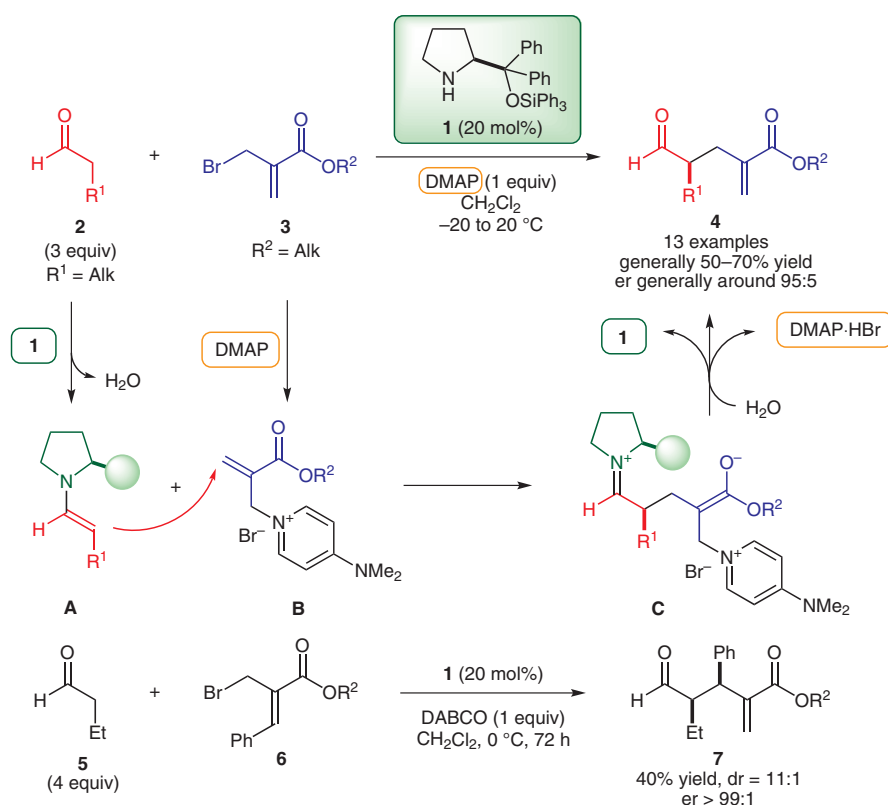


α -Alkylation of Aldehydes via a Conjugate Addition–Elimination Pathway



Significance: A catalytic asymmetric α -alkylation of aldehydes with allylic bromides **3**, proceeding via an S_N2' -type conjugate addition–elimination pathway, has been reported. Stoichiometric DMAP and catalytic amounts of secondary amine **1** delivered alkylation products **4** in moderate yields with high enantioselectivity. Using a more complex electrophile **6**, product **7** was obtained with excellent enantioselectivity albeit in only 40% yield after three days. In addition to moderate yields, the main drawback of the reported method is the use of three equivalents of the aldehyde.

Comment: The widely pursued catalytic asymmetric α -alkylation of aldehydes has recently been advanced by using secondary amine catalysis via an intramolecular S_N2 pathway, an intermolecular radical pathway, and also via S_N1 -type reactions. However, limitations of available methods with respect to suitable electrophiles prompted further research. In the current paper, Palomo and co-workers designed a system that circumvents catalyst alkylation probably by making it reversible. The crucial step of the reaction is based on a conjugate addition (**A** + **B** \rightarrow **C**) rather than on a direct alkylation. DMAP serves a dual role: activating the electrophile via intermediate **B** (for example, see: Y.-C. Chen et al. *Angew. Chem. Int. Ed.* **2009**, 48, 5737) and acting as a base to remove the liberated acid.