Selective Defluoroaminoxylation of Perfluoroalkylarenes by Organic Photoredox Catalysis

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Fluoroalkyl groups are often utilized in various field such as medicines and agrochemicals because its incorporation can drastically change the properties of biologically active small molecules. A number of methods have been reported for the efficient construction of perfluoroalkylated compounds. A selective transformation of carbon–fluorine (C–F) bond is a straightforward strategy for the synthesis of complicated multi-fluorinated compounds from perfluoroalkyl compounds.¹ Although perfluoroalkyl units are inert and difficult to transform selectively, we recently reported selective defluoroallylation of perfluoroalkylarenes using allylic stannanes by photoredox catalysis.² We envisioned that other radical acceptors also works well. Herein, we report selective defluoroaminoxylation of perfluoroalkylarenes by organic photoredox catalysis.

In the investigation for the reaction of perfluoroalkylarene 1a with TEMPO 2 in the presence of organic photoredox catalysts, photocatalyst 3 was found to be the most effective catalyst, which afforded aminoxylated product 4a. Transient-absorption spectroscopy studies disclosed dimethyl substituent in 3 played an important role in prolongation of excited triplet life time and that enable the reaction to proceed efficiently.



Further C–F bond transformation of aminoxylated product 4 was successful. The reaction of 4b with silyl enol ether 5 in the presence of $AlCl_3$ proceeded to afford fluorinated alcohol 6. This result showed a potential of 4 for precursors of various fluorinated alcohols.



1) Y. Nishimoto, N. Sugihara, M. Yasuda, Synthesis 2022, 2765.

2) N. Sugihara, K. Suzuki, Y. Nishimoto, M. Yasuda, J. Am. Chem. Soc. 2021, 143, 9308.