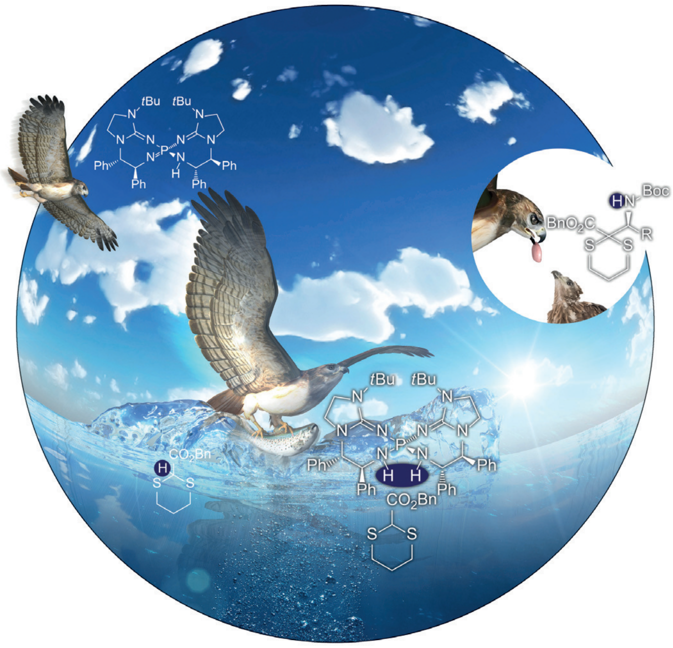
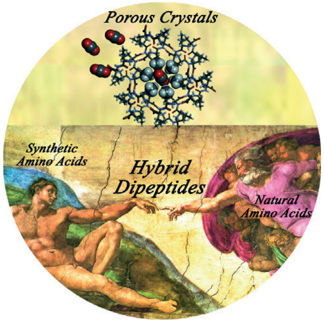
A chiral bis(guanidino) ...

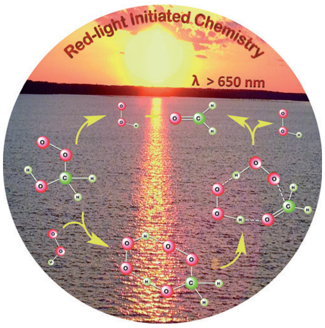


... iminophosphorane catalyzes enantioselective addition reactions of a 1,3-dithiane derivative, which possesses a less-acidic proton, as a pronucleophile. As demonstrated by M. Terada et al. in their Communication on page 15836 ff., the chiral uncharged organosuperbase facilitates the addition of benzylcarbonyl-1,3-dithiane to aromatic *N*-Boc-protected imines to provide optically active α-amino-1,3-dithiane derivatives.

Microporous Materials

In their Communication on page 15684 ff., C. H. Görbitz and co-workers report that dipeptides containing non-proteinogenic residues form crystals with open channels, the diameter of which is tuned by the bulk of the non-proteinogenic units.





Atmospheric Chemistry

J. S. Francisco and M. Kumar study the gas-phase decomposition of the α-hydroxy methylperoxy radical by quantum chemical calculations in their Communication on page 15711 ff.

Photoacoustic Imaging

In their Communication on page 15809 ff., Z. H. Nie, X. Y. Chen, and co-workers report the assembly of chain vesicles that can be used for photoacoustic imaging and drug delivery owing to their strong absorption in the near-infrared region.

How to contact us:

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E-mail: angewandte@wiley-vch.de
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Author Profile

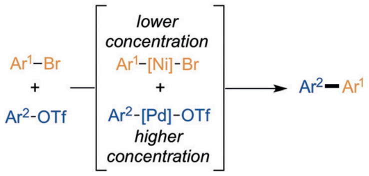
"When I was eighteen I wanted to be an organic chemist! What else?
If I could be anyone for a day, I would be Marcus Antonius, if I could choose the day! …"
This and more about Stéphane Quideau can be found on page 15610.

Obituaries

Richard F. Heck, who shared the Nobel Prize in Chemistry 2010 with Akira Suzuki and Ei-ichi Negishi, passed away on October 10, 2015 at the age of 84. Heck developed the palladium-catalyzed carbon–carbon bond-forming reaction between aryl halides and olefins that is known as the Heck reaction, and also rationalized its mechanism. This reaction has become a standard procedure in modern organic synthesis.

Highlights

Cross-Coupling



Palladium and nickel: This Highlight summarizes recent developments in the area of dual-catalytic Ullman-type coupling reactions of aryl bromides and triflates: Weix and co-workers took advantage of the different selectivities and stabilities of palladium and nickel catalysts to favor the desired cross-coupling and suppress homocoupling.

Essays

History of Chemistry

W. M. Wallau* ______ **15622 – 15631**

The Phenomenon of the Styrian Arsenic Eaters from the Perspective of Literature, Chemistry, Toxicology, and History of Science—“Strong Poison” or “Simple-Minded Reasoning”?

The arsenic eaters of Styria, who were supposedly immunized against the toxic effects of arsenic (As_2O_3), appeared increasingly in scientific and popular literature in the second half of the 19th century. This Essay starts with a depiction of this phenomenon from a detective novel and questions whether the observations and scientific knowledge at that time can confirm this legend. Figure from J. H. Pepper, *The Boy’s Book of Metals*, p. 433.

Fig. 231. Arsenic-eaters of Styria.

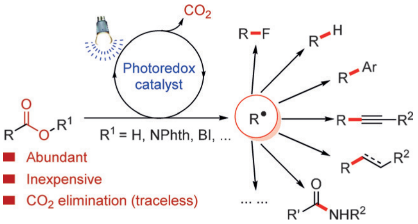
Minireviews

Photochemistry

J. Xuan, Z.-G. Zhang,*
W.-J. Xiao* ______ **15632 – 15641**

Visible-Light-Induced Decarboxylative Functionalization of Carboxylic Acids and Their Derivatives

Photo op: A novel functionalization reaction using visible-light-induced photoredox catalysis has recently been developed (see title). The formed radical species can participate in not only single photocatalytic transformations, but also dual-catalytic reactions by combining photoredox catalysis with other catalytic methods. Recent advances in this research area are discussed herein.

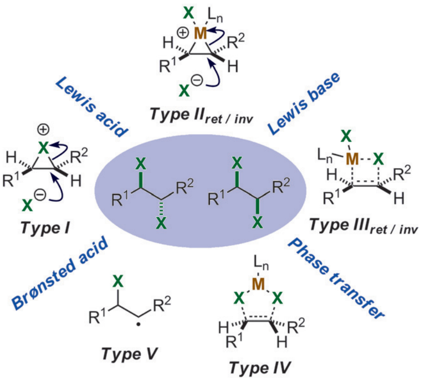


Reviews

Enantioselective Synthesis

A. J. Cresswell, S. T.-C. Eey,
S. E. Denmark* ______ **15642 – 15682**

Catalytic, Stereoselective Dihalogenation of Alkenes: Challenges and Opportunities



One of the most vexing challenges in stereoselective synthesis is catalysis of alkene dihalogenation, under different activation modes, with control over both the absolute and relative stereochemical course of dihalogen addition. Dihalogenations that circumvent the “classical” haliranium intermediates provide new opportunities for catalysis, potentially having broader implications for the design of stereoselective alkene difunctionalizations.

For the USA and Canada:
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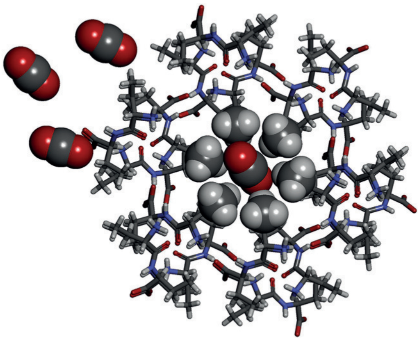
Communications

Crystals of dipeptides comprised of a combination of proteinogenic and non-proteinogenic residues show open channels with variable and tunable diameters modulated by the bulk of the latter units. The accessibility of these novel porous materials from the gas phase is demonstrated by the adsorption isotherms of CO_2 and CH_4. Direct observations of captured CO_2 in the 1D and 2D NMR spectra revealed close gas–matrix interaction.

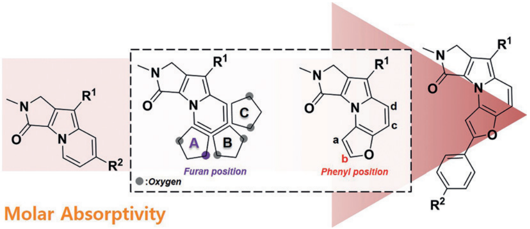


Microporous Materials

V. N. Yadav, A. Comotti,* P. Sozzani, S. Bracco, T. Bonge-Hansen, M. Hennum, C. H. Görbitz* ———— 15684 – 15688

Microporous Molecular Materials from Dipeptides Containing Non-proteinogenic Residues

Frontispiece



Molar absorptivity: Using a rational design strategy guided by the oscillator strength, a furo[3,2-*e*]indolizine-based fluorescent core skeleton with an improved molar absorptivity was synthesized. A furan ring was fused into an indolizine-based Seoul-Fluor to demonstrate the predictablity of their photophysical properties.

Fluorophore Design

Y. Lee, A. Jo, S. B. Park* — 15689 – 15693

Rational Improvement of Molar Absorptivity Guided by Oscillator Strength: A Case Study with Furoindolizine-Based Core Skeleton

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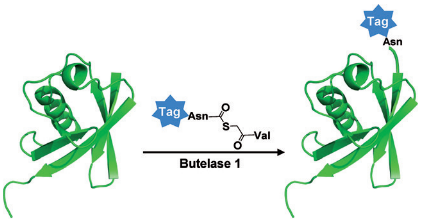


An irreversible butelase-mediated ligation using a thiodepsipeptide substrate is described, with a ligation yield of > 95 % and a minimal excess of substrate and low catalytic amounts of butelase 1. This method was used to introduce a functional tag to ubiquitin and green fluorescent protein with high yields.

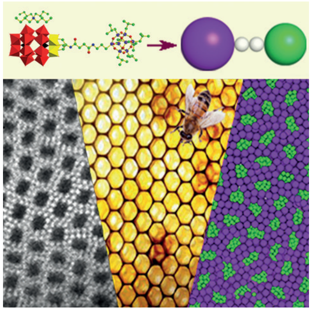
Protein Labeling

G. K. T. Nguyen, Y. Cao, W. Wang, C. F. Liu, J. P. Tam* ——— 15694 – 15698

Site-Specific N-Terminal Labeling of Peptides and Proteins using Butelase 1 and Thiodepsipeptide

---

How to pack dumbbells: The size asymmetry and Janus characteristics of a dumbbell-shaped co-cluster synergistically define its self-assembly in solution into crystals with a filled-honeycomb superstructure. The Janus co-cluster consists of a POM (purple sphere) and a POSS (green sphere) linked by an organic tether.



Cluster-Assembled Materials

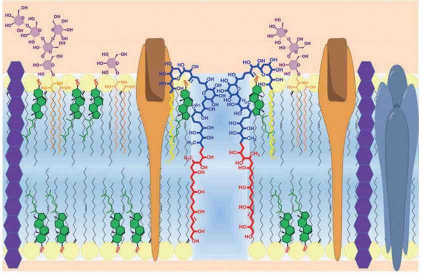
C. Ma, H. Wu, Z.-H. Huang, R.-H. Guo, M.-B. Hu, C. Kübel,* L. T. Yan,* W. Wang* ———— 15699 – 15704

A Filled-Honeycomb-Structured Crystal Formed by Self-Assembly of a Janus Polyoxometalate–Silsesquioxane (POM–POSS) Co-Cluster

Polyketides

A. L. Waters, J. Oh, A. R. Place,
M. T. Hamann* ________ **15705 – 15710**

Stereochemical Studies of the Karlotoxin Class Using NMR Spectroscopy and DP4 Chemical-Shift Analysis: Insights into their Mechanism of Action



In bloom: Harmful algal bloom toxins derived from the dinoflagellate *Karlodinium* sp. produce an interesting suite of complex polyketides which have been shown to have hemolytic, cytotoxic and ichthyotoxic activity. Better understanding the mechanism of action for this class of compounds could lead to the development of new agents for targeting cancer-cell membranes.

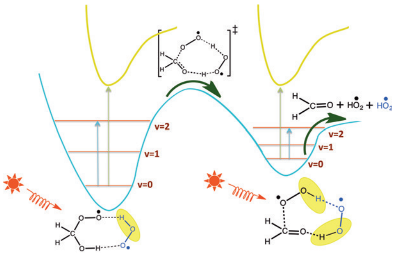
Atmospheric Chemistry

M. Kumar,
J. S. Francisco* ________ **15711 – 15714**

Red-Light-Induced Decomposition of an Organic Peroxy Radical: A New Source of the HO_2 Radical

Inside Back Cover

The gas-phase decomposition of the α-hydroxy methylperoxy radical was examined in the presence of water, a water dimer, the hydroperoxy radical, and a water·hydroperoxy radical complex. The red-light-induced photodissociation of the pre-reaction and post-reaction complexes is suggested as a new mechanism by which the HO_2 radical is released into the atmosphere.

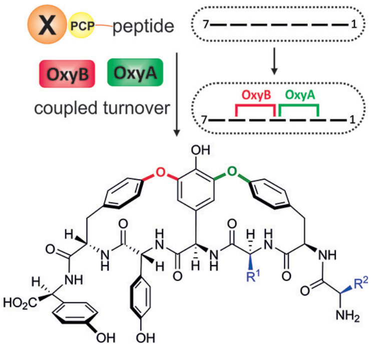


Biosynthesis

C. Brieke, M. Peschke, K. Haslinger,
M. J. Cryle* ________ **15715 – 15719**

Sequential In Vitro Cyclization by Cytochrome P450 Enzymes of Glycopeptide Antibiotic Precursors Bearing the X-Domain from Nonribosomal Peptide Biosynthesis

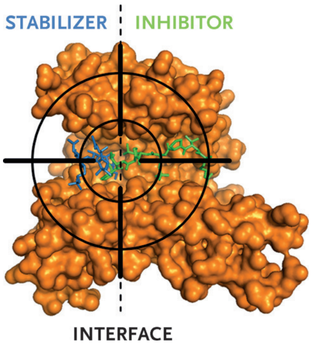
Tying up loose ends: A range of glycopeptide antibiotic precursor peptides were sequentially cyclized to bicyclic peptides by two Cytochrome P450 enzymes (OxyA and OxyB) when presented on non-ribosomal peptide synthetase (NRPS)-derived proteins that include the X-domain. This result indicates that these P450 enzymes show impressive tolerance for alternative substrate structures.



Protein–Protein Interactions

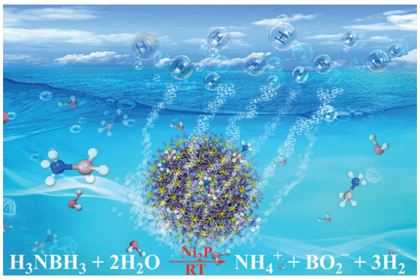
L.-G. Milroy,* M. Bartel, M. A. Henen,
S. Leysen, J. M. C. Adriaans, L. Brunsveld,
I. Landrieu,*
C. Ottmann* ________ **15720 – 15724**

Stabilizer-Guided Inhibition of Protein–Protein Interactions



The rational design of a protein–protein interaction inhibitor was guided by the co-crystal structure of a protein–stabilizer complex and based on a non-covalent tethering approach. The most potent inhibitor of the binding of 14-3-3 to phosphorylated full-length Tau was biochemically and biophysically characterized and has a novel molecular structure that specifically targets the inhibitor–stabilizer interface of 14-3-3.

A low-cost catalytic system using nanostructured Ni_2P as the catalyst was established for the hydrolysis of ammonia–borane. This system exhibits excellent catalytic activity and high sustainability under an air atmosphere and at ambient temperature.



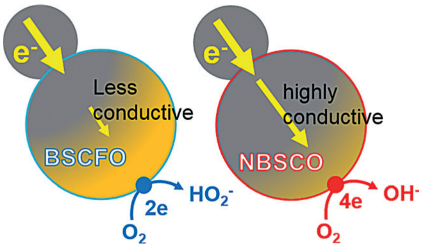
Heterogeneous Catalysis

C.-Y. Peng, L. Kang, S. Cao, Y. Chen, Z.-S. Lin, W.-F. Fu* ______ **15725 – 15729**

Nanostructured Ni_2P as a Robust Catalyst for the Hydrolytic Dehydrogenation of Ammonia–Borane

---

Conductivity makes the difference: Conductive environments surrounding active sites, achieved by more conductive perovskite catalysts (BSCFO, NBSCO) or higher carbon contents, result in a higher number of electrons transferred during complete four-electron (4e) reduction of oxygen, changing the rate-determining step from a two-step 2e process to a single-step 1e process.



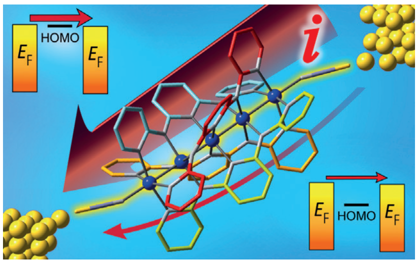
Oxygen Reduction Reaction

D.-G. Lee, O. Gwon, H.-S. Park, S. H. Kim, J. Yang, S. K. Kwak, G. Kim,* H.-K. Song* ______ **15730 – 15733**

Conductivity-Dependent Completion of Oxygen Reduction on Oxide Catalysts

---

Gating the current flow: The transmission efficiency of electron transport across molecular junctions can be controlled electrochemically by potentiostatting the electrode Fermi level (E_F) to be close to the frontier orbitals (E_{FMO}) of the bridging molecule. Transition voltage spectroscopy was utilized to extract quantitative information on the barrier height between E_F and E_{FMO}.



Electrochemistry

VIP

T.-C. Ting, L.-Y. Hsu, M.-J. Huang, E.-C. Horng, H.-C. Lu, C.-H. Hsu, C.-H. Jiang, B.-Y. Jin,* S.-M. Peng,* C.-h. Chen* ______ **15734 – 15738**

Energy-Level Alignment for Single-Molecule Conductance of Extended Metal-Atom Chains

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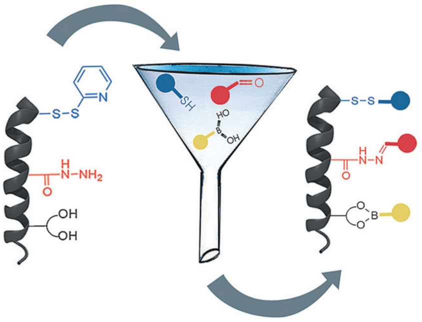


Completely self-absorbed: Tailored chromophores that absorb in the blue, red, and yellow regions can be spatially organized in a desired ratio on a preprogrammed α-helix peptide by the simultaneous use of three orthogonal dynamic covalent reactions (see figure). Energy transfer occurs from the yellow- and red- to the blue-absorbing chromophore, and the helical peptide structure is maintained after the self-assembly process.

Self-Assembly

L. Rocard, A. Berezin, F. De Leo, D. Bonifazi* ______ **15739 – 15743**

Templated Chromophore Assembly by Dynamic Covalent Bonds

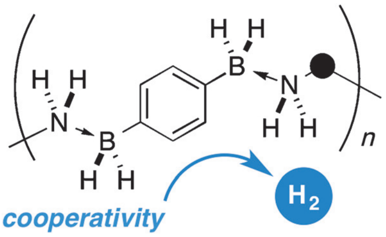
Inside Cover

Polymers

A. Ledoux, P. Larini, C. Boisson, V. Monteil, J. Raynaud,* E. Lacôte* ______ 15744 – 15749

Polyboramines for Hydrogen Release: Polymers Containing Lewis Pairs in their Backbone

Polybor-a-mine of H_2: The one-step polycondensation of diamine and diborane precursors leads to polymer chains assembled by multiple Lewis pairs (see scheme). The new polyboramines are dihydrogen reservoirs that can hydrogenate imines, aldehydes, and ketones. The polyboramines release H_2 thermally with a unique profile, which is a direct consequence of the polymeric nature of the material.

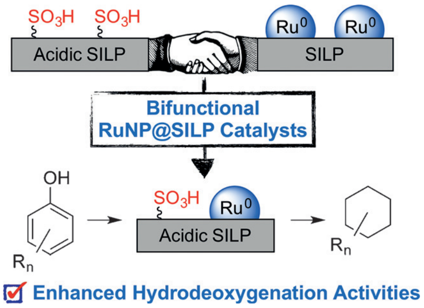


Bifunctional Catalysts

K. L. Luska, P. Migowski, S. El Sayed, W. Leitner* ______ 15750 – 15755

Synergistic Interaction within Bifunctional Ruthenium Nanoparticle/SILP Catalysts for the Selective Hydrodeoxygenation of Phenols

Working hand in hand: Bifunctional catalysts composed of ruthenium nanoparticles immobilized on acid-functionalized supported ionic liquid phases (Ru NPs@SILPs) were designed and synthesized. These catalysts showed enhanced activities for the hydrodeoxygenation of phenolic substrates resulting from a cooperative interaction between the metal and acid components.

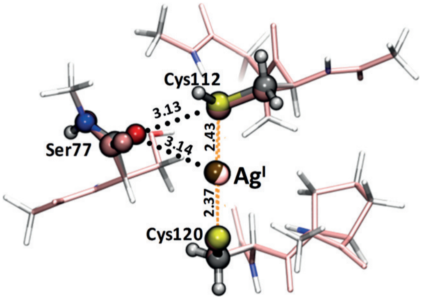


Metalloregulatory Proteins

D. Szunyogh, H. Szokolai, P. W. Thulstrup, F. H. Larsen, B. Gyurcsik, N. J. Christensen, M. Stachura, L. Hemmingsen,* A. Jancsó* ______ 15756 – 15761

Specificity of the Metalloregulator CueR for Monovalent Metal Ions: Possible Functional Role of a Coordinated Thiol?

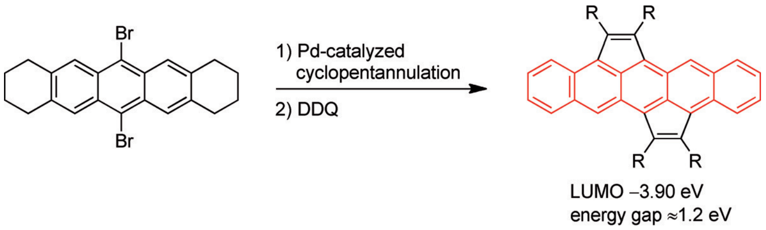
What a difference an H makes: Investigations of Ag^I, Zn^{II}, and Hg^{II} binding to model systems suggest that the selectivity of CueR proteins for monovalent metal ions and their allosteric mechanism may be controlled by the protonation of a coordinating cysteine residue. Quantum chemically optimized structures of the CueR metal site with Cys 112 protonated show that the Ser 77 backbone carbonyl oxygen atom is "pulled" towards the metal site (see picture).



Pentacenes

S. R. Bheemireddy, P. C. Ubaldo, P. W. Rose, A. D. Finke, J. Zhuang, L. Wang, K. N. Plunkett* _ 15762 – 15766

Stabilizing Pentacene By Cyclopentannulation

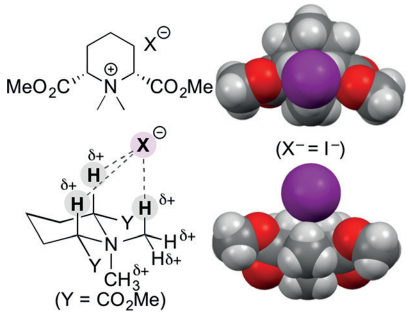


Five in a row: A palladium-catalyzed cyclopentannulation followed by a DDQ-mediated dehydrogenation converts a partially hydrogenated pentacene precursor into stabilized pentacenes. These pentacene derivatives are excellent electron acceptors and have small energy gaps. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Organocatalysis

S. Shirakawa,* S. Liu, S. Kaneko, Y. Kumatabara, A. Fukuda, Y. Omagari, K. Maruoka* ———— 15767 – 15770

Tetraalkylammonium Salts as Hydrogen-Bonding Catalysts

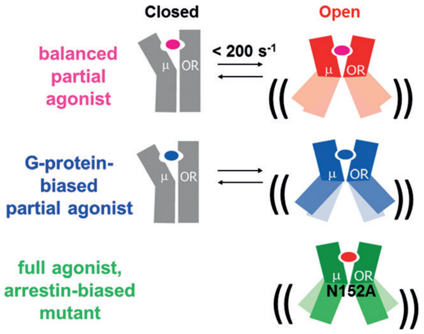


Cats with hitherto unknown talents: Tetraalkylammonium salts are widely used for phase-transfer catalysis. It is now demonstrated that they can also function as hydrogen-bonding catalysts. The hydrogen-bonding ability of appropriately designed ammonium salt catalysts was evaluated in Mannich-type reactions of *N*-acyl isoquinolines and NMR titration studies. Structural information was obtained by X-ray crystallography (see picture).

Receptor Signaling

J. Okude, T. Ueda, Y. Kofuku, M. Sato, N. Nobuyama, K. Kondo, Y. Shiraishi, T. Mizumura, K. Onishi, M. Natsume, M. Maeda, H. Tsujishita, T. Kuranaga, M. Inoue, I. Shimada* —— 15771 – 15776

Identification of a Conformational Equilibrium That Determines the Efficacy and Functional Selectivity of the μ-Opioid Receptor

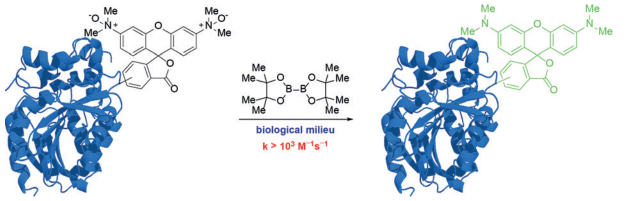


An open and closed case: NMR analysis of different ligand-bound states of the μ-opioid receptor revealed that the intracellular cavity of the receptor exists in an equilibrium between closed and multiple open conformations, and that the population of each open conformation determines the G-protein- and β-arrestin-mediated signaling levels (see picture). These findings provide structural insight into the biased signaling of G-protein-coupled receptors.

Bioorthogonal Chemistry

J. Kim, C. R. Bertozzi* —— 15777 – 15781

A Bioorthogonal Reaction of *N*-Oxide and Boron Reagents

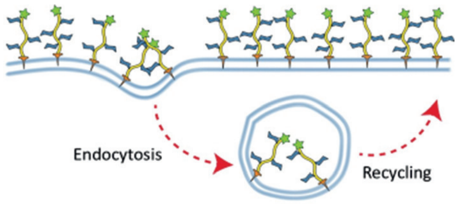


The bond-cleaving reaction between *N*-oxide and diboron reagents features second-order rate constants as high as $2.3\times10^{3}\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Diboron reagents display minimal cell toxicity at millimolar concentrations, penetrate cell membranes, and reduce *N*-oxides inside mammalian cells. This new bioorthogonal reaction is thus well-suited for chemically activating molecules within cells.

Glycoconjugates

E. C. Woods, N. A. Yee, J. Shen, C. R. Bertozzi* ———— 15782 – 15788

Glycocalyx Engineering with a Recycling Glycopolymer that Increases Cell Survival In Vivo



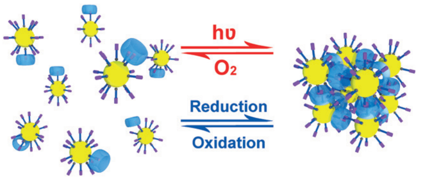
Keepin' it sweet! A panel of glycopolymers bearing a variety of lipids were used to identify constructs that persist on cell membranes. Cholesterylamine-anchored glycopolymers are internalized but recycle to allow for the continuous display of cell-surface glycopolymers for ten days. Furthermore, these mimetics enhance the survival of nonmalignant cells in a zebrafish model of metastasis.

Controllable Self-Assembly

Q. Zhang, D.-H. Qu,* Q.-C. Wang,
H. Tian* ________ 15789 – 15793

Dual-Mode Controlled Self-Assembly of TiO_2 Nanoparticles Through a Cucurbit[8]uril-Enhanced Radical Cation Dimerization Interaction

One way or another: The self-assembly of TiO_2 nanoparticles (NPs) functionalized with methyl viologen (MV^{2+}) can be controlled both by light irradiation and chemical reduction through a cucurbit[8]uril-enhanced radical cation dimerization interaction. This stimuli-responsive self-assembly process can switch the photocatalytic activity of the MV^{2+}–TiO_2 NPs on and off.

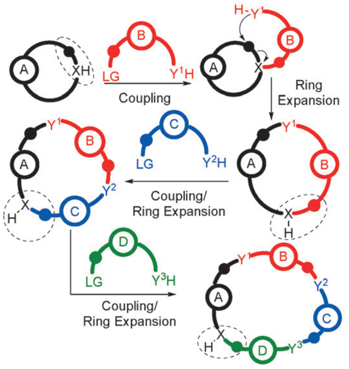


Macrocycles

C. Kitsiou, J. J. Hindes, P. I'Anson,
P. Jackson, T. C. Wilson, E. K. Daly,
H. R. Felstead, P. Hearnshaw,
W. P. Unsworth* ________ 15794 – 15798

The Synthesis of Structurally Diverse Macrocycles By Successive Ring Expansion

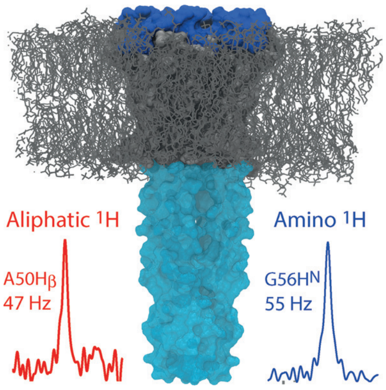
Expanding the family: Macrocycles can be generated using a telescoped acylation/ring-expansion sequence, leading to the insertion of linear fragments into cyclic β-ketoesters without performing a discrete macrocyclization step. The β-ketoester motif is regenerated in the ring-expanded product, therefore the same sequence of steps can be repeated, allowing macrocycles with precise substitution patterns to be "grown" from smaller rings.



Solid-State NMR Spectroscopy

D. Mance, T. Sinnige, M. Kaplan,
S. Narasimhan, M. Daniëls, K. Houben,
M. Baldus,*
M. Weingarth* ________ 15799 – 15803

An Efficient Labelling Approach to Harness Backbone and Side-Chain Protons in ^1H-Detected Solid-State NMR Spectroscopy

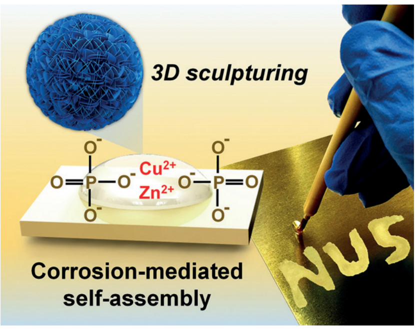


Solid gains: Fractional deuteration in ^1H-detected solid-state NMR provides powerful access to exchangeable and non-exchangeable protons without losing much, if any, spectral resolution compared to that of proteins which are devoid of non-exchangeable protons. Fractional deuteration was successfully applied to study membrane topology and supramolecular interactions of an ion channel.

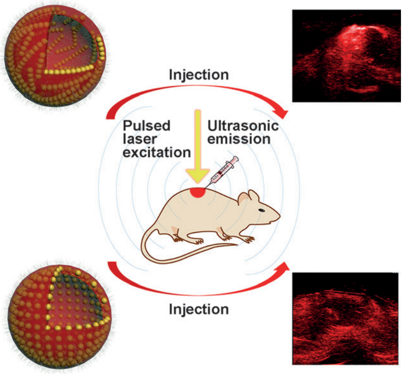
Surface Patterning

J. Wang, G. W. Ho* ________ 15804 – 15808

Corrosion-Mediated Self-Assembly (CMSA): Direct Writing Towards Sculpturing of 3D Tunable Functional Nanostructures



Brass was sculptured into 3D functional nanocomposites by a direct-writing technique induced by corrosion-mediated self-assembly. The resulting nanocomposite served as an effective photocatalyst for enhanced hydrogen generation and organic dye degradation.



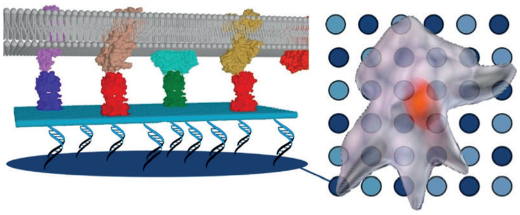
Chain vesicles: Hollow plasmonic vesicles were obtained by the folding up of gold nanoparticle strings. The strong absorption of the chain vesicles in the near-infrared (NIR) region enables their application as contrast agents in photoacoustic imaging and as drug-delivery vehicles with NIR light triggered drug release.

Photoacoustic Imaging

Y. J. Liu, J. He, K. K. Yang, C. L. Yi, Y. Liu, L. M. Nie, N. M. Khashab, X. Y. Chen,* Z. H. Nie* ______ **15809 – 15812**

Folding Up of Gold Nanoparticle Strings into Plasmonic Vesicles for Enhanced Photoacoustic Imaging

Back Cover

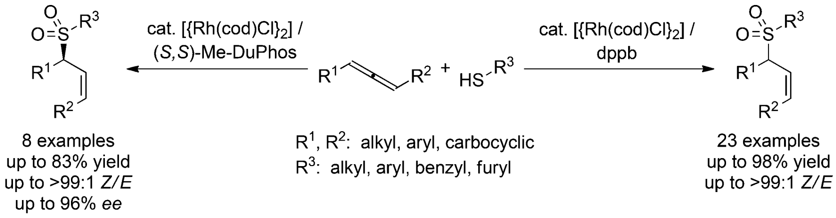


MOSAIC combines DNA micro- and nanostructures to present ligands to living cells on surfaces (see picture) with a full control over their stoichiometry and nanoscale orientation. This technology allows to address fundamental questions in cell signaling.

DNA Nanostructures

A. Angelin, S. Weigel, R. Garrecht, R. Meyer, J. Bauer, R. K. Kumar, M. Hirtz, C. M. Niemeyer* ______ **15813 – 15817**

Multiscale Origami Structures as Interface for Cells



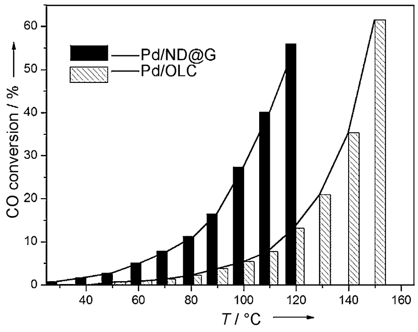
Zelectivity: The title reaction permits the synthesis of valuable allylic thioethers and sulfones in excellent *Z* selectivity. By using unsymmetrically 1,3-disubstituted allenes, good to high regioselectivities were obtained. Asymmetric hydrothiolation of racemic allenes with (*S*,*S*)-Me-DuPhos meets the criteria of a dynamic kinetic resolution. Me-DuPhos = 2′,5′,2″,5″-tetramethyl-1,2-bis(phospholanyl)benzene.

Asymmetric Catalysis

A. B. Pritzius, B. Breit* ______ **15818 – 15822**

Z-Selective Hydrothiolation of Racemic 1,3-Disubstituted Allenes: An Atom-Economic Rhodium-Catalyzed Dynamic Kinetic Resolution

A core–shell material with a nanodiamond core and a defective graphene shell (ND@G) was fabricated and used as a support for palladium nanoparticles (Pd/NG@G). Owing to strong metal–support interactions, Pd/ND@G is a more efficient catalyst of CO oxidation than palladium nanoparticles supported on onion-like carbon (OLC).



Metal–Support Interactions

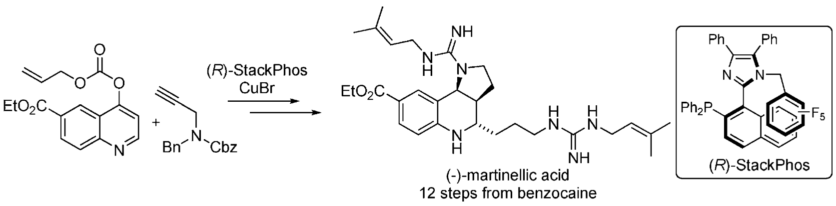
L. Zhang, H. Liu, X. Huang, X. Sun, Z. Jiang, R. Schlögl, D. S. Su* ______ **15823 – 15826**

Stabilization of Palladium Nanoparticles on Nanodiamond–Graphene Core–Shell Supports for CO Oxidation

Natural Products

M. Pappoppula,
A. Aponick* ____________ 15827 – 15830

Enantioselective Total Synthesis of (−)-Martinellic Acid

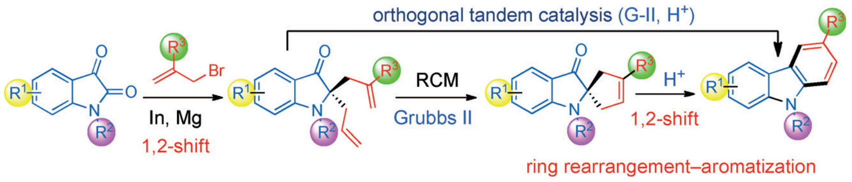


Short and sweet: An enantioselective synthesis of the natural product martinellic acid is reported. The synthesis employs a Cu-catalyzed alkyne addition to a substituted quinoline and requires the use of the axially chiral imidazole-based biaryl ligand StackPhos, and is the most concise enantioselective total synthesis of martinellic acid reported to date. Cbz = benzyloxycarbonyl.

Heterocycle Synthesis

K. Dhara, T. Mandal, J. Das,
J. Dash* ____________ 15831 – 15835

Synthesis of Carbazole Alkaloids by Ring-Closing Metathesis and Ring Rearrangement–Aromatization



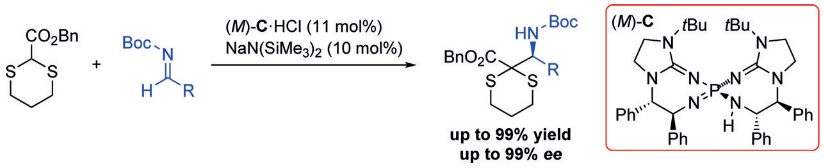
Just a hop, skip, and a jump away: The addition of allyl Grignard/indium reagents to isatins, ring-closing metathesis (RCM), and ring rearrangement–aromatization (RRA) provided carbazole derivatives in high overall yield (see scheme). The RCM step afforded spirocyclic 3-oxindoles, which underwent acid-catalyzed RRA to give carbazoles. A step-economical tandem RCM/RRA process was also developed and applied to the synthesis of carbazole alkaloids.

Organocatalysis

A. Kondoh, M. Oishi, T. Takeda,
M. Terada* ____________ 15836 – 15839

Enantioselective Addition of a 2-Alkoxycarbonyl-1,3-dithiane to Imines Catalyzed by a Bis(guanidino)iminophosphorane Organosuperbase

Front Cover

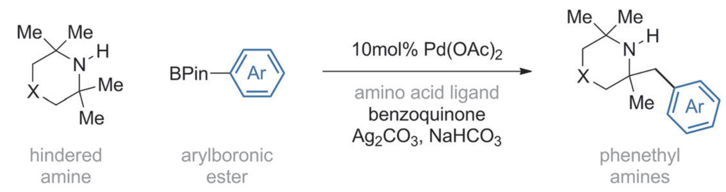


A chiral organosuperbase catalyzes enantioselective addition reactions of a 2-alkoxycarbonyl-1,3-dithiane. In particular, the chiral uncharged bis(guanidino)iminophosphorane catalyst facilitates their addition to aromatic N-Boc-protected imines to provide optically active α-amino-1,3-dithiane derivatives, which are valuable and versatile building blocks in organic synthesis.

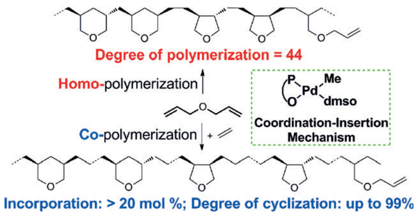
Homogeneous Catalysis

C. He, M. J. Gaunt* ____ 15840 – 15844

Ligand-Enabled Catalytic C–H Arylation of Aliphatic Amines by a Four-Membered-Ring Cyclopalladation Pathway



Four corners: A palladium-catalyzed C–H arylation of aliphatic amines with arylboronic esters is described to proceed by a four-membered-ring cyclopalladation pathway. Crucial to the successful outcome of this reaction is the action of an amino-acid-derived ligand. A range of hindered secondary amines and arylboronic esters are compatible with this process and the products of the arylation can be advanced to complex polycyclic molecules by sequential C–H activation reactions.

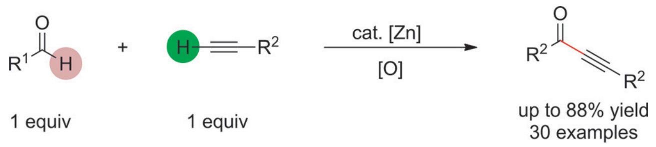


Di-allyl versus mono-allyl monomer: Diallyl ether as a monomer allows for an unprecedented incorporation (20 mol%) and enhanced activity of an allyl monomer in insertion copolymerizations. Even homopolymerization of diallyl ether is possible, thereby yielding poly(diallyl ether) with degrees of polymerization of $\mathrm{DP}_n \approx 44$, which has previously been difficult for allyl monomers by any polymerization mechanism.

Homogeneous Catalysis

Z. Jian, S. Mecking* ______ 15845–15849

Insertion Homo- and Copolymerization of Diallyl Ether



Cross paths: The title reaction for $C(sp^2)$–H/C(sp)–H cross-coupling of terminal alkynes with aldehydes was developed. It provides a simple way to access ynones from readily available materials under mild reaction conditions. Notably, a good reaction selectivity and efficiency could be achieved with a 1:1 ratio of terminal alkyne and aldehyde.

Homogeneous Catalysis

S. Tang, L. Zeng, Y. Liu,
A. Lei* ______ 15850–15853

Zinc-Catalyzed Dehydrogenative Cross-Coupling of Terminal Alkynes with Aldehydes: Access to Ynones

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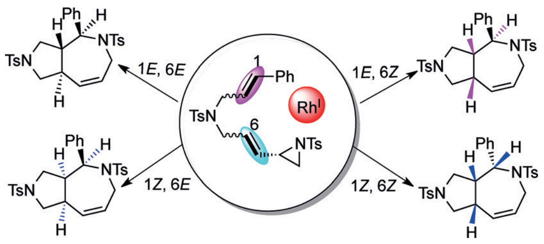

***E/Z* access**: The title reaction was realized and a range of chiral fused bicyclic azepines bearing multiple contiguous stereogenic centers can be obtained in a high-yielding and stereoselective manner. The *E*/*Z* geometry of the C=C bonds in the substrates affect the stereochemistry of the cycloadducts and up to six stereoisomers can be obtained.

Heterocycles

J.-J. Feng, T.-Y. Lin, H.-H. Wu,
J. Zhang* ______ 15854–15858

Modular Access to the Stereoisomers of Fused Bicyclic Azepines: Rhodium-Catalyzed Intramolecular Stereospecific Hetero-[5+2] Cycloaddition of Vinyl Aziridines and Alkenes

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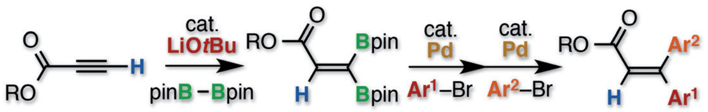


Put a B on it: A method for the synthesis of 1,1-diborylalkenes through a Brønsted base catalyzed reaction between terminal alkynes and bis(pinacolato)diboron has been developed. The procedure allows direct synthesis of functionalized 1,1-diborylalkenes from various terminal alkynes including propiolates, propiolamides, and 2-ethynylazoles.

Boration

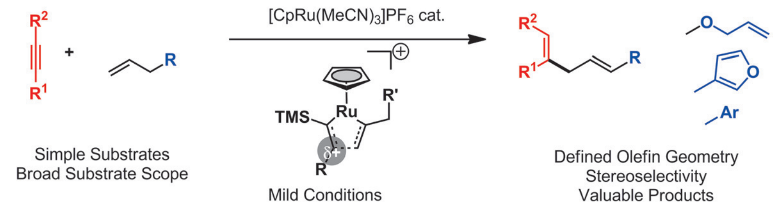
A. Morinaga, K. Nagao, H. Ohmiya,*
M. Sawamura* ______ 15859–15862

Synthesis of 1,1-Diborylalkenes through a Brønsted Base Catalyzed Reaction between Terminal Alkynes and Bis(pinacolato)diboron

Alkyne Cross-Coupling

B. M. Trost,* D. C. Koester,
A. N. Herron ———— **15863 – 15866**

Stereocontrolled Synthesis of Vinyl Boronates and Vinyl Silanes via Atom-Economical Ruthenium-Catalyzed Alkene–Alkyne Coupling

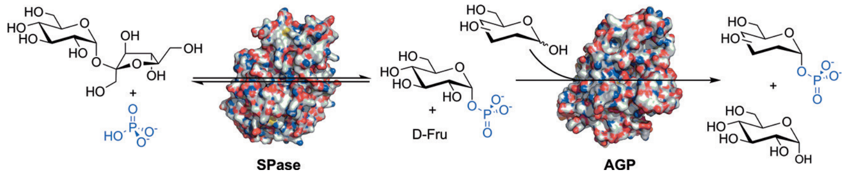


Selectivity at will: A Ru-catalyzed alkene–alkyne coupling reaction of allyl boronates with various alkynes is reported. The double bond geometry in the generated vinyl boranes can be remotely controlled by the juxtaposing boron and silicon groups on the alkyne substrate. The synthetic utility of the coupling products has been demonstrated in a variety of synthetic transformations.

Phosphorylation

P. Wildberger, M. Pfeiffer, L. Brecker,
B. Nidetzky* ———— **15867 – 15871**

Diastereoselective Synthesis of Glycosyl Phosphates by Using a Phosphorylase–Phosphatase Combination Catalyst

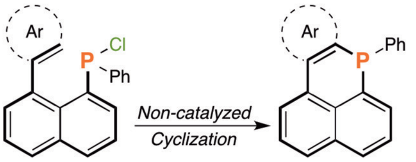


Clever combination: Phosphatase-catalyzed diastereoselective synthesis of various glycosyl phosphates from unprotected aldose substrates was achieved, with α-D-glucose 1-phosphate, derived from the phosphorylase-catalyzed conversion of sucrose and inorganic phosphate, as the phosphoryl donor. Simultaneous and sequential two-step transformations by the phosphorylase–phosphatase combination catalyst gave α-D-/β-L-aldose 1-phosphates in up to 70% yield.

Phosphorus Heterocycles

C. Romero-Nieto,* A. López-Andarias,
C. Egler-Lucas, F. Gebert, J. P. Neus,
O. Pilgram ———— **15872 – 15875**

Paving the Way to Novel Phosphorus-Based Architectures: A Noncatalyzed Protocol to Access Six-Membered Heterocycles

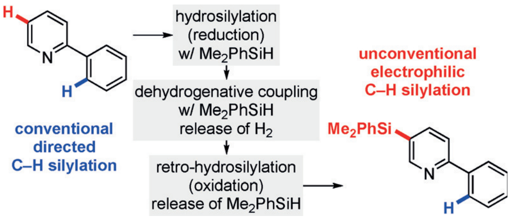


Forging rings: A new synthetic protocol provides access to fused phosphorus heterocycles. The method is compatible with five- and six-membered heterocycles as well as aromatic hydrocarbons. As a result, a series of novel phosphaphenalene derivatives was prepared.

C–H Activation

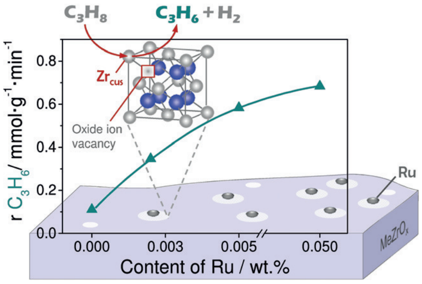
S. Wübbolt,
M. Oestreich* ———— **15876 – 15879**

Catalytic Electrophilic C–H Silylation of Pyridines Enabled by Temporary Dearomatization



Breaking the Law: Reversible 1,4-hydrosilylation of substituted pyridines was used to break and reestablish its aromaticity. The intermediate 1,4-dihydropyridine reacts as an enamine with a catalytically generated silicon electrophile, followed by deprotonation. The whole sequence is promoted by a single catalyst. This strategy addresses the C–H bond at C5 of the electron-deficient arene rather than the C–H bond in proximity to the nitrogen donor.

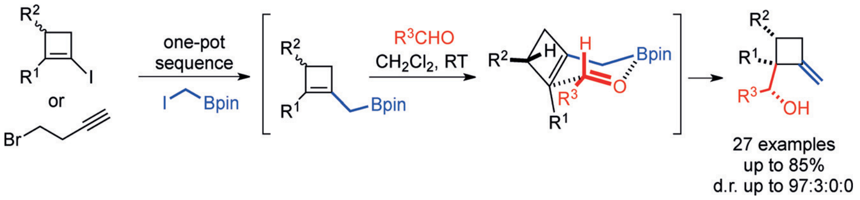
The support is the catalyst: In a new approach to propane dehydrogenation catalysts, surface, coordinatively unsaturated, Zr cations in bulk ZrO_2-based catalysts are the catalytically active sites. Their concentration can be tuned through doping ZrO_2 with metal oxides inducing the formation of such structural defects or by depositing tiny amounts (up to 0.05 wt %) of hydrogenation-active metals that promote ZrO_2 reduction.



Heterogeneous Catalysis

T. Otroshchenko, S. Sokolov, M. Stoyanova, V. A. Kondratenko, U. Rodemerck, D. Linke, E. V. Kondratenko* ——— 15880 – 15883

ZrO_2-Based Alternatives to Conventional Propane Dehydrogenation Catalysts: Active Sites, Design, and Performance



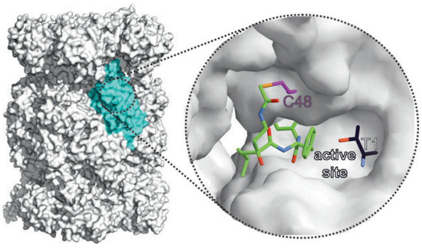
Boron, we have a problem: Difficult-to-access substituted methylenecyclobutanes can be easily and diastereoselectively synthesized in a one-pot reaction that combines boron homologation and boron allylation of an in situ generated metalated cyclobutene intermediate.

Synthetic Methods

M. Eisold, D. Didier* ——— 15884 – 15887

Highly Diastereoselective Synthesis of Methylenecyclobutanes by Merging Boron-Homologation and Boron-Allylation Strategies

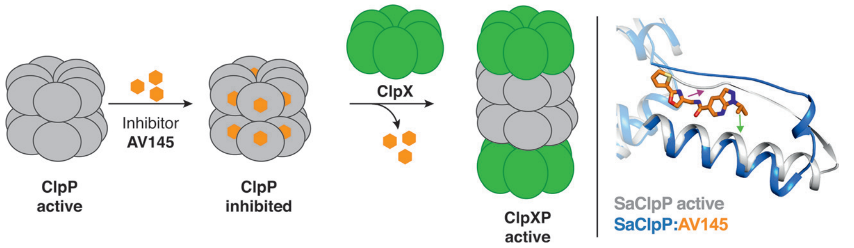
Blocking the channel: Immunoproteasome inhibitors were designed that target an isoform-specific cysteine residue in the substrate binding channel instead of the active site. The compounds display a unique mode of action compared to commonly applied proteasome drugs. They are highly isoform selective and suppress the production of inflammatory cytokines. This new class of inhibitors provides a starting point for the development of anti-inflammatory agents.



Immunoproteasome Inhibition

C. Dubiella,* R. Baur, H. Cui, E. M. Huber, M. Groll* ——— 15888 – 15891

Selective Inhibition of the Immunoproteasome by Structure-Based Targeting of a Non-catalytic Cysteine



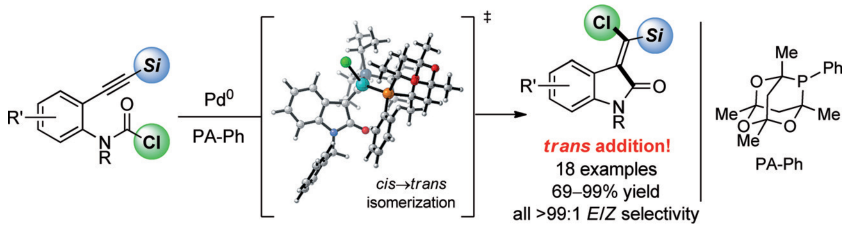
ClpX calls the tune: The first reversible inhibitor for *Staphylococcus aureus* ClpP was identified, and its mode of action was visualized at the molecular level. Structure–activity relationship studies led to improved compounds that inhibit the protease in the nanomolar range. Binding of ClpX overrides the inhibitor-induced conformational lock of ClpP and leads to the formation of an active proteolytic complex.

Drug Development

A. Pahl, M. Lakemeyer, M.-T. Vielberg, M. W. Hackl, J. Vomacka, V. S. Korotkov, M. L. Stein, C. Fetzer, K. Lorenz-Baath, K. Richter, H. Waldmann, M. Groll,* S. A. Sieber* ——— 15892 – 15896

Reversible Inhibitors Arrest ClpP in a Defined Conformational State that Can Be Revoked by ClpX Association

Synthetic Methods

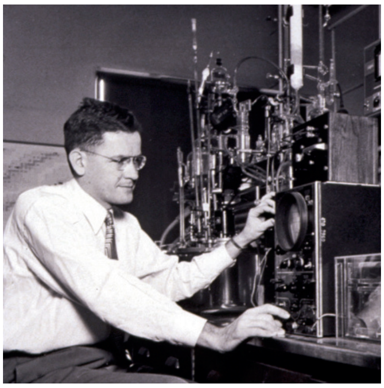


A new *trans*-formation: The use of bulky, electron-deficient phosphaadamantane ligands in combination with sterically hindered alkynes enabled a palladium(0)-catalyzed alkyne chlorocarbamoylation reaction with high reactivity and exclusive *trans* selectivity.

And Finally

John D. Roberts

A 20th century pioneer in physical organic chemistry, John D. Roberts celebrated his 97th birthday in 2015. To mark this occasion, poignant quotes and anecdotes have been collected embodying his philosophies of life and his wide-ranging experiences and interests. A brief summary of Roberts's major scientific accomplishments is also presented. Photograph courtesy John D. Roberts.



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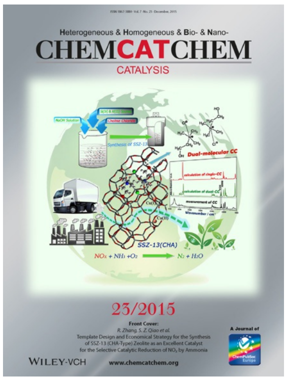

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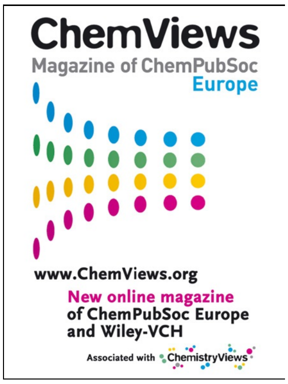

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