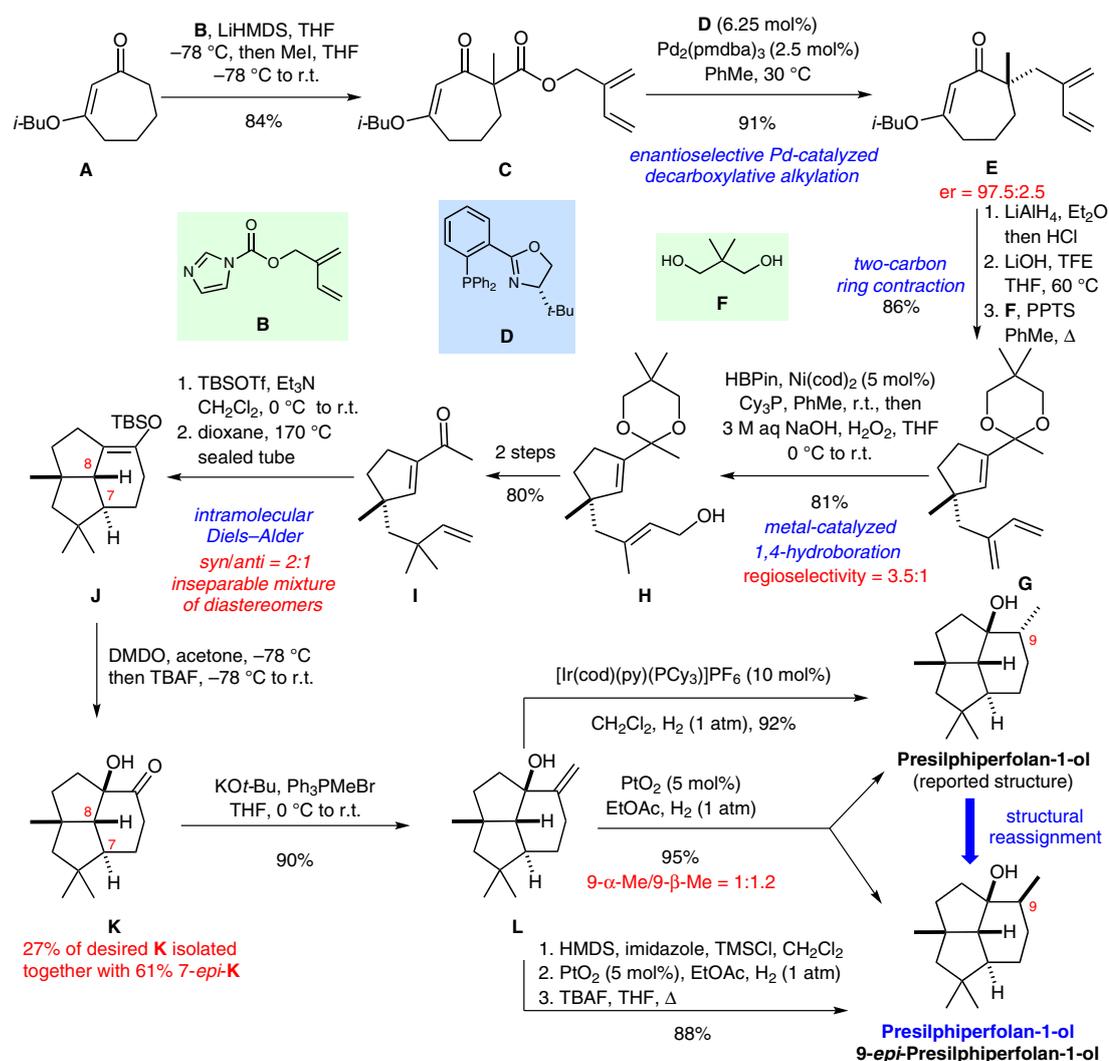


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 Enantioselective Total Synthesis of the Reported Structures of (–)-9-*epi*-Presilphiperfolan-1-ol and
 (–)-Presilphiperfolan-1-ol: Structural Confirmation and Reassignment and Biosynthetic Insights
Angew. Chem. Int. Ed. **2012**, *51*, 9674–9678.

Synthesis of (–)-9-*epi*-Presilphiperfolan-1-ol and (–)-Presilphiperfolan-1-ol



Significance: The title compounds were synthesized for the first time in an elegant and enantioselective manner. Careful analysis of the spectral data obtained prompted the authors to conclude that the actual structure of natural presilphiperfolan-1-ol displays a 9- β -Me group and that the structure with 9- α -Me was most probably misassigned and not a natural product.

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Comment: Ketone **I** was rapidly assembled from enone **A** in eight steps. The subsequent intramolecular Diels–Alder reaction (**I** \rightarrow **J**) allowed the construction of the compact, tricyclic ring system (*cis/trans* = 2:1). While hydrogenation of **L** with PtO₂ gave the two reported structures as a 1:1.2 mixture of C9 epimers, other strategies were reported to obtain both compounds separately in good yield.