Cooperative Catalysis: Radical Addition to Olefins and Asymmetric Protonation

Significance: Jiang and co-workers report the enantioselective radical conjugate addition–protonation of N-aryl glycines to α-branched 2-vinylazaaarenes using a metal-free dual catalytic system (a photosensitizer and a chiral phosphoric acid). The corresponding products are obtained in high yields with good to excellent enantioselectivities, and the methodology is applied to the synthesis of the medicinal compound pheniramine.

Comment: Because α-amino acids are abundant, their use as starting materials for organic synthesis is desirable. In this report, N-aryl α-glycines undergo photooxidative decarboxylation and react further with highly activated olefins in a radical pathway followed by enantioselective protonation. While many examples are shown, the presented substrate scope is still limited to pyridine- and quinoline-containing substances.

**Selected examples:**

- **87% yield**
  - er = 97.3
- **83% yield**
  - er = 94.6
- **69% yield**
  - er = 96.5:3.5
- **95% yield**
  - er = 96:4

**Proposed mechanism:**

1. PMP deprotection
2. reductive amination

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