HUNGARY ITALY GERMANY GREECE

CZECH REPUBLIC FRANCE

ChemPubSoc Europe

SWEDEN BELGIUM

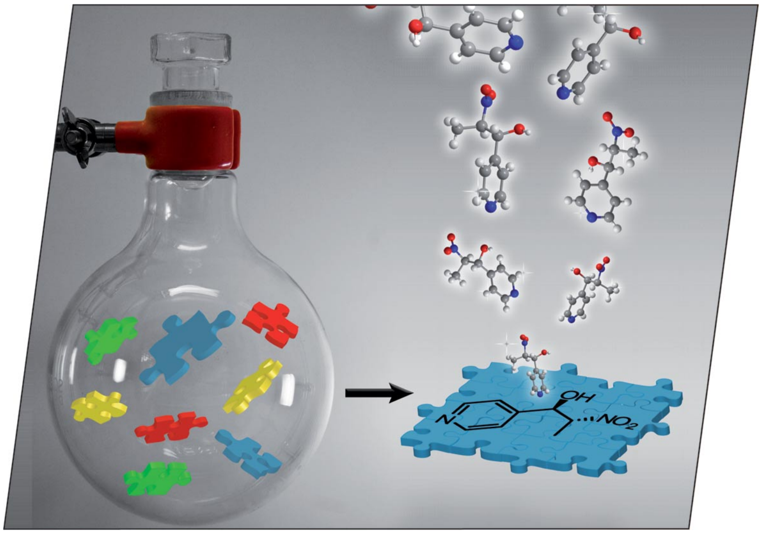
AUSTRIA PORTUGAL POLAND SPAIN NETHERLANDS

EurJOC is a journal of ChemPubSoc Europe, a union of 16 European chemical societies formed for the purpose of publishing high- quality science. All owners merged their national journals to form two leading chemistry journals, the *European Journal of Organic Chemistry* and the *European Journal of Inorganic Chemistry*.

Other ChemPubSoc Europe journals are *Chemistry – A European Journal*, *ChemBioChem, ChemPhysChem*, *ChemMedChem*, *ChemSusChem* and *ChemCatChem.*

COVER PICTURE

The cover picture shows how diastereoselective crystallization selects and amplifies a certain pyridine-nitroalcohol from a dynamic system of chemical compounds (symbolized by puzzle pieces). This serendipitous finding demonstrates the potential of working with dynamic systems for discovery purposes in general and provides an effective asymmetric synthesis protocol for pyridine-nitroalcohols in particular. Details are discussed in the Short Communication by O. Ramström et al. on p. 6315ff.



CONTENTS

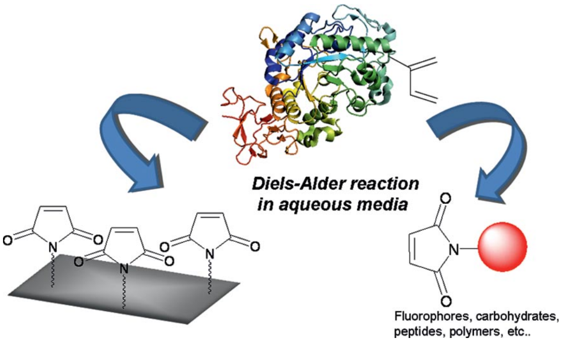
MICROREVIEW

Protein Chemistry

J. M. Palomo* 6303–6314

Diels–Alder Cycloaddition in Protein Chemistry

Keywords: Immobilization / Chemoselectivity / Cycloaddition / Biocatalysis / Chemical modification / Proteins



The Diels–Alder reaction is one of the most powerful methods for C–C bond formation. This Microreview discusses last recent advances in the application of this cycloaddition on protein modification, immobilization and biocatalysis.

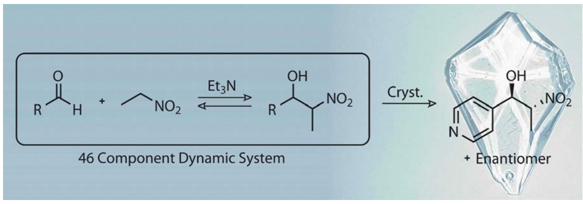
SHORT COMMUNICATIONS

Dynamic Chemistry

M. Angelin, P. Vongvilai, A. Fischer,
O. Ramström* 6315–6318

Crystallization-Driven Asymmetric Synthesis of Pyridine-β-nitroalcohols via Discovery-Oriented Self-Resolution of a Dynamic System

Keywords: Dynamic combinatorial chemistry / Systems chemistry / Aldol reactions / Asymmetric synthesis / Crystallization



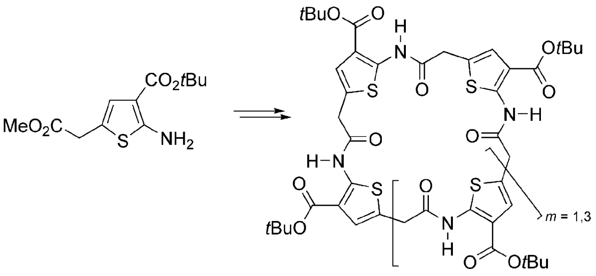
Diastereoselective crystallization of 2-nitro-1-(pyridin-4-yl)propan-1-ol was discovered from a self-screening process of a dynamic nitroaldol system. It was consequently developed into an efficient synthetic procedure and evaluated with a series of other pyridinecarbaldehydes and nitroalkanes as substrates.

Cyclopeptides

H. Özbek, D. Lentz,
H.-U. Reissig* 6319–6322

New Macrocyclic Peptidomimetics Containing 5-Aminothiophene Subunits

Keywords: Amino acids / Peptidomimetics / Sulfur heterocycles / Macrocycles / Hydrogen bonds

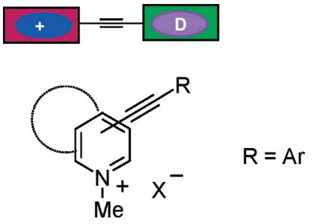


New cyclic peptidomimetics containing 5-aminothiophene subunits show interesting structural features. The compound, composed of four thiophene units (m = 1), has a box-like form in the solid state and bears a hexane molecule in its cavity, which was extracted by the macrocycle from the solvent.

FULL PAPERS

Heteroaromatic Cations

A variety azinium cations (D-π-A$^+$) were synthesized by the Sonogashira reaction in good yields. The hyperpolarizabilities (β) of the chromophores (D-π-A$^+$) were determined by hyper-Rayleigh scattering experiments and ab initio quantum chemical methods.



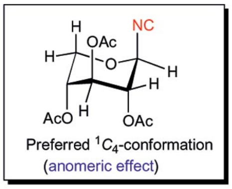
**T. Cañeque, A. M. Cuadro,*
J. Alvarez-Builla, J. Pérez-Moreno,
K. Clays, G. Marcelo, F. Mendicuti,
O. Castaño, J. L. Andrés,
J. J. Vaquero,*** .... **6323−6330**

Heteroaromatic Cation-Based Chromophores: Synthesis and Nonlinear Optical Properties of Alkynylazinium Salts

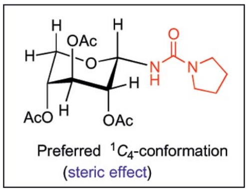
Keywords: Heterocycles / Cations / Chromophores / Synthesis / Nonlinear optics

Anomeric Effect

The anomeric effect associated with the nitrogen atom in the isocyano and urea groups was investigated by ^{1}H NMR spectroscopic analysis of an anomeric pair of xylopyranosyl isocyanides and ureas. We found that the β-xylopyranosyl isocyanide and α-xylopyranosyl urea prefers to exist in the $^1C_4$ conformation, which establishes an anomeric effect of the nitrogen atom in the isocyano group and a normal steric effect of the urea group.



Preferred $^1C_4$-conformation
(anomeric effect)



Preferred $^1C_4$-conformation
(steric effect)

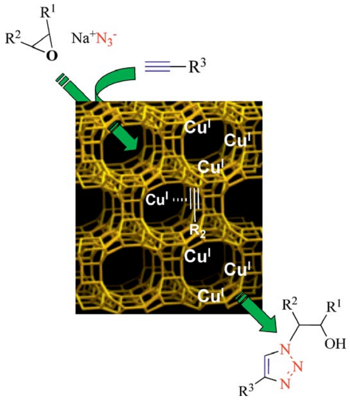
**Y. Ichikawa,* H. Watanabe, H. Kotsuki,
K. Nakano** .... **6331−6337**

Anomeric Effect of the Nitrogen Atom in the Isocyano and Urea Groups

Keywords: Anomeric effect / Isocyanides / NMR spectroscopy / Conformation analysis

Zeo-Click Chemistry

Copper(I)-modified zeolites, especially Cu^{I}−USY, are efficient and reusable heterogeneous catalysts for the one-pot condensation of epoxides with sodium azide and terminal alkynes in water at room temperature. Hydroxymethylated triazoles are thus regio- and stereoselectively obtained in good to high yields.



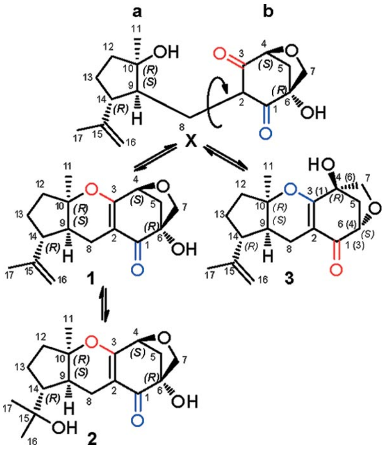
**T. Boningari, A. Olmos, B. M. Reddy,
J. Sommer, P. Pale*** .... **6338−6347**

Zeo-Click Chemistry: Copper(I)−Zeolite-Catalyzed Cascade Reaction; One-Pot Epoxide Ring-Opening and Cycloaddition

Keywords: Alkynes / Copper / Click chemistry / Multicomponent reactions / Regioselectivity / Zeolites

Metabolites of Endophytes

Three new meroterpenes, guignardones A−C (**1**−**3**), were characterized from a culture of *Guignardia mangiferae* associated with normal *Ilex cornuta* leaves.



**W. H. Yuan, M. Liu, N. Jiang, Z. K. Guo,
J. Ma, J. Zhang, Y. C. Song,
R. X. Tan*** .... **6348−6353**

Guignardones A−C: Three Meroterpenes from *Guignardia mangiferae*

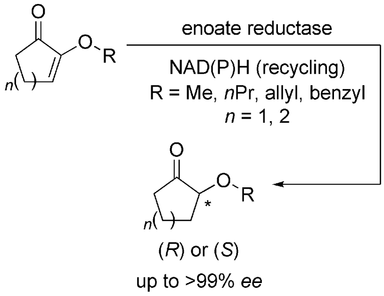
Keywords: Circular dichroism / Configuration determination / Natural products / Structure elucidation / UV/Vis spectroscopy

Bioreduction of α-Alkoxy Enones

C. K. Winkler, C. Stueckler, N. J. Mueller, D. Pressnitz, K. Faber* 6354–6358

Asymmetric Synthesis of *O*-Protected Acyloins Using Enoate Reductases: Stereochemical Control through Protecting Group Modification

Keywords: Biocatalysis / Reduction / Enones / Asymmetric synthesis / Enzymes



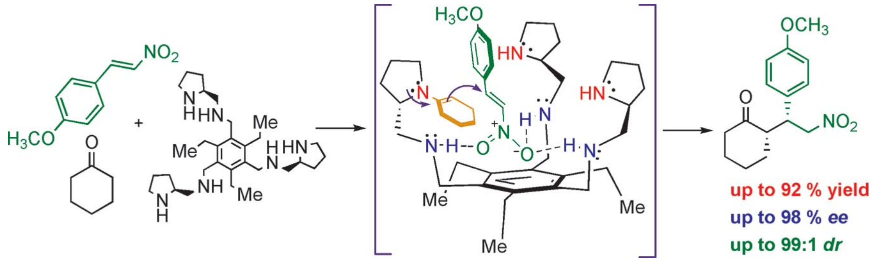
Both stereoisomers of *O*-protected acyloin derivatives were obtained in high *ee* through asymmetric bioreduction of α,β-unsaturated α-alkoxy ketones by using enoate reductases. Stereocontrol was achieved by variation of the size of the protecting group.

Organocatalysis

J. N. Moorthy,* S. Saha 6359–6365

C_3-Symmetric Proline-Functionalized Organocatalysts: Enantioselective Michael Addition Reactions

Keywords: Asymmetric synthesis / Michael addition / Organocatalysis / Amino acids



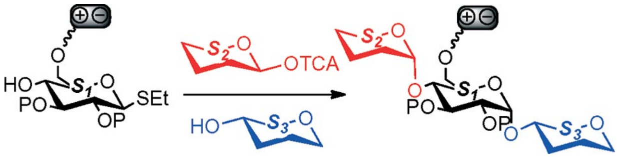
C_3-Symmetric organocatalyst **4** in which the 1,3,5-triethyl groups supposedly ensure that the tethered aminomethylpyrrolidines are *syn* and that the pyrrolidines enjoy conformational flexibility is shown to mediate Michael addition reactions of a variety of carbonyl compounds to β-nitrostyrenes with high diastereo- and enantioselectivity.

Glycosylation on Ionic Liquid Supports

M. Pépin, M. Hubert-Roux, C. Martin, F. Guillen, C. Lange, G. Gouhier* 6366–6371

First Examples of α-(1→4)-Glycosylation Reactions on Ionic Liquid Supports

Keywords: Glycosylation / Ionic liquids / Supported synthesis / Synthetic methods



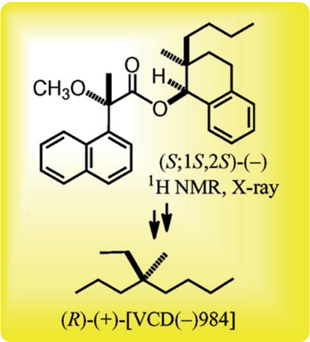
Successive selective α-(1→4)-glycosylation reactions of mono- and disaccharides grafted onto a recyclable ionic support takes place with good yields and stereoselectivities. The purification steps are simple washings or liquid/liquid extractions.

Configuration Determination

T. Fujita, K. Obata, S. Kuwahara, A. Nakahashi, K. Monde, J. Decatur, N. Harada* 6372–6384

(*R*)-(+)-[VCD(−)984]-4-Ethyl-4-methyloctane: A Cryptochiral Hydrocarbon with a Quaternary Chiral Center. (1) Synthesis of the Enantiopure Compound and Unambiguous Determination of Absolute Configuration

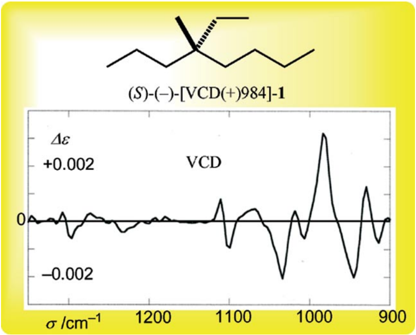
Keywords: Alkanes / Chirality / Configuration determination / Resolution / X-ray diffraction / NMR anisotropy



(*R*)-(+)-[VCD(−)984]-4-Ethyl-4-methyloctane, a fundamental cryptochiral hydrocarbon with a quaternary chiral center, was synthesized in enantiopure form, and its absolute configuration was unambiguously determined by a combination of X-ray crystallographic analysis, ^{1}H NMR anisotropy, and synthesis, whereby two methods were useful for enantioresolution.

Configuration Determination

The enantiopure title compound was synthesized, and its VCD spectrum showed characteristic Cotton effects around 1150–900 cm^{-1}. The VCD spectral curve calculated by the DFT MO method at the B3PW91/6-31G(d,p) level agreed well with the observed VCD spectrum, thus confirming the absolute configuration.

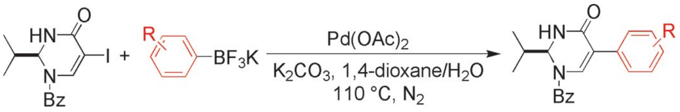


S. Kuwahara, K. Obata, T. Fujita, N. Miura, A. Nakahashi, K. Monde, N. Harada* **6385–6392**

(*R*)-(+)-[VCD(–)984]-4-Ethyl-4-methyloctane: A Cryptochiral Hydrocarbon with a Quaternary Chiral Center. (2) Vibrational CD Spectra of Both Enantiomers and Absolute Configurational Assignment

Keywords: Chirality / Optical rotation / Configuration determination / Density functional calculations / Conformational analysis / Vibrational spectroscopy

Cross-Coupling Reactions



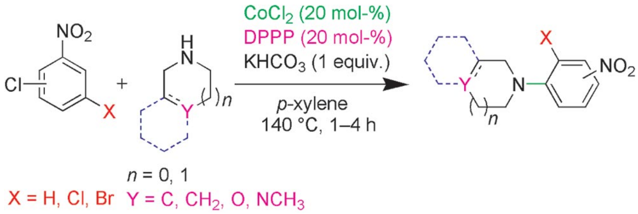
We present a general approach for the synthesis of (2*S*)-isopropyl-5-aryl-2,3-dihydro-4(*H*)-pyrimidin-4-ones by Suzuki–Miyaura reaction of aryltrifluoroborate salts with (2*S*)-isopropyl-5-iodo-2,3-dihydro-4(*H*)-pyrimidin-4-ones in the presence of a palladium catalyst and a base. The arylated compounds were transformed into enantioenriched α-aryl-substituted β-amino acids.

H. A. Stefani,* M. F. Z. J. Amaral, G. Reyes-Rangel, J. Vargas-Caporali, E. Juaristi* **6393–6403**

Functionalization of (2*S*)-Isopropyl-5-iodo-2,3-dihydro-4(*H*)-pyrimidin-4-ones by a Suzuki–Miyaura Cross-Coupling Reaction Using Aryltrifluoroborate Salts: Convenient Enantioselective Preparation of α-Substituted β-Amino Acids

Keywords: Palladium / Borates / Cross-coupling / Nitrogen heterocycles / Amino acids / Enantioselective synthesis

Cobalt Catalysis



The first cobalt-catalyzed C–N bond-forming reaction involving aromatic chlorides and cyclic secondary amines is described. The reaction is *ortho*- and *para*-selective; *meta*-substituted halides are unreactive.

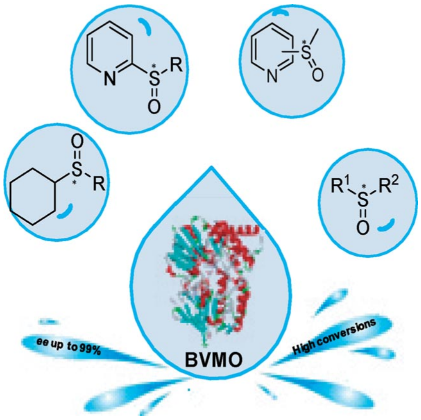
G. Toma,* R. Yamaguchi* **6404–6408**

Cobalt-Catalyzed C–N Bond-Forming Reaction between Chloronitrobenzenes and Secondary Amines

Keywords: Amines / Aryl chlorides / Cobalt / Cross-coupling / C–N bond formation / Phosphane ligands

Enzymatic Catalysis

A large variety of enantiopure sulfoxides have been obtained by using Baeyer–Villiger monooxygenase catalyzed oxidation in aqueous media under mild reaction conditions. Some reaction parameters were studied to improve the catalytic efficiency of these enzymes.



A. Rioz-Martínez, G. de Gonzalo, D. E. Torres Pazmiño, M. W. Fraaije, V. Gotor* **6409–6416**

Enzymatic Synthesis of Novel Chiral Sulfoxides Employing Baeyer–Villiger Monooxygenases

Keywords: Biocatalysis / Monooxygenases / Oxidation / Sulfur / Enantioselectivity

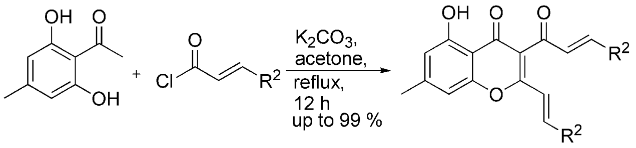
CONTENTS

Heterocycles

P. Königs, O. Neumann, O. Kataeva,
G. Schnakenburg,
S. R. Waldvogel* 6417–6422

Convenient Synthesis of 3-Cinnamoyl-2-styrylchromones: Reinvestigation of the Baker–Venkataraman Rearrangement

Keywords: Heterocycles / Cyclization / Domino reactions / One-pot protocol / Rearrangement



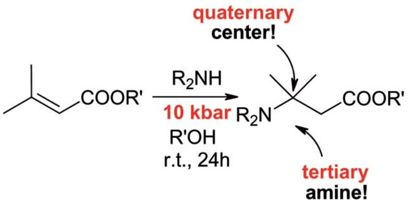
In a one-ps due to the low solubility of the 3-cinnamoyl-2-styrylchromone products. The second hydroxy moiety on the substrate is crucial, because a two-fold cinnamoylated intermediate is required. Earlier reports on such conversions may be corrected.

Bulky Quaternary Centers

A. Yu. Rulev, S. Azad, H. Kotsuki,
J. Maddaluno* 6423–6429

Direct Access to Cumbersome Aminated Quaternary Centers by Hyperbaric Aza-Michael Additions

Keywords: Michael addition / High-pressure chemistry / Chirality / Amines



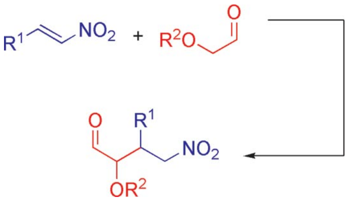
The aza-Michael addition of secondary amines to α,β- or β,β-disubstituted α,β-unsaturated esters was efficiently achieved under high pressure (10–16 kbar) in protic solvents without any catalyst.

Asymmetric Organocatalysis

M. Huťka, V. Poláčková, J. Marák,
D. Kaniansky, R. Šebesta,*
Š. Toma 6430–6435

Enantioselective Organocatalytic Michael Additions of Oxyacetaldehydes to Nitroolefins

Keywords: Aldehydes / Michael addition / Enantioselectivity / Organocatalysis / Density functional calculations



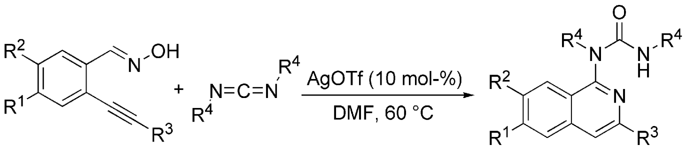
Oxyacetaldehydes enantioselectively add to nitroolefins. Diphenylprolinol trimethylsilyl ether affords products with up 96%*ee*. The reason for lower diastereoselectivity was investigated by computational methods. Reactive intermediates were confirmed by mass spectrometry.

Tandem Reaction

S. Ye, H. Wang, J. Wu* 6436–6439

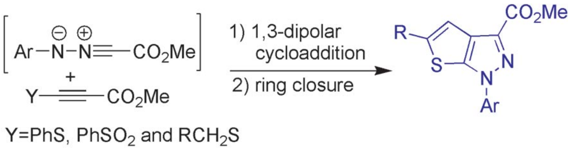
Facile Synthesis of 1-(Isoquinolin-1-yl)-ureas by Silver Triflate Catalyzed Tandem Reactions of 2-Alkynylbenzaldoximes with Carbodiimides

Keywords: Alkynes / Fused-ring systems / Cycloaddition / Cyclization / Rearrangement / Silver



2-Alkynylbenzaldoximes react with carbodiimides under mild conditions and silver triflate catalysis in DMF, leading to a diverse range of 1-(isoquinolin-1-yl)ureas in good to excellent yields. Tandem 6-*endo* cyclization, [3+2] cycloaddition, and subsequent rearrangement are involved in the process.

Dipolar Cycloadditions



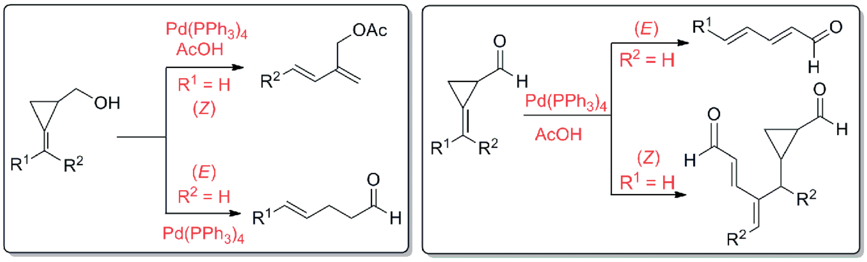
1,3-Dipolar cycloadditions of *C*-carboxymethyl-*N*-arylnitrile imines with substituted acetylenes bearing thiol or sulfone groups were studied. The sulfur controls the regiochemistry of the reaction, and this protocol was applied to the synthesis of ring-fused thieno[2,3-*c*]pyrazoles.

J. Z. Chandanshive, B. F. Bonini, D. Gentili, M. Fochi, L. Bernardi, M. Comes Franchini* **6440–6447**

Regiocontrolled Synthesis of Ring-Fused Thieno[2,3-*c*]pyrazoles through 1,3-Dipolar Cycloaddition of Nitrile Imines with Sulfur-Based Acetylenes

Keywords: Cycloaddition / Regioselectivity / Sulfur / Alkynes / Heterocycles / Fused-ring systems

Synthetic Methods



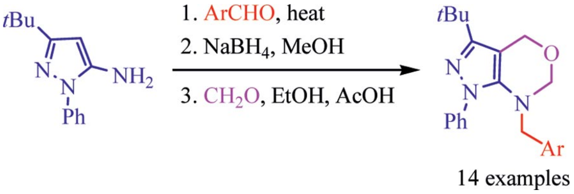
Palladium-catalyzed reactions of 3-substituted methylenecyclopropanes (MCPs), where the substituents can be either hydroxymethyl or formyl, in the presence or absence of an acid source have been thoroughly investigated.

L.-X. Shao, J. Li, B.-Y. Wang, M. Shi* **6448–6453**

Palladium-Catalyzed Reactions of 3-Substituted Methylenecyclopropanes

Keywords: Small ring systems / Palladium / Substituent effects / Synthetic methods

Heterocycles



In an attempt to obtain pyrazolobenzazepine derivatives we serendipitously developed an efficient four-step procedure for the synthesis of new 6,7-dihydro-1*H*,4*H*-pyrazolo[3,4-*d*][1,3]oxazines from 5-amino-3-*tert*-butyl-1-phenylpyrazole as starting material through an unplanned intramolecular etherification process. The structures of the obtained products were confirmed by X-ray diffraction.

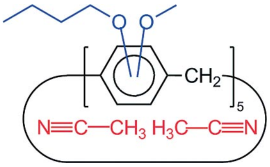
R. Abonia,* J. Castillo, B. Insuasty, J. Quiroga, M. Nogueras, J. Cobo **6454–6463**

An Efficient Synthesis of 7-(Arylmethyl)-3-*tert*-butyl-1-phenyl-6,7-dihydro-1*H*,4*H*-pyrazolo[3,4-*d*][1,3]oxazines

Keywords: 5-Aminopyrazoles / Etherification / Pyrazolo-oxazines / Heterocycles / Cyclization / Fused-ring systems

Host–Guest Chemistry

Nonsymmetric pillar[5]arenes are formed in a statistical ratio of the possible regioisomers but with a high stereoselectivity.



Y. Kou, H. Tao, D. Cao,* Z. Fu, D. Schollmeyer, H. Meier* **6464–6470**

Synthesis and Conformational Properties of Nonsymmetric Pillar[5]arenes and Their Acetonitrile Inclusion Compounds

Keywords: Conformation analysis / Cyclocondensation / Cyclooligomerization / Host-guest chemistry / Regioselectivity

---

* Author to whom correspondence should be addressed.

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