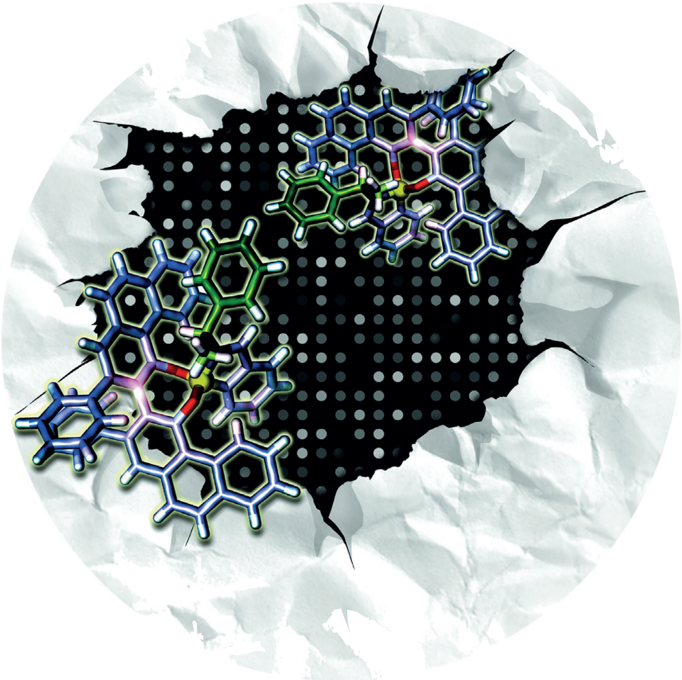
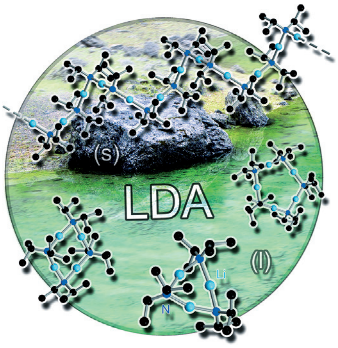
Orthogonal dynamic covalent self-assembly …

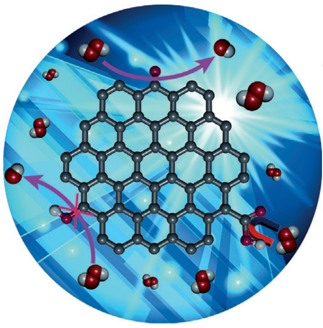


… has been used for high-throughput determination of the enantiomeric purity of chiral amines. The method, described P. Anzenbacher and co-workers in their Communication on page 7130 ff. is based on the self-assembly of 2-formylphenylboronic acid with a chiral diol auxiliary and a chiral amine of unknown chirality to produce two diastereomeric iminoboronates that differ in their fluorescence, as measured using a microplate reader. The approach allows accurate determination of the ee value of chiral amines with errors below 2%.

Lithium Amides

In their Communication on page 6994 ff., D. Stalke and co-workers describe DOSY NMR experiments applied to study the state of aggregation of lithium diisopropyl amide in solution.



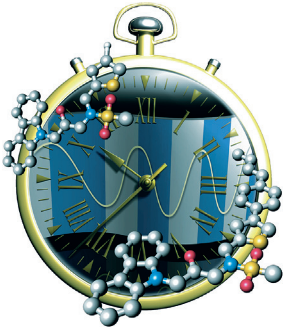


Graphene Quantum Dots

In their Communication on page 7176 ff., X. Qu et al. describe selective deactivation of the oxygen-containing groups on graphene quantum dots (GQDs) to obtain various GQD derivatives and compare their catalytic activities.

Structure–Activity Relationships

In their Communication on page 7193 ff., S. Irle, T. Yoshimura, K. Itami et al. describe the synthesis of a library of KL001 derivatives, a period-lengthening modulator of the mammalian circadian clock, by C–H activation chemistry.



How to contact us:

Editorial Office:
E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

Reprints, E-Prints, Posters, Calendars:
Carmen Leitner
E-mail: chem-reprints@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-327

Copyright Permission:
Bettina Loycke
E-mail: rights-and-licences@wiley-vch.de
Fax: (+49) 62 01–606-332
Telephone: (+49) 62 01–606-280

Online Open:
Margitta Schmitt, Carmen Leitner
E-mail: angewandte@wiley-vch.de
Fax: (+49) 62 01–606-331
Telephone: (+49) 62 01–606-315

Subscriptions:
www.wileycustomerhelp.com
Fax: (+49) 62 01–606-184
Telephone: 0800 1800536 (Germany only)
+44(0) 1865476721 (all other countries)

Advertising:
Marion Schulz
E-mail: mschulz@wiley-vch.de
jspiess@wiley-vch.de
Fax: (+49) 62 01–606-550
Telephone: (+49) 62 01–606-565

Courier Services:
Boschstrasse 12, 69469 Weinheim

Regular Mail:
Postfach 101161, 69451 Weinheim

Angewandte Chemie International Edition is a journal of the Gesellschaft Deutscher Chemiker (GDCh), the largest chemistry-related scientific society in continental Europe. Information on the various activities and services of the GDCh, for example, cheaper subscription to *Angewandte Chemie International Edition*, as well as applications for membership can be found at **www.gdch.de** or can be requested from GDCh, Postfach 900440, D-60444 Frankfurt am Main, Germany.

GDCh
Gesellschaft
Deutscher Chemiker

Editorial

"... There is an unprecedented global consensus that an energetic transition, not to say a revolution, is urgently required. The transition can be defined as the process by which all fossil fuels (and nuclear energy) are replaced by renewable energies. How can we achieve this transition in the shortest time? ..."
Read more in the Editorial by Marc Fontecave.

Service

Author Profile

"My biggest inspiration is my research group and my colleagues.
My favorite principle is the Pauli exclusion principle ..."
This and more about Josep M. Poblet can be found on page 6968.

News


T. Gaich


A. Rentmeister


C. Papp


J. Streuff

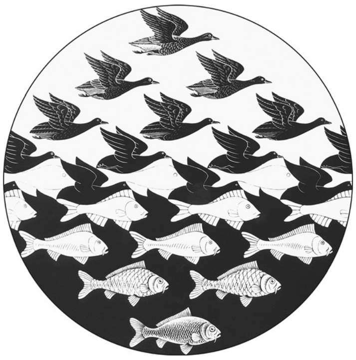

S. Balasubramanian


R. Seshadri

Books

Reviews

Polymorphism

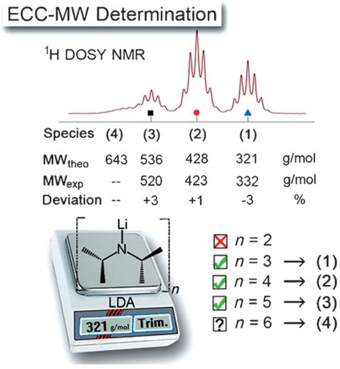


Now you see it, now you don’t: Some of the most captivating accounts of organic solid-state chemistry in recent years concern disappearing polymorphs. This Review features notorious examples and underlines the misconceptions in understanding this phenomenon—both among scientists and in the court of law.

Communications

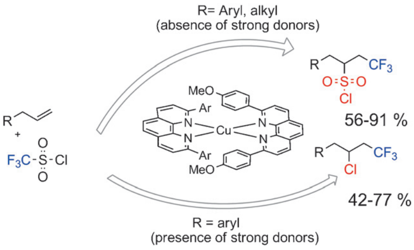
Lithium Amides in Solution

Frontispiece



An important reagent: Lithium diisopropyl amide plays a key role in organic synthesis, serving as a base par excellence for a broad range of deprotonation reactions. However, its state of aggregation in solution in the absence of donor bases was unclear. This problem has been solved by application of a new DOSY NMR experiment.

Photoredox Catalysis



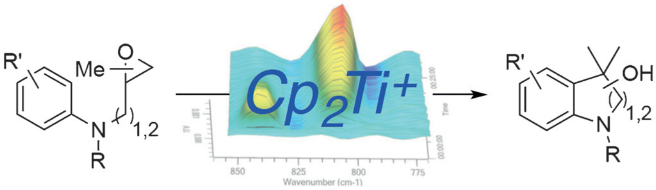
Double role: The trifluoromethylchlorosulfonylation of unactivated alkenes was developed using $[Cu(dap)_2]Cl$ as catalyst (dap = 2,9-bis(*para*-anisyl)-1,10-phenanthroline). $[Cu(dap)_2]Cl$ plays a dual role; acting as an electron transfer reagent as well as coordinating the reactants in the bond forming processes.

For the USA and Canada:
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. US mailing agent: SPP, PO Box 437, Emigsville, PA 17318. Periodicals postage paid at Emigsville, PA. US POSTMASTER: send address changes to *Angewandte Chemie*, John Wiley & Sons Inc., C/O The Sheridan Press, PO Box 465, Hanover, PA 17331. Annual subscription price for institutions: US$ 11.738/10.206 (valid for print and electronic / print or electronic delivery); for 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.

Radical Reactions

A. Gansäuer,* S. Hildebrandt,
A. Michelmann, T. Dahmen,
D. von Laufenberg, C. Kube, G. D. Fianu,
R. A. Flowers, II* ______ **7003 – 7006**

Cationic Titanocene(III) Complexes for Catalysis in Single-Electron Steps

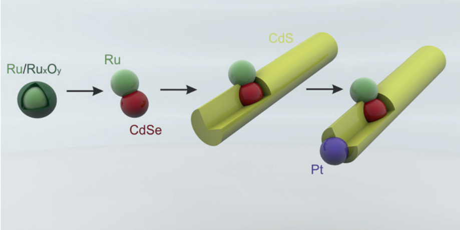


Much simpler surrogate: $[Cp_2Ti]^+$ is a stable and active catalyst for radical arylation proceeding through catalysis in single-electron steps. Its use renders ring substitution for redox tuning obsolete.

Nanoparticles

L. Amirav, F. Oba, S. Aloni,
A. P. Alivisatos* ______ **7007 – 7011**

Modular Synthesis of a Dual Metal–Dual Semiconductor Nano-Heterostructure

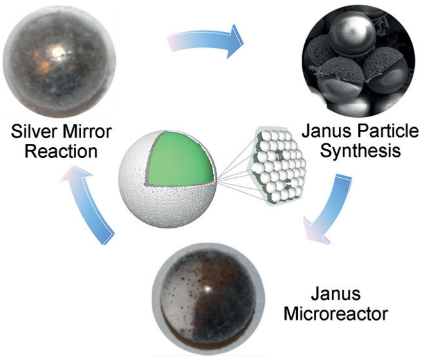


Double duo: Reported is the modular synthesis of a dual metal–dual semiconductor heterostructure with control over the dimensions and placement of its individual components. This multicomponent nanosystem, Ru-CdSe@CdS-Pt, was designed to achieve charge carrier separation and directional transfer across different interfaces toward two separate electrodes.

Microreactors

Y. F. Sheng, G. Q. Sun, J. Wu, G. H. Ma,*
T. Ngai* ______ **7012 – 7017**

Silica-Based Liquid Marbles as Microreactors for the Silver Mirror Reaction



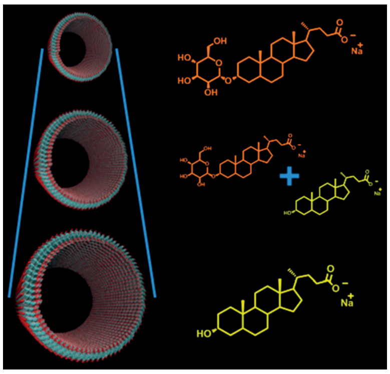
Silver marbles: The silver mirror reaction can take place at liquid marble shells, which are composed of silica particles packing at the air–liquid interface. The appearance of mirrors could be easily modified by the concentration, feeding order, and particle properties. The particles could allow the modification and fabrication of Janus particles from superhydrophobic particles that is not attainable from traditional Pickering emulsion methods.

Nanochannels

M. Gubitosi, L. Travaglini,
M. C. di Gregorio, N. V. Pavel,
J. Vázquez Tato, S. Sennato, U. Olsson,
K. Schillén, L. Galantini* ______ **7018 – 7021**

Tailoring Supramolecular Nanotubes by Bile Salt Based Surfactant Mixtures

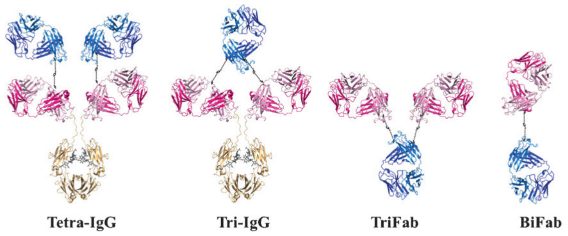
The perfect fit: The tailoring of self-assembled nanotube cross-sections is described for two-component mixtures of a bile acid and its derivative. By controlling the stoichiometry, diameters were found to vary by up to 50%. Starting from pure tubules with a parallel arrangement of the monomer, a progressive inclusion of the second component in an antiparallel orientation is proposed to explain the variation in size.



Cancer Immunotherapy

Y. Cao, J. Y. Axup, J. S. Y. Ma, R. E. Wang, S. Choi, V. Tardif, R. K. V. Lim, H. M. Pugh, B. R. Lawson, G. Welzel, S. A. Kazane, Y. Sun, F. Tian, S. Srinagesh, T. Javahishvili, P. G. Schultz,*
C. H. Kim* ________ **7022 – 7027**

Multiformat T-Cell-Engaging Bispecific Antibodies Targeting Human Breast Cancers



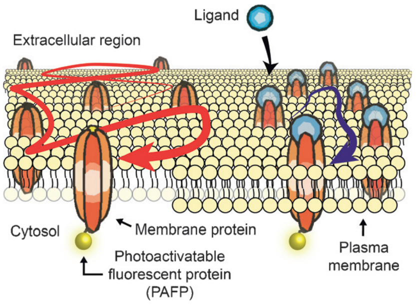
Bispecific antibodies are highly effective for targeting breast cancer cells with antigens of low abundance. It is suggested that the monovalent BiFab in the absence of an Fc domain may be the best bispecific antibody format to trigger antigen-dependent T-cell activation and target tumor eradication for low or heterogeneous Her2-expressing cancers.

Protein Diffusion

D.-H. Kim, K. Zhou, D.-K. Kim, S. Park, J. Noh, Y. Kwon, D. Kim, N. W. Song, J.-B. Lee, P.-G. Suh, N. K. Lee,*
S. H. Ryu* ________ **7028 – 7032**

Analysis of Interactions between the Epidermal Growth Factor Receptor and Soluble Ligands on the Basis of Single-Molecule Diffusivity in the Membrane of Living Cells

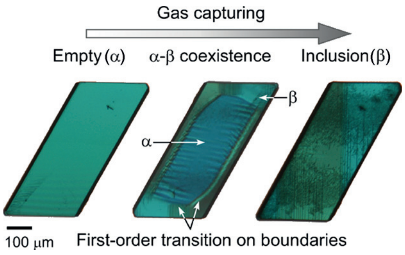
At home in a crowd: The interactions between membrane and soluble proteins in a crowded living-cell membrane (see picture) were analyzed on the basis of single-molecule diffusivity measured by super-resolution microscopy. With this method, biochemical aspects of ligand–receptor interactions that only appear in the intact membrane of living cells can be investigated.



Inclusion Compounds

S. Takamizawa* ________ **7033 – 7036**

Dynamic Gas-Inclusion in a Single Crystal

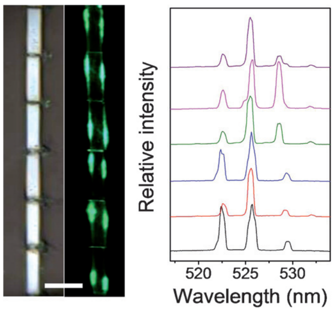


The dynamic inclusion of gas into a single crystal was investigated in situ by single-crystal X-ray diffraction, gas adsorption measurements, and optical microscopy. It was shown that gas inclusion is driven by the spatiotemporal distribution of guest, microscopic structure, and macroscopic phase.

Nanotechnology

Q. Liao, X. Jin, H. H. Zhang, Z. Z. Xu, J. N. Yao, H. B. Fu* ________ **7037 – 7041**

An Organic Microlaser Array Based on a Lateral Microcavity of a Single J-aggregation Microbelt

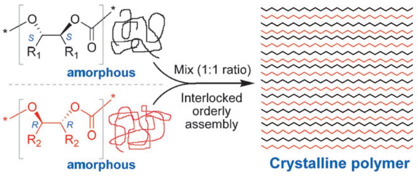


Array of light: A low-threshold lateral-cavity organic microlaser based on a single-crystalline organic microbelt has been developed. By cutting a single microbelt into six pieces by a top-down two-photon processing technique, a compact and uniform 1 × 6 microlaser array with excellent reproducibility and addressable high precision was also successfully fabricated, which could be used in future miniaturized coherent light sources and nanophotonics.

Polymer Assembly

Y. Liu, M. Wang, W.-M. Ren, Y.-C. Xu, X.-B. Lu* ———— **7042 – 7046**

Crystalline Hetero-Stereocomplexed Polycarbonates Produced from Amorphous Opposite Enantiomers Having Different Chemical Structures

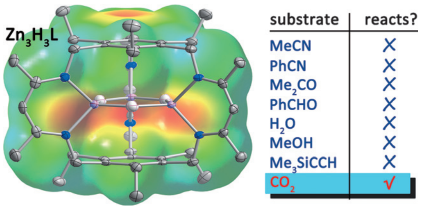


Mixed enantiomers: A unique strategy for polymer assembly was demonstrated through the formation of crystalline hetero-stereocomplexed polymeric materials by the cocrystallization of amorphous isotactic polycarbonates with opposite configurations and different chemical structures. This study is expected to open up a new way to prepare various semi-crystalline materials with a wide variety of physical properties and degradability.

Carbon Dioxide Reduction

D. M. Ermert, I. Ghiviriga, V. J. Catalano, J. Shearer, L. J. Murray* ———— **7047 – 7050**

An Air- and Water-Tolerant Zinc Hydride Cluster That Reacts Selectively With CO_2

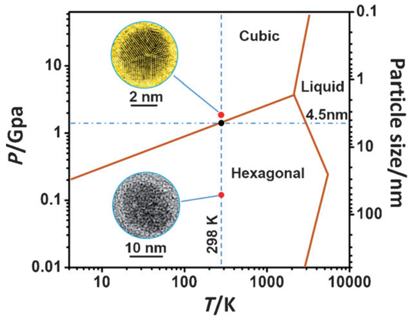


Playing favorites: The reaction of $[Zn_3Cl_3L]$, in which L^{3-} is a tris(β-diketiminate) cyclophane, with $K(sBu)_3BH$ afforded $[Zn_3(\mu\text{-}H)_3L]$ (see picture). This air-stable complex was unreactive towards water, methanol, and other substrates at room temperature but reduced CO_2 to generate $[Zn_3(\mu\text{-}H)_2(\mu\text{-}1,1\text{-}O_2CH)]$. In contrast, $[Zn_3(OH)_3L]$ was found to be unreactive towards CO_2 at 90 °C.

Boron Nitride

H. Liu, P. Jin, Y.-M. Xue, C. Dong, X. Li, C.-C. Tang,* X.-W. Du* ———— **7051 – 7054**

Photochemical Synthesis of Ultrafine Cubic Boron Nitride Nanoparticles under Ambient Conditions

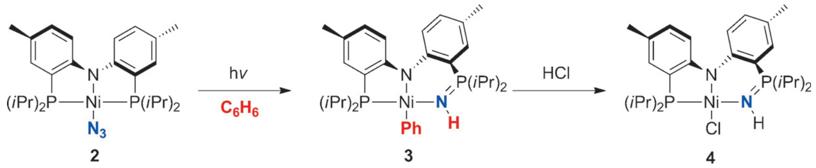


Small phases: A photochemical method is developed to synthesize unprecedentedly small and monodisperse cubic boron nitride (c-BN NPs) nanoparticles of 3.5 nm. Under ambient conditions nanosecond pulsed laser irradiation decomposes ammonia borane (AB) molecules in dioxane solution to give ultrafine c-BN NPs as well as H_2 gas. This approach showed great potential for controllable hydrogen generation.

C–H Activation

V. Vreeken, M. A. Siegler, B. de Bruin, J. N. H. Reek, M. Lutz, J. I. van der Vlugt* ———— **7055 – 7059**

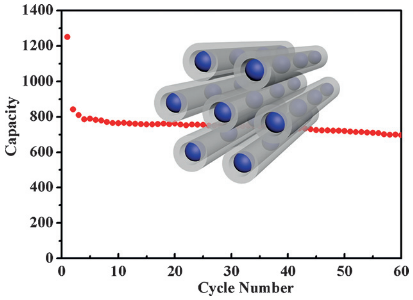
C–H Activation of Benzene by a Photoactivated Ni^{II}(azide): Formation of a Transient Nickel Nitrido Complex



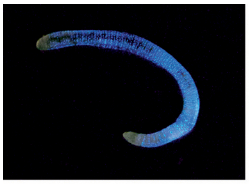
Triple N: Photolysis of nickel-azido complex $[Ni(N_3)(PNP)]$ (**2**) in benzene results in a transient Ni^{IV} nitrido species that bears significant nitridyl character, as supported by DFT calculations. Subsequent insertion of the nitrogen into a Ni–P bond, followed by C_{sp^2}–H activation of solvent yields diamagnetic $[Ni(Ph)(PN^PN^H)]$ (**3**) featuring a parent iminophosphorane ligand. Reaction with HCl provides well-defined $[Ni(Cl)(PN^PN^H)]$ (**4**).

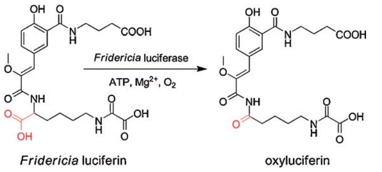
Lithium-Ion Batteries

Trapped in carbon nanotubes: Size-controllable Co_3O_4 nanoparticles exclusively confined in the intratubular pores of the carbon nanotube arrays (CMK-5) have been prepared by a nanocasting method with a Co_3O_4 loading amount of up to 70 wt %. The resultant nanocomposites show excellent performance when used as anode materials for lithium ion batteries.



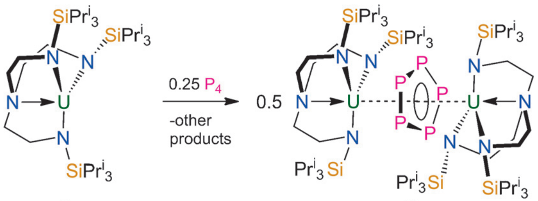
Bioluminescence





Let there be light: The oxyluciferin from the bioluminescent worm *Fridericia heliota* was isolated and its structure elucidated. The results provide insight into a novel bioluminescence mechanism. Oxidative decarboxylation of a lysine fragment of the luciferin supplies energy for light generation, while a fluorescent CompX moiety remains intact and serves as the light emitter.

Cyclo-P_5 Complexes



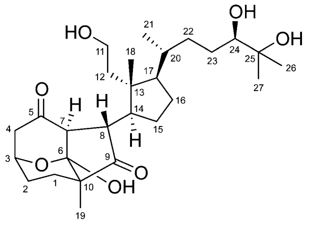
1

2

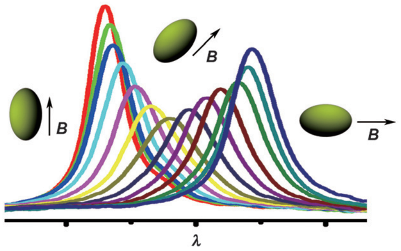
Not your everyday sandwich: Reaction of **1** with P_4 affords the unprecedented actinide inverted-sandwich cyclo-P_5 complex **2**. Theoretical calculations suggest the principal bonding in the $U(P_5)U$ unit is two polarized δ-bonds, and combined characterization data suggest charge transfer from uranium to the cyclo-P_5 unit to give a cyclo-P_5 charge state that approximates to a dianion.

Natural Products

Splitting "hares": A new cytotoxic 9,11-secosteroid with an unprecedented tricyclic γ-diketone structure, aplysiasecosterol A (**1**), was isolated from the sea hare *Aplysia kurodai*. A biosynthetic pathway for **1** from a known cholesterol was proposed and includes two α-ketol rearrangements and an intramolecular acetalization.



Aplysiasecosterol A (**1**)



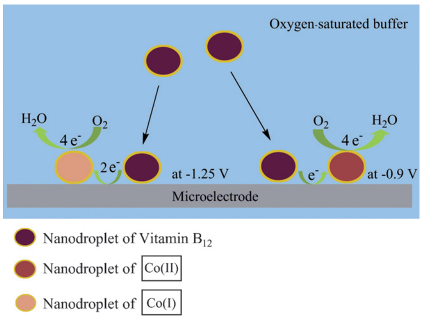
The shape of color to come: Magnetic nanoellipsoidal particles have been assembled into a class of uniquely responsive photonic structures whose photonic properties can be dynamically tuned by controlling the direction of magnetic fields.

Photonic Materials

M. Wang, L. He, W. Xu, X. Wang, Y. Yin* **7077 – 7081**

Magnetic Assembly and Field-Tuning of Ellipsoidal-Nanoparticle-Based Colloidal Photonic Crystals

---



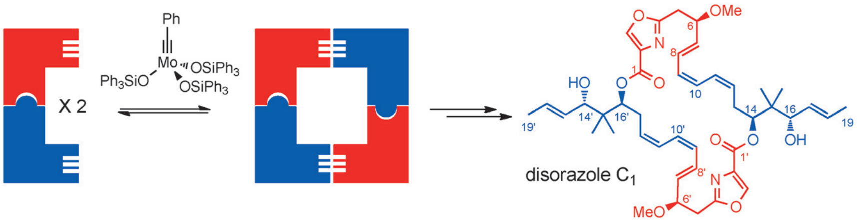
Single vitamin B_{12} (VB_{12}) nanodroplets are used to mediate the reduction of oxygen in neutral buffer (see picture). The mechanism of oxygen reduction mediated by single VB_{12} droplets is revealed as via both Co^{II} and Co^{I} reduced from Co^{III} in VB_{12} through one- or two-electron transfer followed by the four-electron reduction of oxygen.

Electrochemistry

W. Cheng, R. G. Compton* **7082 – 7085**

Oxygen Reduction Mediated by Single Nanodroplets Containing Attomoles of Vitamin B_{12}: Electrocatalytic Nano-Impacts Method

---



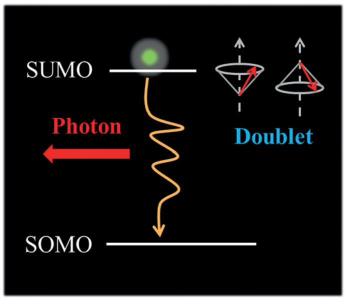
Heads or tails? The self-assembly of disorazole C_1, a cytotoxic bis(lactone) natural product, has been achieved through alkyne cross-metathesis and ring-closing alkyne metathesis. The coupling favored the production of the desired head-to-tail dimer over its head-to-head counterpart with a ratio of 5:1.

Alkyne Metathesis

K. J. Ralston, H. C. Ramstadius, R. C. Brewster, H. S. Niblock, A. N. Hulme* **7086 – 7090**

Self-Assembly of Disorazole C_1 through a One-Pot Alkyne Metathesis Homodimerization Strategy

---



Organic electronics: An organic open-shell molecule (TTM-1Cz) was used as an emitter in organic light-emitting diodes (OLEDs). There is only one electron at the highest occupied molecular orbital (see picture), leading the excited state of TTM-1Cz to be a doublet. The key issue of how to harvest the triplet energy in an OLED is thus circumvented because the radiative decay of the doublet is totally spin-allowed.

Light-Emitting Diodes

Q. Peng, A. Obolda, M. Zhang, F. Li* **7091 – 7095**

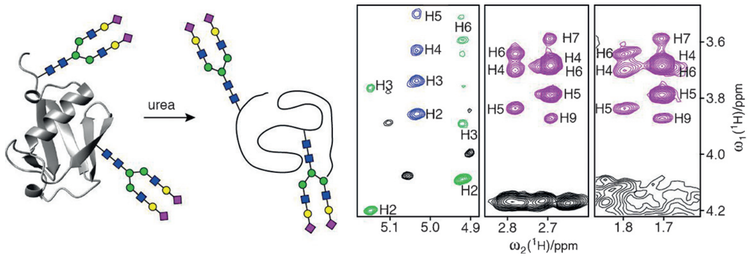
Organic Light-Emitting Diodes Using a Neutral π Radical as Emitter: The Emission from a Doublet

Inside Cover

Protein Modifications

M. Schubert,* M. J. Walczak,* M. Aebi, G. Wider ——— **7096 – 7100**

Posttranslational Modifications of Intact Proteins Detected by NMR Spectroscopy: Application to Glycosylation

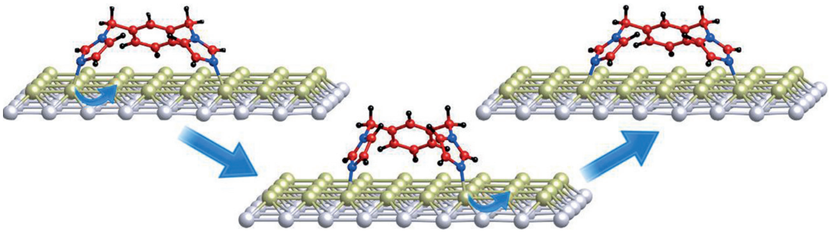


No label required: Characterization of the structure and function of posttranslational modifications (PTMs) can be very challenging especially for glycans. A direct and simple NMR spectroscopic method for the characterization PTMs requires no isotope labeling, can be applied to proteins of any size, and provides information not available by more complicated existing techniques.

Molecular Machines

S. Haq, B. Wit, H. Sang, A. Floris, Y. Wang, J. Wang, L. Pérez-García, L. Kantorovitch,* D. B. Amabilino,* R. Raval* **7101 – 7105**

A Small Molecule Walks Along a Surface Between Porphyrin Fences That Are Assembled In Situ

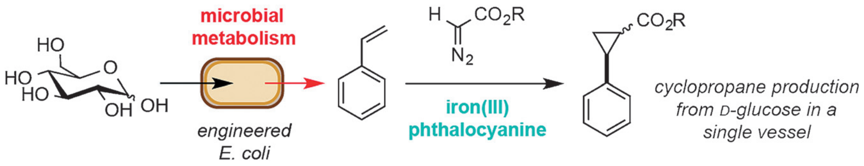


Walk the line: A bis(imidazolyl) compound "walks" along an anisotropic monocrystalline copper surface in one preferred direction with remarkably high selectivity. The motion of the walker can be effectively confined by on-surface synthesis of porphyrin oligomer fences oriented orthogonal to the walking direction, which act as insurmountable barriers.

Synthetic Biology

S. Wallace, E. P. Balskus* — **7106 – 7109**

Interfacing Microbial Styrene Production with a Biocompatible Cyclopropanation Reaction

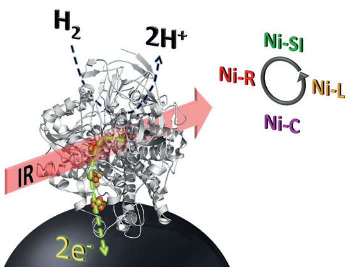


The beauty of bugs: Iron(III) phthalocyanine was identified as a highly active and biocompatible carbene-transfer catalyst capable of cyclopropanating styrene generated by the metabolism of engineered *Escherichia coli*. The biocompatible reaction is nontoxic to the producing organism, thus enabling the near-quantitative production of various phenyl cyclopropanes directly from D-glucose in single-vessel fermentations.

Spectroelectrochemistry

R. Hidalgo, P. A. Ash, A. J. Healy, K. A. Vincent* ——— **7110 – 7113**

Infrared Spectroscopy During Electrocatalytic Turnover Reveals the Ni-L Active Site State During H_2 Oxidation by a NiFe Hydrogenase

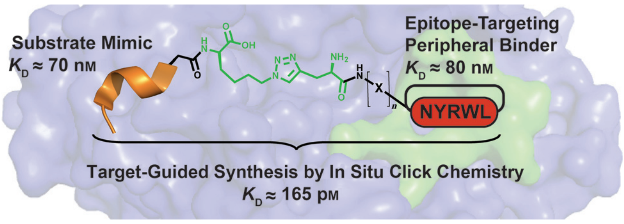


Protein film IR electrochemistry: A combination of precise electrochemical control with infrared spectral acquisition provides fresh insight into catalytic states of the NiFe hydrogenase active site.

Target-Guided Synthesis

B. Farrow, M. Wong, J. Malette, B. Lai,
K. M. Deyle, S. Das, A. Nag, H. D. Agnew,
J. R. Heath* ______ 7114 – 7119

Epitope Targeting of Tertiary Protein Structure Enables Target-Guided Synthesis of a Potent In-Cell Inhibitor of Botulinum Neurotoxin

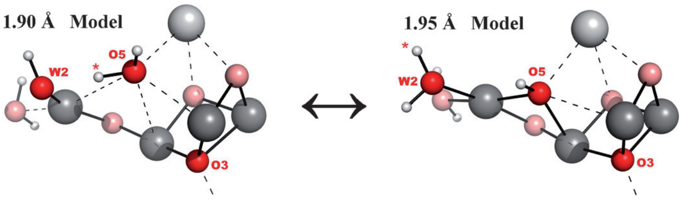


Let the toxins pick their poison: The target-guided synthesis of a divalent peptide ligand that is a potent inhibitor of botulinum neurotoxin both in vitro and in cells was achieved. An active-site-binding substrate mimic was combined with epitope targeting of a nearby site in the folded structure of the toxin to obtain the peripheral binder.

Photosystem II

S. Petrie, R. J. Pace,*
R. Stranger* ______ 7120 – 7124

Resolving the Differences Between the 1.9 Å and 1.95 Å Crystal Structures of Photosystem II: A Single Proton Relocation Defines Two Tautomeric Forms of the Water-Oxidizing Complex

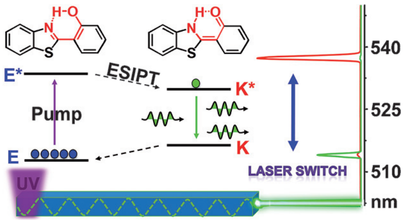


Double act: Assuming the 'low' Mn oxidation state paradigm, DFT calculations show that the structures of the water-oxidizing complex (WOC) of photosystem II in the recent XFEL study at 1.95 Å and the earlier XRD study at 1.9 Å are simply tautomers that are related by a single proton relocation involving W2, O5, and the His337 residue.

Organic Microlaser Switches

W. Zhang, Y. Yan, J. M. Gu, J. N. Yao,
Y. S. Zhao* ______ 7125 – 7129

Low-Threshold Wavelength-Switchable Organic Nanowire Lasers Based on Excited-State Intramolecular Proton Transfer



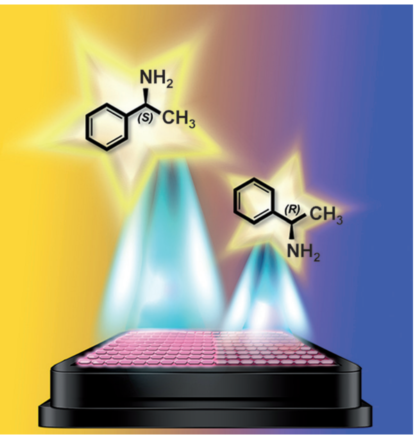
Low-threshold single-mode lasing was achieved via excited-state intramolecular proton transfer (ESIPT)-assisted population inversion in crystal organic nanowires fabricated by the self-assembly of proton-transfer dye molecules. The lasing wavelength can be reversibly switched based on the photoinduced conformation conversion of the excited keto form in the ESIPT process.

Analytical Methods

E. G. Shcherbakova, T. Minami, V. Brega,
T. D. James,
P. Anzenbacher, Jr.* ______ 7130 – 7133

Determination of Enantiomeric Excess in Amine Derivatives with Molecular Self-Assemblies

Front Cover

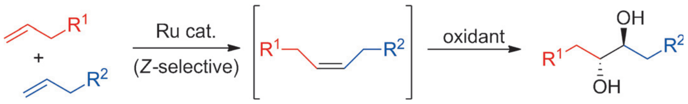


The dynamic covalent self-assembly of chiral amines with chiral fluorescent diols and 2-formylphenylboronic acid produces fluorescent diastereomeric iminoboronates that differ in their fluorescence intensity and polarization. This fluorescence-based assay for the rapid determination of the enantiomeric excess of amine derivatives requires only simple laboratory instrumentation and is amenable to high-throughput screening.

Dihydroxylation

P. K. Dornan, Z. K. Wickens, R. H. Grubbs* ———— 7134–7138

Tandem *Z*-Selective Cross-Metathesis/Dihydroxylation: Synthesis of *anti*-1,2-Diols

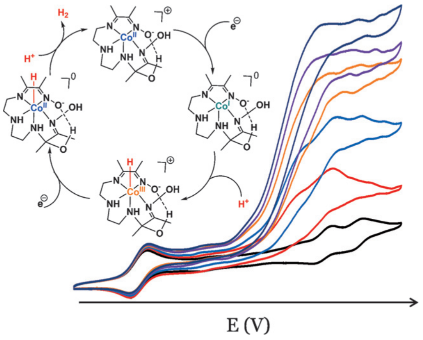


Two steps with one cat.: 1,2-*anti*-Diols are accessible through a tandem *Z*-selective cross-metathesis/dihydroxylation using an assisted tandem catalysis protocol. Both steps are catalyzed by the Ru complex, and the stereocontrol of the cross-metathesis is translated through high stereospecificity in the dihydroxylation step to diastereoselectivity for the 1,2-*anti*-diol.

Water Reduction with Cobalt Oximes

D. Basu, S. Mazumder, X. Shi, R. J. Staples, H. B. Schlegel,* C. N. Verani* ———— 7139–7143

Distinct Proton and Water Reduction Behavior with a Cobalt(III) Electrocatalyst Based on Pentadentate Oximes

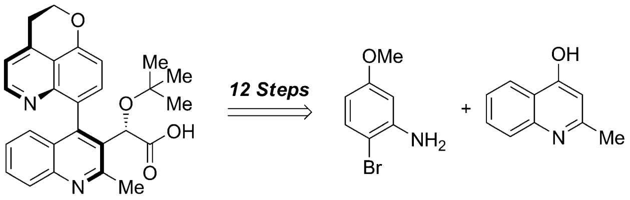


A pentadentate oxime is used for the construction of a new cobalt catalyst, which drives the preferential coordination favored by Co^{I} catalysts in proton/water reduction. This species evolves H_2 in the presence of weak acids in MeCN. Superior catalysis is also observed in water, however, the molecular catalyst yields Co-based nanoparticles.

Asymmetric Synthesis

K. R. Fandrick,* W. Li, Y. Zhang, W. Tang, J. Gao, S. Rodriguez, N. D. Patel, D. C. Reeves, J.-P. Wu, S. Sanyal, N. Gonnella, B. Qu, N. Haddad, J. C. Lorenz, K. Sidhu, J. Wang, S. Ma, N. Grinberg, H. Lee, Y. Tsantrizos, M.-A. Poupart, C. A. Busacca, N. K. Yee, B. Z. Lu, C. H. Senanayake – 7144–7148

Concise and Practical Asymmetric Synthesis of a Challenging Atropisomeric HIV Integrase Inhibitor

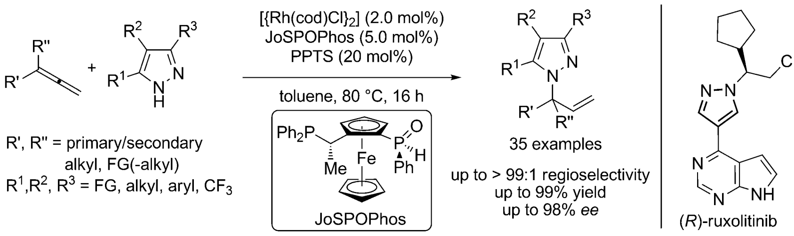


Atropselective: An efficient asymmetric synthesis of an atropisomeric HIV inhibitor has been accomplished. The combination of a copper-catalyzed acylation with the implementation of BI-DIME ligands for a ligand-controlled Suzuki cross-coupling and an unprecedented bis(trifluoromethane)sulfonamide-catalyzed *tert*-butylation renders the synthesis of this complex molecule robust, safe, and economical.

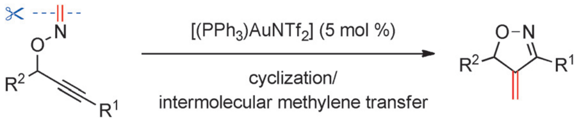
Synthetic Methods

A. M. Haydl, K. Xu, B. Breit* 7149–7153

Regio- and Enantioselective Synthesis of N-Substituted Pyrazoles by Rhodium-Catalyzed Asymmetric Addition to Allenes



Add on: The rhodium-catalyzed regio- and enantioselective addition of terminal allenes and functionalized pyrazoles permits the atom-economic synthesis of valuable branched allylic pyrazoles. The synthesis of the small-molecule pharmaceutical (*R*)-ruxolitinib highlights the potential of this method. FG = functional group.

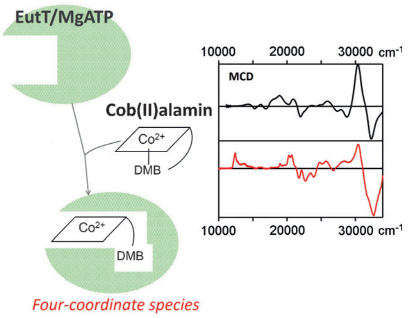


Au is not like Cu: Skeletal rearrangement of *O*-propargylic formaldoximes, in the presence of gold catalysts effectively afforded 4-methylene-2-isoxazolines by intermolecular methylene transfer. The cascade reaction in the presence of gold proceeds by cyclization/methylene transfer and a subsequent ene reaction, whereas with a copper catalyst it proceeds by a 2,3-rearrangement.

Synthetic Methods

I. Nakamura,* S. Gima, Y. Kudo,
M. Terada ———— 7154 – 7157

Skeletal Rearrangement of *O*-Propargylic Formaldoximes by a Gold-Catalyzed Cyclization/Intermolecular Methylene Transfer Sequence

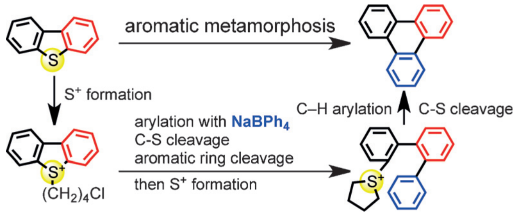


Being specific: Compelling evidence has been found that EutT catalyzes the thermodynamically challenging reduction of Co^{II}rrinoids to form “supernucleophilic” Co^{I} intermediates by a different mechanism to other ATP:corrinoid adenosyltransferases. Spectroscopic, kinetics, and bioassay results suggest that EutT converts cob(II)alamin into an effectively four-coordinate Co^{II} species to facilitate Co^{II} → Co^{I} reduction (DMB = 5,6-dimethylbenzimidazole).

Enzyme Catalysis

K. Park, P. E. Mera, T. C. Moore,
J. C. Escalante-Semerena,
T. C. Brunold* ———— 7158 – 7161

Unprecedented Mechanism Employed by the *Salmonella enterica* EutT ATP:Co^{I}rrinoid Adenosyltransferase Precludes Adenosylation of Incomplete Co^{II}rrinoids

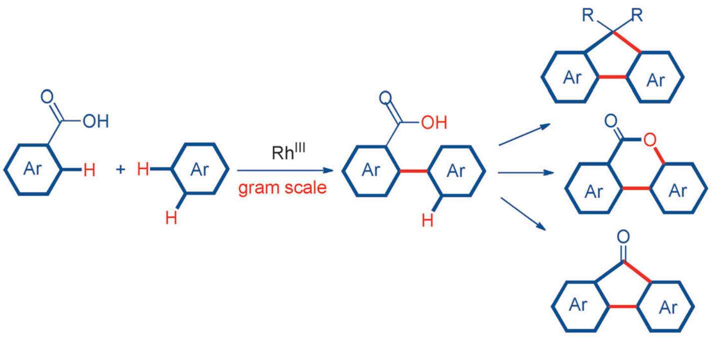


A change of heart: The invention of two palladium-catalyzed arylation reactions of organosulfur compounds enabled the transformation of dibenzothiophenes into triphenylenes and thus a fundamental change in the core aromatic structure (see scheme). Both symmetrical and unsymmetrical triphenylenes were synthesized in a tailor-made fashion in satisfactory overall yield.

Aromatic Compounds

D. Vasu, H. Yorimitsu,*
A. Osuka ———— 7162 – 7166

Palladium-Assisted “Aromatic Metamorphosis” of Dibenzothiophenes into Triphenylenes



Under construction: The highly regioselective title reaction directly furnishes *ortho*-carboxy bi(hetero)aryls. The method has the potential to lead to the rapid construction of a library of appealing polyheterocycles, given the complete regiocontrol, readily available substrates, and functional-group tolerance.

C–H Activation

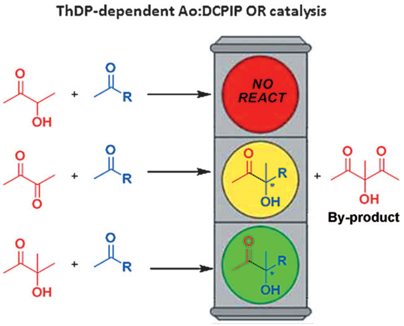
X. Qin, X. Li, Q. Huang, H. Liu, D. Wu,
Q. Guo, J. Lan,* R. Wang,
J. You* ———— 7167 – 7170

Rhodium(III)-Catalyzed *ortho* C–H Heteroarylation of (Hetero)aromatic Carboxylic Acids: A Rapid and Concise Access to π-Conjugated Poly-heterocycles

Asymmetric Synthesis

G. Bernacchia, O. Bortolini,
M. De Bastiani, L. A. Lerin, S. Loschonsky,
A. Massi, M. Müller,
P. P. Giovannini* ________ **7171 – 7175**

Enzymatic Chemoselective Aldehyde–Ketone Cross-Couplings through the Polarity Reversal of Methylacetoin



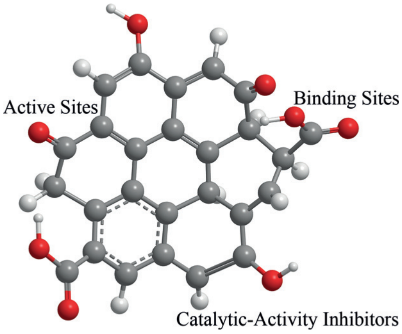
Enzyme catalysis: The substrate scope of the thiamine diphosphase (ThDP)-dependent acetoin:dichlorophenolindophenol oxidoreductase (Ao:DCPIP OR) has been extended to the aldehyde–ketone carboligation reaction. The use of methylacetoin as the acetyl anion donor allows complete control of the chemoselectivity. Some of the resulting tertiary alcohols displayed stereochemistry opposite to that obtained with other ThDP-dependent enzymes.

Graphene Quantum Dots

H. Sun, A. Zhao, N. Gao, K. Li, J. Ren,
X. Qu* ________ **7176 – 7180**

Deciphering a Nanocarbon-Based Artificial Peroxidase: Chemical Identification of the Catalytically Active and Substrate-Binding Sites on Graphene Quantum Dots

Inside Back Cover

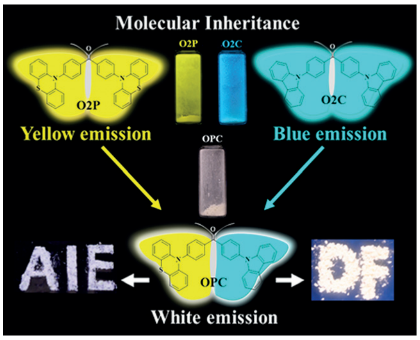


The peroxidase-like activity of graphene quantum dots (GQDs) is studied by means of selective deactivation of the different functional groups on GQDs. Experimental results and theoretical calculations demonstrate that ketone groups are the catalytically active sites whereas carboxylic groups act as substrate-binding sites, and hydroxy groups can decrease the catalytic activity.

White-Light Emission

Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang,*
S. Liu, J. Xu, Z. Chi* ________ **7181 – 7184**

White-Light Emission Strategy of a Single Organic Compound with Aggregation-Induced Emission and Delayed Fluorescence Properties

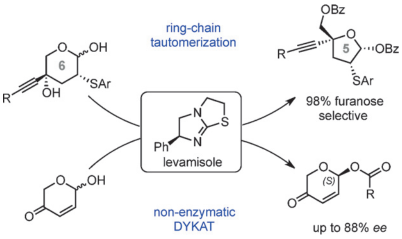


Like fluorescent butterflies: A single white-light-emitting organic compound with aggregation-induced emission-delayed fluorescence (AIE-DF) was achieved by selection of the parent molecules. This novel design principle is a form of molecular inheritance of the tuning properties for a targeted molecule.

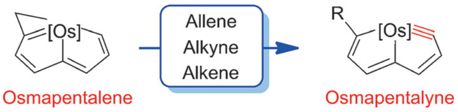
Organocatalysis

A. Ortiz,* T. Benkovics, G. L. Beutner,
Z. Shi, M. Bultman, J. Nye,
C. Sfouggatakis,
D. R. Kronenthal ________ **7185 – 7188**

Scalable Synthesis of the Potent HIV Inhibitor BMS-986001 by Non-Enzymatic Dynamic Kinetic Asymmetric Transformation (DYKAT)

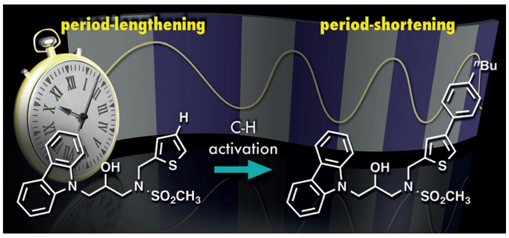


Good dynamic: Described is the synthesis of BMS-986001 by employing two novel organocatalytic transformations: a highly selective pyranose to furanose ring tautomerization, and an unprecedented small-molecule-mediated dynamic kinetic asymmetric transformation (DYKAT) to access enantiopure pyranones. BMS-986001 was synthesized in five steps in an overall yield of 44%. Bz = benzoyl.



General and efficient: Various osmapentalynes were synthesized by a general route via an osmapentalene derivative. The experimental data together with DFT calculations confirm the aromaticity of these fused five-membered rings. Development of this synthetic approach will facilitate the exploration of the reactivities and applications of osmapentalynes, a brand-new aromatic system.

Metallacycles



A change in rhythm: The first functional analysis of KL001 derivatives, which are mammalian circadian-clock modulators, was enabled by cutting-edge C—H activation. The sites of the KL001 derivatives that are critical for their rhythm-changing activity were elucidated, which led to the discovery of the first period-shortening molecules that target the cryptochrome.

Structure–Activity Relationships

Back Cover

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

A video clip is available as Supporting Information on www.angewandte.org (see article for access details).

This article is available online free of charge (Open Access).

This article is accompanied by a cover picture (front or back cover, and inside or outside).

The Very Important Papers, marked VIP, have been rated unanimously as very important by the referees.

The Hot Papers are articles that the Editors have chosen on the basis of the referee reports to be of particular importance for an intensely studied area of research.