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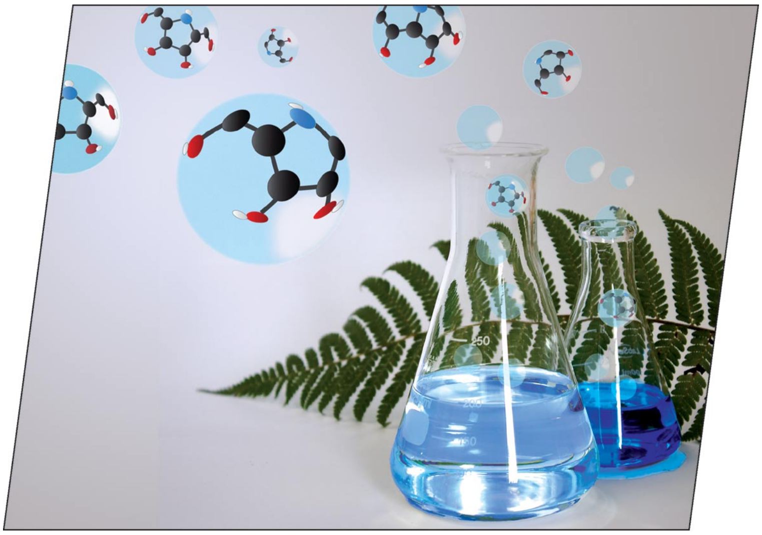
COVER PICTURE

The cover picture shows a representation of the synthesis of several iminosugars. Iminosugars are sugar mimetics found widely in nature. They have potential in the treatment of a number of diseases, and accordingly, much effort has been spent in developing efficient routes for their syntheses. Recent developments in the synthesis of pyrrolidine-containing iminosugars are outlined in the Microreview by B. L. Stocker, M. S. M. Timmer et al. on page 1615ff. The plant in the background is a Ponga (silver fern, *cyathea dealbata*) endemic to New Zealand. It was chosen to highlight the fact that iminosugars are naturally occurring in many plant species from around the world. The authors thank Sam Win-Mason for the photograph used for the cover picture.



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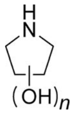
MICROREVIEW

Iminosugars

B. L. Stocker,* E. M. Dangerfield, A. L. Win-Mason, G. W. Haslett, M. S. M. Timmer* 1615–1637

Recent Developments in the Synthesis of Pyrrolidine-Containing Iminosugars

Keywords: Azasugars / Iminosugars / Inhibitors / Total synthesis



Given the enormous potential of iminosugars as inhibitors of glycosidases, and their therapeutic significance, the development of improved synthetic methodologies for their efficient production has become the objective of many synthetic chemists. This review highlights recent developments (post 2005) in the synthesis of pyrrolidine-containing iminosugars.

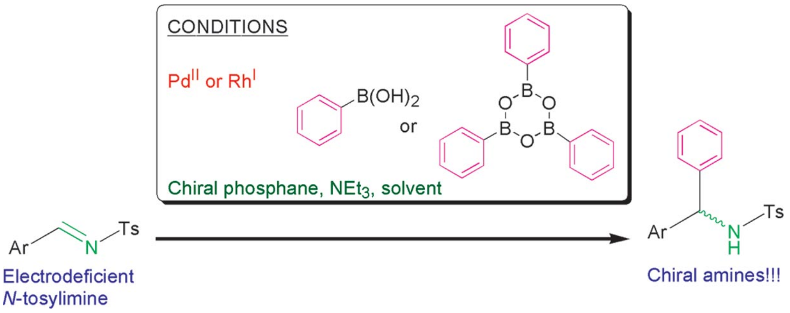
SHORT COMMUNICATIONS

Enantioselective Catalysis

C. S. Marques, A. J. Burke* ... 1639–1643

Catalytic Enantioselective Addition of Phenylboronic Acid and Phenylboroxine to *N*-Tosylimines: Pd^{II} and Rh^{I} Catalysis

Keywords: *N*-Tosylarylimines / Phenylboronic acid / Addition / Chiral amines / Enantioselective catalysis



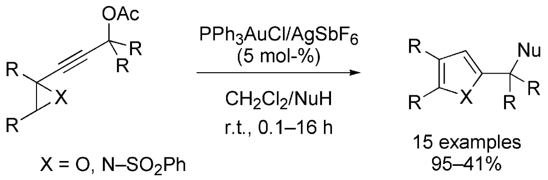
An account of the first successful application of a range of chiral, already known diphosphane ligands in the palladium-catalyzed enantioselective addition of arylboronic acids to *N*-tosylimines is provided; *ee* values of >99% are achieved with good yields.

Gold Catalysis

A. Blanc,* A. Alix, J.-M. Weibel, P. Pale* 1644–1647

Gold(I)-Catalyzed Tandem Rearrangement–Nucleophilic Substitution of α-Acetoxy Alkynyl Oxiranes or Aziridines: Efficient Approach to Furans and Pyrroles

Keywords: Gold / Cyclization / Homogeneous catalysis / Oxygen heterocycles / Nitrogen heterocycles

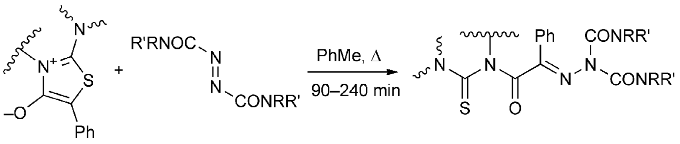


Highly substituted furans and pyrroles were efficiently formed by a new gold(I)-catalyzed tandem rearrangement–nucleophilic substitution of acetoxylated alkynyl oxiranes and aziridines in the presence of various nucleophiles.

Reactivity of Thioisomünchnones

B. Sánchez, I. López, M. E. Light, G. Silvero, J. L. Bravo* 1648–1652

Azodicarboxamides vs. Azodicarboxylates in Reactions against Thioisomünchnones: 1,3-Dipolar Cycloaddition or Nucleophilic Addition?



Azodicarboxamides react with thioisomünchnones to produce open-chain thioureido compounds. Experimental evidence and theoretical calculations hint that azodicarboxamides, unlike azodicarboxylates, could follow a nucleophilic addition/rearrangement mechanism rather than a 1,3-dipolar cycloaddition.

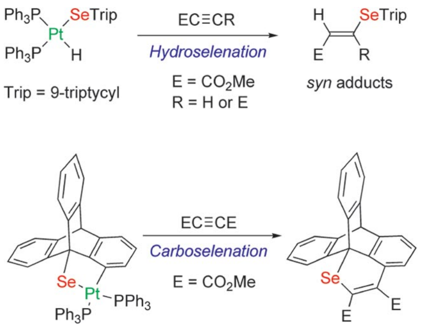
Keywords: Azo compounds / Thioisomünchnones / Mesoionic compounds / 1,3-Dipolar cycloadditions / Thioureas

FULL PAPERS

Hydro- and Carboselenation

A. Ishii,* H. Kamon, K. Murakami, N. Nakata 1653–1659

Hydroselenation and Carboselenation of Electron-Deficient Alkynes with Isolable (Hydrido)(selenolato)platinum(II) Complexes and a Selenaplatinacycle Bearing a Triptycene Skeleton



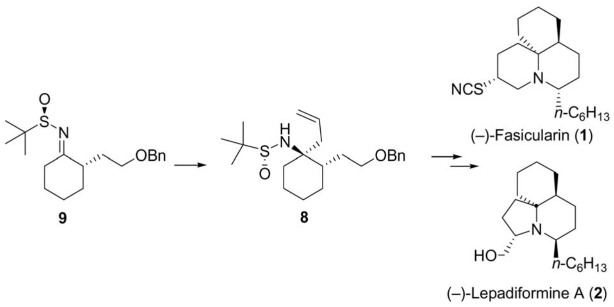
An isolable (hydrido)(selenolato)platinum(II) complex reacts with activated alkynes to yield *syn* adducts. This hydroselenation requires dissociation of a PPh_3 ligand prior to insertion of alkyne. The reaction of a selenaplatinacycle, which is a thermal reaction product of the hydrido complex, with dimethyl acetylenedicarboxylate produces the carboselenation product, a 1*H*-2-benzoselenin derivative.

Keywords: Platinum / Insertion / Hydride ligands / Phosphane ligands / Selenium

Natural Product Synthesis

S.-L. Mei, G. Zhao* 1660–1668

Total Synthesis of (−)-Fasicularin and (−)-Lepadiformine A Based on Zn-Mediated Allylation of Chiral *N-tert*-Butanesulfinyl Ketimine



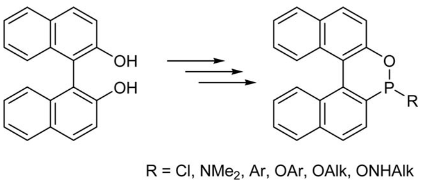
The allylation of the chiral *N-tert*-butanesulfinyl ketimine **9** produced sulfinamide **8** with a *dr* of 12:1 in 89% yield, which allowed for the stereoselective synthesis of fasicularin (**1**) and lepadiformine A. The stereochemical result of this transformation was tentatively explained by a chelated, chair-like, transition state model, in which the allyl-Zn could coordinate to the sulfinyl oxygen.

Keywords: Total synthesis / Alkaloids / Fasicularin / Lepadiformine A / Zinc / Allylation

Cyclic Phosphanes

I. A. Shuklov, N. V. Dubrovina,* H. Jiao, A. Spannenberg, A. Börner* ... 1669–1680

A Highly Diastereoselective Route to Dinaphtho[*c*,*e*][1,2]oxaphosphinines and Their Application as Ligands in Homogeneous Catalysis



A new method for the preparation of 6*H*-dinaphtho[*c*,*e*][1,2]oxaphosphinines starting from BINOL has been developed. This procedure allows the synthesis of these cyclic phosphanes with extremely high diastereoselectivities. The stereochemistries were elucidated by ^{31}P NMR and X-ray analysis. The phosphanes were successfully tested as ligands in the Rh-catalysed hydroformylation of terminal olefins.

Keywords: Phosphane ligands / P ligands / Density functional calculations / Hydroformylation

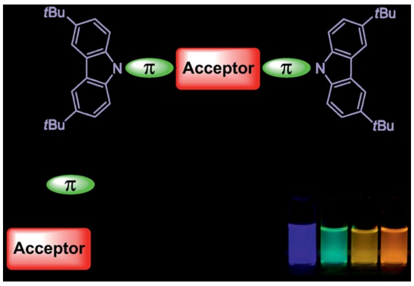
CONTENTS

HOMO–LUMO Gap Tuning

H. Zhang, X. Wan,* X. Xue, Y. Li, A. Yu, Y. Chen* **1681–1687**

Selective Tuning of the HOMO–LUMO Gap of Carbazole-Based Donor–Acceptor–Donor Compounds toward Different Emission Colors

Keywords: Nitrogen heterocycles / Fused-ring systems / Donor–acceptor systems / Molecular electronics / Luminescence



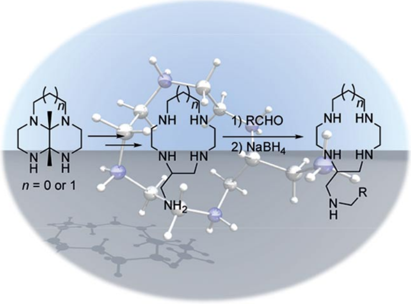
Carbazole-based donor–acceptor compounds with tunable HOMO–LUMO gaps were synthesized and fully characterized. These compounds show redshifted optoelectronic properties with different emission colors ranging from blue to green to orange.

Nitrogen Macrocycles

Y. Rousselin, N. Sok, F. Boschetti, R. Guilard, F. Denat* **1688–1693**

Efficient Synthesis of New *C*-Functionalized Macrocyclic Polyamines

Keywords: Amines / N ligands / Bifunctional chelating agents / Macrocycles



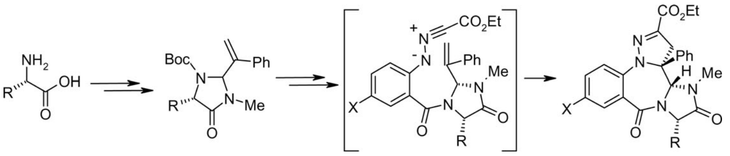
We report a very convenient synthesis of cyclen and [13]aneN4 derivatives bearing an aminomethyl pendant group on a carbon atom. The cyclization step is performed by using chloroacetaldehyde and benzotriazole. The benzotriazole moiety is then replaced by a nitrile group, which is reduced to yield the target compounds. Such macrocycles can be further functionalized to give bifunctional chelating agents.

Tetracyclic 1,4-Benzodiazepin-5-ones

L. Basolo, E. M. Beccalli,* E. Borsini, G. Broggini, M. Khansaa, M. Rigamonti **1694–1703**

Access to a Novel Class of Tetracyclic 1,4-Benzodiazepin-5-ones Starting from α-Amino- Acids by Pd-Catalyzed Amination/1,3-Dipolar Cycloaddition as the Key Steps

Keywords: Fused-ring systems / Nitrogen heterocycles / Palladium / Cycloaddition / Diastereoselectivity



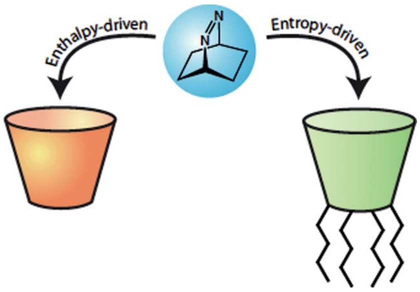
A procedure for the synthesis of enantiopure tetracyclic imidazo[2,1-*c*]pyrazolo[1,5-*a*][1,4]benzodiazepine-5,8-diones from cheap and easily accessible α-amino acids has been developed in which the key steps are an intramolecular palladium-catalyzed amination process to form the imidazole nucleus and an intramolecular 1,3-dipolar cycloaddition reaction to yield the pyrazole and 1,4-diazepine rings.

Molecular Recognition

J. Cui, V. D. Uzunova, D.-S. Guo, K. Wang, W. M. Nau,* Y. Liu* **1704–1710**

Effect of Lower-Rim Alkylation of *p*-Sulfonatocalix[4]arene on the Thermodynamics of Host–Guest Complexation

Keywords: Molecular recognition / Thermodynamics / Lower-rim substitution / Calixarenes



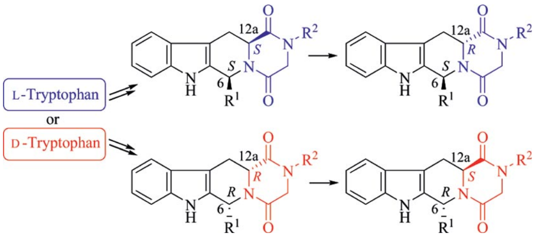
Complex stability constants and thermodynamic parameters for the complexation of *p*-sulfonatocalix[4]arene (SC4A) and 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(*n*-butyl)calix[4]arene (SC4A-Bu) with organic ammonium cations and neutral spherical organic molecules have been determined by isothermal titration calorimetry. These results show that, upon complexation with these guests by SC4A-Bu, the enthalpy changes become less favorable, whereas the entropy changes become more favorable relative to SC4A complexation.

Heterocyclic Chemistry

S. Xiao, X.-X. Shi,* F. Ni, J. Xing, J.-J. Yan, S.-L. Liu 1711–1716

An Efficient and General Method for the Stereodivergent Syntheses of Tadalafil-Like Tetracyclic Compounds

Keywords: Nitrogen heterocycles / Epimerization / Tadalafil analogue / Stereodivergent synthesis



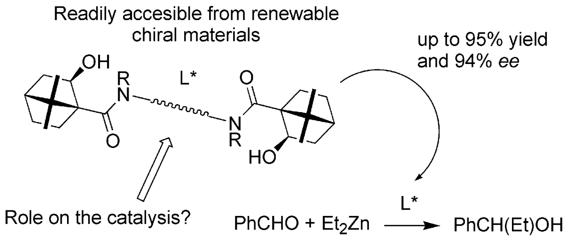
A clean and general DBU-catalyzed epimerization at C-12a position of the tadalafil-like tetracyclic compounds has been fully studied. In addition, by using this clean epimerization as the key step, four stereomers of 6-d_1-tadalafil were stereodivergently synthesized from both L- and D-tryptophan methyl ester hydrochlorides and deuterated piperonal.

Asymmetric Catalysis

T. de las Casas Engel, B. Lora Maroto, S. de la Moya Cerero* 1717–1727

Ketopinic Acid Derived Bis(hydroxy amides) as Cheap, Chiral Ligands for the Enantioselective Ethylation of Aromatic Aldehydes

Keywords: Asymmetric catalysis / Zinc / Hydroxy amides / Chiral pool / Structure–activity relationships



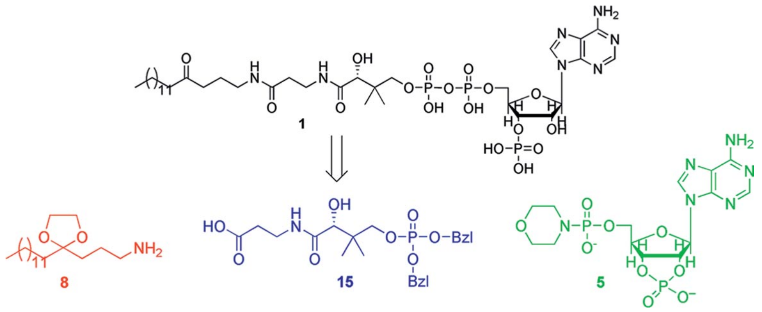
Readily accessible bis(hydroxy amides) are promising, cheap, chiral ligands for the enantioselective addition of organozinc reagents to aldehydes. A series of these ligands has been synthesized and investigated in the enantioselective ethylation of different aldehydes. The role of the diamine moiety in tuning the ligand activity is discussed on the basis of consistent empiric models.

Acyl Coenzyme A Analogues

L. Tautz, J. Rétey* 1728–1735

A Highly Convergent Synthesis of Myristoyl-carba(dethia)-coenzyme A

Keywords: *N*-Myristoylation / Coenzyme A / Antifungal agents / Antiviral agents / Inhibitors



A highly convergent synthesis of myristoyl-carba(dethia)-coenzyme A (**1**) is presented. Compound **1** is a non-hydrolysable substrate analogue and potent inhibitor of *N*-myristoyltransferase (Nmt), a potential drug target for anticancer, antiepilepsy, antifungal and antiviral agents.

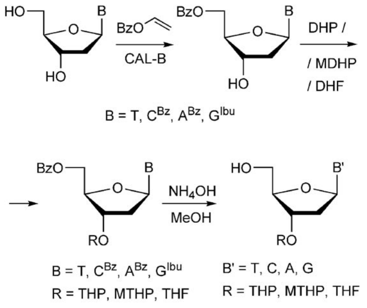
Protected Nucleosides

T. Rodríguez-Pérez, S. Fernández, S. Martínez-Montero, T. González-García, Y. S. Sanghvi, V. Gotor,* M. Ferrero* 1736–1744

Chemoenzymatic Synthesis of 3′-*O*-Acetal-Protected 2′-Deoxynucleosides as Building Blocks for Nucleic Acid Chemistry

Keywords: Nucleosides / Enzymes / Acylation / Protecting groups / Green chemistry

A simple and convenient chemoenzymatic strategy for the preparation of tetrahydropyranyl, 4-methoxytetrahydropyranyl, and tetrahydrofuranyl ethers of 2′-deoxynucleosides, which are useful building blocks for nucleic acid chemistry, has been developed. The three-step process is expected to enable the large-scale synthesis of protected nucleosides.



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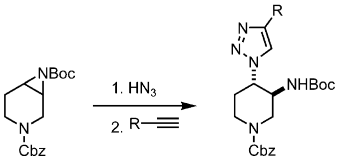
Clicked Piperidines

H. Schramm, W. Saak, C. Hoenke, J. Christoffers* 1745–1753

Synthesis of Triazolyl-Substituted 3-Amino-piperidines by Huisgen-1,3-Dipolar Cycloaddition – New Scaffolds for Combinatorial Chemistry

Keywords: Nitrogen heterocycles / Cycloaddition / Click reaction / Amines



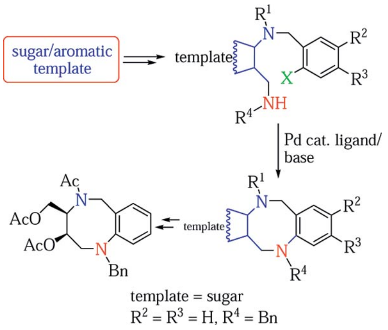
Orthogonally protected 3-aminopiperidine-scaffolds with a triazole-moiety in the 4-position are prepared by ring-opening of an aziridine building block with NaN_3 followed by copper-catalyzed Huisgen 1,3-dipolar cycloaddition with ten different alkynes.

Intramolecular Aryl Amination

N. D. Adhikary, P. Chattopadhyay* 1754–1762

Palladium-Catalyzed Intramolecular Aryl Amination Reaction: An Expeditious Approach to the Synthesis of Chiral Benzodiazocine Derivatives

Keywords: Palladium / Catalysts / Ligands / Amination / Diazocine



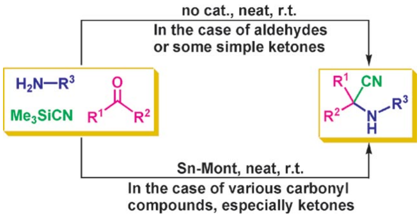
An efficient route to multifunctional benzodiazocines in chiral form by Pd catalyzed intramolecular aryl amination has been reported using D-glucose-derived substrate. The findings could also be extended to synthesize dibenzodiazocine derivatives.

α-Amino Nitrile Synthesis

J. Wang, Y. Masui, M. Onaka* 1763–1771

Synthesis of α-Amino Nitriles from Carbonyl Compounds, Amines, and Trimethylsilyl Cyanide: Comparison between Catalyst-Free Conditions and the Presence of Tin Ion-Exchanged Montmorillonite

Keywords: Heterogeneous catalysis / Clays / Tin ion exchanged montmorillonite / Strecker synthesis / Catalyst-free conditions



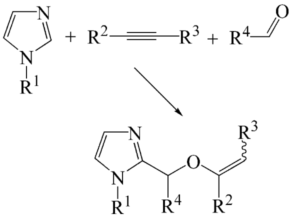
A facile synthesis of α-amino nitriles has been developed by using one-pot reactions of carbonyl compounds, amines, and trimethylsilyl cyanide under mild conditions either without a catalyst or in the presence of tin ion-exchanged montmorillonite. The latter is reusable, increases reaction rates greatly, and enables the reaction to be applied to sterically hindered ketones.

Three-Component Reactions

B. A. Trofimov,* L. V. Andriyankova, K. V. Belyaeva, A. G. Mal'kina, L. P. Nikitina, A. V. Afonin, I. A. Ushakov 1772–1777

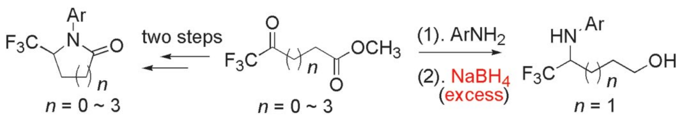
C2-Functionalization of 1-Substituted Imidazoles with Aldehydes and Electron-Deficient Acetylenes: A Novel Three-Component Reaction

Keywords: Nitrogen heterocycles / Electron-deficient compounds / Aldehydes / Multicomponent reactions / Alkynes



Facile interaction of 1-substituted imidazoles with electron-deficient acetylenes and aldehydes leads to a novel class of fascinating imidazole derivatives functionalized at the C2 position with substituents combining the enol ether, acrylate, nitrile, and styrene moieties. Thus, new aspects of fundamental and applied imidazole and acetylene chemistry are unveiled.

Trifluoromethylated Lactams



Synthesis of trifluoromethylated four- to seven-membered ring lactams by reductive amination/cyclization from simply prepared ω-trifluoromethyl keto esters has been described. Unexpected trifluoromethylated δ-amino alcohols were also obtained only from reduction of the corresponding γ-imino esters in the presence of an excess amount of $NaBH_4$.

W. Wan, J. Hou, H. Jiang, Z. Yuan, G. Ma, G. Zhao, J. Hao* **1778–1786**

Reductive Amination/Cyclization of ω-Trifluoromethyl Keto Esters to Trifluoromethylated δ-Amino Alcohols and Lactams 💻

Keywords: Fluorine / Amination / Cyclization / Lactams / Reduction / Cyclization

Pyridine Synthesis

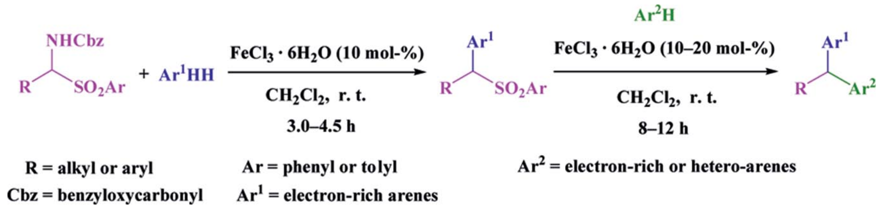
N-{2-[Alkynyl(hetero)aryl]methylene}indolin-1-amines **3** undergo, upon treatment with silver nitrate in chloroform at 60 °C, electrophilic cyclization reactions to afford annulated pyridine derivatives **4**. The reaction can be performed in air and even in the presence of water in the reaction medium. Quantum chemical calculations have been applied in order to gain additional information about the reaction mechanism and the key reactive intermediates.

N. Ghavtadze,* R. Fröhlich, E.-U. Würthwein* **1787–1797**

Indole as Neutral Leaving Group in Silver Nitrate Induced Cyclization Reactions of *N*-{2-[Alkynyl(hetero)aryl]methylene}indolin-1-amines for the Synthesis of Annulated Pyridine Derivatives 💻

Keywords: Lewis acids / Cyclization / Nitrogen heterocycles / Silver / Quantum chemical calculations

Fe-Catalyzed Alkylations



Ferric chloride hexahydrate has been employed for Friedel–Crafts alkylation reactions. The process was further extended to the synthesis of unsymmetrical or bis-symmetrical triarylmethanes.

P. Thirupathi, S. S. Kim* **1798–1808**

Regioselective Arylations of α-Amido Sulfones with Electron-Rich Arenes through Friedel–Crafts Alkylations Catalyzed by Ferric Chloride Hexahydrate: Synthesis of Unsymmetrical and Bis-Symmetrical Triarylmethanes 💻

Keywords: Iron / C–C coupling / α-Amido sulfones / Arenes / Heteroarenes / Triarylmethanes

APOLOGY

Keywords: Iron / C–C coupling / α-Amido sulfones / Arenes / Heteroarenes / Triarylmethanes

Regioselective Arylations of α-Amido Sulfones with Electron-Rich Arenes through Friedel–Crafts Alkylations Catalyzed by Ferric Chloride Hexahydrate: Synthesis of Unsymmetrical and Bis-Symmetrical Triarylmethanes

P. Thirupathi, S. S. Kim* **1809**

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* Author to whom correspondence should be addressed.

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