Palladium-Catalyzed Long-Range Deconjugative Isomerization of Highly Substituted α,β-Unsaturated Carbonyl Compounds

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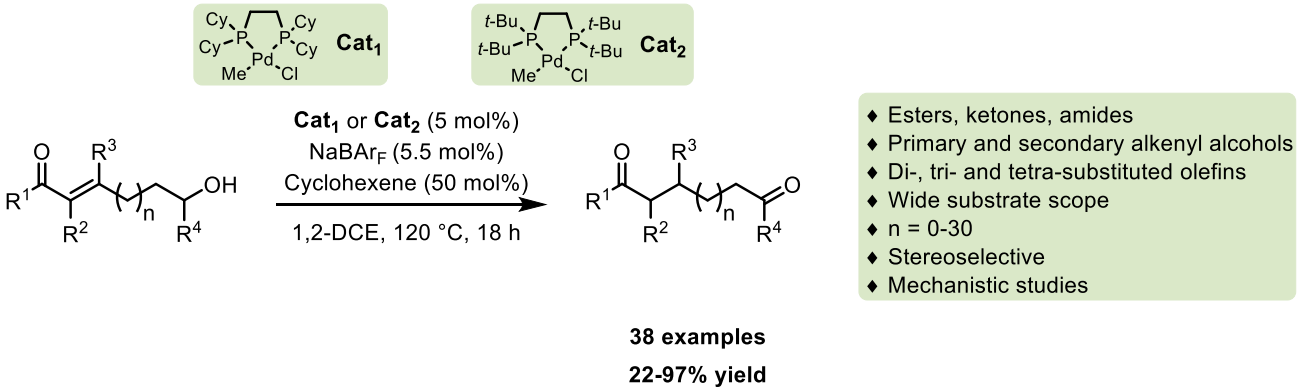
The long range isomerization/refunctionalization of olefins has emerged as an effective method for the construction of functionalized molecules starting from readily available precursors. This redox neutral methodology relies mostly on the use of transition metal complexes, with the economic and environmental advantage to avoid the formation of stoichiometric waste.[1] However, the main challenges for the successful development of such processes are (i) the difficult coordination of highly substituted (prochiral) olefins with metal catalysts,[2] severely narrowing the scope of these methodologies, and (ii) the control of the regioselectivity of metal hydride insertion across the C=C bond.[3]

Building on previous studies in our group,[4] we report herein the application of two Pd catalysts to the deconjugation, isomerization and refunctionalization of α,β-unsaturated carbonyls in good to high yields. Our system successfully isomerizes di-, tri- and tetra-substituted olefins to highly valuable aldehydes and ketones regardless the chain length (up to 38 examples). We also conducted mechanistic studies in order to understand the factors that govern such reaction. Preliminary results of the asymmetric variant of the reaction will also be presented.



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