A. S. Burns, S. D. Rychnovsky* (University of California, Irvine, USA)

Total Synthesis and Structure Revision of (−)-Ilisimonin A, a Neuroprotective Sesquiterpenoid from the Fruits of Illicium simonsii


Total Synthesis of Illisimonin A

Significance: Burns and Rychnovsky report on the first total synthesis of illisimonin A, a sesquiterpenoid isolated from the fruits of Illicium simonsii. The combination of an intramolecular Diels–Alder reaction with a semi-pinacol rearrangement enables the rapid access of the target molecule’s core structure. Using a resolution strategy, the authors are also able to produce enantioenriched (−)-ilisimonin A.

Comment: Enone B is generated from simple starting materials. A 1,3-dioxa-2-silacyclohexene-templated Diels–Alder reaction yields the congested intermediate D. Functional group interconversion leading to epoxide F pave the route for the crucial semi-pinacol rearrangement. Ultimately, functional group interconversions and a final directed C–H oxidation give rise to the natural product.