CHAPTER IV

CONCLUSION

The work had focused on the Barbier-type allylation of aldimines with a combination of allyl bromide and indium powder in alcoholic solvents to give homoallylic amines. The results described herein indicated that the desired addition took place readily in commercial absolute alcoholic solvents without any attempts to exclude moisture and air. Furthermore, for the allylation employing substituted allyl bromide, the γ-allylation products were obtained exclusively and no α-products were observed. We also investigated a variety of chiral amines potentially useful as an auxiliary for asymmetric allylation of aldimines. Among all chiral amines tested, (*R*)-phenylglycinol was found to give the most impressive results whereby the desired allylation products are virtually obtained as a single diastereoisomer as shown by ^{1}H- and ^{13}C-NMR spectroscopy. Asymmetric allylation reaction employing a variety of chiral aldimines derived from (*R*)-phenylglycinol is applicable to a wide range of substrates to give the products in good yields and excellent diastereoselectivity including the aldimines derived from aliphatic aldehydes.

Removal of the phenylglycinol auxiliary was initially attempted by $Pb(OAc)_4$ oxidation followed by acid hydrolysis of the resulting imine. Unfortunately, this method gave low yield and caused extensive racemization. A mechanistic interpretation of racemization and by-product formation was proposed. An improved auxiliary cleavage mwthode was then developed whereby the imines were treated with hydroxylamine hydrochloride. The absolute configuration of the newly formed stereogenic center in the homoallylic amine was determined by comparison of the ^{1}H-NMR spectra of the diastereomeric amides resulted from coupling of the homoallyl amine with Boc-(*R*)-phenylglycine and Boc-(*S*)-phenylglycine respectively. According to this method, the absolute configuration of the homoallyl amines derived from (*R*)-phenylglycinol auxiliary was proved to be *R* while using (*S*)-phenylglycinol as chiral auxiliary gave the product with the opposite configuration. A transition state model explaining the diastereoselectivity observed has been proposed.