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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