C–C Bond Formation Using Nickel-Photoredox Catalysis

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\begin{align*}
R^1 Cl & + H_2R^2 \overset{\text{Ir[(CF}_3\text{)ppy}}_2(\text{dtbbpy})PF_6 (0.5 \text{ mol%})}{\text{Ni(cod)}_2 (4 \text{ mol%})} \text{dtbbpy (5.2 mol%)} \\
& \text{K}_2\text{PO}_4 (2.0 \text{ equiv}) \text{NaWO}_4 \cdot 2\text{H}_2\text{O (1.0 equiv)} \\
& \text{PhH, 34 W Blue LEDs} \text{34–40 °C, 48 h} \\
\end{align*}
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Selected examples:

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\begin{align*}
&\text{PhO}_2\text{C} \quad 62\% \text{ yield} \\
&\text{PhO}_2\text{C} \quad 68\% \text{ yield} \quad (\alpha:\beta:\gamma = 1:8:4.6) \\
&\text{PhO}_2\text{C} \quad 66\% \text{ yield} \quad (c:\beta = 32:1) \\
&\text{CO}_2\text{Ph} \quad 60\% \text{ yield} \\
&\text{CO}_2\text{Ph} \quad 64\% \text{ yield} \\
&\text{PhO}_2\text{C} \quad 55\% \text{ yield} \\
&\text{PhO}_2\text{C} \quad 73\% \text{ yield} \\
&\text{PhO}_2\text{C} \quad 85\% \text{ yield} \quad (\beta:\gamma:\delta = 2.1:5.4:1) \\
&\text{PhO}_2\text{C} \quad 57\% \text{ yield} \quad (\alpha:\beta:\gamma:\delta = 1:3:20.5:4) \\
&\text{PhO}_2\text{C} \quad 40\% \text{ yield} \quad (\alpha:\beta:\gamma:\delta = 1.6:3.1, \text{dr} 1.8:1)
\end{align*}
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**Significance:** The authors developed a nickel-photoredox-catalyzed C(sp^3)–H functionalization of a variety of unactivated alkyl or benzyl 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.