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Enantiocontrolled Synthesis of a Chiral Building Block via Diastereoselective Ring-Closing Metathesis
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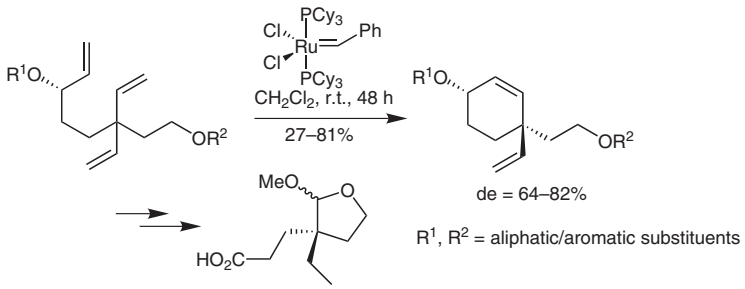
Diastereoselective Ring-Closing Metathesis to Build a Quaternary Carbon Center



Significance: Diastereoselective ring-closing metathesis (RCM) was used to create a quaternary stereogenic center induced by protected hydroxyl groups. The initial stereogenic center was conveniently installed by Sharpless asymmetric epoxidation. The chiral RCM product cyclohexene was converted into a key chiral precursor used for the total synthesis of indole-containing alkaloid (–)-eburnamonine.

Comments: Stereoselective quaternary carbon center formation is still a problematic step in many natural product syntheses. The authors explored a RCM strategy to give a cyclohexene system with functionalizable groups on the quaternary center. Fine-tuning the selectivity by varying the protecting group on the hydroxy moieties gave a de of 81% using Grubbs' 1st-generation catalyst when R^1 = TMS, R^2 = Bz. Unfortunately, the conversion seems to be low for the substrates which provide the highest de's.

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Key Words
ring-closing metathesis (RCM)
indole alkaloids
diastereoselective synthesis
asymmetric induction