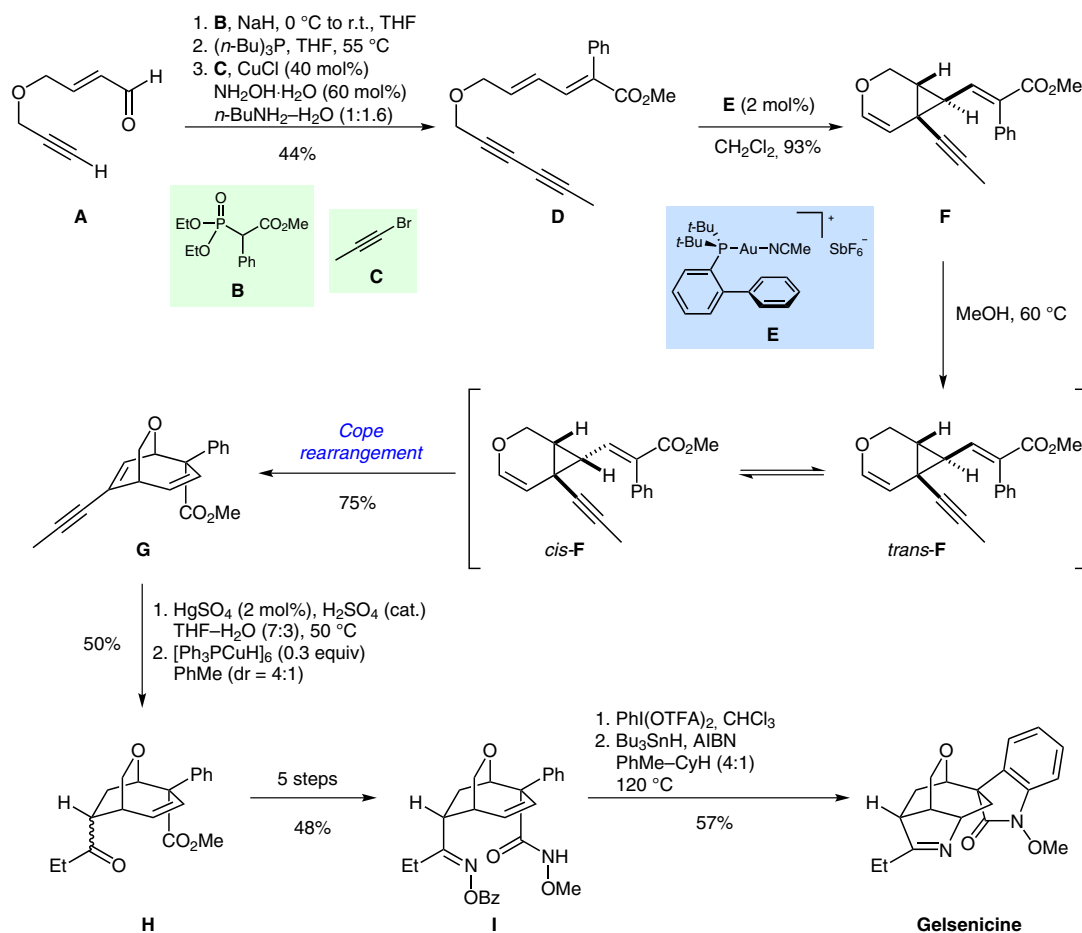


Synthesis of Gelsenicine



Significance: Gelsenicine is an oxindole alkaloid isolated from *Gelsemium Elegans*, a toxic plant widely distributed in Southeast Asia and used in traditional Chinese medicine. The structure features an oxabicyclo[3.3.2] system, an oxindole, and a pyrrole. Ferreira and co-workers disclose the first total synthesis of gelsenicine relying on a gold-mediated cycloisomerization followed by a Cope rearrangement that enabled the quick construction of the gelsenicine core.

Comment: Cycloisomerization precursor **D** was prepared from known aldehyde **A** using Horner–Wadsworth–Emmons olefination followed by Cadiot–Chodkiewicz coupling. Upon exposure to [Au(JohnPhos)(MeCN)SbF₆] (**E**), **D** underwent cycloisomerization to **F**. Heat-induced *cis/trans* isomerization and subsequent Cope rearrangement provided **G**. HgSO₄-mediated regioselective alkyne hydration followed by oxindole and radical pyrrole formation culminated in the synthesis of gelsenicine in 13 steps and 4.2% overall yield.