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.