



The following Communications have been judged by at least two referees to be “very important papers” and will be published online at www.angewandte.org soon:

K. Ohmori, T. Shono, Y. Hatakoshi, T. Yano, K. Suzuki*
An Integrated Synthetic Strategy for Higher Catechin Oligomers

K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada, K. Nozaki*
Synthesis of Stereogradient Poly(propylene carbonate) by Stereo- and Enantioselective Copolymerization of Propylene Oxide with Carbon Dioxide

X. Wurzenberger, H. Piotrowski, P. Klüfers*
A Stable Square-Planar High-Spin- d^6 Molecular $\text{Fe}^{\text{II}}\text{O}_4$ Chromophore From Rare Iron(II) Minerals

I. Piel, M. Steinmetz, K. Hirano, R. Fröhlich, S. Grimme,*
F. Glorius*
Highly Asymmetric NHC-Catalyzed Hydroacylation of Unactivated Alkenes and Mechanistic Insights

Y. Han-ya, H. Tokuyama, T. Fukuyama*
Total Synthesis of (–)-Conophylline and (–)-Conophyllidine

I. Garcia-Bosch, A. Company, C. W. Cady, S. Styring, W. R. Browne, X. Ribas, M. Costas*
Evidence for a Precursor Complex in C–H Hydrogen-Atom-Transfer Reactions Mediated by a Manganese(IV) Oxo Complex

N. Dietl, C. van der Linde, M. Schlangen, M. K. Beyer, H. Schwarz*
The Final Piece in an Intriguing Puzzle: Diatomic $[\text{CuO}]^+$ and Its Role in Spin-Selective Hydrogen- and Oxygen-Atom Transfer in the Thermal Activation of Methane

G. N. Newton, S. Yamashita, K. Hasumi, J. Matsuno, N. Yoshida, M. Nihei, T. Shiga, M. Nakano, H. Nojiri, W. Wernsdorfer, H. Oshio*

Redox-Controlled Optimization of the Magnetic Properties of Keggin-Type $\{\text{Mn}_{13}\}$ Clusters

J. J. Murphy, A. Quintard, P. McArdle, A. Alexakis,* J. C. Stephens*
Asymmetric Organocatalytic 1,6-Conjugate Addition of Aldehydes to Dienic Sulfones

J. M. Lee, W. Shim, J.-S. Noh, W. Lee*
Highly Mobile Thin Films on an Elastomeric Substrate as Gas Sensors: Palladium-Based Nanogap Hydrogen-Gas Sensors

C. C. Lee, Y. Hu,* M. W. Ribbe*
Tracing the Hydrogen Source of Hydrocarbons Formed by Vanadium Nitrogenase

S. R. Waldvogel,* J. Kulisch, M. Nieger, F. Stecker, A. Fischer
Efficient and Stereodiverse Electrochemical Synthesis of Optically Pure Menthylamines

Author Profile



“What I look for first in a publication is a surprising phenomenon.
The most important thing I learned from my parents is to not give up ...”
This and more about Jin-Quan Yu can be found on page 5014.

Jin-Quan Yu _____ 5014

News



J. A. Dumesic



A. S. K. Hashmi



A. Vinu



C.-L. Bai

Boudart Award: J. A. Dumesic _____ 5015

Hector Research Award:
A. S. K. Hashmi _____ 5015

Bessel Research Award:
A. Vinu _____ 5015

Appointed President:
C.-L. Bai _____ 5015

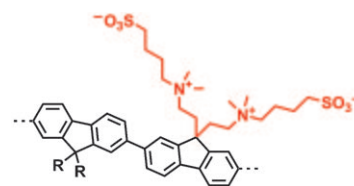
Highlights

Conjugated Polyelectrolytes

U. Scherf* — 5016–5017

Counterion Pinning in Conjugated Polyelectrolytes for Applications in Organic Electronics

Immobilizing counterions: Cationic, conjugated polyelectrolytes can be used to improve the electron injection from low-work-function metal electrodes into the active layers of organic light-emitting diodes. The problem of mobile counterions has now been solved through the use of zwitterionic, conjugated polyelectrolytes as thin injection layers. These polyelectrolytes (see structure) are made from neutral precursor polymers in a simple one-step reaction.



Essays

Synthetic Methods

A. Studer,* D. P. Curran* — 5018–5022

Organocatalysis and C–H Activation Meet Radical- and Electron-Transfer Reactions

A radical outlook: Recently published “organocatalytic C–H activation reactions” have now been interpreted as base-promoted homolytic substitutions. The addition of an aryl radical to an arene followed by deprotonation (see above) and electron transfer form part of the chain reaction. Although these new results are not conceptual breakthroughs, they could be experimental breakthroughs because they presage new transformations in radical (anion) chemistry.

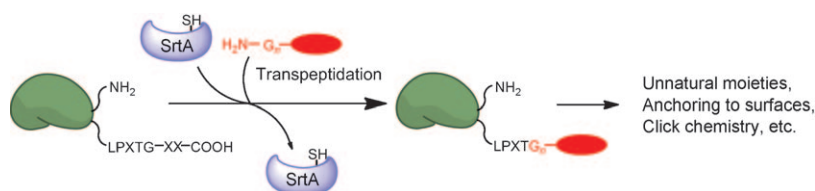


Minireviews

Protein Engineering

M. W.-L. Popp,
H. L. Ploegh* — 5024–5032

Making and Breaking Peptide Bonds: Protein Engineering Using Sortase



It takes all sortases: Enzymatic formation of a peptide bond using the sortase A transpeptidase (SrtA) provides a convenient and mild means for engineering proteins to contain nongenetically tem-

plated modifications. Myriad applications are possible, from producing homogeneous post-translational modification mimics, assembling protein domains, to anchoring proteins to solid surfaces.

For the USA and Canada:

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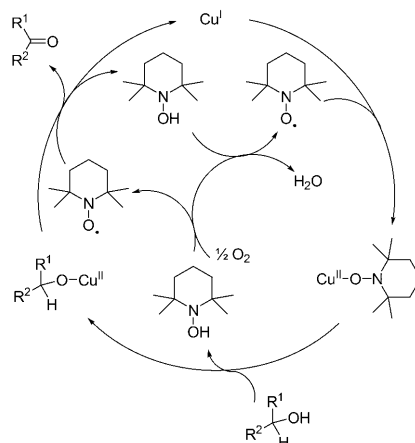
Reviews

Synthetic Methods

L. Tebben, A. Studer* — 5034–5068

Nitroxides: Applications in Synthesis and in Polymer Chemistry

The many faces of radicals: Nitroxides can be applied as stoichiometric and catalytic oxidants in the oxidation of alcohols (see scheme) and carbanions, as well as in oxidative C–C bond-forming reactions. Stable radicals of this class can also be used as precursors for C-centered radicals as well as for the formation of such radicals for synthesis or polymerization.

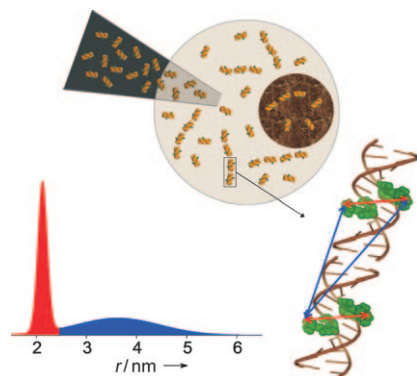


Communications

Pulsed EPR Spectroscopy in Cells

I. Krstić, R. Hänsel, O. Romainczyk, J. W. Engels, V. Dötsch, T. F. Prisner* — 5070–5074

Long-Range Distance Measurements on Nucleic Acids in Cells by Pulsed EPR Spectroscopy



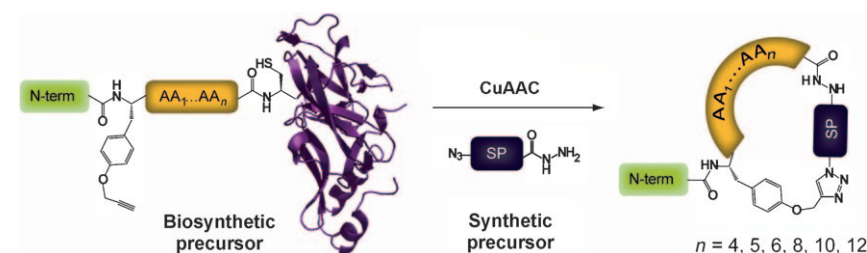
Mapping the structure of nucleic acids:

Pulsed electron–electron double-resonance (PELDOR) spectroscopy has been applied for the first time to map the global structure of nucleic acids inside *Xenopus laevis* oocytes (see picture). The distances measured in vitro and in cells are the same, which implies the existence of stable overall conformations of the hairpin RNA and the neomycin-sensing ribo-switch studied.

Protein Chemistry

J. M. Smith, F. Vitali, S. A. Archer, R. Fasan* — 5075–5080

Modular Assembly of Macrocyclic Organo–Peptide Hybrids Using Synthetic and Genetically Encoded Precursors



Mix, click, cyclize: Conformationally constrained organo–peptide hybrids can be constructed by a tandem chemoselective reaction between a synthetic molecule and a recombinant protein. Diverse mac-

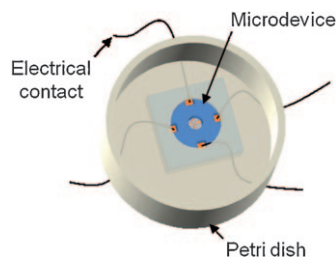
rocyclic structures were obtained in cyclic, lariat, and protein-tethered configurations by varying the nature of the synthetic and biosynthetic precursors.

Bioanalysis

A. Meunier, O. Jouannot, R. Fulcrand,
I. Fanget, M. Bretou, E. Karatekin,
S. Arbault, M. Guille, F. Darchen,
F. Lemaître, C. Amatore* — **5081 – 5084**



Coupling Amperometry and Total Internal Reflection Fluorescence Microscopy at ITO Surfaces for Monitoring Exocytosis of Single Vesicles



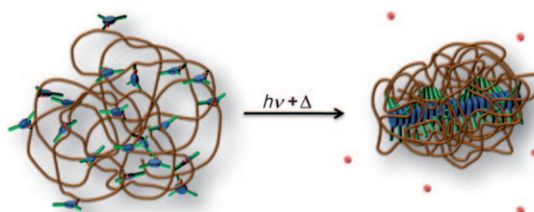
More transparency in bioanalysis: A microdevice based on transparent indium tin oxide (ITO) electrodes allows simultaneous total internal reflection fluorescence microscopy and amperometric measurements. Use of the device in the coupled optical and electrochemical detection of single exocytotic events is demonstrated with enterochromaffin BON cells (see picture).

Folding Processes

T. Mes, R. van der Weegen,
A. R. A. Palmans,*
E. W. Meijer* — **5085 – 5089**



Single-Chain Polymeric Nanoparticles by Stepwise Folding



Light-induced self-assembly leads to the folding of synthetic random-coil polymers into highly stable single-chain polymeric chiral nanoparticles (see picture; green:

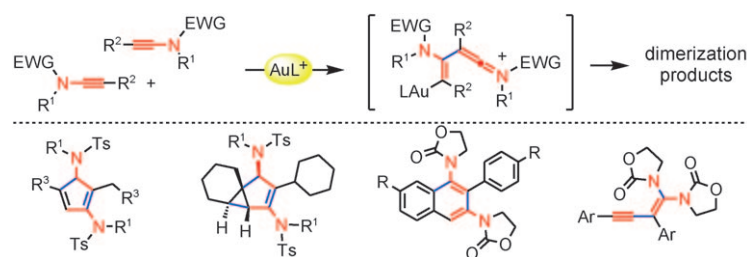
side chains, blue: phenyl rings, red: nitrophenyl leaving groups). The folding of the polymer was aided by heating and cooling steps.

Gold Catalysis

S. Kramer, Y. Odabachian, J. Overgaard,
M. Rottländer, F. Gagosz,*
T. Skrydstrup* — **5090 – 5094**



Taking Advantage of the Ambivalent Reactivity of Ynamides in Gold Catalysis: A Rare Case of Alkyne Dimerization



A gold mine of results: A series of ynamides have been dimerized in the presence of a gold(I) complex. This unprecedented transformation involves the formation of a key keteniminium intermediate that reacts to form a variety

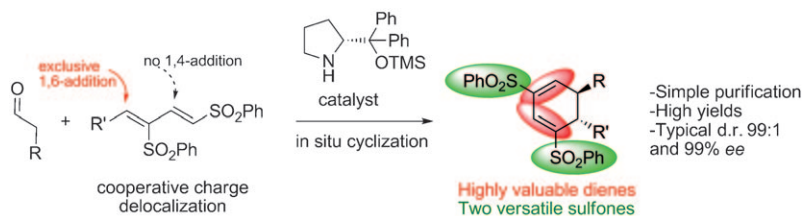
of cyclic and acyclic products. The substitution pattern of the ynamide determines which product is formed (see scheme; EWG = electron-withdrawing group, Ts = *p*-toluenesulfonyl).

Asymmetric Catalysis

J. J. Murphy, A. Quintard, P. McArdle,
A. Alexakis,*
J. C. Stephens* — **5095 – 5098**

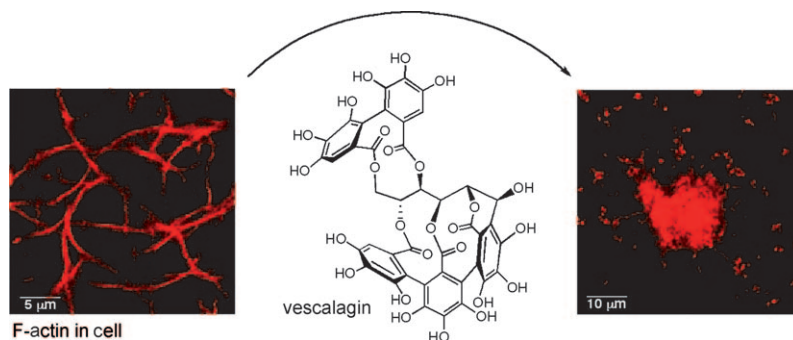


Asymmetric Organocatalytic 1,6-Conjugate Addition of Aldehydes to Dienic Sulfones



An unprecedented 1,6-enamine conjugate addition exploiting the charge delocalization in 1,3-bis(sulfonyl) butadienes has been developed. By appropriately designing a Michael acceptor, unique reactivities

were obtained for the formation of highly valuable dienes containing two versatile vinyl sulfones (see scheme, TMS = trimethylsilyl).



F-actin in cell

Winding it up: The plant polyphenolic metabolite vescalagin fulfills all the requirements for use as an antiactin agent in cellular biological investigations. Despite its high hydrophilicity, it rapidly enters cells and disturbs the organization

of the actin cytoskeleton in a dose-dependent reversible manner by binding fibrillar actin and forcing the actin filaments (left) to wind themselves into ball-like fibrillar aggregates (right).

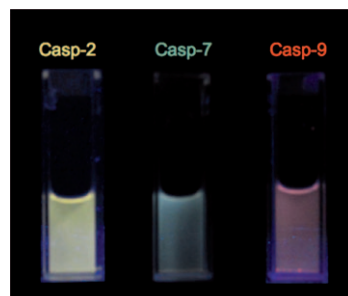
Polyphenolic Natural Products

S. Quideau,* C. Douat-Casassus, D. M. Delannoy López, C. Di Primo, S. Chassaing, R. Jacquet, F. Saltel, E. Genot* _____ 5099–5104

Binding of Filamentous Actin and Winding into Fibrillar Aggregates by the Polyphenolic C-Glucosidic Ellagitannin Vescalagin



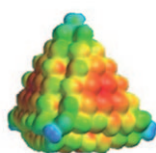
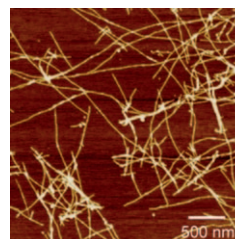
Shaken, not stirred: A novel design for protease sensors is described, in which peptides are conjugated to a DNA backbone carrying multiple fluorophores. The multispectral oligodeoxyfluoroside (ODF) fluorophores are strongly quenched by a dabcyI group at the end of each peptide. In vitro and cellular selectivity assays showed that a mixture of three sensors could be used to identify different caspase activities by the fluorescence outcome (see picture).



Chemosensors

N. Dai, J. Guo, Y. N. Teo, E. T. Kool* _____ 5105–5109

Protease Probes Built from DNA: Multispectral Fluorescent DNA–Peptide Conjugates as Caspase Chemosensors

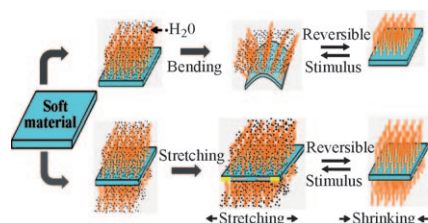


Nanoparticles for amyloid diseases: CdTe nanoparticles (NPs) can efficiently prevent fibrillation of amyloid peptides; the process is based on the multiple binding of A β oligomers to CdTe NPs. The molar efficiency and the inhibition mechanism displayed by the NPs are analogous to the mechanism found for proteins responsible for the prevention of amyloid fibrillation in the human body.

Protein Functionalities

S. I. Yoo, M. Yang, J. R. Brender, V. Subramanian, K. Sun, N. E. Joo, S.-H. Jeong, A. Ramamoorthy, N. A. Kotov* _____ 5110–5115

Inhibition of Amyloid Peptide Fibrillation by Inorganic Nanoparticles: Functional Similarities with Proteins



A redhead: Surface-grafted hydrophilic polymer brushes (see picture) with high molecular weight and graft density caused reversible bending and stretching of soft polymeric substrates on a macroscale. The shape change of the substrate was tuned to respond to different stimuli including humidity, temperature, and pH.

Smart Soft Materials

Y. Zou, A. Lam, D. E. Brooks, A. Srikantha Phani,* J. N. Kizhakkedathu* _____ 5116–5119

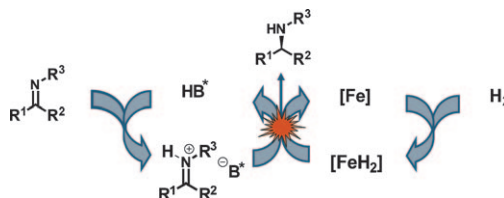
Bending and Stretching Actuation of Soft Materials through Surface-Initiated Polymerization





Iron Catalysis

S. Zhou, S. Fleischer, K. Junge,
M. Beller* — 5120–5124



Control with an iron hand: A broad range of ketimines underwent enantioselective hydrogenation in the presence of a chiral Brønsted catalyst and a well-defined non-chiral iron catalyst (see scheme). This

procedure constitutes an attractive and environmentally favorable alternative to well-established asymmetric hydrogenation reactions with precious-metal catalysts.



Cooperative Transition-Metal and Chiral Brønsted Acid Catalysis: Enantioselective Hydrogenation of Imines To Form Amines

Atropisomeric Scaffolds

J. L. Gustafson, D. Lim, K. T. Barrett,
S. J. Miller* — 5125–5129



A selective sequence: An enantioselective synthesis (see scheme) of atropisomerically defined *p*-terphenyls, as well as tetra- and pentaaryl compounds is reported. The synthesis proceeds through sequen-

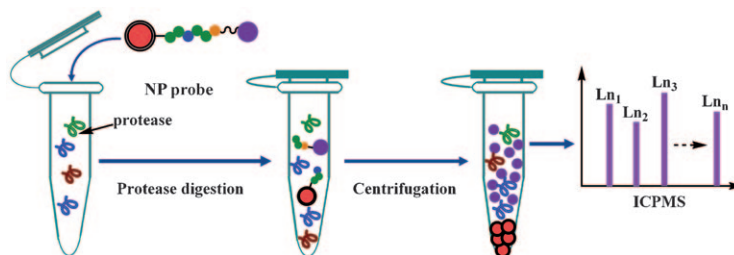
tial atropisomer-selective electrophilic aromatic substitution and regioselective palladium-catalyzed cross-coupling reactions.



Synthesis of Atropisomerically Defined, Highly Substituted Biaryl Scaffolds through Catalytic Enantioselective Bromination and Regioselective Cross-Coupling

Multiplex Protease Assay

X. W. Yan, L. M. Yang,
Q. Q. Wang* — 5130–5133



Coded messages: Lanthanide (Ln) coded protease-specific peptide–nanoparticle (NPs) conjugates act as probes for a multiplex protease assay (MPA) using inductively coupled plasma mass spec-

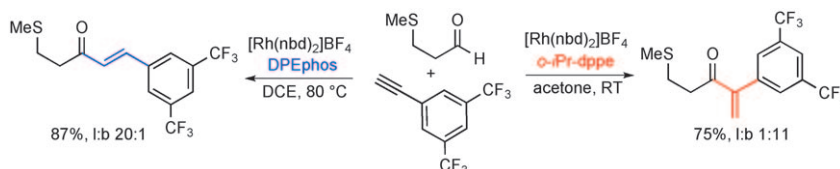
trometry (ICP-MS; see picture). MPA can be achieved by centrifugal separation of the protease-cleaved and uncleaved probes and subsequent determination of the released Ln tags.



Lanthanide-Coded Protease-Specific Peptide–Nanoparticle Probes for a Label-Free Multiplex Protease Assay Using Element Mass Spectrometry: A Proof-of-Concept Study

Regioselective Hydroacylation

C. González-Rodríguez, R. J. Pawley,
A. B. Chaplin, A. L. Thompson,
A. S. Weller,* M. C. Willis* — 5134–5138

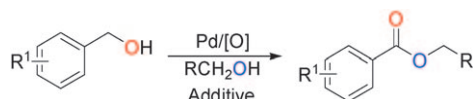


It's all in the ligand: By choice of the appropriate diphosphine ligand a previously linear-selective alkyne hydroacylation process can be “switched” to be highly branched-selective (see scheme,

l = linear, *b* = branched). Structural data for the *ortho*-*i*Pr-dppe–rhodium catalyst suggest restricted rotation of the phosphine aryl units may be responsible for the observed selectivity.



Rhodium-Catalyzed Branched-Selective Alkyne Hydroacylation: A Ligand-Controlled Regioselectivity Switch



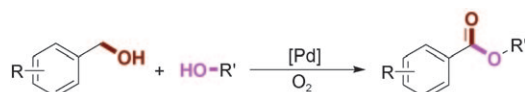
Selectively esterified: Primary alcohols react with dioxygen as a benign oxidant in a palladium-catalyzed oxidative esterification (see scheme). The corresponding aldehydes and esters are formed highly

selectively depending on the catalyst system. The reactions take place in the presence of commercially available ligands without the need for additional organic hydrogen acceptors.

Oxidative Esterification

S. Gowrisankar, H. Neumann, M. Beller* _____ **5139–5143**

General and Selective Palladium-Catalyzed Oxidative Esterification of Alcohols



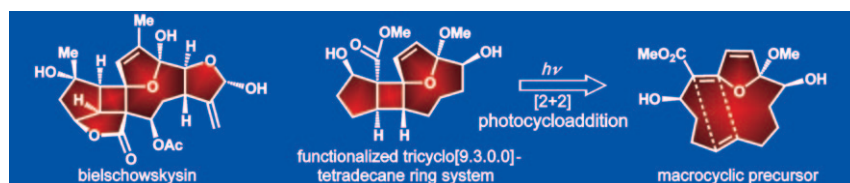
One step from alcohol to ester: A palladium-catalyzed oxidative esterification of various benzylic alcohols with methanol and long-chain aliphatic alcohols was carried out in the presence of molecular

oxygen as the oxidant (see scheme). By considering the effects of substitution and potential mechanistic pathways, the applicability of this method to a range of different substrates was shown.

Oxidative Esterification

C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li, A. Lei* _____ **5144–5148**

Palladium-Catalyzed Aerobic Oxidative Direct Esterification of Alcohols



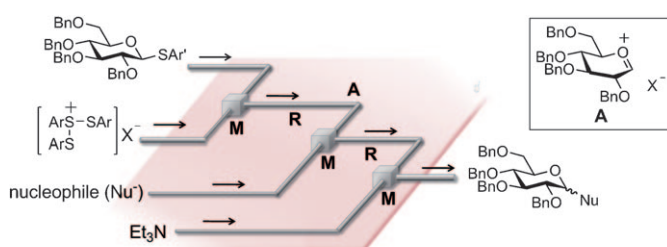
Photons in action: Cascade sequences, brevity, and efficiency are the hallmarks of the synthesis of a functionalized tricyclo[9.3.0.0]tetradecane ring system of the marine natural product bielschowskysin.

The synthesis is achieved in five steps, with the key step being an exquisite intramolecular [2+2] photocycloaddition of a macrocyclic precursor (see scheme).

Natural Product Synthesis

K. C. Nicolaou,* V. A. Adsool, C. R. H. Hale _____ **5149–5152**

An Expedient Synthesis of a Functionalized Core Structure of Bielschowskysin



Go with the flow: The indirect cation-flow method based on the generation of highly reactive organic cations from their precursors using electrochemically generated [ArS(ArSSAr)]⁺ was developed in flow microreactor systems (see scheme;

Bn = benzyl, M = micromixer, R = microtube reactor). The method was applied to evaluate glycosyl cations such as **A** or their equivalents and glycosylation reactions.

Microreactors

K. Saito, K. Ueoka, K. Matsumoto, S. Suga, T. Nokami, J. Yoshida* _____ **5153–5156**

Indirect Cation-Flow Method: Flash Generation of Alkoxycarbenium Ions and Studies on the Stability of Glycosyl Cations



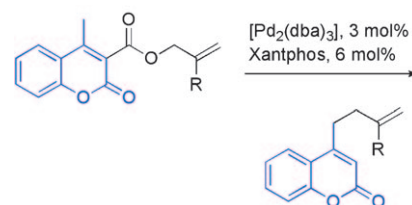
Allylation

R. Jana, J. J. Partridge,
J. A. Tunge* _____ 5157–5161



Migratory Decarboxylative Coupling of Coumarins: Synthetic and Mechanistic Aspects

On the move: Decarboxylative coupling of allyl 4-methyl-3-carboxycoumarins provides the products of γ -allylation of the methyl group rather than the typical regioselective α -allylation. Mechanistic studies show that intramolecular proton transfer from the 4-methyl group to the 3-carboxylate allows allylation of the remote methyl group. The resulting 4-butenyl-3-carboxyl coumarin undergoes Pd⁰-catalyzed decarboxylation to provide the observed products (see scheme).

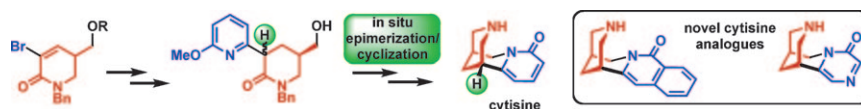


Alkaloid Synthesis

C. Hirschhäuser, C. A. Haseler,
T. Gallagher* _____ 5162–5165



Core Modification of Cytisine: A Modular Synthesis



Getting down to the core: A novel, modular, and more robust synthesis of cytisine, a partial agonist selective for the $\alpha 4\beta 2$ nicotinic acetylcholine receptor, also allows modification of the core structure, as exemplified by the first azacytisine and

a cytisine–varenicline hybrid. Key steps include Stille coupling of heteroarylstananones with a bromolactam motif and an in situ epimerization/alkylative cyclization to complete the tricyclic core (see scheme).

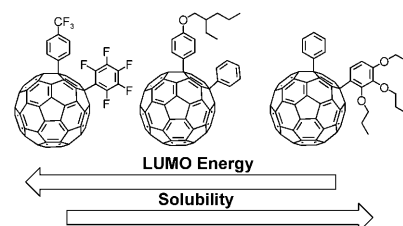
Organic Solar Cells

A. Varotto, N. D. Treat, J. Jo, C. G. Shuttle,
N. A. Batara, F. G. Brunetti, J. H. Seo,
M. L. Chabinyc, C. J. Hawker, A. J. Heeger,
F. Wudl* _____ 5166–5169



1,4-Fullerene Derivatives: Tuning the Properties of the Electron Transporting Layer in Bulk-Heterojunction Solar Cells

Tune me up: The increasing number of new donor materials for organic solar cells requires compatible electron acceptors. A series of 1,4-fullerene adducts with tunable chemical, electronic, and material properties is introduced to effectively influence the photovoltaic characteristics of solar cells.

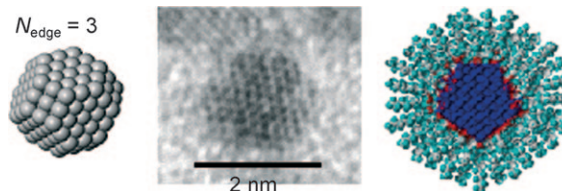


Nanoparticles

K. Pelzer,* M. Hävecker, M. Boualleg,
J.-P. Candy, J.-M. Basset* _____ 5170–5173



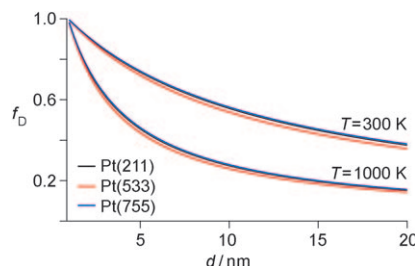
Stabilization of 200-Atom Platinum Nanoparticles by Organosilane Fragments



Three's a charm: Platinum nanoparticles of 2 nm diameter and containing approximately 200 atoms covered with *n*-octylsilyl groups (see picture, right; Pt blue, Si red, C gray, H turquoise) form when

[Pt(dba)₂] (dba = dibenzylideneacetone) decomposes in the presence of *n*-octylsilane. The particles adopt a cuboctahedral structure with an edge length of three atoms.

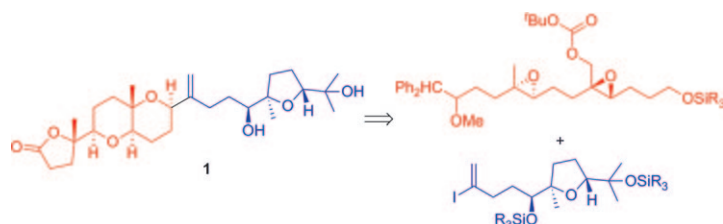
The fraction of dissociation processes f_D for H_2 on platinum that take place on low-coordinate sites of nanoparticles is strongly dependent on the gas temperature of the incoming molecules and on the diameter d of the nanoparticles (see picture). For high gas temperatures and large nanoparticles, dissociation occurs mostly on terraces. Therefore, assumptions that steps always dominate reaction in heterogeneous catalysis cannot be justified.



Heterogeneous Catalysis

I. M. N. Groot,* A. W. Kleyn,
L. B. F. Juurlink _____ **5174–5177**

The Energy Dependence of the Ratio of Step and Terrace Reactivity for H_2 Dissociation on Stepped Platinum



Cascading epoxides: The squalene-derived polyether lactodehydrothysiferol (**1**) has been prepared through a convergent sequence that features an epoxide-opening cascade to construct the tetrahydrofuran and tetrahydropyran subunits.

Additional features include a stereodivergent diene diepoxidation, a monodeoxygenation of a triol, and complex fragment couplings through Suzuki and Nozaki–Hiyama–Kishi reactions.

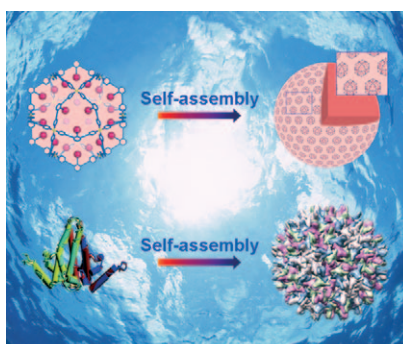
Natural Product Synthesis

D. J. Clausen, S. Wan,
P. E. Floreancig* _____ **5178–5181**

Total Synthesis of the Protein Phosphatase 2A Inhibitor Lactodehydrothysiferol



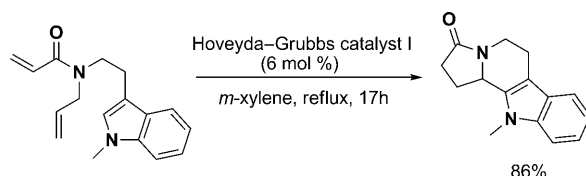
Without the thorn: In polar solvents, cationic $M_{12}L_{24}$ nanocages slowly assembled into hollow spherical “blackberry” structures, the size of which could be tuned by changing the counterion concentration or solvent polarity. The self-assembly process showed similar kinetic and thermodynamic features to viral-capsid formation. (Copyright (2005) National Academy of Sciences, USA. The image of the hepatitis B virus capsid is from the RCSB PDB (ID: 1QGT).)



Blackberry Structures

D. Li, W. Zhou, K. Landskron, S. Sato,
C. J. Kiely, M. Fujita,* T. Liu* **5182–5187**

Viral-Capsid-Type Vesicle-Like Structures Assembled from $M_{12}L_{24}$ Metal–Organic Hybrid Nanocages



Tandem bicycle: In the title reaction double bonds created during ring-closing metathesis isomerize to generate reactive iminium intermediates that undergo intramolecular cyclization reactions with tethered heteroatom and carbon nucleo-

philes. In this way, a series of biologically interesting heterocyclic compounds can be made, including a known precursor for the total synthesis of the antiparasitic natural product harmicine.

Tandem Reactions

E. Ascic, J. F. Jensen,
T. E. Nielsen* _____ **5188–5191**

Synthesis of Heterocycles through a Ruthenium-Catalyzed Tandem Ring-Closing Metathesis/Isomerization/N-Acyliminium Cyclization Sequence

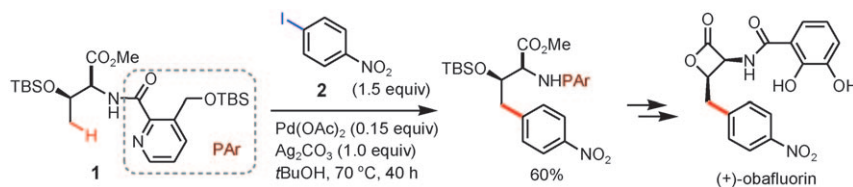


C–H Functionalization

G. He, G. Chen* 5192–5196



A Practical Strategy for the Structural Diversification of Aliphatic Scaffolds through the Palladium-Catalyzed Picolinamide-Directed Remote Functionalization of Unactivated C(sp³)–H Bonds



Hats off to the director: High levels of regio- and stereoselectivity were observed for a broad range of amine substrates with aryl and vinyl iodide coupling partners in the title reaction. The synthetic utility of this strategy was highlighted by the ready

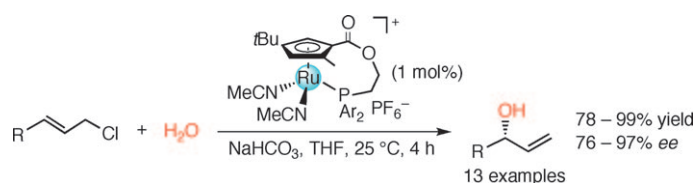
preparation from threonine of **1**, with a removable picolinamide auxiliary PAR, and its coupling with **2** in a concise formal synthesis of (+)-obafluorin. TBS = *tert*-butyldimethylsilyl.

Asymmetric Hydroxylation

N. Kanbayashi, K. Onitsuka* 5197–5199



Ruthenium-Catalyzed Regio- and Enantioselective Allylic Substitution with Water: Direct Synthesis of Chiral Allylic Alcohols



Less is more: A new route to access chiral allylic alcohols through the regio- and enantioselective substitution of mono-substituted allylic chlorides with water has

been developed. The reaction is catalyzed effectively by planar-chiral cyclopentadienyl ruthenium complexes (see scheme).

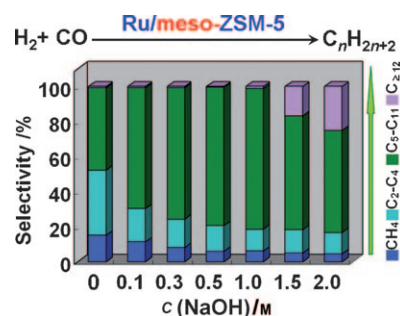
Fischer–Tropsch Synthesis

J. Kang, K. Cheng, L. Zhang, Q. Zhang,* J. Ding, W. Hua, Y. Lou, Q. Zhai, Y. Wang* 5200–5203



Mesoporous Zeolite-Supported Ruthenium Nanoparticles as Highly Selective Fischer–Tropsch Catalysts for the Production of C₅–C₁₁ Isoparaffins

A highly selective catalyst based on mesoporous zeolites for the production of C₅–C₁₁ isoparaffins from syngas has been developed. The selectivity to C₅–C₁₁ hydrocarbons over Ru/meso-ZSM-5 reaches about 80% with a ratio of isoparaffins to *n*-paraffins of 2.7:1. The mesoporous structure and the unique acidity of meso-ZSM-5 play key roles in tuning the product selectivity by controlling the secondary hydrocracking reactions.

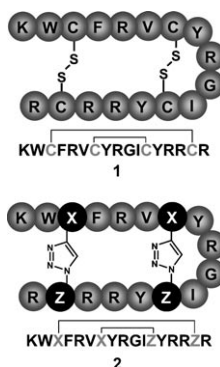


Peptidomimetics

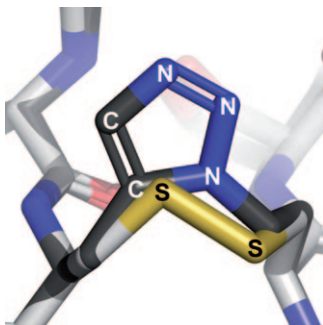
K. Holland-Nell, M. Meldal* 5204–5206



Maintaining Biological Activity by Using Triazoles as Disulfide Bond Mimetics



Click into place: Tachyplesin-I (TP-I) analogues in which both disulfide bridges (**1**) have been replaced with triazoles (**2**) represent structural mimetics of TP-I that display similar or slightly improved anti-bacterial activity. Optimized structures were obtained by replacing the cysteine residues in TP-I by azido- and alkyno-functionalized amino acids.



A good impression: A modular approach using a ruthenium(II) catalyst during peptide synthesis gives rigid and well-defined triazole bridges as tailor-made substitutes for natural disulfide bridges (see structures). The corresponding modification of the monocyclic sunflower trypsin inhibitor-1 yielded an equally potent peptidomimetic containing a redox stable 1,5-disubstituted 1,2,3-triazole bridge.

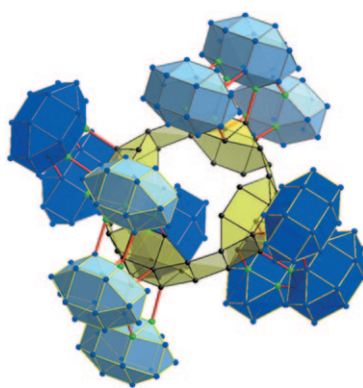
Disulfide Mimics

M. Empting, O. Avrutina, R. Meusinger, S. Fabritz, M. Reinwarth, M. Biesalski, S. Voigt, G. Buntkowsky, H. Kolmar* _____ **5207 – 5211**

“Triazole Bridge”: Disulfide-Bond Replacement by Ruthenium-Catalyzed Formation of 1,5-Disubstituted 1,2,3-Triazoles



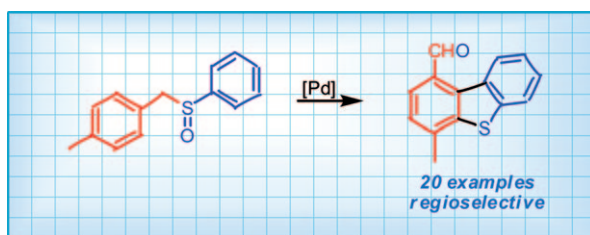
In a nutshell: A 4.3 nm core-shell aggregate of 16 polyoxotungstate building units (see picture of the W/Mn skeleton) delineates the upper limit for structural complexity in molecular metal oxide cluster chemistry to date. This structure is defined by a backbone network of dual Mn–O=W bridges; a retroanalysis of their formation suggests the importance of templation and kinetic control in the self-assembly of the {Mn^{III}₄₀W^{VI}₂₂₄} polyanion.



Polyoxometalates

X. Fang,* P. Kögerler,* Y. Furukawa, M. Speldrich, M. Luban _____ **5212 – 5216**

Molecular Growth of a Core-Shell Polyoxometalate



S=O shows where to go: A novel double C–H activation of aromatic compounds with a sulfoxide as a directing group results in the highly regioselective synthesis of polysubstituted dibenzothio-

phenes (see scheme). The reaction cascade consists of palladium-catalyzed double C–H activation and a Pummerer rearrangement followed by palladium-catalyzed C–S bond formation.

C–H Functionalization

R. Samanta, A. P. Antonchick* _____ **5217 – 5220**

Palladium-Catalyzed Double C–H Activation Directed by Sulfoxides in the Synthesis of Dibenzothiophenes



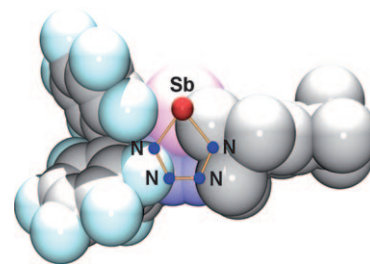
Sb–N Chemistry

M. Lehmann, A. Schulz,*
A. Villinger* _____ 5221 – 5224



An Unusual Isomerization to Tetraazastiboles

A protective shield makes it possible: The synthesis and full characterization of a tetraazastibole is presented for the first time. The conversion of $[\text{N}_3\text{Sb}(\mu\text{-NMes}^*)_2\text{SbN}_3]$ ($\text{Mes}^* = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) into tetraazastibole, $\text{Mes}^*\text{N}_4\text{Sb}$, is an unusual isomerization triggered by the action of the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$, which is also needed for adduct formation: the N_4Sb ring is kinetically protected between the large Mes^* and $\text{B}(\text{C}_6\text{F}_5)_3$ units.



Supporting information is available on www.angewandte.org (see article for access details).



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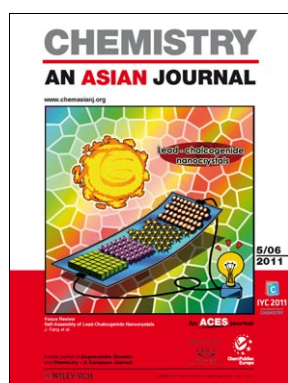
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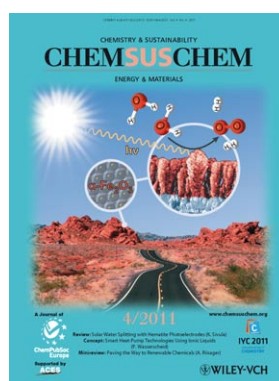
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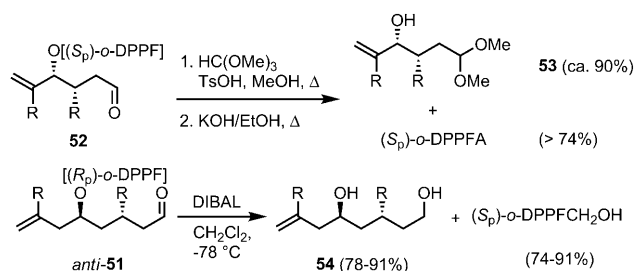
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Corrigendum

Scheme 45 of this Communication contains an error. The correct scheme is shown below. In addition, extra citations are added to references [15, 16, 134]. The full references are shown below.



Scheme 45. Removal and recovery of the catalyst-directing *o*-DPPF group. DPPFA = *o*-diphenylphosphanyl ferrocene carboxylic acid, DIBAL = diisobutylaluminum hydride.

- [15] C. E. Houlden, M. Hutchby, C. B. Bailey, J. Gair Ford, S. N. G. Tyler, M. R. Gagné, G. C. Lloyd-Jones, K. I. Booker-Milburn, *Angew. Chem.* **2009**, *121*, 1862–1865; *Angew. Chem. Int. Ed.* **2009**, *48*, 1830–1833; for the use of the same directing group for palladium-catalyzed *ortho*-alkenylation, see: W. Rauf, A. L. Thompson, J. M. Brown, *Chem. Commun.* **2009**, 3874–3876.
- [16] First example of such a reaction: R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14082–14083; for other recent directed CH-activation reactions from the Yu group see also Ref. [134].
- [134] R. Giri, J. Liang, J.-G. Lei, J.-J. Li, D.-H. Wang, X. Chen, I. C. Naggar, C. Guo, B. M. Foxman, J.-Q. Yu, *Angew. Chem.* **2005**, *117*, 7586–7590; *Angew. Chem. Int. Ed.* **2005**, *44*, 7420–7424; J.-J. Li, T.-S. Mei, J.-Q. Yu, *Angew. Chem.* **2008**, *120*, 6552–6555; *Angew. Chem. Int. Ed.* **2008**, *47*, 6452–6455; R. Giri, J.-Q. Yu, *J. Am. Chem. Soc.* **2008**, *130*, 14082–14083; Y.-H. Zhang, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 14654–14655; D.-H. Wang, K. M. Engle, B.-F. Shi, J.-Q. Yu, *Science* **2010**, *327*, 315–319; B.-F. Shi, Y.-H. Zhang, J. K. Lam, D.-H. Wang, J.-Q. Yu, *J. Am. Chem. Soc.* **2010**, *132*, 460–461.

Removable Directing Groups in Organic Synthesis and Catalysis

G. Rousseau, B. Breit* — 2450–2494

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