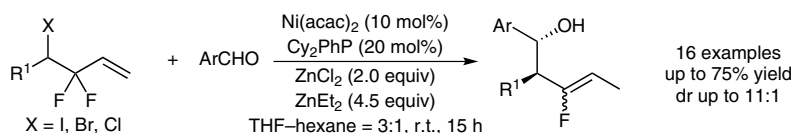
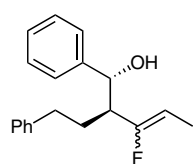


X. LIN, F. ZHENG, F.-L. QING* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY AND DONGHUA UNIVERSITY, SHANGHAI, P. R. OF CHINA)
Regio- and Diastereoselective Nickel-Catalyzed Allylation of Aromatic Aldehydes with α -Halo- β,β -difluoropropene Derivatives
J. Org. Chem. **2012**, *77*, 8696–8704.

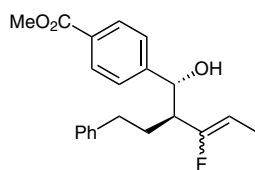
Nickel-Catalyzed Synthesis of γ -Fluorinated Homoallylic Alcohols



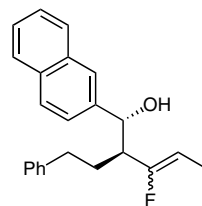
Selected examples:



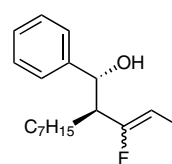
X = I, 60% yield, dr = 8:1



X = Br, 54% yield, dr = 3.5:1

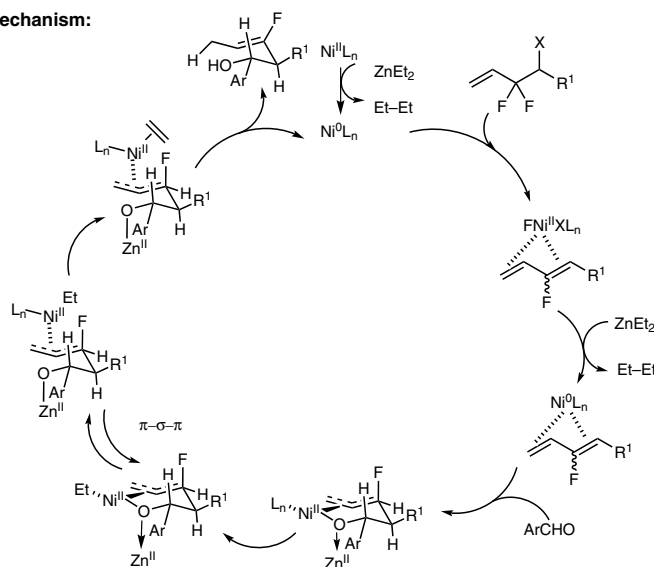


X = Br, 66% yield, dr = 11:1



X = Br, 56% yield, dr = 8:1

Proposed mechanism:



Significance: Functionalized fluoro olefins have been synthetic targets due to the ability of fluorine to alter the biological activity of organic compounds. In response to the high demand of fluorinated olefins, the authors developed a nickel-catalyzed reductive coupling of fluorinated dienes and carbonyl compounds to synthesize fluoro olefinic alcohols.

Comment: Both electron-rich and electron-deficient aromatic aldehydes undergo allylation, albeit with lower regioselectivity for electron-deficient aldehydes. The authors rationalize the *Z/E*-selectivity by the coordination ability of the aldehyde to ZnCl_2 : for electron-rich aldehydes, the coupling reaction proceeds faster than diene isomerization, and the *Z/E*-ratio remains unchanged in the product.

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