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

Preparation of catalyst:

\[
\text{Ti powder (0.3 g)} \rightarrow \text{HCl (10 mL, 2 M)} \rightarrow 220 ^\circ C, 12 \text{h} \rightarrow \text{Ti}^{3+}\text{@TiO}_2
\]

([4+2] annulation):

\[
\begin{align*}
\text{R}_1^1 & \quad \text{H} & \quad \text{N} & \quad \text{R}_2^1 \\
\text{Ph} & \quad \text{Ph} & \quad \text{Ph} & \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{f-BuOH} & \quad \text{Ti}^{3+}\text{@TiO}_2 (10 \text{ mol\%}) & \quad \text{visible light (18 W LED), air}
\end{align*}
\]

Selected results:

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

Comparison with rose bengal:

\[
\begin{align*}
\text{R}_1^1 & \quad \text{H} & \quad \text{N} & \quad \text{R}_2^1 \\
\text{H} & \quad \text{Ph} & \quad \text{Ph} & \quad \text{Ph}
\end{align*}
\]

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

**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 annulation products \(1\text{a}–\text{d}\) 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 \(1\text{a}\) (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).