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Catalytic Asymmetric Synthesis of Enantiopure Isoprenoid Building Blocks: Application in the Synthesis of Apple Laefminer Pheromones

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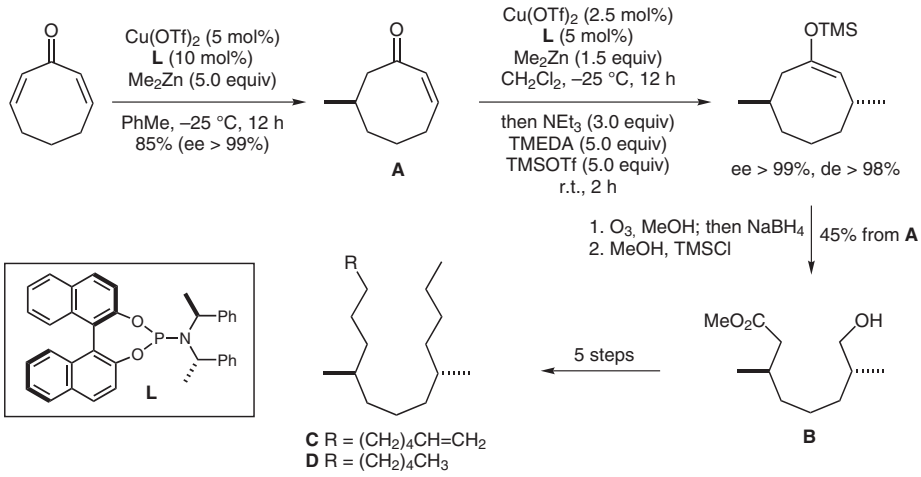
Catalytic Asymmetric Synthesis of Apple Leafminer Pheromones



Significance: Starting from cycloocta-2,7-dienone, all four diastereoisomeric 8-hydroxy-3,7-dimethyloctanoic acids were prepared in four steps (38% overall) and one of them (**B**) was transformed to pheromones **C** and **D** of the apple leafminer (*Lyonetia prunifoliella*) in a further four steps. A new method for the desymmetrization of cross-conjugated dienones is presented.

Comment: The key step in the synthesis is the powerful Cu-phosphoramidite-catalyzed enantioselective conjugate addition of dialkylzincs to enones. The method offers a general solution to the construction of carbon chains with alkyl groups in a 1,5-relationship. It complements the procedures of Noyori (Ru-catalyzed asymmetric hydrogenation of allylic alcohols) and Negishi (Zr-catalyzed enantioselective carboalumination) for the synthesis of isoprenoid chains. For reviews of enantioselective Cu-catalyzed conjugate addition see: A. Alexakis, C. Benhaim *Eur. J. Org. Chem.* **2002**, 3221-3236; B. L. Feringa *Acc. Chem. Res.* **2000**, *33*, 346-353.

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Category

Synthesis of Natural Products and Drugs

Key Words

enantioselective catalytic 1,4-addition
desymmetrization
catalyst control
remote stereocontrol
organozinc reagents
phosphoramidite