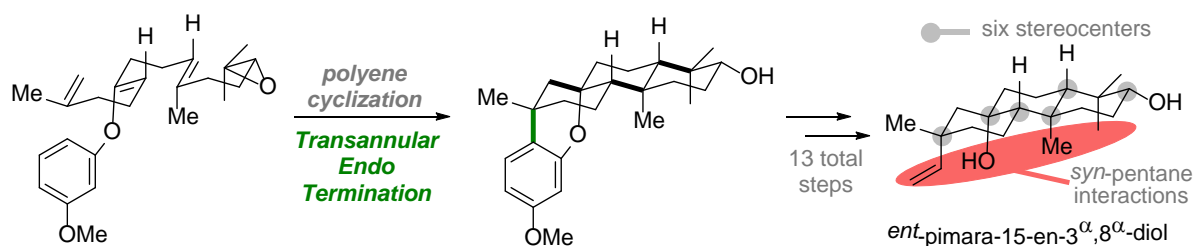


Polyene Cyclizations 2.0: Total Synthesis of a Pimarediol

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The tricyclic natural product *ent*-pimara-15-en-3 α -8 α -diol was first isolated from *Gnaphalium gaudichaudianum* in 2003.^[1] The pimarane skeleton comprises three quaternary carbons and six stereocenters, four of which are adjacent. *Syn*-pentane interactions of all four axial substituents generate considerable strain in the molecule. We present a 13-step synthesis of this synthetically challenging target. The strategy features an unprecedented polyene cyclization of a heteroatom-substituted olefin involving a unique transannular *endo*-termination.



[1] T. Meragelman, G. L. Silva, E. Mongelli, R. R. Gil, *Phytochemistry* **2003**, 62, 569–572.