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 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:**

- O
  - t-Bu
  - 55% yield
- O
  - F
  - 62% yield
- PhO₂C
  - 68% yield (α:β:γ 1:8:4.6)
- PhO₂C
  - 66% yield (c:β 32:1)
- CO₂Ph
  - 60% yield
- CO₂Ph
  - 64% yield
- PhO₂C
  - 55% yield
- PhO₂C
  - 73% yield
- PhO₂C
  - 85% yield (β:γ:δ 2.1:5.4:1)
- PhO₂C
  - 57% yield (α:β:γ:δ 1:3:20.5:4)
- PhO₂C
  - 40% yield (α:β:γ:δ 1:1.6:3.1, dr 1.8:1)

**Reaction conditions:**

- R1 = OAr, Ar, Cy
- R2, R3 = various substituted alkyl or aryl moieties
- PhH, 34 W Blue LEDs
- 34–40 °C, 48 h
- up to 85% yield