Contents

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:

*T. Lewis, M. Faubel, B. Winter, J. C. Hemminger**
CO_2 Capture in an Aqueous Solution of an Amine: Role of the Solution Interface

*Y. H. Kim, S. Banta**
Complete Oxidation of Methanol in an Enzymatic Biofuel Cell by a Self-Assembling Hydrogel Created from Three Modified Dehydrogenases

A. W. Fay, M. A. Blank, C. C. Lee, Y. Hu, K. O. Hodgson,* B. Hedman,* M. W. Ribbe**
Spectroscopic Characterization of a Precursor Isolated from NifEN of an Iron–Molybdenum Cofactor

P. G. Cozzi, A. Gualandi, E. Emer, M. G. Capdevila*
Highly Enantioselective α Alkylation of Aldehydes with 1,3-Benzodithiolylium Tetrafluoroborate: A General Formal Organocatalytic α Alkylation of Aldehydes by Carbenium Ions

*V. Zinth, T. Dellmann, H.-H. Klauss, D. Johrendt**
Recovery of a Parentlike State in $Ba_{1-x}K_xFe_{1.86}Co_{0.14}As_2$

*I. Coin, M. H. Perrin, W. W. Vale, L. Wang**
Photo-Cross-Linkers Incorporated into G-Protein-Coupled Receptors in Mammalian Cells: A Ligand Comparison

*C. Nilewski, N. R. Deprez, T. C. Fessard, D. Bo Li, R. W. Geisser, E. M. Carreira**
Synthesis of Undecachlorosulfolipid A: Reevaluation of the Nominal Structure

*S. Kawamorita, H. Ohmiya, T. Iwai, M. Sawamura**
Palladium-Catalyzed Borylation of Sterically Demanding Aryl Halides with a Silica-Supported Compact Phosphane Ligand

*F. Freire, A. M. Almeida, J. D. Fisk, J. D. Steinkruger, S. H. Gellman**
Impact of Strand Length on the Stability of Parallel-β-Sheet Secondary Structure

*K. A. B. Austin, E. Herdtweck, T. Bach**
Intramolecular [2+2]-Photocycloaddition of Substituted Isoquinolones: Enantioselectivity and Kinetic Resolution Induced by a Chiral Template

Editorial

The Importance of Chemistry for the Future of the Pharma Industry — H. Wild,* D. Heimbach, C. Huwe — **7452–7454**

Author Profile

*"The biggest problem that scientists face is willful scientific illiteracy.
My biggest motivation is seeing my students leading the hunt …"*
This and more about Emmanuel Lacôte can be found on page 7474. — Emmanuel Lacôte — **7474**

Books

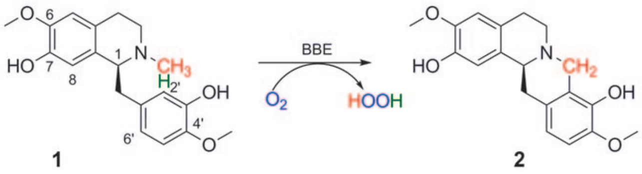
Vom Mikrofilm zur Wissensmaschine — Michael Buckland — *reviewed by H. Hennig* — **7475**

Highlights

Enzymes

J. E. Vick,
C. Schmidt-Dannert* ______ 7476 – 7478

Expanding the Enzyme Toolbox for Biocatalysis

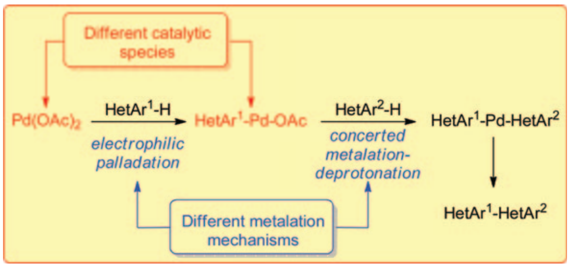


We've got talent: New enzymes with novel reactivity are constantly added to the enzyme toolbox as exemplified by the berberine bridge enzyme (BBE). Analogues of **2**, which are bioactive, have been successfully made from analogues of **1** using BBE. Such new enzymes hold the promise of convenient synthesis of potentially useful nonnatural products.

Oxidative Cross-Coupling

X. Bugaut, F. Glorius* ______ 7479 – 7481

Palladium-Catalyzed Selective Dehydrogenative Cross-Couplings of Heteroarenes



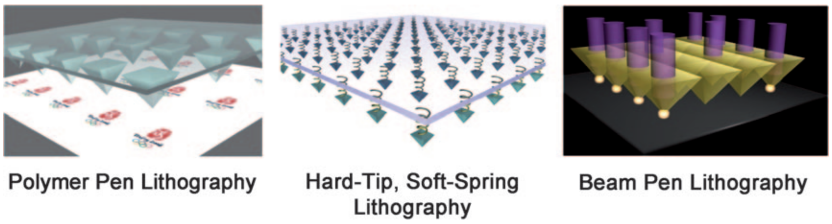
A nice couple: Two heteroaryls bearing no prefunctionalization can be cross-coupled efficiently through Pd^{II} catalysis to afford the biheteroaryl. The selectivity of this transformation probably finds its origin in the two mechanistically different metalation steps of C–H bonds.

Essays

Surface Patterning

L. R. Giam, C. A. Mirkin* ___ 7482 – 7485

Cantilever-Free Scanning Probe Molecular Printing


Polymer Pen Lithography

Hard-Tip, Soft-Spring Lithography

Beam Pen Lithography

25 and 30 years after the invention of AFM and STM, respectively, cantilever-free scanning probe lithography tools such as polymer pen lithography (see picture) mark an important development in the evolution of molecular printing. These simple, robust, and inexpensive approaches allow researchers to create nanoscale and microscale features of various organic and inorganic materials on surfaces in arbitrary patterns.

For the USA and Canada:
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Contents

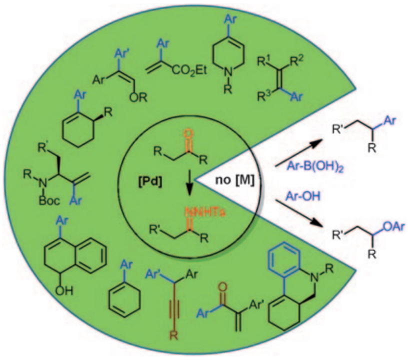
Minireviews

Cross-Coupling

J. Barluenga,* C. Valdés* ___ **7486 – 7500**

Tosylhydrazones: New Uses for Classic Reagents in Palladium-Catalyzed Cross-Coupling and Metal-Free Reactions

Never too old to rock 'n' roll: The investigation of tosylhydrazones—widely used intermediates in organic synthesis—as coupling partners in palladium-catalyzed and metal-free cross-coupling reactions has led to the discovery of powerful C–C and C–O bond-forming transformations. These reactions offer novel possibilities for the unconventional modification of carbonyl compounds (see examples of product types; Ts = *p*-toluenesulfonyl).



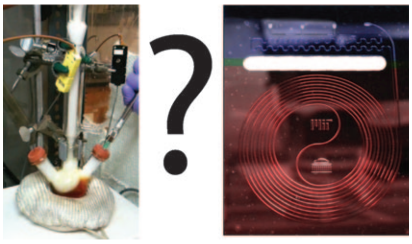
Reviews

Flow Chemistry

R. L. Hartman, J. P. McMullen,
K. F. Jensen* ___ **7502 – 7519**

Deciding Whether To Go with the Flow: Evaluating the Merits of Flow Reactors for Synthesis

Flow or batch? The fine chemicals and pharmaceutical industries are transforming how their products are manufactured, where economically favorable, from traditional batchwise processes to continuous flow. This evolution is impacting synthetic chemistry on all scales—from the laboratory to full production. This Review discusses the relative merits of batch and microflow reactors for performing synthetic chemistry in the laboratory.

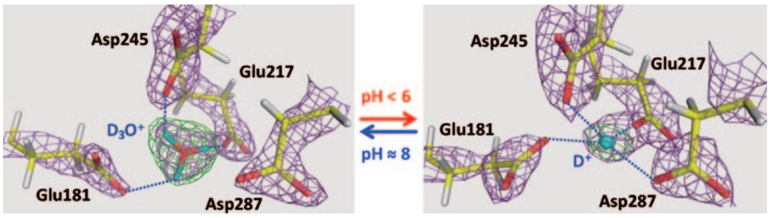


Communications

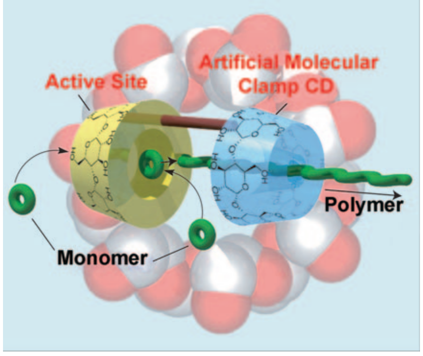
X-ray/Neutron Crystallography

A. Y. Kovalevsky,* B. L. Hanson,
S. A. Mason, T. Yoshida, S. Z. Fisher,
M. Mustyakimov, V. T. Forsyth,
M. P. Blakeley, D. A. Keen,
P. Langan* ___ **7520 – 7523**

Identification of the Elusive Hydronium Ion Exchanging Roles with a Proton in an Enzyme at Lower pH Values



Visible to neutrons: Although thought to be involved in biological processes, hydronium ions had never been identified in biomacromolecular crystallographic structures. A hydronium ion has now been found by neutron and X-ray crystallography to interchange with metal cofactors in the active site of an enzyme. Under more acidic conditions, the hydronium ion is dehydrated to a proton, and the binding site collapses (see picture).



Synthetic polymerases composed of a cyclodextrin (CD) dimer yield high-molecular-weight polymers of cyclic esters without using solvents and co-catalysts. One CD moiety is attached to the active site of a supramolecular catalyst and propagates the polymerization by serving as artificial molecular clamp (see picture). The other CD moiety initiates the ring-opening polymerization.

Supramolecular Catalysis

Y. Takashima, M. Osaki, Y. Ishimaru, H. Yamaguchi, A. Harada* ____ **7524 – 7528**

Artificial Molecular Clamp: A Novel Device for Synthetic Polymerases

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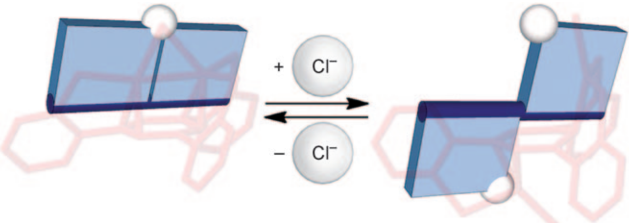


The dinickel chloride affair: In dinuclear nickel(I) complexes supported by a tris(phosphinoaryl)benzene and stabilized by metal–arene interactions, chloride addition causes reversible Ni–Ni bond cleavage that induces 180° rotation around an aryl–aryl bond (see scheme). A dinickel–chloride moiety was found to rotate around the bridging arene by a mechanism involving breaking and forming Ni–P bonds.

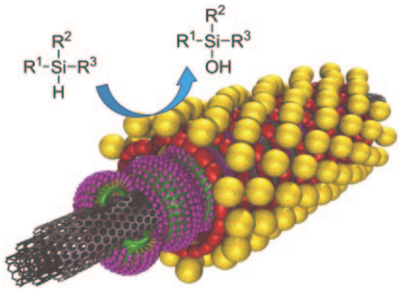
Dinickel Complexes

S. T. Chao, N. C. Lara, S. Lin, M. W. Day, T. Agapie* ____ **7529 – 7532**

Reversible Halide-Modulated Nickel–Nickel Bond Cleavage: Metal–Metal Bonds as Design Elements for Molecular Devices

---

Turning over silanes: The first nanotube-based catalytic system for silane oxidation is reported (see scheme). The reusable gold–nanotube hybrid cleanly oxidizes both alkyl and aryl silanes in high yields, under mild reaction conditions, and compares most favorably to any other catalytic system in terms of overall efficacy and turnover values.



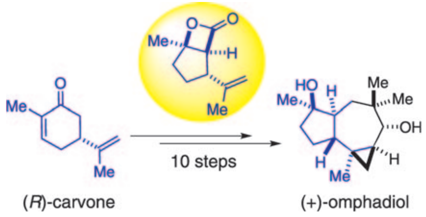
Heterogeneous Catalysis

J. John, E. Gravel, A. Hagège, H. Li, T. Gacoin, E. Doris* ____ **7533 – 7536**

Catalytic Oxidation of Silanes by Carbon Nanotube–Gold Nanohybrids

---

A smooth transition from (*R*)-carvone to a β-lactone and then to (+)-omphadiol characterizes the first total synthesis of this sesquiterpene, which was achieved in ten steps and 18% overall yield. All six contiguous stereogenic centers were introduced in a highly diastereoselective manner. Key steps include a nucleophile-promoted aldol lactonization, a single-pot, sequential intra-/intermolecular di-alkylation, a tandem olefin isomerization/RCM, and a cyclopropanation with unusual facial selectivity.



Total Synthesis

G. Liu, D. Romo* ____ **7537 – 7540**

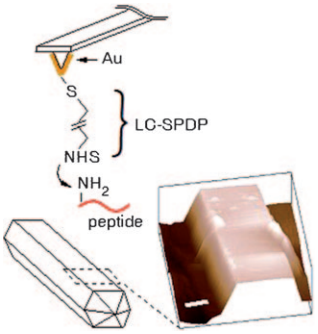
Total Synthesis of (+)-Omphadiol

Protein–Mineral Interactions

R. W. Friddle, K. Battle, V. Trubetskoy, J. Tao, E. A. Salter, J. Moradian-Oldak, J. J. De Yoreo,* A. Wierzbicki* ____ 7541 – 7545

Single-Molecule Determination of the Face-Specific Adsorption of Amelogenin's C-Terminus on Hydroxyapatite

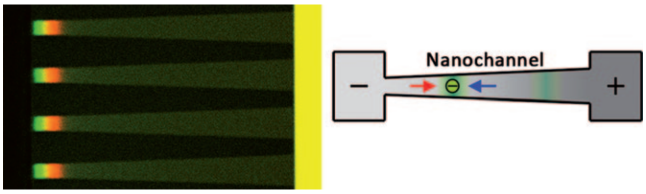
On the face of it: An atomic force microscopy tip, functionalized with Amelogenin protein (Amel), is used to directly determine the single-molecule, face-specific free energy of Amel binding to crystalline hydroxyapatite (see picture). The experimental values compare well with those from molecular dynamics simulations and enable the key interactions controlling face-specific binding to be identified.



Nanotechnology

D. W. Inglis,* E. M. Goldys, N. P. Calander ____ 7546 – 7550

Simultaneous Concentration and Separation of Proteins in a Nanochannel

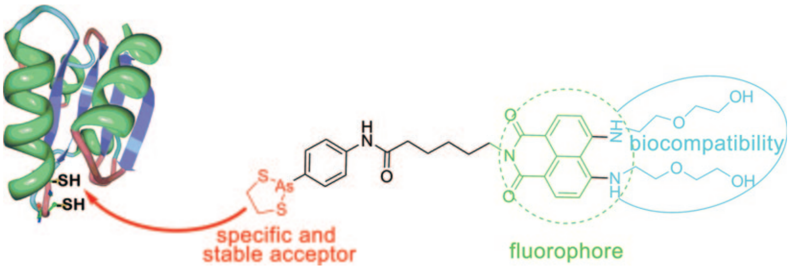


Balancing the forces: Conductivity gradient focusing in a nanochannel achieves simultaneous separation and concentration of proteins without a temperature gradient, membrane, matrix, ampholytes, or external pump. The electrophoretic force (see picture; red arrow) that dominates at the low-salt side (−) balances the electro-osmotic force (blue) at the high-salt side (+).

Redox Proteomics

C. Huang, Q. Yin, W. Zhu,* Y. Yang,* X. Wang, X. Qian, Y. Xu* ____ 7551 – 7556

Highly Selective Fluorescent Probe for Vicinal-Dithiol-Containing Proteins and In Situ Imaging in Living Cells

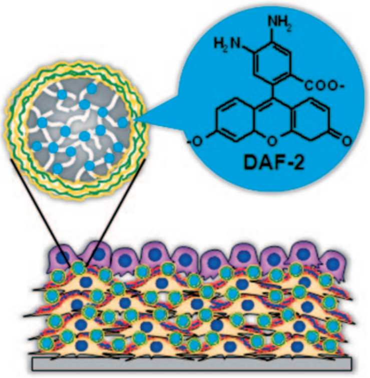


It pays to be direct: In a rapid and specific approach to the detection of vicinal-dithiol-containing proteins (VDPs), the use of a fluorescent probe (see picture) enabled the direct readout of fluorescence. This approach based on fluorescence polarization, electrophoresis, and the direct imaging of VDPs permits the noninvasive study of VDPs both in vitro and in living cells and offers insight into their potential roles in cell function.

Biosensors

M. Matsusaki, S. Amemori, K. Kadowaki, M. Akashi* ____ 7557 – 7561

Quantitative 3D Analysis of Nitric Oxide Diffusion in a 3D Artery Model Using Sensor Particles

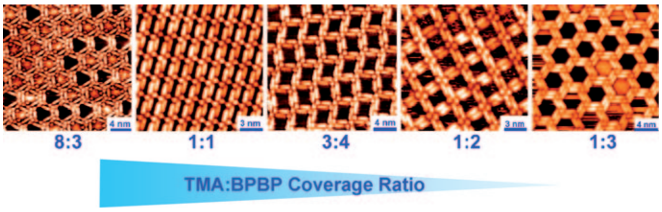


NO blood lost: Three-dimensional analysis of nitric oxide (NO) diffusion in a blood vessel in response to drug stimulation was achieved by using 3D artery models including NO sensor particles (see picture). The quantity and diffusion distance of NO in the five-layered models were almost the same as those for the in vivo blood vessel response. This method enables an in vitro bioassay of tissue responses instead of animal experiments.

Porous Networks

H. Liang, W. Sun, X. Jin, H. Li, J. Li, X. Hu,* B. K. Teo,* K. Wu* ________ 7562 – 7566

Two-Dimensional Molecular Porous Networks Formed by Trimesic Acid and 4,4′-Bis(4-pyridyl)biphenyl on Au(111) through Hierarchical Hydrogen Bonds: Structural Systematics and Control of Nanopore Size and Shape

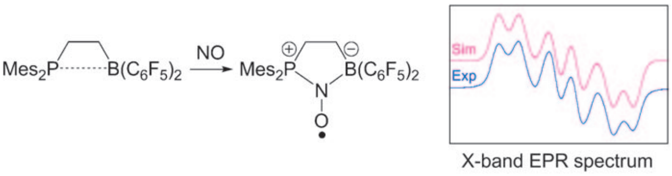


Pores for thought: The pore size and pore shape (including “rectangular”, triangular, tetragonal, diamond, pentagonal, and hexagonal) in binary molecular porous networks formed by trimesic acid (TMA) and 4,4′-bis(4-pyridyl)biphenyl (BPBP) molecules on Au(111) is tuned simply through changing the TMA:BPBP ratio (see picture).

Frustrated Lewis Pairs

A. J. P. Cardenas, B. J. Culotta, T. H. Warren,* S. Grimme,* A. Stute, R. Fröhlich, G. Kehr, G. Erker* ________ 7567 – 7571

Capture of NO by a Frustrated Lewis Pair: A New Type of Persistent *N*-Oxyl Radical



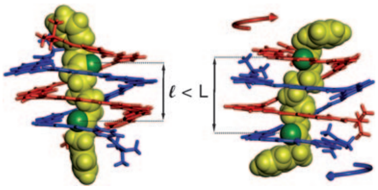
NO your pairs: The intramolecular frustrated Lewis pair (FLP) $Mes_2PCH_2CH_2B(C_6F_5)_2$ captures NO to give the novel *N*-oxyl radical P/B-FLP-NO$^•$ (see scheme). Coordination of NO to the FLP incites H-atom abstraction reactivity with cyclohexene and ethylbenzene to give P/B-FLP-NOH and the O-functionalized P/B-FLP-NOR species.

Molecular Machines

Y. Ferrand, Q. Gan, B. Kauffmann, H. Jiang,* I. Huc* ________ 7572 – 7575

Template-Induced Screw Motions within an Aromatic Amide Foldamer Double Helix

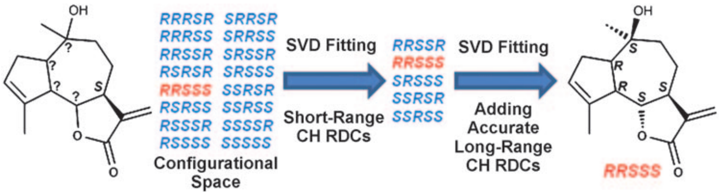
Screwed in place: An anti-parallel double-helical aromatic oligoamide foldamer was shown to bind to a series of rodlike guests of various lengths upon the winding of the duplex around the guests (see scheme). Solid-state crystal structures of the host–guest complexes show that the two strands of the duplex undergo a relative screw motion to adjust the distance between hydrogen-bond donors located at the end of one of their extremities so that they bind to hydrogen-bond acceptors of the guest.



NMR Spectroscopy

P. Trigo-Mouriño, A. Navarro-Vázquez, J. Ying, R. R. Gil,* A. Bax* __ 7576 – 7580

Structural Discrimination in Small Molecules by Accurate Measurement of Long-Range Proton–Carbon NMR Residual Dipolar Couplings

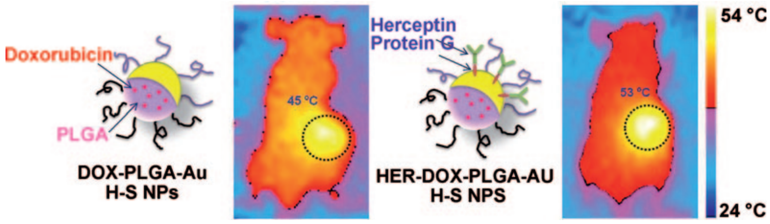


Accurate measurement of long-range CH residual dipolar couplings (RDCs; $^2D_{CH}$ and $^3D_{CH}$) by a new selective *J*-scaled HSQC experiment significantly improves the structural discrimination power of RDCs in small molecules with multiple stereogenic centers. The current approach was demonstrated with 10-epi-8-deoxycumambrin B, a tricyclic natural compound with five stereogenic centers (see figure; SVD = singular value decomposition).

Cancer Therapeutics

S.-M. Lee, H. Park, J.-W. Choi, Y. N. Park, C.-O. Yun, K.-H. Yoo* ______ 7581 – 7586

Multifunctional Nanoparticles for Targeted Chemophotothermal Treatment of Cancer Cells

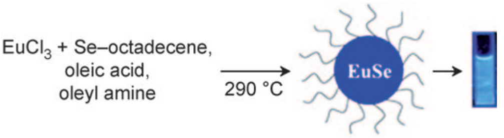


Drug and heat delivery to tumors by active targeting with Herceptin-conjugated doxorubicin-loaded poly(ethylene glycol)–poly(lactic-*co*-glycolic acid)–Au half-shell nanoparticles (HER-DOX-PLGA-Au H-S NPs) is more effective than passive targeting with their HER-free counterparts (DOX-PLGA-Au H-S NPs). Thus, on NIR irradiation, higher intratumoral temperatures were reached in tumor-bearing mice that were treated with the HER-conjugated particles (see picture).

Functional Nanocrystals

C. Wang, D. Zhang, L. Xu, Y. Jiang, F. Dong, B. Yang, K. Yu,* Q. Lin* ______ 7587 – 7591

A Simple Reducing Approach Using Amine To Give Dual Functional EuSe Nanocrystals and Morphological Tuning



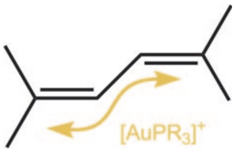
Amine for improvement: A non-injection approach using an amine as a reducing agent is developed to produce spherical EuSe nanocrystals (NCs) exhibiting blue emission (peaking at 403 nm with 2.8% quantum yield) and room-temperature magnetic coercivity of 80.2 Oe (see scheme). The NC morphologies can be controlled easily to be hollow, spherical, or rodlike.

VIP

Gold Cations

R. A. Sanguramath, T. N. Hooper, C. P. Butts, M. Green,* J. E. McGrady, C. A. Russell* ______ 7592 – 7595

The Interaction of Gold(I) Cations with 1,3-Dienes



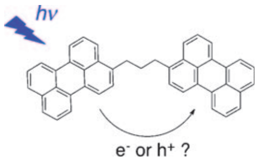
Slip-sliding away: Gold(I) cations bind to only one double bond of a 1,3-diene unit but can glide over the C_4 backbone on a low-activation-energy pathway. However, the binding mode is influenced by substituents on the diene backbone, which also induces a significantly higher barrier to migration.

Ultrafast Dynamics

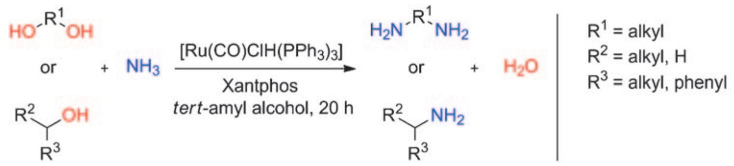
V. Markovic, D. Villamaina, I. Barabanov, L. M. Lawson Daku, E. Vauthey* ______ 7596 – 7598

Photoinduced Symmetry-Breaking Charge Separation: The Direction of the Charge Transfer

Even flow: Photoinduced symmetry-breaking charge separation takes place in a few picoseconds in a 1,3-bis-(perylene)propane dyad in polar solvents. Polarized transient absorption measurements show that the direction of the charge flow is random and entirely governed by the fluctuations of the solvent orientation around the dyad.



Catalytic Amination



Diamination of diols: The first homogeneously catalyzed diaminations of primary and secondary diols with ammonia give the corresponding diamines. Other primary as well as secondary alcohols including hydroxy-substituted esters can also be efficiently converted to primary amines. This atom-efficient and selective amination method proceeds in an ammonia atmosphere without additional hydrogen sources.

S. Imm, S. Bähn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas, M. Beller* ______ **7599 – 7603**

Improved Ruthenium-Catalyzed Amination of Alcohols with Ammonia: Synthesis of Diamines and Amino Esters

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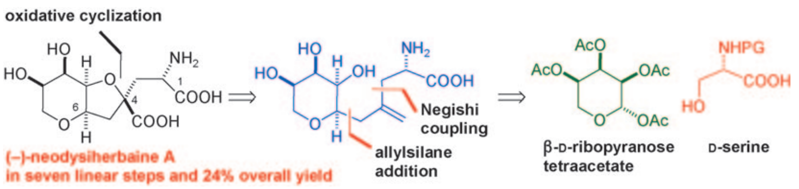
Natural Products



To the point: The synthesis of the title compound was achieved with 24 % overall yield through a sequence that has just seven linear steps (see scheme). Key points are the facial selectivity displayed by an oxocarbenium ion derived from a ribopyranose system and an osmium-catalyzed oxidative cyclization that is compatible with several acid-sensitive groups.

T. J. Donohoe,* P. C. M. Winship, M. R. Tatton, P. Szeto ______ **7604 – 7606**

A Short and Efficient Synthesis of Neodysiherbaine A by Using Catalytic Oxidative Cyclization

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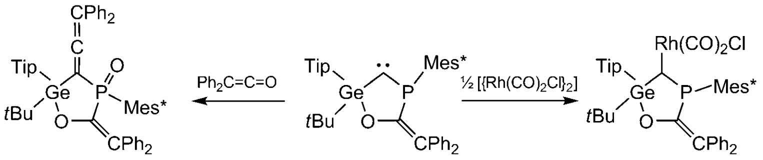
Carbenes



A highly reactive phosphagermacarbene (PGeHC) was synthesized by [3+2] cycloaddition between phosphagermaallene Tip(*t*Bu)Ge=C=PMes* (Tip = 2,4,6-triisopropylphenyl; Mes* = 2,4,6-tris-*tert*-butylphenyl) and diphenylketene. It forms complexes with $[\{Rh(CO)_2Cl\}_2]$ and Me_3P, and undergoes a Wittig-type reaction with diphenylketene (see scheme).

D. Ghereg, S. Ladeira, N. Saffon, J. Escudié,* H. Gornitzka* ______ **7607 – 7610**

Electronic Properties and Reactivity of an Isolable Phosphagermaheterocyclic Carbene

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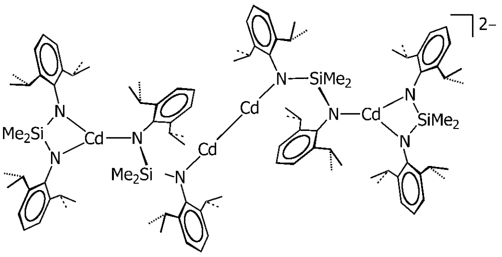
Metal–Metal Bonds



Two Mn–Mn-bonded dimanganese complexes, as well as the tetracadmium complex shown in the picture, were obtained by reduction of $[M_2\{\mu\text{-}\kappa^2\text{-}Me_2Si(NDipp)_2\}_2]$ (M = Mn, Cd; Dipp = 2,6-*i*$Pr_2C_6H_3$). Their structures are consistent with those of calculated intermediates in the reduction of $[Zn_2\{\mu\text{-}\kappa^2\text{-}Me_2Si(NDipp)_2\}_2]$.

D.-Y. Lu, J.-S. K. Yu, T.-S. Kuo, G.-H. Lee, Y. Wang, Y.-C. Tsai* ______ **7611 – 7615**

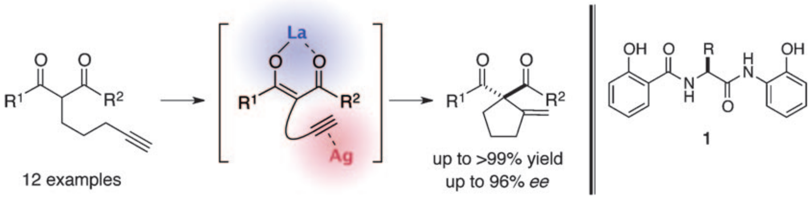
Theory-Guided Experiments on the Mechanistic Elucidation of the Reduction of Dinuclear Zinc, Manganese, and Cadmium Complexes

Contents

Homogeneous Catalysis

A. Matsuzawa, T. Mashiko, N. Kumagai,*
M. Shibasaki* ______ **7616–7619**

La/Ag Heterobimetallic Cooperative Catalysis: A Catalytic Asymmetric Conia-Ene Reaction

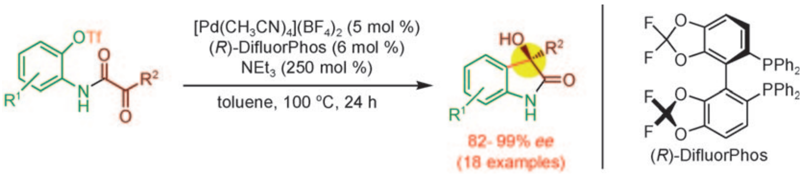


A dual catalyst system: The cooperative function of a hard and soft Lewis acid (La^{III} and Ag^{I}, respectively) in a catalyst system that includes an amide-based ligand **1** is crucial for simultaneous activation of intramolecular 1,3-dicarbonyl and alkyne moieties to afford enantioenriched cyclopentane derivatives (see scheme).

Asymmetric Catalysis

L. Yin, M. Kanai,*
M. Shibasaki* ______ **7620–7623**

A Facile Pathway to Enantiomerically Enriched 3-Hydroxy-2-Oxindoles: Asymmetric Intramolecular Arylation of α-Keto Amides Catalyzed by a Palladium–DifluorPhos Complex

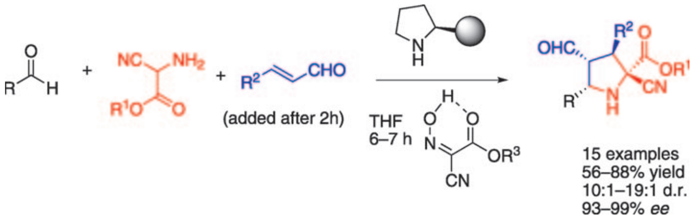


Less metal wastes: The first catalytic, enantioselective intramolecular aryl-transfer reaction of aryl triflates to ketones has been developed (see scheme; $R^1 = R^2 =$ aromatic and aliphatic). This method features overall practicality, including substrate stability and accessibility (protecting-group free) plus no need for the use of stoichiometric amounts of metals.

Multicomponent Reactions

S. Lin, L. Deiana, G.-L. Zhao, J. Sun,
A. Córdova* ______ **7624–7630**

Dynamic One-Pot Three-Component Catalytic Asymmetric Transformation by Combination of Hydrogen-Bond-Donating and Amine Catalysts

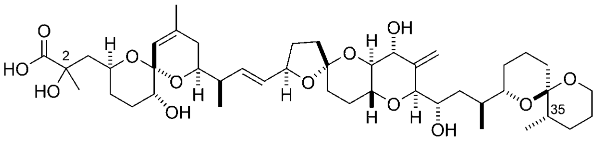


In control: The first dynamic one-pot three-component asymmetric transformation between aldehydes, protected α-cyanoglycine esters, and enals catalyzed by a combination of a simple hydrogen-bond-donating catalyst and a chiral amine catalyst is disclosed. Polysubstituted proline derivatives, which have a quaternary α stereocenter, were synthesized with high *endo*-, diastereo-, and enantioselectivities (93–99 % *ee*).

Natural Products

Y. Pang, C. Fang, M. J. Twiner, C. O. Miles,
C. J. Forsyth* ______ **7631–7635**

Total Synthesis of Dinophysistoxin-2 and 2-*epi*-Dinophysistoxin-2 and Their PPase Inhibition



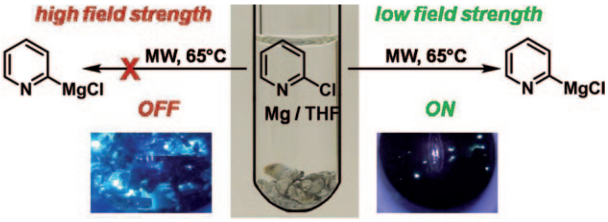
(2*R*)-DTX-2: IC_{50}=1.35 nM (PP2A), 82.6 nM (PP1)
2-*epi*-DTX-2: IC_{50}=137 nM (PP2A), 3114 nM (PP1)

The first total syntheses of the title compounds highlight novel assemblies of the C1–C14 and C28–C38 domains, including an unexpected diastereoselectivity in the Sharpless asymmetric dihydroxylation of an alkene at C1=C2. PPase inhibition assays revealed that 2-*epi*-DTX-2 is at least 1 to 2 orders of magnitude less potent than DTX-2, thus indicating that the configuration at C2 in DTX-2 is crucial for potent inhibition (see picture).

Microwave Chemistry

B. Gutmann, A. M. Schwan, B. Reichart,
C. Gspan, F. Hofer,
C. O. Kappe* ———— **7636–7640**

Activation and Deactivation of a Chemical Transformation by an Electromagnetic Field: Evidence for Specific Microwave Effects in the Formation of Grignard Reagents

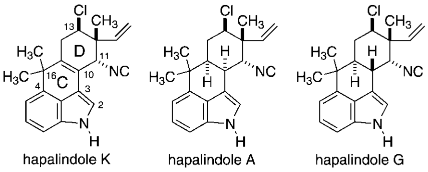


It's field density, not temperature! Modifying the electric field strength in a microwave experiment can completely change the outcome of a reaction. Whereas a low field strength in Grignard reagent formation from Mg metal and aryl halide leads to acceleration of the initiation step, using a high field strength at the same temperature suppresses Mg insertion, favoring solvent decomposition and passivation of the Mg metal (see scheme).

Natural Products

A. Chandra, J. N. Johnston* **7641–7644**

Total Synthesis of the Chlorine-Containing Hapalindoles K, A, and G

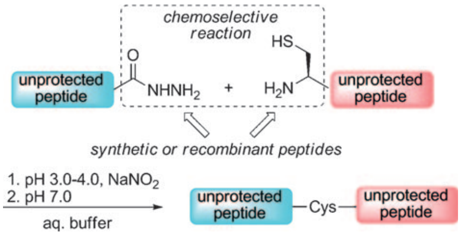


A common approach: Overall brevity in the synthesis of the title compounds (see scheme) is achieved by a sequential electrophilic aromatic substitution of indole and a regio- and diastereoselective intermolecular Diels–Alder cycloaddition to establish the key precursor—a neopentyl chloride. A stereoselective Ritter reaction and dehydration are used for the installation of the isonitrile unit.

Protein Chemical Synthesis

G.-M. Fang, Y.-M. Li, F. Shen, Y.-C. Huang,
J.-B. Li, Y. Lin, H.-K. Cui,
L. Liu* ———— **7645–7649**

Protein Chemical Synthesis by Ligation of Peptide Hydrazides

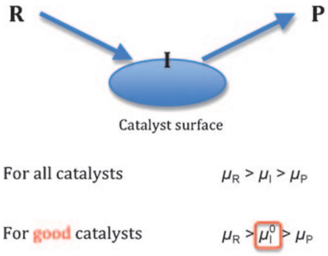


pH determines selectivity: The ligation of peptide hydrazides is a new method for protein chemical synthesis that is complementary to native chemical ligation. Peptide hydrazides may be the long-sought reagent equivalent to a "thioester synthon", one that is stable to the conditions of native chemical ligation.

Heterogeneous Catalysis

J. Cheng,* P. Hu* ———— **7650–7654**

Theory of the Kinetics of Chemical Potentials in Heterogeneous Catalysis



Simple and powerful: The reaction kinetics at surfaces of heterogeneous catalysts is reformulated in terms of the involved chemical potentials. Based on this formulism, an approach of searching for good catalysts is proposed without recourse to extensive calculations of reaction barriers and detailed kinetic analyses. (see picture; R = reactant, I = surface intermediate, P = product, and μ° = standard chemical potential).

Contents

Trifluoromethylation

O. A. Tomashenko, E. C. Escudero-Adán, M. Martínez Belmonte, V. V. Grushin* **7655 – 7659**

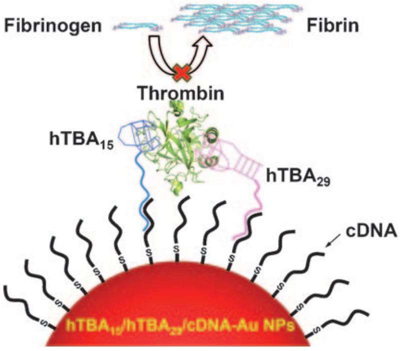
Simple, Stable, and Easily Accessible Well-Defined $CuCF_3$ Aromatic Trifluoromethylating Agents

Give me an F: Exceptionally easy to make in over 90% yield (see scheme) and air-stable in the solid state, $[(Ph_3P)_3Cu(CF_3)]$ is a remarkable example of a rarely encountered well-defined Cu(I) trifluoromethylating agent and a convenient starting material for the synthesis of other $CuCF_3$ complexes, such as $[(phen)Cu(PPh_3)(CF_3)]$.

Anticoagulant Nanoparticles

Y.-C. Shiang, C.-L. Hsu, C.-C. Huang,* H.-T. Chang* **7660 – 7665**

Gold Nanoparticles Presenting Hybridized Self-Assembled Aptamers That Exhibit Enhanced Inhibition of Thrombin

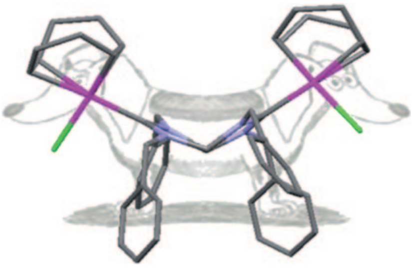


DNA hybridization of thrombin-binding aptamers (TBAs) to form a self-assembled arranged monolayer on gold nanoparticles (Au NPs) was used to control the coagulation activity of thrombin. The $hTBA_{15}/hTBA_{29}/cDNA$-Au NPs provided flexibility and a suitable orientation and distance between the $hTBA_{15}$ and $hTBA_{29}$ units for bivalent binding, allowing strong interactions with thrombin and extremely high anticoagulant potency.

N-Heterocyclic Carbenes

A. Prades, M. Poyatos, J. A. Mata, E. Peris* **7666 – 7669**

Double C–H Bond Activation of $C(sp^3)H_2$ Groups for the Preparation of Complexes with Back-to-Back Bisimidazolinylidenes

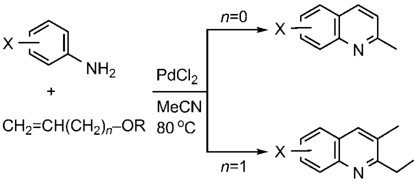


Two-headed carbenes: N-heterocyclic carbene complexes of rhodium and iridium were obtained by the double C–H activation of CH_2 groups in N heterocycles (see structure: C gray, N blue, Cl green, Ir pink). The reaction constitutes a valuable approach to new carbene ligands with unprecedented architectures.

Synthetic Methods

Y. Matsubara,* S. Hirakawa, Y. Yamaguchi, Z.-i. Yoshida* **7670 – 7673**

Assembly of Substituted 2-Alkylquinolines by a Sequential Palladium-Catalyzed C–N and C–C Bond Formation

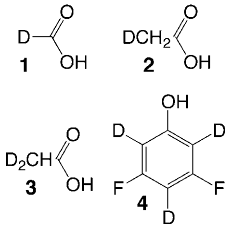


Diversity: A range of substituted 2-alkylquinolines can be prepared in a general and efficient synthetic approach that employs mild reaction conditions (see scheme). The synthesis is based on a sequential palladium-catalyzed C–N and C–C bond formation, followed by palladium-catalyzed aromatization, and results in the formation of the desired compounds in one step.

Isotope Effects

C. L. Perrin,* A. Flach — 7674–7676

No Contribution of an Inductive Effect to Secondary Deuterium Isotope Effects on Acidity

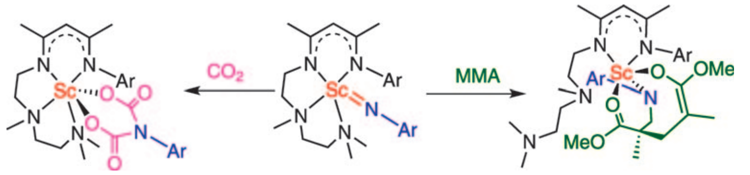


Effect and cause: Secondary deuterium isotope effects on the acidity of the deuterated compounds **1**–**4** were measured by using an NMR titration method applicable to a mixture and capable of very high accuracy. Variable-temperature experiments show that these isotope effects are due only to changes in vibrational frequencies. These findings refute an inductive origin for these isotope effects.

Organometallic Complexes

J. X. Chu, E. L. Lu, Z. X. Liu, Y. F. Chen,* X. B. Leng, H. B. Song — 7677–7680

Reactivity of a Scandium Terminal Imido Complex Towards Unsaturated Substrates

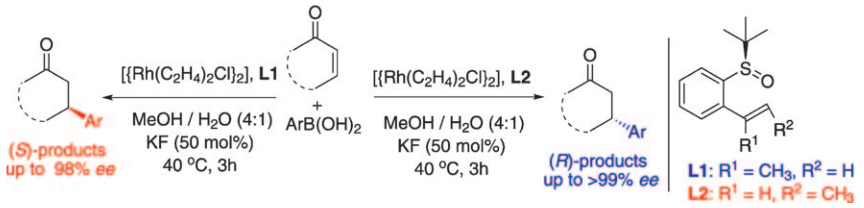


A complex complex: The reactions of a scandium terminal imido complex with a series of unsaturated substrates, including CO_2, PhCN, methyl methacrylate (MMA), cyclopentadiene, PhNCO, and propylene oxide, are presented (see scheme). A variety of intriguing products are formed from this complex. Ar = 2,6-$(i\mathrm{Pr})_2C_6H_3$.

Asymmetric Catalysis

G. Chen, J. Gui, L. Li, J. Liao* — 7681–7685

Chiral Sulfoxide-Olefin Ligands: Completely Switchable Stereoselectivity in Rhodium-Catalyzed Asymmetric Conjugate Additions

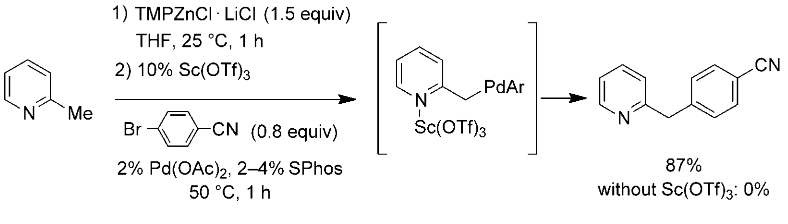


Have it both ways: A novel class of chiral sulfoxide-olefin ligands was synthesized from a single chiral source. These ligands were evaluated in rhodium-catalyzed 1,4-additions of arylboronic acids to electron-deficient olefins, and remarkable olefin-directed reversal of stereoselectivity (up to > 99% *ee*, *R* isomer; 98% *ee*, *S* isomer) was observed when the reversal ligand pair **L1** (branched olefin) and **L2** (linear olefin) were utilized (see scheme).

Arylation Reactions

S. Duez, A. K. Steib, S. M. Manolikakes, P. Knochel* — 7686–7690

Lewis Acid Promoted Benzylic Cross-Couplings of Pyridines with Aryl Bromides



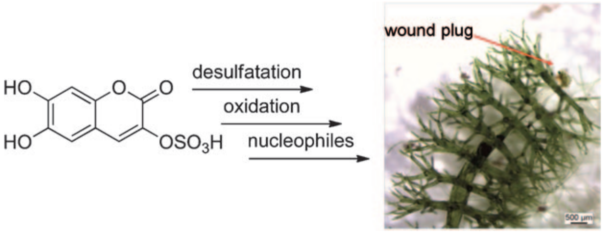
Either $ZnCl_2$, $Sc(OTf)_3$, or BF_3·OEt_2 can promote the palladium-catalyzed arylation of methylpyridines and related heterocycles (see example). The complexation of the Lewis acid to the nitrogen atom in the heterocycle facilitates the reductive elimination, leading to various arylated pyridines in high yields. BF_3·OEt_2 was also found to promote highly regioselective metalations in the case of 2,4-lutidine.

Contents

Phytochemistry

M. Welling, C. Ross,
G. Pohnert* ———— **7691 – 7694**

A Desulfatation–Oxidation Cascade Activates Coumarin-Based Cross-Linkers in the Wound Reaction of the Giant Unicellular Alga *Dasycladus vermicularis*



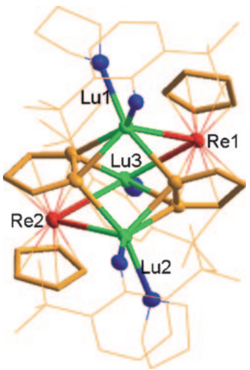
Plugged up: A rapid and efficient cascade of desulfatation, oxidation, and cross-linking mediates wound sealing in the giant-celled alga *Dasycladus vermicularis* (see picture). UV and fluorescence studies and mass spectrometry show the wound plug is a coumarin-based polymer.

Metal–Metal Bonding

M. V. Butovskii, O. L. Tok, V. Bezugly,
F. R. Wagner,* R. Kempe* — **7695 – 7698**

Molecular Lanthanoid–Transition-Metal Cluster through C—H Bond Activation by Polar Metal–Metal Bonds

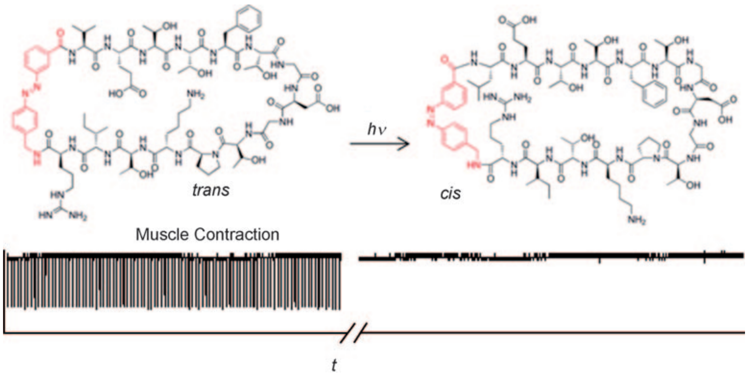
Cp glue: A chiral four-coordinate organolanthanoid complex, which has an unsupported metal–metal bond, reacts to give a lanthanoid–transition-metal cluster with two-electron multicenter metal–metal bonds (see structure). The reaction proceeds through C—H bond activation by the polar metal–metal bonds and affords a 1,2-dimetallation of one Cp ligand of the metallocene moiety.



Muscle Contraction

C. Hoppmann,* P. Schmieder,
P. Domaing, G. Vogelreiter, J. Eichhorst,
B. Wiesner, I. Morano, K. Rück-Braun,
M. Beyermann ———— **7699 – 7702**

Photocontrol of Contracting Muscle Fibers



A twitch in time: Light-directed inhibition of the interaction between α-1-syntrophin and neuronal NO synthase (nNOS) in living skeletal muscle with a cell-permeable photoswitchable nNOS-derived peptide ligand results in photocontrol of muscle performance and nitric oxide signaling.

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

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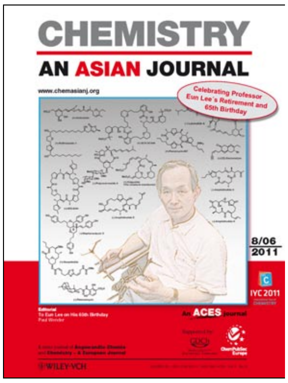

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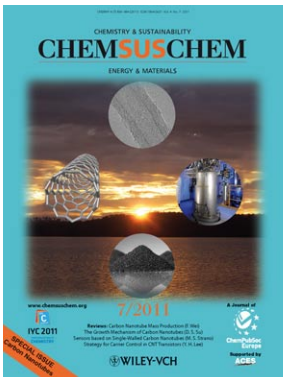

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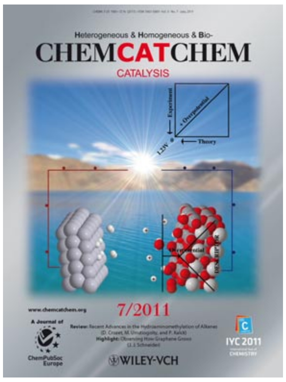

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