Unnatural Amino Acid Derivatives through Click Chemistry: Synthesis of Triazolylalanine Analogues
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Abstract: A novel tert-butyl 2-(1-oxoisodolin-2-yl)acetate derivative is selectively alkylated with propargyl bromide in the presence of lithium hexamethyldisilazide. After removal of the tert-butyl protecting group, the resulting N-isoindolinyl (ethynylalanine) derivative is reacted with a series of azides under ‘click conditions’. The click reactions afford an array of N-isoindolinyl-1,2,3-triazolylalanine derivatives as the free carboxylic acids. Following esterification, the N-isoindolinone protecting group is then transformed into the more easily removable phthaloyl group by selective oxidation at the benzylic position.

One-Pot Coupling–Cyclization–Alkylation Synthesis of 1,2,5-Tribstituted 7-Azaindoles in a Consecutive Three-component Fashion
Timo Lessing and Thomas J. J. Müller

Abstract: 1,2,5-Trisubstituted 7-azaindoles are rapidly and efficiently prepared in a one-pot, copper-free alkylation–cyclization–alkylation sequence starting from unprotected 2-aminopyridyl halides in a consecutive three-component fashion. By extension to a consecutive four-component coupling–cyclization–iodination–alkylation synthesis of 3-iodo-1-methyl-2-phenyl-1H-pyrrolo[2,3-b]pyridine, a concise synthesis of SIS3, a selective TGF-β1 and signaling inhibitor, was realized.

Boron Trifluoride Facilitated Transesterification of Dioxaborolanes
Chathuri J. Kombala, Dulamini I. Ekanayake, Dustin E. Gross

Abstract: The direct transesterification of dioxaborolanes (alkane-1,2-diol based boronate esters) was explored. Using BF₃·OEt₂, alkane-1,2-diol based mono- and bis-boronate esters (i.e., pinacol and ethylene glycol) have been converted quantitatively to either benzene-1,2-diol or alkane-1,3-diol based boronate esters. In the case of pinacol esters, esterification is facilitated by the accompanying pinacol rearrangement, thus shifting the reaction equilibrium.
Organocatalyzed Deracemization of \( \alpha^2 \)-Pyrrolin-4-ones

Sebastijan Ričko, Anže Meden, Anže Ivančič, Andrej Perdih, Bogdan Štefane, Jurij Svetec, and Uroš Groselj


DOI: 10.1002/adsc.201700539

Abstract: Racemic pyrrolin-4-ones, accessible from \( \alpha \)-amino acids, undergo asymmetric stereoselective organocatalyzed 1,4-additions to trans-\( \beta \)-nitrostyrenes (up to 98% ee; dr up to 97:3). From a series of typical organocatalysts, the best performance was achieved using (+)-camphor-1,3-diamine-derived bifunctional organocatalysts. A broad substrate scope and some follow-up modifications have been demonstrated.

Sharpless Asymmetric Dihydroxylation on \( \alpha,\beta \)-Unsaturated Diazoketones: A New Entry for the Synthesis of Disubstituted Furanones

Alexánder G. Talero and Antonio C. B. Burtoloso

*Synlett* 2017, 28, 1748–1752.*

DOI: 10.1055/s-0036-1590977

Abstract: The synthesis of enantiomerically pure 4,5-disubstituted 2-furanones is accomplished in three steps from aldehydes. The steps involve a highly enantioselective Sharpless asymmetric dihydroxylation of \( \alpha,\beta \)-unsaturated diazoketones, followed by a photochemical Wolff rearrangement.

Amine-Urea-Mediated Asymmetric Cycloadditions between Nitrile Oxides and \( \omega \)-Hydroxystyrenes by Dual Activation

Hiroyuki Suga, Yohei Hashimoto, Yasunori Toda, Kazuaki Fukushima, Hiroyoshi Esaki, and Ayaka Kikuchi


DOI: 10.1002/anie.201705662

Abstract: The first example of asymmetric 1,3-dipolar cycloadditions between nitrile oxides and \( \omega \)-hydroxystyrenes, mediated by cinchona-alkaloid-based amine-ureas is reported. The method is based on a dual activation involving both LUMO and HOMO activations. In addition to the stoichiometric asymmetric induction, a catalytic amount of amine-urea enables the cycloadditions to proceed in an enantioselective manner. Computational studies strongly support the HOMO activation of \( \omega \)-hydroxystyrenes and LUMO activation of nitrile oxides by hydrogen-bonding interactions with the Bronsted acid/base bifunctional catalyst.
Synthesis of bis-8-Hydroxyquinolines via an Imination or a Suzuki–Miyaura Coupling Approach
Rob De Vreese, Koen Muylaert, Cedric Maton, Lise Dereu, Frederique Taillieu, Thomas Harth, Rik Van Deun, Henk Vrielinck, Christian V. Stevens, Matthias D’hooghe
DOI: 10.1016/j.tetlet.2017.08.039

Abstract: Bis-8-hydroxyquinolines represent an important yet underexplored class of potential ligands for the preparation of various coordination polymers, which can be used in a plethora of applications. In this work, the synthesis of two types of bis-8-hydroxyquinolines, prepared via either an imination or a Suzuki–Miyaura coupling approach, as well as their analysis is discussed. Imination was pursued through the condensation of quinolinecarbaldehydes with diamines or aminoquinolines with dialdehydes, and the Suzuki–Miyaura coupling reactions were evaluated using a bromoquinoline substrate and diboronic acids.

A One-Pot Methodology for the Synthesis of the Yohimban Skeleton
Claudio Parra, Pablo Solis, Josep Bonjoch and Ben Bradshaw
DOI: 10.1055/s-0036-1589092

Abstract: A simple and straightforward assembly of the yohimban skeleton was achieved by condensation of an acyclic β-keto ester with tryptamine, followed by consecutive cross metathesis and tandem cyclization reactions, leading to the formation of three new rings. The whole process was readily carried out in the one-flask providing a rapid entry to the pentacyclic scaffold of yohimbine alkaloids.

LiAlH₄-Induced Thia-Aza-Payne Rearrangement of Functionalized 2-(Thiocyanatomethyl)aziridines into 2-(Aminomethyl)thiiranes as an Entry to 5-(Chloromethyl)thiazolidin-2-ones
Jeroen Dolfen, Kristof Van Hecke, and Matthias D’hooghe
DOI: 10.1002/ejoc.201700549

Abstract: Non-activated 2-(thiocyanatomethyl)aziridines with diverse substitution patterns were deployed as substrates to effect a LiAlH₄-promoted thia-aza-Payne rearrangement, providing access to functionalized 2-(aminomethyl)thiiranes in good to excellent yields (78-94%). The developed strategy is based on a hydride reduction of the thiocyanate moiety followed by intramolecular aziridine ring opening. Subsequent exposure of the obtained 2-(aminomethyl)episulfide intermediates to triphosgene resulted in the formation of 5-(chloromethyl)thiazolidin-2-ones.
Synthesis and Reactivity of 2-Arylquinazoline Halidoruthenacycles in Arylation Reactions
Petra Kuzman, Franc Požgan, Anton Meden, Jurij Svete and Bogdan Štefane

The halogen plays a role

Abstract: The synthesis of a range of new cyclometallated organoruthenium(II) complexes through the ortho-C–H activation of the aryl group in 2-aryl-substituted quinazolines with \([\text{RuX}_2(\mu\text{-cymene})_2]\) is described. The beneficial effect of the carboxylate ligand on both the cyclometallation and the further arylation reaction step was demonstrated. Mechanistic studies reveal that bromide and iodide anions decelerate the arylation process by an in situ ligand exchange reaction. Additionally, a detailed NMR spectroscopy investigation was performed to explain some elementary steps in the arylation of 2-(aryl)quinazoline halidoruthenacycles.

Direct Aziridination of Nitroalkenes Affording N-Alkyl-C-nitroaziridines and the Subsequent Lewis Acid Mediated Isomerization to β-Nitroenamines
Feiyue Hao, Haruyasu Asahara and Nagatoshi Nishiwaki
Org. Lett. 2017, 19, 5442–5445. DOI: 10.1021/acs.orglett.7b02724

Abstract: A mild and highly diastereoselective one-pot synthesis of trans-N-alkyl-C-nitroaziridines was achieved by the treatment of nitroalkenes with aliphatic amines and N-chlorosuccinimide. Treatment of the obtained aziridines with a Lewis acid resulted in a facile ring opening reaction, accompanied by rearrangement and isomerization into functionalized (Z)-β-nitroenamines.

Efforts Toward a Synthesis of Crotogoudin and Crotobarin
Duy N. Mai, Dmitriy Uchenik, and Christopher D. Vanderwal

Abstract: Two synthesis designs for the diterpenoid crotogoudin are discussed, and efforts to achieve each are described. First, a Cope rearrangement/intramolecular Diels–Alder cascade reaction was investigated. Second, a bioinspired sequence of cationic bicyclization and A-ring oxidative fragmentation set-up for a lactonization induced by a phenolic oxidation, ultimately providing a tricyclic intermediate that required only installation of the bridging ring of the salient bicyclo[2.2.2]octane system. This last endeavor was fraught with difficulty, but did lead to the development of conditions for cyclization of related keto-alkenes via manganese(III)-based radical chemistry.