Total Synthesis (±)-Garcibracteatone

Significance: Garcibracteatone (K) is the structurally most complex polycyclic polypropenylated acylphloroglucinol natural product that has so far been isolated. The four-step total synthesis presented makes use of a biomimetic radical cascade reaction to build up four rings in one transformation. Additionally, the previously unknown relative stereochemistry at C-5 was assigned.

Comment: Precursor F for the key transformation is synthesized from phloroglucinol A in three steps by Friedel–Crafts acylation followed by subsequent diprenylation and alkylation with (±)-lavanudulyl iodide (E). Oxidation of F by using Mn(OAc)₃–Cu(OAc)₂ initiates a radical cascade, which ultimately leads to the formation of the natural product garcibracteatone K (14% yield) along with its C5-epimer L (8% yield). This key transformation constructs four rings and five stereocenters.