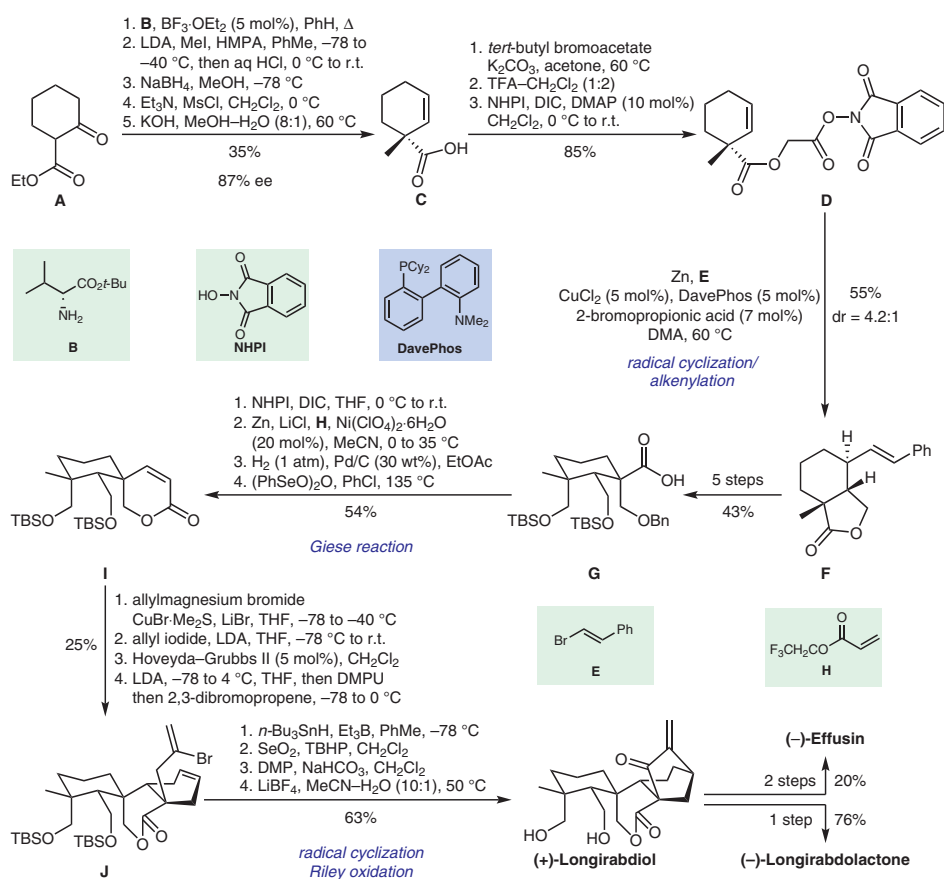


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Tandem Decarboxylative Cyclization/Alkenylation Strategy for Total Syntheses of (+)-Longirabdiol, (-)-Longirabdolactone, and (-)-Effusin

J. Am. Chem. Soc. **2019**, *141*, 8372–8380.

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 spiro lactone *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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 Synfacts 2019, 15(08), 0833 Published online: 18.07.2019
 DOI: 10.1055/s-0039-1690443; Reg-No.: C04119SF