## Et<sub>2</sub>Zn-Mediated Cross-Coupling Reactions between Dibromoketones and Monobromo Carbonyl Compounds

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Chiral 1,4-dicarbonyls are core structures found in natural products and pharmaceuticals. As they are useful synthetic intermediates, the development of efficient methods for their catalytic asymmetric synthesis is highly desirable. The construction of the C2–C3 bond is one of the strategies commonly used for the formation of chiral 1,4-dicarbonyl compounds. Although effective methods that employ chiral auxiliaries have been reported,<sup>1</sup> few methods have been developed for catalytic asymmetric variants to synthesize enantioenriched 1,4-dicarbonyl compounds.<sup>2</sup>

Here, we have developed a novel route to synthesize chiral or racemic 1,4-dicarbonyl compounds.<sup>3</sup> Chiral 1,4-dicarbonyl compounds can be obtained via the enantioselective bromination of aldehydes using a chiral secondary amine catalyst and a subsequent crossreaction between the resulting chiral coupling α-bromoaldehydes and α.αdibromoacetophenones.<sup>4</sup> a,a-Dibromoketones generate zinc enolates through a diethylzincmediated halogen–metal exchange and react with  $\alpha$ -bromocarbonyl compounds to furnish 1,4dicarbonyl compounds via a second generation of zinc enolates. This cross-coupling reaction is enabled by the chemoselective formation of zinc enolates from  $\alpha, \alpha$ -dibromoketones in the presence of  $\alpha$ -bromocarbonyl compounds. This approach provides various chiral 1,4dicarbonyl compounds with high enantioselectivity from readily available aldehydes and  $\alpha, \alpha, \alpha$ tribromoketones under mild conditions.



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