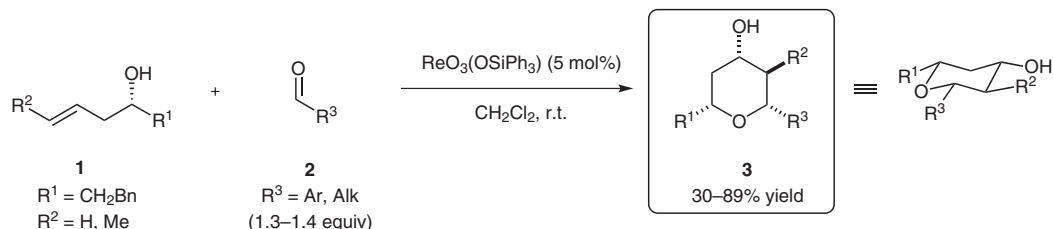
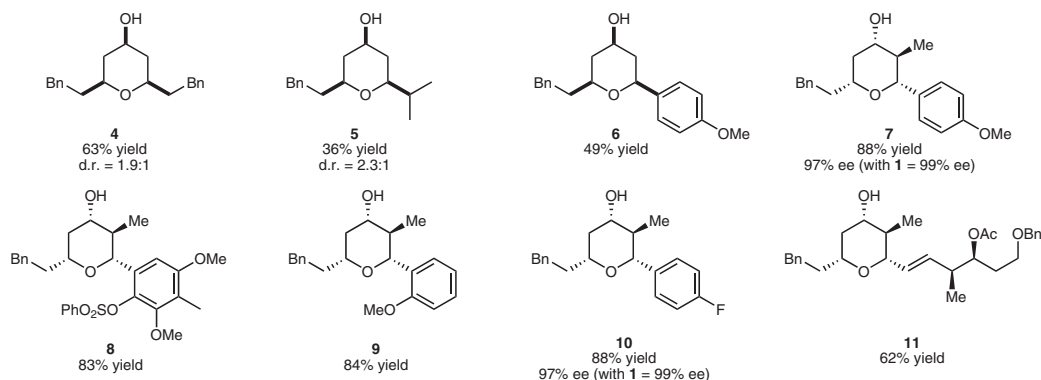


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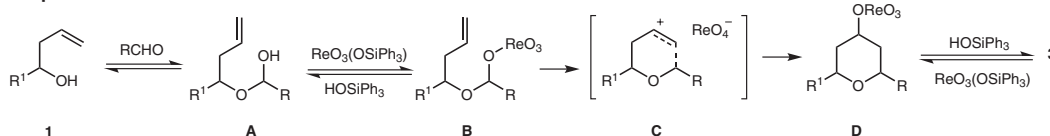
Rhenium(VII) Catalysis of Prins Cyclization Reactions

Org. Lett. **2008**, *10*, 4839-4842.Stereocontrolled Synthesis of Highly
Substituted Tetrahydropyrans

Selected examples:



Proposed mechanism:



Significance: A Re(VII) complex catalyzed the highly selective condensation of easily accessible starting materials using a very mild and simple protocol to give densely functionalized tetrahydropyrans **3** (THP). Aromatic aldehyde partners **2** give a single diastereomer where all substituents are equatorially oriented. Whereas aliphatic aldehydes give diastereomeric mixtures (**4** and **5**), alkenyl aldehydes provide an alternative, as illustrated by complex THP **11**. Achieving high atom-efficiency, the catalytic Prins cyclization reported improves previous protocols using excess acid (the conjugate base moiety is generally incorporated into the THP at the end of the reaction).

Comment: Both $\text{ReO}_3(\text{OH})$ and Re_2O_7 were shown to be effective catalysts to mediate the transformation. The authors were inspired by seminal work on allylic alcohol isomerization done by Osborn and co-workers (*Angew. Chem. Int. Ed.* **1997**, *36*, 976), as well as later investigations done by Grubbs and co-workers (*J. Am. Chem. Soc.* **2005**, *127*, 2842). These early studies invoked a cationic intermediate suggesting that intermediate **C** might be a viable species in the above process. A potential limitation of the reaction is seen with aliphatic aldehydes **2**, which are prone to form side-products arising from competing oxonia-Cope rearrangements under these conditions.

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