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New General Asymmetric Synthesis of Versatile γ -Alkylated Butenolides and Its Application to Expeditious Synthesis of the Chiral Geissman-Waiss Lactones Useful for (+)-Retronecine Synthesis.

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A new method for general asymmetric synthesis of chiral butenolides is established by utilizing excellent diastereocontrolled alkylation at the γ -position of hydroxy butenolides with the chiral tin (II) enolate, prepared in situ from 3-acetyl-4(*S*)-isopropyl-1,3-thiazolidine-2-thione by the reaction with $\text{Sn}(\text{OSO}_2\text{CF}_3)_2$ and *N*-ethylpiperidine. The absolute configuration of the γ -alkylated butenolides was established by *X*-ray analysis. An efficient utility of the chiral butenolides is exemplified with the expeditious synthesis of the optically pure Geissman-Waiss lactone derivatives.

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Stabilizing 1,3-Diaxial Interaction between a Metal (Group 14) and a Heteroatom. Fixation of Six-Membered Carbocycles to the 1,3-Diaxial Conformer.

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Fixation of the molecular geometry of six-membered carbocycles to the 1,3-diaxial conformer by a stabilizing 1,3-diaxial interaction between tin and nitrogen atoms is described. Intramolecular hypervalent interaction biases the structure of chlorodimethyl(*cis*-3-(dimethylamino)cyclohexyl)-stannane toward the 1,3-diaxial conformation, whereas (*cis*-3-(benzyloxy)cyclohexyl)chlorodimethylgermane and (*cis*-3-(benzyloxy)cyclohexyl)dimethylfluorosilane prefer the diequatorial conformation. The difference between the preferred conformations is discussed in terms of the *A* values of $(\text{CH}_3)_3\text{M}$ groups and the polarizability of C-M (M=Sn, Ge, and Si) bonds.

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Efficient Preparation of New Chiral Synthons Useful for (+)-Carbacyclin Synthesis by Utilizing Enzymatic Hydrolysis of Prochiral σ -Symmetric Diesters.

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Enzymatic hydrolyses of prochiral σ -symmetric dimethyl esters employing porcine liver esterase and porcine pancreatic lipase were investigated, resulting in the enantioselective preparation of the corresponding new monoesters useful for (+)-carbacyclin synthesis. It was also demonstrated that the hydrolysis with porcine liver esterase was remarkably affected by acetone as a co-solvent.