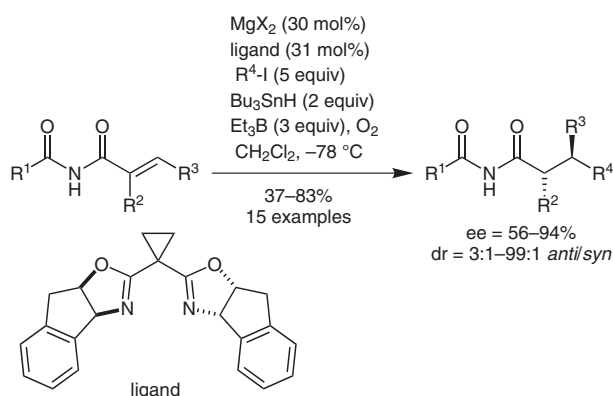


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Enantioselective Radical Addition/Trapping Reactions with α,β -Disubstituted Unsaturated Imides, Synthesis of *anti*-Propionate Aldols
J. Am. Chem. Soc. **2005**, *127*, 2390-2391.

Enantioselective Synthesis of *anti*-Propionate Aldols via Radical Addition



Significance: Currently, there are relatively few methods for the synthesis of *anti*-propionate aldols with extremely high diastereo- and enantioselectivity. Furthermore, standard aldol reactions are performed under basic conditions; limiting the functional group compatibility of the reagents. This method employs radical addition under neutral and fairly mild reaction conditions, providing products with extremely high diastereoselectivity (generally >95:5 *anti/syn*) and good enantioselectivity (generally >70% ee). This high degree of selectivity was obtained with various Mg^{2+} -based Lewis acids, alkyl halides, and vinylic substituents, presenting an interesting new route towards aldol-like products.

Comment: It is believed that the ligand controls the enantioselectivity of the initial β -addition of the alkyl radical; and subsequent orientation of the β -stereocenter controlling the diastereoselectivity of hydrogen atom transfer. H-atom transfer is thought to occur quickly, as a rotameric equilibrium would not provide the observed diastereoselectivities (for examples see: M. P. Sibi, J. Chen *J. Am. Chem. Soc.* **2001**, *123*, 9472, where slower transfer from allyltributyltin gave moderate diastereoselectivity). In addition, it was found that the N–H imide was essential for good yield and selectivity, as oxazolidinone imides afforded <10% yield.

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