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Asymmetric Total Synthesis of Twin Bufogargarizins A and B
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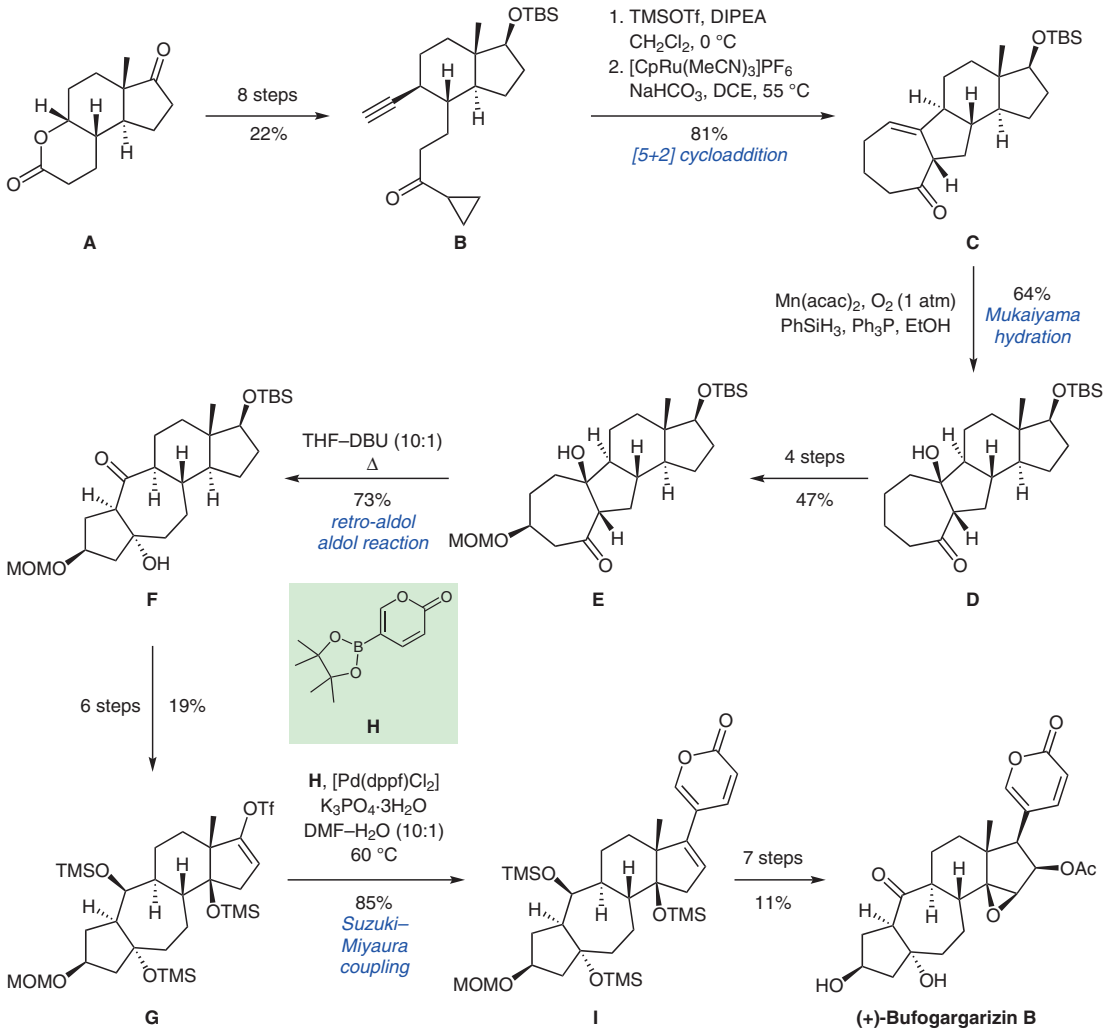
Total Synthesis of (+)-Bufogargarizin B



Significance: Li and co-workers report the total synthesis of the *abeo*-steroid (+)-bufogargarizin B from commercially available sitolactone (**A**). Their synthetic strategy features a Ru-catalyzed [5+2] cycloaddition to forge the seven-membered ring. This transformation, which was pioneered by Wender and Trost, was adopted by the authors to convert silyl enol ether cyclopropane-ynes into cyclohept-3-en-1-ones.

Comment: Ketone **B** is converted into the silyl enol ether, which in situ undergoes the [5+2] cycloaddition. *Retro*-aldol-aldol reaction mediated by DBU in refluxing THF rearranges the carbon skeleton to **F** under high diastereocontrol. The 2-pyrone moiety is installed by a Suzuki–Miyaura coupling of enol triflate **G** with boronic ester **H**. After seven consecutive operations, (+)-bufogargarizin B is obtained. The authors also report the total synthesis of (–)-bufogargarizin A using ketone **D** as a common intermediate.

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Category
Synthesis of Natural Products

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