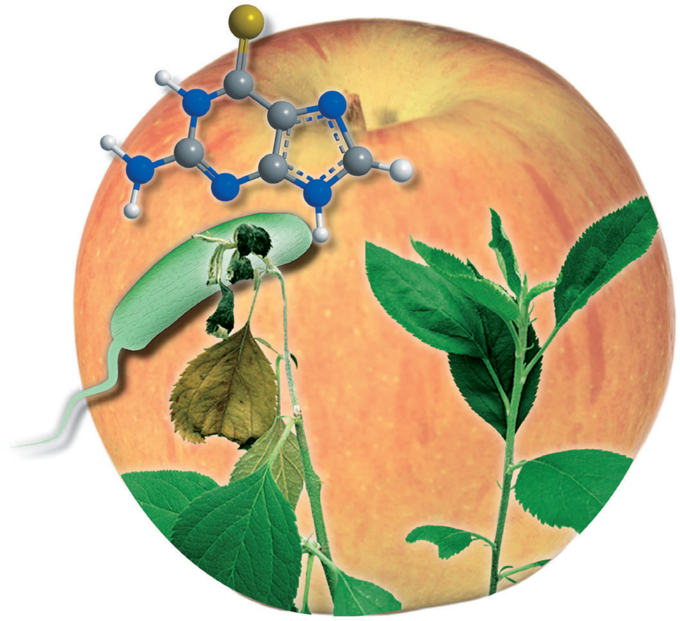
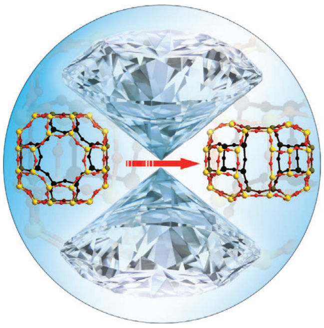
Fire blight ...

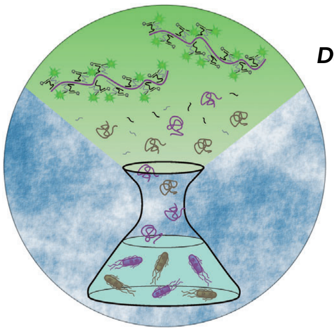


... , a devastating plant disease that mainly affects apple and pear trees, is caused by the bacterium *Erwinia amylovora*. In their Communication on page 10564 ff. C. Hertweck et al. unveil a key role of the antimetabolite 6-thioguanine in fire blight of apple plants. Biosynthetic studies indicate that the protein YcfA mediates guanine thionation in analogy to 2-thiouridylase. (The authors thank Nico Ueberschaar for his contribution to the cover picture.)

High-Pressure Zeolites

The compression of a common zeolite into a new zeolite structure is described by A. Corma and co-workers in their Communication on page 10458 ff. This new zeolite gives improved separation of propene from propane, an important industrial process.





Detection of RNA

In their Communication on page 10586 ff., Y. V. Gerasimova and D. M. Kolpashchikov present a simple and rapid assay for the detection of bacteria in clinical, food, or environmental specimens.

Synthetic Biology

J. M. Gibbs-Davis et al. report the use a cross-catalytic strategy for rapid, isothermal self-replication of DNA in their Communication on page 10577 ff. A destabilizing abasic site in the replicating strand is key to consistent, efficient replication cycles.

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Service

Author Profile

"I lose track of time when I climb a mountain. My biggest motivation is to reach the summit. …"
This and more about Stephan A. Sieber can be found on page 10416.

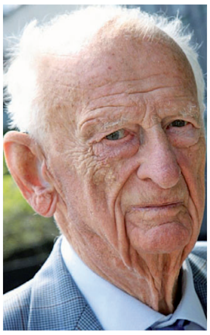
News

N. Maulide

D. Enders

K. Ray

Obituaries



Dr. Haldor Topsøe, founder and Chairman of the Board of Haldor Topsøe A/S, passed away on May 21, 2013, only four days before his one-hundredth birthday. He made significant technological and scientific contributions toward solving key global challenges related to energy, food, and the environment.

Books

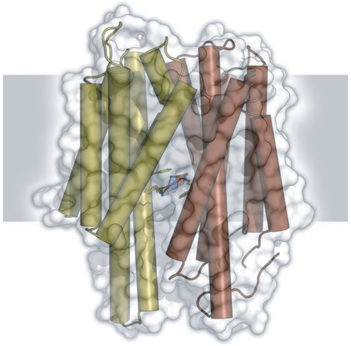
Highlights

Membrane Transport

S. L. A. Andrade,
O. Einsle* ———— **10422–10424**

The Tricky Task of Nitrate/Nitrite Antiport

Subtle differences: Two recent crystal structures have provided the first insight into nitrate/nitrite exchangers (example shown with bound nitrite), which are crucial to bacterial metabolism. A direct comparison of the structures reveals how the proteins can distinguish between their highly similar substrates and translate this into a conformational change to translocate ions across the membrane.

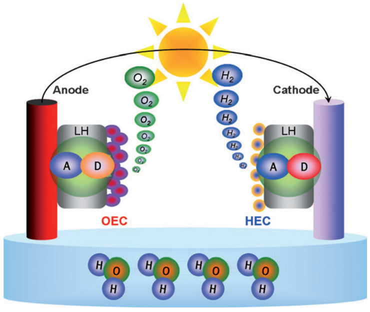


Minireviews

Artificial Photosynthesis

K. S. Joya,* Y. F. Joya, K. Ocakoglu,
R. van de Krol* ———— **10426–10437**

Water-Splitting Catalysis and Solar Fuel Devices: Artificial Leaves on the Move



Turning a new leaf: Electrochemical and light-driven electrocatalytic water oxidation assemblies have been targeted to develop artificial photosynthetic system. Such "Artificial Leaves" are used to make H_2 and O_2 using water as a raw material. The design and performance of the water oxidation systems and standalone solar-to-fuel conversion devices are presented. Progress in the field and future perspectives of water splitting are also discussed.

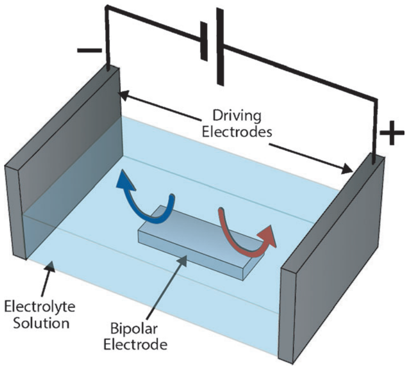
Reviews

Electrochemistry

S. E. Fosdick, K. N. Knust, K. Scida,
R. M. Crooks* ———— **10438–10456**

Bipolar Electrochemistry

A bipolar electrode is a single conductive object that drives both electrochemical oxidations and reductions simultaneously. They have been used for many important applications and advances, for example, in sensors or as mobile electrodes that are able to move freely in solution.



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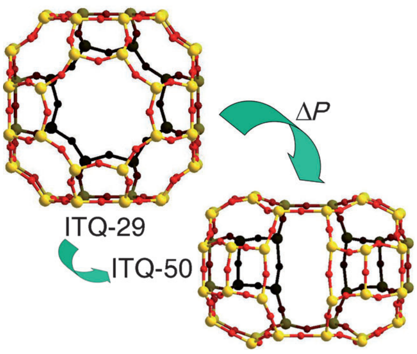
Communications



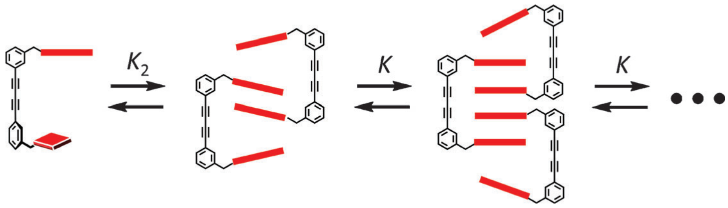
The first pressure-induced solid-phase synthesis of a zeolite has been found through compression of a common zeolite, ITQ-29 (see scheme, Si yellow, O red). The new microporous structure, ITQ-50, has a unique structure and improved performance for propene/propane separation with respect the parent material ITQ-29.

High-Pressure Zeolites

J. L. Jordá, F. Rey, G. Sastre, S. Valencia, M. Palomino, A. Corma,* A. Segura, D. Errandonea, R. Lacomba, F. J. Manjón, Ó. Gomis, A. K. Kleppe, A. P. Jephcoat, M. Amboage, J. A. Rodríguez-Velamazán ______ **10458 – 10462**

Synthesis of a Novel Zeolite through a Pressure-Induced Reconstructive Phase Transition Process

Frontispiece



Arm wrestling: Backbone-directed “arm-to-arm” aggregation of a newly designed perylene bisimide (PBI) dyad with a defined intramolecular space leads to the growth of kinetically stable extended PBI π-stacks. This PBI dyad was shown to assemble into oligomers up to 21 units in length.

Supramolecular Chemistry

C. Shao, M. Stolte, F. Würthner* ______ **10463 – 10467**

Backbone-Directed Perylene Dye Self-Assembly into Oligomer Stacks

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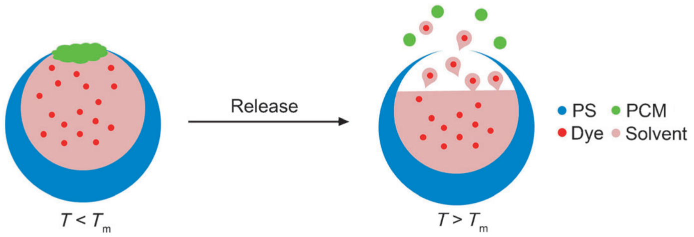

Keep your wine chilled! Microscale polystyrene (PS) bottles are loaded with dye molecules and then corked with a phase-change material (PCM). When the temperature is raised beyond its melting point, the PCM quickly melts and triggers an instant release of the encapsulated dye. The release profiles can be manipulated by using a binary mixture of PCMs with different melting points.

Functional Particles

D. C. Hyun, P. Lu, S.-I. Choi, U. Jeong, Y. Xia* ______ **10468 – 10471**

Microscale Polymer Bottles Corked with a Phase-Change Material for Temperature-Controlled Release

Sharp and refreshing

Angewandte Chemie

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2012–124/17

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4,5-Dihydroxy-2,3-pentandion …

… (DPD) ist die gemeinsame Vorstufe der bakteriellen Quorum-Sensing-Moleküle der Autoinducer-2-Klasse. DPD wurde als universelles Signalmolekül Gram-positiver und Gram-negativer Bakterien vorgeschlagen. In der Zuschrift auf S. 4280 ff. beschreiben K. D. Janda et al. ein komplexes Spektrum an DPD-Strukturisomeren, was darauf hindeutet, dass Bakterien über eine umfangreichere chemische Signalsprache verfügen, als bisher angenommen (Copyright für das Detektivbild: Martin Malchev/ Dreamstime.com).

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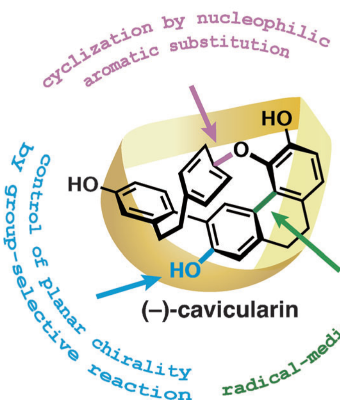
Total Synthesis

H. Takiguchi, K. Ohmori,*
K. Suzuki* 10472 – 10476

Synthesis and Determination of the Absolute Configuration of Cavicularin by a Symmetrization/Asymmetrization Approach

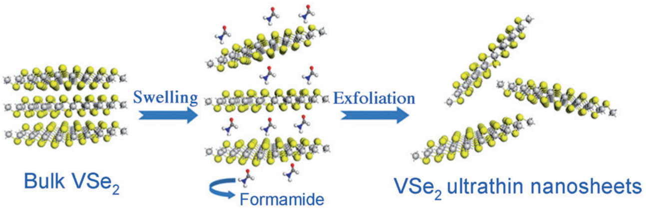
Taking the strain: The asymmetric total synthesis and stereochemical assignment of (−)-cavicularin, which features a highly strained polycyclophane ring system, has been achieved. The key features of this synthesis are 1) macrocyclization by an S_NAr reaction, 2) group-selective reaction to induce planar chirality in a highly stereoselective manner, and 3) radical transannulation to construct the highly strained ring system.



Inorganic Graphene Analogues

K. Xu, P. Z. Chen, X. L. Li, C. Z. Wu,*
Y. Q. Guo, J. Y. Zhao, X. J. Wu,
Y. Xie* 10477 – 10481

Ultrathin Nanosheets of Vanadium Diselenide: A Metallic Two-Dimensional Material with Ferromagnetic Charge-Density-Wave Behavior

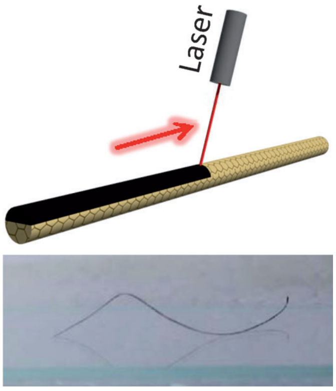


A new metallic 2D material with high electrical conductivity ($1\times10^3\ \mathrm{S\,m^{-1}}$) consists of VSe_2 ultrathin nanosheets with 4–8 Se-V-Se atomic layers. This is the first 2D transition-metal dichalcogenide with intrinsic room-temperature ferromagnetism. The nanosheets increase the charge-density-wave transition temperature to 135 K by dimensional reduction.

Graphene Actuators

H. Cheng, J. Liu, Y. Zhao, C. Hu, Z. Zhang,
N. Chen, L. Jiang, L. Qu* 10482 – 10486

Graphene Fibers with Predetermined Deformation as Moisture-Triggered Actuators and Robots



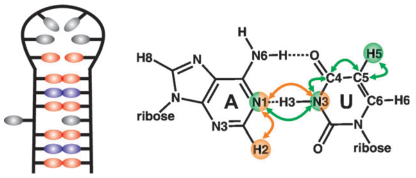
Enough to make your hair curl! Moisture-responsive graphene (G) fibers can be prepared by the positioned laser reduction of graphene oxide (GO) counterparts. When exposed to moisture, the asymmetric G/GO fibers display complex, well-controlled motion/deformation in a predetermined manner. These fibers can function not only as a single-fiber walking robot under humidity alternation but also as a new platform for woven devices and smart textiles.

RNA Dynamics

A. Dallmann, B. Simon, M. M. Duszczyk,
H. Kooshapur, A. Pardi, W. Bermel,
M. Sattler* 10487 – 10490

Efficient Detection of Hydrogen Bonds in Dynamic Regions of RNA by Sensitivity-Optimized NMR Pulse Sequences

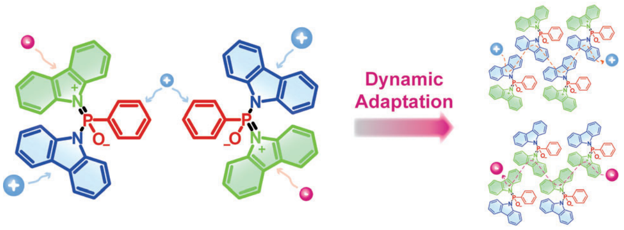
Improved Sensitivity: Efficient NMR experiments are presented for determining the secondary structure in large and dynamic RNAs using *J*-couplings across hydrogen bonds (see picture). The experiments provide up to eight-fold improved sensitivity and thus enable detection of base pairs in dynamic regions even in large RNAs.



Organic Optoelectronics

Y. Tao, J. J. Xiao, C. Zheng, Z. Zhang, M. K. Yan, R. Chen,* X. H. Zhou, H. H. Li, Z. F. An, Z. X. Wang, H. Xu,* W. Huang* ______ **10491 – 10495**

Dynamically Adaptive Characteristics of Resonance Variation for Selectively Enhancing Electrical Performance of Organic Semiconductors

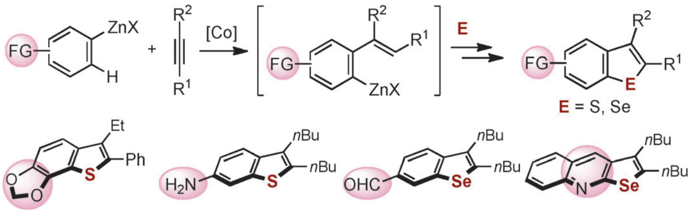


Increased resonance: The selective tuning of the optoelectronic properties of organic semiconductors is possible by enantiotropic resonance variation. Using resonance forms of $N^+{=}P{-}O^-$ in a series of arylamine-phosphine oxide hybrids afforded low-voltage-driven phosphorescent OLEDs with outstanding performances.

Synthetic Methods

B. Wu, N. Yoshikai* ______ **10496 – 10499**

Versatile Synthesis of Benzothiophenes and Benzoselenophenes by Rapid Assembly of Arylzinc Reagents, Alkynes, and Elemental Chalcogens

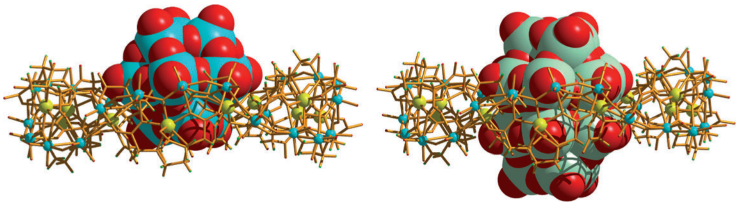


Rapidly aSSembled: The combination of cobalt-catalyzed migratory arylzincation and copper-mediated/catalyzed chalcogenative cyclization allows the construction of benzothiophenes and benzoselenophenes from arylzinc reagents, alkynes, and elemental chalcogens. Benzothiophenes and benzoselenophenes diversely functionalized at the benzene ring moiety can be prepared, which are not readily accessible by conventional methods.

Supramolecular Chemistry

X. Fang,* L. Hansen, F. Haso, P. Yin, A. Pandey, L. Engelhardt, I. Slowing, T. Li, T. Liu, M. Luban, D. C. Johnston ______ **10500 – 10504**

$\{Mo_{24}Fe_{12}\}$ Macrocycles: Anion Templation with Large Polyoxometalate Guests



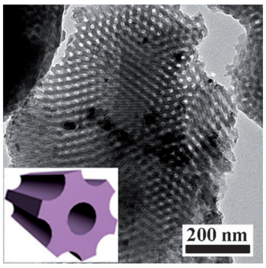
POM and circumstance: Nanometer-sized polyoxometalates (POMs) bring a new direction to anion-templated supramolecular chemistry. The Keggin (left) and Dawson-type (right) polyoxoanions direct the assembly of giant metallomacrocycles through an array of weak hydrogen-bonding interactions. The concerted action of multiple hydrogen bonds keeps the templating guests embedded within the hosts, even in the solution state.

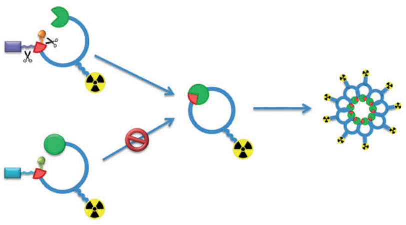
Mesoporous Materials

W. Luo, Y. H. Li, J. P. Dong, J. Wei, J. Q. Xu, Y. H. Deng,* D. Y. Zhao* ______ **10505 – 10510**

A Resol-Assisted Co-Assembly Approach to Crystalline Mesoporous Niobia Spheres for Electrochemical Biosensing

Templated pores: A resol-assisted solvent-evaporation-induced self-assembly (RA-EISA) gives unique ordered mesoporous niobia spheres by using the amphiphilic diblock copolymer PEO-*b*-PS as a template. The mesoporous Nb_2O_5 spheres have ordered hexagonal structures, large pore size and high surface area, and a nanocrystalline framework (see picture). They show excellent electrochemical sensing of hydrogen peroxide.





Drug Design: An ^{18}F-labeled caspase-3-sensitive nanoaggregation positron emission tomography tracer was prepared and evaluated for imaging the caspase-3 activity in doxorubicin-treated tumor xenografts. Enhanced retention of the ^{18}F activity in apoptotic tumors is achieved through intramolecular macrocyclization and in situ aggregation upon caspase-3 activation (see picture).

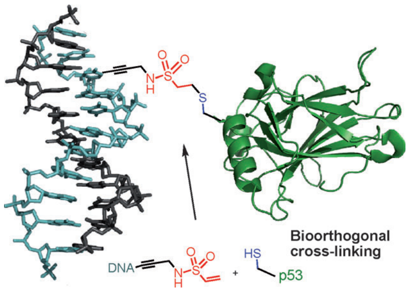
Radiopharmacology

B. Shen, J. Jeon, M. Palner, D. Ye, A. Shuhendler, F. T. Chin,* J. Rao* ———— **10511 – 10514**

Positron Emission Tomography Imaging of Drug-Induced Tumor Apoptosis with a Caspase-Triggered Nanoaggregation Probe

Inside Cover

Bioorthogonal covalent cross-linking of DNA-binding proteins (p53) to DNA was achieved through novel DNA probes bearing a reactive vinylsulfonamide (VS) group. The VS-modified dCTP served as building block for polymerase synthesis of modified DNA, which was readily conjugated with cysteine-containing peptides and proteins by Michael addition.



DNA–Protein cross-linking

J. Dadová, P. Orság, R. Pohl, M. Brázdová, M. Fojta, M. Hocek* ———— **10515 – 10518**

Vinylsulfonamide and Acrylamide Modification of DNA for Cross-linking with Proteins

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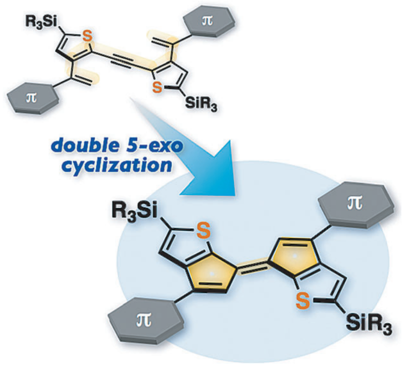

Smooth and selective: Upon photoirradiation, bis(3-alkenyl-2-thienyl)acetylenes smoothly and selectively undergo double 5-*exo-dig* cyclization to produce a series of thiophene-fused pentafulvalenes with various aryl substituents. In this fused π-conjugated skeleton, the fused thiophene rings and the aryl substituents significantly modulate the electronic structure of the pentafulvalene skeleton.

Alkyne Cyclization

A. Fukazawa,* T. Karasawa, H. Zhang, K. Minemura, C. Camacho, J. Wang, S. Irle,* S. Yamaguchi* ———— **10519 – 10523**

Photochemical Double 5-*exo* Cyclization of Alkenyl-Substituted Dithienylacetylenes: Efficient Synthesis of Diarylated Dithienofulvalenes

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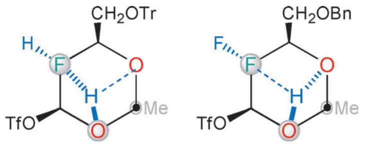


An intramolecular bifurcated H-bond from the axial HO-2 group to the axial F-4 atom and to the O5 atom of α-D-hexopyranosides in apolar solvents is evidenced in ^{1}H NMR spectra. The H-accepting properties of the F atom are modulated by the orientation of the O-substituent at the C3 atom and by an additional F atom at the C4 atom (see picture).

Hydrogen Bonding

G. T. Giuffredi, V. Gouverneur,* B. Bernet* ———— **10524 – 10528**

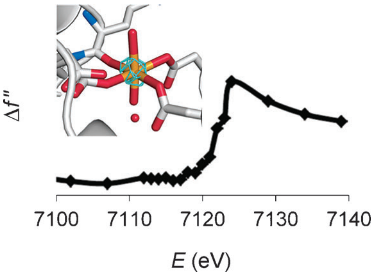
Intramolecular OH⋯FC Hydrogen Bonding in Fluorinated Carbohydrates: CHF is a Better Hydrogen Bond Acceptor than CF_2

Nitrogenase

L. M. Zhang, J. T. Kaiser, G. Meloni,
K. Y. Yang, T. Spatzal, S. L. A. Andrade,
O. Einsle, J. B. Howard,
D. C. Rees* ________ **10529 – 10532**

The Sixteenth Iron in the Nitrogenase MoFe Protein

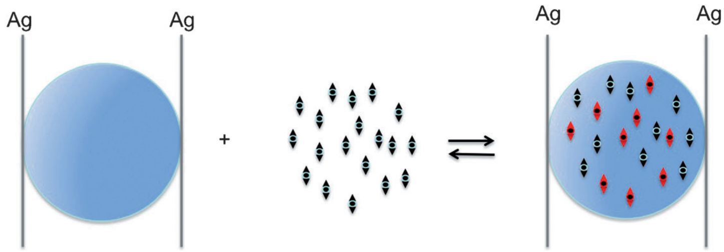
Another iron in the fire: X-ray anomalous diffraction studies on the nitrogenase MoFe protein show the presence of a mononuclear iron site, designated as Fe16, which was previously identified as either Ca^{2+} or Mg^{2+}. The position of the absorption edge indicates that this site is in the oxidation state +2. The high sequence conservation of the residues coordinated to Fe16 emphasizes the potential importance of the site in nitrogenase.



Strong Coupling

A. Canaguier-Durand, E. Devaux,
J. George, Y. Pang, J. A. Hutchison,
T. Schwartz, C. Genet, N. Wilhelms,
J.-M. Lehn,
T. W. Ebbesen* ________ **10533 – 10536**

Thermodynamics of Molecules Strongly Coupled to the Vacuum Field

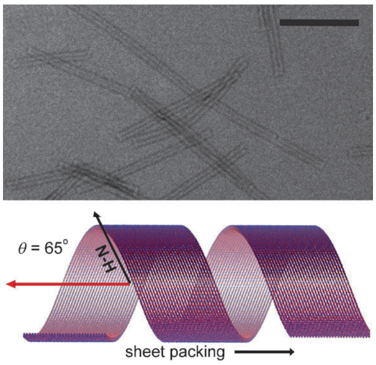


The thermodynamics of strong coupling between molecules and the vacuum field is analyzed and the Gibbs free energy, the enthalpy, and entropy of the coupling process are determined for the first time. The thermodynamic parameters are a function of the Rabi splitting and the microscopic solvation. The results provide a new framework for understanding light-molecule strong coupling.

Peptide Nanotubes

D. A. Middleton,* J. Madine,
V. Castelletto,
I. W. Hamley ________ **10537 – 10540**

Insights into the Molecular Architecture of a Peptide Nanotube Using FTIR and Solid-State NMR Spectroscopic Measurements on an Aligned Sample

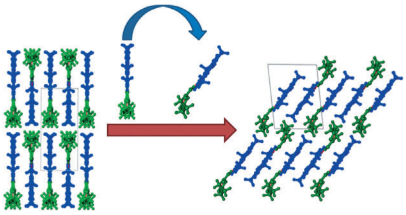


Queuing up: Molecular orientation within macroscopically aligned nanotubes of the peptide AAAAAAK can be studied by solid-state NMR and IR spectroscopy. Line shape analysis of the NMR spectra indicates that the peptide N–H bonds are tilted 65–70° relative to the nanotube long axis. Re-evaluation of earlier X-ray fiber diffraction data suggests that the peptide molecules are hydrogen-bonded in a helical arrangement along the nanotube axis.

Surface Analysis

R. Thakuria, M. D. Eddleston,
E. H. H. Chow, G. O. Lloyd, B. J. Aldous,
J. F. Krzyzaniak, A. D. Bond,
W. Jones* ________ **10541 – 10544**

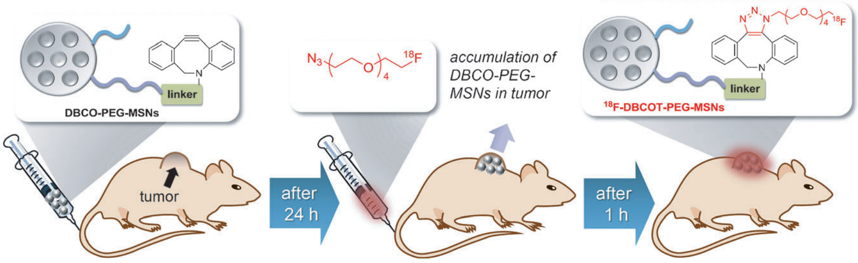
Use of In Situ Atomic Force Microscopy to Follow Phase Changes at Crystal Surfaces in Real Time



AFM of cocrystals: Atomic force microscopy can be used to observe phase changes at crystal surfaces where the transformation is accompanied by a change in the spacing between layers of molecules (see picture). The conversion of a metastable polymorph of the caffeine–glutaric acid cocrystal into the thermodynamically stable form was analyzed continuously in situ using intermittent-contact-mode atomic force microscopy.

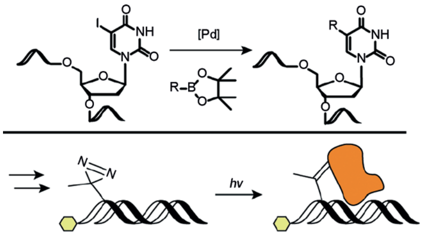
Let's get together: Racemic samples of *d*- and *l*-enantiomorphous $NaBrO_3$ (or $NaClO_3$) crystals aggregate with nearly complete enantioselection. Centimeter-sized enantiopure megacrystals are often produced, and these can be sorted easily.

Crystal Growth



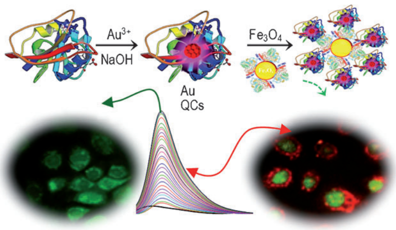
Last-minute labeling: Mesoporous silica nanoparticles (MSNs) were modified with a very short half-life fluorine-18-labeled azide radiotracer by a cycloaddition reaction after the MSNs had reached the tumor site in mice. The tumor could then be visualized successfully with positron emission tomography.

In Vivo Labeling



Quick and clean: A method for Pd-catalyzed Suzuki–Miyaura cross-coupling to iododeoxyuridine (IdU) in DNA is described. Key to the reactivity is the choice of the ligand and the buffer. A covalent [Pd]–DNA intermediate was isolated and characterized. Photocrosslinking probes were generated to trap proteins that bind to epigenetic DNA modifications.

DNA Modification



Nanoprobes based on quantum clusters (QC) with near-infrared fluorescence, magnetic-resonance-imaging contrast, and singlet-oxygen-sensitized intracellular fluorescence are studied. The generation of singlet oxygen and singlet-oxygen-sensitized fluorescence uncaging by magnetic and NIR-emitting nanoparticles are exploited for multimodal bioimaging in vitro.

Photochemistry

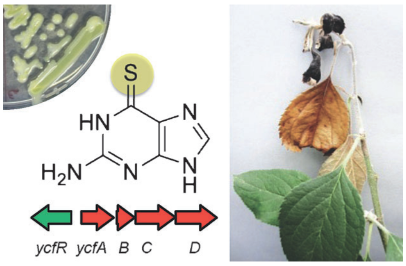
Natural Products

S. Coyne, C. Chizzali, M. N. A. Khalil, A. Litomska, K. Richter, L. Beerhues, C. Hertweck* ———— **10564 – 10568**

Biosynthesis of the Antimetabolite 6-Thioguanine in *Erwinia amylovora* Plays a Key Role in Fire Blight Pathogenesis

Front Cover

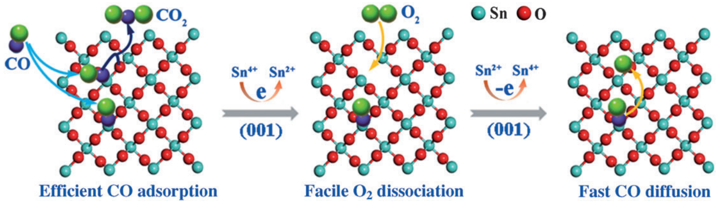
Sulfur for fire: The molecular basis for the biosynthesis of the antimetabolite 6-thioguanine (6TG) was unveiled in *Erwinia amylovora*, the causative agent of fire blight. Bioinformatics, heterologous pathway reconstitution in *E. coli*, and mutational analyses indicate that the protein YcfA mediates guanine thionation in analogy to 2-thiouridylase. Assays in planta and in cell cultures reveal for the first time a crucial role of 6TG in fire blight pathogenesis.



Heterogeneous Catalysis

Y. F. Sun, F. C. Lei, S. Gao, B. C. Pan, J. F. Zhou, Y. Xie* ———— **10569 – 10572**

Atomically Thin Tin Dioxide Sheets for Efficient Catalytic Oxidation of Carbon Monoxide

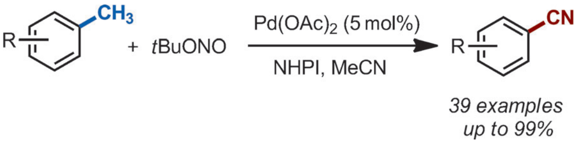


The thinner the better: SnO_2 sheets that are five atomic layers thick are an efficient catalyst for the oxidation of CO (see picture). These sheets, which have 40% surface atom occupancy and are fabricated by a scalable ethylenediamine-assisted pathway, show remarkably improved catalytic performances compared to other SnO_2 species, with the apparent activation energy lowered to 59.2 kJ mol^{-1} and the full-conversion-temperature lowered to 250 °C.

Synthetic Methods

Z. Shu, Y. Ye, Y. Deng, Y. Zhang,* J. Wang* ———— **10573 – 10576**

Palladium(II)-Catalyzed Direct Conversion of Methyl Arenes into Aromatic Nitriles



From methyl to nitrile: A mild ammoxidation method, which directly converts methyl arenes into aromatic nitriles, has been developed by using $Pd(OAc)_2$ and *N*-hydroxyphthalimide (NHPI) as the catalysts, and *tert*-butyl nitrite as the nitrogen source and oxidant.

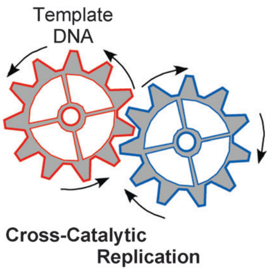
Synthetic Biology

A. Kausar, C. J. Mitran, Y. Li, J. M. Gibbs-Davis* ———— **10577 – 10581**

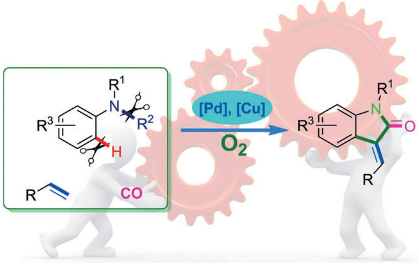
Rapid, Isothermal DNA Self-Replication Induced by a Destabilizing Lesion

Back Cover

You spin me round: Using a destabilizing abasic site and high concentration of ligase, rapid DNA self-replication in an isothermal ligase chain reaction (LCR) was produced. Both destabilization and rapid ligation are essential for proper LCR replication. This method also provides insight into prebiotic nucleotide replication and is a potential amplification method for biodiagnostics.



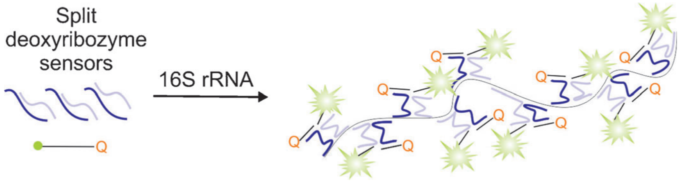
Synthetic Methods



C–H/C–N activation: The first palladium/copper-catalyzed aerobic oxidative C–H alkenylation/*N*-dealkylative carbonylation of tertiary anilines has been developed. Various functional groups were tolerated and acrylic ester could also be suitable substrates. This transformation provided efficient and straightforward synthesis of biologically active 3-methyleneindolin-2-one derivatives from cheap and simple substrates.

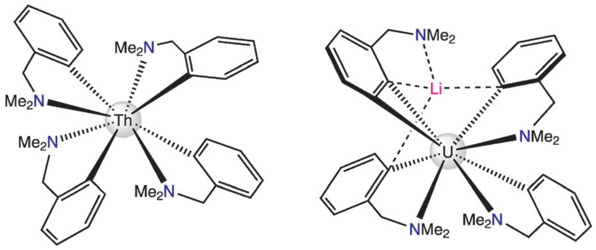
Detection of RNA

Inside Back Cover



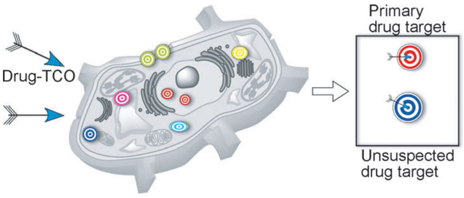
Sixty-four DNA strands hybridize to 16S rRNA to form 32 deoxyribozyme catalytic cores that produce a fluorescent signal. The approach allows detection of 0.6 pM 16S rRNA, or about 3×10^4 bacterial cells in a PCR-free format.

Uranium Chemistry



Why do U react like that? Reaction of 2-Li-$C_6H_4CH_2NMe_2$ with $[MCl_4(DME)_n]$ (M = Th, $n=2$; M = U, $n=0$) results in the formation of a thorium aryl complex, $[Th(2\text{-}C_6H_4CH_2NMe_2)_4]$ or a uranium benzyne complex, $[Li][U(2,3\text{-}C_6H_3CH_2NMe_2)(2\text{-}C_6H_4CH_2NMe_2)_3]$. A DFT analysis suggests that the formation of a benzyne complex with U but not with Th is a kinetic and not thermodynamic effect.

Proteomics

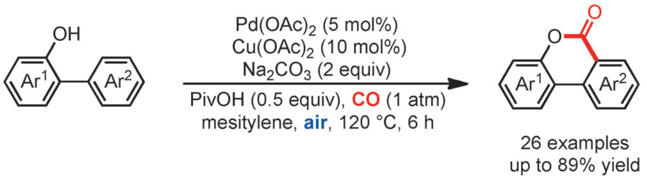


A proteomics method to pull down secondary drug targets from live cells is described. The drug of interest is modified with *trans*-cyclooctene (TCO) and incubated with live cells. Upon cell lysis, the modified drug bound to the protein is pulled down using magnetic beads decorated with a cleavable tetrazine-modified linker. Samples are then run on an SDS-PAGE gel and isolated bands are submitted for mass spectrometry analysis to identify drug targets.

C–H Carbonylation

S. Luo, F.-X. Luo, X.-S. Zhang,
Z.-J. Shi* ______ **10598 – 10601**

Synthesis of Dibenzopyranones through Palladium-Catalyzed Directed C–H Activation/Carbonylation of 2-Arylphenols

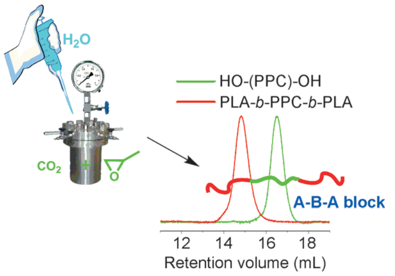


Dibenzopyranones were synthesized by a palladium-catalyzed phenol-directed C–H activation/carbonylation of 2-phenylphenol derivatives in the presence of CO. Pd(OAc)$_2$ was used as a catalyst and Cu(OAc)$_2$ as a catalytic oxidant in the presence of air.

Coordination Copolymerization

D. J. Darensbourg,*
G.-P. Wu ______ **10602 – 10606**

A One-Pot Synthesis of a Triblock Copolymer from Propylene Oxide/Carbon Dioxide and Lactide: Intermediacy of Polyol Initiators

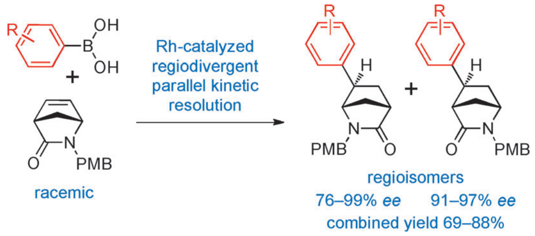


Just add water: The copolymerization of propylene oxide and CO$_2$ catalyzed by a cobalt complex is tolerant to the addition of water as chain-transfer reagent to afford polyols (HO-(PPC)-OH) with narrow molecular weight distributions (see picture; PPC = poly(propylene carbonate); PLA = polylactide). The addition of an organocatalyst to these polyols in the presence of lactides produces well-defined triblock copolymers (PLA-*b*-PPC-*b*-PLA).

Kinetic Resolution

A. S. Kamlet,* C. Préville, K. A. Farley,
D. W. Piotrowski ______ **10607 – 10610**

Regioselective Hydroarylations and Parallel Kinetic Resolution of Vince Lactam

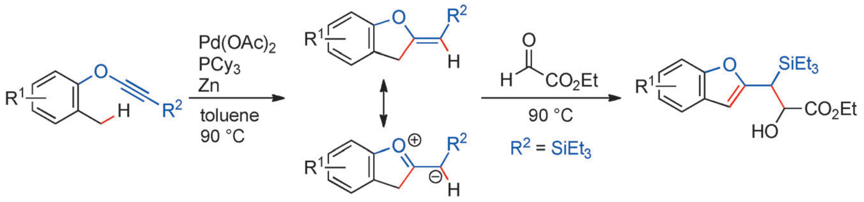


Two regioselective and complementary hydroarylation reactions of an unsymmetrical cyclic olefin have been developed. The products can be transformed in one step into constrained γ-amino acids. Regioselective arylation of Vince lactam is controlled by the choice of phosphine ligand enantiomer and the substituent on the amide nitrogen atom. The method was extended to a general regiodivergent parallel kinetic resolution of the racemic lactam.

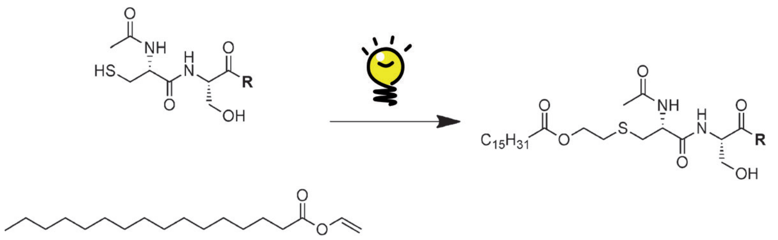
Heterocycles

Y. Minami,* K. Yamada,
T. Hiyama* ______ **10611 – 10615**

Palladium-Catalyzed Hydrobenzylation of *ortho*-Tolyl Alkynyl Ethers by Benzylic C−H Activation: Remarkable Alkynoxy-Directing Effect



It's selective: The title reaction involves palladium(0)-catalyzed insertion of C≡C bonds into benzylic C(sp^3)−H bonds, thus providing efficient access to 2-methylene-2,3-dihydrobenzofurans, which transform into benzofurans upon treatment with a weak acid (e.g., AcOH) and electrophiles. The alkynoxy group serves as a directing group in promoting C−H bond functionalization.

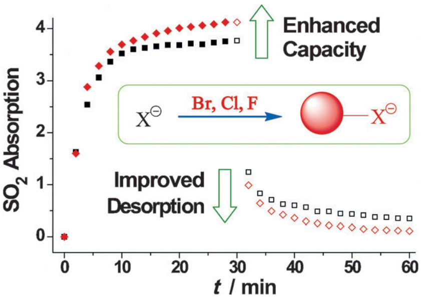


A radical lipidation: Application of a novel thiol–ene lipidation enables the one-step synthesis of self-adjuvanting antigenic peptides as vaccine candidates. The resultant monoacyl lipopeptides are shown to activate monocytes in a robust manner.

Lipopeptides

T. H. Wright, A. E. S. Brooks, A. J. Didsbury, G. M. Williams, P. W. R. Harris, P. R. Dunbar, M. A. Brimble* ________ **10616 – 10619**

Direct Peptide Lipidation through Thiol–Ene Coupling Enables Rapid Synthesis and Evaluation of Self-Adjuvanting Vaccine Candidates



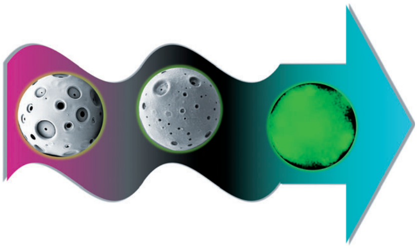
You can have your cake and eat it too: A "dual-tuning" strategy for improving the capture of SO$_2$ was developed by introducing electron-withdrawing sites on the anions to produce several kinds of functionalized ionic liquids. Those functionalized with a halogen group exhibited improved performance over their nonhalogenated counterparts, leading to highly efficient and reversible capture.

Gas Separation

G. Cui, J. Zheng, X. Luo, W. Lin, F. Ding, H. Li, C. Wang* ________ **10620 – 10624**

Tuning Anion-Functionalized Ionic Liquids for Improved SO$_2$ Capture

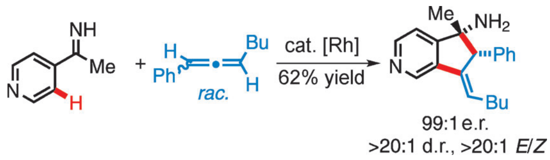
Taking advantage of photothermal conversion, the surface pores of water-dispersible single-walled carbon nanotubes assembled on polymer particles were rapidly closed by NIR irradiation to produce macroporous polymeric microspheres with multiple interconnected chambers. These particles can act as smart containers to encapsulate and hold DNA molecules.



DNA Trapping

Q. Qian, X. Huang, X. Zhang, Z. Xie, Y. Wang* ________ **10625 – 10629**

One-step Preparation of Macroporous Polymer Particles with Multiple Interconnected Chambers: A Candidate for Trapping Biomacromolecules



Racemization required: Rhodium(I)-catalyzed C–H activation directed by unprotected ketimines initiates selective [3+2] cycloaddition with allenes, providing access to highly substituted indenylamines. The reaction proceeds through the dynamic kinetic asymmetric transformation of racemic allenes. The catalyst controls the enantio- and diastereoselectivity, the regioselectivities of the C–H activation and allene incorporation, as well as the *E*/*Z* ratio.

Asymmetric Catalysis

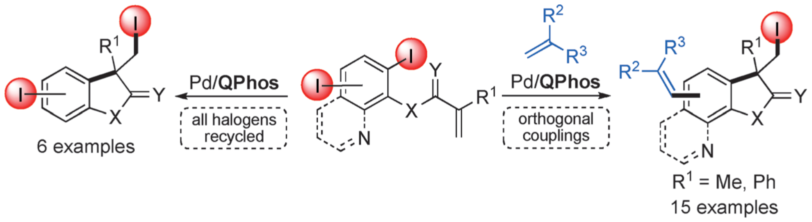
D. N. Tran, N. Cramer* ________ **10630 – 10634**

Rhodium-Catalyzed Dynamic Kinetic Asymmetric Transformations of Racemic Allenes by the [3+2] Annulation of Aryl Ketimines

Simultaneous Catalysis

D. A. Petrone, M. Lischka,
M. Lautens* ———— **10635 – 10638**

Harnessing Reversible Oxidative Addition: Application of Diiodinated Aromatic Compounds in the Carboiodination Process

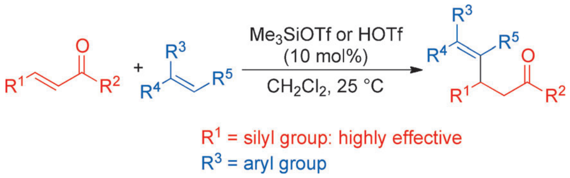


An I for an I: Conditions for the intramolecular carboiodination and the simultaneous convergent intramolecular carboiodination/intermolecular Heck reaction of various diiodoarenes were developed. The ability of the Pd^0/QPhos catalyst/ligand combination to undergo reversible oxidative addition allows these reactions to proceed well, thus increasing both the appeal and utility of this class of substrates in site-selective cross-coupling reactions.

Conjugate Addition

K. Okamoto,* E. Tamura,
K. Ohe* ———— **10639 – 10643**

Acid-Catalyzed Direct Conjugate Alkenylation of α,β-Unsaturated Ketones

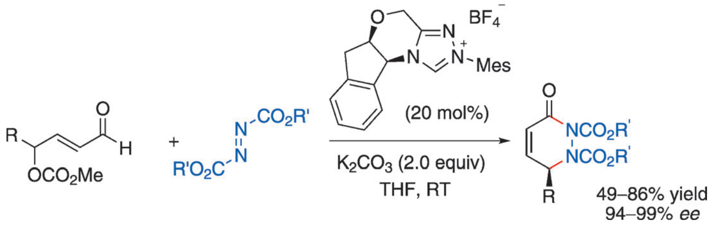


New tricks, old reaction: The title reaction proceeds under mild and transition-metal-free conditions (see scheme; Tf = trifluoromethanesulfonyl). Various combinations of substrates are applicable to the synthesis of γ,δ-unsaturated ketones by employing silicon substituents at the β-position of the enones. The silicon substituents play a key role in stabilization of the cationic intermediate by hyperconjugation.

Synthetic Methods

X.-Y. Chen, F. Xia, J.-T. Cheng,
S. Ye* ———— **10644 – 10647**

Highly Enantioselective γ-Amination by N-Heterocyclic Carbene Catalyzed [4+2] Annulation of Oxidized Enals and Azodicarboxylates



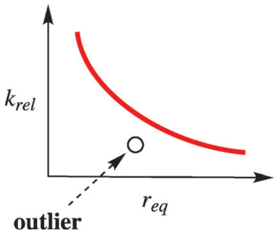
γ-Amination: The title reaction was developed to give the corresponding dihydropyridazinones in good yields with excellent enantioselectivities (see scheme; Mes = 2,4,6-trimethylphenyl). The annulation reaction worked well for γ-aryl, γ-alkyl, or γ-alkenyl oxidized enals. Highly enantiopure tetrahydropyridazinones and γ-amino acid derivatives could be easily prepared by chemical transformations of the resulting dihydropyridazinones.

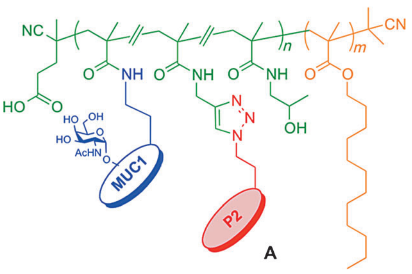
Reactive molecules

G. Markopoulos,*
J. Grunenberg* ———— **10648 – 10651**

Predicting Kinetically Unstable C–C Bonds from the Ground-State Properties of a Molecule

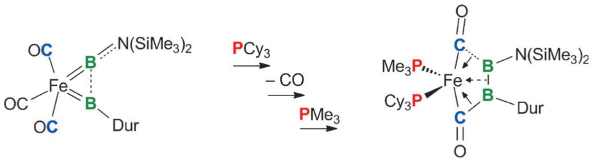
Determining the weakest link: A simple analysis pinpoints kinetically unstable carbon–carbon bonds. No prior knowledge of reaction pathways is necessary and the approach is particularly helpful for the prediction of novel molecules. k_{rel} = relaxed force constant, r_{eq} = bond length.





A

Highly decorated: Tumor-associated MUC1 glycopeptide and tetanus toxoid T-cell epitope P2 can be attached to water-soluble poly(*N*-(2-hydroxypropyl)methacrylamide) carriers by orthogonal ligation techniques. Fully synthetic vaccine **A** with additional nanostructure-promoting domains induced antibodies that exhibit high affinity to tumor cells.



The chain gang: By treatment of an iron bis(borylene) complex with PCy_3 and subsequent stepwise substitution of a CO ligand by PMe_3, a catenated 1D OC-B-B-CO chain was generated in the coordination sphere of iron. This is an CO analogue of the recently reported 1D B-B-B-B chain in the iron tetraboron complex $[(OC)_2Fe\{BN(SiMe_3)_2\}_2(BDur)_2]$. Dur = 2,3,5,6-tetramethylphenyl.

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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