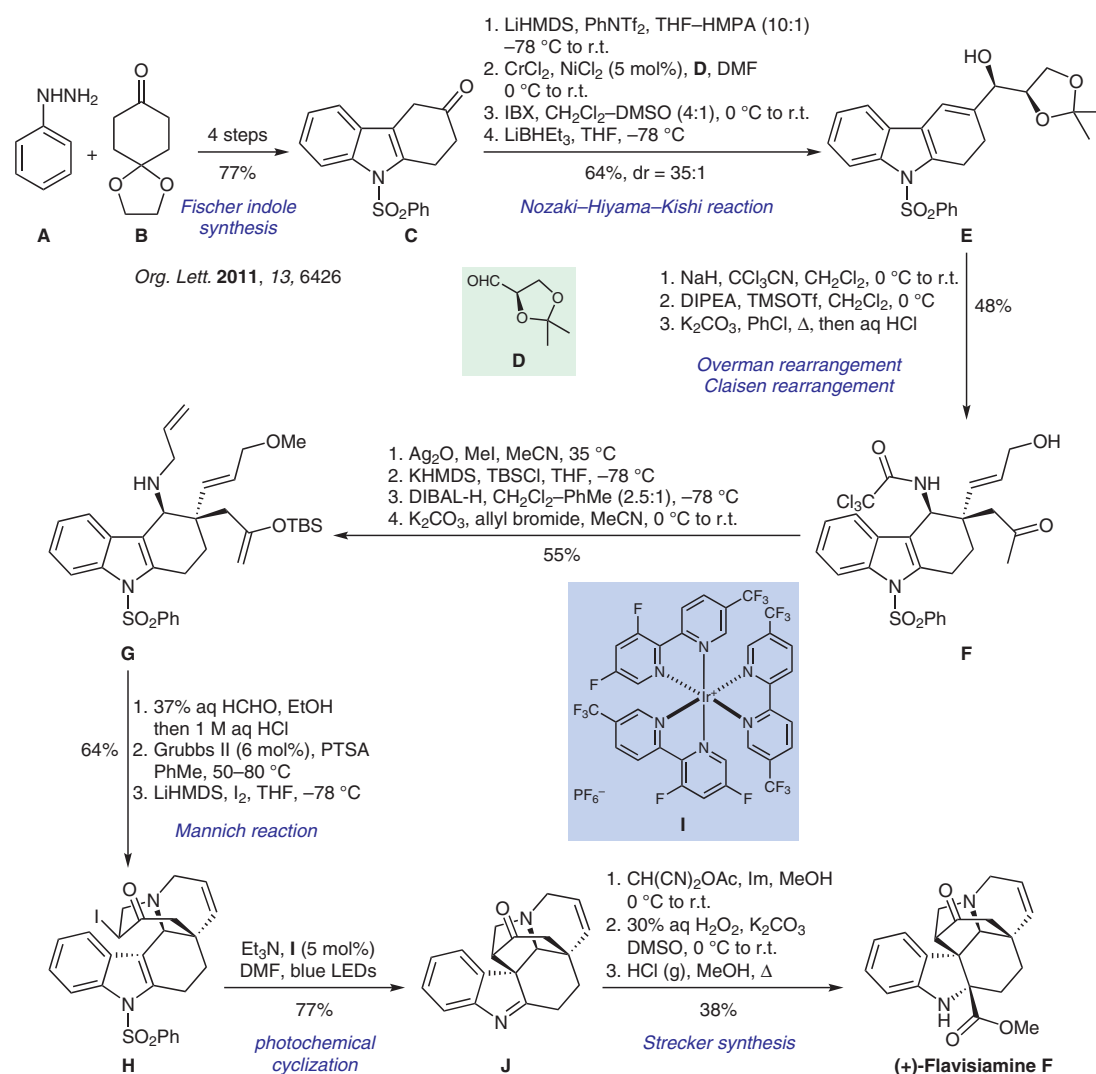


Total Synthesis of (+)-Flavisiamine F



Significance: Xia and co-workers report the first enantioselective total synthesis of the *Kopsia* alkaloid (+)-flavisiamine F. The authors elegantly solve the synthetic puzzle posed by this strained polycyclic natural product by using a strategy involving two [3,3]-sigmatropic rearrangements, ring-closing metathesis, Mannich reaction, and iridium-catalyzed radical cyclization.

Comment: Nozaki–Hiyama–Kishi coupling of the enol triflate derived from **C** followed by oxidation and stereoselective reduction gave **E**. Sequential Overman and Claisen rearrangements afforded ketone **F** en route to allyl amine **G**, which then underwent Mannich reaction and ring-closing metathesis. Halogenation and iridium-mediated photocyclization provided **J**, which was elaborated into the target molecule by Strecker reaction and hydrolysis.