

Transition Metal-free Catalytic C-C Cross -coupling at Room Temperature

C-C cross-coupling reactions have been dominated by the Pd-based catalysis and such catalysis has been earlier recognized with Nobel prize in 2010 because of its various industrial applications. However, the use of heavy, rare and expensive Pd-based catalysts was one of the drawbacks of such reactions and recently there are several alternative attempts using earth-abundant transition metal based catalysts. One of the partners in such coupling reactions is aryl halide which is activated in the first step of catalytic cycle by metal based oxidative addition reaction. Accomplishing such a process without transition metals is extremely challenging.

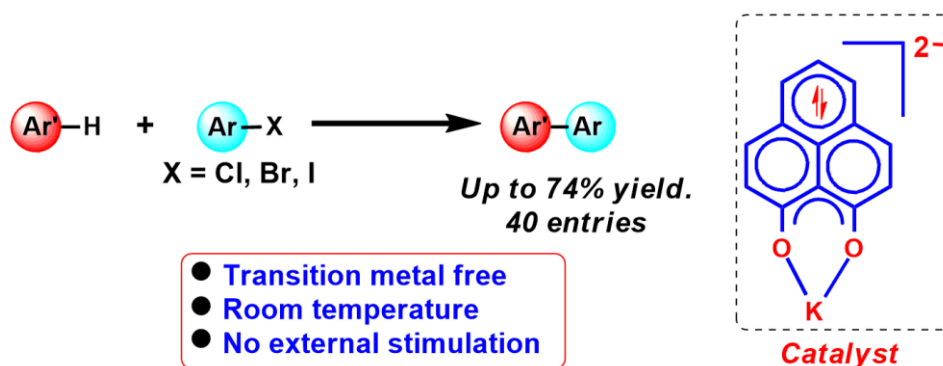


Figure 1: Transition metal-free catalytic aryl halides activation at room temperature accomplishing C-C cross-coupling reactions.

This work establishes a new strategy of aryl halide activation towards direct C-H arylation of arenes and heteroarenes under transition metal-free and ambient conditions (Figure 1). A phenalenyl based catalyst was chemically tuned to a super electron donor by double chemical reduction converting gradually a 12π electrons species to a 14π electrons species. The strategy utilizes the non-bonding molecular orbital of the phenalenyl, which can take up two electrons without significantly compromising the aromaticity. After consecutive acceptance of electrons, it accumulates the energy sufficiently high for promoting a single electron transfer process to the LUMO of aryl halides. Such electron transfer to aryl halide prompts its activation, generating a highly reactive aryl radical, which further reacts with arenes/heteroarenes. Such a method does not require constant supply of electrons (through cathodic reduction or chemical reduction) or light irradiation and works under ambient conditions.

Ref: J. Ahmed, P. Datta, A. Das, S. Jomy, S. K Mandal, *Chem. Sci.*, **2021**, *Advanced Article*, DOI: 10.1039/d0sc05972b.