Theoretical analysis and reactivity of fluorinated radicals

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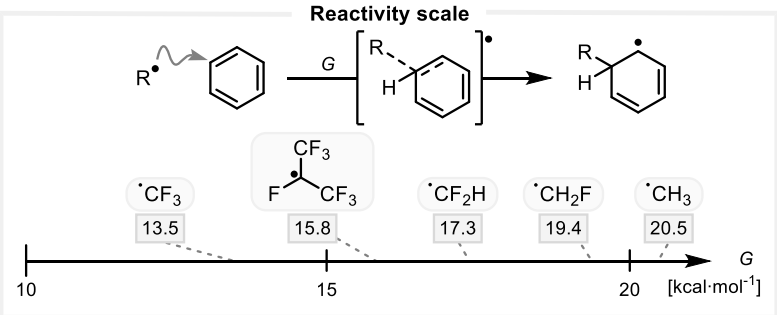
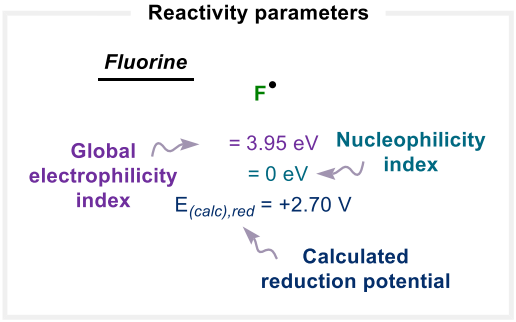
The ability of fluorine atom to alter the properties of a compound at the molecular or macromolecular level is overwhelming. Indeed, insertion of a single fluorine atom nearby a reactive center can have major impact on the chemical reactivity or the properties of a species. For this reason, installation of fluorine atoms and fluorinated motifs onto molecules has become an important synthetic endeavour. Nowadays, a powerful method to facilitate this challenge relies on the design of fluorinated Functional Group Transfer Reagents (FGTRs) which are capable of releasing the desired fluorinated radical upon activation with various stimuli (*e.g.* heat, light, electricity). The influence of the fluorine substitution on radical species was thoroughly investigated and documented by W. R. Dolbier.[1] To help in the design of new chemical transformations involving fluorinated radicals, we have developed a reactivity scale for over 40 radicals based on the calculated energy barriers for their addition to benzene.[2] Other relevant reactivity parameters have been obtained (*e.g.* electrophilicity, nucleophilicity, redox potential) to provide a broader picture of a radical's possible preference or incompatibilities vis-à-vis a given class of reaction partners. We hope that this analysis will stimulate the design of original FGTRs and novel transformations.





[1] W. R. Dolbier, in *Fluorinated free radicals* (Ed.: R. D. Chambers), Springer, Berlin, **1997**, pp. 97.
[2] A. J. Fernandes, R. Giri, K. N. Houk, D. Katayev, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318377.