Photoinduced Cobalt-Catalyzed Enantioselective Reductive Addition of Aryl Iodides to Aldehydes

Significance: A photoredox cobalt-catalyzed enantioselective approach to a Grignard-type addition of aryl iodides to aldehydes is reported. Notably, the mild reaction conditions enable a wide range of functional groups and heterocycles to be tolerated.

Comment: 4CzIPN is used as the photocatalyst, which can be excited under visible-light irradiation. The use of Hantzsch ester as the reductant is notable because it avoids the generation of stoichiometric metal waste.

Selected examples:

- **1-naph**
  - R¹ = COMe, 99% yield, 97% ee
  - R¹ = Br, 92% yield, 97% ee
- **Ph**
  - R¹ = Br, 92% yield, 97% ee
- **N**
  - R¹ = OH, 97% yield, 98% ee
- **Cl**
  - R¹ = OH, 93% yield, 95% ee
- **KOH, CH₂Cl₂**
  - 98% yield
- **D-cloperastine**
  - R¹ = OH, 99% yield, 99% ee
- **R₂ = 4-biphenyl**
  - 72% yield, 95% ee
- **R₂ = 72% yield, 95% ee**
- **R₂ = 91% yield, 97% ee, Z/E > 19:1**
- **Br**
  - R² = OH, 74% yield, 94% ee

Proposed mechanism:

- **Ar⁻I**
  - 4CzIPN⁻
- **Ar**
  - 4CzIPN⁺
- **Py**
  - OH
  - **HE⁻**
  - **PyPh⁺**
  - **HE⁺**

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