



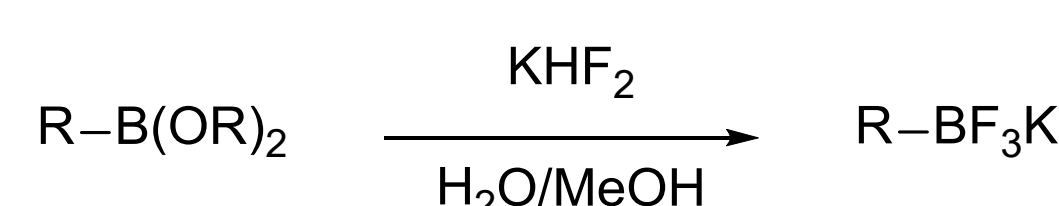
# Accessible Synthesis of Organofluorosilicates

Jarett M. Posz, Stephan Harruff, and Ryan Van Hoveln\*

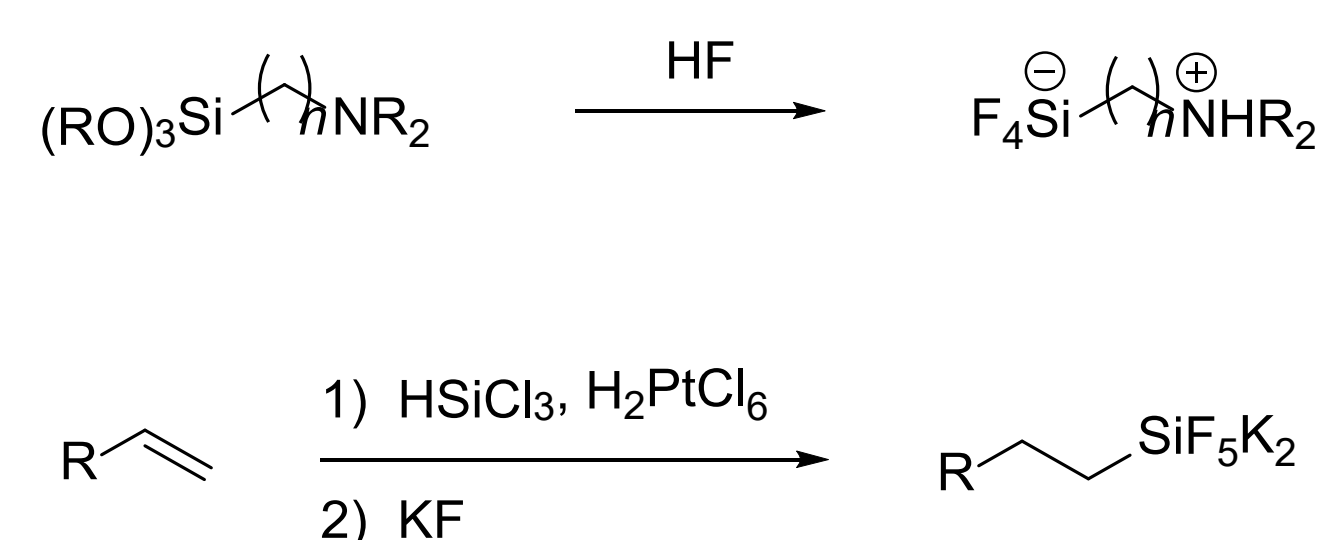
Department of Chemistry and Physics, Indiana State University, Terre Haute, IN 47809

## Introduction

Organotrifluoroborate salts have enjoyed substantial success over the past several years. This is, in part, due to their easy synthesis, high reactivity, and benchtop stability.<sup>1</sup>



However, the analogous synthesis of organotetrafluorosilicates has not been well developed. Organofluorosilicates have been prepared by treating alkoxy silanes with water-free hydrogen fluoride in ether solution<sup>2</sup> or by reacting organotrichlorosilanes with KF.<sup>3</sup> Both of these syntheses rely on starting materials that are not readily synthetically available and require the use of dangerous reagents such as HF.



Several research groups have reported on the synthetically useful electrophilic cleavage reactions of the carbon-silicon bond, however, organofluorosilicates have not received much attention in part due to their inaccessibility.<sup>3,4</sup> Currently, there is one report of using alkoxy silanes to make organofluorosilicates, but they do not report a yield and their procedure has not been reproducible in our hands.<sup>5</sup>

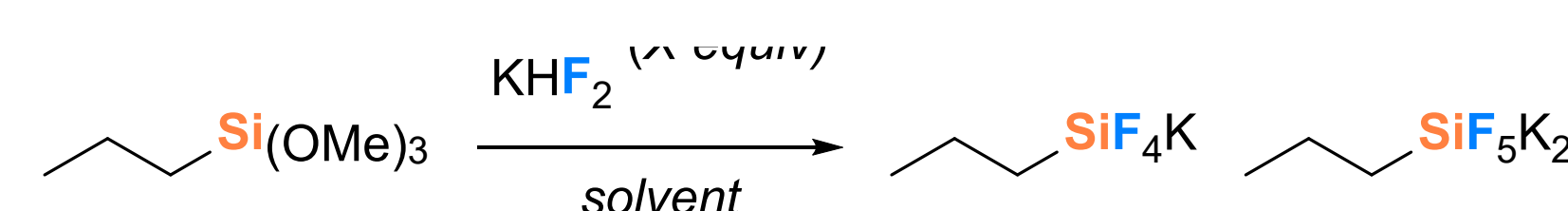
## Hypotheses

A procedure similar to the one used to make organotrifluoroborates, which uses KHF<sub>2</sub> instead of HF, will be able to effectively make the organotetrafluorosilicate.

## Objectives

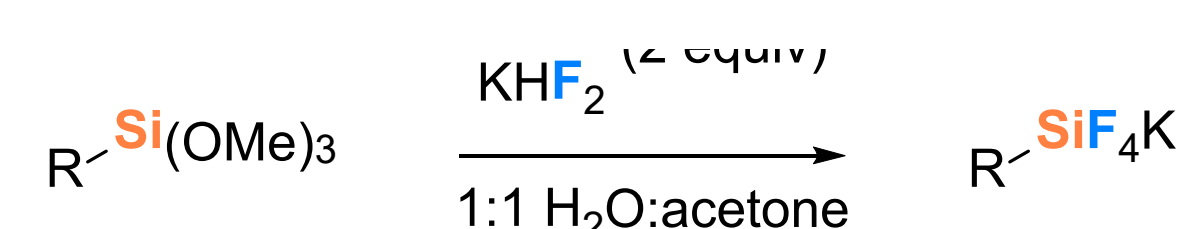
1. Optimize reaction conditions to form the tetrafluorosilicate in good yield.
2. Establish a substrate scope to demonstrate the functional group tolerance of the new method.
3. Use tetrafluorosilicate products in a variety of reactions to demonstrate their utility.

## Optimization of Reaction Conditions



| entry | solvent                      | equiv | tetraF              | pentaF |
|-------|------------------------------|-------|---------------------|--------|
| 1     | 1:1 H <sub>2</sub> O:MeOH    | 10    | mixture of products |        |
| 2     | 1:1 H <sub>2</sub> O:DMSO    | 2     | mixture of products |        |
| 3     | 1:1 H <sub>2</sub> O:acetone | 2     | 89%                 | 0      |
| 4     | 1:2 H <sub>2</sub> O:acetone | 2     | 86%                 | 0      |
| 5     | 1:5 H <sub>2</sub> O:acetone | 2     | 77%                 | 0      |
| 6     | 2:1 H <sub>2</sub> O:acetone | 2     | 51%                 | 0      |
| 7     | 5:1 H <sub>2</sub> O:acetone | 2     | 57%                 | 0      |

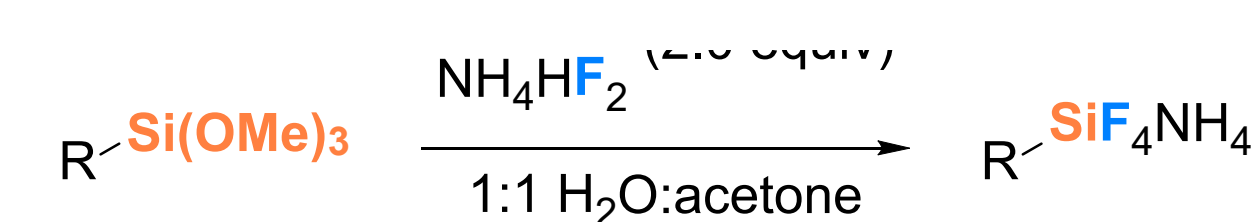
## Current Substrate Scope



| entry | substrate | yield                        |
|-------|-----------|------------------------------|
| 1     |           | 89%                          |
| 2     |           | 95%<br>(scale up to 15 mmol) |
| 3     |           | 86%                          |
| 4     |           | 75%                          |
| 5     |           | 96%                          |
| 6     |           | 77%                          |
| 7     |           | 77%                          |
| 8     |           | 78%                          |
| 9     |           | 95%                          |

The majority of the reactions were run on a 1.5 mmol scale. Yields represent isolated, dry yields. Notably, this reaction seems reasonably functional group tolerant, withstanding the presence of both an alkyl halide, epoxides, and esters, all of which could react with a fluoride nucleophile.

## Reactions with other Bifluorides

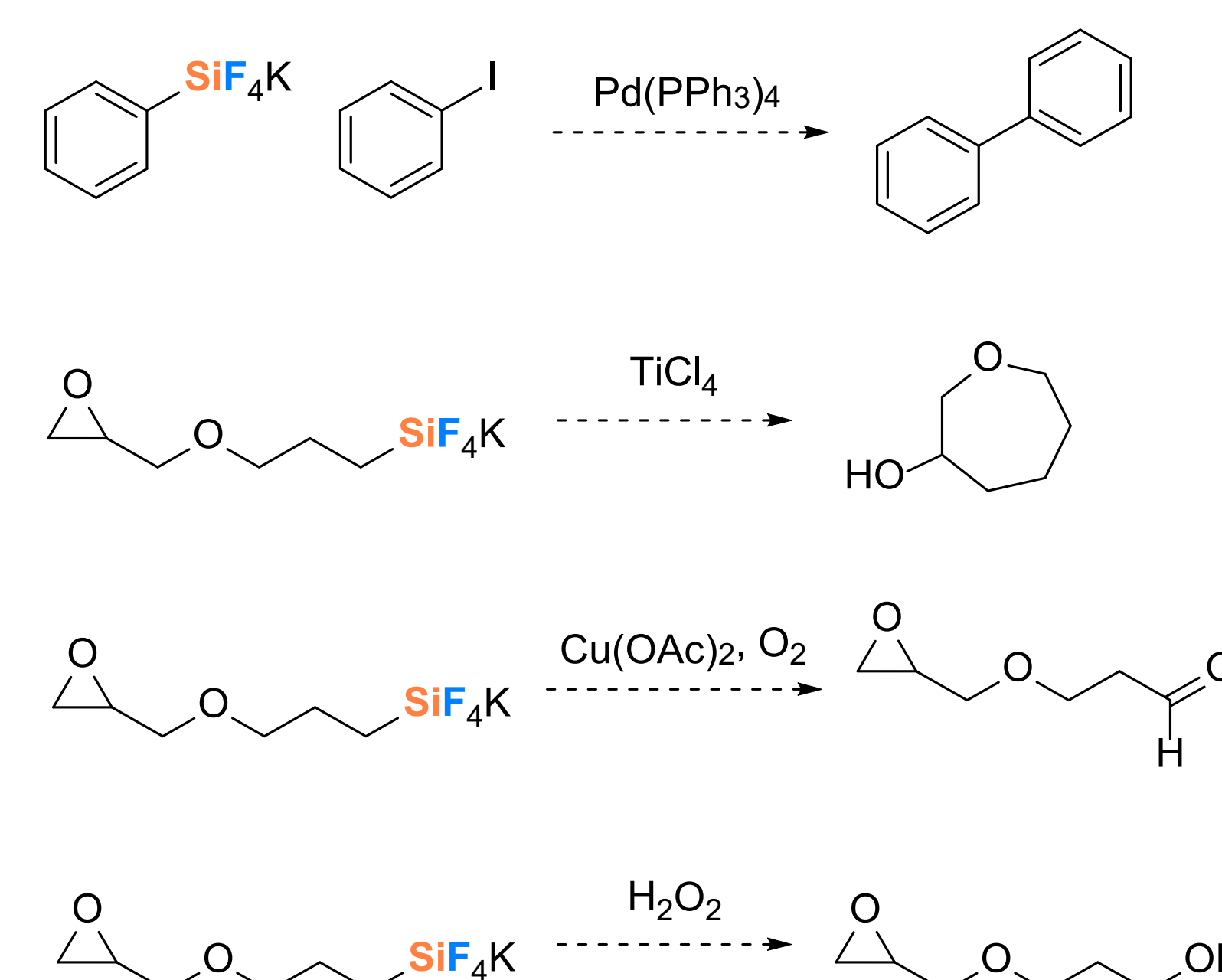


| entry | substrate | % conversion |
|-------|-----------|--------------|
| 1     |           | 100%         |
| 2     |           | 100%         |
| 3     |           | 100%         |

When using NH<sub>4</sub>HF<sub>2</sub> the tetrafluorosilicate stays in solution rather than precipitating out with KHF<sub>2</sub>. This is beneficial due to the fact that we can then perform other reactions *in situ* to demonstrate the utility of a tetrafluorosilicate.

## Future Directions

1. Continue to develop the substrate scope and include other functional groups such as allyl, phosphonate, and nitro groups.
2. Use the tetrafluorosilicates in a variety of reactions that demonstrate their usefulness, such as:



3. Determine the mechanism of fluorination by studying kinetics by NMR, studying reactive intermediates, and optimizing a pathway computationally.

## Conclusions

We have shown that a trialkoxysilane can be a good starting material to form an organotetrafluorosilicate. The reaction is highly selective as the organopentafluorosilicate does not form. The reaction displays good functional group tolerance so far as epoxides, carbonyls, and alkyl halides are tolerated by the reaction conditions. Additionally, ammonium tetrafluorosilicates exhibit higher solubility in water. This allows the tetrafluorosilicate to be used in further transformations. Future work will focus on continuing to develop the substrate scope and utilizing the tetrafluorosilicate product for a number of different transformations such as Hiyama couplings, Fleming-Tamao oxidations, cyclizations and copper-catalyzed oxidations to aldehydes. The mechanism will also be investigated both experimentally and computationally.

## Acknowledgements

We would like to thank Prof. Rick Fitch for many helpful conversations and the Department of Chemistry and Physics for their generous support.

## Funding

NSF grant CHE-0521075 (MRI 400 MHz NMR) Start-up funds provided Indiana State University Center for Student Research and Creativity at ISU

## References

1. Darses, S.; Genet, J.-P. *Chem. Rev.* **2008**, *108*, 288-325.
2. Reinhold, T.; Pfrommer, B.; Lunkenheimer, K.; Hirte, R. *Organometallics* **1998**, *17*, 3670-3676.
3. Yoshida, J.-I.; Tamao, K.; Kurita, A.; Kumada, M. *Tetrahedron Lett.* **1978**, *21*, 1809-1812.
4. Yoshida, J.-I.; Tamao, K.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, M. *Organometallics* **1982**, *1*, 369-380.
5. Ting, R.; Adam, M. J.; Ruth, T. J.; Perrin, D. M. *J. Am. Chem. Soc.* **2005**, *127*, 13094-13095.