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Heterogeneous Visible-Light Photoredox Catalysis with Graphitic Carbon Nitride for α-Aminoalkyl Radical Additions, Allylations, and Heteroarylations


Desilylative or Decarboxylative Photoadditions with Graphitic Carbon Nitride

**Significance:** A graphitic carbon nitride (g-C₃N₄) catalyzed the desilylative addition of α-silylamines to alkenes or heteroaryl chlorides under visible-light irradiation to give the corresponding adducts in up to 96% yield (eq. 1). g-C₃N₄ also promoted the decarboxylative additions of α-amino acids to alkenes under similar conditions to afford the corresponding products in up to 79% yield (eq. 2).

**Comment:** In the desilylative addition of N-methyl-N-[(trimethylsilyl)methyl]aniline to 4-(2,2-dicyanoethenyl)toluene, g-C₃N₄ was reused eight times without significant loss of its catalytic activity. g-C₃N₄ was applied for the continuous-flow reaction of N-methyl-N-[(trimethylsilyl)methyl]aniline with cyclohexanone to afford the desired amine in 85% yield.

**Desilylative additions:**

\[
\begin{align*}
R^1 & \quad \text{TMS} \\
R^2 & \quad \text{or} \\
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{Me} \\
\text{Me} & \quad \text{CN} \\
\text{R}^3 & \quad \text{R}^4 & \quad \text{R}^5 & \quad \text{R}^6 \\
\text{g-C}_3\text{N}_4 \quad \text{(20 mg)} & \quad \text{blue LED (12 W)} & \quad \text{CsF (0.4 mmol)} & \quad \text{MeOH (2 mL)}
\end{align*}
\]

Selected results:

- 92% yield
- 96% yield
- 83% yield
- 88% yield

**Decarboxylative additions:**

\[
\begin{align*}
R^1 & \quad \text{H} & \quad \text{COOH} \\
R^2 & \quad \text{or} \\
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{Me} \\
\text{Me} & \quad \text{CN} \\
\text{N} & \quad \text{Me} & \quad \text{N} & \quad \text{Me} \\
\text{R}^3 & \quad \text{R}^4 & \quad \text{R}^5 & \quad \text{R}^6 \\
\text{g-C}_3\text{N}_4 \quad \text{(20 mg)} & \quad \text{blue LED (12 W)} & \quad \text{CsF (0.4 mmol)} & \quad \text{MeOH (2 mL)}
\end{align*}
\]

Selected results:

- 79% yield
- 71% yield
- 78% yield
- 78% yield