive Surfaces

Frontispiece

Rotate and connect! The shape evolution of a helical 1D/2D semiconductor nano-heterostructure (NHS) consisting of CdS and $ZnIn_2S_4$ is demonstrated. This NHS exhibits enhanced performance in photoelectrochemical cells, which is explained by the interface electronic states and the tailored band alignment.



Nano-Heterostructures



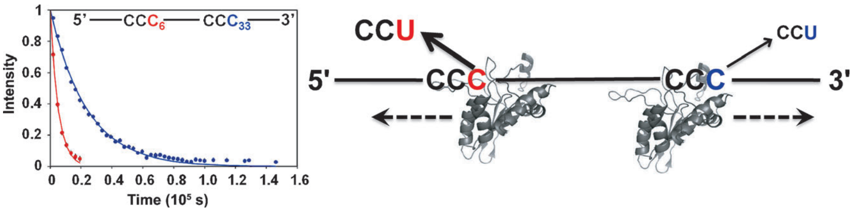
A high-throughput microfluidic chip with 3120 microchambers was used to monitor mesenchymal migration. Through imaging of the whole chip and statistical analysis (see picture), the percentage of migrating cells and the migration velocity were evaluated at different cell densities. The device was also used to screen drugs for their ability to inhibit mesenchymal migration and thus prevent metastatic malignancy.

Microfluidic Systems

Real-Time NMR Spectroscopy

A. Furukawa, K. Sugase, R. Morishita,
T. Nagata, T. Kodaki, A. Takaori-Kondo,
A. Ryo, M. Katahira* ______ **2349 – 2352**

Quantitative Analysis of Location- and Sequence-Dependent Deamination by APOBEC3G Using Real-Time NMR Spectroscopy



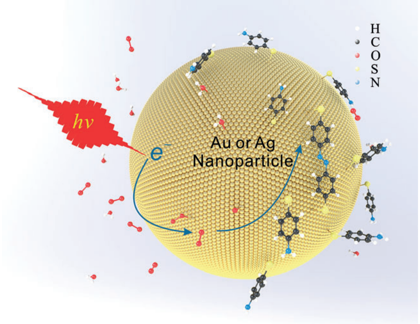
APOBEC3G (A3G) efficiently deaminates cytidines that are located close to the 5′ end of the single-stranded minus DNA of the HIV-1 genome. This process could be quantitatively analyzed using a newly developed real-time NMR spectroscopy method. As a result, the location-dependent deamination can be explained by two catalytic rate constants that depend on the direction of the approach to the target cytidine.

Catalysis

Y. F. Huang, M. Zhang, L. B. Zhao,
J. M. Feng, D. Y. Wu,* B. Ren,*
Z. Q. Tian ______ **2353 – 2357**

Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances

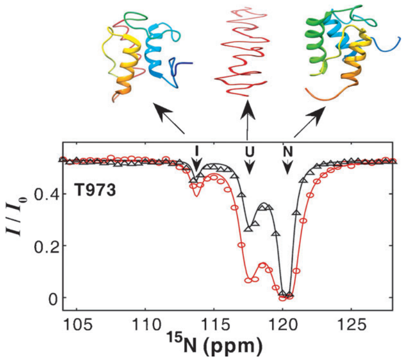
Plasmon-assisted reactions: Surface plasmon resonances (SPRs) support the activation of oxygen to yield metallic oxides and hydroxides on surfaces of Au and Ag nanoparticles, which selectively oxidize molecular species on the surface by laser light illumination. The electron donation to oxygen as well as a local heating effect in the presence of SPRs account for the activation of oxygen.



Protein Folding

J. Lim, T. Xiao, J. Fan,
D. Yang* ______ **2358 – 2361**

An Off-Pathway Folding Intermediate of an Acyl Carrier Protein Domain Coexists with the Folded and Unfolded States under Native Conditions



Neither U(p) nor (dow)N: Acyl carrier protein from *Micromonospora echinospora* adopts three conformations; one folded (N), one unfolded (U), and one intermediate (I). These undergo slow conformational exchange under native conditions. The intermediate state, which is an off-pathway rather than on-pathway product, may mediate the formation of oligomers in vitro and play an important role in the recognition of partner enzymes in vivo.

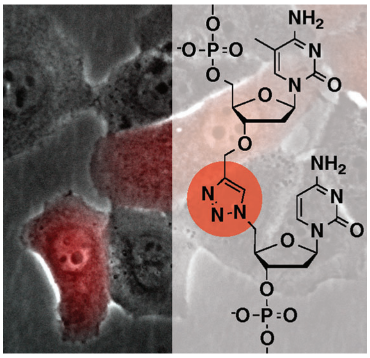
Synthetic Biology

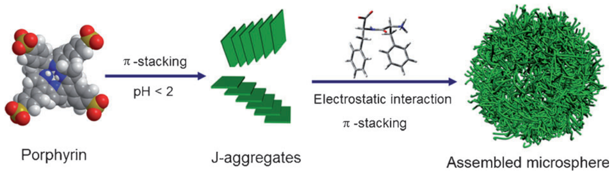
C. N. Birts, A. P. Sanzone,
A. H. El-Sagheer, J. P. Blaydes, T. Brown,
A. Tavassoli* ______ **2362 – 2365**

Transcription of Click-Linked DNA in Human Cells

Inside Back Cover

Just a click away: Human cells are shown to correctly transcribe through a non-natural DNA-backbone linker. Triazole-linked DNA encoding the red fluorescent protein mCherry is shown to be functional in human cells without the need for nucleotide excision repair. These results challenge the idea that a phosphodiester backbone is essential for the biological function of DNA and open up the possibility of total chemical synthesis of genes by click DNA ligation.





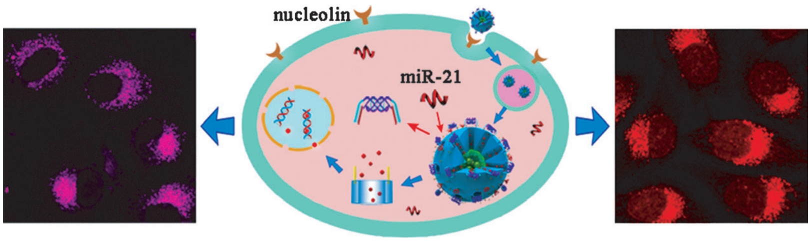
Simple but multifunctional: Photocatalytically active microspheres with highly hydrated, accessible multi-chambered interiors have been prepared by cooperative self-assembly of simple dipeptides and porphyrins (see picture). They serve as a plausible photosynthetic model that could be potentially developed towards studying aspects of primitive abiotic cellularity.

Self-Assembly

Q. Zou, L. Zhang, X. Yan,* A. Wang,
G. Ma, J. Li, H. Möhwald,
S. Mann* 2366 – 2370

Multifunctional Porous Microspheres Based on Peptide–Porphyrin Hierarchical Co-Assembly

---



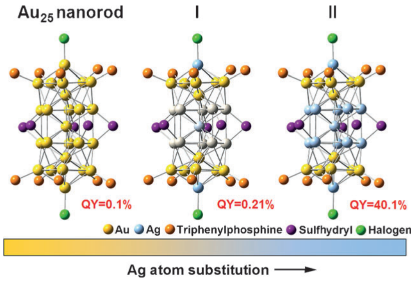
Endogenous uncapping key: A traceable, dual-targeted, and microRNA-controlled drug delivery system was constructed by capping a programmable DNA hybrid onto mesoporous silica-coated quantum dots. Once the nanocarriers had been delivered into the targeted HeLa cells by aptamer-mediated recognition and endocytosis, the overexpressed endogenous miR-21 served as an exclusive key to unlock the gate by competitive hybridization with DNA hybrids.

Drug Delivery

P. Zhang, F. Cheng, R. Zhou, J. Cao, J. Li,
C. Burda, Q. Min,*
J.-J. Zhu* 2371 – 2375

DNA-Hybrid-Gated Multifunctional Mesoporous Silica Nanocarriers for Dual-Targeted and MicroRNA-Responsive Controlled Drug Delivery

---



Shine on, you crazy cluster: Highly fluorescent, silver-doped Ag_xAu_{25-x} nanoclusters (**II**; $x=1$–13; QY = 40.1 %) have been successfully synthesized through the reaction of a silver thiolate complex with Au_{11} clusters. In contrast, species with $x=$ 1–12 (**I**) and undoped Au_{25} nanoclusters are only weakly fluorescent (QY = 0.21 % and 0.1 %, respectively).

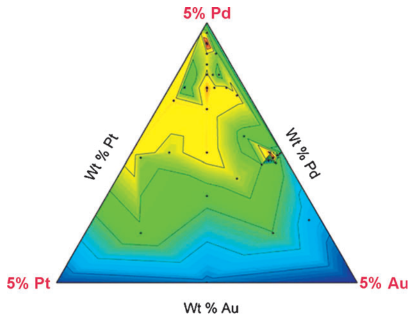
Fluorescent Nanoclusters

S. Wang, X. Meng, A. Das, T. Li, Y. Song,
T. Cao, X. Zhu, M. Zhu,*
R. Jin* 2376 – 2380

A 200-fold Quantum Yield Boost in the Photoluminescence of Silver-Doped Ag_xAu_{25-x} Nanoclusters: The 13th Silver Atom Matters

---

Small change with great effect: The addition of a small amount of Pt to a $AuPd/CeO_2$ catalyst can significantly enhance its performance in the direct synthesis of H_2O_2. The contour diagram shows the productivity of catalysts with different metal ratios (blue/yellow: low/high productivity).

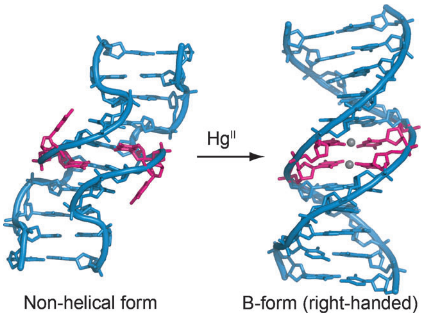


Supported Catalysts

J. K. Edwards,* J. Pritchard, L. Lu,
M. Piccinini, G. Shaw, A. F. Carley,
D. J. Morgan, C. J. Kiely,
G. J. Hutchings* 2381 – 2384

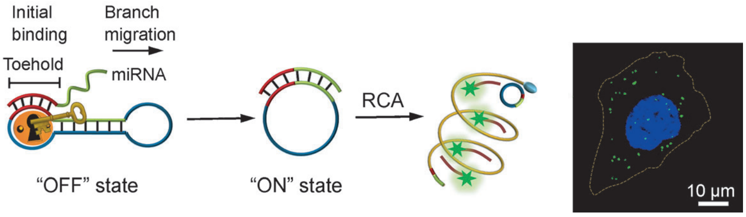
The Direct Synthesis of Hydrogen Peroxide Using Platinum-Promoted Gold–Palladium Catalysts

Structure Elucidation



Paired up: The first crystal structure of a metallo DNA duplex containing consecutive Watson–Crick-like T–Hg^{II}–T base pairs has been solved. The structure itself and the Hg^{II}-induced structural switching from a nonhelical form to the B-form provide the basis for structure-based design of metal-conjugated nucleic acid nanomaterials.

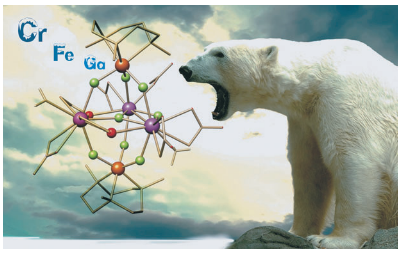
MicroRNA Imaging



Ready to roll: A toehold-initiated strand-displacement (TMSD) process was used to initiate the rolling circle amplification (RCA) of individual miRNAs through the use of a structure-switchable dumbbell-shaped probe. High specificity was achieved through the fine sequence discrimination of TMSD. The amplification produces an extremely long chain containing hundreds of tandem repeats, which allows the visualization of individual microRNAs in situ in single cells.

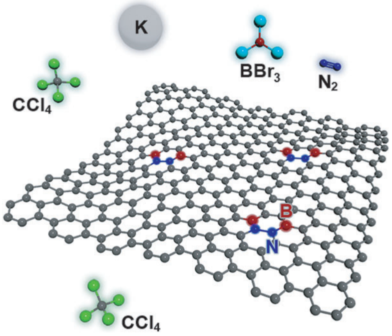
Molecular Refrigeration

Inside Cover

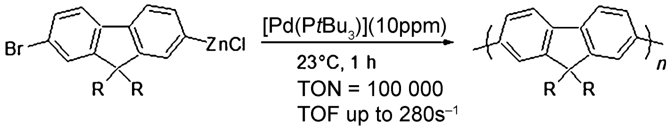


Molecular coolers: Even labile fluoride complexes (see picture; Gd purple, Cr/Fe/Ga orange, F green, O red) are useful precursors for polynuclear, fluoride-bridged 3d–4f systems. Molecular geometry enforces weak exchange interactions, which is rationalized computationally. This, in conjunction with a lightweight auxiliary ligand sphere, gives rise to extremely large magnetic entropy changes.

Modified Graphitic Networks



Mixing it up a bit: B/N-doped graphene was directly synthesized from the reaction of CCl_4, BBr_3, and N_2 in the presence of potassium. It has good dispersibility in *N*-methyl-2-pyrrolidone, allowing solution casting for the fabrication of field-effect transistors with an on/off ratio of 10.7 and an optical band gap of 3.3 eV. The method is scalable and solution processable, making it suitable for many applications.



Kicking it into high gear: Pd/PtBu$_3$-catalyzed Negishi chain-growth polycondensation of AB-type monomers into semiconducting polymers proceeds with unprecedented TONs as high as 100 000 and turnover frequencies of up to 280 s^{-1}. In contrast, related AA/BB-type step-growth polycondensation proceeds with two orders of magnitude lower TONs and TOFs. Similar trends were observed in Suzuki polycondensation.

Catalyst-Transfer Polycondensation

R. Tkachov, V. Senkovskyy, T. Beryozkina, K. Boyko, V. Bakulev, A. Lederer, K. Sahre, B. Voit, A. Kiriy* ———— **2402 – 2407**

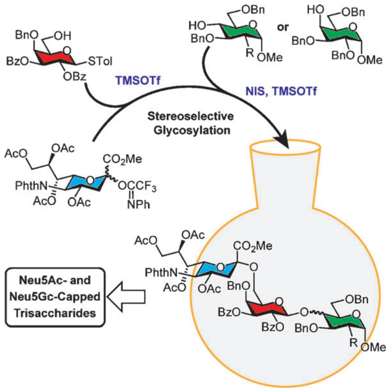
Palladium-Catalyzed Chain-Growth Polycondensation of AB-type Monomers: High Catalyst Turnover and Polymerization Rates

All in a flutter: Significant distortion of the bowl-shaped structure of subphthalocyanine upon the introduction of a seven-membered ring in place of two five-membered rings (see scheme) led to unusual properties and reactivity. Fluttering-dynamic-motion-induced rapid exchange of the *P* and *M* enantiomers as well as markedly split Q-band absorption and distinct ring-current effects arising from the convex and concave surfaces were observed.

Conjugated Molecules

S. Shimizu,* S. Nakano, A. Kojima, N. Kobayashi* ———— **2408 – 2412**

A Core-Expanded Subphthalocyanine Analogue with a Significantly Distorted Conjugated Surface and Unprecedented Properties

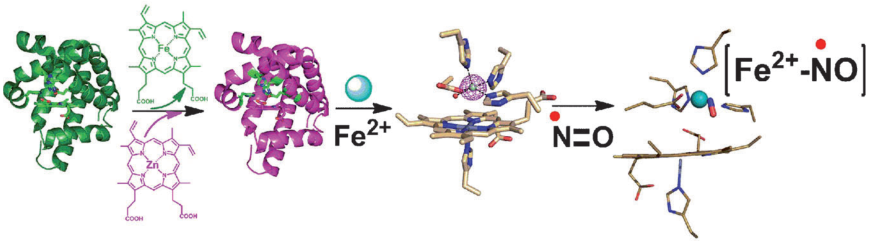


Flu the coop: A stereoselective one-pot assembly and divergent transformation enabled the synthesis of six *N*-acetyl- and *N*-glycolylneuraminic-acid-capped trisaccharides. Two of the *N*-glycolylneuraminic-acid-capped trisaccharides showed inhibitory activities against a common human influenza virus. Bz = benzoyl, NIS = *N*-iodosuccinimide, Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl.

Carbohydrates

Y. Hsu, H.-H. Ma, L. S. Lico, J.-T. Jan, K. Fukase, Y. Uchinashi, M. M. L. Zulueta, S.-C. Hung* ———— **2413 – 2416**

One-Pot Synthesis of *N*-Acetyl- and *N*-Glycolylneuraminic Acid Capped Trisaccharides and Evaluation of Their Influenza A(H1 N1) Inhibition



Ironed out: A nonheme iron nitrosyl complex has been prepared at a rationally designed Fe$_B$ site within a myoglobin-based biosynthetic model of nitric oxide reductases (NORs) that contains a zinc protoporphyrin IX. The designed Fe^{II}-ZnPPFe$_B$Mb1 forms a nitrosyl complex [Fe$_B$$^{2+}$-NO$^{\bullet}$] at the nonheme site. The radical nature of NO is implied to promote N–N bond formation by radical coupling, thus supporting the *trans* mechanism of NORs.

Reaction Mechanisms

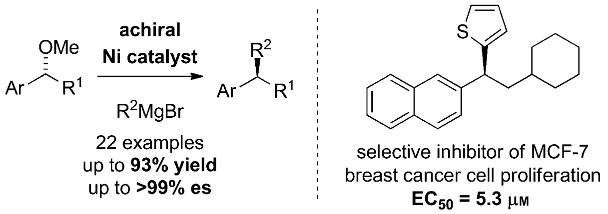
S. Chakraborty, J. Reed, M. Ross, M. J. Nilges, I. D. Petrik, S. Ghosh, S. Hammes-Schiffer, J. T. Sage, Y. Zhang, C. E. Schulz, Y. Lu* ———— **2417 – 2421**

Spectroscopic and Computational Study of a Nonheme Iron Nitrosyl Center in a Biosynthetic Model of Nitric Oxide Reductase

Cross-Couplings

I. M. Yonova, A. G. Johnson,
C. A. Osborne, C. E. Moore,
N. S. Morrissette,
E. R. Jarvo* ______ **2422 – 2427**

Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Grignard Reagents and Identification of Selective Anti-Breast-Cancer Agents

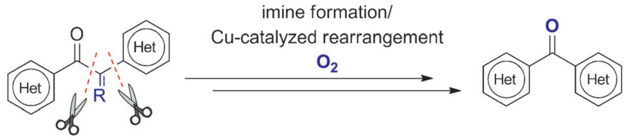


β-Hydrogen atoms welcome! Alkyl Grignard reagents that contain β-hydrogen atoms were used in a stereospecific nickel-catalyzed cross-coupling reaction to form $C(sp^3)-C(sp^3)$ bonds (es = enantiospecificity). Aryl Grignard reagents were also utilized to synthesize 1,1-diarylalkanes. Several compounds that were synthesized by this method exhibited selective inhibition of proliferation of MCF-7 breast cancer cells.

Heterocycles

A. Maji, S. Rana, Akanksha,
D. Maiti* ______ **2428 – 2432**

Synthesis of Bis(heteroaryl) Ketones by Removal of Benzylic CHR and CO Groups

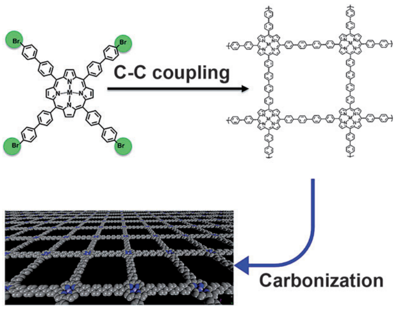


Snip snip: A copper-catalyzed method for synthesis of diaryl ketones by removal of benzylic CH_2, CO, and CHR groups has been discovered. A number of symmetrical and unsymmetrical heterocyclic ketones, which are usually difficult to synthesize, can be prepared in good to excellent yields. Preliminary mechanistic studies indicate that an active Cu/O_2 species mediates the rearrangement.

Oxygen Reduction Reaction

Z. Xiang, Y. Xue, D. Cao,* L. Huang,
J.-F. Chen, L. Dai* ______ **2433 – 2437**

Highly Efficient Electrocatalysts for Oxygen Reduction Based on 2D Covalent Organic Polymers Complexed with Non-precious Metals



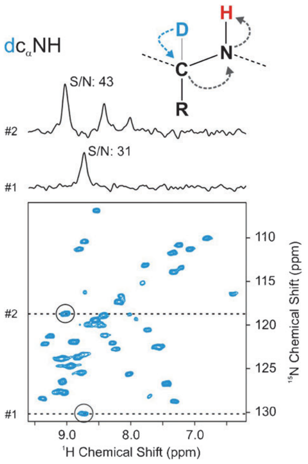
Metal-containing (M = Fe, Co, Mn) 2D covalent organic polymers with precisely controlled locations of N heteroatoms and holes were synthesized from metal–porphyrin complexes by a nickel-catalyzed Yamamoto reaction. Subsequent carbonization led to graphene analogues, which are efficient electrocatalysts for oxygen reduction in both alkaline and acid media and are free from methanol-crossover/CO poisoning.

NMR Spectroscopy

Ü. Akbey,* A. J. Nieuwkoop, S. Wegner,
A. Voreck, B. Kunert, P. Bandara,
F. Engelke, N. C. Nielsen,
H. Oschkinat* ______ **2438 – 2442**

Quadruple-Resonance Magic-Angle Spinning NMR Spectroscopy of Deuterated Solid Proteins

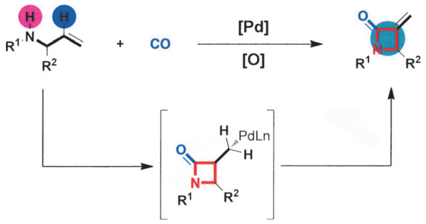
Proton-detected magic-angle spinning solid-state NMR spectroscopy using deuterated proteins facilitates structural biology. Solid deuterated proteins that cannot be unfolded/refolded to exchange the deuterons back with protons and proteins that can only be studied in their native environments show a low intrinsic sensitivity in NMR experiments. For such systems, initial excitation of the deuterons can be very useful.



Heterocycles

W. Li, C. Liu, H. Zhang, K. Ye, G. Zhang,
W. Zhang, Z. Duan, S. You,*
A. Lei* ________ 2443 – 2446

Palladium-Catalyzed Oxidative Carbonylation of *N*-Allylamines for the Synthesis of β-Lactams

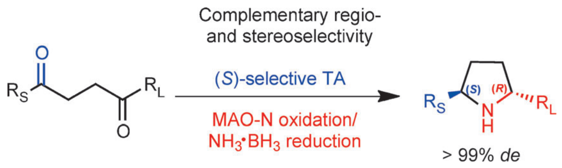


Four corners: The β-lactam scaffold is considered to be an ideal building block for the synthesis of nitrogen-containing compounds. A new, simple, and convenient palladium-catalyzed oxidative carbonylation of *N*-allylamines for the synthesis of α-methylene-β-lactams is reported. DFT calculations suggest that the formation of the β-lactam via a four-membered-ring transition state is favorable.

Biocatalysis

E. O'Reilly, C. Iglesias, D. Ghislieri,
J. Hopwood, J. L. Galman, R. C. Lloyd,
N. J. Turner* ________ 2447 – 2450

A Regio- and Stereoselective ω-Transaminase/Monoamine Oxidase Cascade for the Synthesis of Chiral 2,5-Disubstituted Pyrrolidines

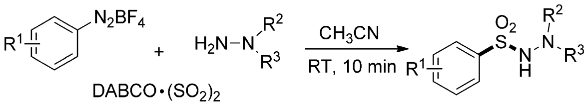


Mirror mirror on the wall: A ω-transaminase (ω-TA)/monoamine oxidase (MAO-N) cascade process for the asymmetric synthesis of chiral 2,5-disubstituted pyrrolidines is reported. The methodology exploits the complementary regio- and stereoselectivity displayed by both enzymes, which ensures that the stereogenic center established by the TA reaction is not affected by the MAO-N catalyzed step.

Aminosulfonylation

D. Zheng, Y. An, Z. Li,*
J. Wu* ________ 2451 – 2454

Metal-Free Aminosulfonylation of Aryldiazonium Tetrafluoroborates with $\mathrm{DABCO\cdot(SO_2)_2}$ and Hydrazines

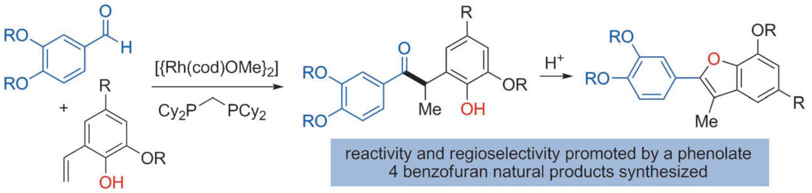


The coupling of aryldiazonium tetrafluoroborates, $\mathrm{DABCO\cdot(SO_2)_2}$, and hydrazines under metal-free conditions leads to the formation of aryl *N*-aminosulfonamides. The reaction proceeds under mild reaction conditions, is fast, has a broad substrate scope, and gives the products in high yields (21 examples). A plausible mechanism that involves a radical process is also proposed.

C–H Activation

S. K. Murphy, A. Bruch,
V. M. Dong* ________ 2455 – 2459

Substrate-Directed Hydroacylation: Rhodium-Catalyzed Coupling of Vinylphenols and Nonchelating Aldehydes



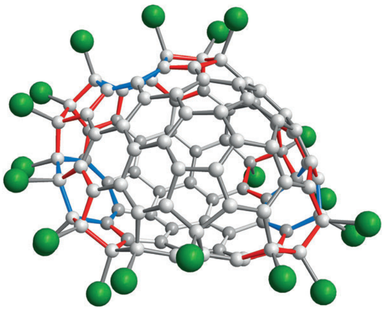
COs with a local branch: A hydroacylation of vinylphenols with aryl, alkenyl, and alkyl aldehydes gave the branched products: α-aryl ketone precursors to benzofurans. This cross-coupling enabled access to eupomatenoid natural products in four steps or less from eugenol (see scheme; cod = 1,5-cyclooctadiene). Aldehyde decarbonylation was avoided by use of an anionic directing group on the alkene and a small-bite-angle diphosphine ligand.

Giant Fullerenes

S.-F. Yang,* S. Wang, E. Kemnitz,*
S. I. Troyanov* ______ **2460 – 2463**

Chlorination of IPR C_{100} Fullerene Affords Unconventional $C_{96}Cl_{20}$ with a Non-classical Cage Containing Three Heptagons

Three heptagons in the fullerene cage were found for the first time in $C_{96}Cl_{20}$ with a nonclassical cage, which was obtained by chlorination of isolated-pentagon-rule C_{100} fullerene. Most of 15 cage pentagons are fused resulting fused pentagon pairs and triples (see structure: gray C, green Cl; pentagons red, heptagons blue).

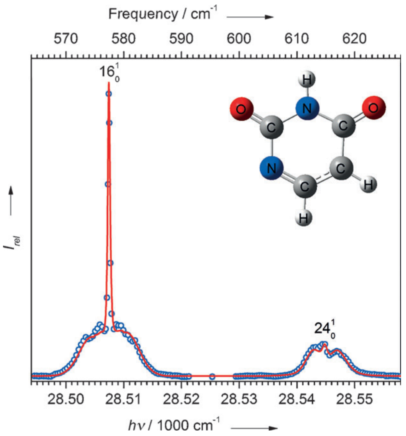


Vibrational Spectroscopy

H. T. Liu, C. G. Ning, D. L. Huang,
L. S. Wang* ______ **2464 – 2468**

Vibrational Spectroscopy of the Dehydrogenated Uracil Radical by Autodetachment of Dipole-Bound Excited States of Cold Anions

The vibrational spectrum of the dehydrogenated uracil radical has been measured by autodetachment from dipole-bound states of cold deprotonated uracil anions. The spectrum shows observed rotational profiles (blue circles) for mode ν_{16} at 577 cm^{-1} (*c*-type) and mode ν_{24} at 615 cm^{-1} (*b*-type), in comparison with the simulated rotational profiles (red line).



DOI: 10.1002/anie.201400409

Flashback: 50 Years Ago …

Vitamin B_{12} had at that time been only partially chemically synthesized (the total synthesis was first published in 1973), and a Review by K. Bernhauer et al. summarized the latest developments in the field, including partial syntheses, coenzyme forms, and enzymatic functions. A Review by Albert Eschenmoser on the origin of the molecular structure of vitamin B_{12} was published in our *Angewandte*'s Centenary Issue (*Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 5–39).

Emanuel Vogel published a Communication on the properties of the cyclodecapentaene system. The system contains 10 π electrons and can thus be expected to have an aromatic character. The proton NMR spectrum of 1,6-methanocyclodecapentane showed it to have a strong ring current, however, it shows olefinic reactivity and cannot be classified as a classical aromatic compound.

Georg Wittig reported a new synthesis of tetraarylphosphonium salts. Reactions of triarylphosphines and *o*-fluorophenyllithium with either fluorene or methyl iodide at −40 °C resulted in the corresponding tetraarylphosphonium salt or its *o*-methyl derivative.

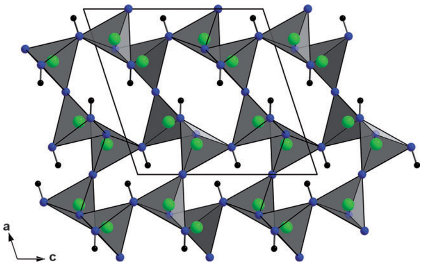
Max Schmidt reported the synthesis of 1,1,1,3,3,3-hexamethyldigermazane ($(CH_3)_3Ge{-}NH{-}Ge(CH_3)_3$). The reaction of trimethylgermanium chloride with ammonia produced the target compound as a colorless liquid. Reaction of dimethylgermanium dichloride under the same conditions resulted in the formation of $[(CH_3)_2GeCl]_3N$.

Read more in Issue 3/1964.

Silica Analogues

A. Marchuk, F. J. Pucher, F. W. Karau, W. Schnick* ———— **2469 – 2472**

A High-Pressure Polymorph of Phosphorus Nitride Imide



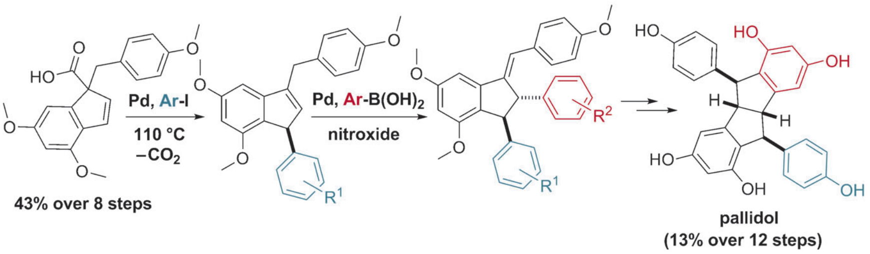
A new form is born: The first high-pressure polymorph of phosphorus nitride imide, β-PN(NH), has been synthesized by treating a single-source precursor at 6 GPa and 1000 °C using the multianvil technique. By adding catalytic amounts of NH_4Cl as a mineralizer single crystals of the product could be obtained and isolated.

Natural Product Synthesis

F. Klotter, A. Studer* ———— **2473 – 2476**

Total Synthesis of Resveratrol-Based Natural Products Using a Palladium-Catalyzed Decarboxylative Arylation and an Oxidative Heck Reaction

Front Cover

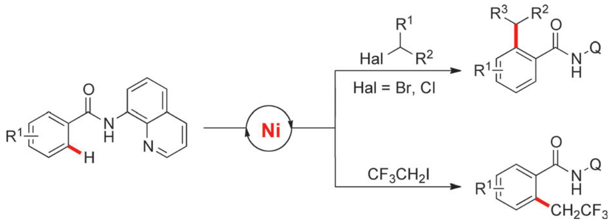


Palladium mediates! A common building block readily available on a large scale serves as the starting material in the title reactions for the introduction of structurally important aryl groups in resveratrol-based natural products. The modular concept is convincingly documented by the synthesis of three racemic resveratrol-based natural products (including pallidol).

C–H Activation

W. Song, S. Lackner, L. Ackermann* ———— **2477 – 2480**

Nickel-Catalyzed C–H Alkylations: Direct Secondary Alkylations and Trifluoroethylations of Arenes

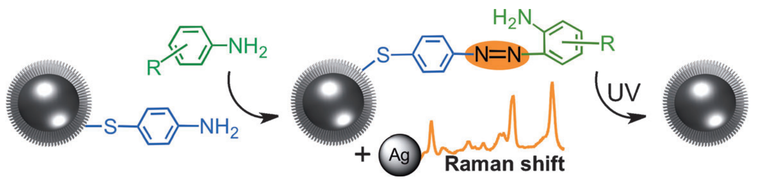


In an absence of activation: A robust nickel(II) catalyst enabled secondary alkylations of unactivated aryl C–H bonds with secondary alkyl bromides and chlorides with ample substrate scope. Based on this system the first C–H trifluoroethylations of arenes with unactivated C–H bonds could be carried out (see scheme; Q = 8-quinolinyl).

Detoxification

X. X. Han, L. Chen, U. Kuhlmann, C. Schulz, I. M. Weidinger,* P. Hildebrandt* ———— **2481 – 2484**

Magnetic Titanium Dioxide Nanocomposites for Surface-Enhanced Resonance Raman Spectroscopic Determination and Degradation of Toxic Anilines and Phenols

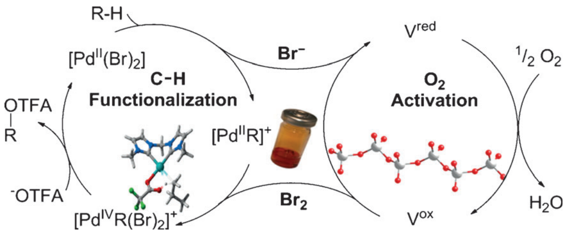


Magnetic TiO_2 nanocomposites (M-TiO_2 NCs) are fabricated and functionalized for determination and elimination of toxic anilines and phenols. The compounds, bound to M-TiO_2 NCs by azo coupling, may be degraded by TiO_2-assisted photocatalysis, making the NCs recyclable. Addition of Ag nanoparticles allows the detection and identification of the azo products by surface-enhanced resonance Raman spectroscopy and accelerates photocatalytic detoxification.

C–H Activation

D. Munz, T. Strassner* ____ **2485 – 2488**

Propane Activation by Palladium Complexes with Chelating Bis(NHC) Ligands and Aerobic Cooxidation



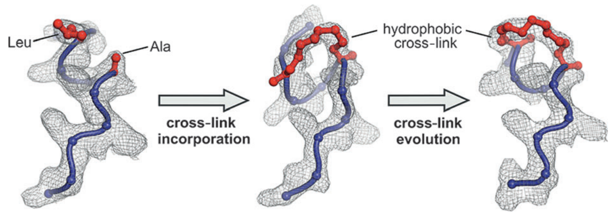
Reoxidation by dioxygen: The combination of C–H activation by a homogeneous catalytic palladium complex with a vanadiumoxo co-catalyst allows the selective aerobic oxidation of propane with dioxygen (see scheme).

PPI Inhibitors

A. Glas, D. Bier, G. Hahne,
C. Rademacher, C. Ottmann,*
T. N. Grossmann* ________ **2489 – 2493**

Constrained Peptides with Target-Adapted Cross-Links as Inhibitors of a Pathogenic Protein–Protein Interaction

Back Cover

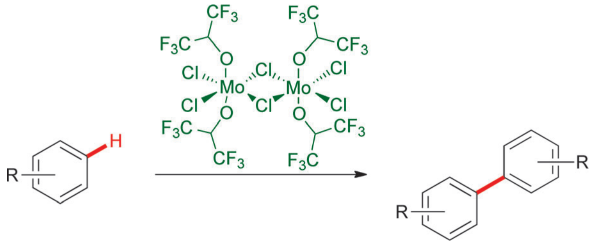


Irregular peptide structures were stabilized using hydrophobic cross-links that replace residues crucially involved in target binding. The cross-links were designed in a rational and iterative process that involved X-ray crystallography. The resulting peptides inhibit the protein–protein interaction between virulence factor ExoS and human protein 14-3-3.

Oxidative Coupling

M. Schubert, J. Leppin, K. Wehming,
D. Schollmeyer, K. Heinze,*
S. R. Waldvogel* ________ **2494 – 2497**

Powerful Fluoroalkoxy Molybdenum(V) Reagent for Selective Oxidative Arene Coupling Reaction

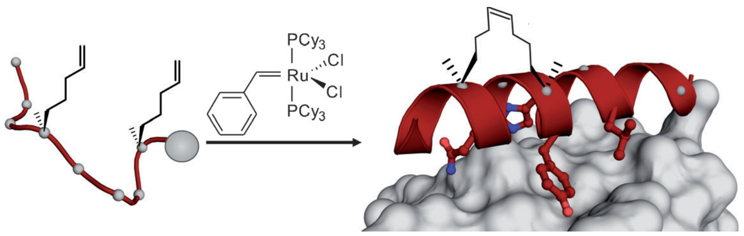


Wait a Mo: A novel molybdenum(V) reagent (see scheme) is superior to the performance of $MoCl_5$ in the oxidative coupling reaction of aryls leading to less by-products and significantly increased yields.

Stapled Peptides

J. Spiegel, P. M. Cromm, A. Itzen,
R. S. Goody, T. N. Grossmann,*
H. Waldmann* ________ **2498 – 2503**

Direct Targeting of Rab-GTPase–Effector Interactions

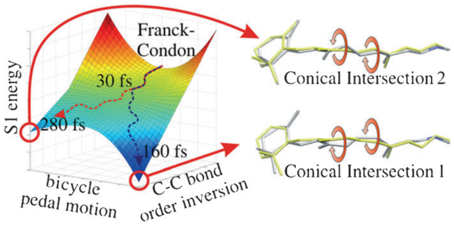


Targeting small GTPases: A library of hydrocarbon-stapled peptides was designed to target Rab GTPases and yielded peptides with significantly increased target affinity. One peptide demonstrates selective binding of activated Rab8a and inhibition of a Rab8a–effector interaction. This work suggests that peptide stapling may enable the development of inhibitors for other small GTPases.

Competitive Deactivation Pathways

D. Polli, O. Weingart, D. Brida, E. Poli, M. Maiuri, K. M. Spillane, A. Bottoni, P. Kukura, R. A. Mathies, G. Cerullo,* M. Garavelli* ______ **2504 – 2507**

Wavepacket Splitting and Two-Pathway Deactivation in the Photoexcited Visual Pigment Isorhodopsin



Follow the right path! In the visual pigment analogue isorhodopsin, the photoexcited wavepacket branches in two competitive deactivation pathways involving two distinct conical intersections. This scenario is deduced from high-level QM/MM simulations of the photoinduced dynamics and is responsible both for the recorded non-exponential two-component decay and for the reduced isomerization quantum yield with respect to rhodopsin.

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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The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.

Angewandte Corrigendum

The table of contents entry for this Highlight (page 11950 in printed issue 46/2013) needs to be corrected as shown below. The editorial office apologizes for this technical mistake.

Metal/N-Heterocyclic Carbene Complexes: Opportunities for the Development of Anticancer Metallodrugs

F. Cisnetti, A. Gautier* __ **11976–11978**

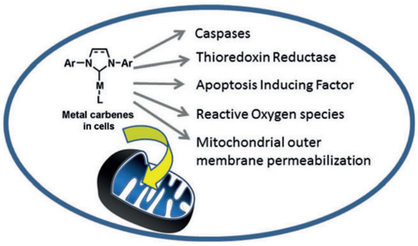
Angew. Chem. Int. Ed. **2013**, *52*

DOI: 10.1002/anie.201306682

Antitumor Agents

F. Cisnetti, A. Gautier* __ **11976 – 11978**

Metal/N-Heterocyclic Carbene Complexes: Opportunities for the Development of Anticancer Metallodrugs



Death trap: The rational design of metal/N-heterocyclic carbene complexes allows mitochondria to be targeted. Activation of several apoptotic processes (which do not include direct DNA damage) induces cell death and significant tumor suppression.