

Total synthesis of 3,4-epoxy-6,9-heneicosadiyne, sex pheromone component of *Thyriniteina arnobia*

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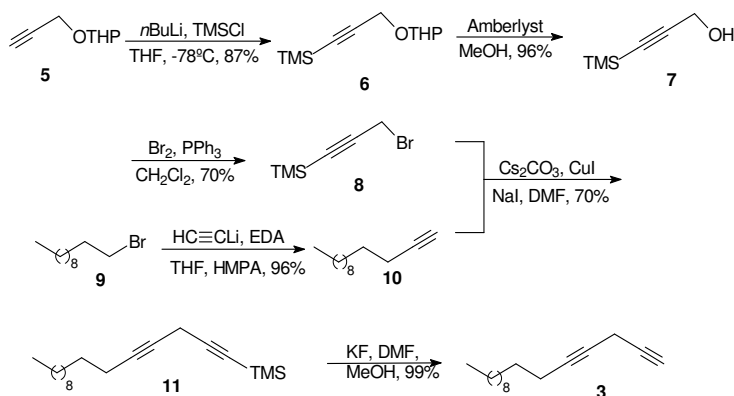
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INTRODUCTION

The Brazilian eucalyptus brown looper, *Thyriniteina arnobia* (Lepidoptera: Geometridae), is the most harmful of the *Eucalyptus* pests in Brazil, causing severe losses in wood production through defoliation. However, no practical and environmentally acceptable method of control currently exists. *T. arnobia* virgin female gland extract was analyzed by GC-EAD and two compounds elicited a strong and reproducible antenna response. GC-MS analyses suggested homoconjugated epoxydiene derivatives as sex pheromone compounds, being the main component identified as 3,4-epoxy-6,9-heneicosadiyne (**1**).¹ In this work we describe the racemic and the studies towards the asymmetric synthesis epoxydiyne **1**.

RESULTS AND DISCUSSION

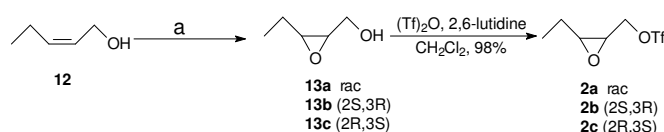
We proposed a convergent synthesis² for compound **1** where the key step is the coupling of epoxytriflate **2** with diyne **3**, which was also prepared in a convergent synthetic route by the reaction of bromide **8** with alkyne **10** (Scheme 1). Diyne **3** is quite unstable, even at low temperature, thus it has to be freshly prepared by deprotecting compound **11** just before the coupling reaction.



Scheme 1: Preparation of diyne **3**.

Racemic epoxialcohol **13a** was prepared by epoxidation of commercially available *cis*-penten-2-ol (**12**) with MCPBA and enantiomerically enriched **13b** and **13c** were prepared employing the

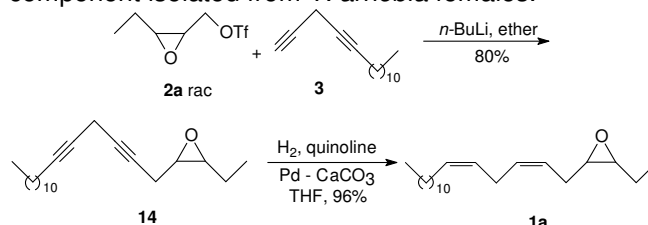
Sharpless asymmetric epoxidation.³ The corresponding epoxytriflates **2** were prepared by reaction with trifluoroacetic anhydride (Scheme 2).³



^aReagents and conditions: (a) MCPBA, CH₂Cl₂, (**13a**, 98%); (b) *t*-BuOOH, 0.20 equiv Ti(O*i*-Pr)₄, 0.22 equiv (L)-DIPT (**13b**, 65%, 70% ee); (c) *t*-BuOOH, 0.20 equiv Ti(O*i*-Pr)₄, 0.22 equiv (D)-DIPT (**13c**, 60%, 70% ee).

Scheme 2: Preparation of epoxytriflates **2**.

The synthesis of racemic **1a** was accomplished by the reaction of the corresponding acetylide of diyne **3** with epoxytriflate **2a**,⁴ followed by hydrogenation of the triple bonds (Scheme 3). GC-MS analysis of synthetic epoxydiene **1** was identical to the major component isolated from *T. arnobia* females.



Scheme 3: Synthesis of racemic epoxydiene **1a**.

CONCLUSION

In conclusion, a very efficient racemic synthesis of 3,4-epoxy-26,29-heneicodiene (**1**) was carried out in 10 steps and 28% overall yield. The enantiomerically enriched epoxydienes are being synthesized by the same methodology. The four stereoisomers will be employed in laboratory and field tests in order to determine the absolute configuration of the natural product and prove its biological role as the major component of *T. arnobia* pheromone blend.

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