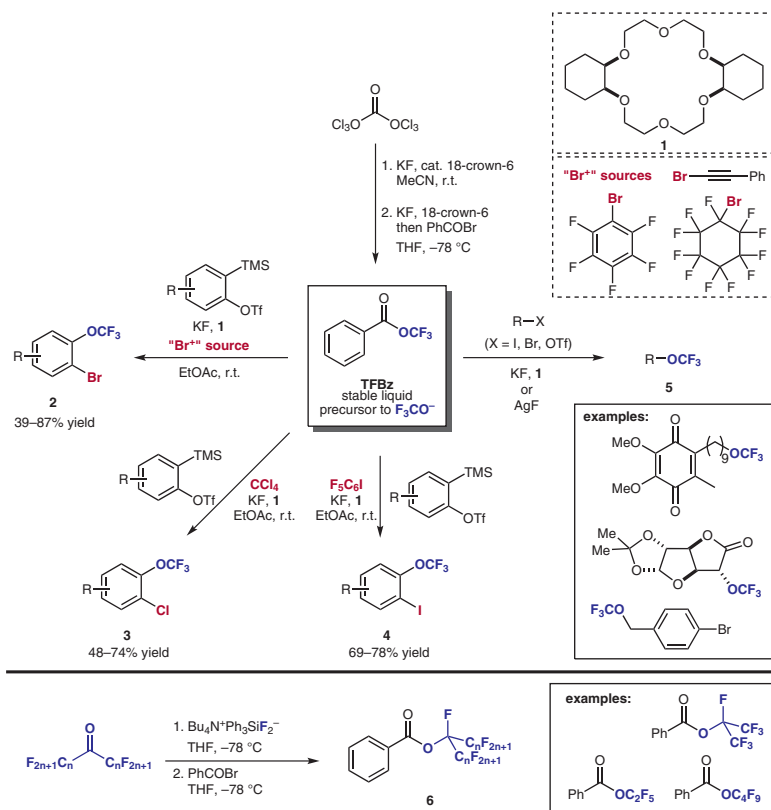


M. ZHOU, C. NI, Y. ZENG, J. HU* (SHANGHAI INSTITUTE OF ORGANIC CHEMISTRY,
P. R. OF CHINA)Trifluoromethyl Benzoate: A Versatile Trifluoromethoxylation Reagent
J. Am. Chem. Soc. **2018**, *140*, 6801–6805.

New Compounds Departing Trifluoromethoxylation Station



Significance: The strongly electron-withdrawing trifluoromethoxy group (OCF_3) has attracted increasing attention as a unique substituent in biologically active compounds and organic materials; however, synthetic methods for installing OCF_3 directly remain rare, due in part to the fact that many of the available sources of or precursors to the trifluoromethoxide anion (OCF_3^-) show limited stability or require specialized equipment for handling. Herein, the authors demonstrate the use of trifluoromethyl benzoate (TFBz) as a stable, liquid reagent for various direct trifluoromethoxylation reactions, acting as a precursor to OCF_3^- , which is generated in situ by treatment of TFBz with a fluoride salt.

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Comment: The use of TFBz was showcased in the trifluoromethoxylation-bromination of arynes. Crown ether **1** and KF were the best combination to generate both the aryne intermediate and OCF_3^- in situ, while several reagents could be employed as “Br⁺” sources to afford the trifluoromethoxylation-bromination products **2**. These conditions were successfully adapted to aryne trifluoromethoxylation-chlorination and trifluoromethoxylation-iodination (products **3** and **4**, respectively). Various reactions using TFBz were also surveyed, including the synthesis of alkyl trifluoromethoxides **5** from the corresponding alkyl halides or pseudo-halides. Finally, other perfluoroalkyl benzoate esters **6** were synthesized from the requisite perfluorinated carbonyl compounds and shown to undergo analogous reactivity to TFBz.