



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*

CO₂ 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

M. Nakanishi, D. Katayev, C. Besnard, E. P. Kündig*

Synthesis of Fused Indolines by Palladium-Catalyzed Asymmetric C–C Coupling Involving an Unactivated Methylene Group

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-Benzodithiolium 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}As₂

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

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

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

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



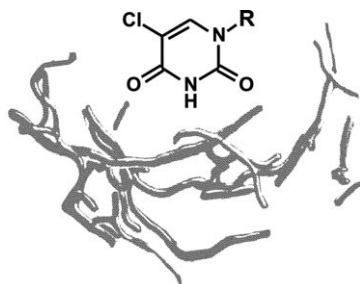
“When I was eighteen I wanted to be a mechanical engineer.

The biggest challenge facing scientists is nonlinearity ...”

This and more about Younan Xia can be found on page 6958.

Author Profile

Younan Xia _____ 6958 – 6959



An automated system for the continuous cultivation of cells in suspension has been used to globally change the composition of the DNA genome of *E. coli*. Thymine was replaced almost completely by 5-chlorouracil through artificial evolution of cells, during which the bacterial genome accumulated hundreds of mutations under permanent conditions of proliferation and selection. The resulting 5-chlorouracil-adapted descendants had the ability to grow on 5-chlorouracil.

Highlights

Organism Chemistry

C. G. Acevedo-Rocha,
N. Budisa* _____ 6960 – 6962

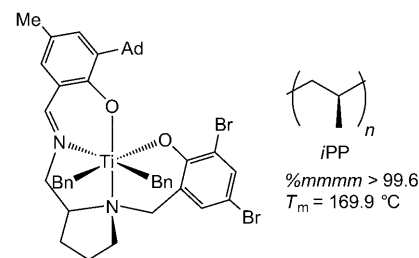
On the Road towards Chemically Modified Organisms Endowed with a Genetic Firewall

Stereoselective Polymerization

L. R. Sita* ————— 6963 – 6965

Duality in Catalyst Design: The Synergistic Coupling of Steric and Stereoelectronic Control over Polyolefin Microstructure

The full picture: In a new strategy for catalyst design, the coupling of steric and stereoelectronic differentiation to develop the salalen–titanium complex pictured resulted in one of the highest degrees of stereocontrol ever observed for the production of isotactic polypropylene (iPP). Ad = adamantyl, Bn = benzyl.



Reviews

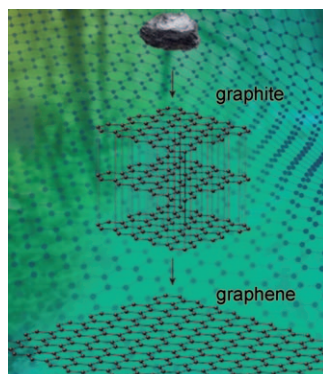
Graphene

A. K. Geim* ————— 6966 – 6985

Random Walk to Graphene (Nobel Lecture)

K. S. Novoselov* ————— 6986 – 7002

Graphene: Materials in the Flatland (Nobel Lecture)



There can be only one: In their Nobel Reviews, the laureates tell the story about the ever changing, exciting scientific pathways that eventually—for example, with the aid of simple adhesive tape—led them to the discovery of graphene. Graphene is a carbon monolayer with almost magical abilities, including exceptional strength, stability, and electronic properties, with massless Dirac fermions as charge carriers.

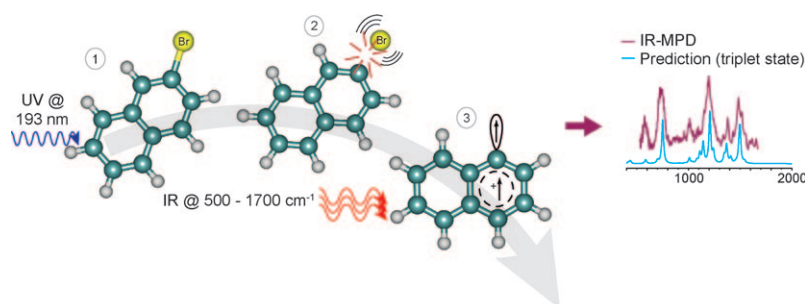
Communications

Triplet Naphthyl Cation

H. Alvaro Galué,
J. Oomens* ————— 7004 – 7007



Spectroscopic Evidence for a Triplet Ground State in the Naphthyl Cation



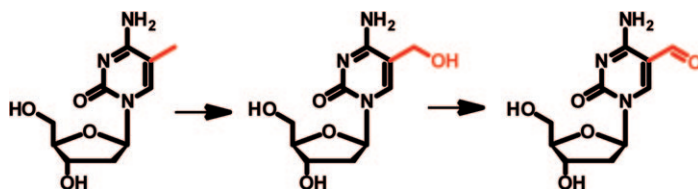
Run to ground: Infrared spectroscopy of the isolated naphthyl carbocation, $C_{10}H_7^+$ (prepared from $C_{10}H_7Br$, see scheme) provides evidence for a triplet electronic ground state ($^3A''$), in which a π electron is promoted to the vacant σ orbital. Previous

computational studies have been ambiguous as to the relative stabilities of the singlet and triplet states; DFT calculations predict both states to be practically iso-energetic.

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individuals who are personal members of a national chemical society prices are available on request. Postage and handling charges included. All prices are subject to local VAT/sales tax.



Touching base: Sophisticated mass spectrometry has shown that 5-formylcytosine is a constituent of mammalian embryonic stem cell DNA. This base is likely produced from methylcytosine via hydroxy-

methylcytosine (see scheme), and it may serve as an intermediate in the long searched for pathway of active DNA demethylation.

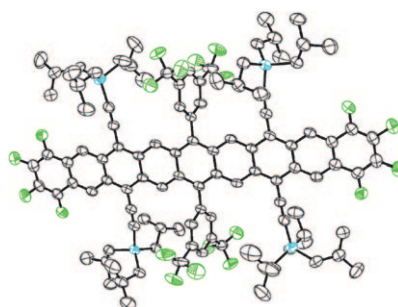
Bioorganic Chemistry

T. Pfaffeneder, B. Hackner, M. Truß,*
M. Münzel, M. Müller, C. A. Deiml,
C. Hagemeier, T. Carell* — 7008 – 7012

The Discovery of 5-Formylcytosine in Embryonic Stem Cell DNA



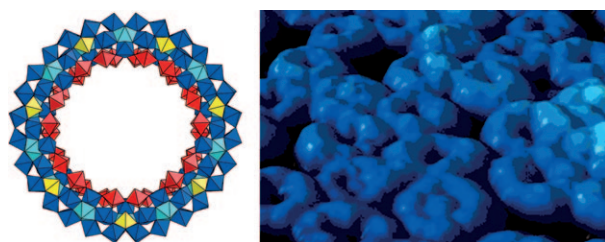
Nine in a line: A multifaceted approach, including a silylethylene functionalization strategy, to the synthesis of stable non-acene derivatives (see picture, F green, Si blue) allows an unprecedented level of characterization, including electrochemical, photophysical, and crystallographic studies. The nonacenes show a strong S_0-S_1 transition and no fluorescence in the visible region.



Oligoacenes

B. Purushothaman, M. Bruzek,
S. R. Parkin, A.-F. Miller,
J. E. Anthony* — 7013 – 7017

Synthesis and Structural Characterization of Crystalline Nonacenes



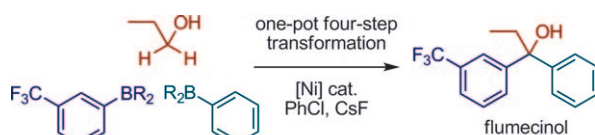
The electrons go in two by two: Scanning tunneling microscopy (STM)/spectroscopy (STS), shows the Mo_{154} giant wheel cluster to have a unique localization of states within each of the 14 identical compartments forming its necklace-type

structure (see picture). Each compartment contains two delocalized electrons. These states make the system different from conventional quantum dots that have completely free electrons or excitonic states.

Polyoxometalate Necklace

D. Zhong, F. L. Sousa, A. Müller,* L. Chi,*
H. Fuchs* — 7018 – 7021

A Nanosized Molybdenum Oxide Wheel with a Unique Electronic-Necklace Structure: STM Study with Submolecular Resolution



All in one pot: A general synthetic platform allows the interconversion of alcohols and carbonyl compounds in a predictable and controlled fashion in one pot. Under the action of a Ni catalyst, PhCl, CsF, and arylboronates, several multistep

alcohol-carbonyl interconversions have been achieved with good overall efficiency (see scheme). A one-pot nickel-catalyzed synthesis of flumecinol (a hepatic microsomal enzyme inducer) has also been demonstrated.

Alcohol-Carbonyl Interconversion

T. Maekawa, H. Sekizawa,
K. Itami* — 7022 – 7026

Controlled Alcohol-Carbonyl Interconversion by Nickel Catalysis

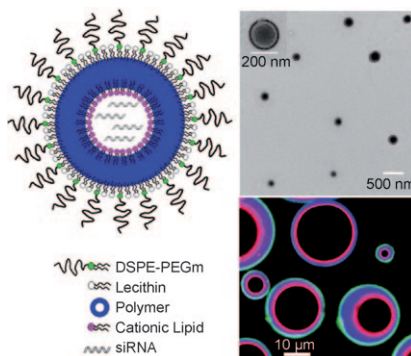


Functional Nanoparticles

J. Shi, Z. Xiao, A. R. Votruba, C. Vilos,
O. C. Farokhzad* ————— **7027 – 7031**



Differentially Charged Hollow Core/Shell Lipid–Polymer–Lipid Hybrid Nanoparticles for Small Interfering RNA Delivery



Speedy delivery: Biodegradable and bio-compatible polymers and lipids form hybrid core/shell nanoparticles (see picture, left) that show promising in vitro and in vivo results for delivering siRNA. The unique lipid–polymer–lipid nanostructure is elucidated by electron and fluorescence microscopy (right) and provides the delivery system with distinct functional features.

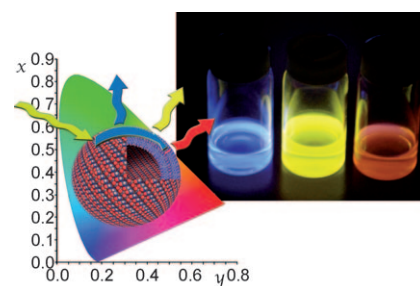
Self-Assembly

K.-P. Tseng, F.-C. Fang, J.-J. Shyue,
K.-T. Wong,* G. Raffy, A. Del Guerzo,
D. M. Bassani* ————— **7032 – 7036**



Spontaneous Generation of Highly Emissive RGB Organic Nanospheres

Over the rainbow: Three highly luminescent compounds use hydrogen-bonding interactions to spontaneously generate hollow nanospheres when dropcast from anhydrous solvents (see picture). Together, they cover more than 75 % of the gamut of a conventional liquid crystalline display.

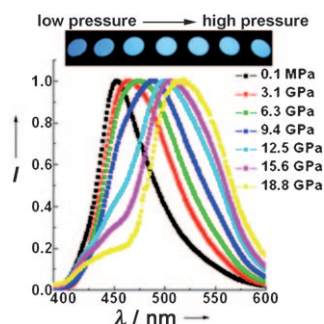


Piezochromic Luminescence

D. P. Yan, J. Lu,* J. Ma, S. H. Qin, M. Wei,*
D. G. Evans, X. Duan ————— **7037 – 7040**



Layered Host–Guest Materials with Reversible Piezochromic Luminescence



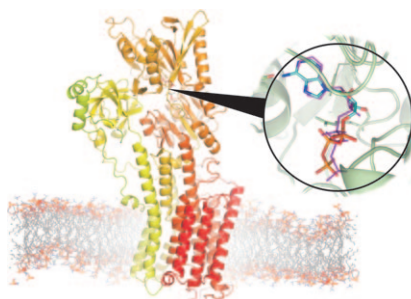
Under pressure: An anionic organic fluorophore (a stilbene derivative, BTZB) assembled into a layered double hydroxide host has reversible optical responses, including changes in absorption spectra, luminescence color, and fluorescence lifetime, on changing the external pressure (see picture). These changes are not observed for pristine BTZB.

Conformation Analysis

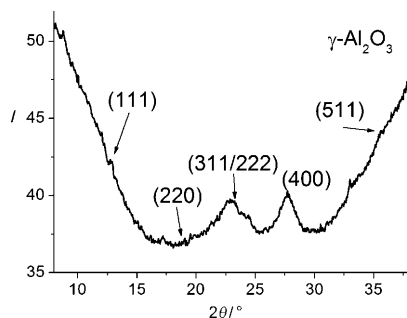
D. A. Middleton,* E. Hughes,
M. Esmann ————— **7041 – 7044**



The Conformation of ATP within the Na,K-ATPase Nucleotide Site: A Statistically Constrained Analysis of REDOR Solid-State NMR Data



Simplification through statistics: The conformation of adenosine triphosphate (ATP) bound to the high-affinity nucleotide site of Na,K-ATPase in its native membrane (see picture) can be determined by REDOR solid-state NMR measurements. The structural analysis of ligands may be improved dramatically by considering their conformational preferences based on the statistical analysis of a limited number of ^{31}P – ^{13}C distances.

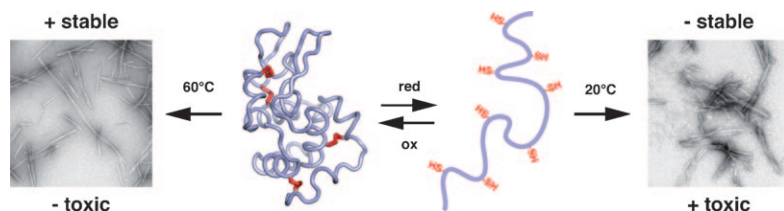


Alumina in flow: Information obtained from in situ synchrotron powder X-ray diffraction (PXRD) measurements was used to develop the first large-scale, rapid, one-step synthesis of $\gamma\text{-Al}_2\text{O}_3$. The data suggest a reaction mechanism that does not involve crystalline intermediates, and $\gamma\text{-Al}_2\text{O}_3$ was prepared at low temperature in a continuous-flow reactor using aluminum isopropoxide in 2-propanol/water without subsequent calcination.

Nanoparticles

N. Lock, M. Christensen, K. M. Ø. Jensen, B. B. Iversen* 7045 – 7047

Rapid One-Step Low-Temperature Synthesis of Nanocrystalline $\gamma\text{-Al}_2\text{O}_3$



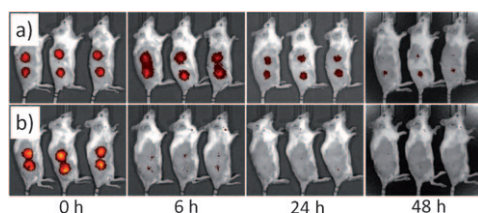
In a stable condition: Disulfide bonds stabilize folded proteins primarily by decreasing the entropic cost of folding. Such cross-links also reduce toxic aggregation by favoring the formation of highly structured amyloid fibrils (see picture). It

is suggested that disulfide bonds in extracellular proteins were selected by evolutionary pressures because they decrease the propensity to form toxic aggregates.

Amyloid Toxicity

M. F. Mossuto, B. Bolognesi, B. Guixer, A. Dhulesia, F. Agostini, J. R. Kumita, G. G. Tartaglia, M. Dumoulin, C. M. Dobson, X. Salvatella* 7048 – 7051

Disulfide Bonds Reduce the Toxicity of the Amyloid Fibrils Formed by an Extracellular Protein



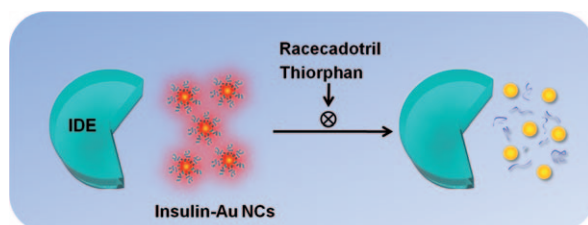
Amphiphilic oligonucleotides synthesized by covalent conjugation between a hydrophobic diacyllipid tail and chemically stabilized RNA or DNA oligonucleotides can directly label tumor cells on injection into solid tumors. In a murine

melanoma tumor model, cell membrane-anchored CpG ODNs with a nuclease-resistant phosphorothioate backbone (row a) exhibited significantly enhanced immunostimulatory activity compared to soluble CpG (row b).

Sticky Oligonucleotides

H. Liu, B. Kwong, D. J. Irvine* 7052 – 7055

Membrane Anchored Immunostimulatory Oligonucleotides for In Vivo Cell Modification and Localized Immunotherapy



Go for gold: As-prepared insulin–Au nanoclusters (NCs) show intense red fluorescence, excellent biocompatibility, and preservation of natural insulin bioactivity in lowering the blood-glucose level.

Their versatility in applications is demonstrated by fluorescence imaging, X-ray computed tomography, and insulin–inhibitor interactions (see picture; IDE = insulin-degrading enzyme).

Gold Nanoclusters

C.-L. Liu, H.-T. Wu, Y.-H. Hsiao, C.-W. Lai, C.-W. Shih, Y.-K. Peng, K.-C. Tang, H.-W. Chang, Y.-C. Chien, J.-K. Hsiao, J.-T. Cheng,* P.-T. Chou* 7056 – 7060

Insulin-Directed Synthesis of Fluorescent Gold Nanoclusters: Preservation of Insulin Bioactivity and Versatility in Cell Imaging



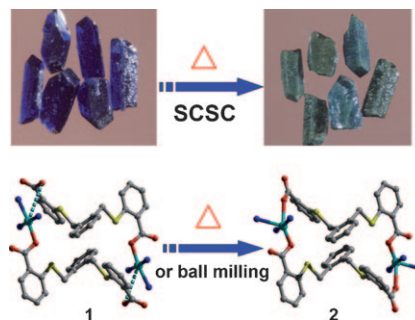
Single-Crystal Transformations

J. Sun, F. Dai, W. Yuan, W. Bi, X. Zhao,
W. Sun, D. Sun* — 7061 – 7064



Dimerization of a Metal Complex through Thermally Induced Single-Crystal-to-Single-Crystal Transformation or Mechanochemical Reaction

Come together: Monomers of copper carboxylate complex **1** (see picture, Cu blue-green, N blue, O red, S yellow, C gray) can dimerize to **2** when previously H-bonded carboxylate groups coordinate to copper. This dimerization can be induced by thermal single-crystal-to-single-crystal transformation or by mechanochemical reaction.

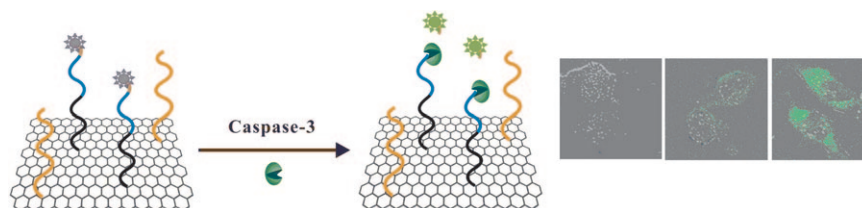


Graphene Conjugates

H. Wang, Q. Zhang, X. Chu,* T. Chen,
J. Ge, R. Yu — 7065 – 7069



Graphene Oxide–Peptide Conjugate as an Intracellular Protease Sensor for Caspase-3 Activation Imaging in Live Cells



All systems GO! An intracellular protease sensor is based on the covalent conjugate of graphene oxide and peptide substrates with fluorophore labels. The conjugate can be delivered into live cells and

provides specific, high-contrast imaging of caspase-3 activation (see picture; orange = cell penetration peptide, blue/black = caspase-3 peptide probe).

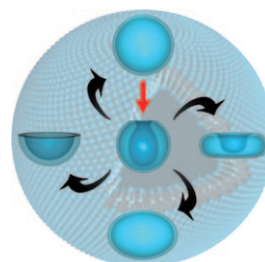
Polymersome Morphologies

S. A. Meeuwissen, K. T. Kim,
Y. Chen, D. J. Pochan,
J. C. M. van Hest* — 7070 – 7073



Controlled Shape Transformation of Polymersome Stomatocytes

Shape up your polymersome: Polymeric vesicles composed of block-copolymers with a glassy hydrophobic segment are no longer merely destined to take on the morphology obtained right after self-assembly. Gradual introduction of plasticizing solvents creates a permeable vesicular membrane, which together with osmotic pressure differences leads to shape transformation (see scheme).

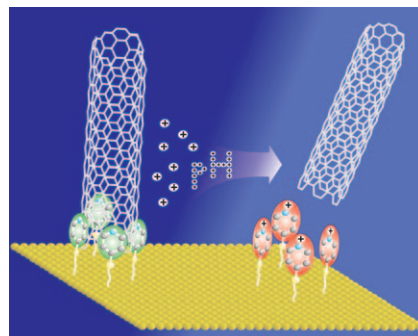


Self-Assembly

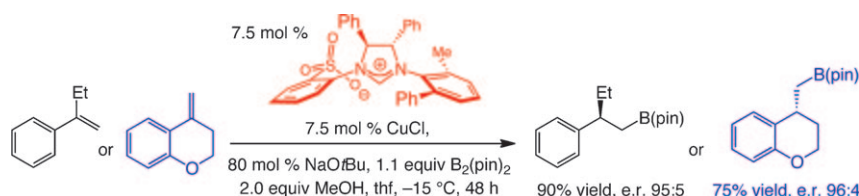
T. Ferri,* D. Frasca, O. Arias de Fuentes,
R. Santucci, M. Frasconi* — 7074 – 7078



Spatially Oriented and Reversible Surface Assembly of Single-Walled Carbon Nanotubes: A Strategy Based on π - π Interactions



Nanotubes released: π - π stacking interactions between single-walled carbon nanotubes (SWCNTs) and a monolayer of aromatic rings anchored on a gold surface result in reversible surface assembly of the SWCNTs. Protonation of a pyridine-based self-assembled monolayer reduces the pyridine-SWCNT interaction and thus releases the SWCNTs (see picture).



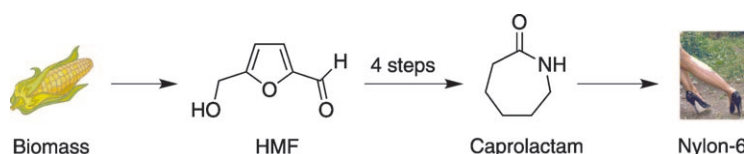
Tough nut to crack: Chiral bidentate N-heterocyclic carbene copper complexes were designed that promote enantioselective hydroborations of one of the most difficult substrate classes: acyclic and

exocyclic 1,1-disubstituted alkenes undergo reaction with > 98 % site selectivity, in up to > 98 % yield and e.r = 96.5:3.5 (see scheme, $B_2(\text{pin})_2$ = bis(pinacolato)diboron).

Enantioselective Catalysis

R. Corberán, N. W. Mszar,
A. H. Hoveyda* — 7079 – 7082

NHC-Cu-Catalyzed Enantioselective Hydroboration of Acyclic and Exocyclic 1,1-Disubstituted Aryl Alkenes



Renewable nylon: 5-Hydroxymethylfurfural (HMF), which can be obtained from renewable resources such as D-fructose, was converted into caprolactone with very good overall selectivity in only three steps.

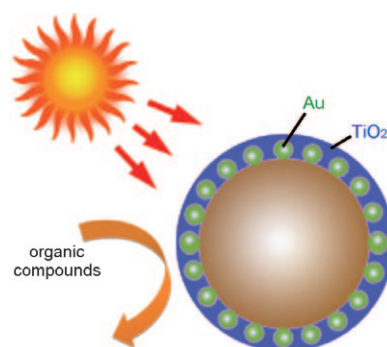
The new route involves two hydrogenation steps to obtain 1,6-hexanediol, which was oxidatively cyclized to caprolactone, and then converted into caprolactam.

Sustainable Chemistry

T. Buntara, S. Noel, P. H. Phua,
I. Melián-Cabrera, J. G. de Vries,*
H. J. Heeres* — 7083 – 7087

Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone

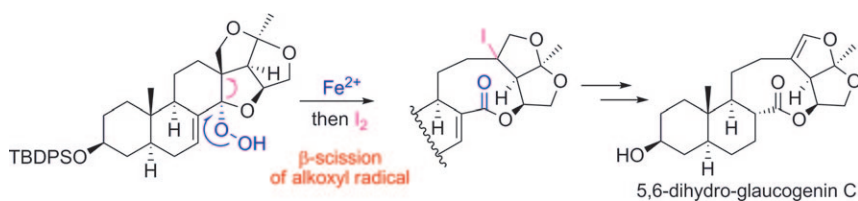
Nicely decorated: A sandwich-structured photocatalyst shows an excellent performance in degradation reactions of a number of organic compounds under UV, visible light, and direct sunlight (see picture). The catalyst was synthesized by a combination of nonmetal doping and plasmonic metal decoration of TiO_2 nanocrystals, which improves visible-light activity and enhances light harvesting and charge separation, respectively.



Photocatalysts

Q. Zhang, D. Q. Lima, I. Lee, F. Zaera,
M. Chi, Y. Yin* — 7088 – 7092

A Highly Active Titanium Dioxide Based Visible-Light Photocatalyst with Nonmetal Doping and Plasmonic Metal Decoration



A skeleton key: A biomimetic synthesis of the title natural product was completed in 19 steps and 6.4 % overall yield. Iron(II)-promoted fragmentation of α -alkoxy hydroperoxide and subsequent trapping

of the resulting tertiary carbon radical by iodide enabled the highly efficient construction of the challenging 13,14:14,15-disecopregnane skeleton (see scheme; TBDSO = *tert*-butyldiphenylsilyl).

Natural Product Synthesis

J. Gui, D. Wang, W. Tian* — 7093 – 7096

Biomimetic Synthesis of 5,6-dihydro-glaucogenin C: Construction of the Disecopregnane Skeleton by Iron(II)-Promoted Fragmentation of an α -Alkoxy Hydroperoxide



Synthetic Methods

D.-G. Yu, Z.-J. Shi* — 7097–7100



Mutual Activation: Suzuki–Miyaura Coupling through Direct Cleavage of the sp^2 C–O Bond of Naphtholate

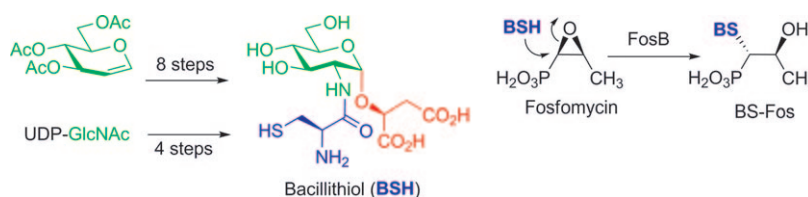


Working together: A new approach of mutual activation between naphtholates and aryl boronic acid derivatives by the formation of borates to facilitate the Suzuki–Miyaura coupling through direct

cleavage of the sp^2 C–O bond by nickel catalysis is described (see scheme; R': annulated ring system). Various naphtholates and aryl boronic acid derivatives could be directly coupled in good yields.

Natural Products

S. V. Sharma, V. K. Jothivasan, G. L. Newton, H. Upton, J. I. Wakabayashi, M. G. Kane, A. A. Roberts, M. Rawat, J. J. La Clair, C. J. Hamilton* — 7101–7104



Chemical and Chemoenzymatic Syntheses of Bacillithiol: A Unique Low-Molecular-Weight Thiol amongst Low G + C Gram-Positive Bacteria

The full monty: The recently discovered thiol cofactor bacillithiol (BSH), its biosynthetic precursors, and its symmetrical disulfide are prepared in two ways. The fosfomycin resistance protein (FosB) is

shown to be a BSH-utilizing enzyme. It displays bacillithiol-S-transferase activity with a strong preference for BSH over L-cysteine as its thiol substrate.

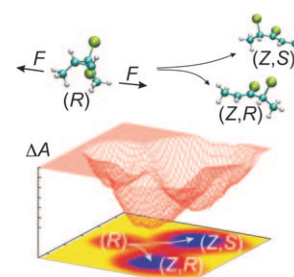
Enforced Ring-Opening

P. Dopieralski,* J. Ribas-Arino,* D. Marx — 7105–7108



Force-Transformed Free-Energy Surfaces and Trajectory-Shooting Simulations Reveal the Mechano-Stereochemistry of Cyclopropane Ring-Opening Reactions

A force to be reckoned with: The force-transformed free-energy surfaces obtained by means of sophisticated ab-initio metadynamics simulations on force-transformed potential-energy surfaces have rationalized the intriguing experimental data on the ring opening of dichlorocyclopropane (see scheme) induced by a mechanical force (F).



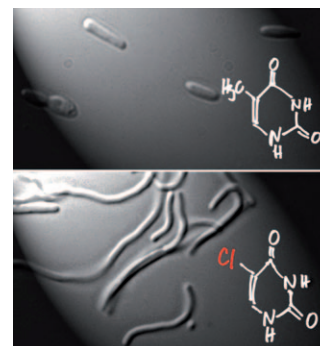
Chemically Modified Organisms

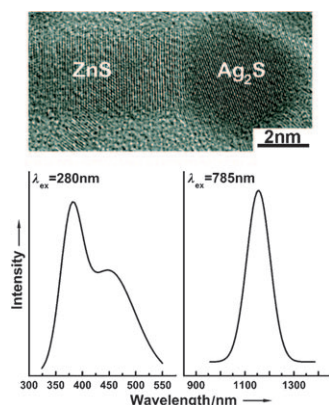
P. Marlière, J. Patrouix, V. Döring, P. Herdewijn, S. Tricot, S. Cruveiller, M. Bouzon, R. Mutzel* — 7109–7114



Chemical Evolution of a Bacterium's Genome

Automated selection was used to evolve an *Escherichia coli* strain unable to synthesize thymine nucleotides into a chemically modified organism whose DNA genome is composed of adenine, cytosine, guanine, and an artificial base, the thymine analogue 5-chlorouracil. Evolving cells were initially observed as irregular filaments and progressively recovered the appearance of short rods typical of wild-type *E. coli* (see picture).



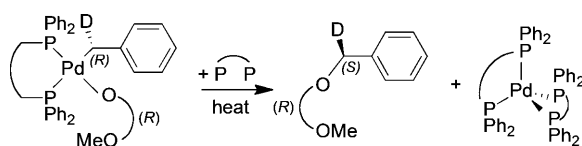


Heterostructured semiconductor matchsticks with Ag_2S heads and ZnS stems (see TEM image) were synthesized by thermal co-decomposition of $\text{Ag}(\text{DDTC})$ and $\text{Zn}(\text{DDTC})_2$ (DDTC = diethyldithiocarbamate). The heteronanostructures show both UV/blue ($\lambda_{\text{ex}} = 280 \text{ nm}$) and near-infrared ($\lambda_{\text{ex}} = 785 \text{ nm}$) photoluminescence.

Heteronanostructures

S. Shen, Y. Zhang, L. Peng, Y. Du, Q. Wang* 7115–7118

Matchstick-Shaped Ag_2S – ZnS Heteronanostructures Preserving both UV/Blue and Near-Infrared Photoluminescence



On the contrary: Isolated benzylpalladium aryloxy complexes undergo $\text{C}(\text{sp}^3)\text{--O}$ bond-forming reductive elimination by a stepwise ionic mechanism (see scheme) distinct from the accepted concerted pathway for reductive elimination of aro-

matic ethers from arylpalladium(II) species. The mechanism is proposed to result from dissociation of the aryloxy ligand followed by nucleophilic attack on the benzylic carbon atom.

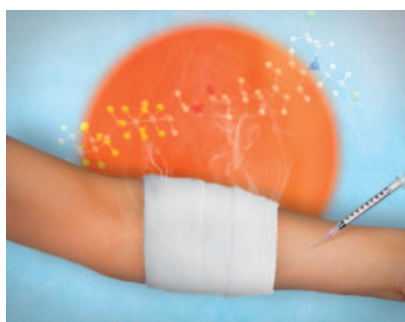
C–O Bond Formation

S. L. Marquard, J. F. Hartwig* 7119–7123

$\text{C}(\text{sp}^3)\text{--O}$ Bond-Forming Reductive Elimination of Ethers from Bisphosphine-Ligated Benzylpalladium(II) Aryloxy Complexes



Putting the heat on: Drugs that are essentially inactive at 37°C and are active under mild hyperthermia can be synthesized by modification of chlorambucil with thermoresponsive groups (see picture; C gray, Cl green, F yellow, H white, N blue, O red). This modification should allow this cytotoxic agent to be used in a more targeted fashion, and consequently, with reduced side-effects.



Antitumor Agents

C. M. Clavel, O. Zava, F. Schmitt, B. Halamoda Kenzaoui, A. A. Nazarov, L. Juillerat-Jeanneret, P. J. Dyson* 7124–7127

Thermoresponsive Chlorambucil Derivatives for Tumour Targeting



Look both ways: Coordination bonding of verdazyl radicals to diamagnetic metal ions dramatically modifies the crystal packing of the electronic spin bearers. The face-to-face positioning of two radicals

leads to a magnetic behavior that is more relevant to a $S=0$ to $S=1$ spin-transition phenomenon than to the usual exchange-interaction view.

Spin Transitions

L. Norel, J.-B. Rota, L.-M. Chamoreau, G. Pilet, V. Robert,* C. Train* 7128–7131

Spin Transition and Exchange Interaction: Janus Visions of Supramolecular Spin Coupling between Face-to-Face Verdazyl Radicals

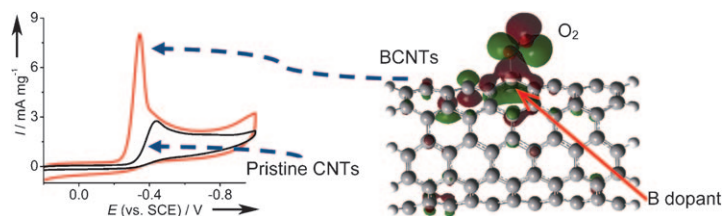


Electrocatalysis

L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen,
X. Wang, Q. Wu, J. Ma, Y. Ma,*
Z. Hu* **7132–7135**



Boron-Doped Carbon Nanotubes as
Metal-Free Electrocatalysts for the Oxygen
Reduction Reaction



A **metal-free** electrocatalyst has been developed by doping carbon nanotubes with electron-deficient boron. The good performance in the oxygen reduction reaction originates from the enhanced O_2

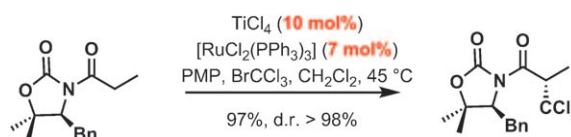
chemisorption and effective utilization of π electrons in the conjugated carbon from the boron doping, as revealed by DFT calculations.

Transition-Metal Catalysis

Z. Gu, A. T. Herrmann,
A. Zakarian* **7136–7139**



Dual Ti–Ru Catalysis in the Direct Radical
Haloalkylation of *N*-Acyl Oxazolidinones



Waste not, want not: A mechanistic study of the ruthenium-catalyzed haloalkylation of titanium enolates led to the development of a process that is catalytic in both metals: titanium and ruthenium (see scheme; Bn = benzyl, PMP = 1,2,2,6,6-

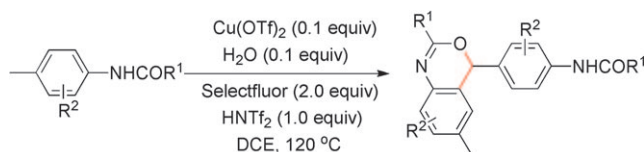
pentamethylpiperidine). Catalytic turn-over was observed in the formation of the titanium enolates from *N*-acyl oxazolidinones, and insight was gained into the inhibitory effect of the amine base.

C–H Activation

T. Xiong, Y. Li, X.-H. Bi,* Y.-H. Lv,
Q. Zhang* **7140–7143**



Copper-Catalyzed Dehydrogenative Cross-
Coupling Reactions of *N*-*para*-Tolylamides
through Successive C–H Activation:
Synthesis of 4*H*-3,1-Benzoxazines



A **novel annulation reaction** of readily available tolylamides was catalyzed by $Cu(OTf)_2$ in the presence of Selectfluor and water through successive intermolecular C–H activated dehydrogenative

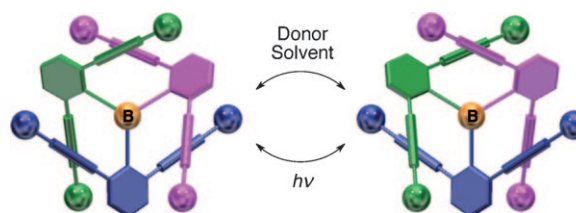
cross-coupling reactions of benzylic methyl $C(sp^3)$ –H and aromatic $C(sp^2)$ –H bonds, and subsequent intramolecular C–O bond formation (see scheme).

Propeller Structures

H. Ito,* T. Abe, K. Saigo* **7144–7147**

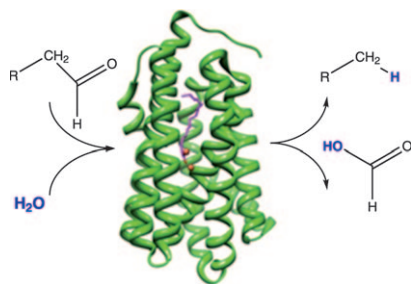


Enantioseparation and Electronic
Properties of a Propeller-Shaped
Triarylborane



Flip out! Bulky substituents induce a high barrier to interconversion of the helically chiral enantiomers of the title triarylborane (see picture) and thus allow the separation of the enantiomers by chiral chromatography. The electronic proper-

ties of the central boron atom play a significant role in the flipping dynamics of the propeller structure, and racemization can be greatly accelerated by UV-light irradiation.

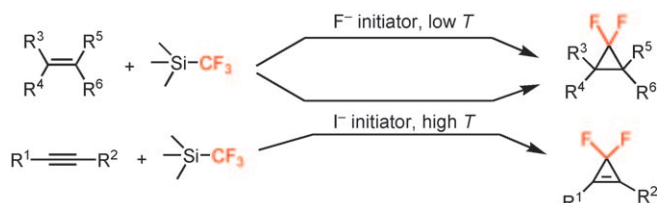


Just add water: Structurally, cyanobacterial aldehyde decarbonylases are members of the non-heme diiron oxygenase family of enzymes. However, the enzyme catalyzes the hydrolysis of aliphatic aldehydes to alkanes and formate (see scheme), in an oxygen-independent reaction. This unusual and chemically difficult reaction most likely involves free radical intermediates.

Enzymology

D. Das, B. E. Eser, J. Han, A. Sciore, E. N. G. Marsh* — 7148–7152

Oxygen-Independent Decarbonylation of Aldehydes by Cyanobacterial Aldehyde Decarbonylase: A New Reaction of Diiron Enzymes



Highly versatile: The Ruppert–Prakash reagent (Me_3SiCF_3) can be an efficient source of difluorocarbene. By varying the nonmetallic initiator that is used (F^- at lower temperatures and I^- at higher

temperatures), a range of structurally diverse alkenes and alkynes can be converted into the corresponding *gem*-difluorinated cyclopropanes and cyclopropenes in good yields (see scheme).

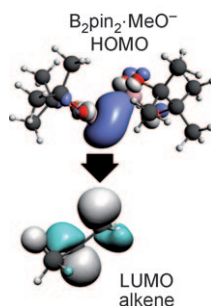
Fluorine Chemistry

F. Wang, T. Luo, J. Hu,* Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash,* G. A. Olah — 7153–7157

Synthesis of *gem*-Difluorinated Cyclopropanes and Cyclopropenes: Trifluoromethyltrimethylsilane as a Difluorocarbene Source



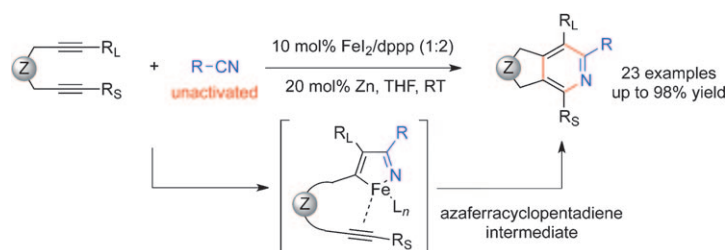
Changing behavior: A nucleophilic sp^2 carbene-type boryl moiety, formed upon interaction of tetraalkoxydiboranes and a Lewis base, can attack non-activated $\text{C}=\text{C}$ bonds. Computational studies identify the interaction as the overlap between the strongly polarized $\text{B}-\text{B}$ σ bond (HOMO) and the antibonding π^* orbital (LUMO) of the $\text{C}=\text{C}$ bond. Conceptually, the normally electrophilic boron becomes nucleophilic and forces the olefin to act as an electrophile.



Boron Chemistry

A. Bonet, C. Pubill-Ulldemolins, C. Bo,* H. Gulyás,* E. Fernández* — 7158–7161

Transition-Metal-Free Diboration Reaction by Activation of Diboron Compounds with Simple Lewis Bases



Joined by iron: The iron catalyst for the formation of pyridines at room temperature (see scheme), which was generated

in situ from an inorganic iron salt and a diphosphine ligand, exhibited high reactivity and regioselectivity.

[2+2+2] Cycloaddition

C. X. Wang, X. C. Li, F. Wu, B. S. Wan* — 7162–7166

A Simple and Highly Efficient Iron Catalyst for a [2+2+2] Cycloaddition to Form Pyridines

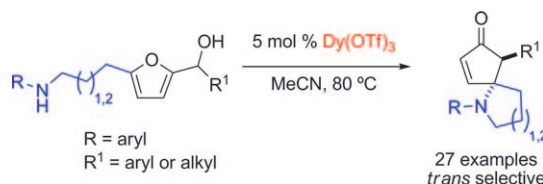


Domino Reactions

L. I. Palmer,
J. Read de Alaniz* 7167–7170



Direct and Highly Diastereoselective Synthesis of Azaspirocycles by a Dysprosium(III) Triflate Catalyzed Aza-Piancatelli Rearrangement



Ring the changes: The first example of an intramolecular aza-Piancatelli rearrangement is reported. Dysprosium(III) trifluoromethanesulfonate efficiently catalyzes the synthesis of functionalized

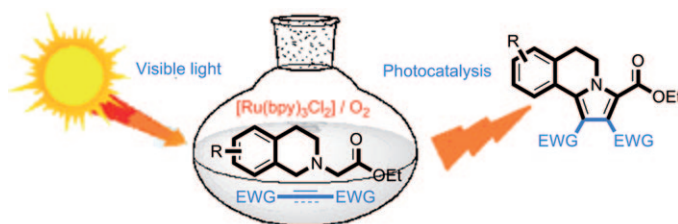
azaspirocycles in a *trans*-selective manner by a 4 π electrocycization of elaborated furylcarbinols (see scheme; Tf = trifluoromethanesulfonyl).

Photochemistry

Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang,
J. Rong, J.-R. Chen,
W.-J. Xiao* 7171–7175



Visible-Light-Induced Oxidation/[3+2] Cycloaddition/Oxidative Aromatization Sequence: A Photocatalytic Strategy to Construct Pyrrolo[2,1-*a*]isoquinolines



A ray of sunshine: The title reaction sequence using ethyl 2-(3,4-dihydroisoquinolin-2(1*H*)-yl)acetates with a series of electron-deficient alkenes and alkynes provides rapid and efficient access to pyrrolo[2,1-*a*]isoquinolines (see scheme;

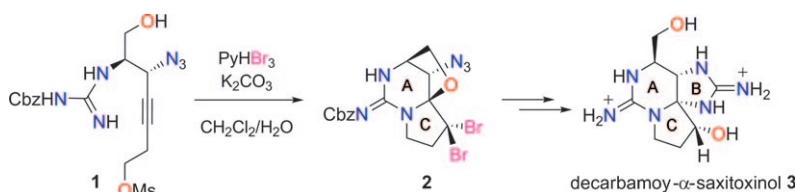
bpy = 2,2'-bipyridine, EWG = electron-withdrawing group). The reaction offers a strategically new protocol for the direct and efficient construction of the core structure of naturally occurring lamellarin alkaloids.

Natural Products

Y. Sawayama, T. Nishikawa* 7176–7178



A Synthetic Route to the Saxitoxin Skeleton: Synthesis of Decarbamoyl α -Saxitoxinol, an Analogue of Saxitoxin Produced by the Cyanobacterium *Lyngbya wollei*



Pick your poison: Salient features of a concise synthetic route for the saxitoxin skeleton are a bromonium-ion-initiated cascade cyclization of readily prepared **1** to give tricyclic intermediate **2** and the transformation of the *gem*-dibromo-

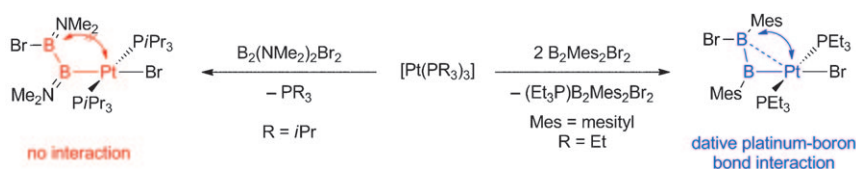
methylene group into an enol acetate unit. This new route enabled the preparation of **3**, a naturally occurring analogue of saxitoxin. Cbz = benzyloxycarbonyl, Ms = methanesulfonyl, Py = pyridine.

Boron Ligands

H. Braunschweig,* A. Damme,
T. Kupfer 7179–7182



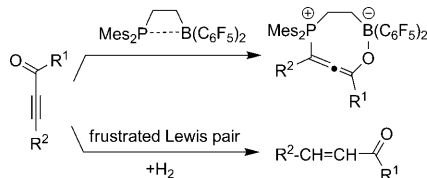
Unexpected Bonding Mode of the Diboran(4)yl Ligand: Combining the Boryl Motif with a Dative Pt–B Interaction



Catching the anchor: Although diboranes(4) commonly react by way of B–B bond activation, reaction of B₂Mes₂Br₂ with [Pt(PEt₃)₃] led to the selective oxidative addition of one B–Br bond; the resulting diboran(4)yl complex shows an unexpected dative Pt–B bonding interac-

tion to the second boron center of the diboran(4)yl ligand. Oxidative addition of one B–Br bond in B₂(NMe₂)₂Br₂ to [Pt-(PEt₃)₃] enabled the isolation of a diboran(4)yl species without any dative Pt–B interaction.

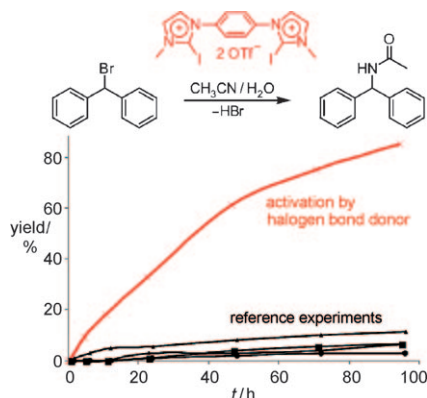
Frustrated, but not frustrating: Frustrated Lewis pairs (FLPs) can undergo selective 1,4-addition reactions with conjugated ynones (see scheme). Upon FLP dihydrogen activation selective hydrogenation of the carbon–carbon triple bond can be achieved, in one case even catalytically.



Frustrated Lewis Pairs

B.-H. Xu, G. Kehr, R. Fröhlich,
 B. Wibbeling, B. Schirmer, S. Grimme,
 G. Erker* _____ 7183–7186

Reaction of Frustrated Lewis Pairs with
 Conjugated Ynones-Selective
 Hydrogenation of the Carbon–Carbon
 Triple Bond



I...Br-iding: Benzhydryl bromide can be activated by novel halogen-bond donors and subsequently undergoes a Ritter-like reaction with acetonitrile (see scheme). Comparative experiments with non-iodinated reference compounds and tests with added acids indicate that halogen bonds are very likely the basis for this effect. The activation seems to be applicable to other substrates as well.

Halogen Bonds

S. M. Walter, F. Kniep, E. Herdtweck,
 S. M. Huber* _____ 7187–7191

Halogen-Bond-Induced Activation of a
 Carbon–Heteroatom Bond



Supporting information is available
 on www.angewandte.org
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 Information on www.angewandte.org
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Corrigendum

Backbone Dynamics of Cyclotide MCoTI-I
Free and Complexed with Trypsin

S. S. Puttamadappa, K. Jagadish,
A. Shekhtman,
J. A. Camarero* ————— 7030–7034

Angew. Chem. Int. Ed. **2010**, 49

DOI 10.1002/anie.201002906

The authors of this Communication have recognized an error in Figure 1 d and Table 1. Because of an error in the scaling of the NOE values for the MCoTI-I/trypsin complex (Figure S2 C and D in the Supporting Information), the reported S^2 values for the MCoTI-I/trypsin complex were not accurate. The correct Figure 1 and Table 1 are shown below.

The text that refers to Figure 1 d and Table 1 (page 7032, left column) is also inaccurate. It should read: “Thus, although loop 1 showed $\langle S^2 \rangle = 0.75 \pm 0.29$, which is slightly lower than the value for the rest of the molecule ($\langle S^2 \rangle = 0.78 \pm 0.23$), Lys⁴ showed a significant lower value of S^2 upon complex formation. Several other residues in loop 2 (Cys⁹), loop 5 (Cys²⁷ and Arg²²), and loop 6 (Val¹) also showed significantly lower values of S^2 upon complex formation (Figures 1 d and 2 c). It is likely that the increase in mobility observed in these loops may help to accommodate the increased flexibility of Lys⁴ in the binding loop (Figure 2 c).

Since our data clearly shows that backbone flexibility of MCoTI-I cyclotide increases in some of the MCoTI-I residues upon binding to trypsin, we decided to estimate the contribution of these motions to the overall Gibbs free energy of binding (ΔG). The energetic benefit of this increase in backbone flexibility can be estimated from the experimental relaxation data, by using the experimentally measured order parameters, S^2 .^[27] The estimated ΔG value was approximately 10 kJ mol^{−1} at 298 K. This value should be compared to the calculated value from the trypsin inhibitory constant of MCoTI-I (the trypsin inhibitory constant of MCoTI-I ($K_i \approx 20$ pM,^[28] $\Delta G \approx -61$ kJ mol^{−1}). The calculated entropic contribution ($-T\Delta S$) at the same temperature was approximately 7 kJ mol^{−1}.”

We have also included modified versions of Figure S2 C and D (showing corrected NOE enhancements and R_{ex} values for the MCoTI/trypsin complex), which are included as Supporting Information. The authors would like to point out that this error does not affect the overall interpretation of the results in the Communication.

[27] A. G. Palmer III, *Annu. Rev. Biophys. Biomol. Struct.* **2001**, 30, 129.

[28] O. Avrutina, H. U. Schmoldt, D. Gabrijelcic-Geiger, D. Le Nguyen, C. P. Sommerhoff, U. Diederichsen, H. Kolmar, *Biol. Chem.* **2005**, 386, 1301.

Table 1: Average order parameters of structural elements in MCoTI-I in the free state and bound to trypsin.

Structural element	Sequence	$\langle S^2 \rangle^{[a]}$	$\langle S^2 \rangle^{[b]}$
		Free MCoTI-I	Trypsin–MCoTI-I
loop 1	3–8	0.81 ± 0.01	0.75 ± 0.29
loop 2	10–14	0.81 ± 0.01	0.93 ± 0.04
loop 3	16–18	0.84 ± 0.02	$0.82^{[c]}$
loop 4	20	$0.88^{[c]}$	$0.98^{[c]}$
loop 5	22–26	0.92 ± 0.02	0.80 ± 0.24
loop 6	28–34	0.76 ± 0.05	0.71 ± 0.34
cystine knot	2,9,15,19,21,27	0.84 ± 0.02	0.62 ± 0.33

[a] S^2 values for residues 5 and 23 from free MCoTI-I are not included in the average because the relaxation data could not be fitted to a monoexponential function. [b] S^2 values for residues 2, 5, 8, 18, 19, 23, 29, 31, 32, and 33 from trypsin-bound MCoTI-I are not included in the average because of the lack of signal intensity or because the relaxation data could not be fitted to a monoexponential function. [c] $\langle S^2 \rangle$ contains the S^2 value for a single residue.

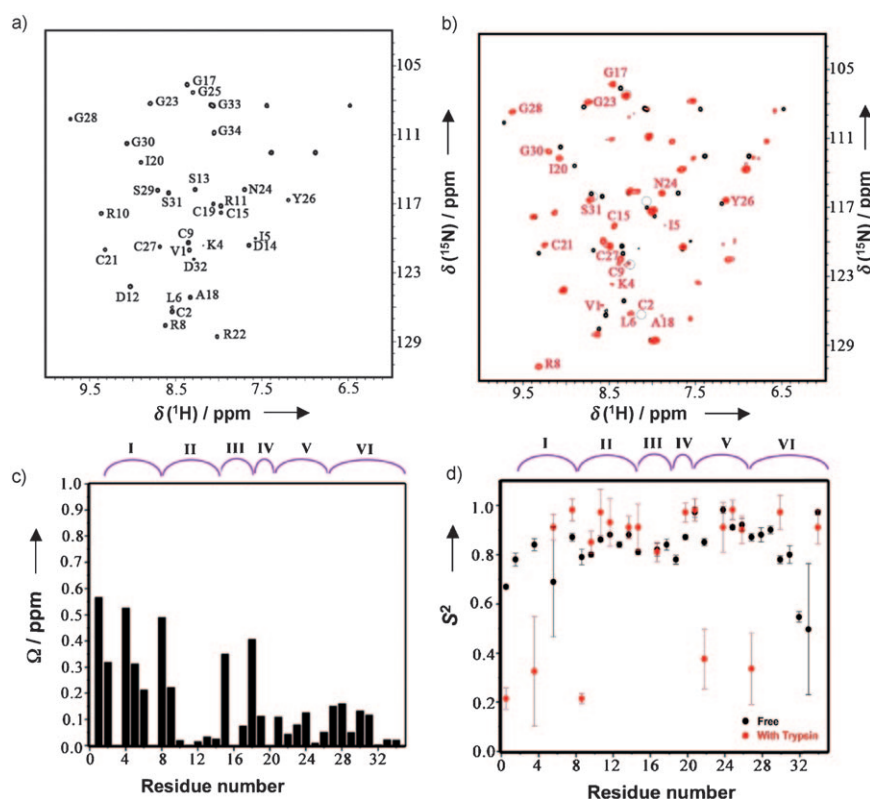


Figure 1. NMR analysis of the backbone dynamic of free and trypsin bound MCoTI-I. a) $\{^{15}\text{N}, ^1\text{H}\}$ NMR heteronuclear single quantum correlation (HSQC) spectrum of free MCoTI-I. Chemical shift assignments of the backbone amides are indicated. b) Overlay of the $\{^{15}\text{N}, ^1\text{H}\}$ HSQC spectra of free (black) and trypsin bound MCoTI-I (red). Residues with large average amide chemical shift differences between two different states (>0.3 ppm) are indicated. Peaks that are broadened in trypsin bound MCoTI-I are indicated by grey circles. c) Average amide chemical shift difference for all the assigned residues in free and trypsin bound MCoTI-I. Chemical shift difference was calculated as: $\Delta\Omega = [(\Delta\Omega_{\text{NH}}^2 + 0.04\Delta\Omega_{\text{N}}^2)/2]^{1/2}$, where $\Delta\Omega_{\text{NH}}$ and $\Delta\Omega_{\text{N}}$ are the changes in the amide proton and nitrogen chemical shifts (ppm), respectively. d) Order parameter, S^2 , for the free (black) and the trypsin bound MCoTI-I (red). The S^2 value is a measure of backbone flexibility and represents the degree of angular restriction of the N-H vector in the molecular frame. The MCoTI-I loops are shown on top of panels (c) and (d). Small unassigned peaks in the spectra of both free and trypsin-bound of MCoTI-I are from a minor conformation of the protein, and result from a known isomerization of the backbone at an Asp-Gly sequence in loop 6 of MCoTI-I.