Y. XUE, S.-H. HOU\*, X. ZHANG, F.-M. ZHANG, X.-M. ZHANG, Y.-Q. TU\* (SHANGHAI JIAO TONG UNIVERSITY AND LANZHOU UNIVERSITY, P. R. OF CHINA) Total Synthesis of the Hexacyclic Sesterterpenoid Niduterpenoid B via Structural Reorganization Strategy J. Am. Chem. Soc. **2024**, 146, 25445–25450, DOI: 10.1021/jacs.4c09555

## Total Synthesis of (±)-Niduterpenoid B



**Significance:** Niduterpenoid B is characterized by a 5/5/5/5/3/5 hexacyclic framework featuring 13 contiguous stereocenters, four of which are quaternary. The total synthesis by Tu and co-workers capitalizes on a cascade reaction wherein the tetraquinane scaffold, with its stereocenters, is rapidly assembled. The full core of the molecule is later accessed via a rhodium-mediated cyclopropanation.

**Comment:** Cyclobutanone **A**, assembled by [2+2] cycloaddition of cyclopentadiene and methoxy(methyl)ketene, was converted into key triene **E**. Exposure of **E** to Lewis and Brønsted acid catalysis initiated the Nazarov cyclization/double ring expansion/elimination reaction which, after Krapcho decarboxylation, returned tetraquinane **F**. The highly strained three-membered ring in **J** was installed via cyclopropanation of diazo ketone **I**, which served as synthetic intermediate to complete the synthesis of niduterpenoid B.

## SYNFACTS Contributors: Erick M. Carreira <sup>©</sup>, Tristano C. Martini Synfacts 2024; 20(12), 1233 DOI: 10.1055/a-2439-7388; **Reg-No.:** C08024SF

## Category

Synthesis of Natural Products

## Key words

(±)-niduterpenoid B

Horner–Wadsworth– Emmons reaction

Knoevenagel condensation

Krapcho decarboxylation

Alcaraz reaction

Johnson–Claisen rearrangement

cyclopropanation

Month