C–C Bond Formation Using Nickel-Photoredox Catalysis

![Chemical Reaction Diagram](image)

\[ R^1 Cl + H_2 R^2 \rightarrow R^1 O \rightarrow R^2 O \]

Significance: The authors developed a nickel-photoredox-catalyzed C(sp³)–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.

**Selected examples:**

- **55% yield**
  - \( \text{O} \text{Ph} \text{O}_2 \text{C} \) (\( \alpha:\beta:\gamma:\delta \) 2.1:5.4:1)

- **62% yield**
  - \( \text{O} \text{Ph} \text{O}_2 \text{C} \) (\( \alpha:\beta:\gamma:\delta \) 1:3:20.5:4, dr 1.8:1)

- **68% yield**
  - \( \text{O} \text{Ph} \text{O}_2 \text{C} \) (\( \alpha:\beta:\gamma:\delta \) 1:8:4.6)

- **66% yield**
  - \( \text{O} \text{Ph} \text{O}_2 \text{C} \) (\( \alpha:\beta \) 32:1)

- **60% yield**
  - \( \text{CO}_2 \text{Ph} \)

- **64% yield**
  - \( \text{NC} \text{CO}_2 \text{Ph} \)

- **55% yield**
  - \( \text{PhO}_2 \text{C} \) (\( \alpha:\beta:\gamma:\delta \) 1:1.6:3.1, dr 1.8:1)

- **73% yield**
  - \( \text{CO}_2 \text{Ph} \)