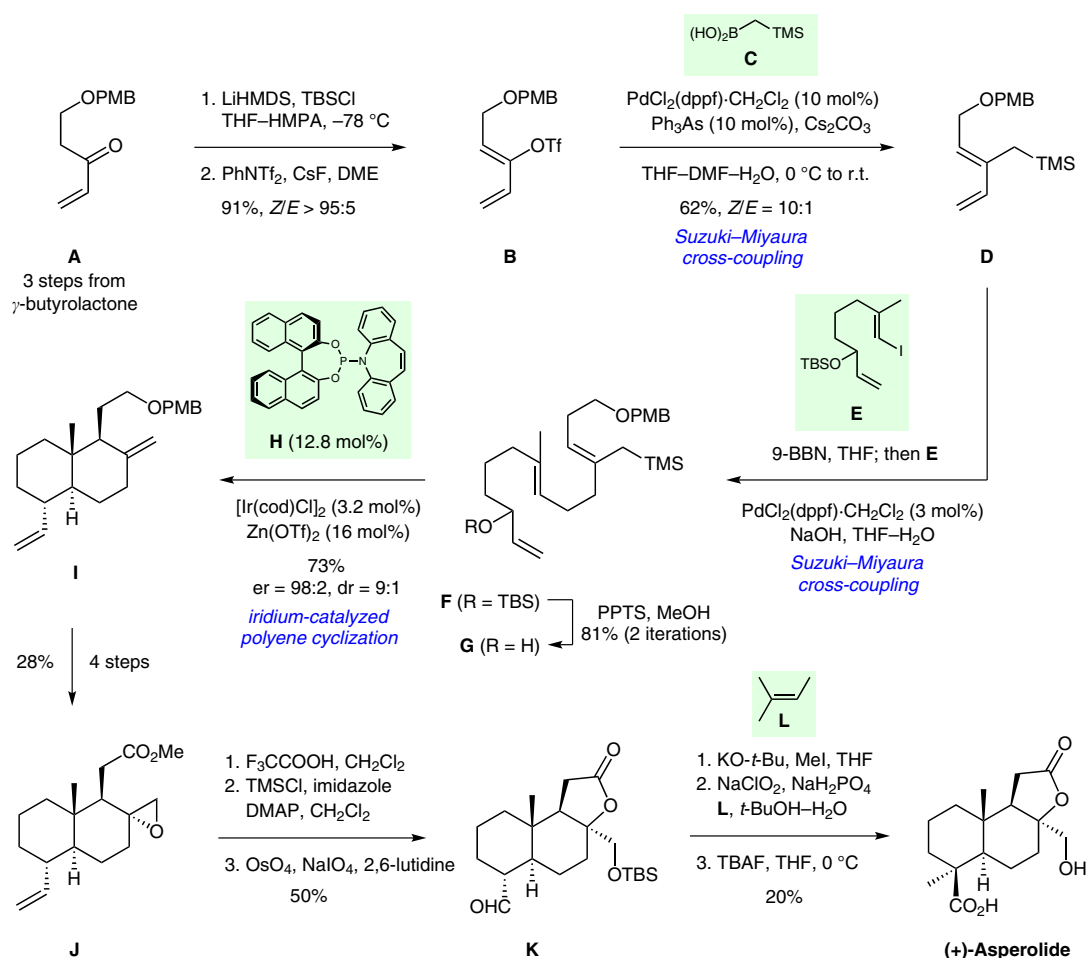


Total Synthesis of (+)-Asperolide C



Significance: The first total synthesis of (+)-asperolide C, a tetranorlabdane diterpenoid isolated from the endophytic fungal strain *Aspergillus wentii* EN-48, is reported including the first thorough characterization of this natural product which previously could only be obtained as an inseparable mixture with another related terpene. The synthetic strategy, which delivers the desired target in 18 steps for the longest linear sequence, could thereby potentially also be used to access other members of the labdane class and related terpenes.

Comment: The key element of the synthesis is the use of an iridium-catalyzed, enantioselective polyene cyclization in which the cationic cascade is terminated by an allyl silane to forge a properly substituted decaline scaffold with the required exocyclic double bond in excellent stereoselectivity. This process, which resembles the currently accepted mechanism for the biogenesis of these terpenes, in fact represents one of only three examples to date applying an asymmetric polyene cyclization cascade in a natural product synthesis.