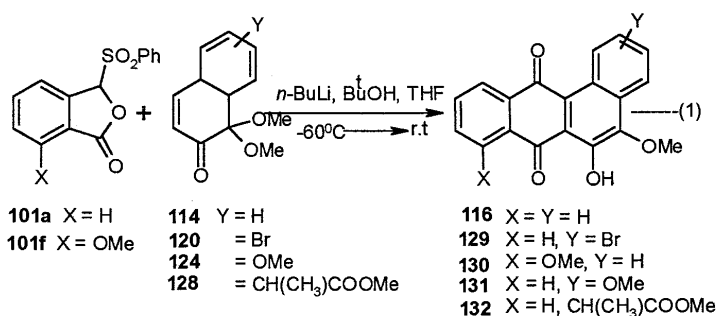


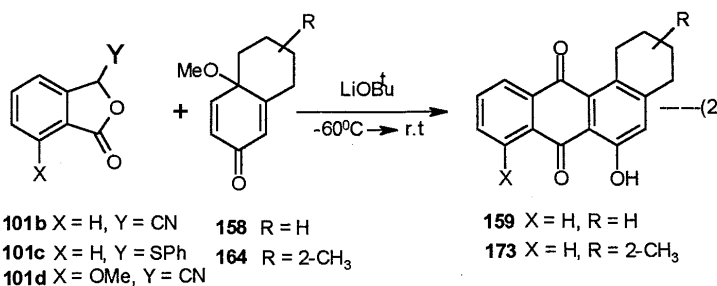
Abstract

The thesis describes the model synthetic studies of hydroxybenz[*a*]anthraquinones, chrymutin and total synthesis of brasiliquinone B (**110**), brasiliquinone C (**109**) and 3-deoxyrabelomycin (**219b**).

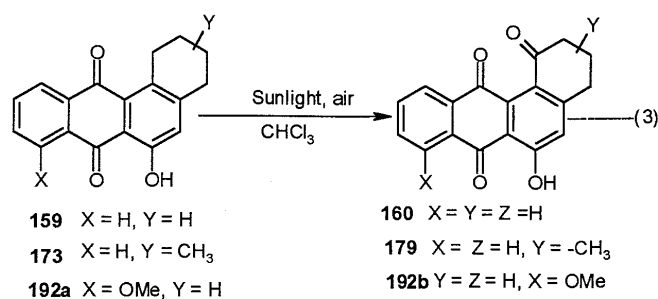
Naphthalenones (**114**, **120**, **124** and **128**) have been prepared by phenyliodonium diacetate (PIDA) assisted dearomatization of the corresponding β -naphthols, and shown to undergo anionic [4+2] annulation with **101** in the presence of LiOBu^t to give benz[*a*]anthraquinones, **116**, **129**, **130**, **131**, and **132** in high yields.



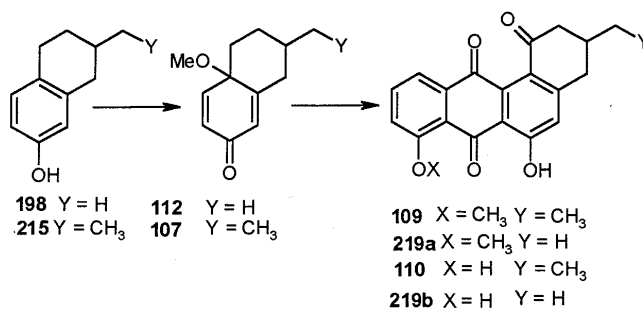
The annulation has also been extended to the synthesis of 1,2,3,4-tetrahydrobenz[*a*]anthraquinones (eq. 2). Naphthalenones (e.g. **158**, **164**) containing an angular methoxy group undergo annulation with 3-cyanophthalide (**101b**) or 3-(phenylthio)phthalide (**101c**) to give tetrahydrobenz[*a*]anthraquinones (**159**, **173**). The annulation of the naphthalenones, however, fails with phthalide sulfone (**101a**).



The general utility of Krohn's photooxidation has been explored. Sunlight mediated oxidation of 1,2,3,4-tetrahydrobenz[*a*]anthraquinones, (**159**, **173** & **192a**) resulted in regiospecific introduction of 1-keto function, giving **160**, **179** & **192b**.

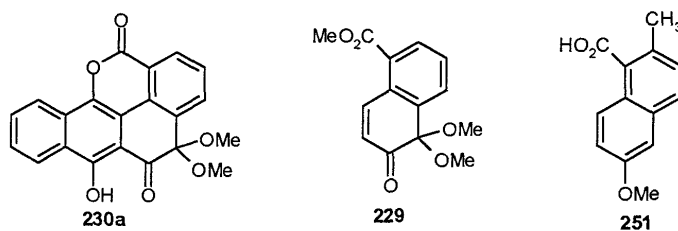


The total synthesis of brasiliquinone B (**110**) & C (**109**) and deoxyrabelomycin (**219b**) has been achieved by the combined use of phthalide annulation and



photochemical oxidation. Methoxynaphthalenone **107**, prepared in few steps from 7-methoxytetralone undergoes annulation with cyanophthalide **101d** yielding 1,2,3,4-tetrahydro-3-ethylbenz[*a*]anthraquinone in 93% yield, which on photochemical oxidation provided brasiliquinone C (**109**). AlCl₃-assisted demethylation of brasiliquinone C (**109**) furnished brasiliquinone B (**110**). Similar strategy has also been exercised to accomplish a synthesis of deoxyrabelomycin **219b**.

Annulation of **101b** with **229** in the presence of LiOBu^t has been shown to undergo an unprecedented Michael-domino reaction to produce chrymutin carbon scaffold **230a** in one pot operation.



An important subsidiary achievement in the synthetic study is the development of a regiospecific synthesis of α -tetralones. Cyclocondensation of homophthalates with acrylates in the presence of bases (e.g. NaOMe) produces 2-carboxy- α -tetralones, selective dealkoxycarbonylation of which results in the synthesis of α -tetralones. This synthesis of α -tetralones has been utilized to prepare **251**, a key intermediate required for the synthesis of chrymutin **224**.