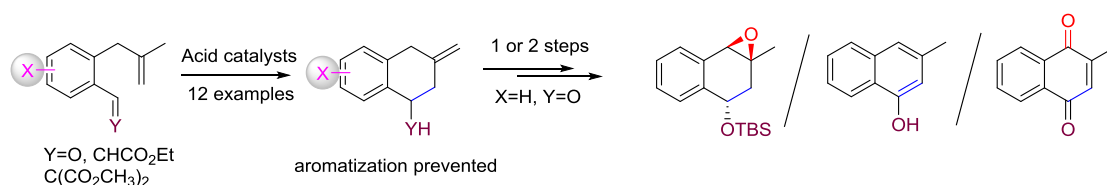
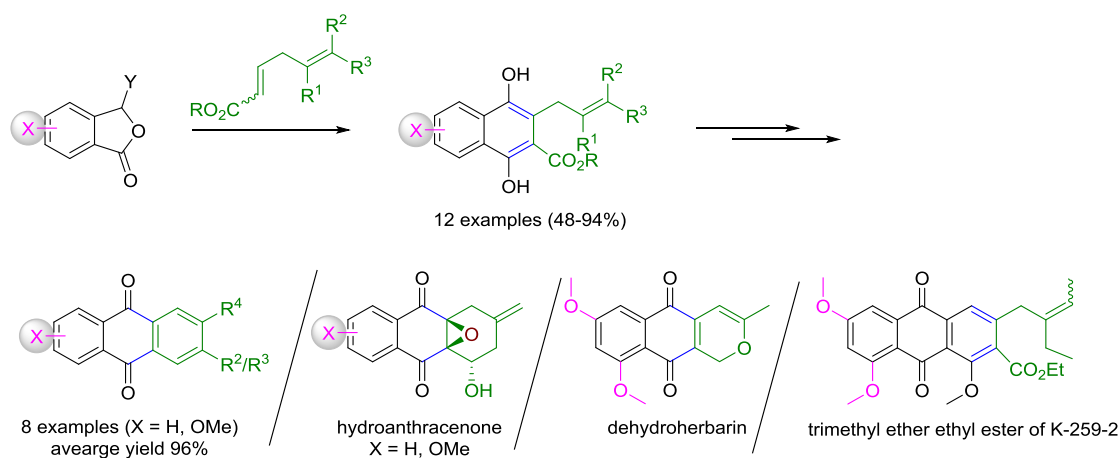


## Abstract

This thesis has dealt with combined application of [4 + 2] anionic annulation and carbonyl-ene reaction for the synthesis of tetralins and hydroanthracenones. 2-Methallyl aromatic aldehydes, synthesized by Suzuki coupling of 2-formylaryl boronic acids, are shown to provide cycloalkylidene products under acidic conditions. The problem of susceptibility of the products to aromatization is circumvented by varying the reaction conditions and catalysts including binol-derived Brønsted acid catalysts. A *peri*-effect is identified as one of the controlling factors for the aromatization. Several oxidative transformations of an ene product are carried out as model studies of hydroaromatic polyketide natural products.



For the extension of the above chemistry to anthracenones, the annulation chemistry of skipped dienoates have been studied. 2,5-Hexadienoates, sensitive to isomerization by acids and bases, are shown to be suitable for the [4 + 2] anionic annulation to give 3-methallylnaphthoates in regiospecific manner. The accessibility of the naphthoates culminated in a new synthesis of anthraquinones, hydroanthracenones based on intramolecular carbonyl-ene reaction. A similar annulation of a skipped dienoate has led to the short synthesis of dehydroherbarin and first synthesis of a trimethyl ether ethyl ester of K-259-2.



*Key Words:* Boronic acid, Ene reaction, Aromatization, *peri*-Effect, Annulation, Dienoate, Isomerisation, 3-Methallylnaphthoates, Anthraquinone, Hydroanthracenones, Total synthesis.