# Abstract

During the last decade benzotriazole-mediated synthetic methodology has developed rapidly and has now become an important synthetic tool for many chemical processes, including multistep preparations of drugs, biologically active compounds, and synthetic analogs of natural products. Benzotriazole has assisted the synthesis of a wide range of useful organic compounds due to the unique properties of the benzotriazolyl group as both a good anion-stabilizing group and a good leaving group. This approach involves the steps of the preparation of benzotriazole stabilized intermediates, their transformations and final displacement of stabilizing group from synthesized derivatives. The principal steps in such sequences are generally the first and the last ones and a variety of benzotriazole assisted transformations is sometimes limited by the availability of the benzotriazole derivatives and by the ability of the final intermediate to eliminate benzotriazolyl moiety. Novel synthetic methods and approaches in benzotriazole chemistry could achieve the desired diversification of chemical objects and methods.

The main goal of this dissertation was the elaboration of new synthetic approaches to *N*-substituted benzotriazoles and their further applications as synthons in heterocyclic and organic chemistry.

**Chapter 1:** gives a brief overview of benzotriazole chemistry, including common methods to obtain the *N*-substituted benzotriazoles and the common types of their transformations.

**Chapter 2:** This chapter highlights the study of the nucleophilic substitution of α-(chloroalkyl)benzotriazoles with C-nucleophiles. Such new transformations opened a direct and general synthetic route for the synthesis of benzotriazoloalkyl(hetero)aromatic

compounds **2.9a-k, 2.12a,b** and **2.13**. Our synthetic route allowed the synthesis of previously known compounds **2.9a,b,e** in superior yields. This methodology required mild reaction conditions that led to novel compound **2.9g-k** derived from aldehydes other than formaldehyde and benzotriazolylalkylheteroaromatic systems **2.12a,b** and **2.13** derived from acid sensitive heterocycles.

**Chapter 3**: highlights our study of the new transformations of (*N,N*-dialkylaminoalkyl)-benzotriazoles **3.1** as a generalized iminium ion equivalent. This new displacement of the Bt-moiety with phenolate anions opened a synthetic route to previously unknown or hard to synthesize Mannich-type products and, thus allowed extension of the Mannich aminomethylation of phenols to heteroalkylation and benzylation.

**Chapter 4**: in this chapter we have introduced a novel alternative synthetic route for the synthesis of α-benzotriazolyl-substituted ketones **4.4** *via* oxidation of silyl enol ethers.**4.2**. Such a synthetic approach has been based on the oxidizing property of 1-chlorobenzotriazole **4.3**. This methodology allowed the preparation of a variety of aromatic, aliphatic and alicyclic ketones **4.4** bearing a benzotriazole moiety at the α-carbon. With a view to extending the synthetic applications of benzotriazole derivatives, we have examined the leaving ability of benzotriazolyl group in α-benzotriazolyl-aromatic and alicyclic ketones. We found that they could be used as two-carbon components in a [3+2+1] pyridine ring annulation in the reaction with chalcones in the presence of ammonium acetate as a nitrogen component to attain 2,4,6-triarylpyridines **4.9a-i,** 2,4-diarylindeno[1,2-b]pyridines **4.9j,k** and 2,4-diaryl-5,6-dihydro-benzo[h]quinolines **4.9l-n**. Our methodology proved to be advantageous alternative route because this synthetic route

provides superior yields and applicable not only with phenacetyl derivatives but also with α-substituted ketones in general.

**Chapter 5**: provides full experimental details for our studies.