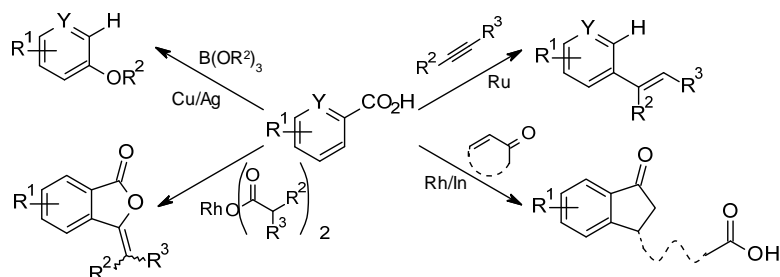


CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION

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Carboxylic acids are versatile substrates for catalytic C-C and C-X bond formations.^[1] A new concept is the use of carboxylates as deciduous directing groups, which stay in place just long enough to direct a C-H functionalization reaction into a specific position and are shed tracelessly as soon as the new C-C or C-heteroatom bond has formed.



In the carboxylate-directed, Ag/Cu-catalyzed C-H alkoxylation,^[2] an alkoxide group is introduced selectively in the ortho position of aromatic carboxylates. The new substituent destabilizes the C-COOH bond to an extent that swift protodecarboxylation occurs, precluding further substitution of the second ortho-C-H bond. A similar reaction concept is utilized in a Ru-catalyzed decarboxylative hydroarylation of alkynes with formation of vinyl arenes^[3] and a regiospecific synthesis of 1,1-disubstituted alkenes from α,β-unsaturated carboxylic acids.^[4] In the presence of a Rh/In catalyst, benzoic acids react with α,β-unsaturated ketones with formation of two new C-C bonds along with the selective cleavage of non-activated C-H, CO-OH and C-COR bonds to give indanones.^[5]

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