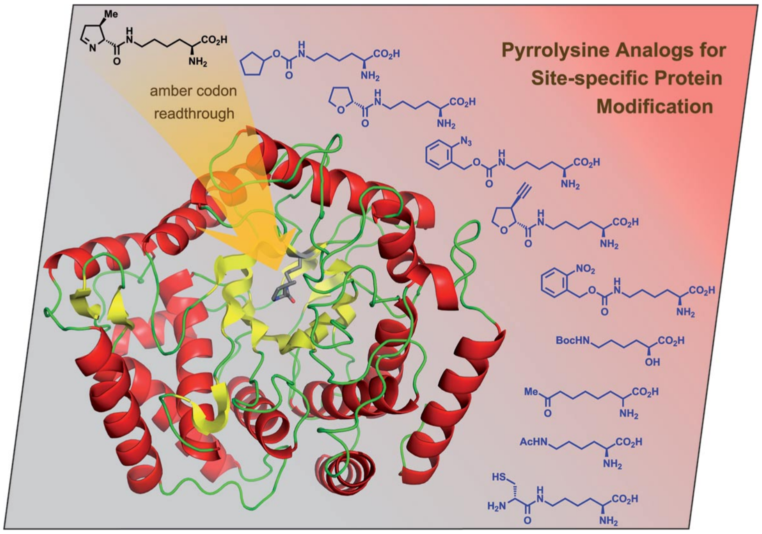
HUNGARY
ITALY
GERMANY
GREECE
CZECH REPUBLIC
ChemPubSoc Europe
FRANCE
SWEDEN
BELGIUM
AUSTRIA
PORTUGAL
POLAND
SPAIN
NETHERLANDS

EurJOC is co-owned by 11 societies of ChemPubSoc Europe, a union of European chemical societies 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*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

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

COVER PICTURE

The cover picture shows the X-ray crystal structure of the monomethylamine methyltransferase from *Methanosarcina barkeri*. It was central to the discovery of pyrrolysine, the 22nd genetically encoded amino acid. The picture is also decorated with the structures of pyrrolysine and some of its analogs. They can be incorporated into proteins in response to an otherwise non-sense amber (UAG) codon upon action of pyrrolysyl-tRNA^{Pyl} synthetases from various *Methanosarcinaceae* working in tandem with their cognate tRNAs. Details are presented in the Microreview by M. K. Chan et al. on p. 4171 ff. The scarlet-and-gray background represents the colors of The Ohio State University.



CONTENTS

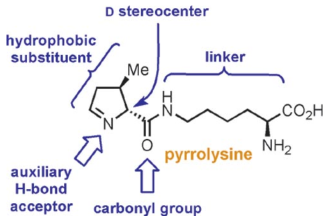
MICROREVIEW

Pyrrolysine

T. Fekner, X. Li,
M. K. Chan* **4171–4179**

Pyrrolysine Analogs for Translational Incorporation into Proteins

Keywords: Pyrrolysine / Amino acids / Amber codon / Protein modifications / Genetic encoding



A combination of crystallographic, biochemical, and synthetic studies related to pyrrolysine and its biochemical machinery led to the formulation of a set of principles for the design of successful analogs for site-specific modification of proteins. The journey leading to it and recent practical applications of the acquired knowledge are discussed.

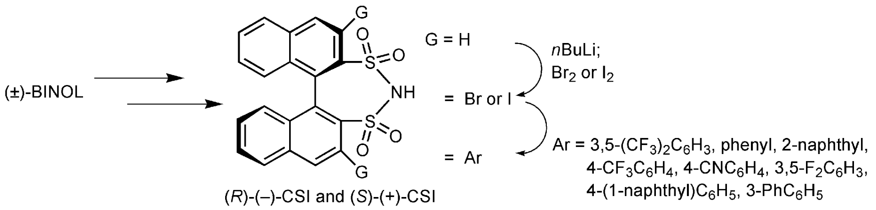
SHORT COMMUNICATIONS

Chiral Brønsted Acids

H. He, L.-Y. Chen,
W.-Y. Wong, W.-H. Chan,
A. W. M. Lee* **4181–4184**

Practical Synthetic Approach to Chiral Sulfonimides (CSIs) – Chiral Brønsted Acids for Organocatalysis

Keywords: Sulfonimides / Brønsted acids / Chirality / Organocatalysis



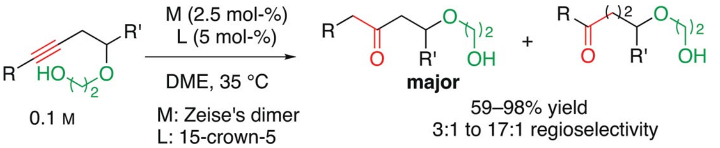
3,3′-Diaryl chiral sulfonimides (CSIs), a new class of Brønsted acids, were synthesized from readily available racemic BINOL. Sulfonyl-group-directed *ortho*-lithiation afforded the dihalides, which serve as the common precursors for the aryl-substituted CSIs.

Platinum Activation of Alkynes

D. Yang, J. Huang,
B. Liu* **4185–4188**

Platinum-Catalyzed Regioselective Formation of β-Alkoxy Ketones from Internal Alkynes

Keywords: Platinum / Alkynes / Ketones / Regioselectivity / Cyclization



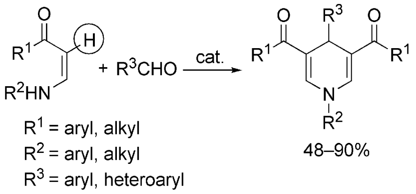
A platinum/crown ether catalyzed method for the regioselective formation of β-alkoxy ketones from internal homopropargyl ethers was achieved. Various β-alkoxy ketones were obtained in up to 98% yield with up to 17:1 selectivity (*exo*/*endo*). Some products could be transformed further into the corresponding β-hydroxy ketones, showing that this method could serve as an aldol reaction alternative.

Cascade Reactions

J. Yang, C. Wang, X. Xie, H. Li,
Y. Li* **4189–4193**

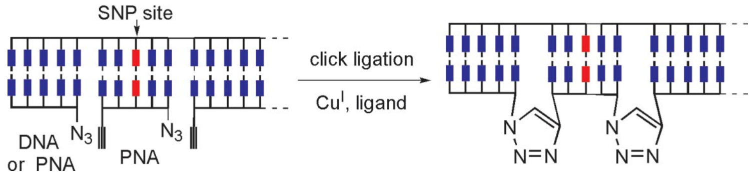
Acid-Catalyzed Cascade Reactions of Enaminones with Aldehydes: C–H Functionalization To Afford 1,4-Dihydropyridines

Keywords: Nitrogen heterocycles / Cyclization / Lewis acids / C–H activation / Domino reactions



The acid-catalyzed efficient synthesis of functional 1,4-dihydropyridines from the reaction of enaminones with aldehydes was described. The 1,4-dihydropyridines could be obtained in a one-pot process without the isolation of the enaminone intermediates.

Sequence-Specific PNA Click Ligation



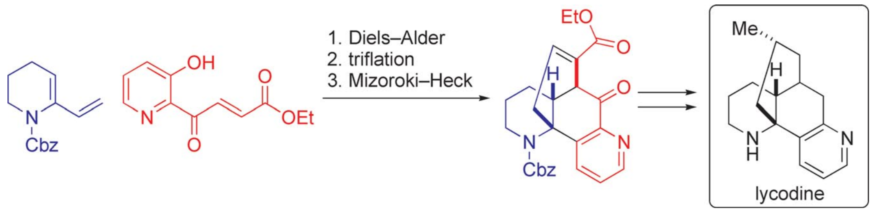
A template-dependent click–click reaction was developed for highly efficient conjugation of PNA with DNA or PNA. The click ligation reaction is capable of discriminating between templates differing by a single nucleotide.

X. Peng,* H. Li, M. Seidman 4194–4197

A Template-Mediated Click–Click Reaction: PNA–DNA, PNA–PNA (or Peptide) Ligation, and Single Nucleotide Discrimination

Keywords: Peptide nucleic acids / Chemical Ligation / Click chemistry / Nucleotides / DNA

Natural Product Synthesis



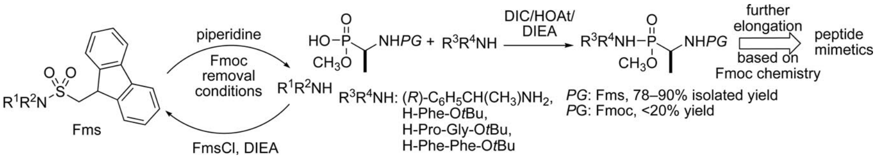
Lycodine was prepared by using Diels–Alder and Mizoroki–Heck reactions as key steps for the construction of the bicyclo[3.3.1]nonane core.

C. Tsukano,* L. Zhao, Y. Takemoto, M. Hirama* 4198–4200

Concise Total Synthesis of (±)-Lycodine

Keywords: Alkaloids / Total synthesis / Heck reaction / Cycloaddition

Protecting Groups



A new Fmoc-type protecting group, (9*H*-fluoren-9-yl)methanesulfonyl (Fms), has been developed. Use of Fms led to successful condensation of Fms-AlaP(OCH_3)-OH with the N-terminus of peptides, avoiding a serious problem associated with Fmoc, and thereby paving a new way to the synthesis of α-amino phosphonic acid containing peptide mimetics without losing the well-established Fmoc chemistry.

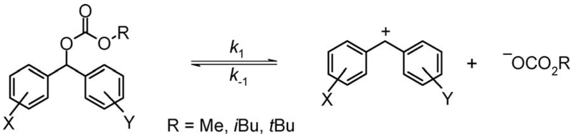
Y. Ishibashi, K. Miyata, M. Kitamura* 4201–4204

(9*H*-Fluoren-9-yl)methanesulfonyl (Fms): An Amino Protecting Group Complementary to Fmoc

Keywords: Protecting groups / Sulfonamides / Phosphorus / Peptides

FULL PAPERS

Kinetics



Kinetics of the combination of alkyl carbonates with benzhydrylium ions as well as the reverse reactions (heterolyses) have been studied by photometry and conductimetry. Thereby an additional advantage of the *t*Boc protecting group for synthetic application is revealed, i.e., its greater stability under neutral and basic conditions compared to other organic carbonates.

N. Streidl, R. Branzan, H. Mayr* 4205–4210

Nucleophilicities and Nucleofugalities of Organic Carbonates

Keywords: Kinetics / Linear free energy relationships / Solvolysis / Correlation analysis / Leaving groups

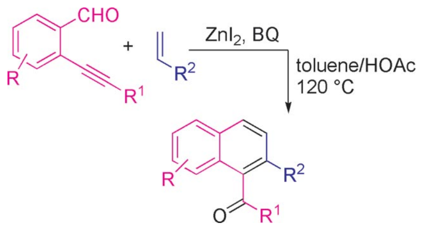
CONTENTS

Naphthalene Synthesis

X. Zhao, X.-G. Zhang, R.-Y. Tang, C.-L. Deng, J.-H. Li* 4211–4217

ZnI_2-Catalyzed Benzannulation of *o*-Alkynylbenzaldehydes with Alkenes Leading to 1-Acyl-2-Substituted Naphthalenes

Keywords: Zinc / Annulation / Fused-ring systems / Alkenes



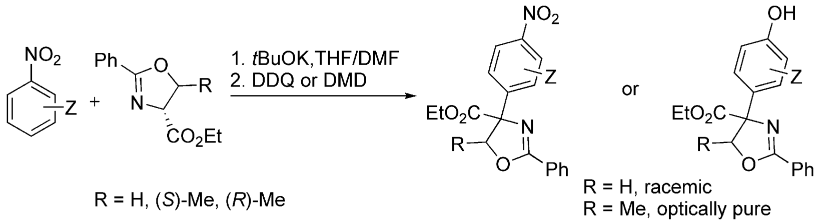
A new, practical route to 1-acyl-2-substituted naphthalenes has been developed by benzoquinone-promoted ZnI_2-catalyzed benzannulation of 2-alkynylbenzaldehydes with alkenes. This method allows three new bonds, two C=C bonds and one C=O bond, to be constructed in a single reaction.

Amino Acids

D. Sulikowski, M. Mąkosza* 4218–4226

Oxidative Nucleophilic Substitution of Hydrogen in Nitroarenes with Carbanions of Protected Serine and Threonine Esters

Keywords: Carbanions / Nitroarenes / Amino acids / Oxidation / Nucleophilic substitution



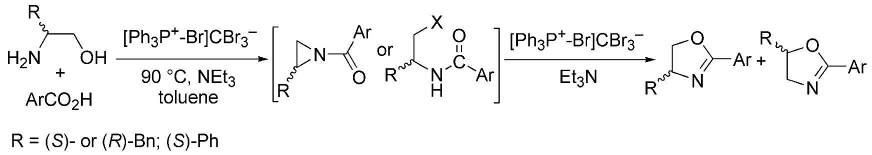
The reactions of oxazoline carbanions lead to the formation σ^H adducts that can be further oxidized with DDQ to give α-(*p*-nitroaryl) derivatives or with DMD to give α-(*p*-hydroxyaryl) derivatives in good and very good yields. The presence of the second chiral center in the oxazolines, obtained from threonine esters, resulted in a reaction that was completely diastereoselective.

Optically Active 2-Aryl-1,3-oxazolines

H. Jiang, S. Yuan, W. Wan, K. Yang, H. Deng, J. Hao* 4227–4236

Bromotriphenylphosphonium Salt Promoted Tandem One-Pot Cyclization to Optically Active 2-Aryl-1,3-oxazolines

Keywords: Heterocycles / Chirality / Cyclization / Amino alcohols



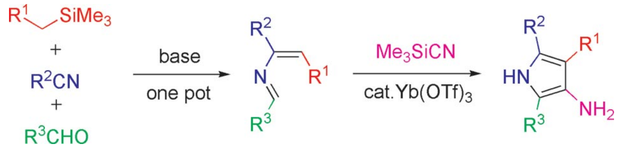
Optically active 4-substituted-2-aryl-1,3-oxazolines and 5-substituted-2-aryl-1,3-oxazolines were successfully prepared through a sequential process involving bromotriphenylphosphonium salt promoted aziridine ring formation and ring opening in a tandem one-pot cyclization of chiral 2-amino-3-phenylpropanol or 2-amino-2-phenyl-1-ethanol with various aryl acids in moderate to excellent yields.

Yb-Catalyzed Annulation

T. Sasada, T. Sawada, R. Ikeda, N. Sakai, T. Konakahara* 4237–4244

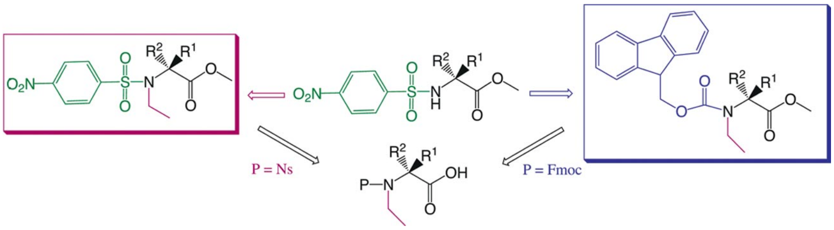
Approach to Trisubstituted 3-Aminopyrrole Derivatives by $Yb(OTf)_3$-Catalyzed [4+1] Annulation of 2-Azadiene with Me_3SiCN

Keywords: Multicomponent reactions / Nitrogen heterocycles / Annulation / Ytterbium



We found a novel approach to the simple and practical synthesis of 3-aminopyrrole derivatives, which proceeds through a four-component coupling reaction of a functionalized silane, a nitrile, an aldehyde, and trimethylsilyl cyanide by $Yb(OTf)_3$-catalyzed annulation of a 2-azabutadiene with trimethylsilyl cyanide.

Get Protected!



A fast and practical synthesis of *N*-ethylated amino acid methyl esters has been described. The protocol is based on the use of the 4-nitrophenylsulfonyl (nosyl, Ns) protecting group and triethyloxonium tetrafluoroborate as the alkylating agent. The method is compatible with standard fluorenylmethyloxycarbonyl (Fmoc) chemistry.

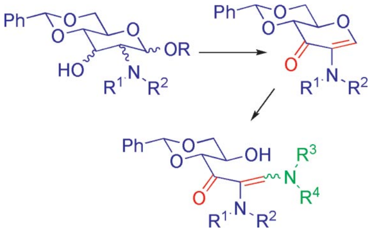
E. L. Belsito, R. De Marco, M. L. Di Gioia, A. Liguori,* F. Perri, M. C. Viscomi **4245–4252**

N-(4-Nitrophenylsulfonyl)- and *N*-(Fluorenylmethoxycarbonyl)-*N*-ethyl Amino Acid Methyl Esters – A Practical Approach

Keywords: Amino acids / Protecting groups / Alkylation / One-pot synthesis

Amino Glycal Synthesis

A general method for the synthesis of new *N*,*N*-disubstituted 2-amino glycals from amino sugars is described. Their reactions with different amines have been explored and an efficient methodology for the synthesis of highly functionalised β-enamino ketones is reported.

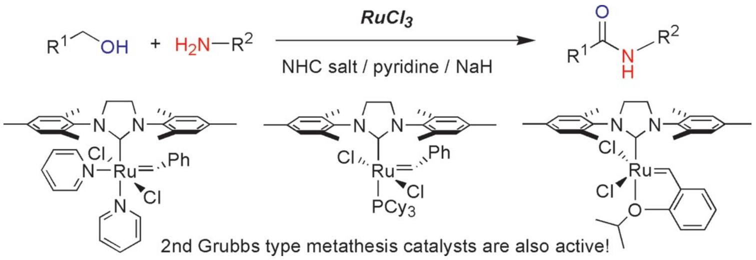


F. Iglesias-Guerra,* I. Periñán, M. Vega-Holm, J. M. Vega-Pérez* **4253–4265**

Synthesis of 2-Amino glycal Derivatives and their Conversion into Highly Functionalised β-Enamino Ketones

Keywords: Synthetic methods / Carbohydrates / Glycosides / Glycals / Amines / Ketones

Amide Synthesis



A catalyst generated in situ from simple and economical RuCl$_3$, an NHC precursor, NaH, and pyridine was developed. The catalyst allows the efficient synthesis of amides directly from alcohols and amines. Grubbs-type NHC-based olefin metathesis catalysts were also found to be active for the amidation of alcohols, suggesting that an Ru complex supported by an NHC ligand can catalyze the reaction.

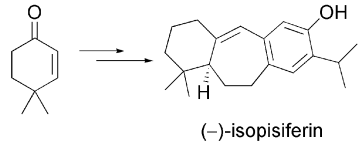
S. C. Ghosh, S. H. Hong* **4266–4270**

Simple RuCl$_3$-Catalyzed Amide Synthesis from Alcohols and Amines

Keywords: Amides / N-heterocyclic carbenes / Carbene ligands / Ruthenium / Grubbs catalyst / Amidation

Natural Product Synthesis

Starting from 4,4-dimethyl-2-cyclohexenone, an enantioselective synthesis of (–)-isopisiferin has been accomplished in 15 steps with an overall yield of 11.4%.



N.-W. Jan, H.-J. Liu,* M.-T. Hsieh, K.-S. Shia* **4271–4275**

Total Synthesis of (–)-Isopisiferin: Confirmation of Absolute Configuration

Keywords: Natural products / Enantioselectivity / Terpenoids / Lithium / Configuration determination

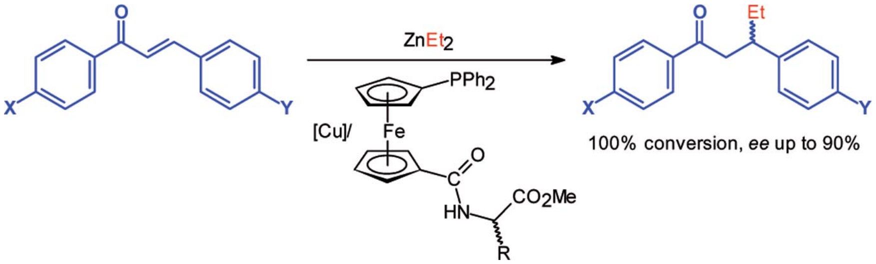
CONTENTS

Chiral Amidophosphanes

J. Tauchman, I. Císařová,
P. Štěpnička* 4276–4287

Chiral Phosphanylferrocenecarboxamides with Amino Acid Pendant Groups as Ligands for Cu-Mediated Asymmetric Conjugate Additions of Diethylzinc to Chalcones – Structural Characterisation of Precursors to the Cu Catalyst

Keywords: Phosphanylferrocene ligands / Amino acids / Amides / Copper / Asymmetric synthesis / Conjugate addition



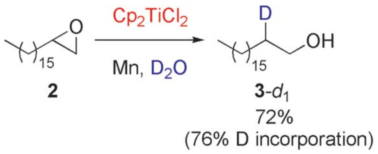
Chiral phosphanylferrocenecarboxamides bearing amino acid pendant groups are efficient ligands for Cu-mediated conjugate additions of diethylzinc to chalcones. Reactions with these donors proceed quickly and with high enantioselectivities (*er* values up to 95:5) under convenient reaction conditions.

Water as HAT Reagent

T. Jiménez, A. G. Campaña, B. Bazdi,
M. Paradas, D. Arráez-Román,
A. Segura-Carretero,
A. Fernández-Gutiérrez, J. E. Oltra,
R. Robles, J. Justicia,*
J. M. Cuerva* 4288–4295

Radical Reduction of Epoxides Using a Titanocene(III)/Water System: Synthesis of β-Deuterated Alcohols and Their Use as Internal Standards in Food Analysis

Keywords: Titanium / Water chemistry / Radicals / Reduction / Natural products



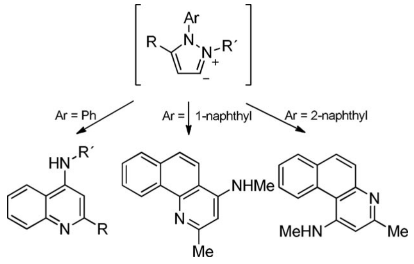
The reductive opening of epoxides mediated by Cp_2TiCl is described. Water was used to access alcohols with anti-Markovnikov regiochemistry. The use of D_2O led to the efficient synthesis of β-deuterated alcohols. A deuterated sample of tyrosol, a bioactive compound contained in the leaf of the olive tree, was prepared and successfully applied as an internal standard in food analysis.

N-Heterocyclic Carbenes

A. Dreger, R. Cisneros Camuña,
N. Münster, T. A. Rokob, I. Pápai,
A. Schmidt* 4296–4305

Rearrangements of N-Heterocyclic Carbenes of Pyrazole to 4-Aminoquinolines and Benzoquinolines

Keywords: Carbenes / Nitrogen heterocycles / Density functional calculations / Reaction mechanisms / Sigmatropic rearrangement / Malaria



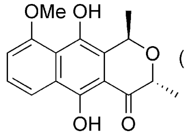
1-Phenyl-substituted pyrazolium salts, formed by quaternization of pyrazoles with benzyl halides or long-chain alkyl halides, deprotonate to pyrazol-3-ylidenes that undergo a sequence of ring-opening, ring-closure, and tautomerization to new substituted 4-aminoquinolines. Similarly, 1-naphthyl-substituted pyrazolium-3-ylidenes give benzoquinolines. DFT calculations elucidate the mechanism.

Asymmetric Synthesis

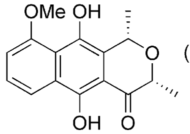
R. A. Fernandes,*
V. P. Chavan 4306–4311

A Concise Asymmetric Synthesis of (–)-Hongconin and (–)-1-*epi*-Hongconin

Keywords: Quinones / Asymmetric synthesis / Annulation / Cyclization / Natural products



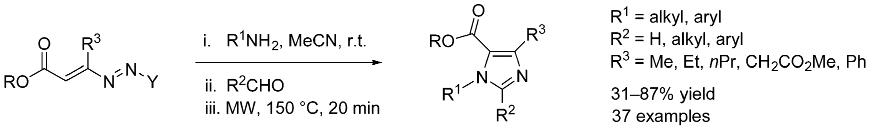
(–)-hongconin



(–)-1-*epi*-hongconin

An efficient asymmetric synthesis of (–)-hongconin and (–)-1-*epi*-hongconin has been achieved by using Dötz benzannulation or lactaldehyde arylation and the oxa-Pictet–Spengler reaction as the key steps.

Microwave-Assisted Synthesis



R^1 = alkyl, aryl
R^2 = H, alkyl, aryl
R^3 = Me, Et, *n*Pr, CH_2CO_2Me, Ph

31–87% yield
37 examples

Reaction of 1,2-diaza-1,3-dienes with primary amines and aldehydes under microwave irradiation affords functionalized imidazole-4-carboxylates in good to excellent yield through a simple one-pot multicomponent procedure. The reaction sequence features the 1,5-electrocyclization of a conjugated azavinyl azomethine ylide species as the key step.

L. Preti, O. A. Attanasi, E. Caselli, G. Favi, C. Ori, P. Davoli, F. Felluga, F. Prati* 4312–4320

One-Pot Synthesis of Imidazole-4-Carboxylates by Microwave-Assisted 1,5-Electrocyclization of Azavinyl Azomethine Ylides 💻

Keywords: Azomethine ylides / Electrocyclic reactions / Microwave chemistry / Multicomponent reactions / Nitrogen heterocycles

CORRECTION

Keywords: Phosphanes / Polyfluoroarenes / Aromatic substitution / Nucleophilic substitution / Ab initio calculations / Bis(phosphane)palladium dichloride complexes

Di- and Trifluorobenzenes in Reactions with Me_2EM (E = P, N; M = $SiMe_3$, $SnMe_3$, Li) Reagents: Evidence for a Concerted Mechanism of Aromatic Nucleophilic Substitution

L. I. Goryunov, J. Grobe,* D. Le Van, V. D. Shteingarts,* R. Mews, E. Lork, E.-U. Würthwein* 4321

---

* Author to whom correspondence should be addressed.

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