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Total Synthesis of Atropurpuran
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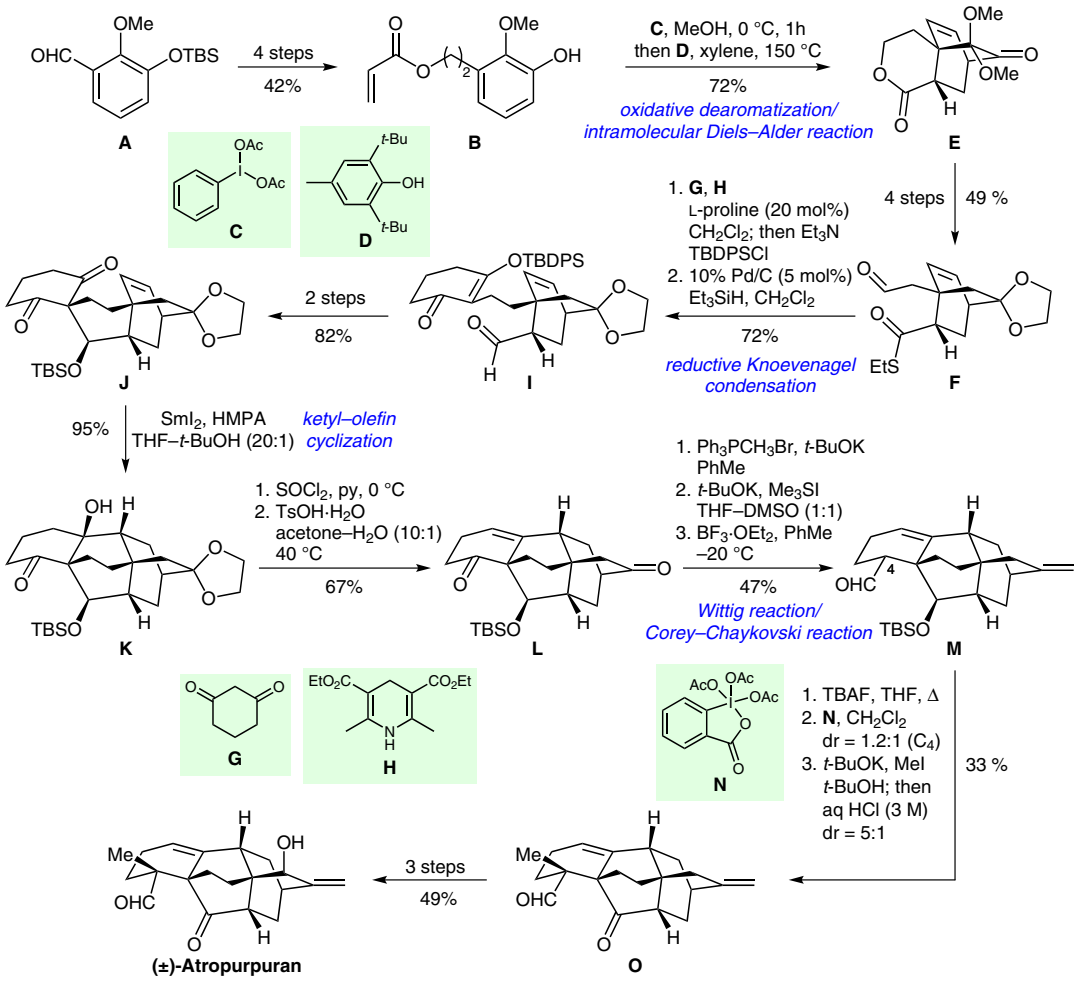
Synthesis of (±)-Atropurpuran



Significance: (±)-Atropurpuran belongs to the arcutane diterpenes and was isolated from *Aconitum hemsleyanum* var. *atropurpureum*. Its complex structure features a tetracyclo[5.3.3.$0^{4,9}$.$0^{4,12}$]tridecane core embedding two quaternary centers and four additional stereocenters. Qin and coworkers disclose the first total synthesis relying on an oxidative dearomatization/intramolecular Diels–Alder cascade to build the bicyclo[2.2.2.]octane ring, a reductive Knoevenagel condensation, and a ketyl–olefin cyclization.

Comment: Oxidative dearomatization of **B** using phenyliodine diacetate (**C**) in methanol followed by heating at 150 °C in xylene afforded tricycle **E** in 72% yield. Opening of the lactone and oxidation followed by a reductive Knoevenagel condensation and an aldol addition reaction furnished key intermediate **J**. Samarium-mediated ketyl–olefin cyclization afforded the (±)-atropurpuran core **K** in 95% yield. The total synthesis of (±)-atropurpuran was completed in a total of 25 linear steps and 0.4% overall yield.

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diterpenes
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