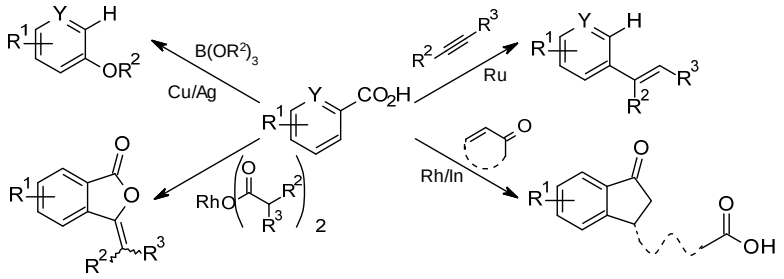
CARBOXYLATES AS DIRECTING AND LEAVING GROUPS IN CATALYTIC BOND FORMATION

Lukas J. Gooßen, G. Zhang, A. Biafora, L. Huang, Y. Gao

Ruhr-Universität Bochum, Lehrstuhl für Organische Chemie I, Bochum, Germany
lukas.goossen@rub.de

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]

[1] M. Pichette Drapeau, J. Bahri, D. Lichte, L. J. Gooßen, *Angew. Chem.* **2019**, *58*, 892-896.

[2] S. Bhadra, W. Dzik, L. J. Gooßen, *Angew. Chem. Int. Ed*. **2013**, *52*, 2959–2962.

[3] a) L. Huang, A. Biafora, G. Zhang, V. Bragoni, L. J. Gooßen, *Angew. Chem. Int. Ed*. **2016**, *55*, 6933–6937.

[4] a) J. Tang, D. Hackenberger, L. J. Gooßen, *Angew. Chem. Int. Ed*. **2016,** *55,* 11296–11299; b) Y. Gao, Y. Ou, L. J. Gooßen, *Chem. Eur. J.,* **2019**, doi: 10.1002/chem.201902022.

[5] G. Zhang, Z. Hu, F. Belitz, Y. Ou, N. Pirkl, L. J. Gooßen, *Angew. Chem. Int. Ed*. **2019**, *58*, 6435-6439.