CHAPTER-6

SUMMARY AND CONCLUSIONS

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The thesis entitled "**Applications of Boronic acids as a Reagent and Starting Material in Organic Synthesis**" described a various applications of aryl, alkyl and vinylboronic acids in synthetic organic chemistry. The content of the thesis has been divided into six chapters including this summary and conclusions.

Chapter-1 provided a general introduction about different boronic acids, their synthesis and applications in different organic transformations as starting material, reagent, catalyst, template, etc. Also the biological applications of various boronic acids have been discussed briefly in this chapter (Figure **6.1**).

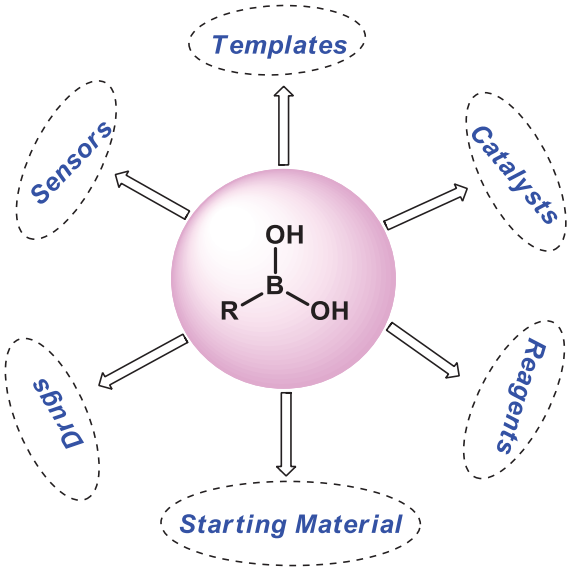
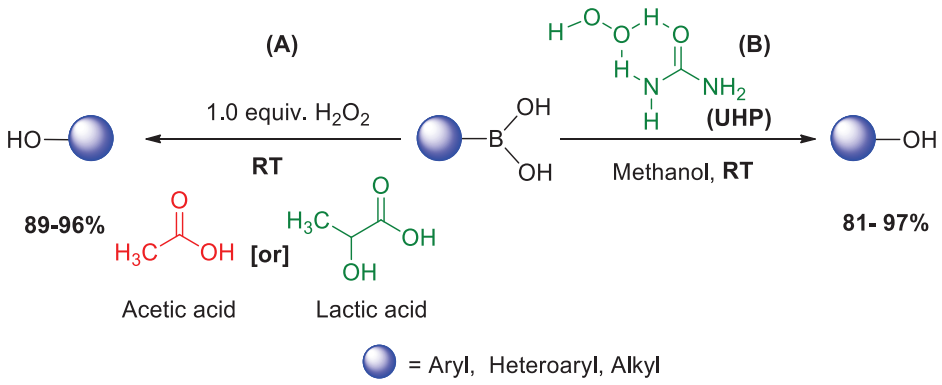


Figure 6.1 Overview of chapter-**1**.

Chapter-2 described the "Oxidative *ipso*-hydroxylation of arylboronic acids with green oxidant hydrogen peroxide under catalyst-free condition". Oxidation of arylboronic acids into corresponding phenols was achieved using 35% aqueous hydrogen peroxide in biomass derived solvents such as lactic acid and acetic acid in the absence of catalysts. The reaction was preceded at room temperature and provided the desire products in 89-96% yields within short reaction time. Similar to arylboronic acids, alkylboronic acids also underwent *ipso*-hydroxylation smoothly under the optimized reaction conditions.

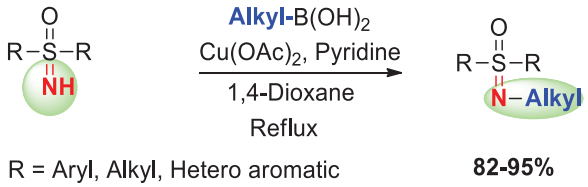


Scheme 6.1. Snapshot of chapter-**2**.

Despite having many advantages, this method also suffered from some disadvantages. For instance, use of acidic medium and functional groups incompatibility are the major problems associated with this protocol **(A)**. Therefore, an alternative protocol has been developed for the chemoselective *ipso*-hydroxylation of arylboronic acids using solid adduct urea-hydrogen peroxide (UHP) (**Scheme 6.1**). The *ipso*-hydroxylation underwent smoothly with urea-hydrogen peroxide at room temperature in common solvents like methanol and acetonitrile **(B)**. During the *ipso*-hydroxylation of boronic acids with

UHP, excellent chemoselectivity was observed where oxidation sensitive functional groups such as olefin, aldehyde, alcohol, ketone, and sulfide as well as heterocycles such as pyridine and thiophene were well tolerated during the *ipso*-hydroxylation with UHP.

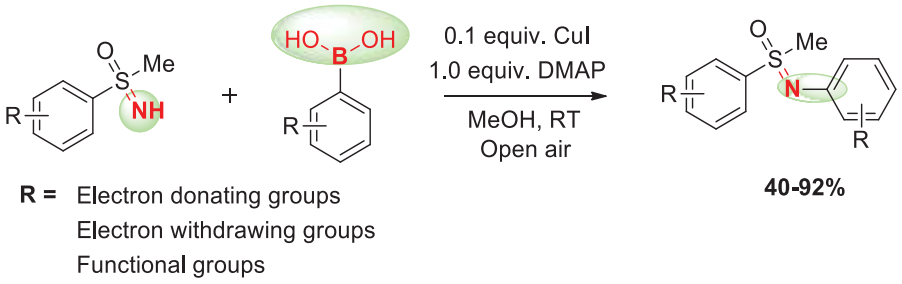
Chapter-3 explicated the "*N*-alkylation of sulfoximines with alkylboronic acids promoted by copper salts". *N*-methylation of various sulfoximines was demonstrated using methylboronic acid as alkylating agent in the presence of copper (II) acetate and pyridine. The reaction was carried out in 1,4-dioxane under reflux condition which provided *N*-methylsulfoximines in 82-95% yields. Similarly, *N*-ethylation, propylation, phenethylation, cyclopropylation and cyclohexylation of different sulfoximines were demonstrated under optimized reaction condition using corresponding alkylboronic acids. Moreover, the optimized condition was also well suited for the *N*-methylation and cyclopropylation of bioactive L-methionine sulfoximine and provided desire product in high yields (**Scheme 6.2**).



Scheme 6.2. Pictorial representation of chapter-**3**.

Chapter-4 highlighted the "Copper catalyzed *N*-arylation of sulfoximine with arylboronic acids". Sulfoximines underwent *N*-arylation with different arylboronic acids in the presence of catalytic amount of copper (I) iodide (0.1 equiv.) and 4-DMAP (1 equiv.).

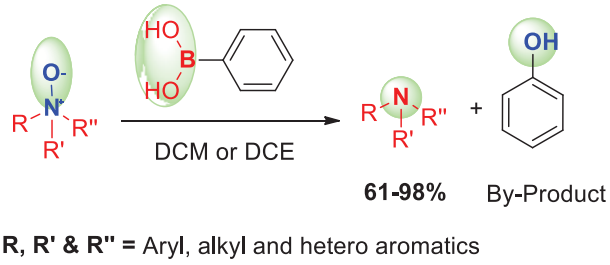
Notably, *N*-arylation of sulfoximines with sterically hindered arylboronic acid (e.g. 2,4,6-trimethylphenylboronic acid and 2,6-dimethylphenylboronic acid etc.) was successfully demonstrated under optimized reaction conditions with good yields. All the reactions took place at room temperature and provided good to excellent yields of the *N*-arylsulfoximines. For the first time, *N*-arylation of biologically relevant L-methionine sulfoximine with different arylboronic acids was demonstrated. Surprisingly, the optimized reaction condition was well suited to the task for *N*-vinylation of sulfoximine with *trans*-2-phenylvinylboronic acid.



Scheme 6.3. Quick look of chapter-**4**.

Chapter-5 presented "Phenylboronic acid mediated deoxygenation of *tertiary* amine *N*-oxides". Deoxygenation of various amine *N*-oxides was demonstrated using a green and economical reagent phenylboronic acid. The *N*,*N*-dialkylaniline *N*-oxides, trialkylamine *N*-oxides and pyridine *N*-oxides underwent for deoxygenation smoothly to provide the desired amines in good to excellent yields. The reaction was provided phenol and boric acid as byproduct which are environmentally benign. Various reduction susceptible functional groups such as ketone, amide, ester, nitro and aryl halides were well

tolerated under the optimized reaction condition. An indirect method for identification and quantification of *tertiary* amine *N*-oxide using UV-Vis spectrometry was also demonstrated by using 4-nitrophenylboronic acid as a deoxygenating reagent.



Scheme 6.4. Graphical illustration of chapter-**5**.

In conclusion, boronic acids have been successfully utilized in various organic transformations as starting materials and reagents. Arylboronic acids underwent *ipso*-hydroxylation to provide various phenols in excellent yields in the presence of hydrogen peroxide derivatives. Alkylboronic acids have been used as *N*-alkylating agents for the sulfoximines in the presence of stoichiometric amount of copper (II) acetate and pyridine. On the other hand, *N*-arylation of sulfoximine was achieved with different arylboronic acids with catalytic amount of copper iodide (0.1 equiv.) and stoichiometric amount of 4-DMAP (1 equiv.). Phenylboronic acid mediated deoxygenation of *tertiary* amine *N*-oxides was also successfully accomplished under mild reaction conditions. All the demonstrated protocols in this thesis are superior to most of the existing protocols in terms of reaction conditions and yields. Hence, we believe the developed methodologies will find wide applications in synthetic organic chemistry.