Enantioselective Radical Addition to Heteroarenes

**Significance:** Heteroarenes with basic nitrogen centers, such as pyridines or quinolines, can be found in pharmaceuticals and in bioactive molecules. Minisci-type reactions are direct methods to synthesize such classes of compounds, but the generation of highly enantioselective stereocenters is challenging. The authors have developed a highly enantio- and regioselective addition of α-amino alkyl radicals to pyridines and quinolines in the presence of an iridium photoredox catalyst and a chiral Brønsted acid catalyst.

**Comment:** The chiral Bronsted acid activates the heteroarene and induces the enantioselectivity of the reaction, whereas the iridium photoredox catalyst plays a role in the electron-transfer process. In addition to being applicable to a broad scope of substrates, the reaction can be used in late-stage functionalizations of molecules in a highly chemo-, regio-, and enantioselective manner.

**Selected examples:**
- 93% yield, 96% ee
- 76% yield, dr > 20:1
- 82% yield, 95% ee
- 80% yield, 92% ee
- 70% yield, 95% ee
- 89% yield, 96% ee

**Proposed mechanism:**
- Radical generation
- Photoredox cycle
- Chiral Bronsted acid cycle
- Oxidation
- Deprotonation
- Radical addition