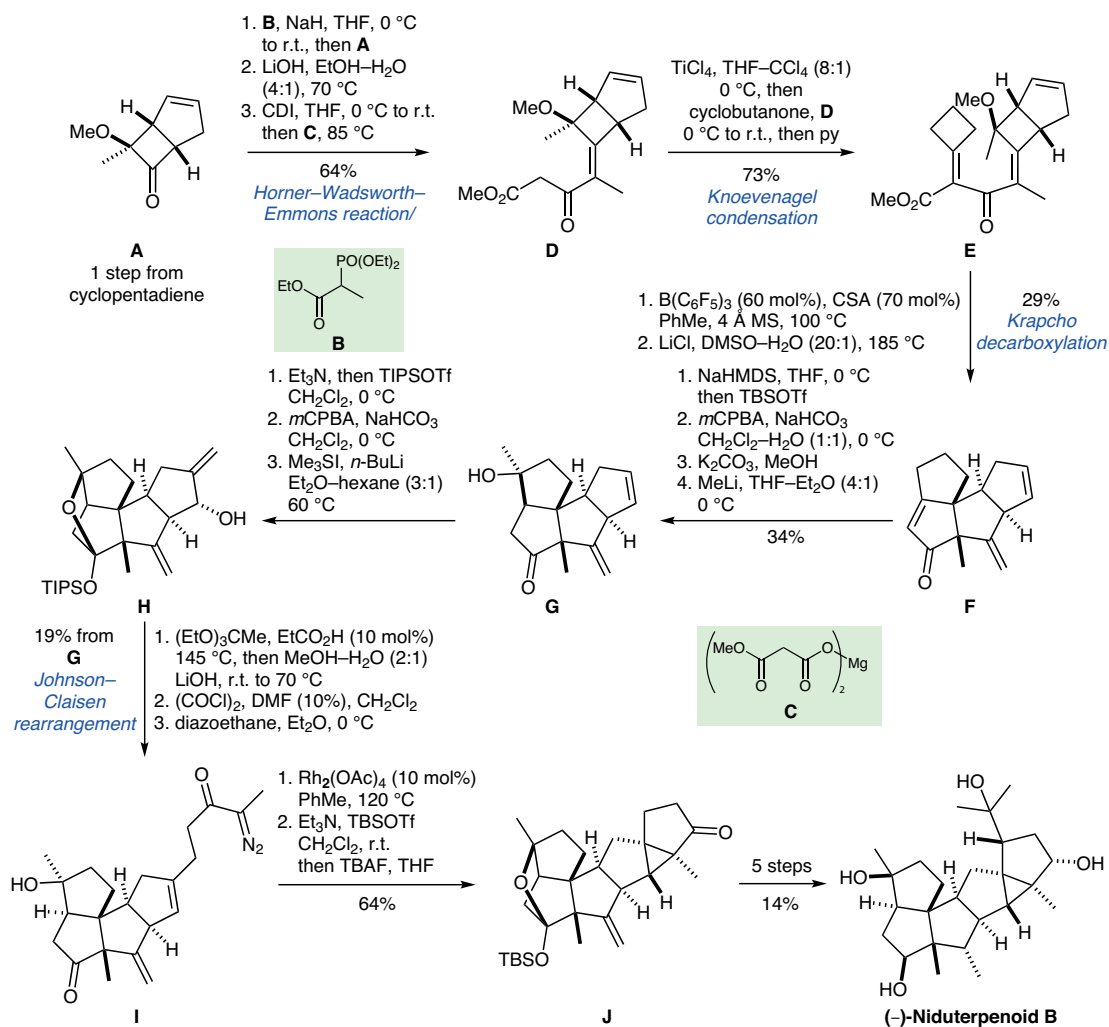


## Total Synthesis of (±)-Niduterpenoid B



**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.