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Tandem Decarboxylative Cyclization/Alkenylation Strategy for Total Syntheses of (+)-Longirabdiol, (–)-Longirabdolactone, and (–)-Effusin

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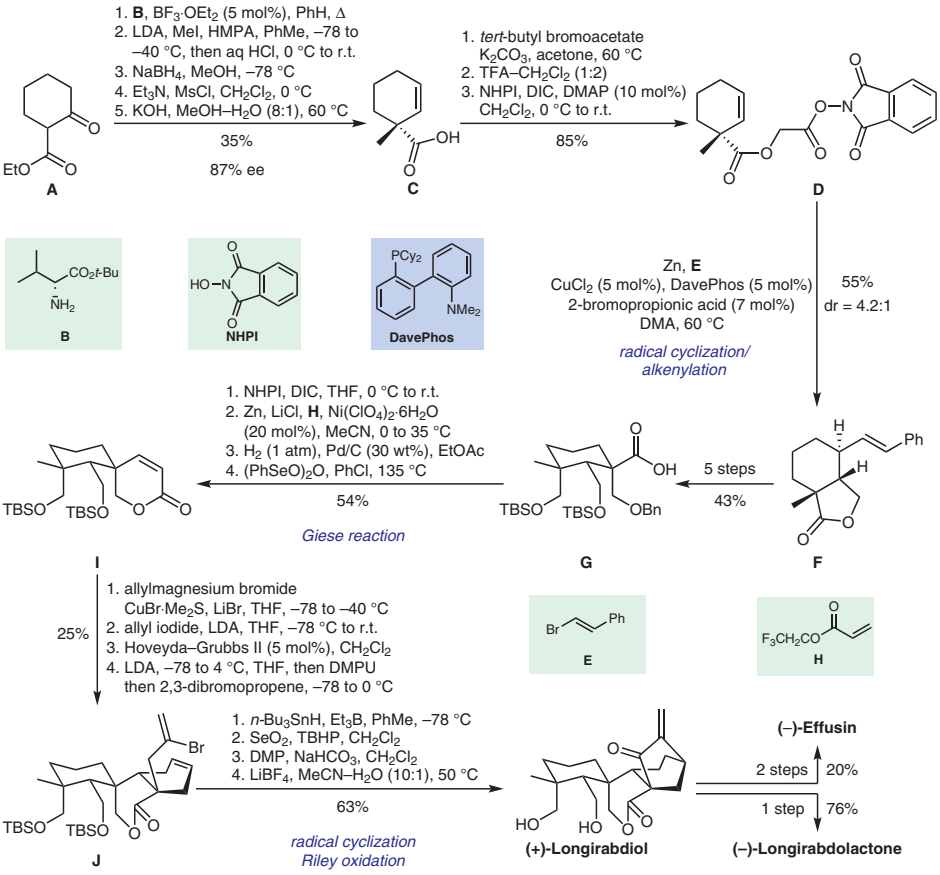
Synthesis of (+)-Longirabdiol, (–)-Longirabdolactone, and (–)-Effusin



Significance: Owing to their well-established biological effects and structural complexity, *ent*-kaurane diterpenoid natural products continue to attract interest from the synthetic community. Li and co-workers present enantioselective total syntheses of three spirolactone *ent*-kauranoids by relying on a sequence involving an elegant tandem decarboxylative cyclization alkenylation. Two additional free radical-based cyclization events allowed the team to access (+)-longirabdiol. Closely related natural products (–)-longirabdolactone and (–)-effusin were synthesized by implementation of few additional transformations.

Comment: The authors initiated their synthetic route by preparation of enantioenriched acid **C** followed by its subsequent transformation into the redox-active ester **D**. Tandem radical cyclization/alkenylation led to the formation of lactone **F** with good diastereoselectivity. Following functional group interconversions, intermolecular decarboxylative Giese reaction and intramolecular lactonization gave rise to spiro-compound **I**. This intermediate was transformed into advanced intermediate **J**, thereby setting the stage for the last radical cyclization, allylic oxidation, and desilylation to afford (+)-longirabdiol.

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Category

Synthesis of Natural Products and Potential Drugs

Key words

(+)-longirabdiol
(–)-longirabdolactone
(–)-effusin
radical cyclization
Giese reaction
Riley oxidation

Synfact of the Month