IRON CATALYZED SUZUKI CROSS COUPLING

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Iron-catalyzed cross-coupling reactions have become a valuable method for C-C bond formation in recent years. However, reactivity patterns and mechanisms are not yet fully understood, which means that other and hitherto unknown manipulations of the catalysis activity by substrate effects are to be expected.[1,2]

The iron catalyzed Suzuki biaryl couplings remained problematic in several publications[3] and to best of our knowledge there is only one known example of the Bedford group.[4]

Fig. 1 shows the studied iron-catalyzed sp^2-sp^2 suzuki cross-coupling. Here, C=X (X = C, N, O) acts as the directing group for the incorporation of the of borinate at the position of the leaving group Y (Y = Hal, OMe). In contrast to the previous work,[4] this reaction proceeds under mild reaction conditions, with a small excess of the borinate and without the use of additives. Crucial appears to be a pre-coordination of the iron catalyst to the carbonyl donor function (ketone, imines, pyridine, etc.), leading to a dramatic acceleration of the elementary steps of the cross-coupling (oxidative addition, transmetallation, reductive elimination), while the thermodynamically favored direct addition of the organometallic species to the electrophilic carbonyl derivative function is suppressed. As a result, a broad substrate scope with a high functional group tolerance is achieved.

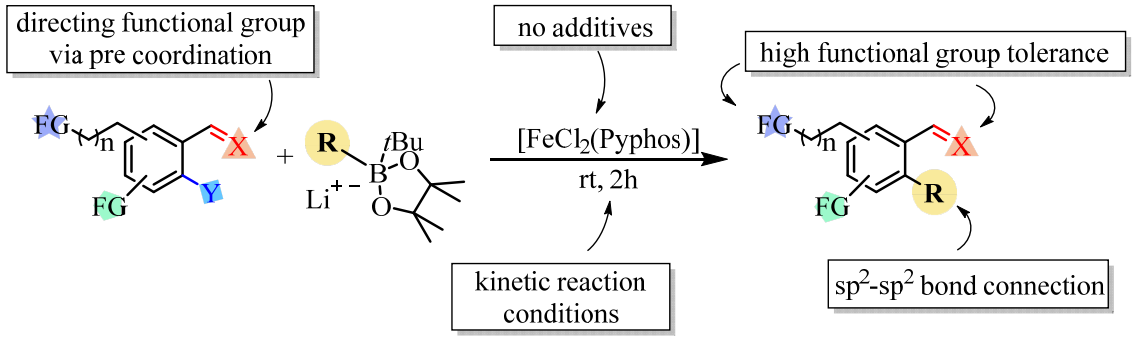

Figure 1: reaction equation of the studied iron-catalyzed sp^2-sp^2 suzuki cross-coupling

[1] Bedford, R*. *Acc. Chem. Res.* **2015**, 48, 5, 1485–1493.

[2] Wu, G., Jacobi von Wangelin*, A. *Nat Catal* **2018**, **1**, 377–378.

[3] a) Crockett M. et al., Angew. Chem. Int. Ed. 2020, 59, 5392 –5397; b) Iwamoto T. et al. Chem. Commun., 2019, 55, 1128-1131; c) Daifuku S. et al. J. Am. Chem. Soc. 2015, 137, 11432−11444; d) Bedford et al. Synthesis 2015, 47, 1761–1765 and more

[4] O'Brien, H., Manzotti M., Abrams R., Elorriaga D., Sparkes H., Davis S., Bedford R.*, *Nat Catal* **2018**, 1, 429–437.