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

Preparation of catalyst:

\[
\text{Ti powder (0.3 g)} \rightarrow \text{HCl (10 mL, 2 M)} \rightarrow \text{220 °C, 12 h} \rightarrow \text{Ti}^{3+}@\text{TiO}_2 \quad (1)
\]

[4+2] Annulation:

\[
\begin{align*}
\text{R}_1^+ & \quad \text{R}_2^- \\
(0.2 \text{ mmol}) & \quad (0.6 \text{ mmol}) \\
\text{Ti}^{3+}@\text{TiO}_2 (10 \text{ mol%}) & \quad \text{t-BuOH, visible light (18 W LED), air} \\
& \quad (2)
\end{align*}
\]

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:

\[
\begin{align*}
\text{R}_1^+ & \quad \text{Ph} \\
\text{t-BuOH, 13 h} & \quad \text{visible light (18 W LED), air} \\
& \quad (3)
\end{align*}
\]

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**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 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-yl benzene 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).