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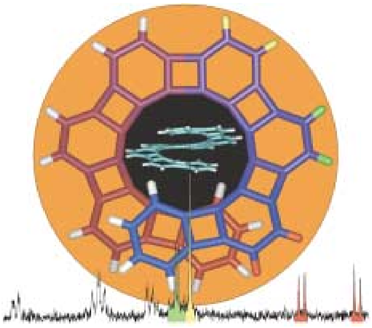
Pages 3071–3296

COVER PICTURE

The cover picture shows the molecular structure of the helically extended angular [8]phenylene. An unprecedented cobalt-catalyzed triple cyclization of an appropriate nonayne was successful in assembling the largest crystallographically characterized helical phenylene (heliphene). Its properties are intriguing; the heliphene is unusually configurationally labile and has a strongly attenuated bathochromic increment in the UV spectrum, shielding of the terminal rings as a result of spatial overlap, and alternating ring-current intensities along the angular frame. The X-ray crystallographic data detail the helical and σ–π distortive features. Most surprisingly, the remarkable flexibility of the heliphene provided an unusually low barrier ($\Delta G^{\neq}$ (−4.5 °C) = 13.4 ± 0.4 kcal mol^{-1}) for enantiomerization. The ^{1}H NMR spectrum was consistent with the alternation of cyclohexatrienoid and aromatic character; the terminal rings are the most diatropic and the penultimate ones the least. Further details about this chiral polycyclic benzenoid hydrocarbon are described by K. P. C. Vollhardt, et al. on p 3227 ff.

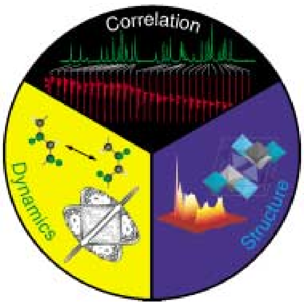


REVIEWS

Contents

Broad, uninterpretable bands in solid-state NMR spectra are a thing of the past. Modern implementations of methods such as magic-angle spinning, cross polarization, hetero- and homonuclear decoupling and recoupling, etc., allow one to obtain multidimensional correlation spectra with a resolution as good as that of liquid-state NMR spectra. In addition, anisotropy parameters characteristic of solids are accessible.

Angew. Chem. **2002**, *114*, 3224–3259



D. D. Laws, H.-M. L. Bitter,
A. Jerschow* 3096–3129

Solid-State NMR Spectroscopic Methods in Chemistry

Keywords: multipulse techniques · NMR spectroscopy · solid-state structures · spin-spin coupling · structure elucidation

Get your teeth into this! Calcium phosphates such as polycrystalline fluoroapatite (top picture) are common minerals which can also be formed in living organisms. This process (biomineralization) is not yet fully understood. A thorough understanding of the structure, formation, and resolution of biominerals should lead to improved treatment of, for example, bone diseases by use of endoprostheses (bottom picture). The significance of biological tissues containing calcium phosphates is reviewed from a chemical point of view, and explained with examples.

S. V. Dorozhkin, M. Epple* 3130–3146

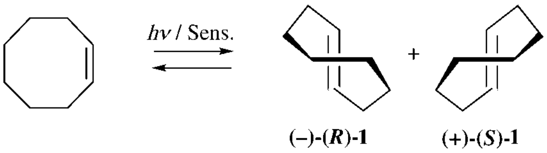
Biological and Medical Significance of Calcium Phosphates

Keywords: bioinorganic chemistry · biomaterials · biomimetic synthesis · biomineralization · materials science

Angew. Chem. **2002**, *114*, 3260–3277

MINIREVIEW

Researching the origins of chirality leads to a strong interest in selective and atom-economic syntheses of enantiomerically pure target molecules from non-chiral starting materials. New developments in the field of asymmetric photochemistry (as an example see the photochemical *cis–trans* isomerization in which the chiral cyclooctene **1** is formed; Sens = sensitizer) and photochirogenesis are described with special emphasis on absolute asymmetric synthesis.



A. G. Griesbeck,*
U. J. Meierhenrich* 3147–3154

Asymmetric Photochemistry and Photochirogenesis

Keywords: asymmetric synthesis · chirality · photochemistry · photochirogenesis

Angew. Chem. **2002**, *114*, 3279–3286

VIPs

The following communications are "Very Important Papers" in the opinion of two referees. They will be published shortly (those marked with a diamond will be published in the next issue). Short summaries of these articles can be found on the *Angewandte Chemie* homepage at the address http://www.angewandte.org

Metallabenzenes and Valence Isomers: Synthesis and Characterization of a Platinabenzene	V. Jacob, T. J. R. Weakley, M. M. Haley*	◆
The Total Synthesis of Diazonamide A	K. C. Nicolaou,* M. Bella, D. Y.-K. Chen, X. Huang, T. Ling, S. A. Snyder	◆
Syntheses and Crystal Structures of the New Ag-S Clusters $[Ag_{70}S_{16}(SPh)_{34}(PhCO_2)_4(\text{triphos})_4]$ and $[Ag_{188}S_{94}(PnPr_3)_{30}]$	X.-J. Wang, T. Langetepe, C. Persau, B.-S. Kang, D. Fenske*	
Protonated Benzene: IR Spectrum and Structure of $C_6H_7^+$	N. Solcà, O. Dopfer*	
Single-Step Assembly of a C_2-Symmetrical Palladium(IV) Spirocyclic Complex	Y. Yamamoto,* T. Ohno, K. Itoh	
Changeable Pore Sizes Allowing Effective and Specific Recognition by a Molybdenum-Oxide Based "Nanosponge": En Route to Sphere-Surface and Nanoporous-Cluster Chemistry	A. Müller,* E. Krickemeyer, H. Bögge, M. Schmidtmann, S. Roy, A. Berkle	

ESSAY

A great researcher, communicator, and human being: Not only was Max Perutz (see picture) a very gifted chemist who shared the Nobel prize for chemistry with John Kendrew in 1962 for their pioneering work on the elucidation of the structures of hemoglobin and myoglobin, he was also the chairman of the extremely successful Laboratory of Molecular Biology. Above all, he was magnanimous and extraordinarily generous, according everyone the same level of respect.

Angew. Chem. **2002**, *114*, 3287 – 3298

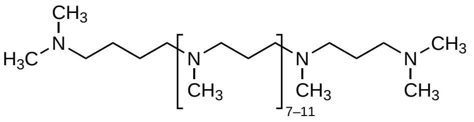
J. M. Thomas* .... 3155 – 3166

The Scientific and Humane Legacy of Max Perutz (1914 – 2002)

Keywords: history of science · Nobel Prize · obituary · Perutz, Max

HIGHLIGHT

Directed precipitation of silicic acid during the formation of diatom cell walls is promoted by polyamines (see picture) and peptides. These species-specific organic matrices, which direct the biomineralization process to amorphous SiO_2, are accessible only after dissolution of the silica cell wall with hydrogen fluoride.



Angew. Chem. **2002**, *114*, 3299 – 3301

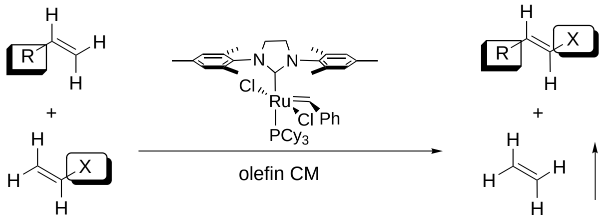
G. Pohnert* .... 3167 – 3169

Biomineralization in Diatoms Mediated through Peptide- and Polyamine-Assisted Condensation of Silica

Keywords: biomineralization · biosynthesis · diatoms · enzymes · silicates

COMMUNICATIONS

Stereoselective and chemoselective olefin cross metathesis can be viewed as a highly selective and efficient set of reactions that provide the same products as would selective C–H activation and allylic oxidation (see scheme for an example). More active catalyst systems will provide an efficient process to functionalized products from readily available olefins. Cy = cyclohexyl.



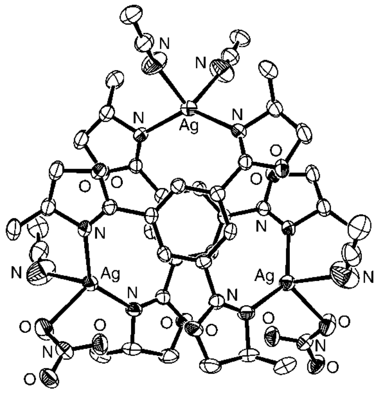
Angew. Chem. **2002**, *114*, 3303 – 3306

A. K. Chatterjee,
R. H. Grubbs* .... 3171 – 3174

Formal Vinyl C–H Activation and Allylic Oxidation by Olefin Metathesis

Keywords: alkenes · C–H activation · cross-coupling · metathesis

Self-recognition of ligand chirality leads to the completely stereospecific self-assembly of a propeller-shaped supramolecular capsule induced by a rigid chiral tris(oxazoline) acting as a tris-monodentate ligand and Ag^I metal ions having a tetrahedral coordination geometry (the structure of one helical complex is shown).



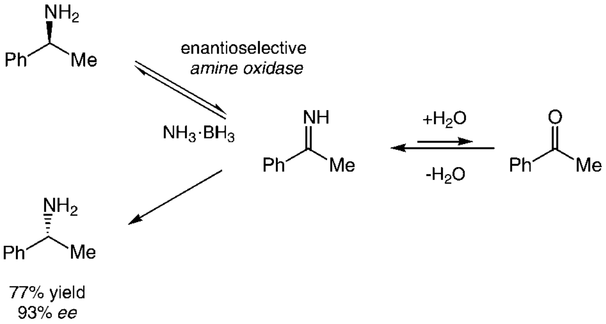
Angew. Chem. **2002**, *114*, 3306 – 3309

H.-J. Kim, D. Moon, M. S. Lah,
J.-I. Hong* .... 3174 – 3177

An Enantiomerically Pure Propeller-Shaped Supramolecular Capsule Based on the Stereospecific Self-Assembly of Two Chiral Tris(oxazoline) Ligands around Three Ag^I Ions

Keywords: chirality · self-assembly · silver · supramolecular chemistry

Both the catalytic activity and enantioselectivity of the amine oxidase used in the deracemization of D,L-α-methylbenzylamine (see scheme) have been enhanced by in vitro evolution methods to give α-methylbenzyamine in 77% yield and 93% *ee*.



Angew. Chem. **2002**, *114*, 3309–3312

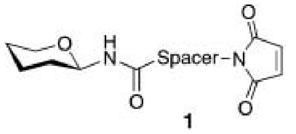
M. Alexeeva, A. Enright, M. J. Dawson, M. Mahmoudian, N. J. Turner* 3177–3180

Deracemization of α-Methylbenzylamine Using an Enzyme Obtained by In Vitro Evolution

Keywords: amino acids · deracemization · enzyme catalysis · reduction

---

A new tool for the high-throughput study of carbohydrate–protein interactions: Maleimide-linked carbohydrates (e.g. **1**) were immobilized on thiol-derivatized glass slides, and the microspots were probed with fluorescein-labeled lectins (see picture). The binding of lectins to the carbohydrates on the slide depends on the concentration of the immobilized carbohydrates and on the length of the tethers.



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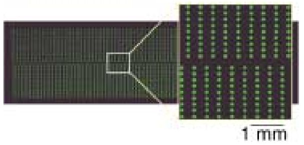

Angew. Chem. **2002**, *114*, 3312–3314

S. Park, I. Shin* 3180–3182

Fabrication of Carbohydrate Chips for Studying Protein–Carbohydrate Interactions

Keywords: carbohydrate chips · fluorescence · glycoconjugates · high-throughput screening · proteins

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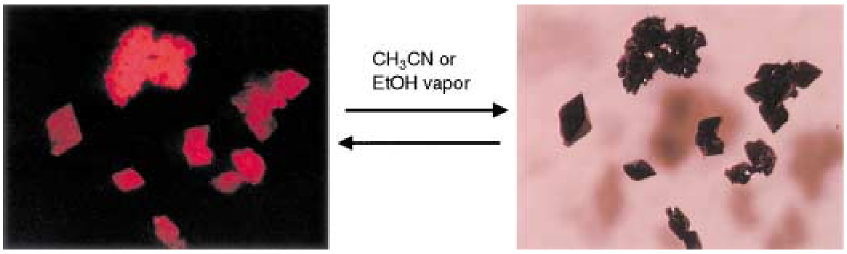
Remarkable vapochromic effects are observed in a dinuclear platinum(II) complex, where changes in luminescence are facilitated in the presence of solvated organic molecules, such as acetonitrile and ethanol (see scheme).



Angew. Chem. **2002**, *114*, 3315–3317

M. Kato,* A. Omura, A. Toshikawa, S. Kishi, Y. Sugimoto 3183–3185

Vapor-Induced Luminescence Switching in Crystals of the *Syn* Isomer of a Dinuclear (Bipyridine)platinum(II) Complex Bridged with Pyridine-2-Thiolate Ions

Keywords: luminescence · platinum · sensors · structure elucidation · vapochromism

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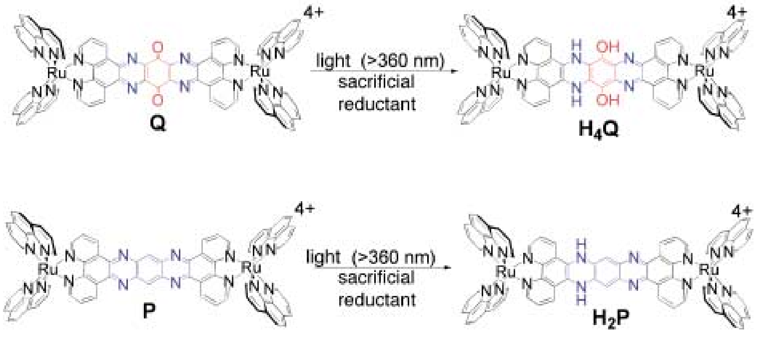
Reversible storage of up to two or four electrons is possible in complexes **P** and **Q**, respectively, upon irradiation with visible light in the presence of triethylamine. This ability could lead to photocatalysts capable of concerted multielectron reduction of important substrates.



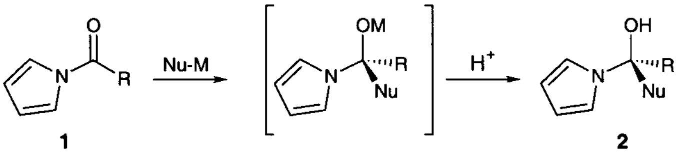
Angew. Chem. **2002**, *114*, 3317–3319

R. Konduri, H. Ye, F. M. MacDonnell,* S. Serroni, S. Campagna, K. Rajeshwar 3185–3187

Ruthenium Photocatalysts Capable of Reversibly Storing up to Four Electrons in a Single Acceptor Ligand: A Step Closer to Artificial Photosynthesis

Keywords: bridging ligands · multielectron storage · photochemistry · ruthenium · spectroelectrochemistry

Sufficiently stable intermediates formed in the reaction of *N*-acylpyrroles (**1**) with hydride and Grignard reagents can undergo further synthetic transformations and chromatographic purification to enable the generation of pyrrolecarbinols **2** in 76–95% yields [Eq. (1)].



(1)

Angew. Chem. **2002**, *114*, 3320–3323

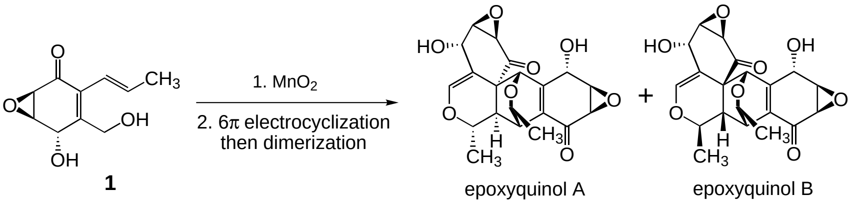
D. A. Evans,* G. Borg,
K. A. Scheidt 3188–3191

Remarkably Stable Tetrahedral Intermediates: Carbinols from Nucleophilic Additions to *N*-Acylpyrroles

Keywords: carbinols · nitrogen heterocycles · nucleophilic addition · reaction intermediates · reaction mechanisms

---

A highly stereoselective $HfCl_4$-mediated Diels–Alder reaction of furan and the chiral acrylate ester of Corey's auxiliary to subsequently give **1**, and the realization of the postulated biosynthetic pathway for the construction of epoxyquinols A and B, namely, oxidative 6π electrocyclization, followed by Diels–Alder reaction of the unprotected monomer are the key steps in the asymmetric total synthesis of (+)-epoxyquinols A and B.



Angew. Chem. **2002**, *114*, 3324–3326

M. Shoji, J. Yamaguchi, H. Kakeya,
H. Osada, Y. Hayashi* 3192–3194

Total Synthesis of (+)-Epoxyquinols A and B

Keywords: asymmetric synthesis · Diels–Alder reaction · dimerization · epoxyquinol · total synthesis

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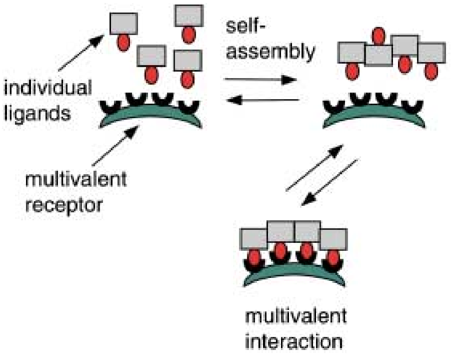
Size is important: Noncovalent nanoparticles are formed by the self-assembly of glycodendrimers containing both a ligand and a self-assembling moiety. Particle size reaches an optimum at the second and third generation, larger dendritic species show less efficient self-assembly. It is the nanoparticles, not the individual molecules, that governs their potency as polyvalent receptor blockers (see scheme), both in vitro and in vivo.



Angew. Chem. **2002**, *114*, 3327–3330

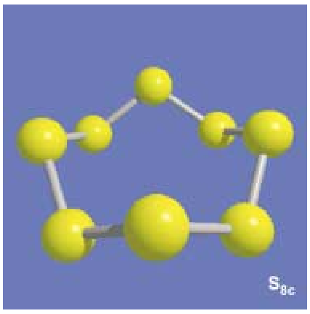
G. Thoma,* A. G. Katopodis,
N. Voelcker, R. O. Duthaler,
M. B. Streiff 3195–3198

Novel Glycodendrimers Self-Assemble to Nanoparticles which Function as Polyvalent Ligands In Vitro and In Vivo

Keywords: aggregation · carbohydrates · dendrimers · polyvalence · supramolecular chemistry

---

A challenging problem is the structure determination of liquid sulfur. By using a quantum thermodynamical model the authors found that liquid sulfur below the λ-transition temperature is predominantly built upon cyclic structures S_{8c} (see structure) accompanied by trace amounts of other ring structures such as S_{7c}, S_{6c}, S_{9c}, S_{10c}, and S_{12c}.

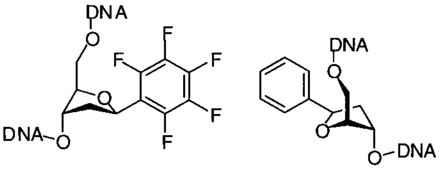


Angew. Chem. **2002**, *114*, 3331–3335

R. Ludwig,* J. Behler, B. Klink,
F. Weinhold 3199–3202

Molecular Composition of Liquid Sulfur

Keywords: ab initio calculations · density functional calculations · liquids · sulfur · structure elucidation



The inverse quadrupolar moments of the phenyl and pentafluorophenyl residues in the non-hydrogen-bonded, artificial base pair shown here promotes strong intramolecular stacking interactions in oligonucleotide duplexes. The greater the number of natural base pairs that are replaced by this novel pair, the higher the thermodynamic stability of the resulting oligonucleotide duplex if they are arranged in an alternating fashion.

Angew. Chem. **2002**, *114*, 3335–3338

G. Mathis, J. Hunziker* 3203–3205

Towards A DNA-Like Duplex without Hydrogen-Bonded Base Pairs

Keywords: DNA recognition · DNA structures · nucleobases · oligonucleotides · pi interactions

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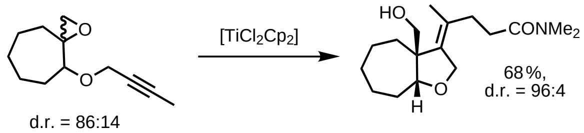
Intramolecular C–C bond formation based on a titanocene-catalyzed epoxide ring opening selectively leads to tri- and tetrasubstituted olefins (see scheme). This represents an excellent method for the otherwise difficult synthesis of such compounds.



Angew. Chem. **2002**, *114*, 3341–3343

A. Gansäuer,* M. Pierobon,
H. Bluhm 3206–3208

Stereoselective Synthesis of Tri- and Tetrasubstituted Olefins by Tandem Cyclization Addition Reactions Featuring Vinyl Radicals

Keywords: alkenes · diastereoselectivity · domino reactions · radical reactions · titanium

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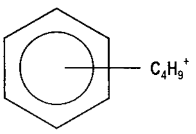

Constantly in motion: The attack of the *tert*-butyl cation on benzene gives a π complex whose stability is similar to that of the σ complex. The frequently employed notation for real or proposed π complexes (see picture) has now to be interpreted as indicating the mobility of the cation along the ring periphery: the position of the cation above the delocalized π-electron belt cannot be established.

Angew. Chem. **2002**, *114*, 3343–3346

D. Heidrich* 3208–3210

Do Isopropyl and *tert*-Butyl Cations Form π Complexes with Benzene?

Keywords: ab initio calculations · arenes · aromatic substitution · carbocations · electrophilic substitution

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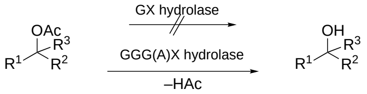


A single amino acid pattern (GGG(A)X motif) in hydrolases controls their activity towards tertiary alcohols. Consequently, a range of active lipases and esterases which catalyze the efficient conversion of acetates of different tertiary alcohols (see scheme) and thereby facilitate access to this class of building blocks for organic synthesis, flavors, and fragrances was identified by sequence comparison. Hydrolases bearing an alternative GX motif were inactive.

Angew. Chem. **2002**, *114*, 3338–3341

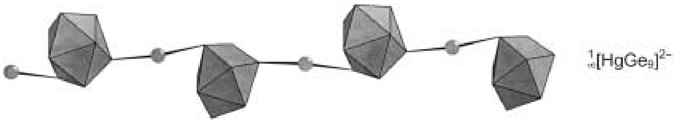
E. Henke, J. Pleiss,
U. T. Bornscheuer* 3211–3213

Activity of Lipases and Esterases towards Tertiary Alcohols: Insights into Structure–Function Relationships

Keywords: biotransformation · enzyme catalysis · esterases · lipases · molecular modeling · tertiary alcohols

---

Teaching an old ion new tricks: Zintl ions can be used as building blocks to construct complex structures with interesting electronic properties. The reaction of Ge_9 ions with elementary mercury leads to the unusual polymer $^1_\infty[HgGe_9]^{2-}$ (see picture) which is structurally characterized in the form of its K[2.2.2]cryptand salt.



Angew. Chem. **2002**, *114*, 3352–3355

A. Nienhaus, R. Hauptmann,
T. F. Fässler* 3213–3215

$^1_\infty[HgGe_9]^{2-}$—A Polymer with Zintl Ions as Building Blocks Covalently Linked by Heteroatoms

Keywords: cluster compounds · germanium · mercury · polymers · Zintl anions

1433-7851/02/4117-3078 $ 20.00+.50/0

Single-molecule sequencing comes into sight: exonuclease III of *E. coli* has been shown to perform the processive sequential hydrolysis of double-stranded DNA with one strand being completely rhodamine-labeled at each pyrimidine base. The performance of the exceptional enzyme was studied by steady-state kinetic analysis based on quantitative fragment-length determination.

Angew. Chem. **2002**, *114*, 3350 – 3352

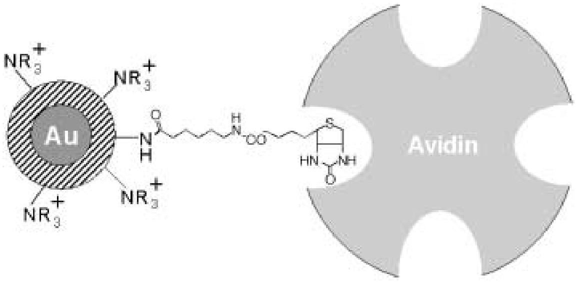
S. Brakmann,*
S. Löbermann .... 3215 – 3217

A Further Step towards Single-Molecule Sequencing: *Escherichia coli Exonuclease* III Degrades DNA that is Fluorescently Labeled at Each Base Pair

Keywords: exonuclease • fluorescence • nucleotides • phosphoric ester hydrolysis • sequence determination

---

An ambitious goal in the area of nanobiosciences is to combine the functionality and stability of nanostructured inorganic solids with the structural variety and the self-organizing abilities of biochemical molecules. How the ligand shell of nanoparticles needs to be built up to achieve a stable and specific conjugation with biological molecules and to coordinate the chemical properties of nanoparticles and biomolecules is exemplified for gold nanoparticles conjugated with avidin (see picture).



Angew. Chem. **2002**, *114*, 3346 – 3350

A. Schroedter, H. Weller* .. 3218 – 3221

Ligand Design and Bioconjugation of Colloidal Gold Nanoparticles

Keywords: colloids • conjugation • nanostructures • sol – gel processes • supramolecular chemistry

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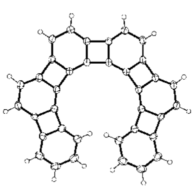
Two plus two plus two times two: A double cobalt-catalyzed cycloisomerization was used to convert appropriate hexaynes into hydrocarbons **1** and **2**. Their X-ray structures reveal pronounced helical topologies, but their barriers to enantiomerization are low compared to those of the helicenes.



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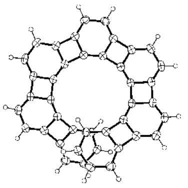


2

Angew. Chem. **2002**, *114*, 3357 – 3361

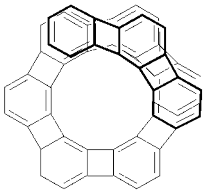
S. Han, A. D. Bond, R. L. Disch,
D. Holmes, J. M. Schulman, S. J. Teat,
K. P. C. Vollhardt,*
G. D. Whitener .... 3223 – 3227

Total Syntheses and Structures of Angular [6]- and [7]Phenylene: The First Helical Phenylenes (Heliphenes)

Keywords: antiaromaticity • cyclotrimerization • helical structures • phenylenes • small ring systems

---

Six of the final cyclobutadiene rings in angular [8]phenylene and [9]phenylene (**1**) are closed in an unprecedented cobalt-catalyzed triple cyclization of appropriate nonaynes. These strained products are the largest known phenylenes and display unusual configurational lability. Their synthesis has enabled a first estimate of the properties of the hypothetical polyheliphene.



1

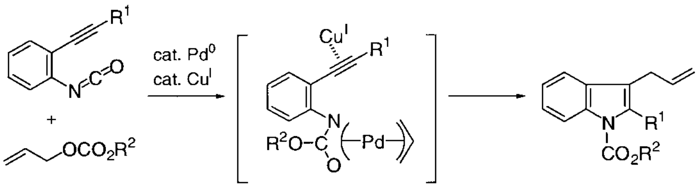
Angew. Chem. **2002**, *114*, 3361 – 3364

S. Han, D. R. Anderson, A. D. Bond,
H. V. Chu, R. L. Disch, D. Holmes,
J. M. Schulman, S. J. Teat,
K. P. C. Vollhardt,*
G. D. Whitener .... 3227 – 3230

Total Syntheses of Angular [7]-, [8]-, and [9]Phenylene by Triple Cobalt-Catalyzed Cycloisomerization: Remarkably Flexible Heliphenes

Keywords: antiaromaticity • cyclotrimerization • helical structures • phenylenes • small ring systems

Carboamination of alkynes is catalyzed by a Pd^0-Cu^I bimetallic species. The Pd^0 species act as a precursor for a π-allylpalladium intermediate while the Cu^I centers behave as a Lewis acid for C≡C bonds. This catalyst allows the synthesis of indoles from isocyanates and allyl carbonates (see scheme).



Angew. Chem. **2002**, *114*, 3364–3367

S. Kamijo, Y. Yamamoto* ... 3230–3233

A New Pd^0-Cu^I Bimetallic Catalyst for the Synthesis of Indoles from Isocyanates and Allyl Carbonates

Keywords: carboamination · copper · homogeneous catalysis · indoles · palladium

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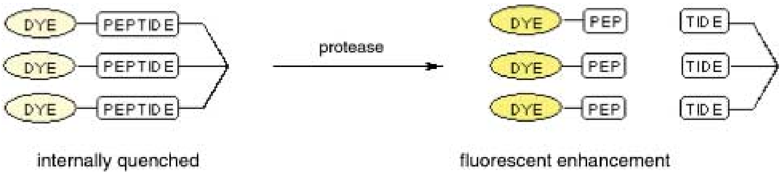
A way to reduce the synthetic work associated with FRET-based techniques for protease analysis and characterization is shown here. Protease-mediated cleavage of fluorescent peptides attached to dendrimers results in large increases in fluorescence (see scheme).



Angew. Chem. **2002**, *114*, 3367–3370

J. M. Ellard, T. Zollitsch, W. J. Cummins, A. L. Hamilton, M. Bradley* 3233–3236

Fluorescence Enhancement through Enzymatic Cleavage of Internally Quenched Dendritic Peptides: A Sensitive Assay for the AspN Endoproteinase

Keywords: dendrimers · fluorescence · lyases · peptides · solid-phase synthesis

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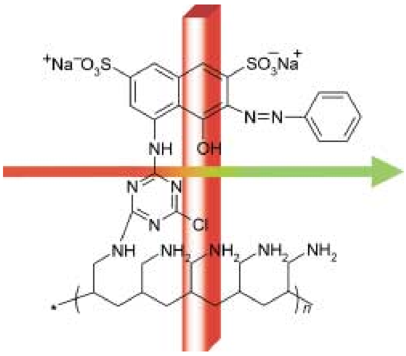
A combination of electrostatic interactions and covalent bonding is used to form films with low-molecular-weight chromophores by a layer-by-layer deposition process. Using a common, commercially available red dye, this deposition process results in noncentrosymmetric films (see scheme) that exhibit second-harmonic generation (red →green), with $\chi^{(2)}$ values as large as 11.3×10^{-9} esu, that is, six times that of quartz.



Angew. Chem. **2002**, *114*, 3370–3372

K. E. Van Cott,* M. Guzy, P. Neyman, C. Brands, J. R. Heflin, H. W. Gibson, R. M. Davis 3236–3238

Layer-By-Layer Deposition and Ordering of Low-Molecular-Weight Dye Molecules for Second-Order Nonlinear Optics

Keywords: chromophores · nonlinear optics · self-assembly · thin films

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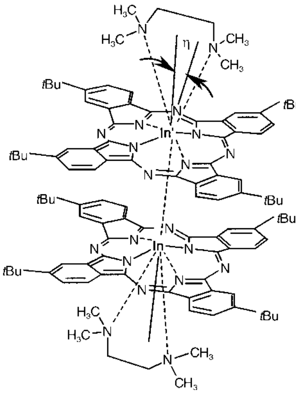
Enhanced nonlinear optical response is observed in a soluble dimeric indium–phthalocyanine (Pc) complex stabilized as a Lewis base adduct. The Pc moieties are tilted 14.5° from an axis connecting the In centers, which are out of plane with respect to the Pc macrocycles (see diagram). The In–In separation was calculated to be 3.24 Å by using extended X-ray absorption fine structure (EXAFS) spectroscopy.



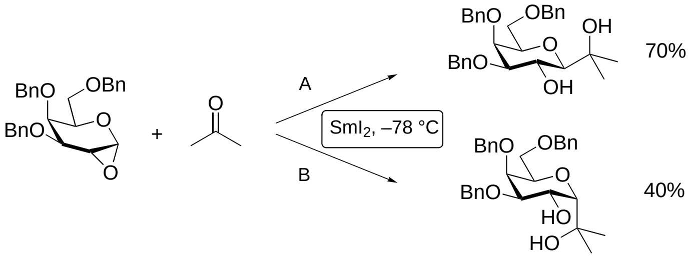
Angew. Chem. **2002**, *114*, 3373–3376

Y. Chen, M. Barthel, M. Seiler, L. R. Subramanian, H. Bertagnolli, M. Hanack* 3239–3242

An Axially Bridged Indium Phthalocyanine Dimer with an In–In Bond

Keywords: dimerization · EXAFS spectroscopy · indium · nonlinear optics · phthalocyanines

Sugar mimics: 1,2-anhydro sugars can be cross-coupled with aldehydes and ketones under very mild conditions and using a wide range of protecting groups to give C-glycosides in good yield in a radical reaction mediated by SmI_2 (see scheme; A = no proton source, B = in the presence of water).



Angew. Chem. **2002**, *114*, 3376–3380

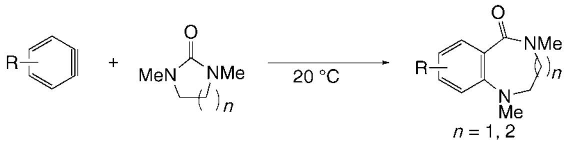
J. L. Chiara,* E. Sesmilo 3242–3246

Samarium Diiodide-Mediated Reductive Coupling of Epoxides and Carbonyl Compounds: A Stereocontrolled Synthesis of C-Glycosides from 1,2-Anhydro Sugars

Keywords: C-glycosides · electron transfer · radical reactions · samarium

---

Seven- and eight-membered heterocycles are formed straightforwardly, in modest to high yields in this novel addition reaction of ureas to arynes (see scheme; R = alkoxy, alkyl, aryl). The reaction of a *meta*-substituted aryne affords the product with perfect regioselectivity, whereas a *para*-substituted aryne gives a mixture of regioisomers.



Angew. Chem. **2002**, *114*, 3381–3383

H. Yoshida, E. Shirakawa,* Y. Honda,
T. Hiyama* 3247–3249

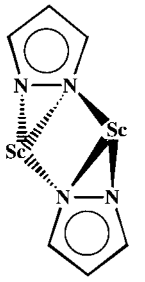
Addition of Ureas to Arynes: Straightforward Synthesis of Benzodiazepine and Benzodiazocine Derivatives

Keywords: arynes · nitrogen heterocycles · regioselectivity · ureas

---

New pyrazolate ligation modes continue to be uncovered: $[Sc_2(Ph_2pz)_6]$ (**1**; Ph_2pz = 3,5-diphenylpyrazolate) displays the new μ-η^2:η^1 binding mode and $[Nd(\eta^2\text{-}Me_2pz)_2(\eta^1\text{-}Me_2pz)(Me_2pzH)_2py)]$ (**2**; Me_2pz = 3,5-dimethylpyrazolate; py = pyridine) displays the first example of unidentate η^1(N) coordination of a pyrazolate to a lanthanide ion.

Angew. Chem. **2002**, *114*, 3383–3385



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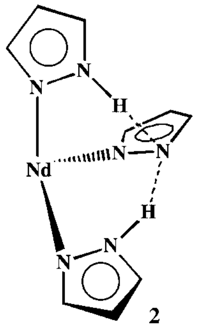


2

G. B. Deacon,* C. M. Forsyth, A. Gitlits,
R. Harika, P. C. Junk, B. W. Skelton,
A. H. White 3249–3251

Pyrazolate Coordination Continues To Amaze—The New μ-η^2:η^1 Binding Mode and the First Case of Unidentate Coordination to a Rare Earth Metal

Keywords: lanthanides · N ligands · neodymium · scandium

$^1\Delta$-O_2 can now be made safely and efficiently from gas–solid reactions between alkali-metal peroxides and hydrogen halides [Eq. (1)]. This method avoids the liquid-phase quenching and instability problems associated with the hydrogen peroxide/chlorine system.

$$Na_2O_2 + 2\,HCl \longrightarrow H_2O + 2\,NaCl + 1/2\,O_2\ (^1\Delta_g) \qquad (1)$$

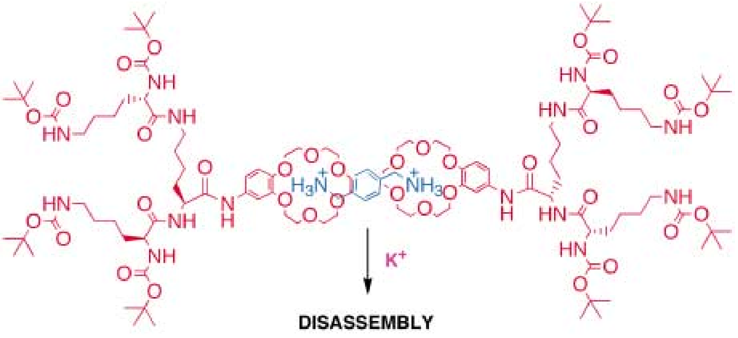
Angew. Chem. **2002**, *114*, 3386–3388

A. J. Alfano, K. O. Christe* 3252–3254

Singlet Delta Oxygen Production from a Gas–Solid Reaction

Keywords: hydrogen halides · oxygen · peroxides · quenching · singlet delta oxygen

Supramolecular dendrimers have been assembled in solution by using the interactions between dendritic branches functionalized with [18]crown-6 and a bis-ammonium cation as a template (see scheme). Disassembly is triggered by the addition of K^+ ions, which enables controlled release of the encapsulated template.



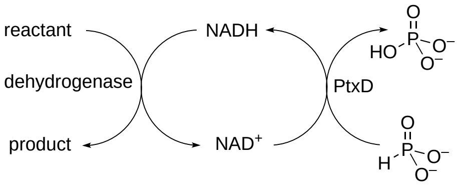
Angew. Chem. **2002**, *114*, 3388 – 3391

G. M. Dykes, D. K. Smith,*
G. J. Seeley . . . . 3254 – 3257

Controlled Release of a Dendritically Encapsulated Template Molecule

Keywords: crown compounds • dendrimers • NMR spectroscopy • self-assembly • supramolecular chemistry

The highly thermodynamically favorable oxidation of phosphite to phosphate by phosphite dehydrogenase (PtxD) makes the enzyme useful for cofactor regeneration (see figure). Deuterium exchange in D_2O provides labeled phosphite for the preparation of deuterated products.



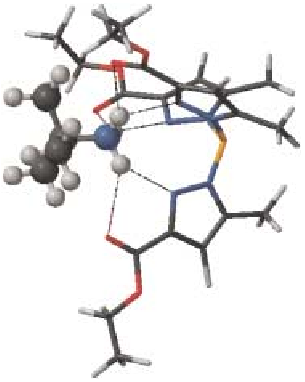
Angew. Chem. **2002**, *114*, 3391 – 3393

J. M. Vrtis, A. K. White, W. W. Metcalf,
W. A. van der Donk* . . . . 3257 – 3259

Phosphite Dehydrogenase: A Versatile Cofactor-Regeneration Enzyme

Keywords: cofactors • enzyme catalysis • isotopic labeling • nucleotides

The ubiquitous tris(pyrazolyl)borate family of ligands can recognize more than metal cations! Host – guest complexes between elaborated tris(pyrazolyl)borate ligands and protonated amines (see picture) and cationic octahedral metal complexes are described. The latter is an example of an alternative bio-inspired paradigm, in which the guest is preorganized to promote recognition, rather than the host.



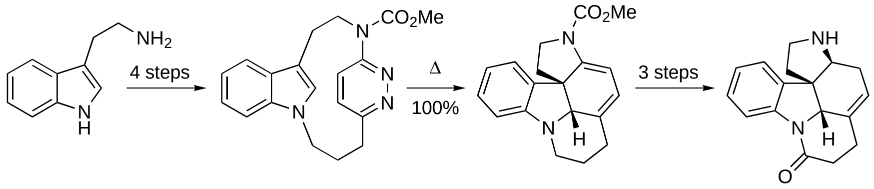
Angew. Chem. **2002**, *114*, 3393 – 3395

B. S. Hammes, X. Luo, M. W. Carrano,
C. J. Carrano* . . . . 3259 – 3261

Guest Preorganization: An Alternative “Bioinspired” Paradigm in Host – Guest Chemistry

Keywords: cooperative effects • host – guest systems • preorganization • supramolecular chemistry • pyrazolylborates

(±)-Strychnine in 12 easy steps! This concise synthesis involves the construction of a [3.3]cyclophane and its transannular inverse-electron-demand Diels – Alder reaction to afford a pentacycle quantitatively (see scheme), which is rapidly converted into Rawal’s key ABCEG intermediate; thus (±)-strychnine can be synthesized from tryptamine in only 12 steps.



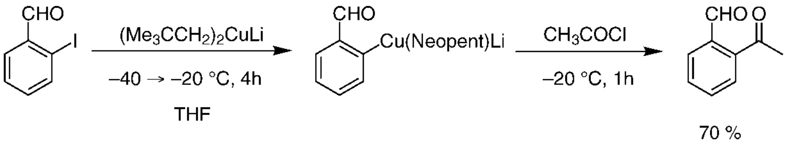
Angew. Chem. **2002**, *114*, 3395 – 3396

G. J. Bodwell,* J. Li . . . . 3261 – 3262

A Concise Formal Total Synthesis of (±)-Strychnine by Using a Transannular Inverse-Electron-Demand Diels – Alder Reaction of a [3](1,3)Indolo[3](3,6)pyridazinophane

Keywords: cycloaddition • cyclophanes • heterocycles • natural products • pericyclic reaction

Even aldehyde and ketone functions are tolerated in mixed organocuprates prepared by copper–halogen exchange using $(Me_3CCH_2)_2CuLi$ ($Neopent_2CuLi$) or $(PhMe_2CCH_2)_2CuLi$ ($Neophyl_2CuLi$). The steric hindrance of the neopentyl and neophyl groups is essential to ensure the chemoselectivity of the reaction (see scheme), and therefore allows a general preparation of polyfunctionalized organocuprates.



Angew. Chem. **2002**, *114*, 3397–3399

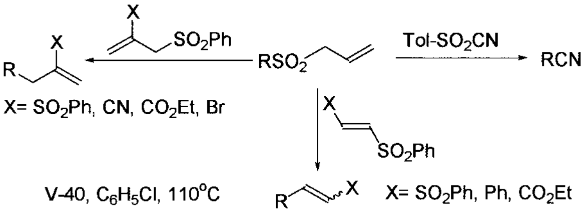
C. Piazza, P. Knochel* 3263–3265

Sterically Hindered Lithium Dialkylcuprates for the Generation of Highly Functionalized Mixed Cuprates through a Halogen–Copper Exchange

Keywords: chemoselectivity • cuprates • halides • metalation • nucleophilic addition

---

Primary alkyl radicals are generated highly efficiently and reliably from alkyl allyl sulfone precursors. The latter are effective in tin-free radical C–C-bond formations, including cyanation, vinylation, and allylation (see scheme; V-40 = 1,1′-azobis(cyclohexane-1-carbonitrile).



Angew. Chem. **2002**, *114*, 3399–3401

S. Kim,* C. J. Lim 3265–3267

Tin-Free Radical-Mediated C–C-Bond Formations with Alkyl Allyl Sulfones as Radical Precursors

Keywords: allylation • C–C coupling • radical reactions • sulfones

---

Switching on chirality: Reversible catenation allows switching between achiral, planar, Pd^{II}-linked rings containing a pentakis(*m*-phenylene) unit and a chiral, double-helical conformation of the catenane (see picture). Molecular chirality is induced in the catenane by an ancillary chiral unit on the metal.

Angew. Chem. **2002**, *114*, 3403–3406

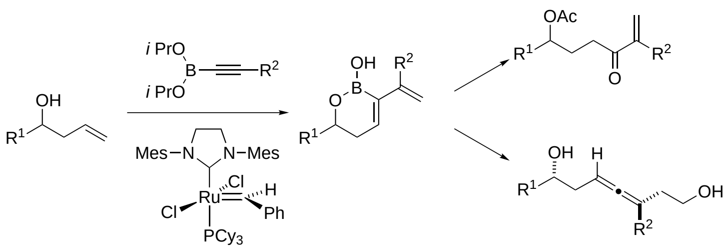
A. Hori, A. Akasaka, K. Biradha, S. Sakamoto, K. Yamaguchi, M. Fujita* 3269–3272

Chirality Induction through the Reversible Catenation of Coordination Rings

Keywords: catenanes • chirality • helical structures • palladium • self-assembly

---

Branched networks of reactions create variety in this synthesis of trisubstituted allenes and functionalized enones from readily available homoallylic alcohols in just two steps, by using a new alkynylboronic ester annulation (see scheme; Mes = 2,4,6-trimethylphenyl, Cy = cyclohexyl).



Angew. Chem. **2002**, *114*, 3406–3410

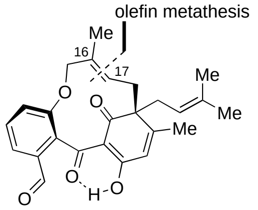
G. C. Micalizio, S. L. Schreiber* 3272–3276

An Alkynylboronic Ester Annulation: Development of Synthetic Methods for Application to Diversity-Oriented Organic Synthesis

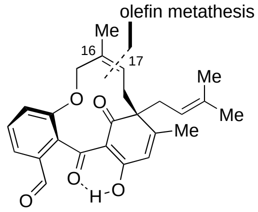
Keywords: allenes • annulation • boronic acids • metathesis • synthetic methods

1433-7851/02/4117-3083 $ 20.00+.50/0

Pushing the frontiers of olefin metathesis: As the coleophomones B (**1**) and C (**2**) differ only in the configuration of the $\Delta^{16,17}$ double bond, ring-closing metathesis was chosen as the method for their construction following an initially convergent route that diverges at a late stage.



1 coleophomone B



2 coleophomone C

Angew. Chem. **2002**, *114*, 3410–3415

K. C. Nicolaou,* G. Vassilikogiannakis,
T. Montagnon 3276–3281

The Total Synthesis of Coleophomones B and C

Keywords: acyl cyanides • metathesis • natural products • total synthesis

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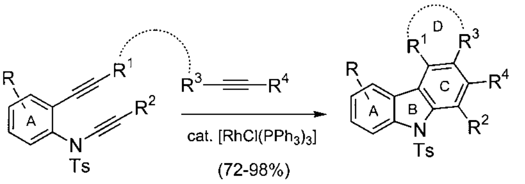
An A →ABC or A →ABCD ring-formation strategy proves extremely efficient for generating substituted carbazoles ([Eq. (1)]; Ts = tosyl). Inter- and intramolecular alkyne cyclotrimerizations mediated by Wilkinson's catalyst provide substituted carbazoles of relevance for natural product and drug-related synthesis. The diynes required for these reactions are obtained in a few steps by a combination of Sonogashira and N-ethynylation reactions.



(1)

Angew. Chem. **2002**, *114*, 3415–3418

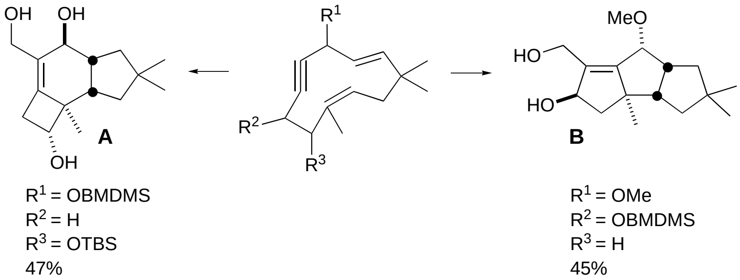
B. Witulski,* C. Alayrac 3281–3284

A Highly Efficient and Flexible Synthesis of Substituted Carbazoles by Rhodium-Catalyzed Inter- and Intramolecular Alkyne Cyclotrimerizations

Keywords: alkynes • cyclotrimerization • natural products • nitrogen heterocycles • ynamides

---

A completely selective entry to the triquinane family is described from a highly strained cycloundecadienyne framework, simply by choosing the correct propargylic position for the radical trigger (see scheme; A: natural protoilludane, B: linear triquinane, BMDMS = (bromomethyl)dimethylsilyl, TBS = *tert*-butyldimethylsilyl).



Angew. Chem. **2002**, *114*, 3418–3421

A.-L. Dhimane, C. Aïssa,
M. Malacria* 3284–3287

Transannular Radical Cascade as an Approach to the Diastereoselective Synthesis of Linear Triquinane

Keywords: cyclization • polycycles • radicals • strained molecules • synthetic methods

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

Accelerated publications

* Author to whom correspondence should be addressed

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CORRIGENDA

In the Communication by A. Gagnon and S. J. Danishefsky in Issue 9, **2002**, pp. 1581–1584, the wrong reagent was accidentally given in Scheme 2. In f), "3-iodoprop-1-ene" should be replaced by "allyltributyltin".

In the Communication by S. Spange et al. in Issue 10, **2002**, pp. 1729–1732, two thematically relevant works on sol–gel techniques were not cited. These were: a) U. Deschler, P. Kleinschmit, P. Panster, *Angew. Chem.* **1986**, *98*, 237–253; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 236–252; b) B. Lebeau, J. Maquet, C. Sanchez, E. Toussacre, R. Hierle, J. Zyss, *J. Mater. Chem.* **1994**, *4*, 1855–1860.

In the Communication by U. Mazurek, D. Schröder, and H. Schwarz in Issue 14, **2002**, pp. 2538–2541 two molecular formulae were inadvertently cut short on the right-hand side of Figure 2. The correct formulae are as follows: $CrC_6F_6O_{10}H_{11}^+$ and $CrC_3F_2O_6H_6^+$ (in place of the incorrectly shown formulae $CrC_6F_6O_{10}H_1$ und CrC_3F_2O). The editorial team apologizes for this oversight.