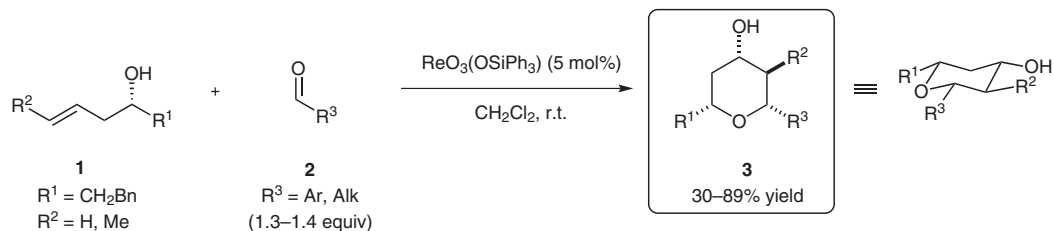
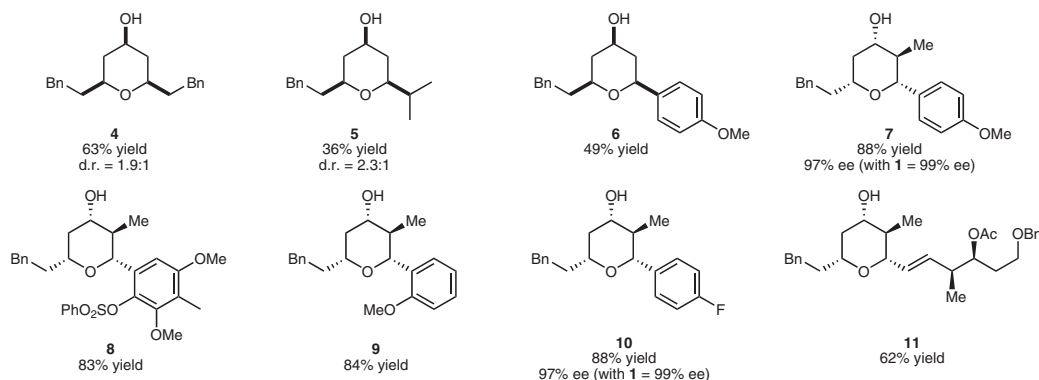


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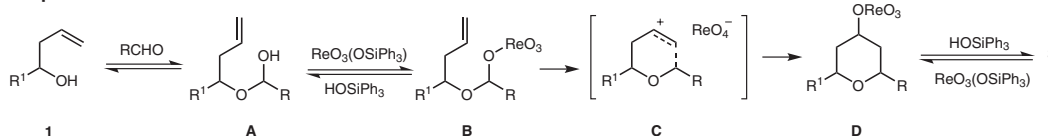
Rhenium(VII) Catalysis of Prins Cyclization Reactions

*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  $\text{Re}_2\text{O}_7$  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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