σ C–O BOND CLEAVAGE AND PROTODECARBOXYLATION OF FORMATES

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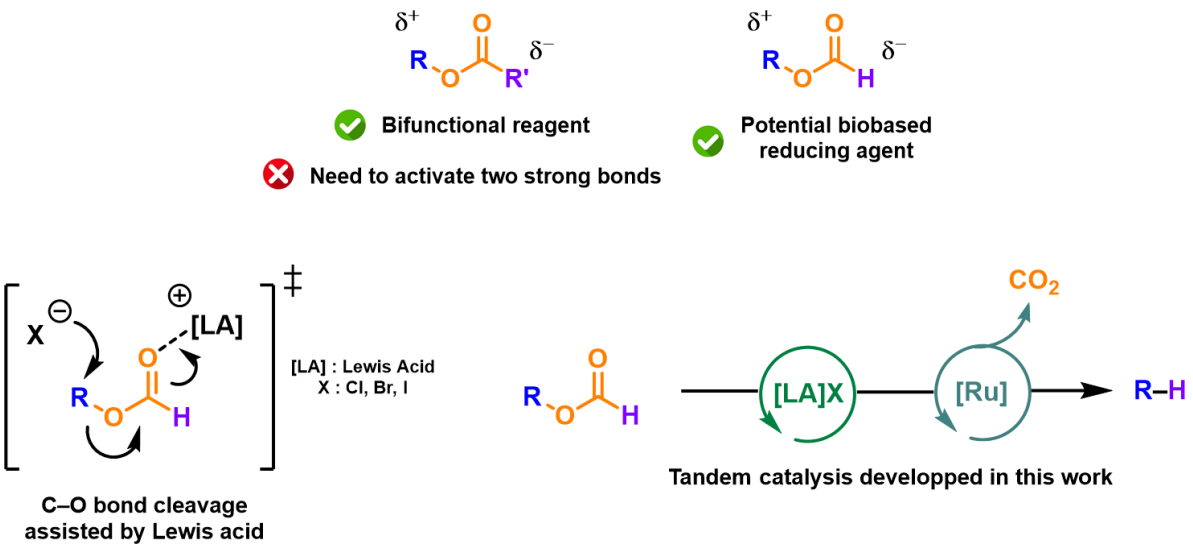
The mitigation of climate change and the transition from petroleum feedstock to biorenewable carbon sources is challenging for academia and industry. This is partly because of the oxidation state, due to the high number of O atoms, and functionalization differences in petroleum and bio-based carbon. Thus, to accomplish this change of paradigm, chemists need to find new catalytic systems able to cleave σ C–O bonds and defunctionalize biomass to unlock its use as starting material.[1,2]

Esters can be readily available or synthesized from biomass. From a reactivity point of view, they are interesting compounds as they can be considered, upon CO_2 extrusion, as bifunctional reagents with both a nucleophilic and an electrophilic moiety. However, such use is currently restricted to allyl and benzyl esters bearing an activated C–O bond.[3,4,5]

To expand the scope of this strategy to alkyl esters, the activation of their strong σ C–O bond is critical. In this work, we demonstrate that catalytic Lewis acidic salts enable this strategic cleavage and are compatible with organometallic catalysts, able to perform the subsequent decarboxylation. This tandem catalysis unlocks the decarboxylative recombination of formate esters, thereby providing a deoxygenation pathway of alcohols to alcanes, using formic acid as reducing agent.



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