ABSTRACT

Enantioselective Synthesis of Bicyclic *cis*-Dihydroarenediols and Related Biomolecules

Over the past several years synthetic organic chemistry has witnessed tremendous use of *cis*-dihydroarenediols as chiral pool molecules. These species are mainly available via enzymatic transformation. However, this methodology has many drawbacks especially from the standpoint of regioselectivity and isolable yields. Thus, development of a chemical method for ready access to these compounds was desirable. The thesis entitled "**Enantioselective Synthesis of Bicyclic *cis*-Dihydroarenediols and Related Biomolecules**" is an embodiment of our efforts in this direction and consists of two chapters. Chapter 1 is further subdivided in two parts (1A and 1B).

Chapter 1A presents a brief overview on oxidative metabolites of aromatic hydrocarbons with an emphasis on bicyclic *cis*-dihydroarenediol metabolites. It highlights several enzymes which produce these small optically pure molecules and their utility in synthetic organic chemistry.

Chapter 1B describes an enantioselective strategy for the synthesis of bicyclic *cis*-dihydroarenediols involving Barrett's asymmetric hydroxyallylation and ring-closing metathesis (RCM) reaction as key steps. This methodology was also extended to synthesise bicyclic conduritol analogues. Furthermore, it was envisioned that bicyclic *cis*-dihydroarenediols as such or in their protected form could be ideal precursors for several naturally occurring bioactive *cis*-keto-diol motif containing natural products. Indeed this was realized in the context of the synthesis of an *ent*-scytalone derivative wherein heteroatom-directed Wacker oxidation was the pivotal step.

Chapter 2 illustrates further extension and utilization of our novel strategy for the synthesis of *ent*-scytalone derivative as described in the previous chapter. In this regard two natural products, e.g. (−)-chrysanthone A and (−)-heliophenanthrone were selected each of which features a methyl ether containing keto-diol motif in their structural outlay. In addition to the successful model study for (−)-chrysanthone A, this chapter describes the first enantioselective six-step synthesis of (−)-heliophenanthrone without employing any protection-deprotection protocol at an overall yield of 28%.

***Keywords*:** *cis*-dihydroarenediol, hydroxyallylation, Wacker oxidation, ring closing metathesis (RCM), scytalone, (−)-heliophenanthrone.