

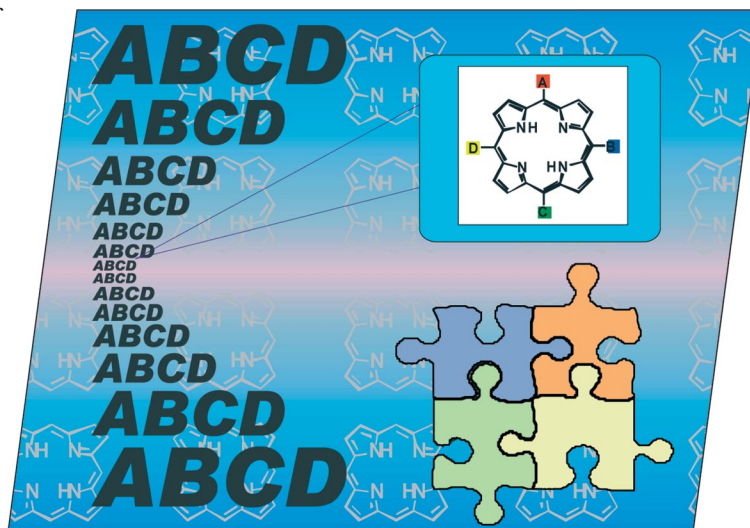


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COVER PICTURE

The cover picture shows that the preparation of ABCD-type porphyrins from porphyrin precursors is not as difficult as an eye exam or a puzzle. The use of porphyrin precursors and modern organometallic methods allow the preparation of all types of A_x - and ABCD-type porphyrins. Details are discussed in the article by M. O. Senge et al. from Trinity College Dublin on p. 237ff.



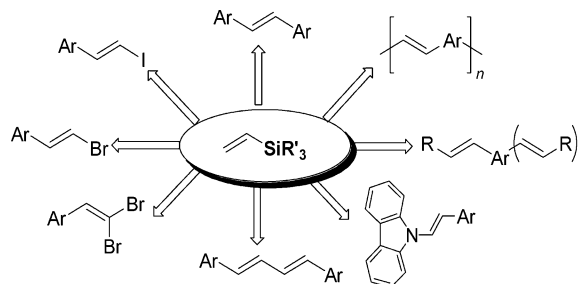
MICROREVIEW

Silylative Coupling

P. Pawluć, W. Prukała,
B. Marciniak* 219–229

Silylative Coupling of Olefins with Vinylsilanes in the Synthesis of π -Conjugated Double Bond Systems

Keywords: Silylative coupling / Arylvinyl derivatives / Cross-coupling / Halogenation / Desilylative coupling / Silanes



From simple vinylsilanes to complex π -conjugated molecules: recent applications of sequential silylative coupling/desilylative

coupling methodology to the synthesis of functionalized arylvinyl derivatives are reviewed.

SHORT COMMUNICATION

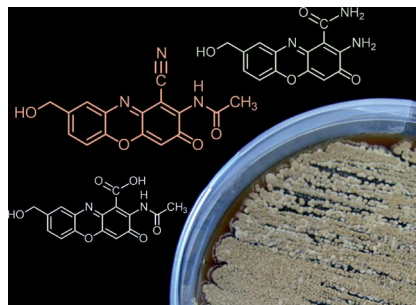
Natural Products

P. B. Gomes, M. Nett, H.-M. Dahse,
I. Sattler, K. Martin,
C. Hertweck* 231–235



Bezerramycins A–C, Antiproliferative Phenoxazinones from *Streptomyces griseus* Featuring Carboxy, Carboxamide or Nitrile Substituents

Keywords: *Streptomyces griseus* / Antiproliferative activity / Phenoxazinone / Natural products / Biosynthesis



Three phenoxazinones, which primarily differ in the carboxy, carboxamide and nitrile substituents at C-1, were isolated from a *Streptomyces griseus* strain. The cooccurrence of the rare nitrile-functionalized bezerramycin C with carboxy and carboxamide substituted congeners implies a biogenetic relationship.

FULL PAPERS

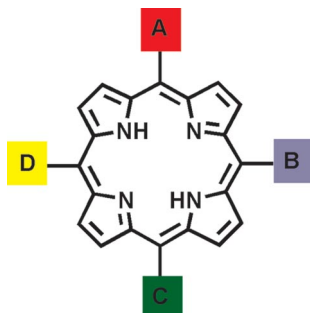
Porphyrins

M. O. Senge,* Y. M. Shaker, M. Pintea,
C. Ryppa, S. S. Hatscher, A. Ryan,
Yu. Sergeeva 237–258



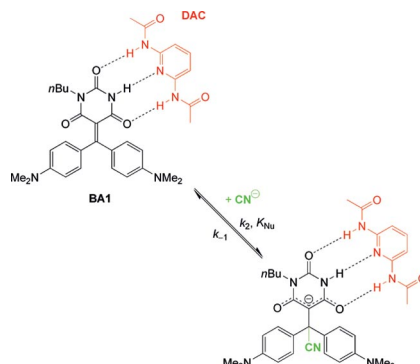
Synthesis of *meso*-Substituted ABCD-Type Porphyrins by Functionalization Reactions

Keywords: Porphyrinoids / Tetrapyrroles / C–C coupling / Conformation analysis



A comprehensive study of contemporary synthetic methods by using organolithium and Pd-catalyzed C–C coupling reactions for ABCD-porphyrins reveals that it is now possible to prepare almost any desired *meso*-substituted porphyrin.

For the first time it is demonstrated that it is possible to influence the reactivity of a neutral electrophile which possesses a hydrogen bonding motif by using a complementary receptor: Upon complexation of **BA1** with the receptor **DAC** both the electrophilicity and the Lewis acidity of **BA1** are markedly increased.



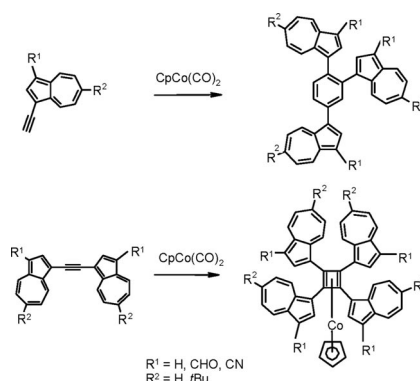
M. Bauer, S. Spange* 259–264

Enhancing the Reactivity of an Electrophilic Barbiturate Dye by Cooperative Hydrogen Bonding



Keywords: Donor-acceptor systems / Supramolecular chemistry / Hydrogen bonds / Lewis acids / Acidity / Electrophilicity

Co-catalyzed cyclooligomerization of ethynylazulenes as well as diazulenylethyne to the corresponding azulenyl-substituted cyclobutadienes and benzenes is described.

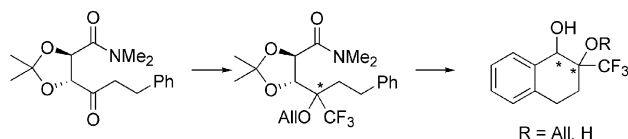


A. H. M. Elwahi,
K. Hafner* 265–274

Cyclooligomerization of Mono- and Diazulenylethyne Catalyzed by Transition Metal Complexes

Keywords: Cobalt catalyst / Ethynylazulenes / Azulenylbenzenes / Azulenylcyclobutadienes / Cyclooligomerization / Cross-coupling / Polycycles

Nucleophilic Trifluoromethylation



The enantiopure stereoisomers of the title compound were prepared and charac-

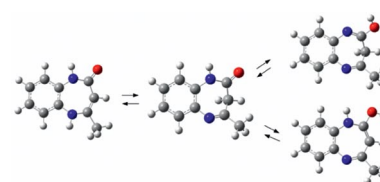
terized, starting from a tartaric acid derived keto amide.

F. Massicot, J. Nonnenmacher,
F. Grellepois, C. Portella* 275–279

Enantiopure 2-(Trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-1,2-diols from a Tartaric Acid Derived Scaffold

Keywords: Aromatic substitution / Asymmetric synthesis / Chiral pool / Cyclization / Fluorine

An exhaustive study of tautomerization in three kinds of dihydro-1,5-benzodiazepin(e)-2-(thi)one systems through theoretical calculations is reported.



S. I. Okovytyy,* L. K. Sviatenko,
A. A. Gaponov, L. I. Kasyan,
I. N. Tarabara, J. Leszczynski ... 280–291

DFT Study on Tautomerism of Dihydro-2H-1,5-benzodiazepin-2-ones and Dihydro-2H-1,5-benzodiazepine-2-thiones



Keywords: Nitrogen heterocycles / Tautomerism / Density functional calculations

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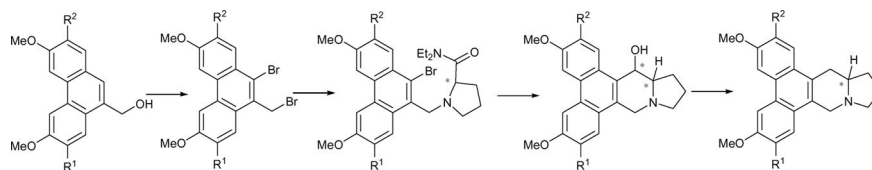
Phenanthro-indolizidine Alkaloids

Z. Wang, Z. Li, K. Wang,
Q. Wang 292–299



Efficient and Chirally Specific Synthesis of Phenanthro-Indolizidine Alkaloids by Parham-Type Cycloacylation

Keywords: Alkaloids / Synthetic methods / Metalation / Cyclization / Reduction / Cycloacylation



A series of enantiopure phenanthro-indolizidine alkaloids have been synthesized in excellent overall yields and with very high *ee* values with Parham-type cycloacylation

as the key step. The large-scale preparation of enantiomerically pure alkaloids is now feasible.

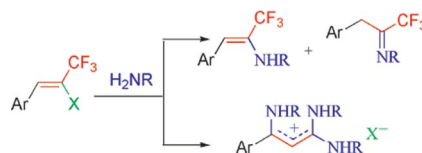
Trifluoromethylated Enamines

A. Yu. Rulev,* V. M. Muzalevskiy,
E. V. Kondrashov, I. A. Ushakov,
A. V. Shastin, E. S. Balenkova, G. Haufe,
V. G. Nenajdenko* 300–310



A Cascade Approach to Captodative Trifluoromethylated Enamines or Vinylogous Guanidinium Salts: Aromatic Substituents as Switches of Reaction Direction

Keywords: Amines / Nucleophilic substitution / Domino reactions



The electronic natures of the aromatic substituents on β -halo- β -(trifluoromethyl)styrenes govern the outcomes of their reactions with nitrogen nucleophiles bearing primary amino groups, the reaction products being either captodative trifluoromethylated enamines or vinylogous guanidinium salts.

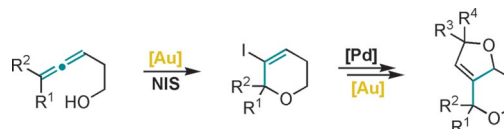
Gold-Catalyzed Transformations

B. Gockel, N. Krause* 311–316



Synthesis of Bicyclic Ethers by a Gold/Palladium/Gold-Catalyzed Cyclization/Cross Coupling Sequence

Keywords: Allenes / Cycloisomerization / Gold / Homogeneous catalysis / Oxygen heterocycles



The stereoselective gold-catalyzed 6-*endo* cyclization of various β -hydroxyallenes in the presence of *N*-iodosuccinimide affords iodinated dihydropyrans in good yield. Subsequent functionalization by pal-

ladium-catalyzed cross coupling opens an access to α -hydroxyallenes that are converted in a second gold-catalyzed cyclization into bicyclic ethers which occur in various natural products.

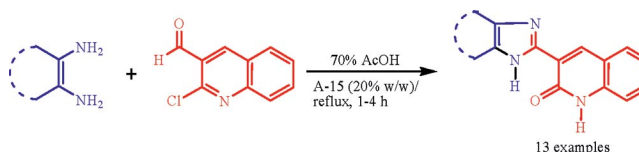
Heterocyclic Antitumor Agents

R. Abonia,* J. Castillo, P. Cuervo,
B. Insuasty, J. Quiroga, A. Ortíz,
M. Nogueras, J. Cobo 317–325



A Simple One-Pot Synthesis of New Imidazol-2-yl-1*H*-quinolin-2-ones from the Direct Reaction of 2-Chloroquinolin-3-carbaldehyde with Aromatic *o*-Diamines

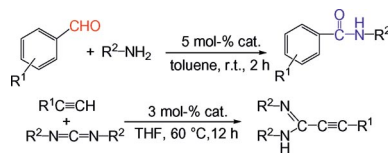
Keywords: Antitumor agents / Synthetic methods / Biological activity / Cyclization / Nitrogen heterocycles / Hydrolysis



We implemented an efficient, one-step procedure for the direct synthesis of new imidazol-2-yl-1*H*-quinolin-2-ones from the reaction of 2-chloroquinolin-3-carbaldehyde

with aromatic *o*-diamines using Amberlyst®-15 as catalyst. This approach involved simultaneous C–Cl hydrolysis and condensation processes in the same pot.

Cyclopentadienyl-free rare-earth metal amides $[\{(CH_2SiMe_2)\{(2,6-iPr_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ have been found to be versatile catalysts for C–N and C–C bond formation.



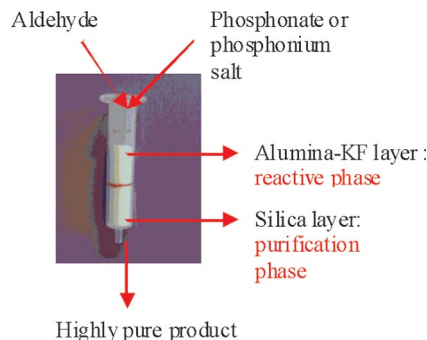
Y. Wu, S. Wang,* L. Zhang, G. Yang,
X. Zhu, Z. Zhou, H. Zhu,
S. Wu 326–332

Cyclopentadienyl-Free Rare-Earth Metal Amides $[\{(CH_2SiMe_2)\{(2,6-iPr_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ as Highly Efficient Versatile Catalysts for C–C and C–N Bond Formation

Keywords: Lanthanides / N,O ligands / Amides / Amidines

On-Column Reactions

The synthesis of some natural bioactive compounds, including (*E*)-stilbenes, alkylidenesorcinols, and 5-aryl-2,4-pentadienoates, over a column of alumina-KF under microwave irradiation was investigated by using the Wittig and Horner–Emmons reactions.

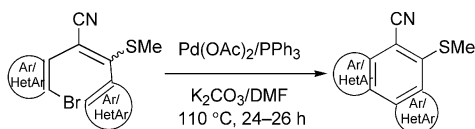


S. C. Dakdouki, D. Villemin,*
N. Bar 333–337

Solid-Phase Reactive Chromatography (SPRC): A New Methodology for Wittig and Horner–Emmons Reactions on a Column under Microwave Irradiation

Keywords: Wittig reactions / Solid-phase synthesis / Supported catalysis / Reactive chromatography / Microwave chemistry

Pd-catalyzed Cyclization



An efficient route to substituted phenanthrenes and polycyclic heteroarenes by a direct, Pd-catalyzed, intramolecular aryl-

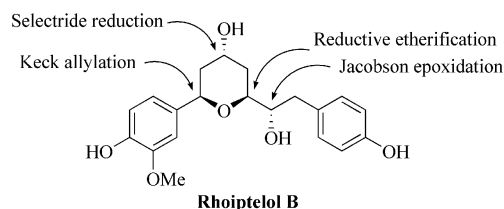
ation/heteroarylation of 2-(2-bromoaryl/heteroaryl)-3-(aryl/heteroaryl)-3-(methylthio)acrylonitriles has been reported.

A. K. Yadav, H. Ila,*
H. Junjappa 338–344

Synthesis of Novel Substituted Phenanthrenes and Polycyclic Heteroarenes by Pd-Catalyzed, Direct, Intramolecular Arylation/Heteroarylation

Keywords: Cyclization / Heteroarenes / Palladium / Phenanthrenes / Polycycles

Natural Product Synthesis



The first total synthesis of rhoiptelol B has been achieved in 15 steps in a stereoselective and convergent fashion. The key steps used were Keck allylation, Jacobson reso-

lution, lithium-mediated aldol reaction and reductive etherification for the generation of required chiral centers.

C. R. Reddy,* N. N. Rao,
B. Srikanth 345–351

Total Synthesis of a Diarylheptanoid, Rhoiptelol- B

Keywords: Rhoiptelol B / Total synthesis / Natural products / Reductive etherification / Aldol reactions

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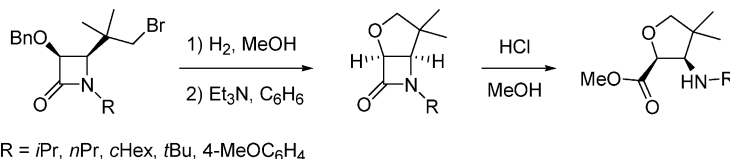
β -Lactam Chemistry

E. Leemans, M. D'hooghe, Y. Dejaegher,
K. W. Törnroos, N. De Kimpe* 352–358



Synthesis of 3,4-Fused Bicyclic β -Lactams
and Their Transformation into Methyl *cis*-
3-Aminotetrahydrofuran-2-carboxylates

Keywords: β -Lactams / β -Amino acids /
Oxolanes / Cyclization / Stereoselectivity



cis-3-Benzoyloxy-4-(2-bromo-1,1-dimethyl-
ethyl)azetidin-2-ones were transformed into
novel *cis*-2-oxa-6-azabicyclo[3.2.0]heptan-
7-ones by a two-step procedure. The latter

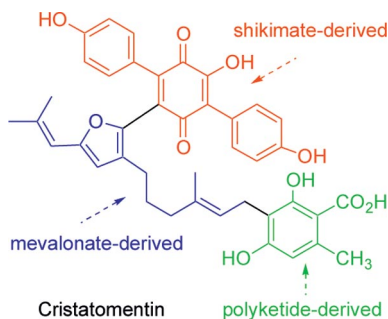
cis-2-oxa-6-azabicyclo[3.2.0]heptan-7-ones
were subsequently converted into *cis*-
3-amino-tetrahydrofuran-2-carboxylates
through acidic methanolysis.

Green Toadstool Pigment

B. Koch, C. Kilpert,
W. Steglich* 359–362

Cristatomentin, a Green Pigment of Mixed
Biogenetic Origin from *Albatrellus cristatus*
(Basidiomycetes)

Keywords: Natural products / Meroter-
penoids / Quinones / Furans / Fungi



The structure of cristatomentin has been
elucidated by MS studies and comparison
of its NMR spectrum with those of cristatic
acid and albatrellin. The furylbenzoquin-
one chromophore of cristatomentin may
arise from cristatic acid and 2-*O*-acetyl-
atromentin, which co-occur with the title
compound in the fungus.

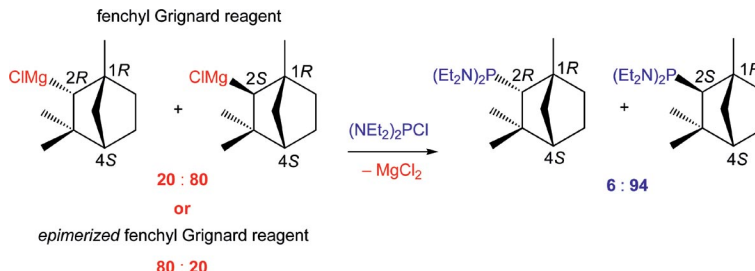
Diastereoselective Grignard Reactions

J. Beckmann,* A. Schütrumpf 363–369



Reactions of the Bornyl and Fenchyl Grig-
nard Reagent with Chlorophosphanes –
Diastereoselectivity and Mechanistic Im-
plications

Keywords: Grignard reaction / Nucleophilic
substitution / Radical reactions



The reaction of the fenchyl Grignard re-
agent (ratio *endo:exo* = 20:80) or the *epi*-
merized fenchyl Grignard reagent (ratio
endo:exo = 80:20) with $(\text{NEt}_2)_2\text{PCl}$ gave
rise to a mixture of α - and β -fenchylbis(di-
ethylamino)phosphane with an *endo:exo*

ratio of 6:94 regardless of the original
endo:exo ratio. The results of the substi-
tution reactions are consistent with a SET
mechanism involving the fenchyl radical as
intermediate.

CORRECTION

J. A. Morales-Serna, Y. Díaz,
M. I. Matheu, S. Castellón* 371

Efficient Synthesis of β -Glycosphingolipids
by Reaction of Stannylceramides with Gly-
cosyl Iodides Promoted by TBAI/AW 300
Molecular Sieves

Keywords: Glycosylation / Glycolipids /
Sphingolipids / Tin / Ethers

* Author to whom correspondence should be addressed.

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