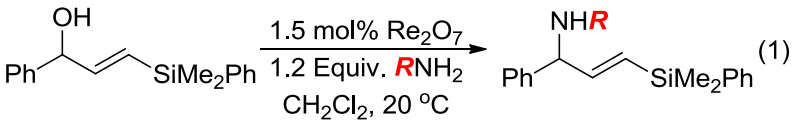
ACSAC Final Report

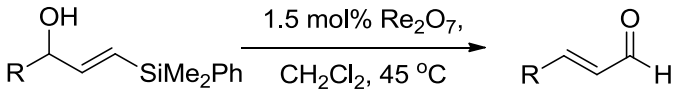
We have developed new and innovative chemistry throughout the project and although not all of the objectives of the original proposal have been accomplished to date many are at a stage whereby they will be soon.

The research developed within the ACSAC project has provided a new method for the selective synthesis of allylic amines which are very useful synthetic building blocks in organic synthesis. This was achieved through the development of a new rhenium catalysed reaction whereby allylic alcohols could be very rapidly converted into their corresponding amines. This reaction provided a wide range of synthetically useful compounds and a significant amount of mechanistic work was performed to elucidate the mechanism. The reaction appears to be catalysed by perrhenic acid [$Re_2O_7(H_2O)_2$] which forms an allylic cation which undergoes outer sphere attack by the amine nucleophile (Eq. 1).



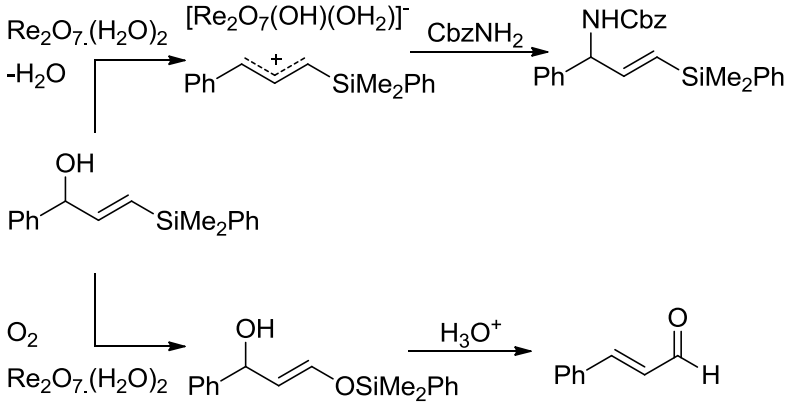
(1)

We also discovered the first example of a rhenium catalysed Flemming-Tamao oxidation which utilises aerobic oxygen as the terminal oxidant. The result of this reaction is the formation of a silyl enol ether bearing an adjacent alcohol which upon hydrolysis undergoes a dehydration reaction to provide cinnimaldehyde (Eq. 2).



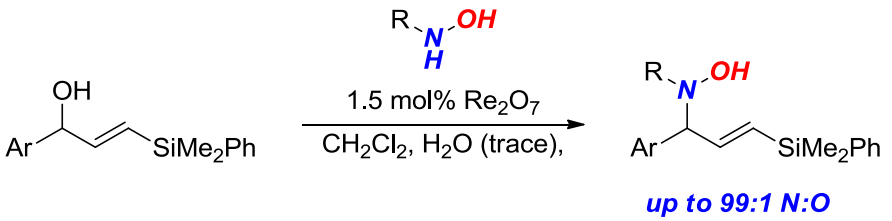
(2)

Through thorough mechanistic investigations the following pathways were elucidated.



Mor recently, this method has been applied to the reaction of hydroxylamine derivatives which can potentially react at either the *N* or the *O* terminus and others have observed mixtures of *N* and *O* isomers. Our system provides almost a single regioisomer (>98:2) and is very general when Cbz carbamate was used. Lower selectivities were observed with other carbamates although when electron rich aromatics are used much higher selectivities are obtained due to the reversible nature of the reaction. This is one of the only general methods

for selective N allylation of hydroxylamines and provides one of the four possible regioisomers in excellent yields. We expect this reaction to have many applications within the pharmaceutical and specialty chemical sectors.



(3)