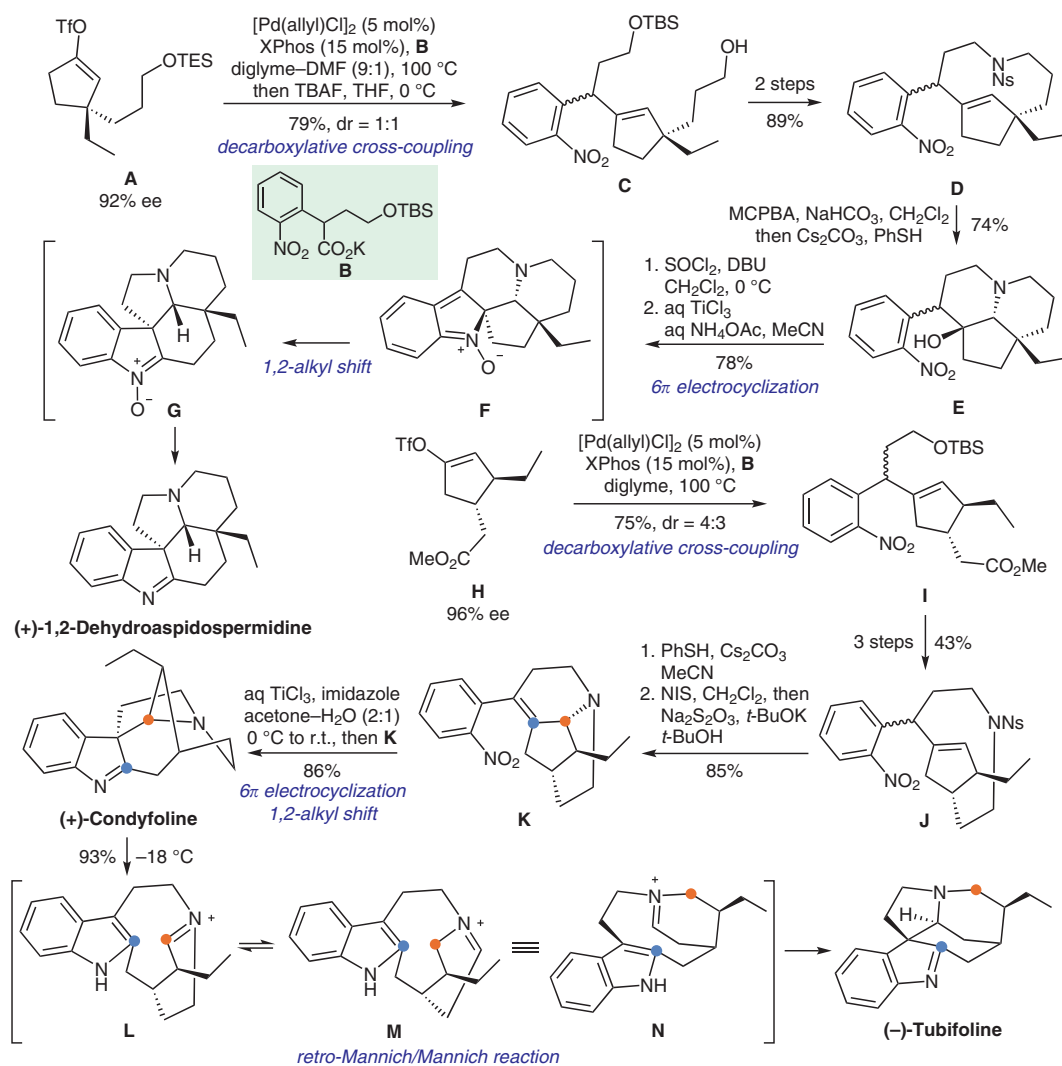


Total Synthesis of (+)-1,2-Dehydroaspidospermidine, (+)-Condyfoline, and (-)-Tubifoline



Significance: Zhu and co-workers report the synthesis of 2,3,3-trisubstituted indolenines through a TiCl₃-mediated reductive cyclization of tetrasubstituted alkenes bearing a 2-nitrophenyl substituent. An unprecedented sequence of reduction of nitroarene, 6π electrocyclization, 1,2-alkyl shift, and final nitrone reduction resulted in the syntheses of (+)-1,2-dehydroaspidospermidine, (+)-condyfoline, and (-)-tubifoline.

Comment: Palladium-catalyzed decarboxylative cross-coupling between enantioenriched vinyl triflate **A** and racemic potassium carboxylate **B** furnished cyclopentene **C**. Epoxidation, deprotection, and subsequent transannular epoxide ring opening provided **E** which was converted into (+)-1,2-dehydroaspidospermidine through reductive cyclization. Isomerization of (+)-condyfoline to (-)-tubifoline occurred by a retro-Mannich/Mannich reaction.