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 phosphoramidate 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:

- 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:

Intermolecular examples:

- 8% yield dr > 10:1 er = 75:25
- 85% yield dr = 8:1 er = 66:34