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**Title:** Morita–Baylis–Hillman Reaction of  $\beta,\beta$ -Disubstituted Enones: An Enantioselective Organocatalytic Approach for the Synthesis of Cyclopenta[b]annulated Arenes and Heteroarenes

**Authors:** Satpathi, B. (/jspui/browse?type=author&value=Satpathi%2C+B.)  
Ramasastry, S.S.V. (/jspui/browse?type=author&value=Ramasastry%2C+S.S.V.)

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**Abstract:** The first enantioselective organocatalytic intramolecular Morita–Baylis–Hillman (MBH) reaction of sterically highly demanding  $\beta,\beta$ -disubstituted enones is presented. The MBH reaction of  $\beta,\beta$ -disubstituted- $\alpha,\beta$ -unsaturated electron-withdrawing systems was previously considered to be unfeasible. Towards this end, designer substrates, which under simple and practical reaction conditions generate a variety of cyclopenta[b]annulated arenes and heteroarenes in excellent enantiopurities and near-quantitative yields in remarkably short reaction times, are described. The reason for the unusually facile nature of this reaction is attributed to the synergy guided and entropically favored intramolecular reaction. Further, this strategy provides easy access to a substantial number of bioactive natural products and pharmaceutically significant compounds.

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