

The ISHC Bulletin

Recent Publications of ISHC Members

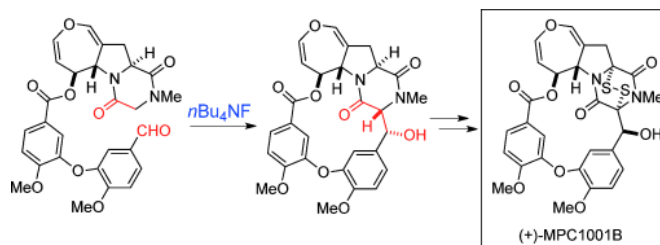
Issue 1; May 1, 2016

Total Synthesis of (+)-MPC1001B

Taichi Kurogi, Shun Okaya, Hideto Fujiwara, Kentaro Okano, Hidetoshi Tokuyama

Angew. Chem. Int. Ed. **2016**, *55*, 283–287

DOI: 10.1002/anie.201507830



Abstract

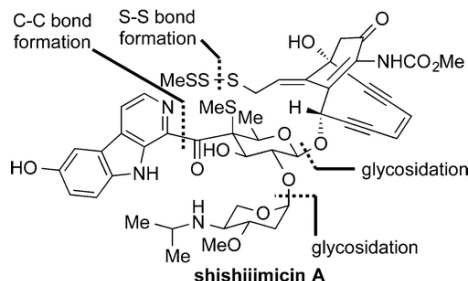
The first total synthesis of an epidithiodiketopiperazine alkaloid, (+)-MPC1001B, was accomplished. This synthesis features a tetra-*n*-butylammonium fluoride mediated intramolecular aldol reaction for forming the 15-membered macrolactone ring, and the construction of an epidithiodiketopiperazine substructure 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

J. Am. Chem. Soc. **2015**, *137*, 8716–8719

DOI: 10.1021/Jacs.5b05575



Abstract

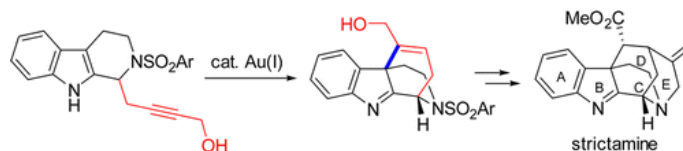
The total synthesis of the rare but extremely potent antitumor agent shishijimicin A has been achieved via a convergent strategy involving carboline disaccharide **3** and hydroxy enediyne thioacetate **4**.

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

Org. Lett. **2016**, *18*, 1670–1673.

DOI: 10.1021/acs.orglett.6b00536



Abstract

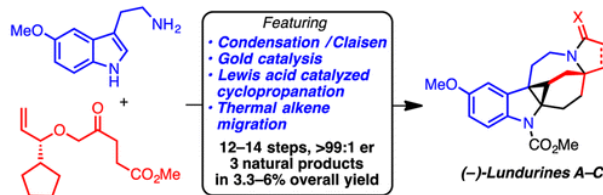
A gold-catalyzed cyclization of 1-propargyl-1,2,3,4-tetrahydro- β -carboline led to formation the D-ring of strictamine. Functional group modifications of the resulting tetracyclic indolenine led to the formal total synthesis of (±)-strictamine.

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

J. Am. Chem. Soc. **2016**, *138*, 3671–3674

DOI: 10.1021/jacs.6b01428



Abstract

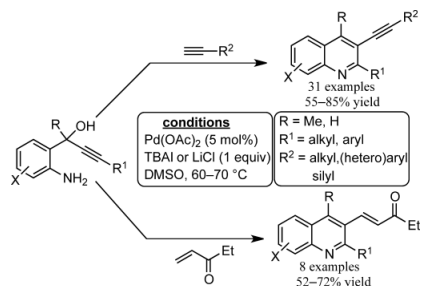
The total synthesis of lundurines A–C has been accomplished in racemic and enantiopure forms in 11–13 and 12–14 steps, respectively, without protection/deprotection of functional groups, by a novel tandem double condensation/Claisen rearrangement, a gold(I)-catalyzed alkyne hydroarylation, a cyclopropanation 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

Adv. Synth. Catal. **2016**, *358*, 303–313

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

Org. Lett. **2016**, *18*, 1892–1895.

DOI: 10.1021/acs.orglett.6b00662



Abstract

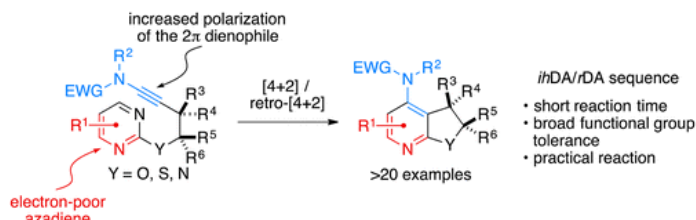
Ir(III)-catalyzed regioselective direct C-7 amidation of indoles in reaction with organic azides has been developed. While its efficiency was varied by the choice of *N*-directing groups, *N*-pivaloylindoles were most effective in undergoing the desired amidation at room temperature over a broad range 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 Bissret, Markus Neuburger, Vincent Gandon, Nicolas Blanchard

Org. Lett. **2016**, *18*, 1610–1613

DOI: 10.1021/acs.orglett.6b00464



Abstract

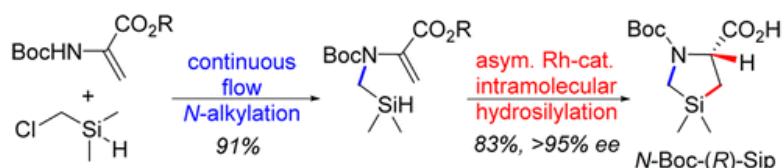
Functionalized polycyclic aminopyridines are central to the chemical sciences, but their syntheses are still hampered by a number of shortcomings. These nitrogenated heterocycles can be efficiently prepared by an intramolecular inverse electron demand hetero Diels–Alder (*ihDA*) cycloaddition of ynamides 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

Org. Lett. **2016**, *18*, 1812–1815.

DOI: 10.1021/acs.orglett.6b00548



Abstract

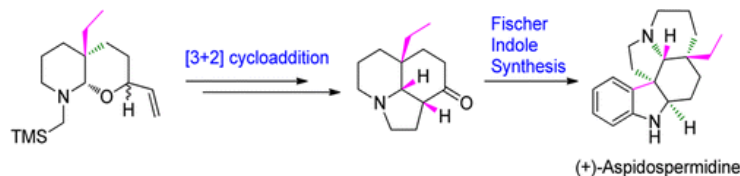
An asymmetric synthesis of a silicon-containing proline surrogate, *N*-Boc-(*R*)-silaproline (**1**), is described. Starting from *N*-Boc-dehydroalanine ester, deprotonation, followed by *N*-alkylation with chloromethyltrimethylsilane under flow conditions, afforded the *N*-alkylated product **8** in 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

Org. Lett. **2016**, *18*, 1558–1561.

DOI: 10.1021/acs.orglett.6b00374



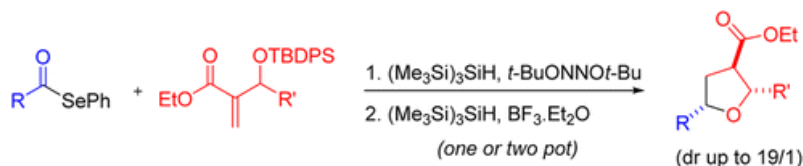
Abstract

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 Desvergnès, Yannick Landais
Org. Lett. **2016**, *18*, 1542–1545.

DOI: 10.1021/acs.orglett.6b00303



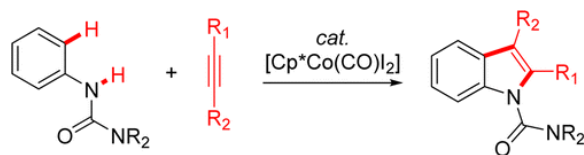
Abstract

2,3,5-Trisubstituted tetrahydrofurans were prepared stereoselectively through a two-step process involving the addition of an acyl radical to a β -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 a 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
Org. Lett. **2016**, *18*, 1776–1779.

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.