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Recent Publications of ISHC Members

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Total Synthesis of (+)-MPC1001B
Taichi Kurogi, Shun Okaya, Hideto Fujiwara, Kentaro Okano, Hidetoshi Tokuyama


DOI: 10.1002/anie.201507830

**Abstract**

The first total synthesis of an epidithiodiketopiperazine alkaloid, (+)-MPC1001B, was accomplished. This synthesis features a tetra-n-butylammonium fluoride mediated intramolecular aldol reaction for forming the 15-membered macrolactone ring, and the construction of an epidithiodiketopiperazine substructure through a stepwise sulfenylation reaction involving a novel trityl trisulfide (TrSSS)-group transfer.

Total Synthesis of Shishijimicin A
K. C. Nicolaou, Zhaoyong Lu, Ruofan Li, James R. Woods, Te-ik Sohn


DOI: 10.1021/Jacs.5b05575

**Abstract**

The total synthesis of the rare but extremely potent antitumor agent shishijimicin A has been achieved via a convergent strategy involving carboline disaccharide 3 and hydroxy enediyne thioacetate 4.

Formal Total Synthesis of (±)-Strictamine Based on a Gold-Catalyzed Cyclization
Daisuke Nishiyama, Ayako Ohara, Hiroaki Chiba, Hiroshi Kumagai, Shinya Oishi, Nobutaka Fujii, Hiroaki Ohno


DOI: 10.1021/acs.orglett.6b00536

**Abstract**

A gold-catalyzed cyclization of 1-propargyl-1,2,3,4-tetrahydro-β-carboline led to formation the D-ring of strictamine. Functional group modifications of the resulting tetracyclic indolenine led to the formal total synthesis of (±)-strictamine.
Concise Total Synthesis of Lundurines A–C Enabled by Gold Catalysis and a Homodienyl Retro-Ene/Ene Isomerization

Mariia S. Kirillova, Michael E. Muratore, Ruth Dorel, Antonio M. Echavarren


DOI: 10.1021/jacs.6b01428

**Abstract**

The total synthesis of lundurines A–C has been accomplished in racemic and enantiopure forms in 11–13 and 12–14 steps, respectively, without protection/deprotection of functional groups, by a novel tandem double condensation/Claisen rearrangement, a gold(I)-catalyzed alkyne hydroarylation, a cyclopropanation via formal [3 + 2] cycloaddition/nitrogen extrusion, and a remarkable olefin migration through a vinylcyclopropane retro-ene/ene reaction that streamlines the endgame.

Palladium(II)-Catalyzed Sequential Aminopalladation and Oxidative Coupling with Acetylenes/Enones: Synthesis of Newly Substituted Quinolines from 2-Aminophenyl Propargyl Alcohols

Nuligonda Thirupathi, Surendra Puri, Thota Jagadeshwar Reddy, Balasubramanian Sridhar, Maddi Sridhar Reddy


DOI: 10.1002/adsc.201500805

**Abstract**

Palladium catalyzed conversion of 1-(2-aminophenyl)-propargyl alcohols to 3-alkynyl quinolines is realized via a cascade that involves aminopalladation, oxidative coupling with alkynes and dehydration. The method is shown to have a broad substrate scope with respect to propargyl alcohols as well as alkynes. Vinyl ketones as coupling partners in the same reaction afforded 3-alkenyl quinolines with equal ease.

A Direct Access to 7-Aminoindoles via Iridium-Catalyzed Mild C–H Amidation of N-Pivaloylindoles with Organic Azides

Youyoung Kim, Juhyeon Park, Sukbok Chang


DOI: 10.1021/acs.orglett.6b00662

**Abstract**

Ir(III)-catalyzed regioselective direct C-7 amidation of indoles in reaction with organic azides has been developed. While its efficiency was varied by the choice of N-directing groups, N-pivaloylindoles were most effective in undergoing the desired amidation at room temperature over a broad range of substrates. The reaction was scalable, and deprotection of the chelation group was also facile.
Inverse Electron-Demand [4 + 2]-Cycloadditions of Ynamides: Access to Novel Pyridine Scaffolds
Guillaume Duret, Robert Quinlan, Rainer E. Martin, Philippe Bisseret, Markus Neuburger, Vincent Gandon, Nicolas Blanchard
Org. Lett. 2016, 18, 1610–1613
DOI: 10.1021/acs.orglett.6b00464

Abstract
Functionalyzed polycyclic aminopyridines are central to the chemical sciences, but their syntheses are still hampered by a number of shortcomings. These nitrogenated heterocycles can be efficiently prepared by an intramolecular inverse electron demand hetero Diels–Alder (ihDA) cycloaddition of ynamides to pyrimidines. This ihDA/rDA sequence is general in scope and affords expedient access to novel types of aminopyridinyl scaffolds that hold great promise in terms of exit vector patterns.

Asymmetric Synthesis of N-Boc-(R)-Silaproline via Rh-Catalyzed Intramolecular Hydrosilylation of Dehydroalanine and Continuous Flow N-Alkylation
John Y. L. Chung, Michael Shevlin, Artis Klapars, Michel Journet
DOI: 10.1021/acs.orglett.6b00548

Abstract
An asymmetric synthesis of a silicon-containing proline surrogate, N-Boc-(R)-silaproline (1), is described. Starting from N-Boc-dehydroalanine ester, deprotonation, followed by N-alkylation with chloromethylsilane under flow conditions, afforded the N-alkylated product 8 in 91% yield. An unprecedented enantioselective (NBD)2RhBF4/Josiphos 404-1 catalyzed 5-endo-trig hydrosilylation afforded the silaproline ester in 85–90% yield and >95% ee. Subsequent saponification and salt formation upgraded 1 to >99% ee.

Efficient Strategy for the Construction of Both Enantiomers of the Octahydropyrroloquinolinone Ring System: Total Synthesis of (+)-Aspidospermidine
Ganesh Pandey, Shiva Kumar Burugu, Pushpendra Singh
DOI: 10.1021/acs.orglett.6b00374

Abstract
An efficient and highly stereoselective intramolecular [3 + 2] cycloaddition of nonstabilized azomethine ylide generated from a designed bicyclic aminal precursor is reported for the synthesis of both (−)- and (+)-octahydropyrroloquinolinone. One of the enantiomers is further advanced to accomplish the total synthesis of (+)-aspidospermidine.
Stereocontrolled \((\text{Me}_3\text{Si})_3\text{SiH}\)-Mediated Radical and Ionic Hydride Transfer in Synthesis of 2,3,5-Trisubstituted THF

Simon Grélaud, Valérie Desvergnes, Yannick Landais


**DOI:** 10.1021/acs.orglett.6b00303

**Abstract**

2,3,5-Trisubstituted tetrahydrofurans were prepared stereoselectively through a two-step process involving the addition of an acyl radical to a \(\beta\)-silyloxy acrylic ester followed by an acid-catalyzed desilylation–ketalization sequence and a final oxocarbenium reduction step. High levels of 1,2- and 1,3-stereocontrol were attained when \((\text{Me}_3\text{Si})_3\text{SiH}\) was used as a radical followed by an ionic hydrogen transfer agent.

Indole Synthesis via Cobalt(III)-Catalyzed Oxidative Coupling of \(N\)-Arylureas and Internal Alkynes

Zhuo-Zhuo Zhang, Bin Liu, Jing-Wen Xu, Sheng-Yi Yan, Bing-Feng Shi


**DOI:** 10.1021/acs.orglett.6b00494

**Abstract**

A mild Co(III)-catalyzed oxidative annulation of \(N\)-arylureas and internal alkynes has been developed. The use of less electrophilic ureas other than acetamides as directing groups is crucial for the reaction. A broad range of synthetically useful functional groups are compatible with this reaction, thus providing a new opportunity for the synthesis of diverse indoles.