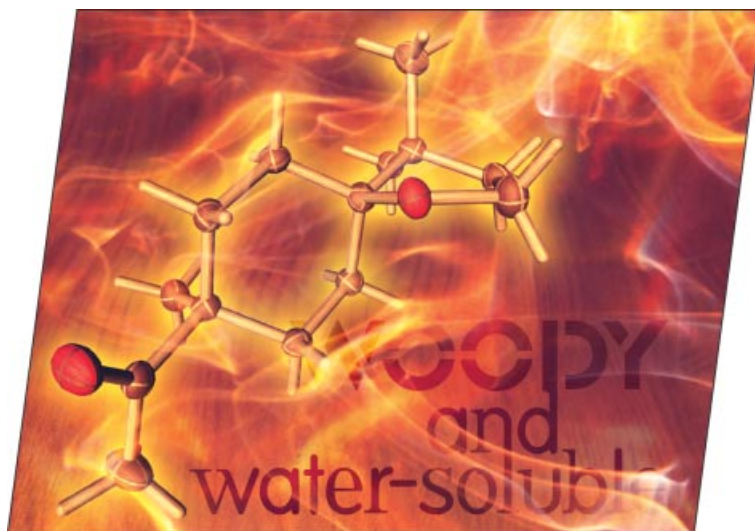




The EUChemSoc Societies have taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further EUChemSoc Societies (Austria, Czech Republic and Sweden) are Associates of the two journals.

COVER PICTURE

The cover picture shows the X-ray crystal structure of a spirocyclic analog of the woody-ambery odorant Iso Gamma, in which the polarity of the γ -double bond is mimicked by the oxygen atom of the spiroannulated 3,3-dimethyltetrahydrofuran-2-yl moiety. The log P_{ow} value thereby improves from 5.7 to 3.2, so that this pleasant woody-ambery odorant, which is reminiscent of Iso E Super with additional agrestic, conifer-type facets of Cashmeran, can indeed be considered the first water-soluble perfumery raw material of the woody-ambery family. According to the European REACH regulations, it is thus classified as being bioavailable and regarded to be nonpersistent in the environment. To emphasize on the paradox of wood being water-soluble, the wooden ORTEP model seems to dissolve into incense smoke that floats like streaks in water above a wood grain that warps like the ground of the ocean. But besides the interesting physical and olfactory properties of the target structure, P. Kraft and K. Popaj also report on an unprecedented tethering effect that was discovered in the course of synthetic attempts towards this and related structures by Diels–Alder reactions, on p. 261 ff.



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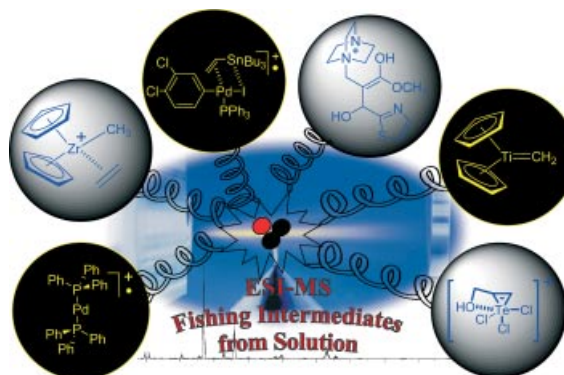
MICROREVIEW

ESI-MS Fishing of Intermediates

L. S. Santos* 235–253

Online Mechanistic Investigations of Catalyzed Reactions by Electrospray Ionization Mass Spectrometry: A Tool to Intercept Transient Species in Solution

Keywords: Mass spectrometry / ESI-MS / Reaction mechanisms / Intermediates / Organometallic catalysis



Reaction mechanisms have been accessed by online monitoring by electrospray ionization mass and tandem mass spectrometric experiments [ESI-MS(/MS)]. Reaction pathways shown by ESI-MS(/MS)

have been probed by gas-phase ion/molecule reactions, and several expanded mechanisms for different reactions have been elaborated based on mass spectrometric data.

SHORT COMMUNICATION

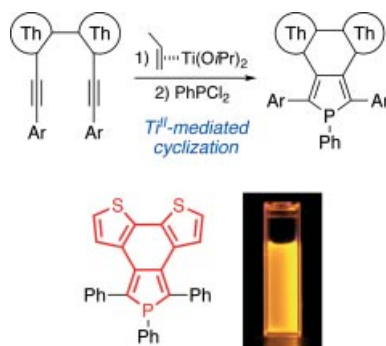
Benzo[c]phospholes

T. Miyajima, Y. Matano,*
H. Imahori 255–259



Bithiophene-Fused Benzo[c]phospholes: Novel P,S-Containing Hybrid π -Conjugated Systems with Small HOMO–LUMO Energy Gaps

Keywords: Phospholes / Thiophenes / Fused-ring systems / Conjugation / Pi interactions



Fusion of a phosphole ring and a bithiophene subunit provides a new class of P,S-containing hybrid π systems. Appropriately ring-annulated systems emit orange light with narrow HOMO–LUMO energy gaps due to the efficient π -electron delocalization over the three conjugated heterole rings.

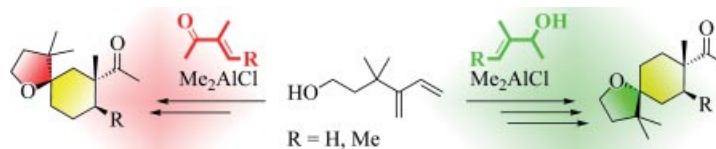
FULL PAPERS

Unexpected Tethering

P. Kraft,* K. Popaj 261–268

Unexpected Tethering in the Synthesis of Methyl-Substituted Acetyl-1-oxaspiro[4.5]decanes: Novel Woody–Ambery Odorants with Improved Bioavailability

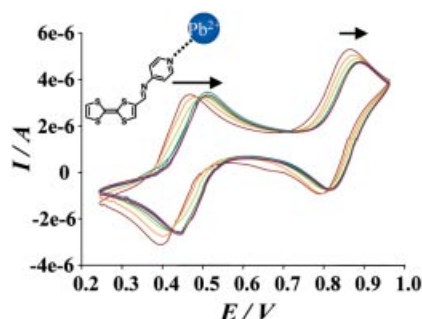
Keywords: Biodegradation / Diels–Alder reactions / Fragrances / Structure–activity relationships / Tethering effects




Woody and water-soluble? As paradoxical as for wood in real life, so it was for woody odorants such as Iso E Super [$\log(P_{ow}) = 5.7$] to be water-soluble. But by spiroannulation of a dimethyltetrahydrofuran moiety, woody odorants with $\log(P_{ow})$

≤ 4.0 could indeed be designed. And on the way, a new unusual tethering effect for Diels–Alder reactions was discovered, which could be “switched on” or “switched off” depending on the functional group of the dienophile.

Tetrathiafulvalene–imine–pyridine assemblies have been synthesized and shown to generate both electrochemical and colorimetric responses upon lead binding.

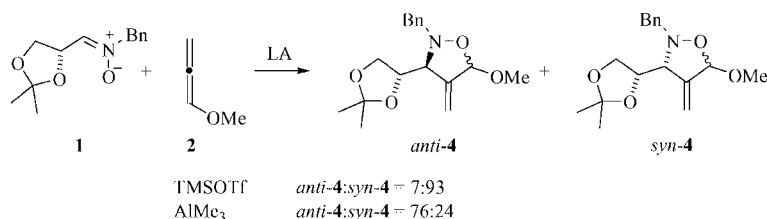


J.-Y. Balandier, A. Belyasmine,
M. Sallé* 269–276

Tetrathiafulvalene–Imine–Pyridine Assemblies for Pb²⁺ Recognition 

Keywords: N ligands / Charge transfer / Conjugation / Imines / Donor–acceptors systems

1,3-Dipolar Cycloadditions



The site selectivity of cycloadditions of nitrone **1** and methoxyallene (**2**) is strongly influenced by Lewis acids which induce exclusive formation of 4-methylene-substituted isoxazolidines **4**.

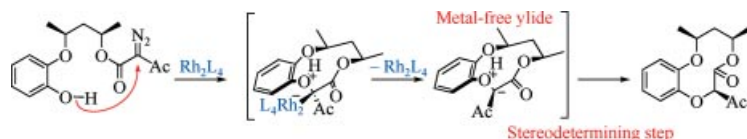
The diastereofacial selectivity of the methoxyallene cycloaddition to nitrone **1** can be controlled just by employing different Lewis acids.

B. Dugović, L. Fišera,
H.-U. Reißig* 277–284

1,3-Dipolar Cycloadditions of *N*-Benzyl-2,3-*O*-isopropylidene-D-glyceraldehyde Nitron to Methoxyallene – Control of Site- and Diastereoselectivity of Isoxazolidine Formation by Lewis Acids

Keywords: Methoxyallene / Nitron / 1,3-Dipolar cycloaddition / Lewis acids / Isoxazolidines

Stereocontrolled O–H Insertion



The intermolecular O–H insertion reaction of rhodium carbenoids generated from diazoacetoacetates is inefficient and poorly stereoselective, but the corresponding intramolecular reaction with a chiral tether is efficient and gives the product in 86 % diastereomeric excess.

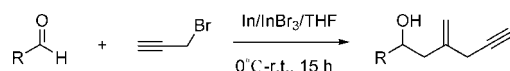
intramolecular reaction with a chiral tether is efficient and gives the product in 86 % diastereomeric excess.

C. Y. Im, T. Okuyama,
T. Sugimura* 285–294

Stereoselective Formation of a Chiral Ether by Intramolecular O–H Insertion Reaction of a Metal Carbenoid Generated from Diazoacetoacetate

Keywords: Stereocontrol / Carbenoids / Insertion / Intramolecular reactions / Chiral tether / Chirality


Tandem Reactions



A chemo- and regioselective method was developed for the synthesis of 1-substituted-3-methylene-5-yn-1-ol by the In-mediated tandem reaction of aldehydes with 3-bromo-1-propyne.

mediated tandem reaction of aldehydes with 3-bromo-1-propyne.

J.-M. Huang,* H.-C. Luo, Z.-X. Chen,
G.-C. Yang, T.-P. Loh* 295–298

An In-Mediated Tandem Reaction of Aldehydes with 3-Bromo-1-propyne To Produce 1-Substituted-3-methylene-5-yn-1-ol Compounds 

Keywords: Aldehydes / Alcohols / Alkynes / Indium / Propargylation / Tandem

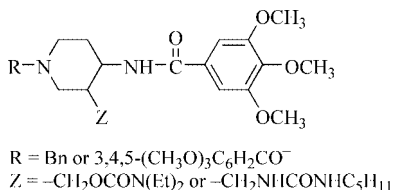
CONTENTS

Trisubstituted 4-Aminopiperidines

H. Benmehdi, A. Lamouri, N. Serradji,
F. Pallois, F. Heymans 299–307

Synthesis of New Trisubstituted 4-Amino-
piperidines as PAF-Receptor Antagonists

Keywords: Aminopiperidines / Diastereoisomers / Enamines / Antagonists / Reduction / Biological activity



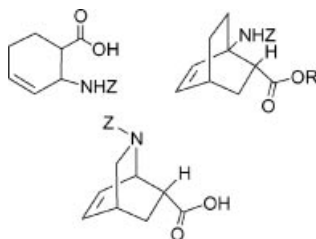
Two pairs of trisubstituted 4-aminopiperidine diastereoisomers have been synthesized, isolated and identified. The key step was the reduction of ester- and cyanide-conjugated enamines to the primary amines.

Cyclic β-Amino Acids

O. Songis, P. Y. Géant, G. Sautrey,
J. Martinez, M. Calmès* 308–318

Asymmetric Diels–Alder Reaction of
Aminodienes with a Nonracemic Acrylate
Bound to Rink Resin: A Comparison of
These Reactions with Their Solution-State
Analogues

Keywords: Asymmetric synthesis / Diels–Alder reactions / Supported synthesis / Cyclic β-amino acids / Microwave activation / Chiral auxiliaries



The asymmetric Diels–Alder reaction between (3*R*)-1-[4-(benzyloxycarbonyl)-phenyl]-4,4-dimethyl-2-oxopyrrolidin-3-yl acrylates and three *N*-*Z*-protected 1-aminodienes has been investigated both in solution and on a solid support. Comparable results for each class of reaction were observed with the formation of the corresponding constrained cyclic β-amino acids in high yields and moderate-to-good selectivity when using optimized conditions.

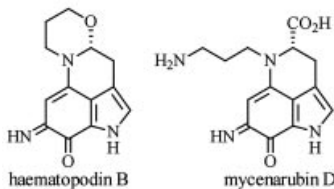
Pyrroloquinoline Alkaloids

S. Peters, R. J. R. Jaeger,
P. Spiteller* 319–323



Red Pyrroloquinoline Alkaloids from the
Mushroom *Mycena haematopus*

Keywords: Alkaloids / Fungi / Metabolic profiling / Natural products / Pyrroloquinolines



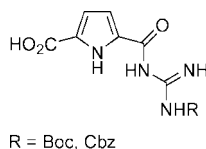
The so far unknown native main pigment haematopodin B was isolated from fruiting bodies of *M. haematopus* along with three new minor pigments named mycenarubins D, E and F. Upon injury of the fruiting bodies, haematopodin B starts to decompose. One of the decomposition products is the already known pigment haematopodin.

Pyrrole Building Blocks

C. Schmuck,* V. Bickert,
M. Merschky, L. Geiger, D. Rupprecht,
J. Dudaczek, P. Wich, T. Rehm,
U. Machon 324–329

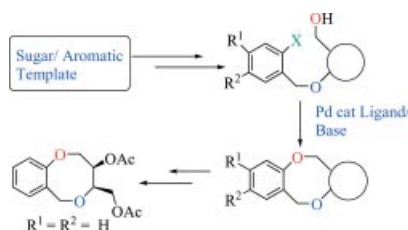
A Facile and Efficient Multi-Gram Synthesis of *N*-Protected 5-(Guanidinocarbonyl)-1*H*-pyrrole-2-carboxylic Acids

Keywords: Guanidinium cations / Pyrroles / Anion receptors / Protecting groups




The synthesis of two versatile building blocks for supramolecular anion binding motifs, *N*-protected 5-(guanidinocarbonyl)-1*H*-pyrrole-2-carboxylic acids, is reported. Using this type of building block, a cationic guanidiniocarbonyl-pyrrole anion binding site can easily be introduced into other molecules by standard amide coupling conditions.

Palladium-catalyzed intramolecular aryl etherification using bulky binaphthylphosphane or bis(diphenylphosphanyl)ferrocene ligands is shown to be a convenient method for the synthesis of eight-membered oxygen heterocycles. Application of this methodology to a sugar derivative led to the synthesis of chiral benzodioxocine.

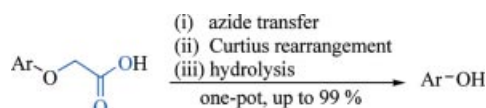


A. Neogi, T. P. Majhi, B. Achari,
P. Chattopadhyay* 330–336

Palladium-Catalyzed Intramolecular C–O Bond Formation: An Approach to the Synthesis of Chiral Benzodioxocines 

Keywords: Palladium / Catalysts / Dioxocine / Ligands / Etherification / Heterocycles


Deprotection Reactions



A reliable and high-yielding one-pot sequence for the removal of *O*-carboxymethyl moieties from phenols is presented. When diethylphosphoryl azide is employed as the azide transfer reagent in the Curtius

rearrangement and glycerol in the subsequent hydrolytic workup, the protocol can be reliably applied to a broad scope of substrates.

A. Spurg, S. R. Waldvogel* 337–342

High-Yielding Cleavage of (Aryloxy)acetates 

Keywords: Azides / Cleavage reactions / Carboxylic acids / Arenes / Rearrangement

Domino Reaction

A variety of 2-acyl-, 2-aro-yl- and 2-formyl-substituted phenols are converted in a one-pot reaction with α,β -unsaturated carboxylic acid chlorides into the corresponding 3-alkenylcoumarins. Especially the labile 3-vinylcoumarins are readily available by the simple to perform protocol.

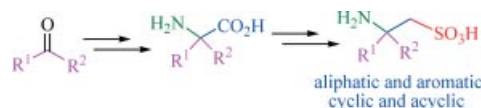


P. Königs, O. Neumann, K. Hackelöer,
O. Kataeva, S. R. Waldvogel* ... 343–349

Versatile One-Pot Synthesis of 3-Alkenylcoumarins

Keywords: Heterocycles / Alkenes / Domino reaction / Coumarin


Amino Acid Synthesis



An effective and versatile method was developed to synthesize *N*-benzyloxycarbonyl-protected and free 2,2-disubstituted taurines. Several novel 2,2-disubstituted

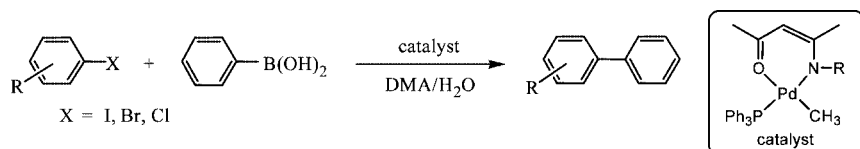
taurines, including aliphatic/aromatic and cyclic/acyclic derivatives, were obtained, which demonstrates the generality of this method.

B. Wang, W. Zhang, L. Zhang, D.-M. Du,
G. Liu, J. Xu* 350–355

Versatile Synthesis of Free and *N*-Benzyloxycarbonyl-Protected 2,2-Disubstituted Taurines 

Keywords: Amino acid / Aminoalkanesulfonic acid / Ketone / Synthesis / Taurine

Palladium Catalysis



(β -Oxoiminato)(phosphanyl)palladium complexes are found to act as highly active catalysts in Suzuki–Miyaura coupling reactions. Various aryl iodides and bromides undergo rapid coupling with phenylboronic

acid with remarkably high turnover frequencies under mild conditions. Furthermore, it has been shown that the catalyst system is also effective in the reactions of aryl chlorides.

D.-H. Lee, J.-Y. Jung, I.-M. Lee,
M.-J. Jin* 356–360

(β -Oxoiminato)(phosphanyl)palladium Complexes as Highly Active Catalysts in Suzuki–Miyaura Coupling Reactions

Keywords: β -Oxoiminate / Palladium / Catalysis / C–C coupling / Suzuki–Miyaura reactions

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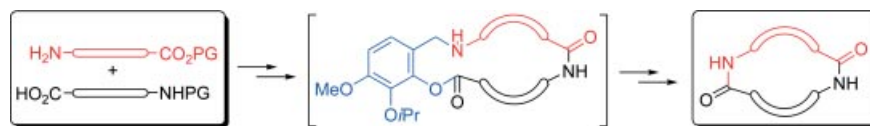
Strained Bis(lactams)

J. Springer, T. P. Jansen, S. Ingemann,
H. Hiemstra,
J. H. van Maarseveen* 361–367



Improved Auxiliary for the Synthesis of Medium-Sized Bis(lactams)

Keywords: Bis(lactams) / Templated synthesis / Auxiliaries / Cyclic peptides



A broadly applicable auxiliary-based method has been developed for the synthesis of bis(lactams). A novel auxiliary is described that is inserted in the backbone of a linear peptide facilitating the mutually reactive

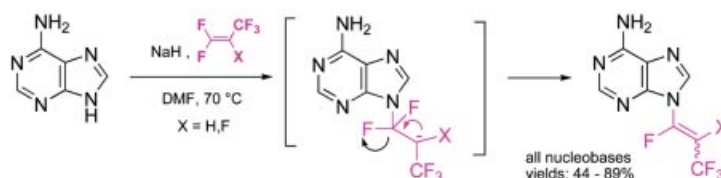
terminal groups to approach one another for a cyclization reaction. Functionalized seven- and eight-membered bis(lactams) have been prepared that are difficult to access using traditional methods.

Nucleobases

H. Wójtowicz-Rajchel,* H. Koroniak,
A. Katrusiak 368–376

A Convenient Method for the Synthesis of Stable α -Fluoro Enamines of Nucleobases

Keywords: Enamines / Nucleobases / Hexafluoropropene / Pentafluoropropene / Addition–elimination reactions



A convenient method for the synthesis of *N*- α,β -difluoro- β -trifluoromethyl enamines and *N*- α -fluoro- β -trifluoromethyl enamines of nucleic acids bases is described. The

procedure is based on a Michael-type addition–elimination reaction and shows high N^9 regioselectivity for purines and N^1 for pyrimidines.

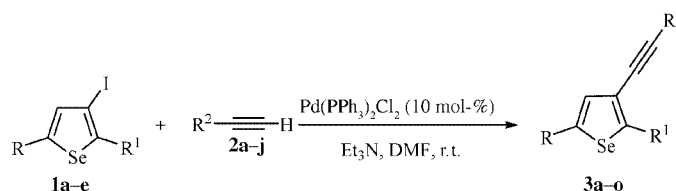
Cu-Free Sonogashira Reactions

D. Alves, J. S. dos Reis, C. Luchese,
C. W. Nogueira, G. Zeni* 377–382



Synthesis of 3-Alkynylselenophene Derivatives by a Copper-Free Sonogashira Cross-Coupling Reaction

Keywords: Palladium / Cross-coupling / Selenium / Selenophene



3-Iodoselenophene derivatives undergo Sonogashira cross-coupling reactions with several terminal alkynes in the presence of a catalytic amount of palladium salt under

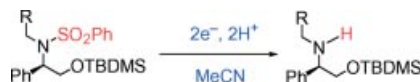
mild conditions to furnish the corresponding 3-alkynylselenophenes in good-to-excellent yields.

Electrochemical Deprotection

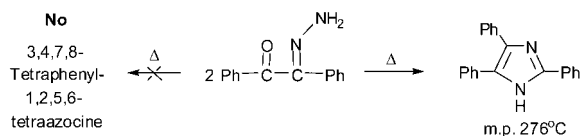
V. Coeffard, C. Thobie-Gautier, I. Beaudet,
E. Le Grognet,* J.-P. Quintard* ... 383–391

Mild Electrochemical Deprotection of *N*-Phenylsulfonyl *N*-Substituted Amines Derived from (*R*)-Phenylglycine

Keywords: Sulfonamides / Protecting groups / Cleavage reactions / Electrolyses / Cyclic voltammetry



The electrochemical reduction of *N*-phenylsulfonyl *N*-substituted amines in a protic medium under constant cathodic potential was found to be a mild desulfonylation method. The influence of the substituents on the nitrogen atom was considered in order to clarify the mechanistic aspects and to evaluate the scope of the method.



Benzil monohydrazone undergoes thermolysis in moist air to produce benzil, benzaldehyde, benzamide, benzil bis(ketazine), benzyl phenyl ketone, 3,4,5,6-tetraphenylpyridazine, benzaldehyde benzil azine,

and small amounts of 2,4,5-triphenylimidazole. In previous work, the last named component was mistaken for the yet unknown 3,4,7,8-tetraphenyl-1,2,5,6-tetraazocine.

J. J. Eisch,* T. Y. Chan,

J. N. Gitua 392–397

Purported Synthesis of 3,4,7,8-Tetraphenyl-1,2,5,6-tetraazocine from Benzil and Hydrazine: Competing Cyclization and Carbon–Carbon σ -Bond Scission

Keywords: Dimerization / Cyclization / Nitrogen heterocycles / C–C bond scission

If not otherwise indicated in the article, papers in issue 1 were published online on December 12, 2007