

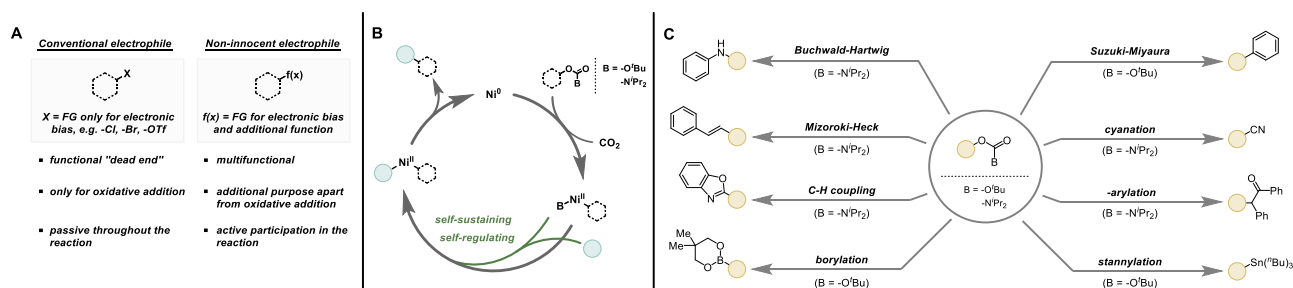
## Non-innocent electrophiles unlock exogenous base-free coupling reactions

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Electrophiles are key parts in countless catalytic reactions and serve almost exclusively two general purposes through their functional group (FG): first, locating the bond-forming site at the corresponding substrate and second, providing the electronic bias for the initiation of the catalytic cycle. Apart from that, such conventional electrophiles (CE) are passive throughout the reaction rendering the functional group and the corresponding prior synthetic efforts to install it highly sacrificial. This work<sup>[1]</sup> introduces the concept of non-innocent electrophiles (NIE), a class of multifunctional electrophiles endowed with a functionality which actively participates in the reaction after oxidative addition (Fig. 1A). This concept was used as a platform for the development of exogenous base-free coupling reactions (Fig. 1B). Considered an inherent requisite for catalytic turnover in numerous transition metal catalyzed couplings, the use of stoichiometric bases simultaneously affects this class of reactions by limiting the accessible chemical space, generating additional waste, and oftentimes rendering reaction conditions heterogeneous thereby restricting the application of emerging technologies such as flow chemistry or high-throughput experimentation. Therefore, a general approach that eludes the need for exogenous bases in coupling reactions would be beneficial in various aspects.



**Figure 1** Graphic summary. **A:** Comparison of CEs and NIEs. **B:** Blueprint for exogenous base-free coupling reactions via NIEs. **C:** Developed exogenous base-free coupling reactions based on NIEs.

In summary, the study confirmed the hypothesis and diisopropylcarbamates as well as *tert*-butyl carbonates were found to release a competent base after oxidative addition. Notably, this catalytic release mechanism generates the base on-demand, establishing self-sustaining catalytic systems with intrinsic self-regulation and efficiently overrides the deleterious effects caused by the use of an exogenous base. As a result, multiple coupling reactions (8 distinct reactions) which traditionally rely on the addition of stoichiometric base could be turned into exogenous base-free, homogeneous processes, that were compatible with base-sensitive functional groups (Fig. 1C). Importantly, C–H/C–O coupling scenarios proved feasible representing a promising avenue for sustainable catalysis.

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