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Organocatalytic Nitrenoid Transfer: Metal-Free Selective Intermolecular C(sp³)–H Amination Catalyzed by an
Iminium Salt

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:

\[
\begin{align*}
\text{PhINSO₂R₄} & \quad \text{A} (20 \text{ mol%}) \\
\text{CH₂Cl₂, r.t.} &
\end{align*}
\]

27 examples
36–87% yield

Mechanistic studies:

Detection of a proposed intermediate:

\[
\begin{align*}
\text{HN} & \quad \text{Me} \quad \text{BF₄} \\
\text{PhINSO₂Ts (10 equiv)} & \\
\text{CH₂Cl₂, r.t.} &
\end{align*}
\]

proposed intermediate
(observable by ESI-MS)

KIE study:

\[
\begin{align*}
\text{HN} & \quad \text{Me} \quad \text{BF₄} \\
\text{PhINSO₂Ts (2 equiv)} & \\
\text{CH₂Cl₂, r.t.} &
\end{align*}
\]

\[
\begin{align*}
\text{HN} & \quad \text{Me} \quad \text{BF₄} \\
\text{PhINSO₂Ts (2 equiv)} & \\
\text{CH₂Cl₂, r.t.} &
\end{align*}
\]

\[
\begin{align*}
k_D/k_H & = 2.5
\end{align*}
\]