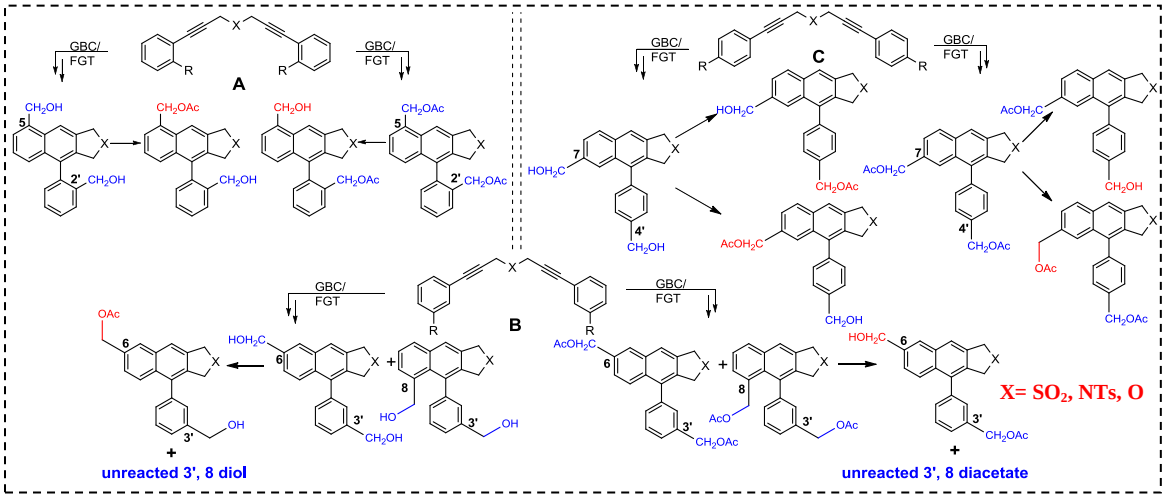
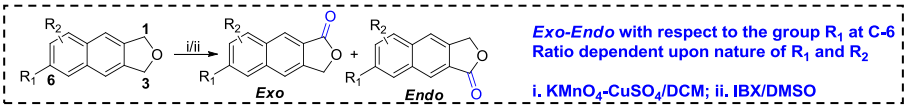
Abstract

Studies on the Synthesis of Regiosomeric Aryl Naphthalene Monoacetates from Diols and Diacetates, Phthalides from Phthalans and Possible Pummerer Route to Oxa-enediyne

A series of aryl naphthalene diol and diacetate derivatives were synthesized *via* Garratt-Braverman cyclization (GBC) of the symmetrically substituted *bis*-propargyl systems having same functionalities at the two ends to study the enzyme (lipase) mediated regioselective transesterification and hydrolysis reactions for the synthesis of differentially substituted heterocycle-based aryl naphthalene derivatives as their monoacetates. In all these cases the selectivity (regioselectivity) during enzyme mediated transformations was excellent. The pattern of selectivity was found to be dependent upon the nature of the fused heterocyclic ring like sulfolene, dihydrofuran or dihydro isoindole. The structure of the regioisomeric monoacetates were elucidated by analyzing different types of NMR spectroscopy. In some cases crystal structures confirmed the structures of the regioisomers. The pattern of selectivity was explained by considering the active site model for *Pseudomonas* lipase and finally by molecular docking, based on the crystal structure of PCL, representing the *Pseudomonas* lipase family.



The nature and extent of regioselectivity during chemical oxidation of unsymmetrical phthalans to their regioisomeric phthalides was also studied. In the process, iodoxy benzoic acid (IBX) was found to be an excellent reagent. The extent of regioselectivity was shown to be dependent upon the electronic nature of the aryl ring (donor or acceptor).



In an attempt to synthesized cyclic oxa-enediyne by Pummerer rearrangement, an acyclic sulfoxide precursor was synthesized (**Figure 1**). However, all attempt to induce intramolecular Pummerer type cyclization failed under all reported conditions.

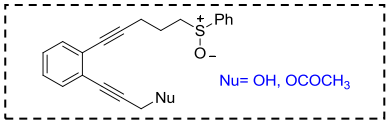


Figure1: Synthesized acyclic enediyne sulfoxide