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

**Preparation of catalyst:**

\[ \text{Ti powder (0.3 g)} \xrightarrow{\text{HCl (10 mL, 2 M)}} 220 ^\circ \text{C, 12 h} \xrightarrow{\text{Ti}^{3+} @ \text{TiO}_2 (0.0006 \text{ mmol})} \]

**[4+2] annulation:**

\[ \begin{aligned}
\text{R}_1^1 \\ \text{H} \\ \text{N} \\ \text{R}_2^1 \\
\end{aligned}
+ \begin{aligned}
\text{R}_1^2 \\ \text{H} \\ \text{N} \\ \text{R}_2^2 \\
\end{aligned}
\xrightarrow{\text{Ti}^{3+} @ \text{TiO}_2 (10 \text{ mol%})}
\begin{aligned}
\text{R}_1^1 \\ \text{H} \\ \text{N} \\ \text{R}_2^1 \\
\text{R}_1^2 \\ \text{H} \\ \text{N} \\ \text{R}_2^2 \\
\end{aligned}
\xrightarrow{\text{t-BuOH, visible light (18 W LED), air}}
\begin{aligned}
\text{R}_1^1 \\ \text{H} \\ \text{N} \\ \text{R}_2^1 \\
\text{R}_1^2 \\ \text{H} \\ \text{N} \\ \text{R}_2^2 \\
\end{aligned}
\]

**Selected results:**

- 1a, 14 h, 79% yield
- 1b, 14 h, 85% yield
- 1c, 18 h, 68% yield
- 1d, 17 h, 71% yield

**Comparison with rose bengal:**

\[ \begin{aligned}
\text{Ph} \\
\text{N} \\
\text{Ph} \\
\text{t-BuOH, 13 h} \\
\text{visible light (18 W LED), air}
\end{aligned}
\xrightarrow{\text{t-BuOH, 13 h}}
\begin{aligned}
\text{Ph} \\
\text{N} \\
\text{Ph} \\
\end{aligned}
\xrightarrow{\text{43% yield for Ti}^{3+} @ \text{TiO}_2 (10 \text{ mol%})}
\begin{aligned}
\text{Ph} \\
\text{N} \\
\text{Ph} \\
\text{rose bengal (sodium salt)}
\end{aligned}
\]

**Significance:** A self-doped Ti$^{3+} @ \text{TiO}_2$ catalyst was prepared as shown in equation 1. The [4+2] annulation of N-cyclobutylanilines with alkynes took place in the presence of Ti$^{3+} @ \text{TiO}_2$ under visible-light irradiation in air to give the corresponding annulation 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$^{3+} @ \text{TiO}_2$ (10 mol%) or rose bengal (5 mol%) for 13 h, product 2 was obtained in yields of 43% and 19%, respectively (eq. 3).