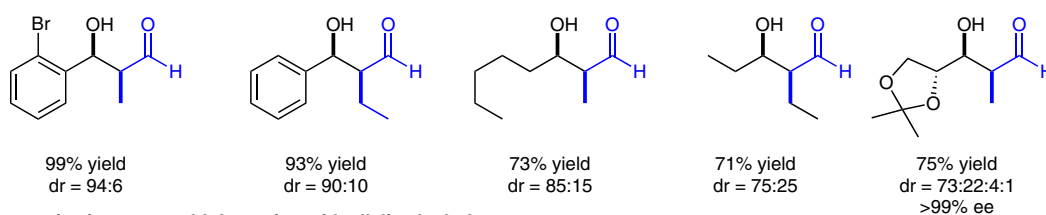
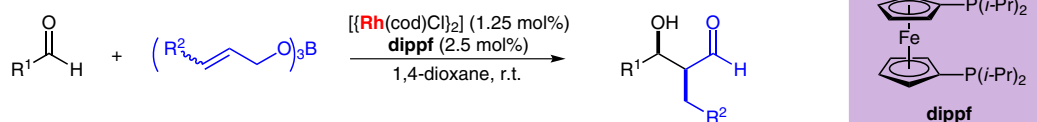
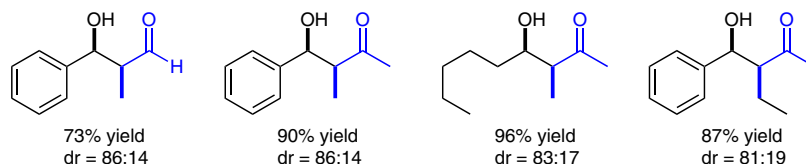


In Situ Aldehyde Enolate Formation by Rhodium-Catalyzed Isomerization

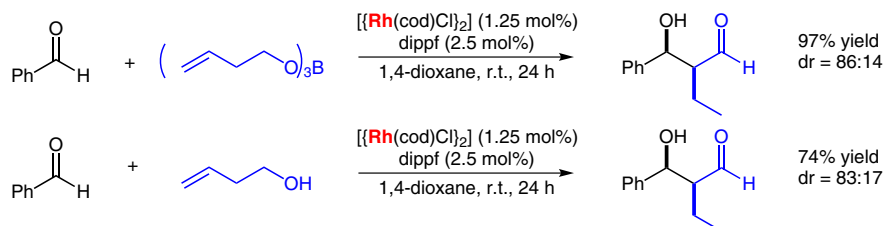
Isomerization–cross-aldol reaction with triallylboranes:



Isomerization–cross aldol reaction with allylic alcohols:



Isomerization–cross aldol with homoallyloxyborane and homoallylic alcohol:



Significance: Aldol reactions in which the aldol donor is derived from an aldehyde, are particularly challenging. This report describes a strategy in which aldehyde enolates are generated in situ by rhodium-catalyzed isomerization of triallylboroxanes. High *syn*-selectivity is obtained for a variety of aldehyde-donor and -acceptor partners.

Comment: Remarkably, the use of triallyloxyboranes is not required; simple primary and secondary allylic alcohols also undergo the isomerization–cross-aldol sequence with similar levels of reactivity and selectivity, presumably through a rhodium-enolate or -enol mechanism.