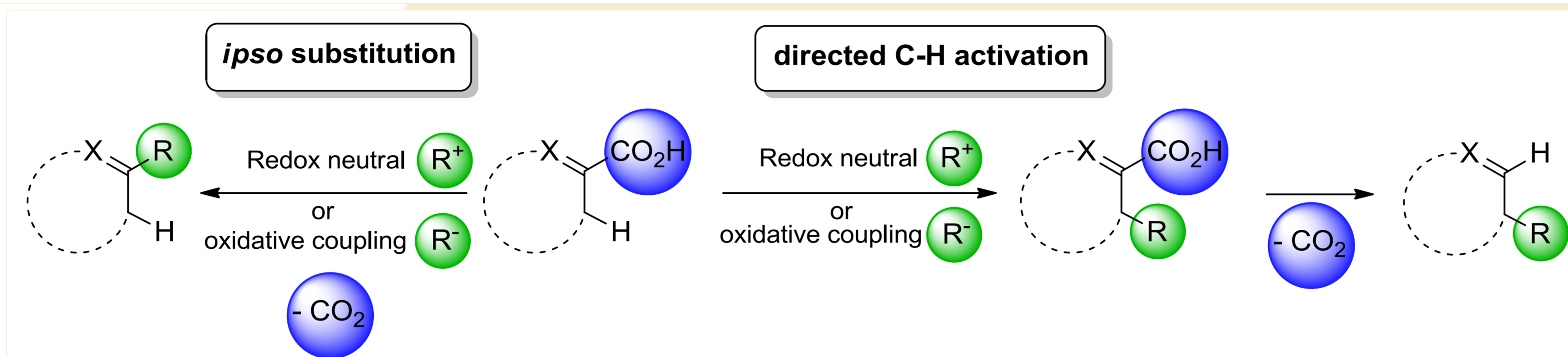


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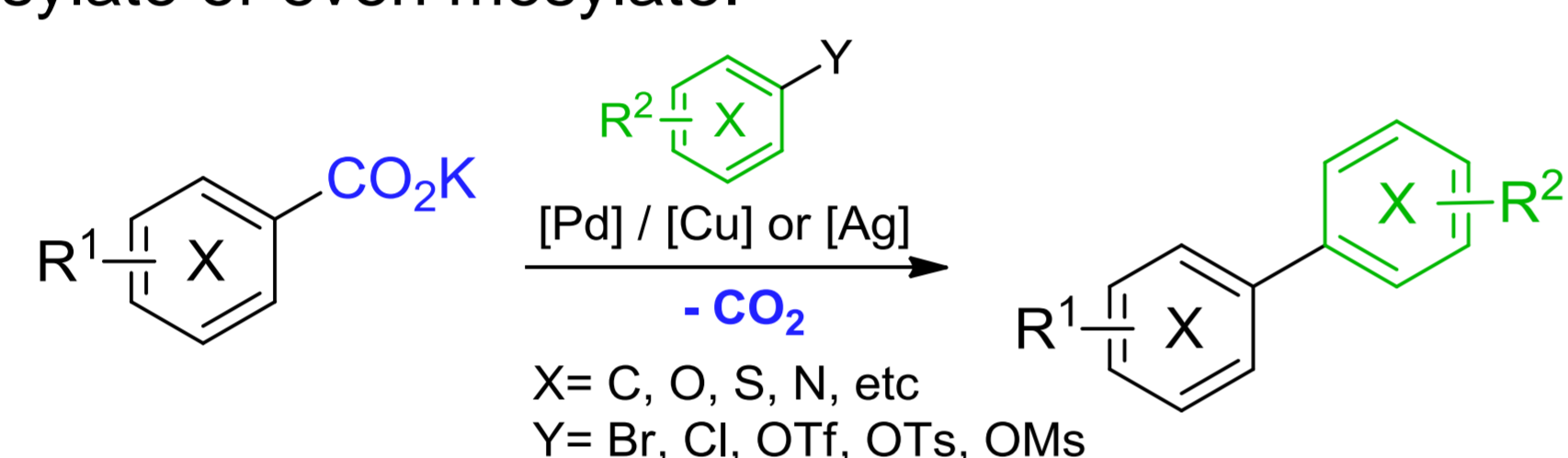
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Abstract: In Goossen's group, carboxylic acid groups are used as functional group for coupling reactions. Decarboxylative coupling reactions in which carboxylate groups are cleaved and in their place, new carbon-carbon or carbon-heteroatom bonds are formed, have recently emerged as a powerful synthetic strategy.^[1] Various decarboxylative cross-couplings have been disclosed that allow e.g. the synthesis of biaryls, vinyl arenes, aryl ketones, azomethines and aryl ethers. Moreover, the carboxylic acid can be used also as directing group to activate C-H bonds in *ortho*-position and can be removed easily by protodecarboxylation. This strategy has been applied for the synthesis of ketones and aryl ethers.

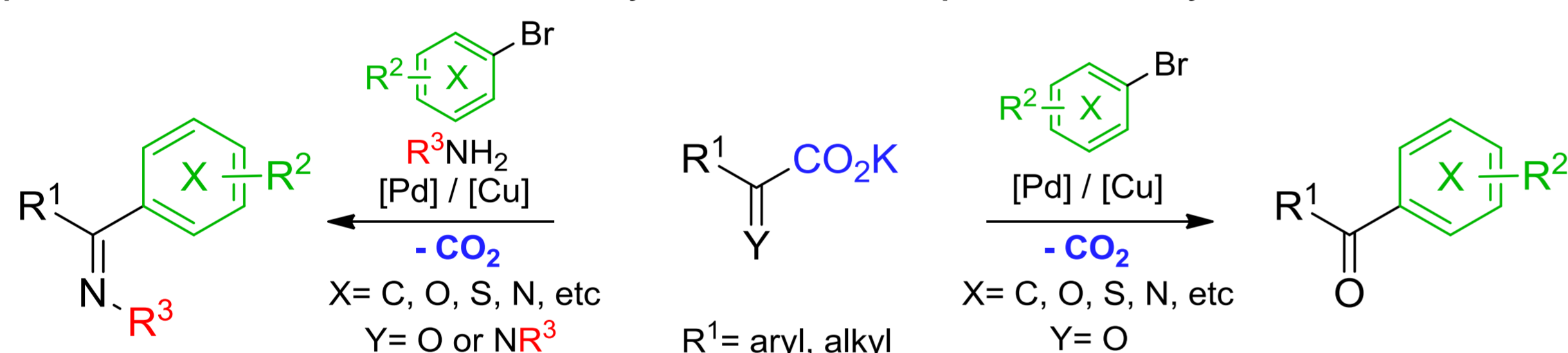


ipso- Substitution of the carboxylate group

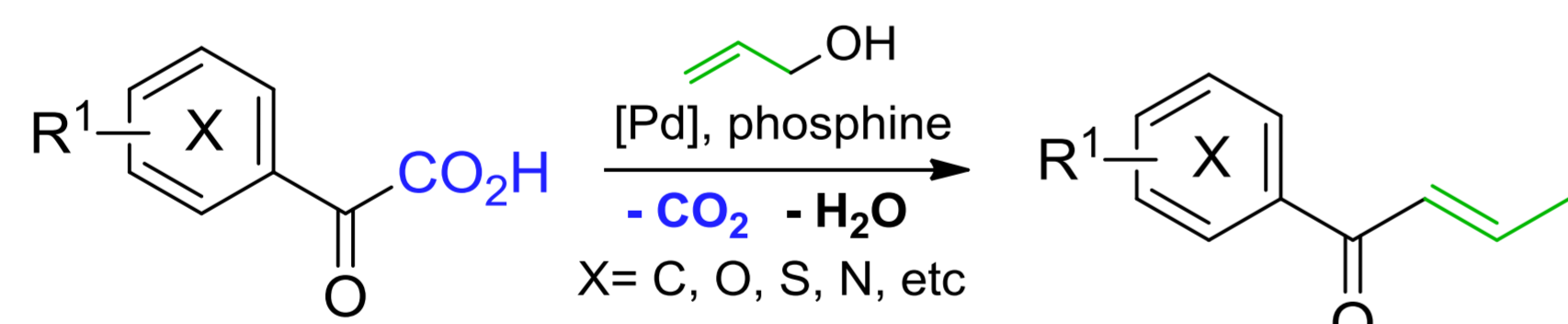
Synthesis of biaryls: A bimetallic system consisting of a copper or silver decarboxylative catalyst and a palladium cross-coupling catalyst are employed and allows the synthesis of biaryls starting from carboxylate salts using several electrophiles such as aryl bromide, chloride, triflate, tosylate or even mesylate.^[2]



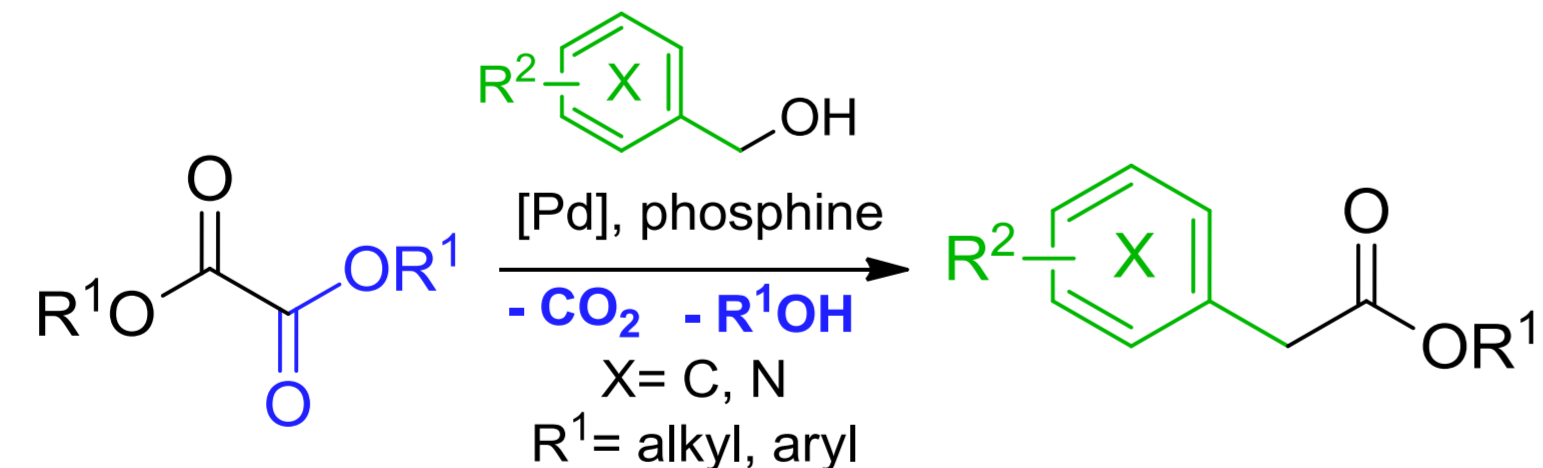
Synthesis of aryl ketones and azomethines: In a presence of modified bimetallic palladium / copper catalyst, the synthesis of aryl ketones and azomethines starting from α -oxocarboxylates or the corresponding imines are performed. In the reaction, an acyl anion equivalent formed *via* decarboxylation are coupled with aryl bromides.^[3]



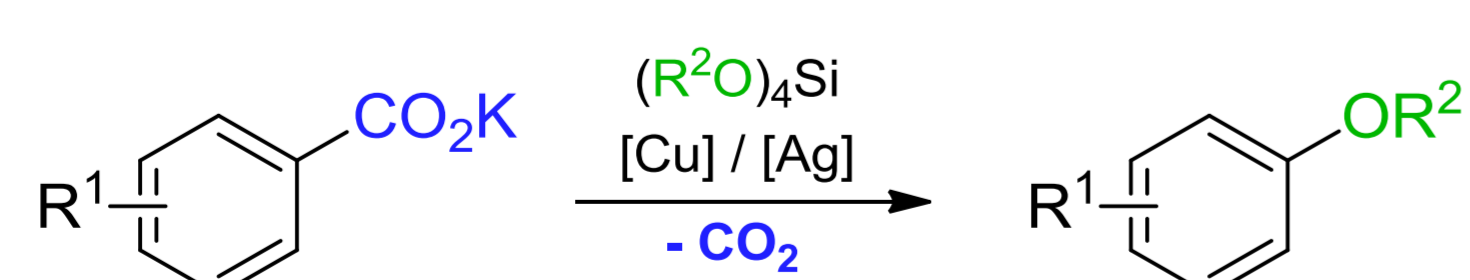
Synthesis of α,β -unsaturated aryl ketones: The decarboxylation of α -oxocarboxylic acids are also combined with an allylation reaction leading to the corresponding α,β -unsaturated ketones. The reaction proceeds *via in situ* esterification with the release of water and the subsequent decarboxylative allylation followed by isomerisation.^[4]



Synthesis of aryl acetates: Aryl acetates can also be synthesized from oxalates and various benzyl alcohols. After an *in situ* transesterification, the corresponding α -aryl ester are formed *via* decarboxylative coupling.^[5]

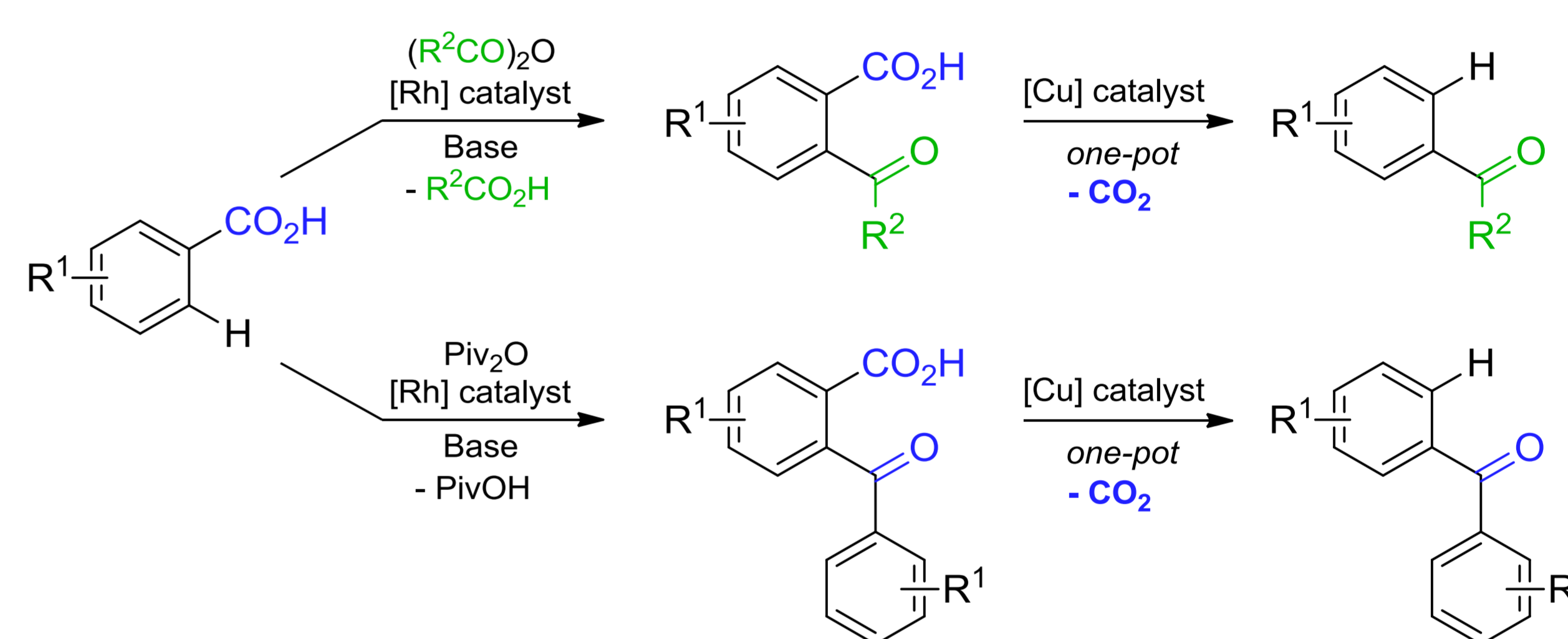


Synthesis of aryl ethers: In the presence of a bimetallic catalyst system consisting of silver as the decarboxylation catalyst and copper(II) as the cross-coupling catalyst *ortho*-substituted aromatic carboxylates undergo decarboxylative *ipso*-etherification with tetraalkoxysilane.^[6]

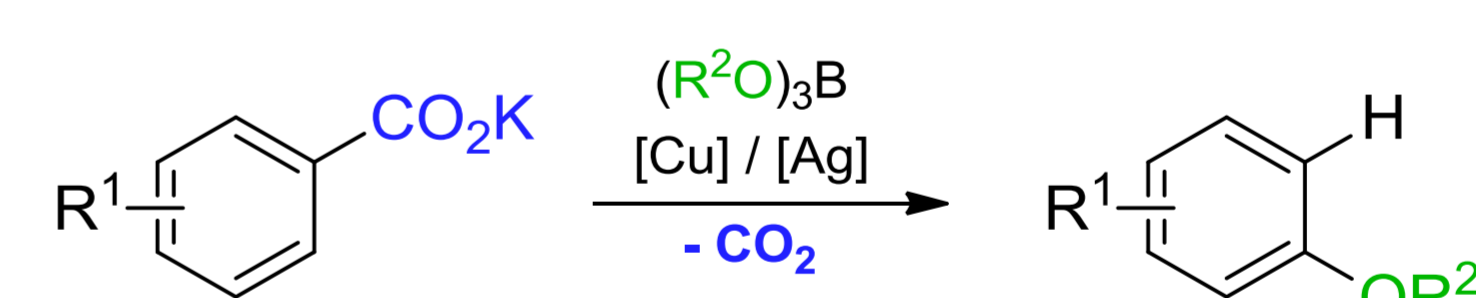


Carboxylate directed C-H activation

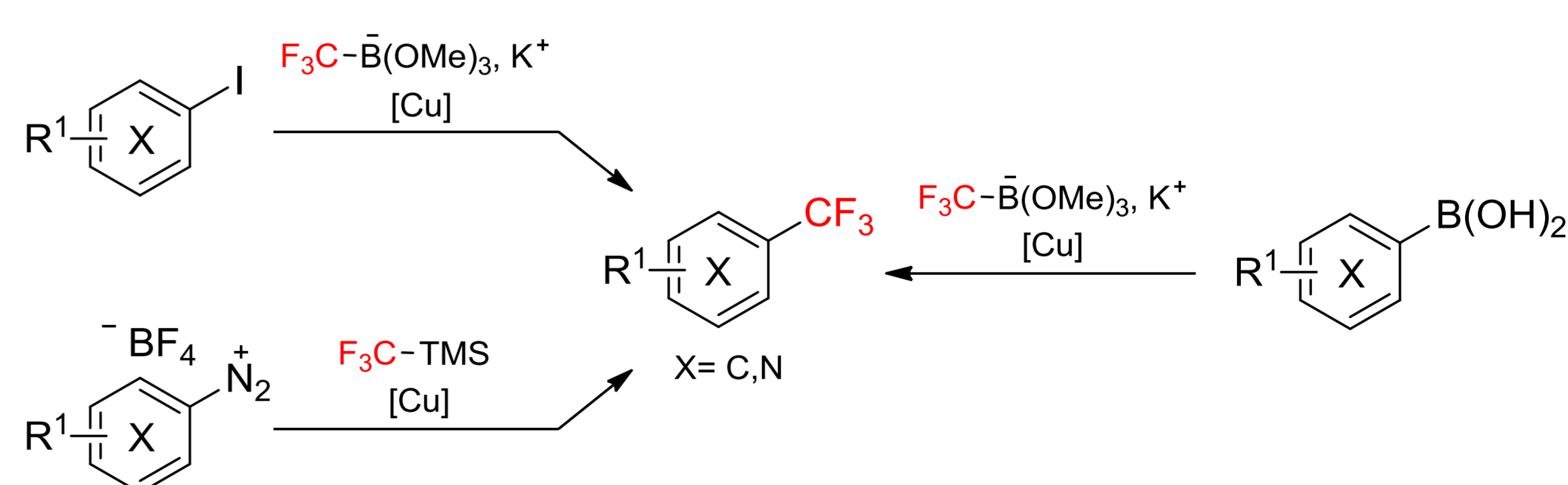
Synthesis of aryl ketones and *ortho*-acylbenzoic acids: The acylation of carboxylic acid can be performed using a rhodium catalyst in combination with an anhydride as acylating agent leading to the formation of *ortho*-acylbenzoic acids. The carboxylic acid group can also be removed later on *via* copper-catalyzed protodecarboxylation in one-pot, affording the corresponding ketones.^[7]



Synthesis of alkyl aryl ethers: In the presence of a modified copper/silver bimetallic system, benzoates with a low tendency to extrude carbon dioxide undergo *ortho*-C-H-alkoxylation with concomitant loss of the carboxylate directing group in a protodecarboxylation step. Thus, the alkoxy group is installed in the *ortho* rather than the *ipso* position of the former carboxylate directing group.^[8]



Synthesis of benzotrifluorides: The air-stable trifluoromethylated agent $K^+[CF_3B(OMe)_3]^-$ allows the trifluoromethylation of aryl iodides in a redox neutral process or of boronic acids in an oxidative process in presence of copper. Diazonium salts can also be used as starting materials in a Sandmeyer type reaction.^[9]



Literature and further reading (see also www.chemie.uni-kl.de/goossen)

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