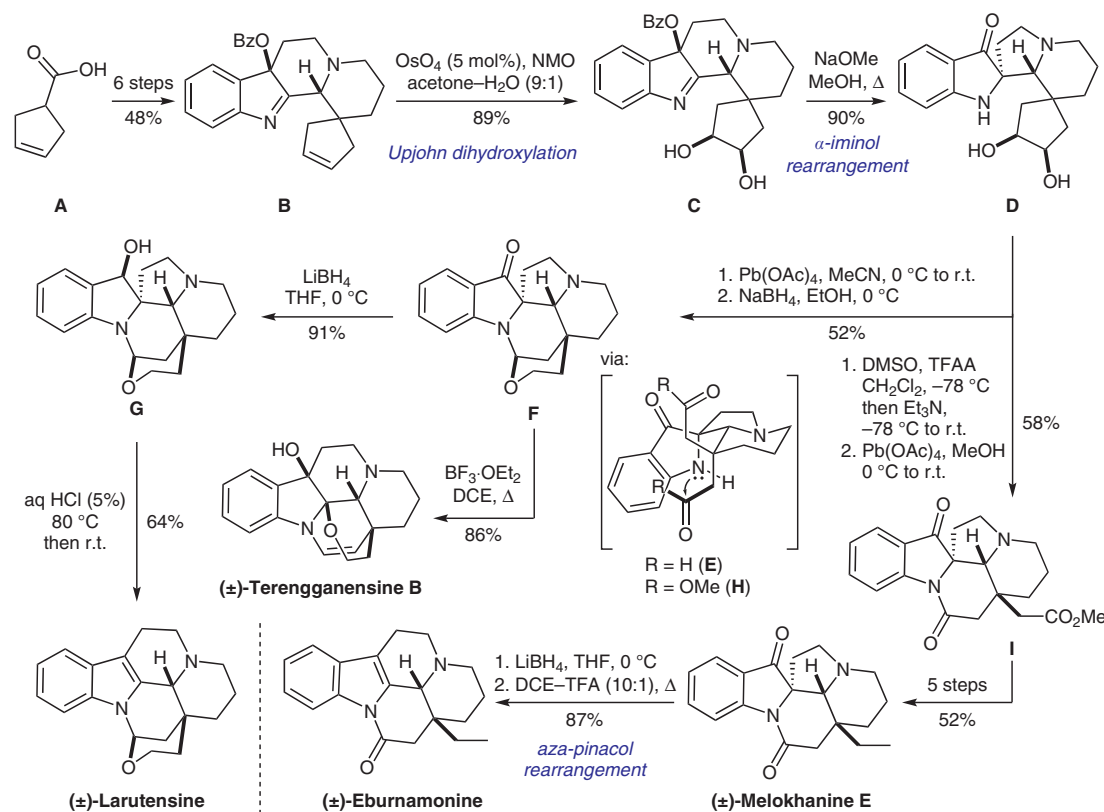


Synthesis of Eburnane-Type Alkaloids



Significance: Zhu and co-workers present their recent efforts to access eburnane-type alkaloids using a highly divergent approach. The presented route features an α -iminol rearrangement to access the *trans*-fused core in intermediate **D**. The conformational bias allowed to close the remaining six-membered ring of the eburnane core in a diastereoselective fashion. The divergent design of the route uses key intermediates **D** and **E** to access four different eburnane alkaloids with good yields.

Comment: α -Iminol rearrangement of **C** led to key intermediate **D**. Oxidative cleavage of the diol and reduction yielded hexacyclic aminal **F** as a single diastereomer. Lewis acid induced 1,2-alkyl shift of **F** furnished (\pm)-terengganensine **B**. Reduction to alcohol **G** and Brønsted acid mediated rearrangement allowed synthesis of (\pm)-larutensine. Oxidation of diol **D** to the corresponding diketone and subsequent oxidative bond cleavage gave pentacyclic amide **I**. (\pm)-Melokhanine **E** was obtained in five additional steps and was then converted into (\pm)-eburnamonine by means of an aza-pinacol rearrangement.