# Carbocations and alkyl radicals as complementary building blocks in reactions with nucleophiles and electrophiles

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Carbocations and alkyl radicals represent some of the most important reactive intermediates in organic synthesis. Due to their high reactivity, reactions typically employ appropriately stabilized derivatives, which facilitates their generation and improves selectivity. Notably, both species are stabilized by the same types of substituents—typically alkyl, aryl, or heteroatom-containing groups—resulting in common structural motifs. The key distinction between them lies in their philicity: carbocations exhibit strong electrophilic character, whereas stabilized alkyl radicals, bearing electron-donating substituents, behave as nucleophiles. Theoretically, the same molecular scaffold can be functionally diversified by introducing fragments of opposite philicity, provided by the suitable reaction conditions. **The objective of my work was to develop synthetically valuable transformations involving either stabilized carbocations or alkyl radicals.**

In the first part of the study, I focused on developing a new method for the ring-opening of donor–acceptor cyclopropanes by reversing their standard reactivity. These strained molecules are commonly used in the synthesis of biologically active compounds. The application of vitamin $B_{12}$ (or its derivatives) catalysis enabled the generation of a carbon-centered radical at the donor-substituted position, initially bearing a partial positive charge. It then reacted with electrophilic olefins, followed by reduction to afford classical saturated addition products. The mild reaction conditions were compatible with a wide range of electron-accepting groups and heteroaromatic systems. Importantly, the nature of the ligands on the cobalt catalyst was found to significantly influence the reaction outcome.

Subsequent efforts were directed at developing a selective diazotization protocol for aliphatic amines. Although this reaction was discovered nearly 150 years ago, it has remained largely confined to the functionalization of aromatic compounds. Its efficient application also for aliphatic amines would make them an important precursor of carbocations. The key breakthrough was the use of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) as the reaction medium. Its unique properties enabled both a more selective diazotization step and acid-promoted conversion of intermediates into the desired products. This strategy afforded approximately 70 distinct products in high yields, including Friedel–Crafts-type alkylation of arenes, as well as transformations of the amine group into chloro, bromo, or carboxylic acid functionalities. Beyond addressing a longstanding synthetic challenge, the process offers good atom economy, uses amines without prefunctionalization, and proceeds under operationally simple, air- and moisture-tolerant conditions without the need for complex equipment.