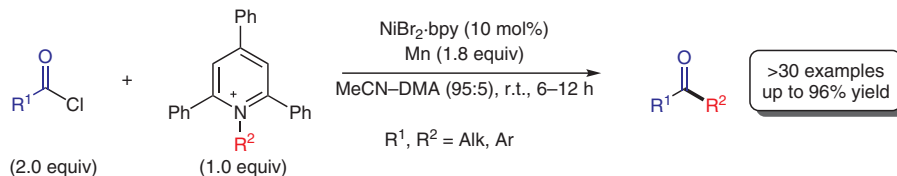
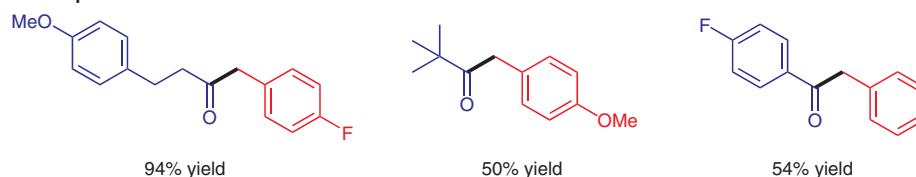


F. T. PULIKOTTIL, R. PILLI, R. V. SUKU, R. RASAPPAN* (INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH THIRUVANANTHAPURAM, VITHURA, INDIA)
Nickel-Catalyzed Cross-Coupling of Alkyl Carboxylic Acid Derivatives with Pyridinium Salts via C–N Bond Cleavage
Org. Lett. **2020**, *22*, 2902–2907.

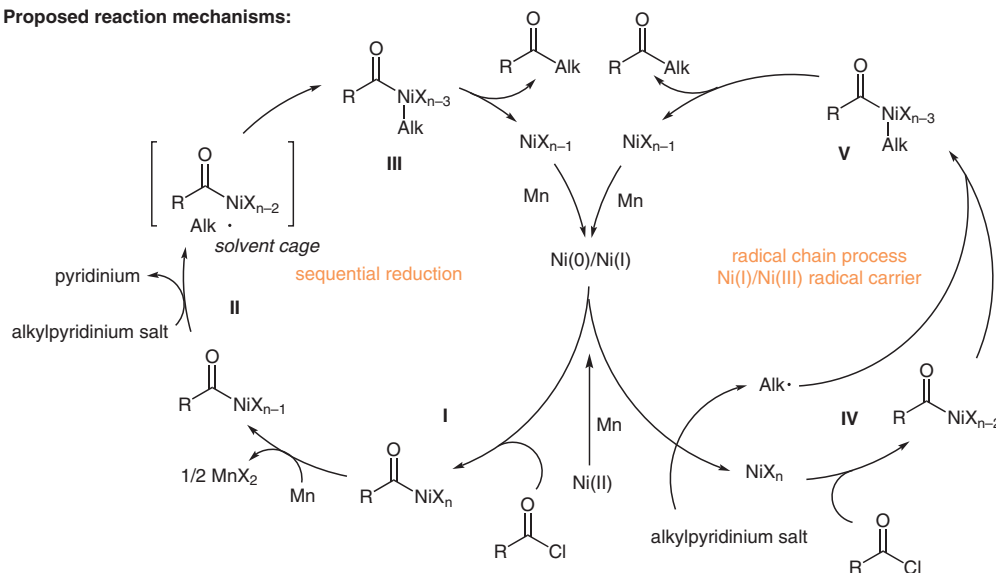
Nickel-Catalyzed Acylation of Pyridinium Salts



Selected examples:



Proposed reaction mechanisms:



Significance: Rasappan and co-workers report the Ni-catalyzed cross-coupling of several alkyl carboxylic acid chlorides with alkylpyridinium salts to afford a range of versatile ketones in good to excellent yields. The authors were able to extend their method to the use of free carboxylic acids by generation of anhydrides in situ.

Comment: The authors proposed two possible mechanistic pathways. In sequential reduction, the low-valent Ni(0)/Ni(I) undergoes oxidative addition with the acid chloride **I**, which is further reduced from the Mn, allowing the reduction of the alkylpyridinium salt **II** to form the desired product **III** after reductive elimination. In the case of a radical chain process, the low-valent Ni species may reduce the alkylpyridinium salt before oxidative addition of the formed Ni-species **IV** into the acid chloride. Combination of the formed Ni intermediate with the formed alkyl radical **V** affords the desired product after reductive elimination.