Nickel-Catalyzed Decarboxylative Alkyl–Alkyl Cross-Coupling

Decarboxylative alkyl–alkyl cross-coupling:

\[
\text{R}_1^1\text{R}_2^2 \quad \text{O} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Zn} \quad \text{R}_3^3 \quad (2 \text{ equiv}) \quad \text{NiCl}_2 \cdot \text{glyme (20 mol%)} \quad \text{ligand L (40 mol%)} \quad \text{DMF–THF, 25 °C, 8–14 h} \quad \text{R}_1^1\text{R}_2^2 \quad \text{up to 89% yield}
\]

Selected examples:

R = Me, 79% yield
R = n-C\text{H}_{13}, 62% yield

Three-component conjunctive cross-coupling:

\[
\text{R}_1^1,\text{R}_2^2 = \text{Alk} \\
\text{R}_3^3 = \text{Alk, O(4-ClC}_6\text{H}_4), \text{OMe, SMe, N(Me)Boc} \\
\text{PhZnCl-LiCl (3 equiv)} \quad \text{NiCl}_2\cdot\text{glyme (20 mol%)} \quad \text{ligand L (40 mol%)} \quad \text{DMF–THF, 25 °C, 8 h} \quad \text{R}_1^1\text{R}_2^2\text{Ph} \quad \text{up to 94% yield}
\]

Selected examples:

68% yield
76% yield
92% yield
49% yield

Significance: Baran and co-workers report a nickel-catalyzed decarboxylative cross-coupling of redox-active alkyl esters with dialky zinc reagents by using a bipyridine ligand to afford a variety of products in very high yields. Remarkable are the high functional group tolerances as well as the mild reaction conditions.

Comment: The authors present a three-component conjunctive cross-coupling by employing benzyl acrylate as an acceptor molecule. The formation of quaternary centers is accomplished by the formation of two C–C bonds and the corresponding products are obtained in very high yields.