Cation Radical Diels–Alder Reactions via Asymmetric Counteranion-Directed Catalysis

**Significance:** The Nicewicz group reports both intra- and intermolecular enantioselective Diels–Alder reactions. The photoredox catalyst system consists of a cationic oxopyrylium photooxidant bearing a chiral N-triflyl phosphoramide anion.

**Comment:** Enantioselective transformations that proceed through a radical ion pair represent a major challenge for asymmetric catalysis. In this report, despite obtaining moderate enantioselectivities, the authors proved the concept by introducing a chiral counteranion. The presented results could provide insights into asymmetric photoredox reactions.

**Presented examples:**
- **X = O, NTs, R = Alk, PMP = p-methoxyphenyl**
  - 72% yield, dr = 6:1, er = 75:25
  - 43% yield, dr = 5:1, er = 73:27
  - 63% yield, dr = 6:1, er = 75:25
  - 10% yield, dr = 5:1, er = 50:50
  - 42% yield, dr = 10:1, er = 50:50

**Proposed mechanism:**
- Photoreduction of the cationic oxopyrylium photooxidant leads to a close ion pair in non-polar media.

**Intermolecular examples:**
- **A (0.5 mol%)**
  - 8% yield, dr > 10:1, er = 75:25

**Key words:**
- chiral counteranion
- photoredox catalysis
- Diels–Alder reaction