Organocatalytic C(sp³)–H Amination through Nitrenoid Transfer

**Significance:** The Hilinski group reports a C(sp³)–H amination through a nitrenoid transfer catalyzed by iminium salt A. The reaction proceeds in moderate to high yields, and the method is applicable to several natural products having other functional groups.

**Comment:** In contrast to reported nitrenoid-transfer reactions catalyzed by transition metals, the authors developed an organocatalytic variant of the transformation. They proposed the diaziridinium salt as critical intermediate, which is supported by ESI-MS analysis, but not yet fully characterized. A kinetic isotopic effect study suggested C–H cleavage as the rate-determining step.

**Selected examples:**

- \( \text{R}^1, \text{R}^2, \text{R}^3 = \text{Alk, Ar} \)
- \( \text{R}^4 = \text{Ar, OCH}_2 \text{CCl}_3 \)

- **R1**: 
  - H (64% yield)
  - Br (37% yield)
  - Br (69% yield)
  - O (56% yield)
  - O (71% yield)

- **R2**: 
  - Me
  - CF₃

- **R3**: 
  - NHTs
  - Br
  - NHTs
  - NHTs

- **R4**: 
  - OCH₂CCl₃
  - SO₂Ph
  - BF₄⁻

**Mechanistic studies:**

Detection of a proposed intermediate:

- \( \text{PhI} \text{NSO}_2 \text{R}^4 (2 \text{ equiv}) A (20 \text{ mol}%) \quad \text{CH}_2\text{Cl}_2, \text{r.t.} \quad 27 \text{ examples} 36–87\% \text{ yield} \)

KIE study:

- \( \text{H} \quad \text{H} \quad \text{D} \quad \text{D} \)
- \( \text{PhI} \text{NSO}_2 \text{Ts} (2 \text{ equiv}) A (20 \text{ mol}%) \quad \text{CH}_2\text{Cl}_2, \text{r.t.} \quad k_\text{H}/k_\text{D} = 2.5 \)