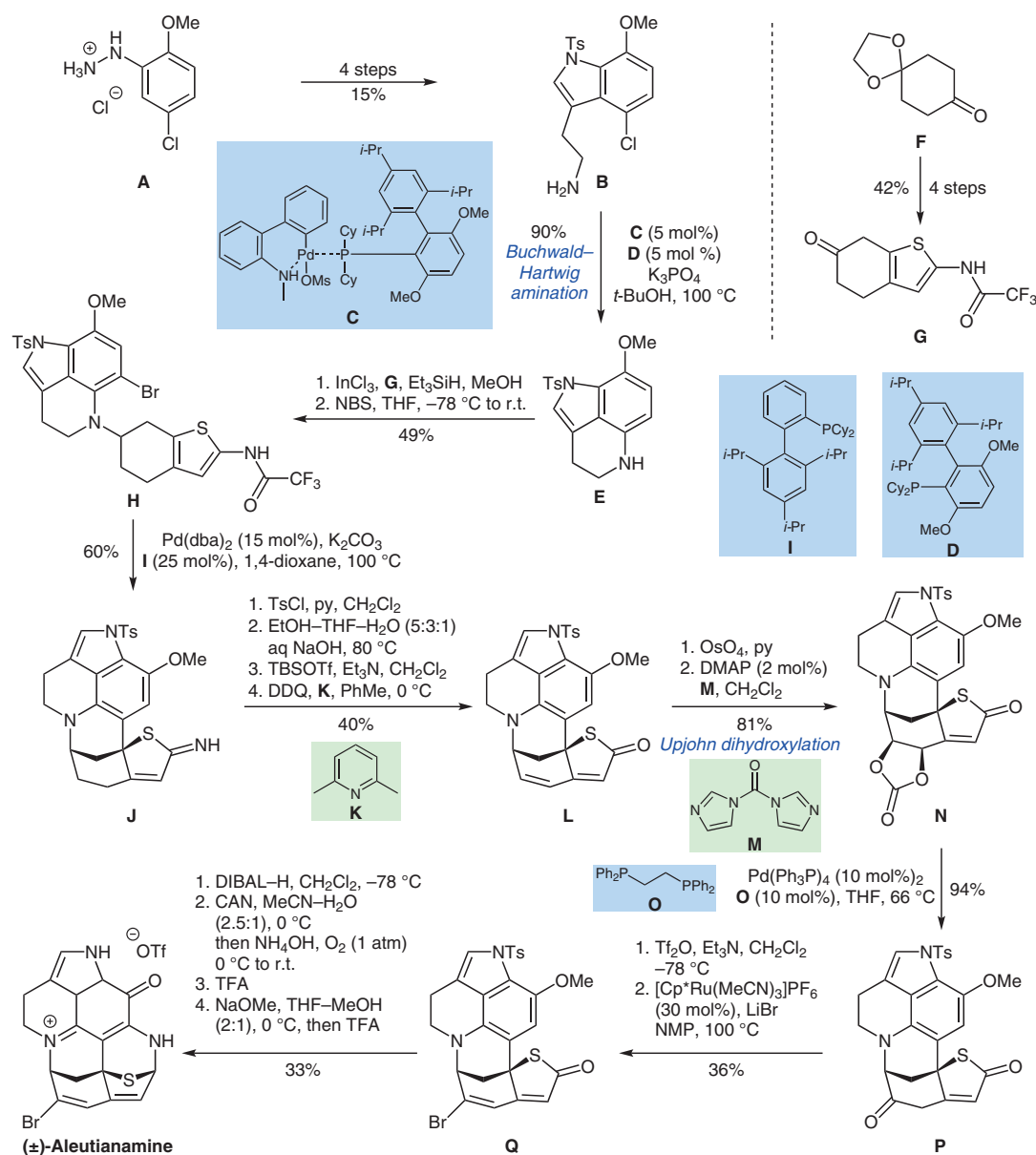


Synthesis of (±)-Aleutianamine



Significance: Stoltz and co-workers report the total synthesis of the recently isolated pyrroloiminoquinone alkaloid (±)-aleutianamine. Key to their approach is a palladium-catalyzed dearomative thiophene functionalization to construct the [3.3.1]ring system and the thioimide.

Comment: Tricycle **E** was accessed from hydrazine **A** in five steps. Reductive amination of amidothiophene **G** and subsequent bromination yielded tertiary amine **H**. Treatment with $Pd(dba)_2$ and XPhos in the presence of a base led to dearomative cyclization and acetamide cleavage, resulting in thioimide **J**.