

**A SEARCH FOR SHORTER, MORE CONVERGENT
ROUTES TO ENANTIOPURE NAPHTHOPYRANS
RELATED TO THE APHID INSECT PIGMENTS**

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BY

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I declare that this thesis is my own account of my research and contains, as its main content, work that has not been submitted for a degree at any tertiary institution.

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Abstract

The naphtho[2,3-*c*]pyran ring system is generally found amongst natural products as the 5,10- or 6,9-quinones. These compounds display a wide range of biological activities, and as such, have been synthesised by various research groups. The synthetic work described in this thesis is directed towards finding shorter, more convergent routes to enantiopure quinone A **10**, quinone A' **11** and quinone-*pm* **13**, three derivatives of the aphid insect pigments protoaphin-*fb* **6**, protoaphin-*sl* **7** and protoaphin-*pm* **9**, respectively.

The first chapter describes the previous syntheses of some naphtho[2,3-*c*]pyrans including those relating to the aphid insect pigment derivatives. Also detailed is the ability of these naphthopyranquinones to act as potential bioreductive alkylating and dialkylating agents. The latter part of the chapter records some of the previously achieved assemblies of quinones A **10** and A' **11** in both racemic and enantiopure form, as well as the only synthesis of enantiopure quinone-*pm* **13**.

Chapter 2 involves the preparation of regioselectively halogenated aryldioxolanes starting with the allylation of brominated and chlorinated phenols. The isomerisation of these dioxolanes into the corresponding halogenated 2-benzopyrans is then investigated.

Chapter 3 examines the regioselectivity of the Diels-Alder reaction between protected benzopyranquinones and the substituted diene 1-methoxy-1,3-bis(trimethylsilyloxy)-buta-1,3-diene **80**. Such protection involves preparing the acetates and methoxymethyl ethers of

the benzopyranquinones. The latter part of the chapter describes the direct bromination of benzopyranquinones.

Chapter 4 reports on the stereoselective reaction between metal phenolates and the chiral aldehyde **108** to subsequently afford naphthyldioxolanes **264**, **291**, **292** and **295**. The rearrangement reaction of the derived naphthyldioxolane **295** is then investigated.

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Abbreviations

Ac	acetyl
dba	(<i>E,E</i>)-dibenzylidene acetone
(DHQ) ₂ -PHAL	Bis(dihydroquinino)phthalazine
(DHQD) ₂ -PHAL	Bis(dihydroquinidino)phthalazine
DMSO	dimethyl sulfoxide
Et	ethyl
EtOAc	ethyl acetate
Ether	diethyl ether
Glc	glucoside
<i>i</i> -Pr	isopropyl
IR	infrared
mp	melting point
Me	methyl
NMR	nuclear magnetic resonance
TMS	tetramethylsilane
TLC	thin layer chromatography
Ts	toluenesulfonyl