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Selective late-stage oxidation of C—H bonds in the synthesis of complex natural diterpenes

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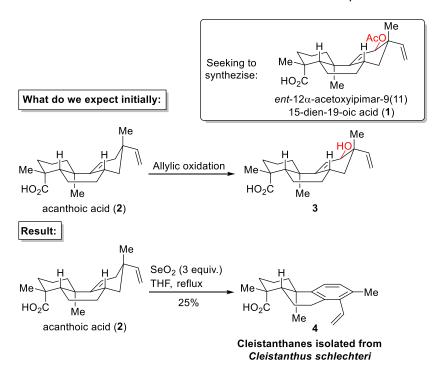
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ABSTRACT

One of the main challenges in the area of C—H bond oxidation is the development of selective reactions due to the ubiquity of this type of bond in organic molecules and its low reactivity. In the case of transformations applied at a late-stage, obtaining chemoselectivity is of great interest. In this sense, our main goal is to use complex natural diterpenes as platforms to perform selective C—H oxidations in the synthesis of other natural products in a higher oxidative level.

In order to synthesize the natural product **1**, we envisioned that the *ent*-pimarane acanthoic acid (**2**)¹ could be converted to the allylic alcohol **3**. However, the allylic oxidation of compound **2** with three equivalents of SeO₂ in THF at reflux furnished the aromatic compound **4** in 25% yield (Scheme 1).

This result enabled us to access the cleistanthanes class of natural products² in a biomimetic way.



Scheme 1. Allylic oxidation of acanthoic acid with SeO₂

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