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1,3-Dicarbonyl compounds represent a prominent family of structures that are easily available and can provide rapid access to complex molecules. When doubly substituted, these compounds can be rapidly converted to valuable tetrasubstituted stereocenters via asymmetric transformations. Here, we report a prolinol- or pipecolinol-derived tetradentate ligand scaffold that can house two zinc centers or a single magnesium atom to desymmetrize a wide range of malonic esters and 1,3-diketones. The reductive desymmetrization of disubstituted malonic ester via hydrosilylation has enabled the stereoselective synthesis of various enantioenriched building blocks, including quaternary stereocenters, tertiary alkyl halides, α -tertiary amines, and tertiary alcohols. Consequently, novel and expeditious approaches to bioactive natural metabolites, such as 2-dechlorohalomon, conagenin, and yezo'otogirins, were devised. Meanwhile, the magnesium-catalyzed desymmetric cyanosilylation of acyclic 1,3-diketones using the same ligand scaffolds afforded two vicinal tetrasubstituted carbons. The polyfunctionalized nature of the chiral cyanohydrin products can be used to access molecules of higher complexity, particularly those with consecutive stereocenters.

