**VIP** ***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:***



## News

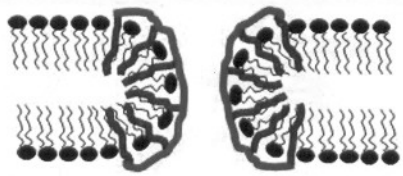


## Books



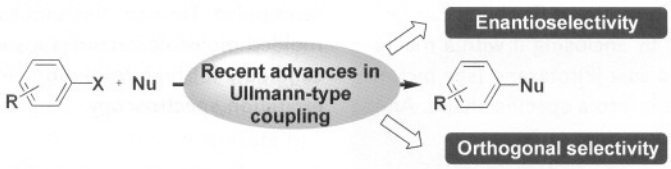
## Highlights

**Better channeling**: The insertion of amphiphilic, charged homo, graft, or block copolymers into lipid membranes is a way of forming defined membrane channels or pores. New insights into the mechanism of pore formation are discussed; for example, the picture shows the carpet mechanism for the insertion of amphiphilic graft polymers into a membrane.



***Artifical Membrane Pores***






**Copper makes the difference**: Important challenges have been overcome in copper-catalyzed Ullmann reactions since its renaissance in the early 2000s. Significant advances in this field have recently been made in regards to carrying out enantioselective and chemoselective arylation of nucleophiles (Nu) by using a copper catalyst (see scheme).

***Arylation***

# Contents

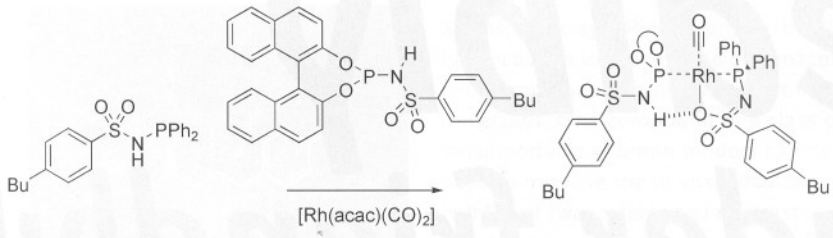
## Reviews



## Communications




**For the USA and Canada:**
ANGEWANDTE CHEMIE International Edition (ISSN 1433-7851) is published weekly by Wiley-VCH, PO Box 191161, 69451 Weinheim, Germany. Air freight and mailing in the USA by Publications Expediting Inc., 200 Meacham Ave., Elmont, NY 11003. Periodicals postage paid at Jamaica, NY 11431. US POSTMASTER: send address changes to *Angewandte Chemie*, Wiley-VCH, 111 River Street, Hoboken, NJ 07030. Annual subscription price for institutions: US$ 7225/6568 (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.

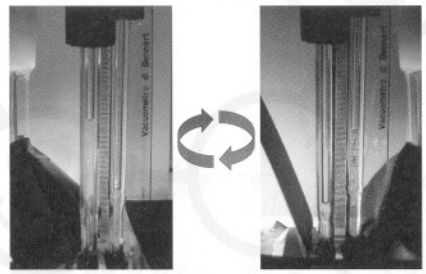



**Adapt to react**: METAMORPhos ligands are a class of flexible and adaptive hydrogen-bonded multidentate sulfonamide-based phosphorus ligands. Selective formation of complexes with two different METAMORPhos ligands (see scheme) that display unusual kinetic behavior leads to the proposal of a new mechanism. These complexes are highly reactive and enantioselective in the rhodium-catalyzed asymmetric hydrogenation of alkenes.

***Supramolecular Ligands***

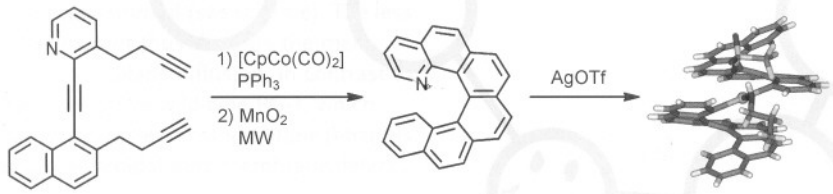


**En route to a clean engine**: The concentration of a chemical system containing an azobenzene derivative can be varied cyclically by light, and this variation has been exploited to produce continuous work. The cyclic concentration change of the system is the result of a light-controlled self-assembly/disassembly process.



***Energy Conversion***



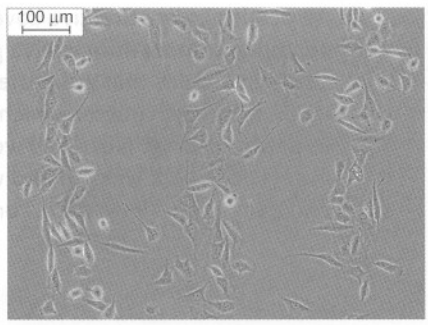



**The taming of the screw**: The $Co^{I}$-catalyzed cyclotrimerization of triynes and microwave (MW) assisted aromatization with $MnO_2$ are central to the practical synthesis of diaza[5]helicene and aza[6]-helicenes. The aza[6]helicene racemates have been resolved, the absolute configuration of the enantiomers assigned, the energy barriers to racemization determined, and X-ray structures of their Ag complexes obtained (see picture; Cp = $C_5H_5$, OTf = triflate).

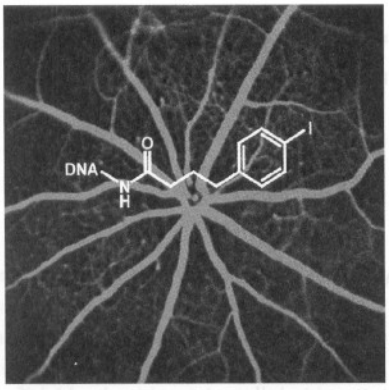
***Helical Structures***



**Restrained potential**: A caged cyclic peptide attached to a surface is able to trigger cell attachment to the surface with spatiotemporal definition upon exposure to light ($\lambda = 351$ nm). The peptide shows no integrin-binding activity in its caged form, but mediates cell adhesion effectively after irradiation (see optical microscopy image of cells on a surface irradiated through a mask in bands 100 μm in width).




***Cell–Surface Interactions***

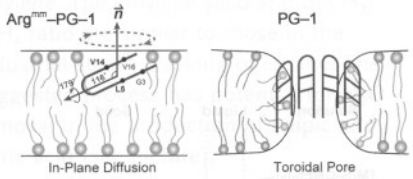



**Seeing eye to eye**: Plasma-protein binding is effective in improving the pharmacokinetic properties of otherwise short-lived molecules. One compound in a class of small portable albumin binders can be used to improve the in vivo circulatory half-life of two widely used contrast agents. It improves the imaging performance of fluorescein in angiographic analysis of the retina of mice (see picture).

***Protein Binding***

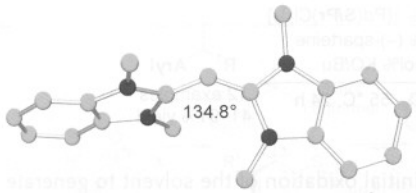


**Barreling through**: Guanidinium–phosphate hydrogen bonding significantly affects the structure and activity of the antimicrobial peptide PG-1. Solid-state NMR data show that a mutant of PG-1, having dimethylated Arg residues, adopts an in-plane orientation, interfacial location, and fast uniaxial motion around the membrane normal (see scheme). The less active mutant thus disrupts the membrane by in-plane diffusion, in contrast to the more active wild-type PG-1, which forms immobile transmembrane β-barrels to cause toroidal-pore membrane defects.




***Transmembrane peptides***



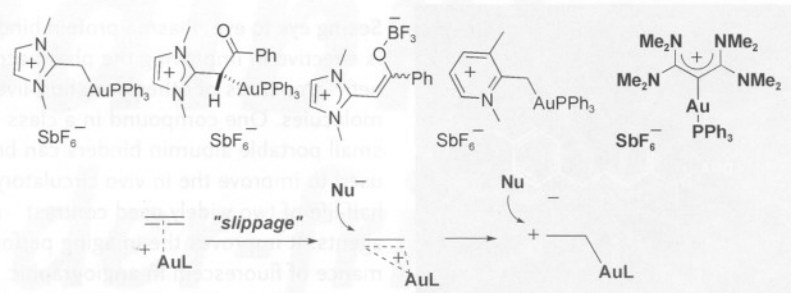



**Pushed to the limit**: Pushing C=C π bonds to the breaking point by using a push–push substitution pattern forces allenes to bend (see structure; C light blue, N dark blue). An acyclic allene featuring a C=C=C bond angle of 134.8° has been isolated in which the typically sp-hybridized central carbon atom approaches a configuration that has two lone pairs of electrons, and acts as a very strong $\eta^1$-donor ligand for transition metals.

***Bent Allenes***

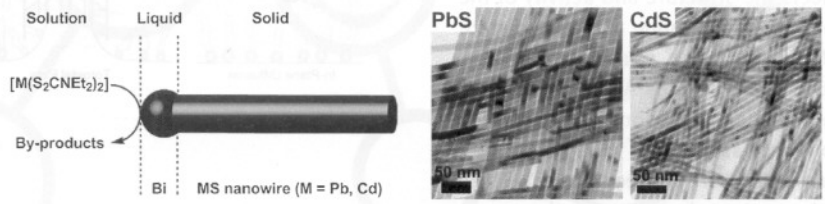
# Contents





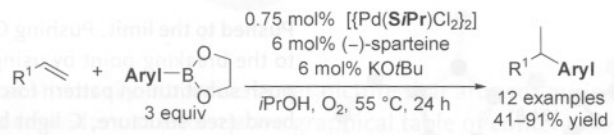

**Carbophilic Lewis acids** can polarize a coordinated π-bond by a slippage mechanism. A series of stable ylid- or enolate gold complexes of ene-1,1-diamines not only emulate this property, but also reveal the exceptional donor capacity of such electron-rich olefin ligands. Moreover, the first metal complex of a tetraaminoallene is reported, which features a prototype "carbodicarbene" ligand bound to a transition-metal template.



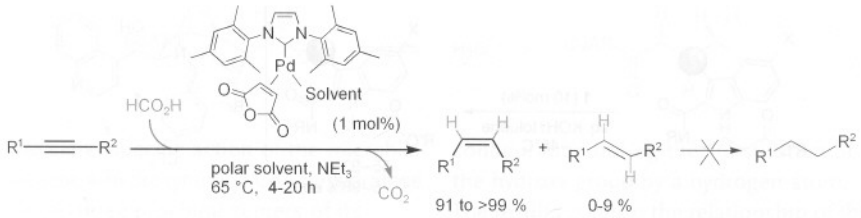



**All wired up!** High-quality colloidal PbS and CdS nanowires were grown from Bi nanoparticles by the solution–liquid–solid (SLS) mechanism. The single-source-precursor strategy could provide a general approach for the synthesis of colloidal semiconductor nanowires.





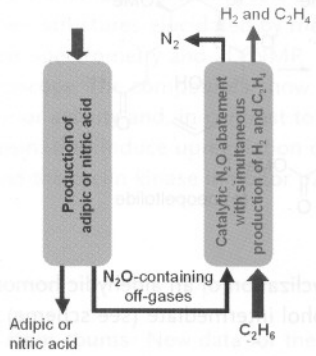

**An oxidation exercise**: An aerobic alcohol oxidation coupled with a regioselective palladium-catalyzed reductive functionalization of styrenes and arylboronic esters has been developed (see scheme). The mechanism is thought to proceed by initial oxidation of the solvent to generate a $Pd^{II}$-hydride species, which subsequently reacts with the alkene and arylboronic ester to ultimately generate a new C–C bond.




**Beyond Lindlar and without hydrogen**: Transfer hydrogenation of internal alkynes catalyzed by a palladium(0) catalyst containing an N-heterocyclic carbene ligand gives *Z* alkenes without over-reduction to alkanes (see scheme). Contrary to most transfer hydrogenations, ketones are not reduced. As such, this is the first catalyst that shows excellent stereo- and chemoselectivity for the semihydrogenation of alkynes without the need for hydrogen gas.

***Transfer Hydrogenation***

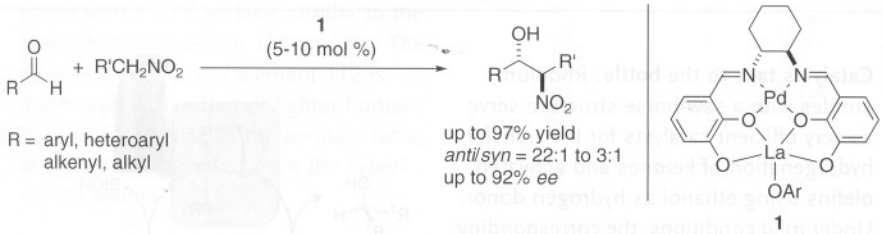





**Chemicals come clean**: Calcium oxide doped with small amounts of sodium oxide is used as catalyst in the abatement of $N_2O$ by ethane to produce $H_2$ and ethylene. The ethylene yield and the $H_2$/$C_2H_4$ ratio are similar to those in the industrial steam cracking of ethane. The suggested process has potential for $N_2O$ removal in the production of adipic and nitric acid (see picture).

***Environmental Chemistry***

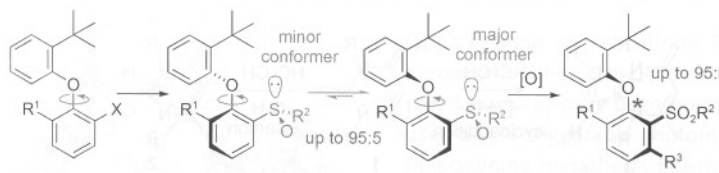





**Two metals in a pod**: The combination of Pd and La with a dinucleating Schiff base was developed for *anti* selectivity in the catalytic asymmetric nitroaldol reaction (see scheme). Short syntheses of β-adrenoceptor agonists by using the heterobimetallic catalyst are presented.

***Nitroaldol Reaction***





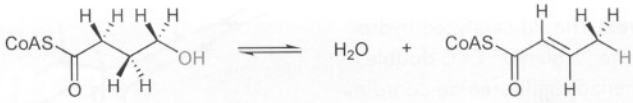

**Twisted ethers**: Introduction of a bulky alkylsulfinyl substituent *ortho* to the C–O axis of a diaryl ether imposes a powerful conformational preference (see scheme). The preference persists upon oxidation of the sulfoxide to a sulfone, leading to dynamic thermodynamic resolution of the atropisomeric ether. This is the first enantioselective synthesis of an atropisomeric diaryl ether not forming part of a macrocyclic ring.

***Atropisomeric Ethers***

# Contents



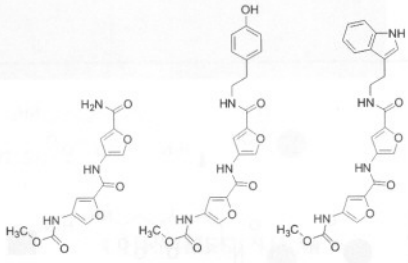



**The stereospecific action** of the microbial enzyme 4-hydroxybutyryl-CoA dehydratase on the three prochiral centers of its substrate 4-hydroxybutyryl-CoA can now be described as *anti* elimination of the 2*Re* and 3*Si* hydrogen atoms with retention of configuration during the substitution of the hydroxy group by a hydrogen atom. The results confirm the relationship of the dehydratase to acyl-CoA dehydrogenases and the view that the $Fe_4S_4$ cluster acts as a Lewis acid.

## Enzyme Mechanisms



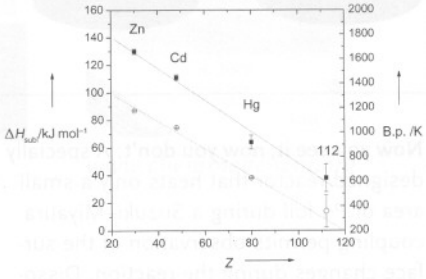
**Drugs from the sea**: Three new netropsin-type antibiotics (**1**–**3**) with a hitherto unknown furan core structure have been isolated from marine actinomycete strains and their structures elucidated by means of mass spectrometry and 2D NMR spectroscopy. The compounds show antitumor activity and, in contrast to netropsin, they induce upregulation of p53 and the cyclin kinase inhibitor p21.




## Marine Natural Products

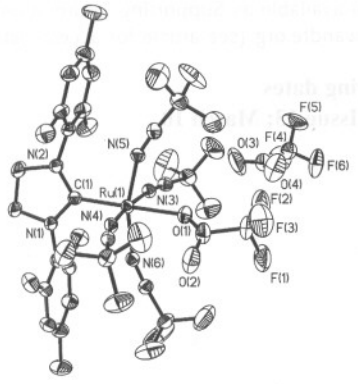


**Every atom counts**: New data for the adsorption chromatographic behavior of single atoms of element 112 confirm a metallic character involved in their interaction with a gold surface, similar to the lighter homologues Zn, Cd, and Hg. The elemental volatility of element 112 is much higher than that of lighter homologues of Group 12 of the periodic table, as empirically deduced from the experimental results.




## Transactinides






**Open sesame**: Novel cationic $Ru^{II}$ complexes with N-heterocyclic carbene ligands (see structure) have been prepared and used as UV-triggerable photoinitiators for ring-opening metathesis polymerization. They may be used for the high-yield synthesis of bulk polymers as well as for surface functionalization. Laser pulse radiolysis and NMR spectroscopy experiments supported by quantum chemical calculations give insight into the initiation mechanism.

## Photochemical ROMP

# Contents




**The issues for March 2008 appeared online on the following dates**
**Issue 10: February 15. · Issue 11: February 22. · Issue 12: March 3. · Issue 13: March 10**

## Service





# Corrigendum

The last sentence in the left column on page 8802 of this Communication should read: "These two β-lactam-resistant bacterial cells contained different kinds of β-lactamases (TEM-1 in plasmid encoded *E. coli* Bl21 and ESBL; SHV-18 in *K. pneumoniae*)." In the Supporting Information on page 1, the enzyme activity was not indicated correctly. The third sentence should read: "β-lactamases were obtained from Biologics Process Development, Inc, CA, USA and Sigma–Aldrich (6–18 units/mg corresponds to the amount of enzyme which hydrolyzes 1 μmol of benzylpenicillin per minute at pH 7.0 and 25 °C or 50–150 units/mg protein by using cephaloridine)."

A Simple and Specific Assay for Real-Time Colorimetric Visualization of β-Lactamase Activity by Using Gold Nanoparticles




*Angew. Chem. Int. Ed.* **2007**, *46*

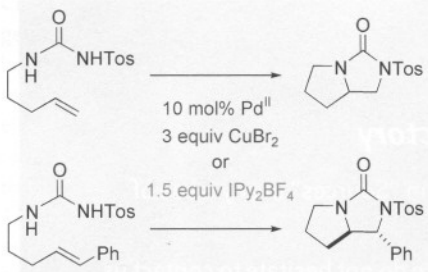
DOI 10.1002/anie.200702773

## Amination

K. Muñiz,* C. H. Hövelmann, E. Campos-Gómez, J. Barluenga,* J. M. González, J. Streuff, M. Nieger

Intramolecular Diamination of Alkenes with Palladium(II)/Copper(II) Bromide and $IPy_2BF_4$: The Role of Halogenated Intermediates

*Chem. Asian J.*
DOI: **10.1002/asia.200700373**



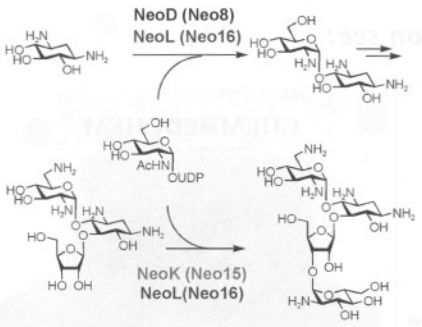

**Complementary procedures** for the diamination of terminal and internal alkenes with tethered ureas and related groups as the nitrogen source provide access to cyclic urea, sulfamide, and guanidine derivatives. Opposite stereochemical pathways were identified for the diamination of terminal alkenes with $IPy_2BF_4$ and under palladium catalysis with the reoxidant $CuBr_2$, but identical ones were found for internal alkenes.

## Biosynthesis

K. Yokoyama, Y. Yamamoto, F. Kudo, T. Eguchi*

Involvement of Two Distinct *N*-Acetylglucosaminyltransferases and a Dual-Function Deacetylase in Neomycin Biosynthesis

*ChemBioChem*
DOI: **10.1002/cbic.200700717**



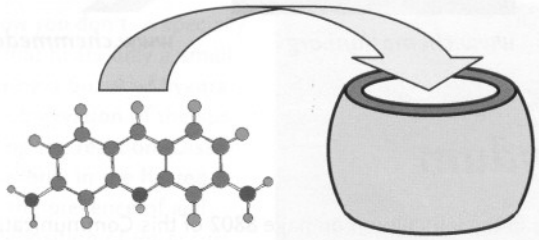

**A new enzyme family**: The glycosylation steps in the biosynthesis of neomycin were clarified through recombinant enzyme assays. NeoD catalyzes the first transglucosaminylation, and NeoK catalyzes the second, while NeoL catalyzes both deacetylations. We found that NeoK and its homologous proteins constitute a novel glycosyltransferase family.

## Host–Guest Complexes

P. Montes-Navajas, A. Corma, H. Garcia*

Complexation and Fluorescence of Tricyclic Basic Dyes Encapsulated in Cucurbiturils

*ChemPhysChem*
DOI: **10.1002/cphc.200700735**



**Encapsulating cucurbiturils:** Tricyclic dyes can be inserted into cucurbiturils to form host–guest complexes (see figure). These complexes vary in stoichiometry, depending on the cucurbituril involved. The stoichiometry of the complex plays a major role in the photophysical behaviour of the dyes.

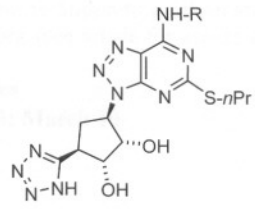
## Receptor Antagonist

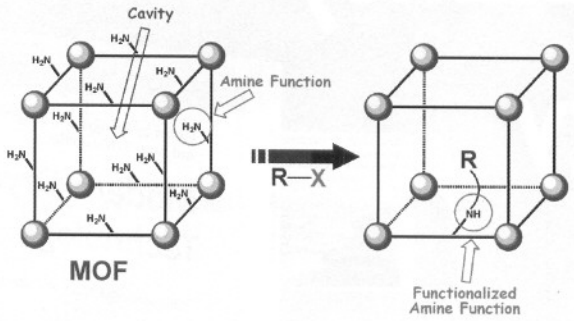
H. Ye, C. Chen, H.-C. Zhang,* B. Haertlein, T. J. Parry, B. P. Damiano, B. E. Maryanoff*

Carba-nucleosides as Potent Antagonists of the Adenosine 5′-Diphosphate (ADP) Purinergic Receptor ($P2Y_{12}$) on Human Platelets

*ChemMedChem*
DOI: **10.1002/cmdc.200700310**

**Antagonizing a key platelet purinergic receptor.** The wide clinical use of clopidogrel has highlighted the importance of platelet ADP receptor ($P2Y_{12}$) antagonists for preventing adverse cardiovascular events. We synthesized a series of novel carba-nucleosides and examined their usefulness as $P2Y_{12}$ antagonists. Some tetrazole derivatives were high-affinity receptor antagonists and potent inhibitors of human platelet aggregation.






### Post-Synthetically Modified MOFs

J. S. Costa, P. Gamez,* C. A. Black, O. Roubeau, S. J. Teat, J. Reedijk

Chemical Modification of a Bridging Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure

A new metal–organic framework with amino groups oriented inside the pores has been synthesized. The post-synthetic modification of the cavities in this MOF with two different functionalities is for the first time clearly evidenced by X-ray crystallography. The cavities of the MOF can be transformed without modifying the original 3D structure of the MOF.

*Eur. J. Inorg. Chem.*
DOI: **10.1002/ejic.200800002**

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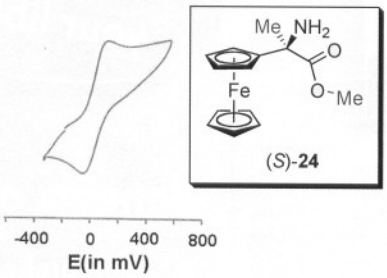
Are α-ferrocenyl-α-amino esters stable? The answer is yes provided that the α-carbon is tetrasubstituted and that very mild reaction conditions are involved in their generation. Thus, the (*S*) enantiomer of methyl α-ferrocenylalaninate **24**, prepared in around 90% *ee* from 2-ferrocenylpropene, is a stable compound that can be stored for prolonged periods of time without appreciable decomposition.




### Ferrocenyl Amino Acids

R. M. Moreno, M. Catasús, C. López, A. Moyano*

Enantiocontrolled Preparation of the First Stable α-Ferrocenylalanine Derivatives

*Eur. J. Org. Chem.*
DOI: **10.1002/ejoc.200800029**

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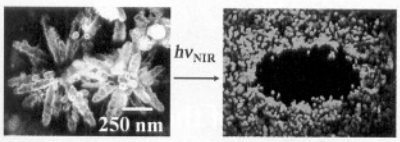


**Gold–silver therapy**: Core-free $Au_xAg_{1-x}$ nanostructured dendrites have been developed that show absorption in the NIR region, exhibiting potential as photothermal therapeutic agents. An effective photothermal capability was found in hollow $Au_{0.3}Ag_{0.7}$ nanostructured dendrites treated with A549 lung cancer cells.

### Gold–Silver Nanostructures

K.-W. Hu, C.-C. Huang, J.-R. Hwu, W.-C. Su, D.-B. Shieh, C.-S. Yeh*

A New Photothermal Therapeutic Agent: Core-Free Nanostructured $Au_xAg_{1-x}$ Dendrites

*Chem. Eur. J.*
DOI: **10.1002/chem.200800114**

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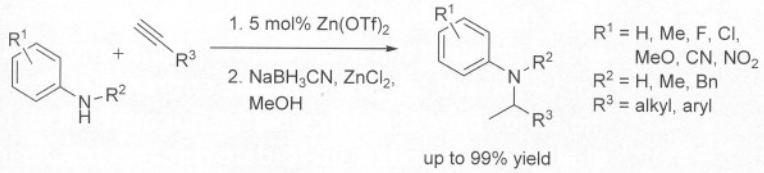


**Zinc green**: Easily available zinc salts are active and practical catalysts for the intermolecular hydroamination of terminal alkynes with anilines. The reactions proceed in the presence of $Zn(OTf)_2$ with excellent regioselectivity (>99%) and with high yields. Moreover, difficult functional groups such as nitro and cyano substituents are tolerated by the catalyst.

### Homogeneous Catalysis

K. Alex, A. Tillack, N. Schwarz, M. Beller*

General Zinc-Catalyzed Intermolecular Hydroamination of Terminal Alkynes

*ChemSusChem*
DOI: **10.1002/cssc.200700160**