

## Catalytic hydrogenation of mono-carboxylic acid using iridium complexes and its application to di-carboxylic acids

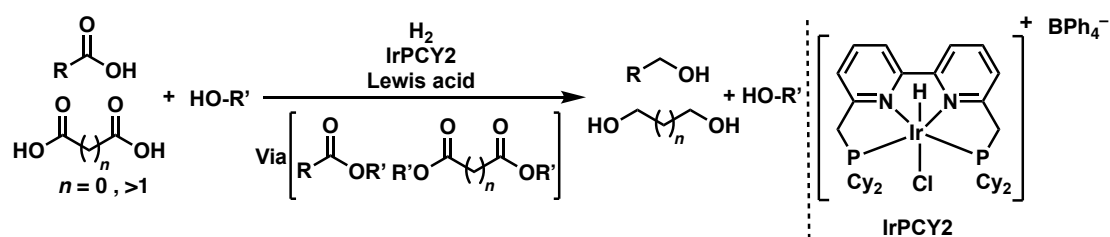
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Catalytic hydrogenation of carboxylic acids to alcohols by hydrogen gas represents a green method to cheaply obtain platform chemicals from biomass. In recent years, several systems have been reported for this transformation, but the selectivity and substrate scope of the current systems have been unsatisfactory<sup>1</sup>. In particular, hydrogenation of di-carboxylic acids is scarcely reported, due to the amount of side reactions that can occur. The selective transformation of dicarboxylic acids to diols represents a green method to obtain important polymer precursors and platform chemicals and thus warrants further research. In particular, the hydrogenation of oxalic- and glycolic acid to yield ethylene glycol is highly sought after.

Our group has in the past years been developing a novel structurally robust PNNP-Ir catalyst, IrPCY2, for hydrogenation of lactones and esters that maintains its functionality in the presence of a wide range of functional groups and additives<sup>2</sup>. Herein, we show that IrPCY2 in the presence of a simple Lewis acid additive can catalyze the one-pot esterification and hydrogenation of a wide range of mono- and di-carboxylic acids, giving desired alcohols in high to quantitative selectivity at low catalyst loadings. The developed system is highly effective for a plethora of industrial relevant substrates, including long-chained dicarboxylic acids, oxalic acid and glycolic acid, all of which has never before been reported using a homogeneous system. Kinetic studies in conjunction with electron spray ionization measurements elucidates a plausible reaction mechanism, and clarifies why the interplay between IrPCY2 and Lewis acid additive was found to be essential for obtaining high reactivity.



1) Selected examples: a) T. J. Korstanje, J. I. van der Vlugt, C. J. Elsevier, B. de Bruin, *Science* **2015**, 350, 298. b) J. Ullrich, B. Breit, *ACS Catal.* **2018**, 8, 785. c) M. Naruto, S. Saito, *Nat. Commun.* **2015**, 6, 8140. d) M. Naruto, S. Agrawal, K. Toda, S. Saito, *Sci. Rep.* **2017**, 7, 3425. e) S. Yoshioka, S. Saito, *Chem. Commun.* **2018**, 54, 13319. f) A. Saito, S. Yoshioka, M. Naruto, S. Saito, *Adv. Synth. Catal.* **2019**, 362, 424. 2) S. Yoshioka, S. Nimura, M. Naruto, S. Saito, *Science Advances* **2020**, 6, 43