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Enantioselective Total Synthesis of (-)-Hunterine A Enabled by a Desymmetrization/Rearrangement Strategy *J. Am. Chem. Soc.* **2024**, *146*, 4340–4345, DOI: 10.1021/jacs.3c13590.

Total Synthesis of (-)-Hunterine A

Significance: Stoltz and co-workers present the first total synthesis of (-)-hunterine A. This rearranged monoterpene indole alkaloid was isolated in 2019 and features a pentacyclic core structure. The synthesis hinges on a desymmetrization, an aza-Cope/Mannich sequence, and an azide-alkene dipolar cycloaddition.

Comment: Desymmetrization of diketone **A** was achieved through Noyori transfer hydrogenation, furnishing ketone **C**. Upon treatment with silver(I) nitrate in ethanol, allylic alcohol **G** underwent an aza-Cope/Mannich sequence, giving rise to ketone I, which is the substrate for an azide-alkene dipolar cycloaddition. Triazoline J was transformed to (-)-hunterine A through irradiation, opening of the resulting putative aziridine with acetic acid, and hydrolysis.

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Synthesis of Natural

Key words

(-)-hunterine A

rearranged monoterpene indole alkaloid

Noyori transfer hydrogenation

aza-Cope/Mannich reaction

azide-alkene dipolar cycloaddition

