

Abstract of Main Thesis

Studies on Controlled Coupling Cyclization of Unsymmetric Quinones

ふ いんしゅん
HU YINJUN

The mono-protected quinones, quinone monoacetals (QMAs), which can be easily prepared *via* oxidations from phenols developed in our laboratory, have attracted considerable interest due to their broad utilities in organic synthesis. Recently, rising interest in the development of utilization of QMAs has been fuelled, owing to their uniqueness of the privileged bifunctionalities possessing enone and allylactal moieties in only one skeleton. The varied reactivities in nucleophilic attacks on QMAs can be operative by all the electrophilic ring carbons, for instance, conjugated addition to an enone moiety and addition to a carbonyl carbon. Being different from these established *addition chemistry* under basic conditions, the utility of QMAs in *substitution chemistry* under acidic conditions is quite limited.

This thesis principally deals with the progress of the emerging theme for the latter, in which the general successes are listed below.

1) First, an efficient Brønsted acid-controlled strategy for the [3+2] coupling of QMAs with π -nucleophilic alkenes has been successfully developed. This novel and expeditious [3+2] coupling, triggered by the particular use of the catalytic system of a specific acid promoter, perfluorinated acid, and a hydrogen bond donor solvent, fluoroalcohol, could smoothly proceed to provide diverse dihydrobenzofurans and other derivatives in high yields.

2) Further investigations in this strategy with regard to the acid modifications have led to the development of the fluorophthalic acid catalyst with minimal loading (5 mol%). In addition, a unique solid acid catalyst (PS-PFBA) including immobilized perfluorobenzoic acid (PFBA) sites in the polystyrene (PS) backbones has also been successfully prepared for this coupling reaction as a recyclable alternative for green chemistry.

3) Finally, several applications, such as the synthesis of naturally occurring modules and preparation of regio-controlled benzofuran oligomers by utilizing this strategy, were presented for proving the usability of this work in the future development of organic chemistry.