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 co-workers 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 phenylidene 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.