C–C Bond Formation Using Nickel-Photoredox Catalysis

**Significance:** The authors developed a nickel-photoredox-catalyzed C(sp3)–H functionalization of a variety of unactivated alkyl or benzylic compounds using chloroformate derivatives. Mild coupling conditions allow the tolerance of several functional groups, leading to the corresponding carbonyl compounds in good yields.

**Comment:** From a mechanistic point of view, the authors hypothesized a catalytic cycle, which starts with an oxidative addition of chloroformate to a nickel(0) species. A SET forms a nickel(III) intermediate, which undergoes subsequent photoelimination, leading to a chlorine radical. Following H-abstraction results in a carbon-centered radical. Addition of the nickel(II) complex and subsequent reductive elimination affords the carbonyl compound.

**Selected examples:**

- 55% yield
- 62% yield
- 68% yield (α:β:γ 1:8:4.6)
- 66% yield (α:β 32:1)
- 60% yield
- 64% yield
- 55% yield
- 73% yield
- 85% yield (β:γ:δ 2.1:5.4:1)
- 57% yield (α:β:γ:δ 1:3:20.5:4)
- 40% yield (α:β:γ:δ 1:6.3:1, dr 1:8:1)

**Equation:**

\[
\text{R}^1 \text{Cl} + \text{H}_2\text{R}^2 \rightarrow \text{R}^1 \text{O} = \text{R}^2
\]

\[
\begin{align*}
\text{I}r[\text{dF(CF}_3\text{)ppy}]_2(\text{dtbppy})\text{PF}_6 (0.5 \text{ mol%}) \\
\text{Ni(cod)}_2 (4 \text{ mol%}) \\
\text{dtbppy} (5.2 \text{ mol%}) \\
\text{K}_2\text{PO}_4 (2.0 \text{ equiv}) \\
\text{NaWO}_4 \cdot 2\text{H}_2\text{O} (1.0 \text{ equiv}) \\
\text{PhH, 34 W Blue LEDs} \\
34–40 °C, 48 h
\end{align*}
\]

up to 85% yield

**Key words:**

nickel catalysis
photoredox catalysis
C–H functionalization

**Category:** Metals in Synthesis

**Synfacts of the Month**

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