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

**Significance:** A catalytic asymmetric α-allylation of aldehydes with allylic bromides, proceeding via an $S_N^2$-type conjugate addition–elimination pathway, has been reported. Stoichiometric DMAP and catalytic amounts of secondary amine delivered alkylation products in moderate yields with high enantioselectivity. Using a more complex electrophile, product 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-allylation of aldehydes has recently been advanced by using secondary amine catalysis via an intramolecular $S_N^2$ pathway, an intermolecular radical pathway, and also via $S_N^1$-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 → 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.