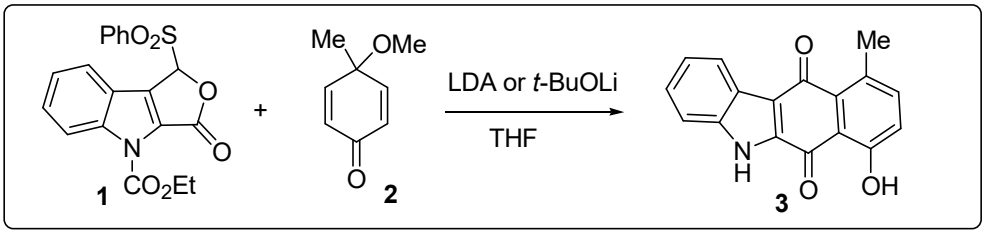
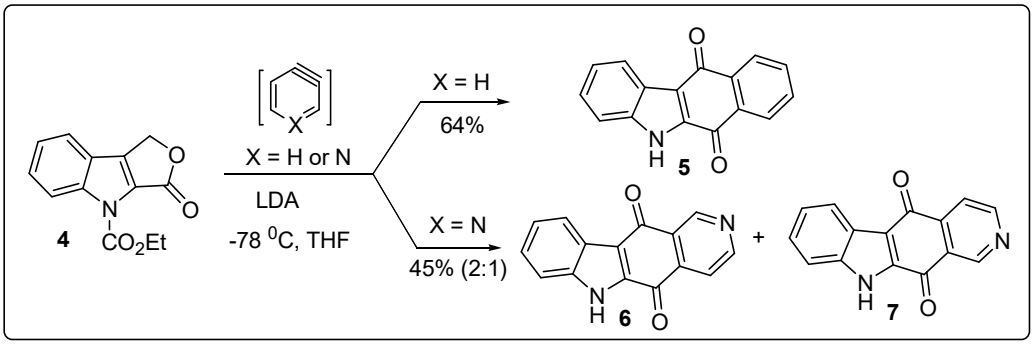
Abstract

This thesis entitled "**Anionic [4+2] Cycloaddition in the Synthesis of Carbazoles and Synthetic Studies towards Furanosteroids"** describes the synthetic studies of **carbazole-1,4-quinones**, **1-oxygenated carbazoles**, **densely substituted carbazoles**, **furonaphthoquinones** skeletons and related naturally occurring alkaloids **ellipticine** and **murrayafoline A** based upon the exploration of anionic [4+2] cycloaddition reaction.

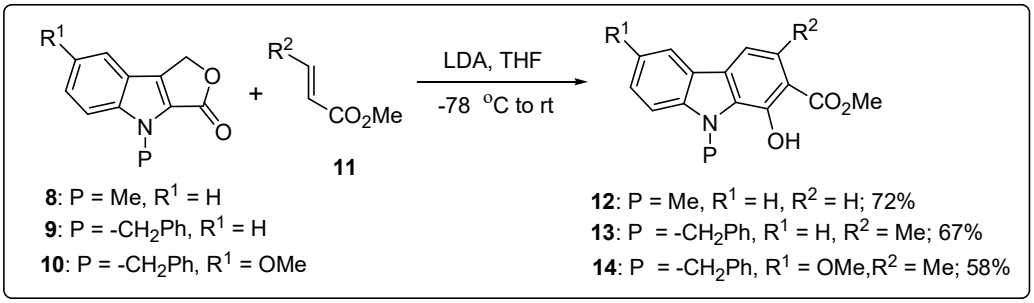
In part A, the Hauser annulation, alternatively known as [4+2] cycloaddition of 1-phenylsulfonyl *N*-ethoxycarbonyl protected furoindolone **1** with quinol ether **2** in the presence of LDA or *t*-BuOLi has been described as a tool for synthesizing carbazole-1,4-quinone **3** (more than 8 examples).



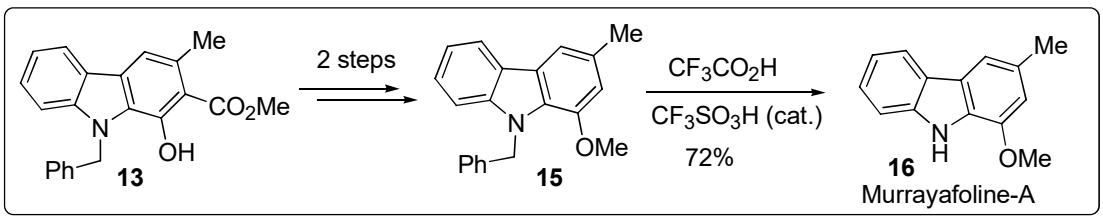
The anionic [4+2] cycloaddition between C-1 unsubstituted furoindolone **4** and bromobenzene in the presence of LDA allowed one-pot regiospecific construction of 5*H*-benzo[*b*]carbazole-6,11-dione **5**, present in various natural products. Similar cycloaddition between furoindolone **4** and 3-bromopyridine afforded an inseparable mixture (2:1) of ellipticine quinone **6** and isoellipticine quinone **7**, constituting the formal syntheses of ellipticine and isoellipticine alkaloids respectively.



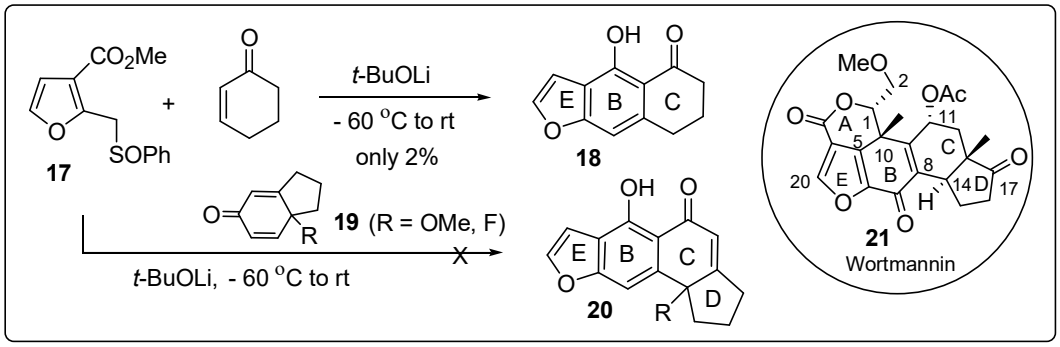
The LDA promoted anionic [4+2] cycloaddition of *N*-methyl and *N*-benzyl protected furoindolones (**8**, **9** & **10**) with simple Michael acceptors (e.g. **11**) is developed to be as a regiospecific and efficient route for synthesizing 1-oxygentaed carbazoles (**12**-**14**). It has been exemplified with 10 examples.



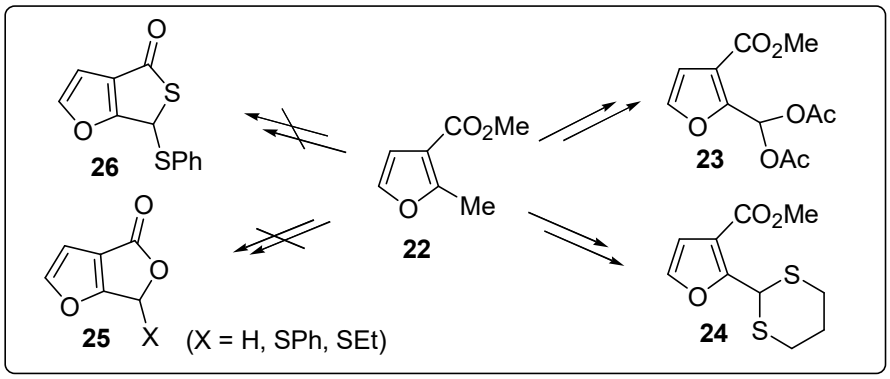
The choice of *N*-protection in **8**, **9** and **10** was crucial for the success of the annulation. Similar attempts for the annulations with **1** and **4** were not successful. *N*-Benzyl protected carbazole **13**, obtained from the above study was utilized for a short synthesis of naturally occurring carbazole alkaloid murrayafoline A (**16**) as shown below.



In part B, the study directed towards the synthesis of core structure (EBC ring system) of furanosteroids (e.g. wortmannin **21**) has been described. The model study based on annulation between sulfoxide derivative **17** and 2-cyclohexenone produced tricyclic EBC moiety **18** of furanosteroids only in 2% yield. Other attempts such as the annulation between **17** with quinol ethers **19** were without success.



Commercially available methyl 2-methyl-furan-3-carboxylate **22** has been functionalized to give **23** and **24** in good yields. Unfortunately, the attempted cycloaddition between the d^4 furan annulating agents (**23** and **24**) and 2-cyclohexenone failed to give expected tricyclic EBC ring system of furanosteroids.



Attempts at transforming **22** to furofuranones **25** and furothiofuranone **26** have been described.