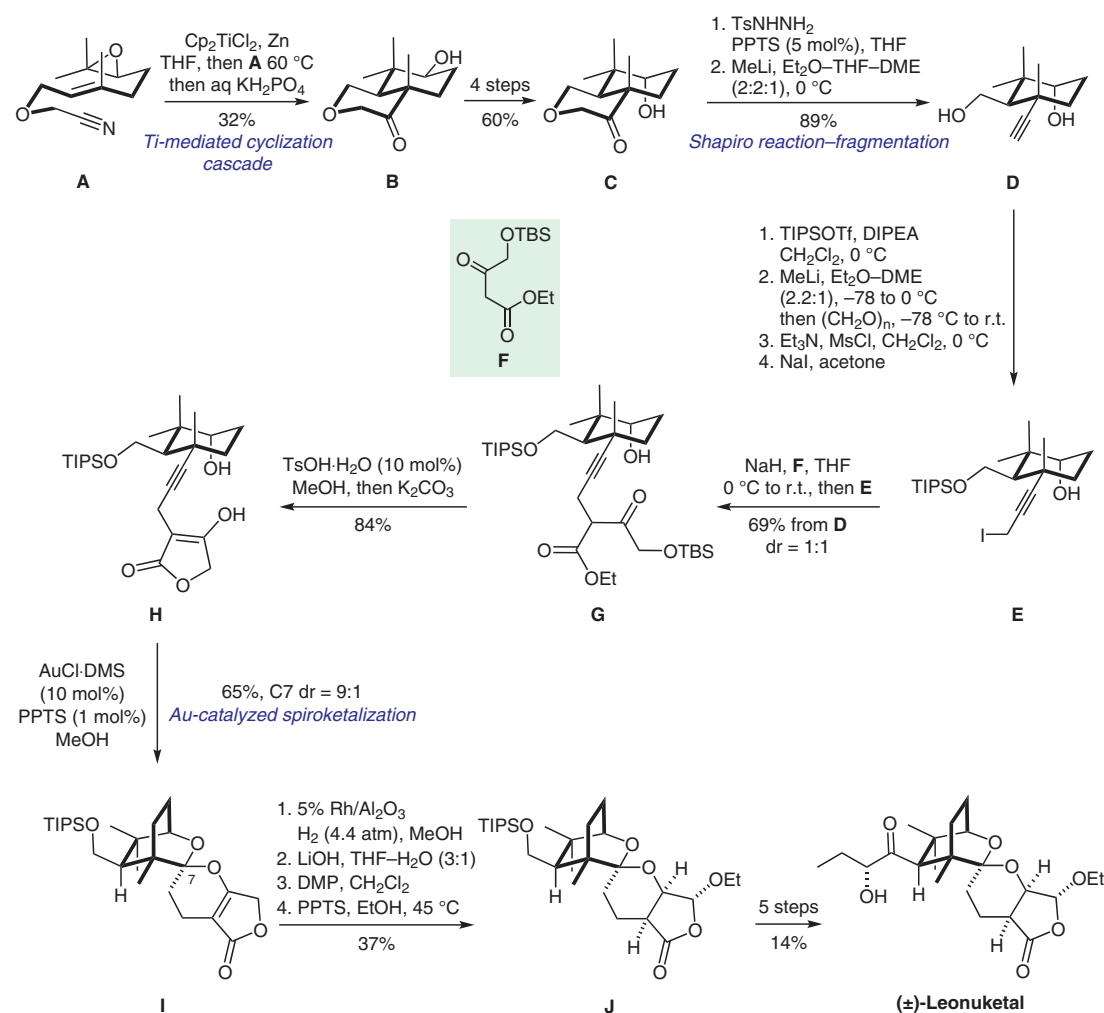


Synthesis of (±)-Leonuketal



Significance: The tetracyclic 8,9-*seco*-labdane terpenoid (–)-leonuketal was isolated from the Chinese liverwort *Leonurus japonicus* and shows significant vasorelaxant activity against KCl-induced contraction of rat aorta. The authors present the first total synthesis relying on a Ti-mediated cyclization, a Shapiro reaction–fragmentation and an Au-catalyzed spirocyclization.

Comment: Epoxide **A** was subjected to Ti-mediated radical cyclization to obtain bicyclic ketone **B**. Shapiro reaction–fragmentation was applied to furnish alkyne **D**. Alkylation of ketoester **F** with iodide **E** afforded alkyne **G** which was cyclized to butenolide **H**. Au-catalyzed spirocyclization delivered spiroketal **I** which was transformed into the natural product in additional 9 steps.