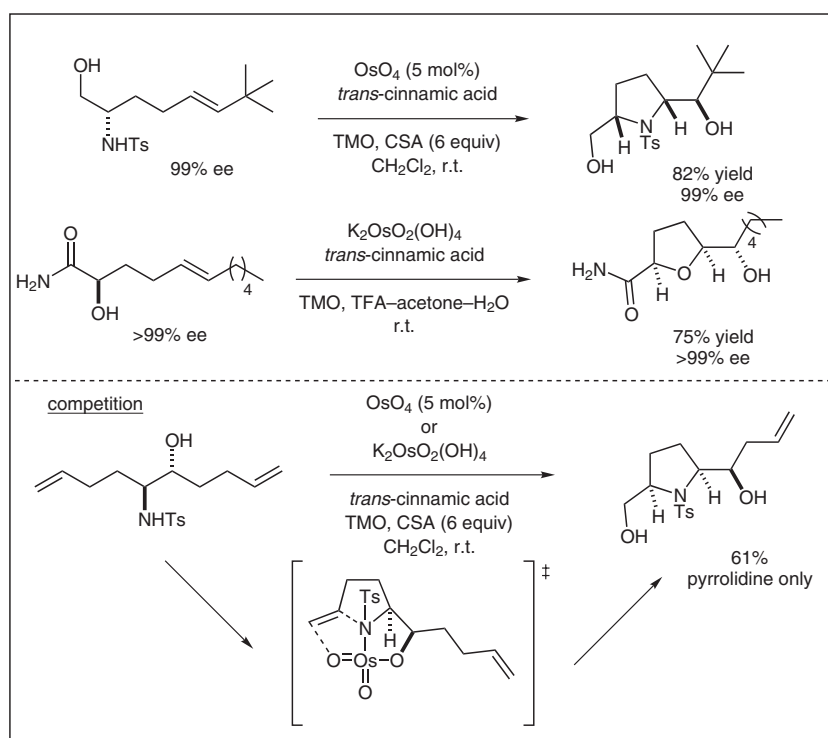


Catalytic Oxidative Cyclizations Mediated by Osmium



Significance: An osmium-catalyzed oxidative cyclization of hydroxy amines has been developed which generates pyrrolidines or THFs in high yield with high diastereoselectivity. Preferentially five-membered rings are formed (THFs if alcohol is appropriately located, pyrrolidine if amine is appropriately located), but the nitrogen heterocycle dominated in a competition experiment (see above). OsO_4 was found to be the best catalyst for pyrrolidine synthesis, while $\text{K}_2\text{OsO}_2(\text{OH})_4$ was the catalyst of choice for THF synthesis. A variety of substituted hydroxy amines are tolerated including those with bulky *t*-Bu groups appended directly to the alkene. A nice competition experiment was performed which showed only formation of the pyrrolidine with no sign of THF formation.

Comment: This is a very nice synthesis of pyrrolidines as well as an extension on the group's previous finding shown by the synthesis of THFs and showcased by the formal synthesis of (+)-*cis*-solumin (*Angew. Chem. Int. Ed.* **2005**, *44*, 4766–4768). This protocol allows for easy access to these five-membered heterocycles (THFs and pyrrolidines) that are tolerant to various functional groups and do not show competitive formation of six-membered rings. The authors also explain that the *trans*-cinnamic acid is a sacrificial alkene which is dihydroxylated by Os(VIII) generating Os(VI), which is a competent catalyst for the oxidative cyclization. The proposed transition state should be useful for a number of other applications.

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