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:

S.-T. Wu, Y.-R. Wu, Q.-Q. Kang, H. Zhang, L.-S. Long, Z. Zheng,* R.-B. Huang, L.-S. Zheng*
Chiral Symmetry Breaking by Chemically Manipulating Statistical Fluctuation in Crystallization

*F. Arnesano, S. Scintilla, G. Natile**
Interaction between Platinum Complexes and a Methionine Motif Found in Copper Transport Proteins

*F. Akagi, T. Matsuo, H. Kawaguchi**
Dinitrogen Cleavage by a Diniobium Tetrahydride Complex: Formation of a Nitride and Its Conversion to Imide Species

J.-H. Jang, D. Dendukuri, T. A. Hatton, E. L. Thomas, P. S. Doyle**
A Route to Three-Dimensional Structures in a Microfluidic Device: Stop-Flow Interference Lithography

Y. Zhao, A. W. Mitra, A. H. Hoveyda, M. L. Snapper**
Kinetic Resolution of 1,2-Diols through Highly Site- and Enantioselective Catalytic Silylation

X. Wang, L. Andrews, S. Riedel, M. Kaupp**
Mercury Is a Transition Metal: The First Experimental Evidence for HgF_4

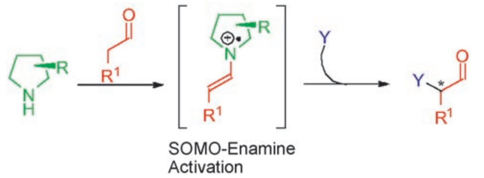
News

Books

Highlights

Asymmetric Catalysis

Radicals in Asymmetric Organocatalysis

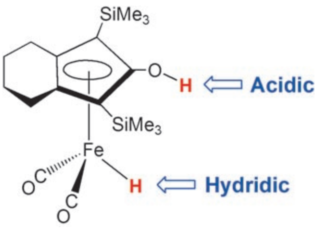


Radical turn to organocatalysis: Aminocatalysis has developed into a versatile tool for the stereoselective functionalization of carbonyl species. In the search for new organocatalytic transformations, attention has been focused on radicals to expand the scope of aminocatalysis. The successful application of the SOMO(singly occupied molecular orbital)-enamine activation has led to a number of novel transformations.

Non-Precious-Metal Catalysts

An Iron Catalyst for Ketone Hydrogenations under Mild Conditions

Doing it on the cheap: An iron-based homogeneous catalyst for ketone hydrogenation was reported, thus avoiding the use of a precious metal. Excellent yields and chemoselectivity for hydrogenation are found under mild conditions (25 °C, 3 atm H_2). An ionic hydrogenation mechanism allows the delivery of a proton from the OH group and a hydride from the metal center (see picture).

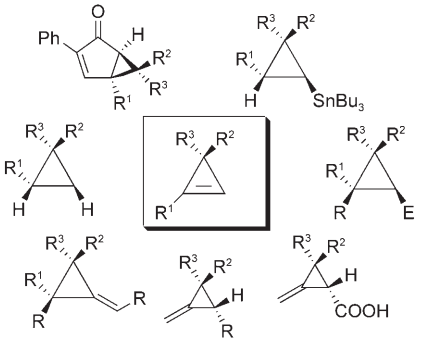


Reviews

Synthetic Methods

I. Marek,* S. Simaan,
A. Masarwa ______ 7364 – 7376

Enantiomerically Enriched Cyclopropene Derivatives: Versatile Building Blocks in Asymmetric Synthesis



Straining at the leash: Chiral cyclopropenes are versatile reactive building blocks in organic synthesis, in particular for the production of enantiomerically enriched methylene- and alkylidenecyclopropanes. The simple route to chiral cyclopropenes forms an excellent basis for the discovery of new reactivity.

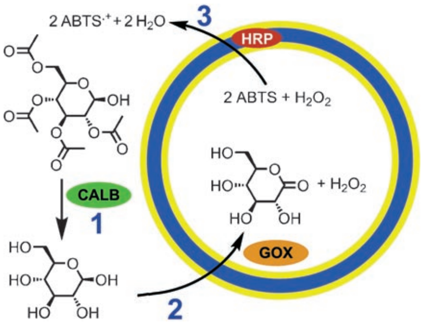
Communications

Nanoreactors

D. M. Vriezema, P. M. L. Garcia,
N. Sancho Oltra, N. S. Hatzakis,
S. M. Kuiper, R. J. M. Nolte, A. E. Rowan,*
J. C. M. van Hest* ______ 7378 – 7382

Positional Assembly of Enzymes in Polymersome Nanoreactors for Cascade Reactions

In a good position: Nanoreactors can be constructed by the controlled positioning of glucose oxidase (GOX) and horseradish peroxidase (HRP) within the central water pool and block-copolymer membrane of polymersomes. A one-pot multistep reaction sequence is performed with the nanoreactor in combination with free *Candida antarctica* lipase B (CALB) in the bulk solution (see picture; ABTS: 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)).

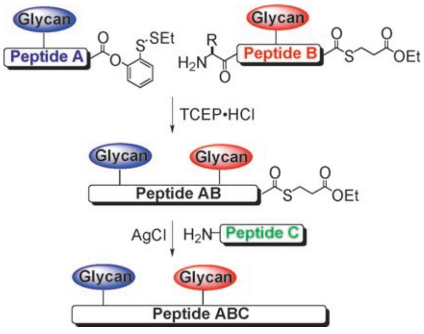


Glycopeptides

G. Chen, Q. Wan, Z. Tan, C. Kan,
Z. Hua, K. Ranganathan,
S. J. Danishefsky* ______ 7383 – 7387

Development of Efficient Methods for Accomplishing Cysteine-Free Peptide and Glycopeptide Coupling

As simple as A, B, C: Non-cysteine-based reiterative fragment coupling of glycopeptides involves a metal-free (TCEP) coupling of a peptidyl C-terminal phenolic ester containing an *ortho*-disulfide moiety (A) with an N-terminal glycopeptide whose C terminus is an alkyl thioester (B) to produce AB, whose N terminus contains an alkyl thioester. A AgCl-mediated coupling of AB with peptide C then produces the tridomainal peptide ABC. TCEP = tris(2-carboxyethyl)phosphine.



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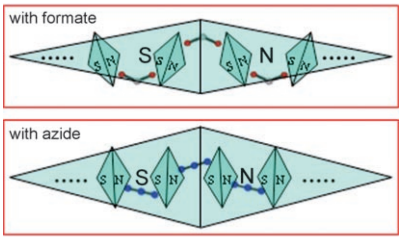
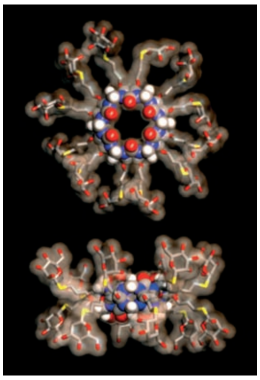


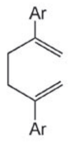
Magnetic strings: Single-molecule-magnet-like $[Mn_3^{III}O]$ units are strung into two chain compounds along the magnetic easy axis with formate and azide anions, respectively, as bridges (see picture). The enhanced uniaxial anisotropy and intrachain coupling of these two chain compounds mean that they act as single-chain magnets with a high energy barrier for magnetization relaxation.

Single-Chain Magnets



Steering wheels: Cucurbit[6]uril (CB[6]) can be used as a scaffold to synthesize carbohydrate clusters in which about 11 carbohydrate moieties are attached to the periphery of the rigid macrocycle like a wheel (see picture). The clusters show enhanced selectivity and affinity in binding to specific proteins through multivalent interactions. The CB[6] cavity allows formation of host–guest complexes that can be delivered to specific cells.

Carbohydrate Clusters



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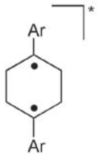

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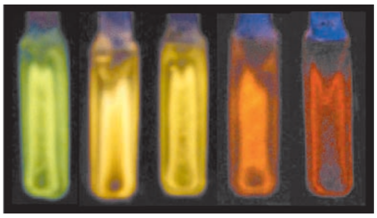
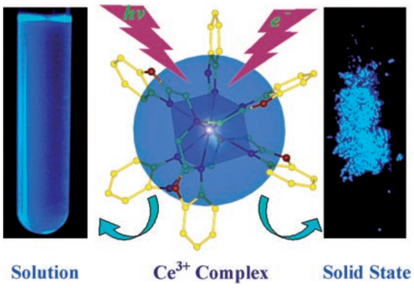


Light from an unobservable source: Annealing a γ-irradiated glassy matrix containing 2,5-diaryl-1,5-hexadiene **1** gives rise to an intense thermoluminescence (TL) that is assigned to the singlet excited state of the corresponding cyclohexane-1,4-diyl ($^1\mathbf{2}^{\bullet\bullet}$*) on the basis of substituent effects on λ_{TL} and DFT calculations (see picture showing thermoluminescence of $^1\mathbf{2}^{\bullet\bullet}$*; Ar = 4-$XC_6H_4$; from left to right: X = F, H, Me, Cl, Br).

Biradical Intermediates

Sky-blue research: Studies of the photoluminescence and electroluminescence of a series of Ce^{3+} coordination complexes with tripodal benzimidazole ligands reveals effective energy transfer from both metal- and ligand-based transitions and efficient blue metal-centered emission. A blue-emitting LED device was fabricated using one such cerium complex, suggesting their potential application as light-emitting materials.



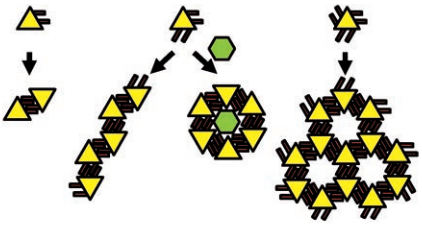
Lanthanide Luminescence


A Journal of the Gesellschaft Deutscher Chemiker
Angewandte
Chemie
International Edition
2006–45/42
WILEY-VCH

Hierarchical Self-Assembly

D. Bléger, D. Kreher, F. Mathevet, A.-J. Attias,* G. Schull, A. Huard, L. Douillard, C. Fiorini-Debuischert, F. Charra* **7404 – 7407**

Surface Noncovalent Bonding for Rational Design of Hierarchical Molecular Self-Assemblies



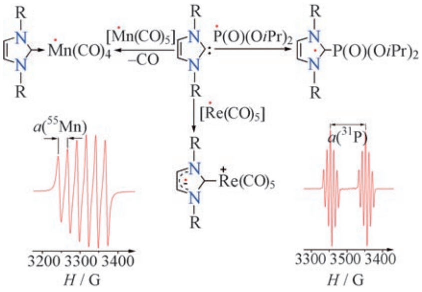
Clip chemistry: When a fully deterministic strategy that parallels polymer chemistry is used, mono-, bi-, and trifunctional clip-bearing building blocks form noncovalent surface-self-assembled dimers, polymers, and 2D networks, respectively (see scheme). These entities can then be subjected to further higher-level manipulations, as shown by controlled reorganization (cyclization) of a polymerlike chain around a molecular block.

Carbenes

B. Tumanskii,* D. Sheberla, G. Molev, Y. Apeloig* **7408 – 7411**

Dual Character of Arduengo Carbene–Radical Adducts: Addition versus Coordination Product

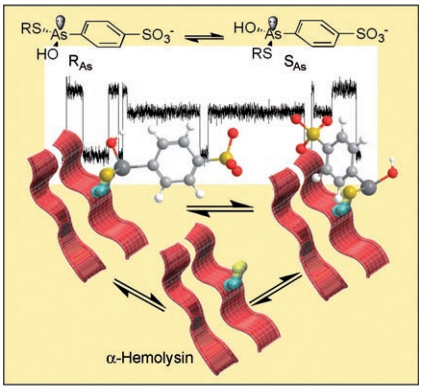
At last, two general types of radical adducts have been obtained by the addition of radicals to a stable N-heterocyclic carbene. Addition products were obtained with $(iPrO)_2(O)P^{\bullet}$ and $[(CO)_5Re^{\bullet}]$, while with $[(CO)_5Mn^{\bullet}]$ and $[(CO)_3CpMo^{\bullet}]$ (Cp = η^5-cyclopentadienyl) substitution of one carbonyl ligand and coordination to the metal center occurred to give novel metal-centered radicals (see scheme).



Chiral Organoarsenic Compounds

S.-H. Shin, M. B. Steffensen, T. D. W. Claridge, H. Bayley* **7412 – 7416**

Formation of a Chiral Center and Pyrimidal Inversion at the Single-Molecule Level

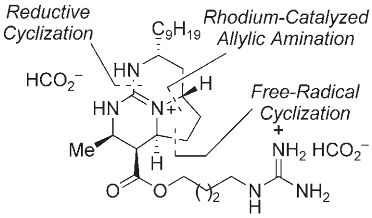


One-at-a-time stereochemistry: As–S bond-making and bond-breaking reactions are important in pharmacology, toxicology, and cell biology. The aqueous covalent chemistry of individual As^{III} molecules can be monitored inside a protein nanoreactor. The approach is used to follow the creation of a chiral center at As^{III}, through the formation of a short-lived As–S bond, and to monitor inversion at that center (see picture).

Polycyclic Guanidines

P. A. Evans,* J. Qin, J. E. Robinson, B. Bazin **7417 – 7419**

Enantioselective Total Synthesis of the Polycyclic Guanidine-Containing Marine Alkaloid (−)-Batzelladine D



Batzelladine D

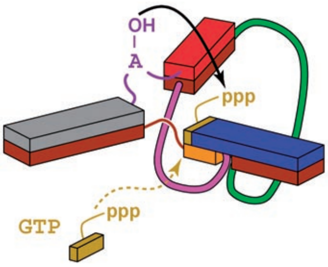
Addressing the marine core: The enantioselective total synthesis of the polycyclic guanidine-containing marine alkaloid (−)-batzelladine D has been accomplished using a convergent 14-step reaction sequence (longest linear sequence) in 10% overall yield. The ability to accomplish the selective homolytic cleavage of an alkyl iodide in the presence of an azide circumvents the necessity for nitrogen-protecting groups.

Catalytic DNA

C. Höbartner,
S. K. Silverman* _______ **7420 – 7424**

Engineering a Selective Small-Molecule Substrate Binding Site into a Deoxyribozyme

A small goal: An RNA ligase deoxyribozyme is engineered to accept a small-molecule NTP substrate in a multiple-turnover fashion. Selective binding is enforced by hydrogen bonding, and structural preorganization within the NTP itself is important for its efficient utilization as a substrate. This study points the way toward a broader use of small-molecule substrates with nucleic acid enzymes.

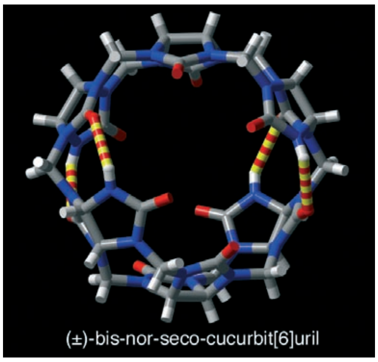


Chiral Recognition

W.-H. Huang, P. Y. Zavalij,
L. Isaacs* _______ **7425 – 7427**

Chiral Recognition inside a Chiral Cucurbituril

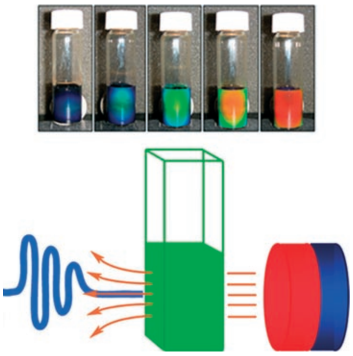
Picky host: The isolation, characterization, and recognition properties of the first chiral cucurbit[*n*]uril—(±)-bis-nor-seco-CB[6]—are reported. The (±)-bis-ns-CB[6] undergoes diastereoselective recognition events with guests that contain stereogenic centers including amino acids, amino alcohols, and *meso* compounds.



Photonic Crystals

J. Ge, Y. Hu, Y. Yin* _______ **7428 – 7431**

Highly Tunable Superparamagnetic Colloidal Photonic Crystals

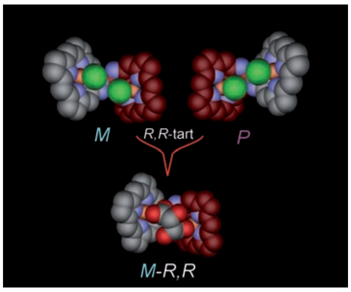


Tuning crystal: Superparamagnetic nanocrystal clusters can self-assemble into colloidal photonic crystals in solution, whose stop bands can be magnetically tuned across the entire visible spectrum. Owing to the high magnetization and the highly charged polyacrylate-capped surface of each cluster, the colloidal photonic crystals show a rapid, reversible, and widely tunable optical response to external magnetic fields.

Porphyrinoids

M. Siczek,
P. J. Chmielewski* _______ **7432 – 7436**

Synthesis, Characterization, and Chirality of Dimeric N-Confused Porphyrin–Zinc Complexes: Toward the Enantioselective Synthesis of Bis(porphyrinoid) Systems

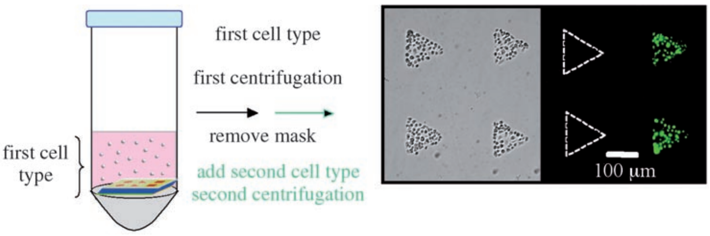


A chiral bivalve: Upon insertion of zinc ions, the 3,3′-bis(N-confused porphyrin) adopts a bent transoid structure with homochiral subunits that are capable of the supramolecular binding of alcohols. The introduction of a dianionic ligand of defined configuration results in the racemic mixture being converted into a pure enantiomer (see picture; tart = tartrate dianion) as determined by circular dichroism studies.

Cell Patterning

D. G. Barrett, M. N. Yousaf* **7437 – 7439**

Rapid Patterning of Cells and Cell Co-Cultures on Surfaces with Spatial and Temporal Control through Centrifugation

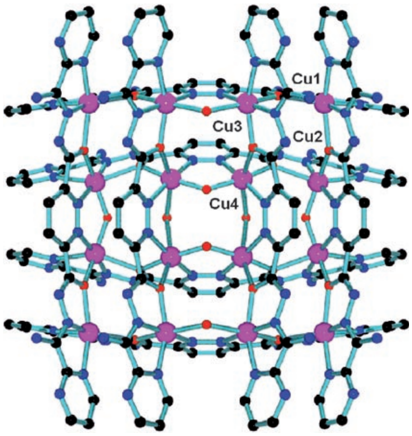


Cultural events: A methodology that combines surface chemistry with soft lithography and centrifugation allows the rapid, inexpensive, and complete patterning of cells and cell co-cultures (yellow and red) on gold surfaces (green) covered by a self-assembled monolayer (blue). Sequential masking of the surface with a polydimethylsiloxane membrane (gray) allows the controlled patterning of multiple cell lines (see picture).

Magnetic Grid Complexes

L. N. Dawe,
L. K. Thompson* **7440 – 7444**

A Self-Assembled, Magnetically Coupled Square Cu_{16} 4 × [2 × 2] Grid

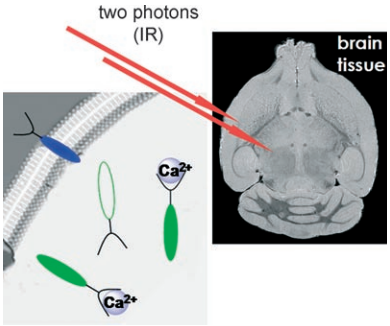


Grid ion: A Cu_{16} grid prepared with a tetratopic bishydrazone ligand has metal ions in a [4 × 4] array linked by a combination of μ-$O_{hydrazone}$ and μ-$NN_{pyridazine}$ bridges. The six-coordinate copper ions display Jahn–Teller distortion, leading to some orbitally orthogonal bridges. Multiple intragrid magnetic-exchange pathways are present and are modeled simply by taking the molecular symmetry and the orthogonal connections into account.

Fluorescent Probes

H. M. Kim, B. R. Kim, J. H. Hong,
J.-S. Park, K. J. Lee,
B. R. Cho* **7445 – 7448**

A Two-Photon Fluorescent Probe for Calcium Waves in Living Tissue



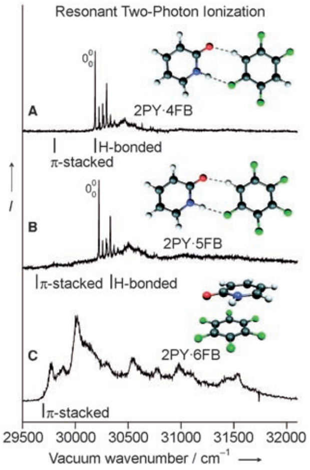
Intracellular messaging: The novel two-photon fluorescent probe ACa1 can visualize calcium waves in cells and living tissue for a long period of time and without any mistargeting problems (see picture). The probe is capable of monitoring the calcium waves at a depth of about 150 µm in living tissues for more than 1100 s and with no photobleaching artifacts.

2-Pyridone–Fluorobenzene Complexes

R. Leist, J. A. Frey, P. Ottiger, H.-M. Frey, S. Leutwyler,* R. A. Bachorz, W. Klopper* **7449 – 7452**

Nucleobase–Fluorobenzene Interactions: Hydrogen Bonding Wins over π Stacking

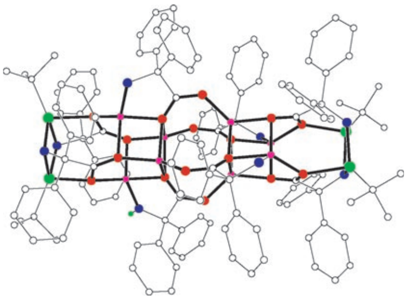
The relative importance of H-bonding and π stacking in isolated cold complexes of 2-pyridone (2PY) with 1,2,4,5-tetrafluorobenzene (4FB), pentafluorobenzene (5FB), and hexafluorobenzene (6FB) was investigated. Unexpectedly, only 2PY·6FB exhibits π stacking in the gas phase and a broad UV spectrum. The other 2PY·*n*FB complexes show narrow absorption spectra characteristic of doubly H-bonded dimers (see picture).



Organozinc Chemistry

C. Redshaw,* M. R. J. Elsegood **7453 – 7457**

Synthesis of Tetra-, Hexa-, and Octanuclear Organozinc Ring Systems



Zinc joins the magic circle: Use of the acids $Ph_2C(X)CO_2H$ (X = OH, NH_2) allows access to novel organozinc ring systems. Intriguing solid-state structures (see picture; O red, Zn green, N blue, Li pink), elucidated by X-ray crystallography using synchrotron radiation, form depending on the nature of X. These complexes serve as an entry point into new organozinc ring chemistry.

Natural Products Synthesis

S. Akai, K. Kakiguchi, Y. Nakamura, I. Kuriwaki, T. Dohi, S. Harada, O. Kubo, N. Morita, Y. Kita* **7458 – 7461**

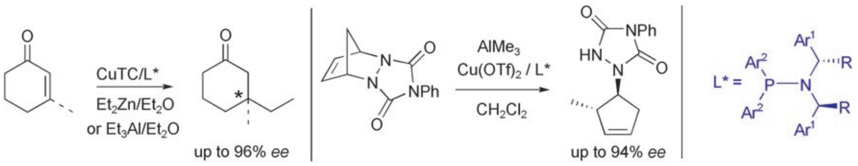
Total Synthesis of (±)-γ-Rubromycin on the Basis of Two Aromatic Pummerer-Type Reactions

Double or nothing: In a convergent synthesis of the title compound, a potent inhibitor of human telomerase, two different aromatic Pummerer-type reactions were employed to construct the pivotal bisbenzannelated spiroketal skeleton from the two fragments shown in the scheme. This methodology offers convenient access to a wide range of substituted bisbenzannelated spiroketals from naphthol derivatives. MOM = methoxymethyl.

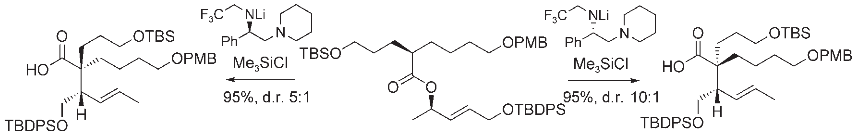
Asymmetric Catalysis

L. Palais, I. S. Mikhel, C. Bournaud, L. Micouin, C. A. Falciola, M. Vuagnoux-d'Augustin, S. Rosset, G. Bernardinelli, A. Alexakis* **7462 – 7465**

SimplePhos Monodentate Ligands: Synthesis and Application in Copper-Catalyzed Reactions



A simple choice: Ligands termed SimplePhos (**L***), based on a chiral amino and flexible aryl groups on the phosphorus atom, induce high enantioselectivity in the copper-catalyzed conjugate addition and allylic substitution of dialkyl zinc and trialkyl aluminum reagents (see scheme; CuTC = copper thiophene carboxylate).



To overcome the limitation of the poor diastereoselectivity of the title reaction with α-branched esters, chiral amides were used to generate the enolate intermediates diastereoselectively. The desired rearrangement then took place with efficient transfer of chirality to give densely functionalized products with at least one quaternary stereocenter (see scheme; PMB, TBS, and TBDPS are protecting groups).

Synthetic Methods

Y.-c. Qin, C. E. Stivala,
A. Zakarian* ______ **7466 – 7469**

Acyclic Stereocontrol in the Ireland–Claisen Rearrangement of α-Branched Esters

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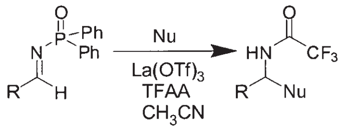

Hydrated lanthanum triflate has been shown to be an effective and highly active Lewis acid catalyst for nucleophilic addition to *N*-phosphinylimines in the presence of trifluoroacetic anhydride (TFAA; see scheme). Unexpectedly, trifluoroacetamide products are produced in a novel process which likely involves consecutive acylation/hydration of *N*-phosphinylimine substrates and subsequent nucleophilic addition.

Synthetic Methods

W. W. Ong, A. B. Beeler, S. Kesavan,
J. S. Panek, J. A. Porco, Jr.* _ **7470 – 7472**

Nucleophilic Addition to *N*-Phosphinylimines by Rare-Earth-Metal Triflate/Trifluoroacetic Anhydride Activation

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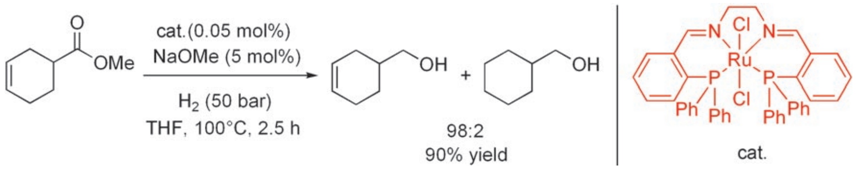

The missing link: The presence of two N,P bridges in the ruthenium complexes used as catalysts for the title reaction is essential. Esters that contain isolated C=C bonds are reduced to the corresponding unsaturated alcohols in high yields with high chemoselectivity (see example).

Catalytic Hydrogenation

L. A. Saudan,* C. M. Saudan, C. Debieux,
P. Wyss ______ **7473 – 7476**

Dihydrogen Reduction of Carboxylic Esters to Alcohols under the Catalysis of Homogeneous Ruthenium Complexes: High Efficiency and Unprecedented Chemoselectivity

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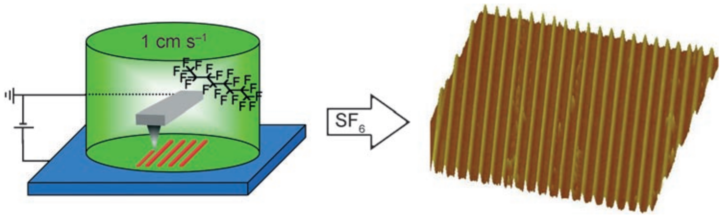


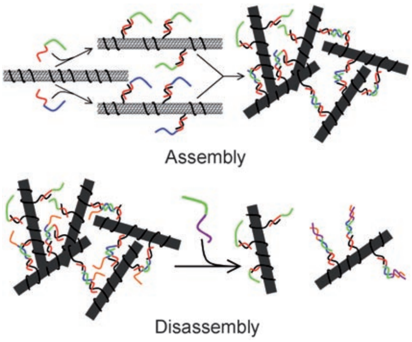
Quick as a flash: High-speed scanning probe lithography in perfluorooctane leads to direct deposition of fluorinated amorphous carbon at velocities in the cm s^{-1} range. Features as small as 27 nm are fabricated on 100-μm^2 areas within seconds. The nanoscale patterns are characterized by using photoelectron emission microscopy and secondary ion mass spectrometry.

Nanofabrication

M. Rolandi, I. Suez, A. Scholl,
J. M. J. Fréchet* ______ **7477 – 7480**

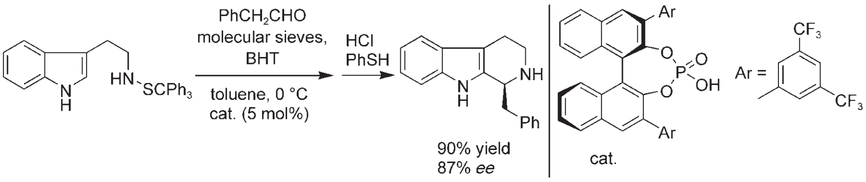
Fluorocarbon Resist for High-Speed Scanning Probe Lithography

Carbon Nanotubes



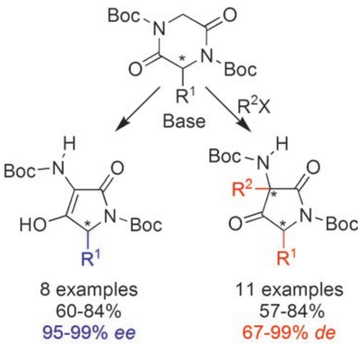
Carbon nanotubes made smart: Single-walled carbon nanotubes (SWNTs) bearing multiple highly hybridizable DNA sequences were prepared, and the hybridization-driven aggregation and redispersion of the conjugates were realized (see picture). The DNA–SWNT conjugates could be used as building blocks for DNA-programmed material self-assembly and should be able to parallel or even outperform regularly employed systems.

Organocatalysis



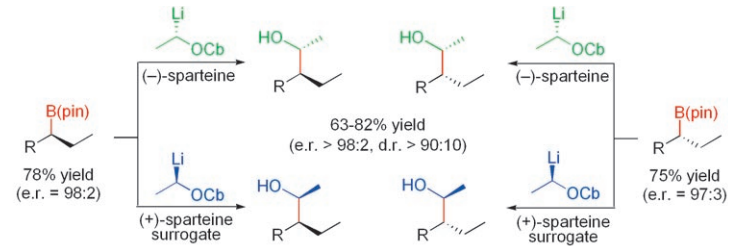
From cations to chiral products: β-Carbolines can be synthesized with good enantioselectivity by the title reaction catalyzed by a chiral binol-derived Brønsted acid (see scheme, BHT = 3,5-di(*tert*-butyl)-4-hydroxytoluene). The procedure commences from tryptamine and can be scaled up readily, as both the installment and the removal of the auxiliary proceed in high yield under mild conditions.

C–C Activation

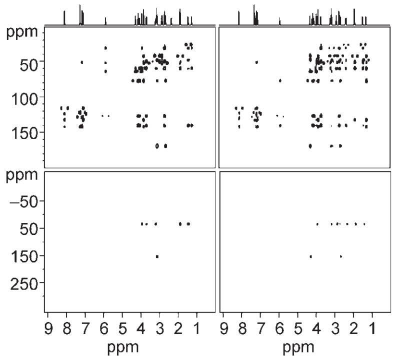


The surprising reactivity under basic conditions of 2,5-diketopiperazines activated by *N*-Boc substituents provides a highly stereoselective pathway to pyrrolidine-2,4-diones. A wide range of valuable pharmaceutical scaffolds can be synthesized by adding an alkylating reagent during the course of the reaction (see scheme). R^1 = alkyl; R^2 = alkyl, benzyl; Boc = *tert*-butoxycarbonyl.

Asymmetric Synthesis



Take your pick: Either enantiomer of either diastereomer of substrates bearing adjacent stereogenic centers is accessible through reaction of an (*R*)- or (*S*)-lithiated carbamate with an (*R*)- or (*S*)-boronic ester (see scheme; pin = pinacolate, OCb = substituted carbamate).



One experiment, four NMR spectra: By combining the principles of time-sharing evolution and multiple FID acquisition within the same scan, several fully complementary NMR spectra can be obtained in a single-shot acquisition. Four different HMBC and HMBC-relayed experiments (see spectra) can be carried out simultaneously for ^{13}C and ^{15}N at natural abundance, with a saving in measuring time of up to 75%.

NMR Spectroscopy

P. Nolis, M. Pérez-Trujillo,
T. Parella* ———— **7495 – 7497**

Multiple FID Acquisition of Complementary HMBC Data

Slow dance: Long believed to be impossible, migration of a phosphorus ligand via a bridging intermediate is observed between two metal centers in a diiron complex containing an asymmetric bridging ligand. This process occurs in a similar fashion to the migration of carbonyl ligands but at a rate slow enough to be studied by NMR spectroscopy.

Phosphorus Ligand Migration

H. Sun,* J. Gu, Z. Zhang, H. Lin, F. Ding,
Q. Wang ———— **7498 – 7500**

Slow Migration of a Phosphorus Ligand between Two Metal Centers

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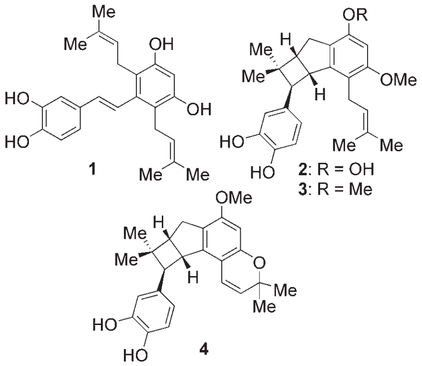
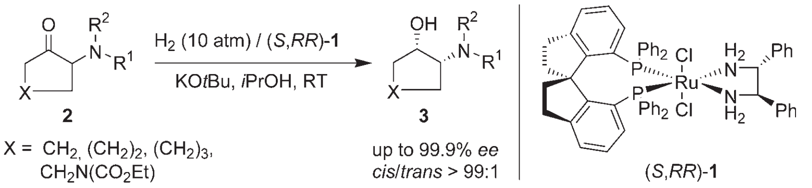
State of the artochamins: Total syntheses of artochamins F (**1**), H (**2**), I (**3**), and J (**4**; see scheme) have been achieved through a flexible and expedient strategy that features a cascade sequence involving two concurrent [3,3] sigmatropic rearrangements and an unusual intramolecular formal [2+2] thermal cycloaddition reaction between an electron-rich stilbene and a prenyl group.



Cascade Reactions

K. C. Nicolaou,* T. Lister, R. M. Denton,
C. F. Gelin ———— **7501 – 7505**

Cascade Reactions Involving Formal [2+2] Thermal Cycloadditions: Total Synthesis of Artochamins F, H, I, and J

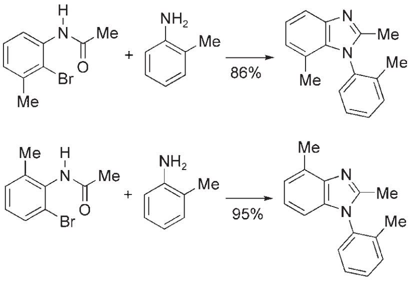


Resolutely dynamic hydrogenation: A highly efficient asymmetric hydrogenation of racemic *N*,*N*-disubstituted α-aminocycloalkanones involving dynamic kinetic resolution in the presence of a ruthenium catalyst gives chiral α-aminocycloalkanols with excellent enantioselectivities and *cis* diastereoselectivities (see scheme). A synthesis of optically pure U-(−)-50488 based on this reaction is reported.

Asymmetric Catalysis

S. Liu, J.-H. Xie, L.-X. Wang,
Q.-L. Zhou* ———— **7506 – 7508**

Dynamic Kinetic Resolution Allows a Highly Enantioselective Synthesis of *cis*-α-Aminocycloalkanols by Ruthenium-Catalyzed Asymmetric Hydrogenation



Highly tolerated: A catalytic method employing [$Pd_2(dba)_3$] and XPhos or RuPhos permits the efficient synthesis of *N*-aryl benzimidazoles in regioisomerically pure form starting from *ortho*-haloanilides (see scheme), and tolerates a wide range of functional groups. dba = *trans*,*trans*-dibenzylideneacetone.

Supporting information is available on the WWW (see article for access details).

A video clip is available as Supporting Information on the WWW (see article for access details).

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