Visible-Light-Mediated [4+2] Annulation of N-Cyclobutylanilines on Self-Doped Titania

Preparation of catalyst:

\[
\text{Ti powder (0.3 g)} \xrightarrow{\text{HCl (10 mL, 2 M)}} \text{Ti}^{3+}\text{@TiO}_2
\]  

([4+2] annulation):

\[
\begin{align*}
\text{R}_1^\text{H} & \quad \text{N} & \quad \text{R}_2^\text{H} \\
\text{Ph} & \quad \text{N} & \quad \text{Ph} \\
\text{t-Bu} & \quad \text{N} & \quad \text{Ph} \\
\text{F}_3\text{C} & \quad \text{N} & \quad \text{Ph} \\
\end{align*}
\]

Selected results:

\[
\begin{align*}
\text{1a}, 14 \text{ h}, 79\% \text{ yield} \\
\text{1b}, 14 \text{ h}, 85\% \text{ yield} \\
\text{1c}, 18 \text{ h}, 68\% \text{ yield} \\
\text{1d}, 17 \text{ h}, 71\% \text{ yield}
\end{align*}
\]

Comparison with rose bengal:

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{Ph} \\
\text{t-BuOH, 13 h} & \quad \text{visible light (18 W LED), air}
\end{align*}
\]

Selected results:

\[
\begin{align*}
\text{2}, 43\% \text{ yield for Ti}^{3+}\text{@TiO}_2 (10 \text{ mol}) & \quad \text{19\% yield for rose bengal (5 mol)}
\end{align*}
\]

Significance: A self-doped Ti\(^{3+}\)@TiO\(_2\) catalyst was prepared as shown in equation 1. The [4+2] annulation of N-cyclobutylanilines with alkynes took place in the presence of Ti\(^{3+}\)@TiO\(_2\) under visible-light irradiation in air to give the corresponding annihilation products 1a–d in up to 85% yield (eq. 2; 15 examples).

Comment: The catalyst was recovered by centrifugation, washed with t-BuOH, and reused four times for the formation of 1a (fifth run: 79% yield). When the reaction of 4-t-butyl-N-cyclobutylaniline and prop-1-yn-1-ylbenzene was carried out in the presence of Ti\(^{3+}\)@TiO\(_2\) (10 mol%) or rose bengal (5 mol%) for 13 h, product 2 was obtained in yields of 43% and 19%, respectively (eq. 3).