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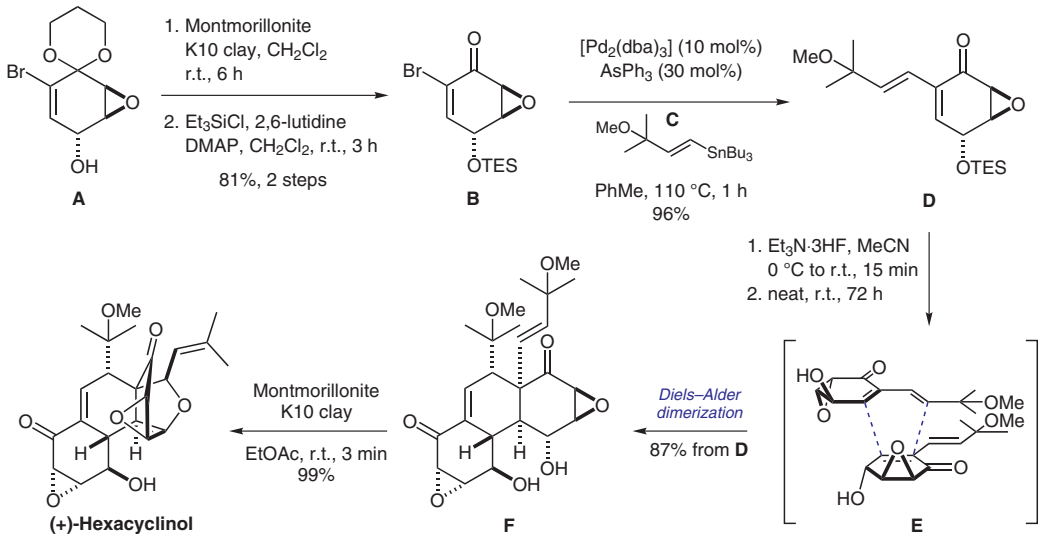
Total Synthesis and Structure Assignment of (+)-Hexacyclinol
Angew. Chem. Int. Ed. **2006**, *45*, 5790-5792.

Synthesis of (+)-Hexacyclinol



Significance: (+)-Hexacyclinol is a metabolite isolated from *Panus rudis* strain HKI 0254 in 2002. The structure of this natural product has been the cause of recent controversy [*Chem. Eng. News* **2006**, *84(31)*, 11]. A synthesis of the proposed structure (J. La Clair *Angew. Chem. Int. Ed.* **2006**, *45*, 2769-2773) has recently been revised on the basis of calculated ^{13}C NMR shifts (S. D. Rychnovsky *Org. Lett.* **2006**, *8*, 2895-2898). This work substantiates the revised structure and relates to a recent biomimetic synthesis of (+)-panepophenanthrin by Porco and co-workers (*Angew. Chem. Int. Ed.* **2003**, *42*, 3913-3917) that amply displays the virtues of biomimetic strategy in natural product synthesis.

Comment: Stille coupling of bromide **B** and vinyl stannane **C** gave **D** that, upon silyl cleavage, underwent Diels–Alder dimerization via *exo* transition state **E** to afford **F**. Subsequent treatment with K10 clay induced S_N2' substitution of the allylmethoxy group by the proximal *Re* face hydroxyl group giving the target.

Reviews: *The Stille Reaction*, V. Farina, V. Krishnamurthy, W. J. Scott *Org. React (N.Y.)* **1997**, *50*, 1-652. *Clay and Clay-Supported Reagents in Organic Synthesis*, R. S. Varma *Tetrahedron* **2002**, *58*, 1235-1255.

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