

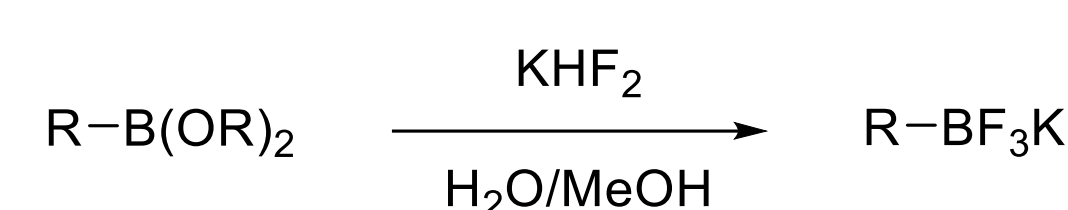


# Palladium-catalyzed coupling of organotetrafluorosilicate salts and aryldiazonium salts under mild conditions

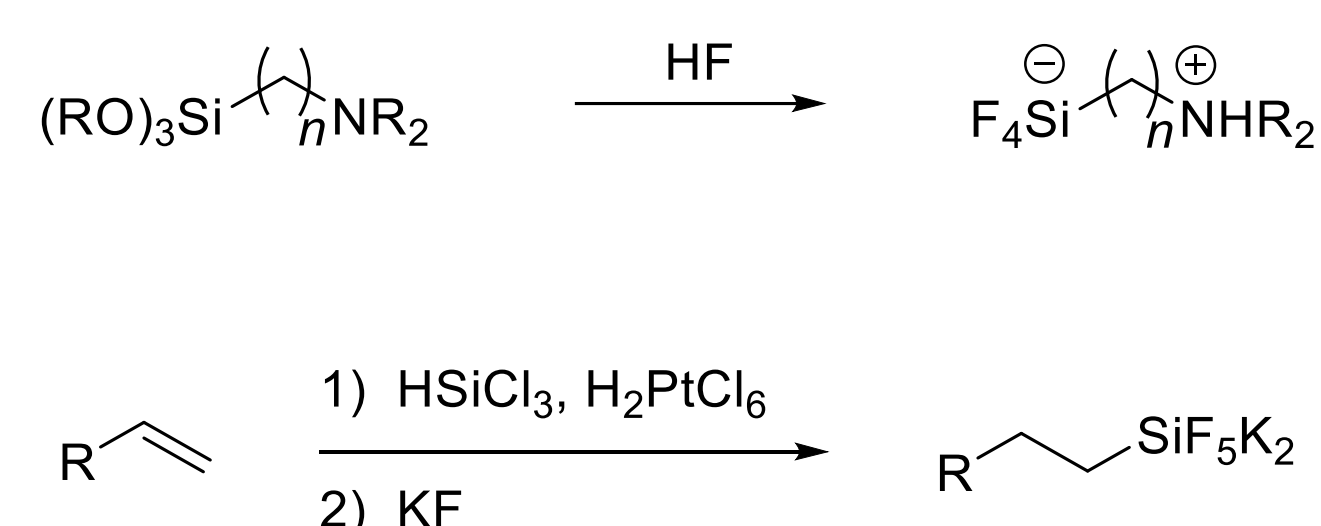
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## Introduction

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, facile synthesis of organotetrafluorosilicates has recently been developed by our lab.<sup>2</sup> Organofluorosilicates have also been prepared by treating alkoxy silanes with water-free hydrogen fluoride in ether solution<sup>3</sup> or by reacting organotrichlorosilanes with KF.<sup>4</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>4,5</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>6</sup>

Current best coupling reactions, like Suzuki couplings and Sonogoshira couplings, are limited by their use of basic conditions, which cannot tolerate base-sensitive functional groups. Organotetrafluorosilicate salts have not been explored as coupling partners until recently and show significant potential.<sup>7</sup> The activated silicon does not seem to require a base additive in order to couple effectively. Initial results show that tetrafluorosilicates will couple with aryldiazonium salts in the presence of a palladium catalyst, producing easily removable byproducts.

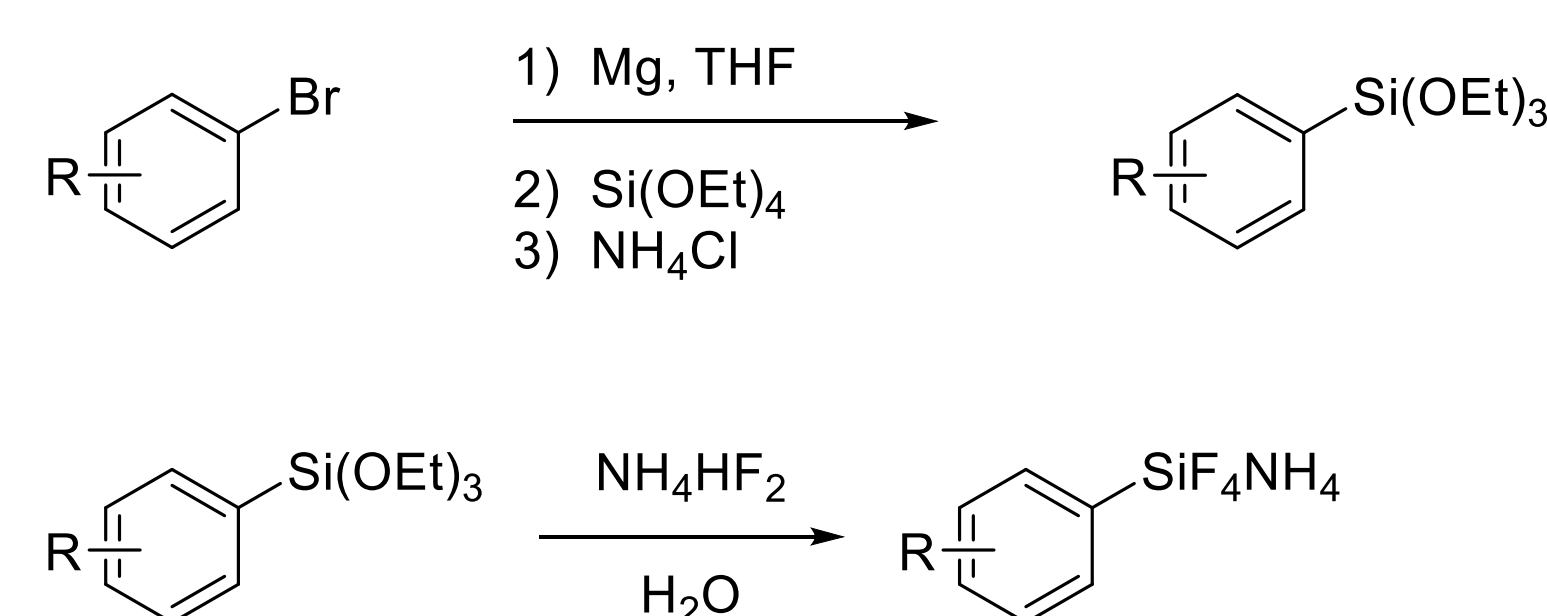
## Hypothesis

An ammonium organotetrafluorosilicate will tolerate coupling conditions, which will allow couplings to occur in mildly acidic conditions and without the need for a basic additive.

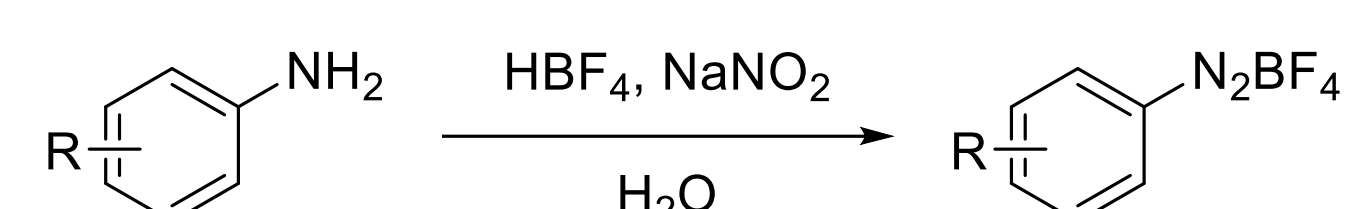
## Substrate Synthesis

Aryltrialkoxysilanes can be easily synthesized by Grignard attack of tetraethylorthosilicate. Ammonium organotetrafluorosilicates can be readily synthesized with ammonium bifluoride in water. While many diazonium salts are known to be explosive, the tetrafluoroborate salts are usually stable up to 300 °C and are stable to shock. They can be prepared from the aniline.

### synthesis of tetrafluorosilicate:

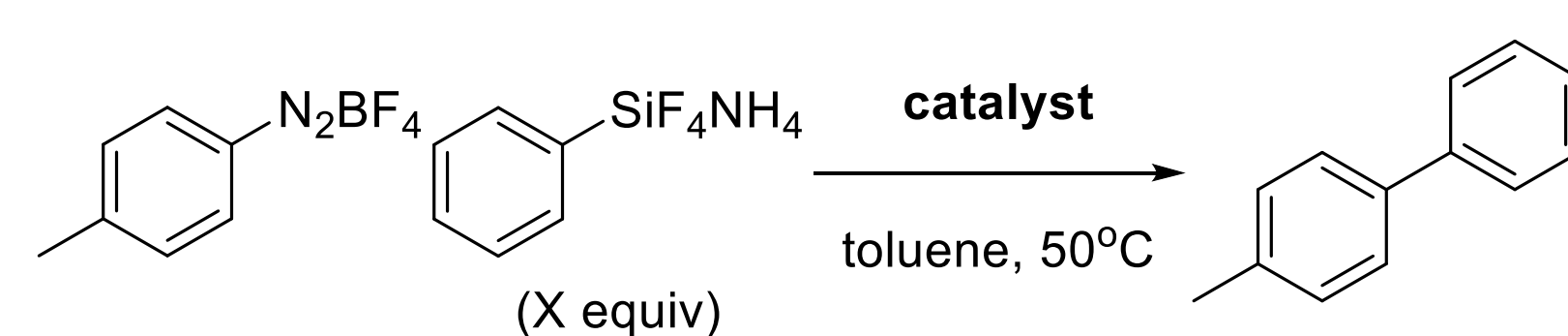


### synthesis of diazonium salt:



## Optimization of Reaction Conditions

Initial optimization began with a selection of Pd with different ligands. The equivalents of the aryldiazonium salt proved to be important to the final yield. Other conditions that were optimized includes solvents, concentration, metal catalyst, and additives.



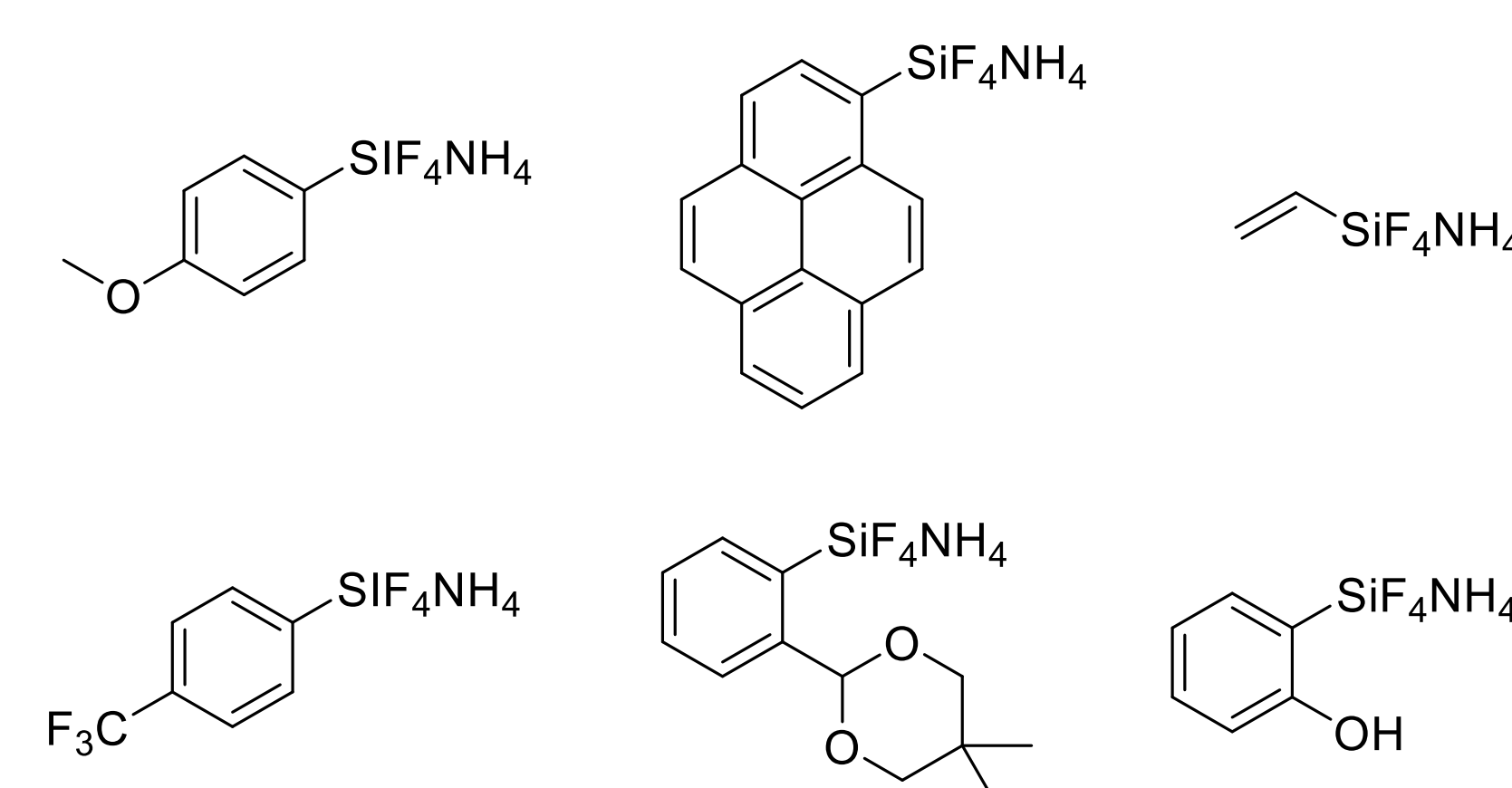
entry	equiv of PhSiF <sub>4</sub> NH <sub>4</sub>	catalyst	yield
1	1.2	Pd(PPh <sub>3</sub> ) <sub>4</sub> (1%)	13%
2	1.2	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), dppf (2%)	10%
3	1.2	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PCy <sub>3</sub> (10%)	8%
4	1.2	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PtBu <sub>3</sub> (10%)	15%
5	1.2	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PAd <sub>2</sub> Bu (10%)	20%
6	1.2	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PAd <sub>2</sub> Bu (5%)	34%
7	2.0	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PAd <sub>2</sub> Bu (5%)	53%
8	5.0	Pd <sub>2</sub> (dba) <sub>3</sub> (1%), PAd <sub>2</sub> Bu (5%)	90%

Yields determined by NMR using 1,1,1,2-tetrachloroethane as an internal standard

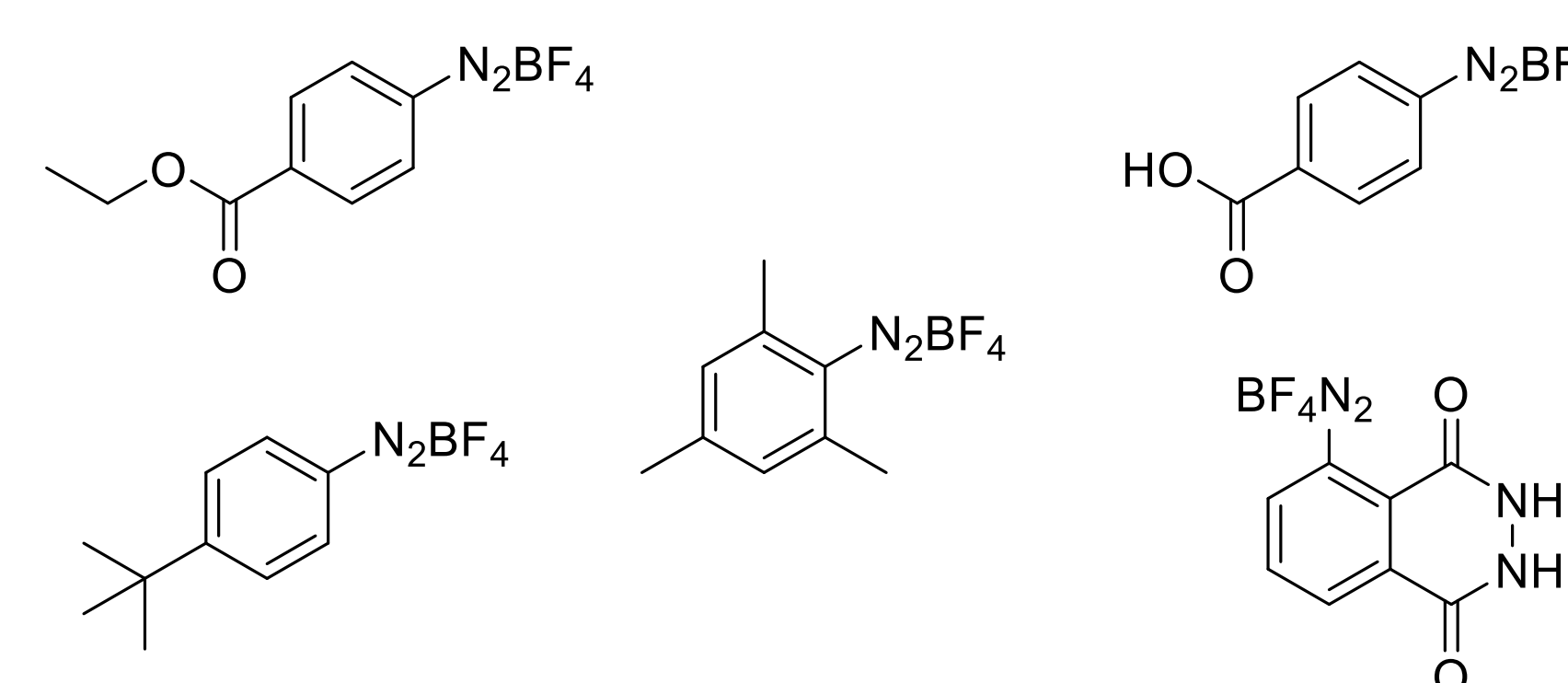
## Future Substrate Scope

Using the optimized reaction conditions, the substrate scope will be explored. A sampling of the substrates that will be used are shown below.

### silicate substrates:

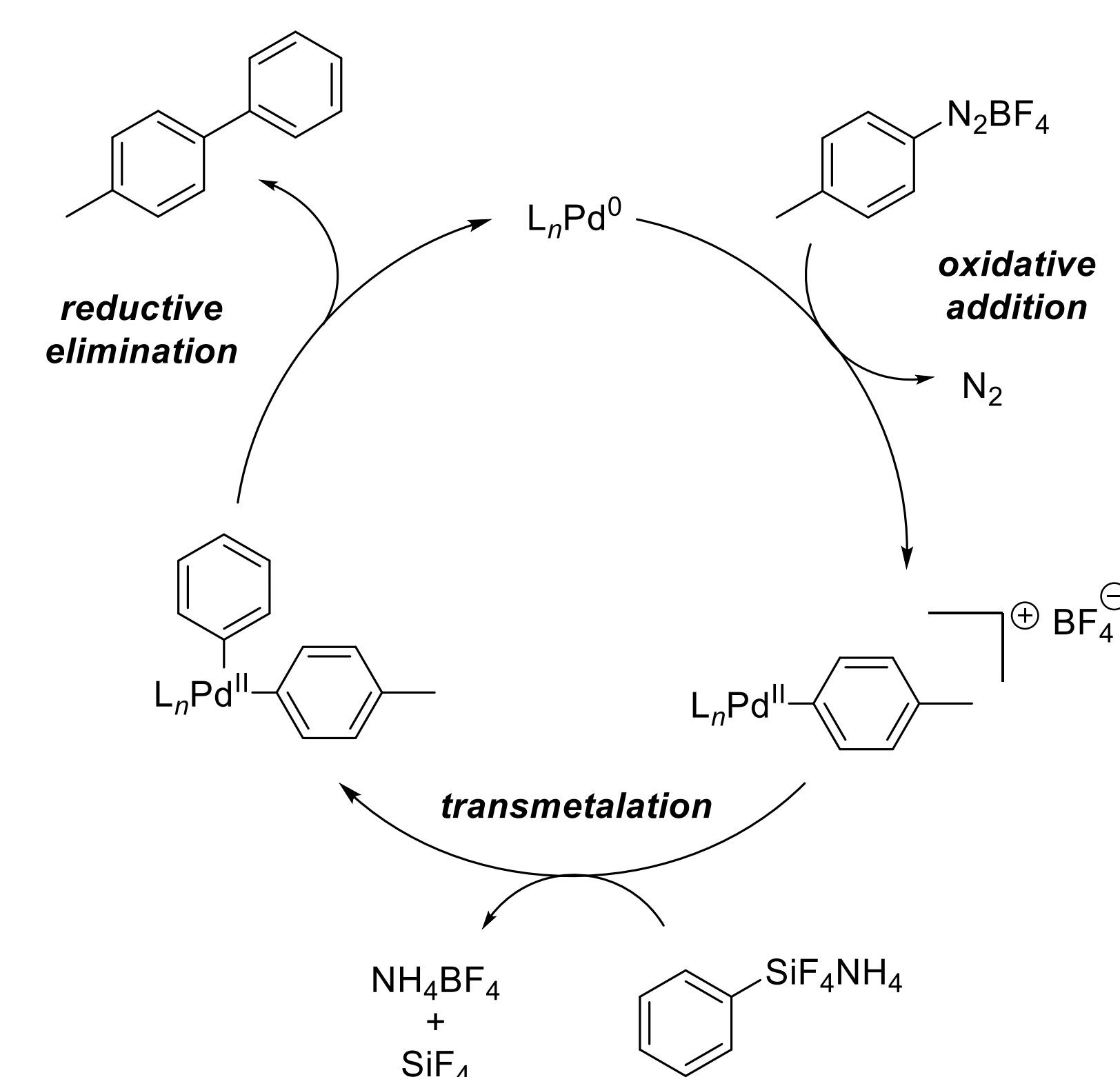


### diazonium substrates:



## Proposed Mechanism

We believe this reaction proceeds by a fairly standard mechanism while producing by-products that are easily removed from the desired product.



## Future Directions

1. Use the coupling to establish a substrate scope that includes other functional groups such as carbonyls, acids, and phenols.
2. Explore other coupling reactions using tetrafluorosilicates

## Conclusions

We have shown that an organotetrafluorosilicate can participate in a coupling reaction. We expect the reaction to be highly tolerant of a variety of functional groups. Future work will focus on continuing to develop the Pd-catalyzed coupling of aryldiazonium salts with aryldiazonium salts by exploring the substrate scope.

## Acknowledgements

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