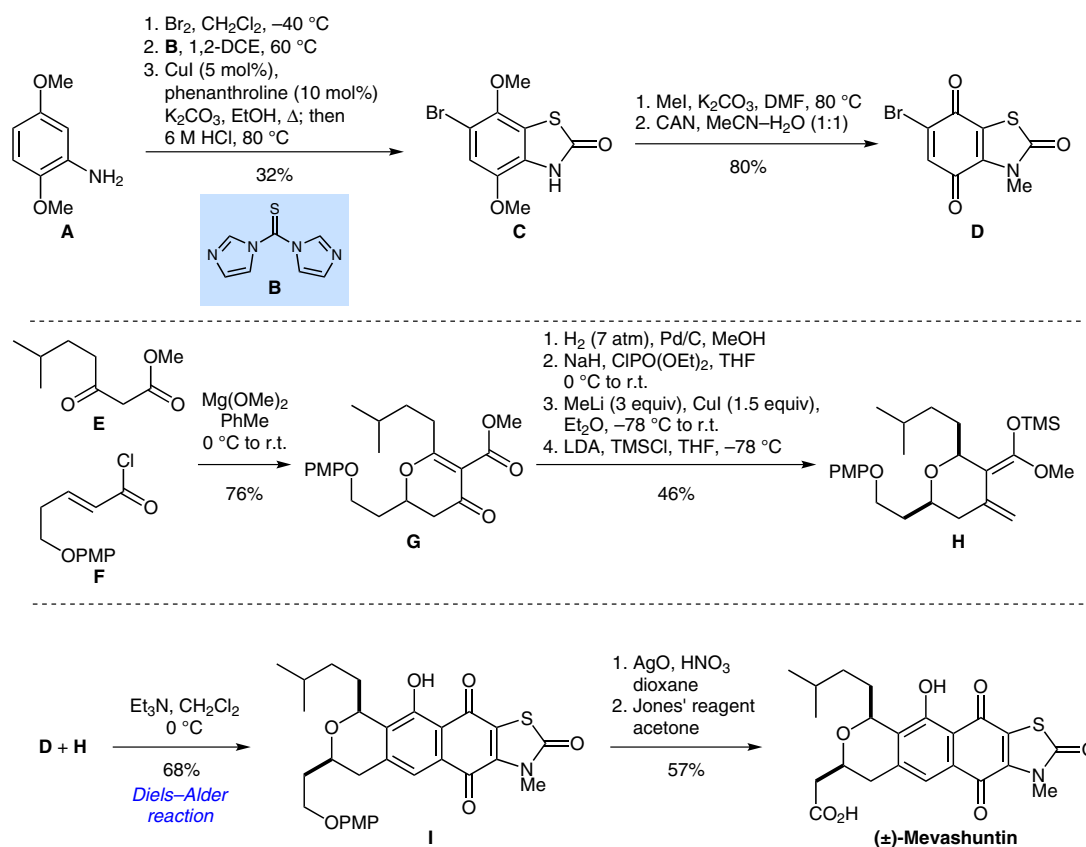


Synthesis of (±)-Mevashuntin



Significance: Mevashuntin was reported in 2005 by Shin-ya and co-workers (*Tetrahedron Lett.* 2005, 46, 1273). The relative and absolute configuration of the pyran substituents, as well as the relative positions of the sulfur and nitrogen atoms in the heteroaromatic ring were unknown. During characterization of the natural product, the NMR data was found to be concentration-dependent; therefore, comparison with reported data for the natural product was difficult. To circumvent this, the acid was converted into the methyl ester with TMS-diazomethane. The spectra of the ester matched very closely with the reported data for the natural product.

Comment: Removal of the ketone present in **G** was achieved by conversion into the enol phosphate followed by displacement with MeLi. Formation of the γ -TMS enolate provided diene **H**. A late-stage Diels–Alder reaction provided access to the core, with the regioselectivity controlled by a bromine substituent.