

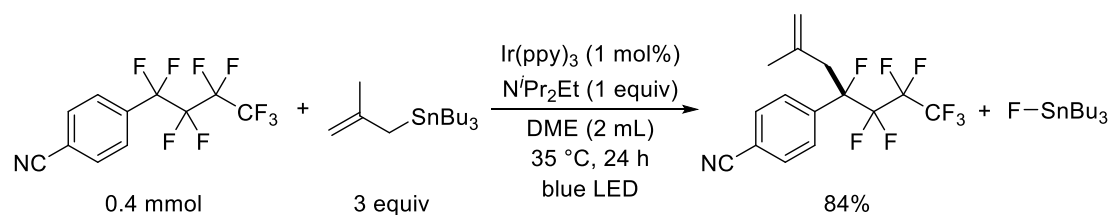
## Photoredox-Catalyzed C–F Bond Transformation at the Benzylic Position in Perfluoroalkyl Arenes

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**Keywords:** Photoredox Catalyst; C–F Bond Transformation; Perfluoroalkyl Compound; Organostannane; Radical Reaction

Various organofluorine compounds play an important role in pharmaceutical, agrochemical and electronic material sciences. Fluorine group affects the structural and physicochemical properties owing to the electronegativity of fluorine atom. In particular, perfluoroalkyl compounds have attracted great interest because polyfluoroalkyl moieties dramatically enhance thermal stability and provide novel surface effect toward surfactants and lubricants. Hence, many types of perfluoroalkylation have been developed. However, there are few methods to transform C–F bond in perfluoroalkyl group selectively. Therefore, the establishment of C–F bond transformation of readily-available perfluoroalkyl compounds is highly desired for preparing various functionalized fluorinated compounds. There are two examples to transform C–F bond in  $C_2F_5$  group via two electron reduction.<sup>1</sup> However, these methods have narrow substrate scope due to highly reactive carbanion intermediates. We envisioned that utilization of a radical intermediate via single electron reduction enabled to transform C–F bond in various perfluoroalkyl moieties.

The reaction of *p*-(nonafluorobutyl)benzonitrile with methallyltributyltin proceeded in the presence of  $Ir(ppy)_3$  and *N,N*-diisopropylethylamine under blue LED irradiation for 24 h to afford the defluoroalkylated product in 84% yield. The C–F bond transformation exclusively occurred at the benzylic position. Formation of stable tin fluoride is a driving force in the reaction progress. Organostannanes act as fluoride ion scavenger and prevent reconstruction of C–F bond, and their high reactivity toward radicals allows the allylation of steric hindered perfluoroalkyl radical species.



(1) a) Y. Nakamura, K. Uneyama, *J. Org. Chem.* **2007**, 72, 5894-5897; b) Y. Yamauchi, K. Sakai, T. Fukuhara, S. Hara, H. Senboku, *Synthesis* **2009**, 20, 3375-3377