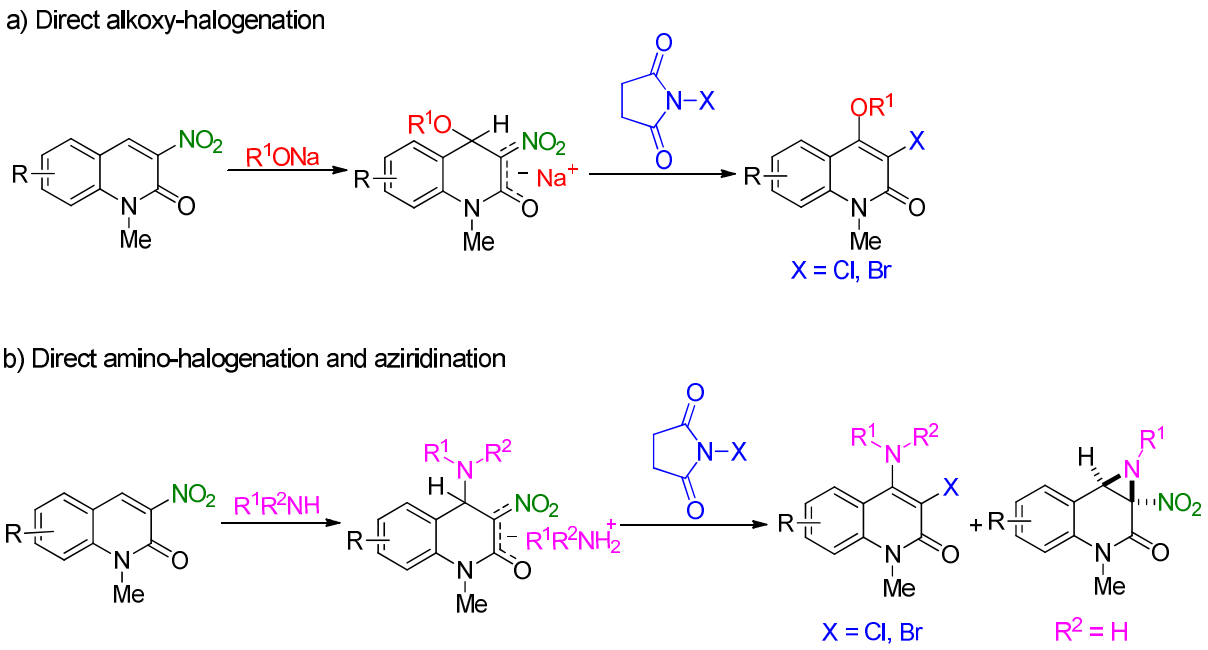
論 文 内 容 の 要 旨

Natural as well as unnatural 1-methyl-2-quinolones (**MeQone**s) are heterocyclic compounds with a wide range of pharmacologically important activities. In addition, they also serve as important building blocks and intermediates in organic synthesis. Therefore, a number of methods have been studied in great detail for the preparation of **MeQone**s. However, among these methods, only a few methods for direct functionalization of the **MeQone** framework are currently available because of the inertness caused by the aromaticity. Accordingly, development of a facile method for direct modification of the **MeQone** framework is one of the highly demanded projects.

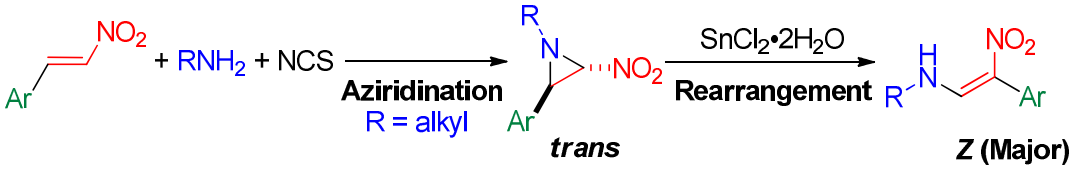
A nitro group is one of the most important functional groups in organic syntheses because of its strongly electron-withdrawing ability to activate the scaffold, facilitating the reaction with nucleophilic reagents. Moreover, a nitro group serves not only as a precursor of versatile functionalities but also as a good leaving group. Inspired by these properties of the nitro group, I successfully achieved the direct 4-alkoxylation and 3-halogenation of the **MeQone** framework by a sequential treatment of 3-nitrated **MeQone**s with sodium alkoxides and *N*-halosuccinimide under mild conditions (Scheme 1, a). In addition, direct amino-halogenation and aziridination of the **MeQone** framework was also developed by replacing sodium alkoxides with amines as nucleophiles (Scheme 1, b).



Scheme 1. Direct functionalization of the **MeQone** framework

C-Nitroaziridines serve as useful building blocks in organic synthesis because of the high reactivity caused by strongly electron-withdrawing nitro group and ring strain. Although direct aziridination of nitroalkenes is the most efficient approach to *C*-nitroaziridines, there is no report with regard to preparing *N*-alkyl derivatives.

I demonstrate here an efficient and highly diastereoselective one-pot synthesis of *trans*-*N*-alkyl-*C*-nitroaziridines upon treatment of nitroalkenes with aliphatic amines and *N*-chlorosuccinimide. The resultant aziridines are found to isomerize into (*Z*)-β-aryl-β-nitroenamines with high diastereoselectivity through Lewis acid-mediated ring opening and rearrangement of the aryl group (Scheme 2).



Scheme 2. Direct aziridination of nitroalkenes and the subsequent isomerization

Overall, several facile and efficients methods for direct functionalization of the **MeQone** framework and nitroalkenes were successfully developed. The tolerance of a wide range of functional groups and operational simplicity are the notable advantages of these protocol. The resultant products can be easily transformed into other useful building blocks. Therefore, these methods will be surely useful as powerful tools for preparation of novel compounds with structural diversity and complexity. The results of these investigations are disclosed in this thesis.