

## Transformation of Glycals to Chiral Fused Aromatic Cores via Annulative $\pi$ -Extension Reaction with Arynes

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**Abstract :** Carbohydrate-derived chiral intermediates which contain arrays of defined stereocenters have found enormous applications in organic synthesis due to their inherent functional group, stereochemical and structural diversities as well as their ready availability. Stereodiversity of these classes of molecules has motivated synthetic organic chemistry over the years. One major challenge is control of relative configuration during construction of acyclic fragments. Here, we show that The Diels Alder addition of arynes to appropriately substituted vinyl/aryl glycals followed by  $\pi$ -extension via pyran ring opening smoothly furnished meta-disubstituted fused aromatic cores containing a stereo-defined orthogonally protected chiral side chain. The method is broad in terms of aryl homologation affording benzene, naphthalene, and phenanthrene derivatives. Base-induced deprotonation followed by cleavage of the allylic C-O bond appears to be the crucial steps leading to the development of aromaticity, which is the driving force behind the annulative  $\pi$ -extension process. The present protocol can be used for the synthesis of meta-disubstituted naphthalene aldehydes and substrates for aldolases.

**Keywords :** vinyl/C-2 aryl glycal, arynes, cyclization, ring opening

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