Allylboration of Aldehydes

Significance: A highly enantioselective allylboration of aldehydes catalyzed by the chiral Brønsted acid (R)-TRIP is reported by the authors. This transformation shows a broad substrate scope: aryl, heteroaryl, $\alpha,\beta$-unsaturated and aliphatic aldehydes can all be efficiently allylated. Furthermore, the crotylboration of benzaldehyde also proceeded smoothly with high diastereo- and enantioselectivity in the presence of this acid catalyst.

Comment: Simple starting materials and a commercially available catalyst make this protocol a useful and efficient method for the synthesis of enantoenriched homoallylic alcohols. A transition state where the boronate is activated by protonation of the boronate oxygen with a chiral phosphoric acid is proposed by the authors. To confirm this activation model, further mechanistic investigation may be required.

Selected examples:
- PhOH, 99% yield, er = 99:1
- PhCH=CHPh, 94% yield, er = 98:2
- PhCH=CHCH=CHPh, 98% yield, er = 55:3
- with (E)-boronate: 96% yield (anti), er = 98:2
- with (Z)-boronate: 95% yield (syn), er = 97:3