



**SYNTHESIS AND EFFECTIVENESS OF A NEW CYCLOHEXYL  
CHIRAL AUXILIARY  
AND  
STUDIES TOWARDS THE SYNTHESIS OF  
BICYCLO[4.4.4]TETRADECA-3,8,12-TRIENE.**

A Thesis Submitted in fulfilment of the requirements  
for the degree of Master of Science

by

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# DECLARATION

To the best of my knowledge, this thesis contains no material previously submitted for a degree or diploma and contains no material previously published or written by any other person except where due reference has been given.

I give consent to this thesis being made available for loan and copying.

Hamish Saul Christie.

28/2/99

# ABSTRACT

Attempts to optimise the synthesis of (1R,2S,5R)-5-*tert*-butyl-2-phenylcyclohexanol (**6**) were made. This molecule is considered a potentially useful chiral auxiliary, bearing a similarity to Whitesell's successful chiral auxiliary *trans*-2-phenylcyclohexanol. The alcohol is generated in two steps from 4-*tert*-butylphenylcyclohexene. The key step is an asymmetric dihydroxylation of the alkene to yield two enantiomerically pure diastereomeric diols **7** and **9**.

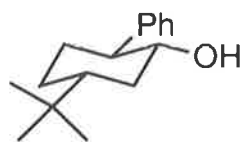
Previously diol **7** has been hydrogenolysed, in modest yield, to alcohol **6**. Methods were investigated to improve the yield of deoxygenation of diol **7** and also to make use of the diastereomeric diol **9** to produce the enantiomer of alcohol **6**. The effectiveness of alcohol **6** as a chiral auxiliary was examined utilizing a known asymmetric alpha amino acid synthesis and comparing the results with those achieved with (-)-8-phenylmenthol as chiral auxiliary. The new chiral auxiliary **6** was found to induce diastereoselectivity, however, not to the degree that is attained with 8-phenylmenthol.

In an attempt to demonstrate an effective kinetic resolution using Sharpless' asymmetric dihydroxylation reaction (3(RS),6(RS))-3-*tert*-butyl-1,6-diphenylcyclohex-1-ene (**44**) was synthesised as a potentially useful alkene candidate for effective resolution. This alkene was found to be unreactive under Sharpless' dihydroxylation conditions.

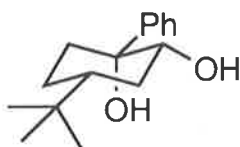
As a potential precursor to the as yet unknown (out,out)-bicyclo[4.4.4]tetradecane, and a curious molecule in its own right, the highly symmetrical molecule bicyclo[4.4.4]tetradeca-3,8,12-triyne (**59**) was considered as a synthetic target.

Progress towards the synthesis of this molecule was made via tetramethyl-3,8-cyclodecadiyne-1,1,6,6-tetracarboxylate (**75a**).

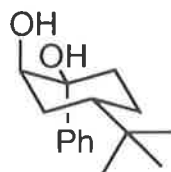
Diyne **75a** has been previously synthesised, however, it was found that it can be produced in two steps from simple starting materials, six fewer steps than previously reported. This tetraester was converted into a diester and attempts were made to alkylate it. The triyne **59** remains unknown, however, further pursuit of the strategies considered may yield the desired result. The explosive properties of some of the lower molecular weight alkyne precursors was noted.



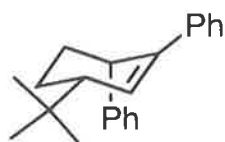
**6**



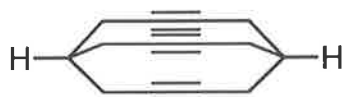
**(-)7**



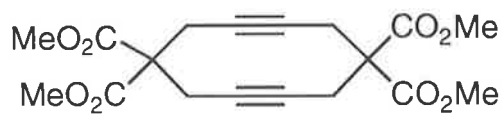
**(-)9**



**44**



**59**



**75a**