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:

![Chemical structures of presented examples](image)

Proposed mechanism:

![Proposed mechanism](image)

Intermolecular examples:

![Chemical structures of intermolecular examples](image)