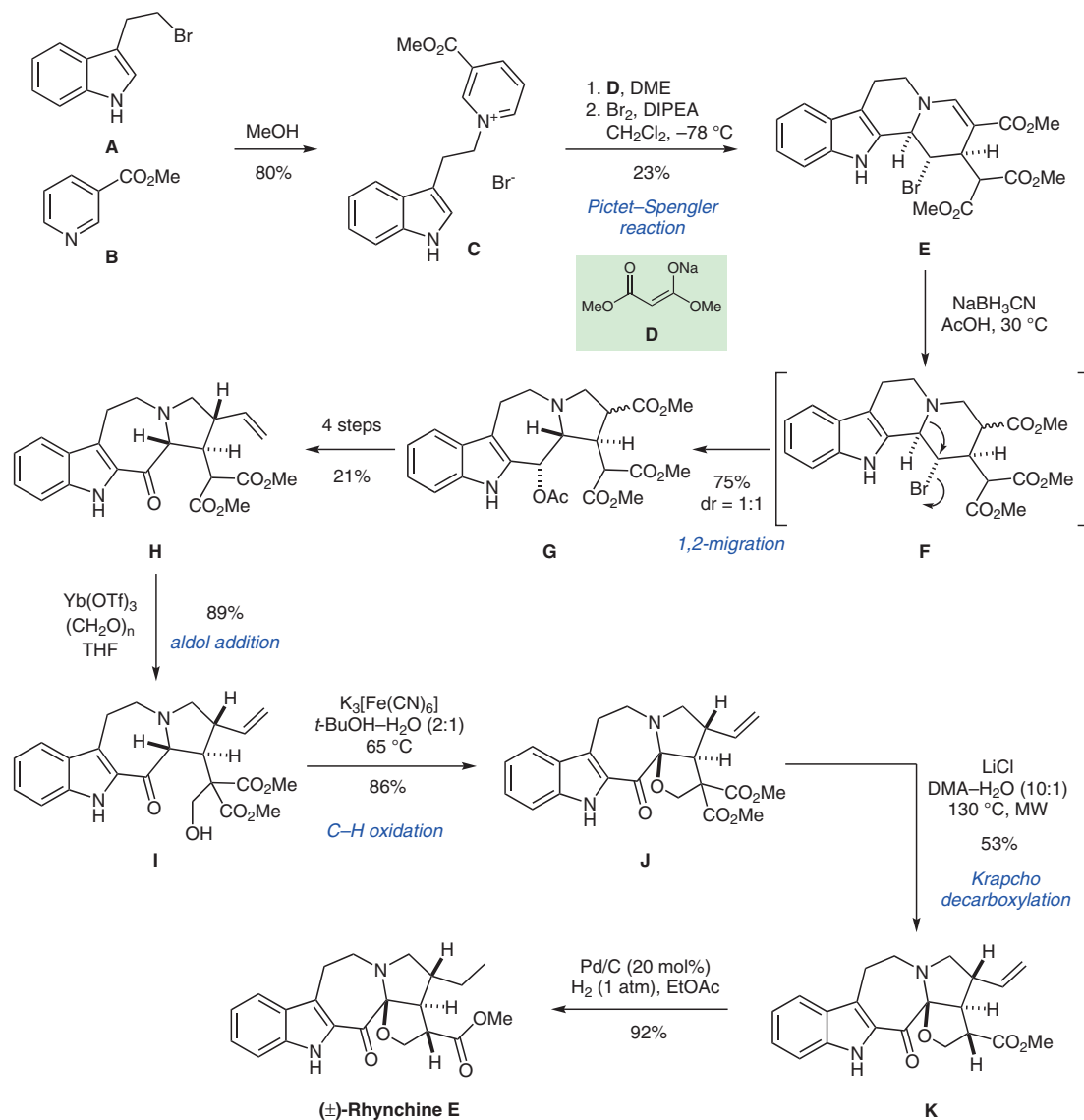


## Total Synthesis of (±)-Rhynchine E



**Significance:** In 2021, a new class of structurally unique monoterpene indole alkaloids was isolated from *Uncaria rhynchophylla*, rhynchines A–E. Zhao and co-workers now report the first racemic total synthesis of rhynchine E as well as rhynchine A–D. A biosynthetic relationship of the rhynchines natural products to hirsuteine, which is also commonly found in the isolation plant, was proposed.

**Comment:** The synthesis commenced with the formation of tetracyclic triester **E** from pyridinium salt **C**, through a Pictet–Spengler reaction. Subsequent treatment with NaBH<sub>3</sub>CN in AcOH, triggered conjugated reduction and a 1,2-migration, forming the core tetrahydroazepine **G**. The tetrahydrofuran ring of (±)-rhynchine **E** was formed via C–H oxidation using K<sub>3</sub>[Fe(CN)<sub>6</sub>].