**Significance:** The group of Zhu reports an organocatalytic asymmetric acyloin rearrangement of disubstituted α-hydroxy acetals. This rearrangement is carried out in the presence of a chiral N-triflyl phosphoramide catalyst to give the desired α-alkoxy ketones in good to high yields and high to excellent enantioselectivities.

**Comment:** The acyloin (α-ketol) rearrangement is employed in the biosynthesis of many different natural products. The generation of an ion pair between the oxocarbenium ion and the chiral phosphoramide catalyst is presumably responsible for the asymmetric induction of this 1,2-carbon-shift reaction.

**Selected examples:**

- **Catalyst:**
  - **R1 = Ar**
  - **R2 = Alk**
  - 23 examples
  - 50–97% yield
  - er from 82:18 to 96:4

- **82% yield**
  - er = 95:5

- **91% yield**
  - er = 96:4

- **95% yield**
  - er = 95:7.5

- **75% yield**
  - er = 96:4

- **52% yield**
  - er = 92.5:7.5

**Further derivatizations:**

- **92% yield**
  - er = 95:5
  - dr > 20:1

- **98% yield**
  - er = 94.5:5.5
  - dr > 20:1

- **93% yield**
  - er = 94.5:5.5
  - dr > 20:1

- **99% yield**
  - er = 96:4
  - dr > 20:1