Chiral Brønsted Acid Catalyzed 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 enantioenriched 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.

\[
\begin{align*}
R = & \text{Ar, Alk} \\
\text{Ph} & \text{OH} \\
\text{with (E)-boronate: } 96\% \text{ yield (anti), } er = 98:2 \\
\text{with (Z)-boronate: } 95\% \text{ yield (syn), } er = 97:3
\end{align*}
\]

Selected examples:

1. **Ph**<sub>2</sub>OH, 99% yield, er = 99:1
2. **Ph**<sub>2</sub>OH, 94% yield, er = 98:2
3. **Ph**<sub>2</sub>OH, 98% yield, er = 95:5

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