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Total Synthesis and Structure Revision of (–)-Illisimonin A, a Neuroprotective Sesquiterpenoid from the Fruits of *Illicium simonsii*

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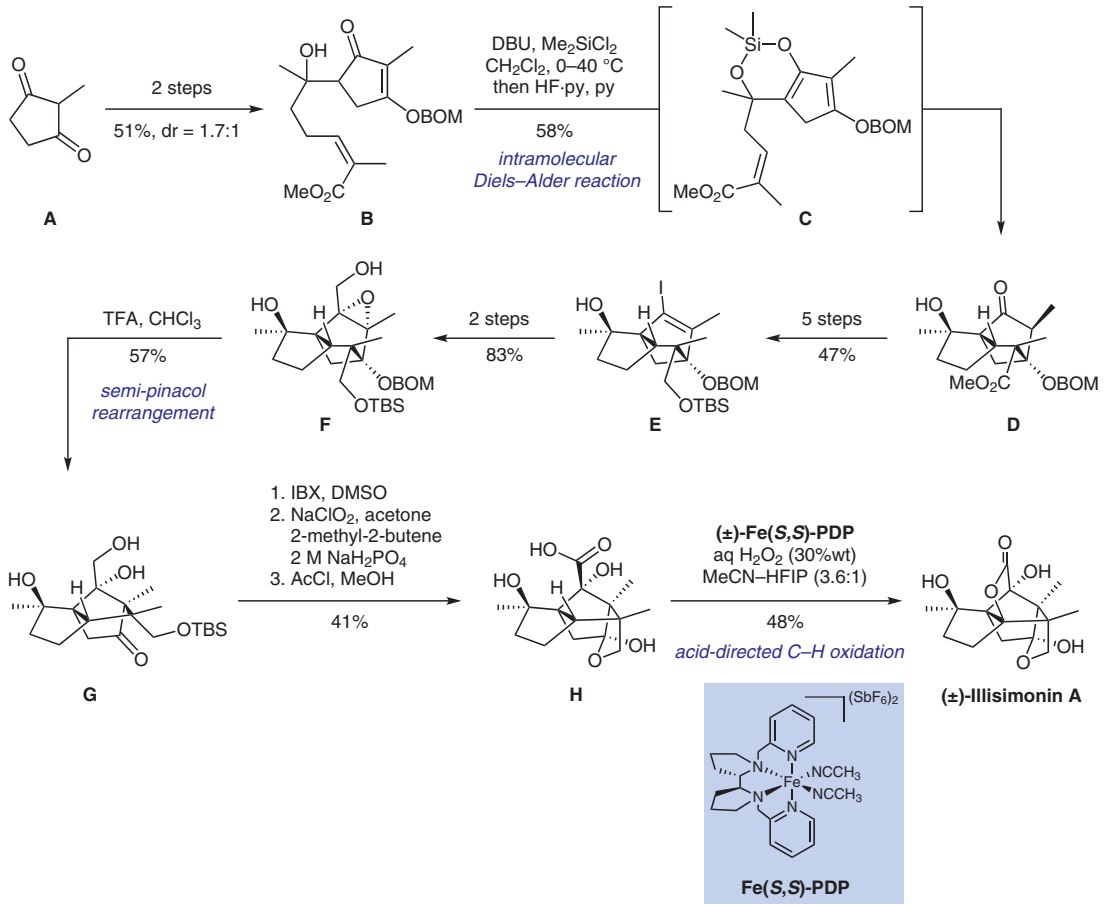
Total Synthesis of Illisimonin A



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.

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