

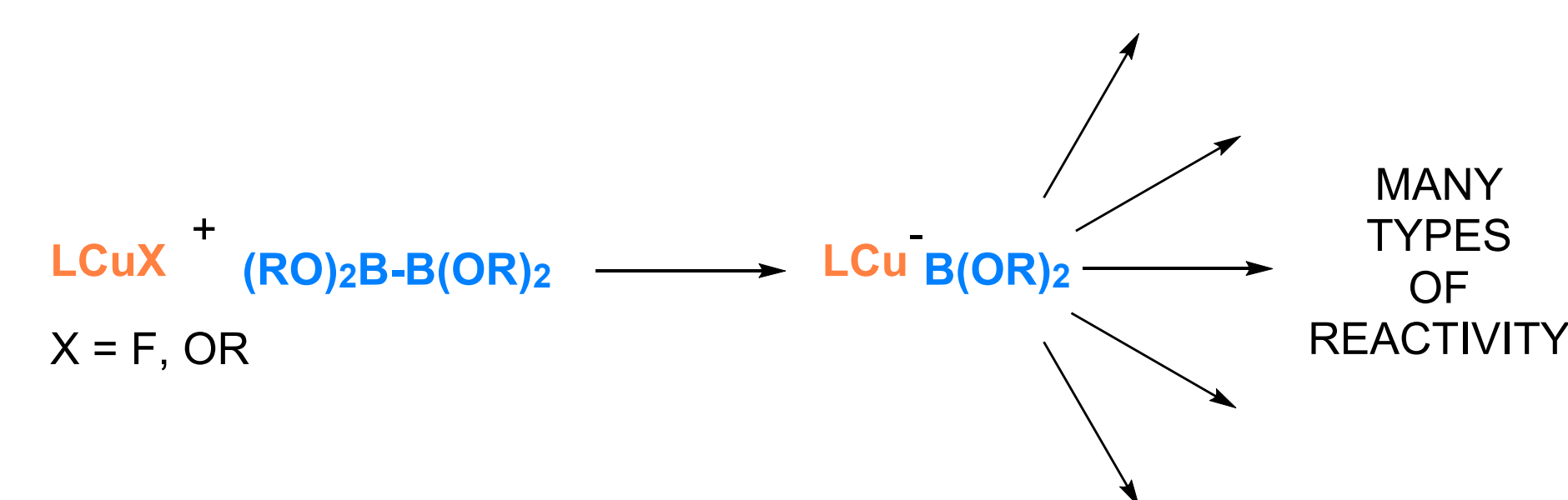


Progress Towards Synthesis of an Acylsilane *via* Copper Catalysis

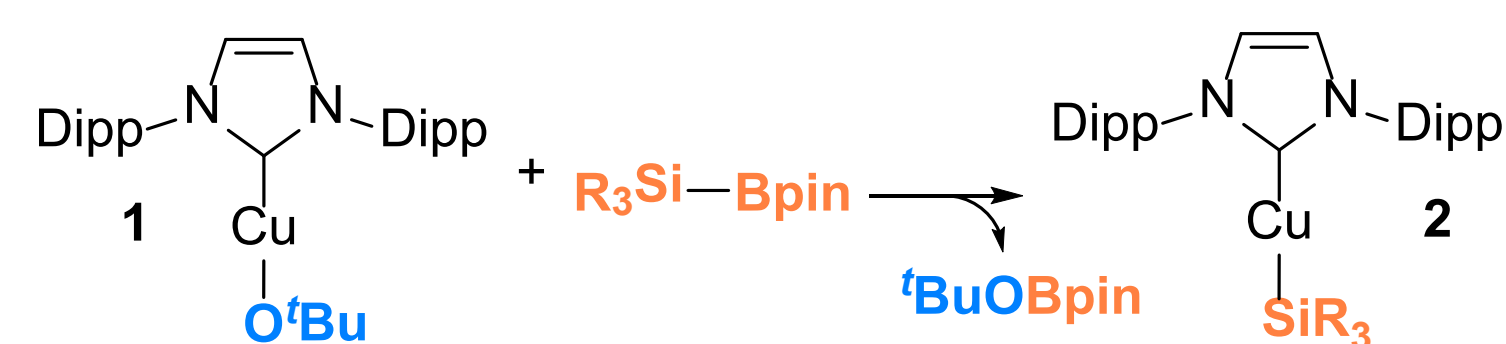
Jake R. Wilkinson, Travis H. Reiner, Brogan M. Thomas, and Ryan Van Hoveln*
Department of Chemistry and Physics, Indiana State University, Terre Haute, IN 47809

Introduction

Considerable work has shown that diborons can react with copper alkoxides and fluorides to break the boron-boron bond, creating a strong boron-oxygen/fluorine bond and a copper-boron bond. This copper-boron bond has been used extensively in catalysis to incorporate boron into a wide range of organic molecules. These reactions include hydroboration and diboration of alkynes, alkenes, and carbonyls, as well as borylation of aromatic halides.¹

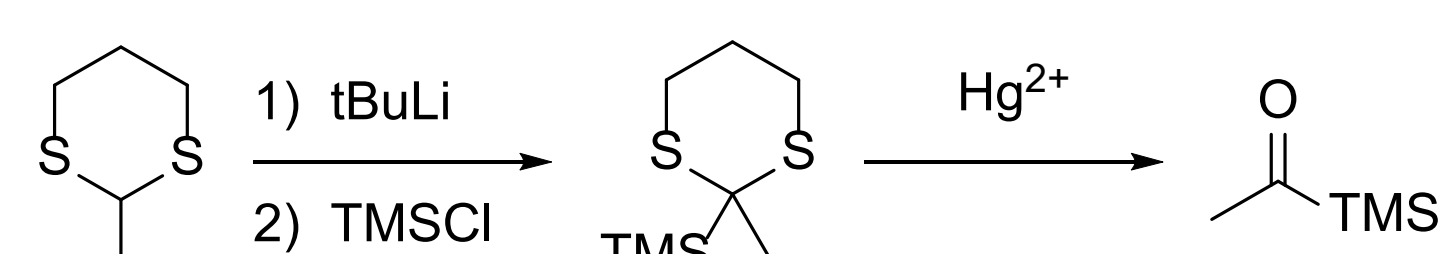


Silylboranes have been used in similar transformations as silylating reagents, however, these reagents are difficult to synthesize and air/water sensitive.² Disilanes could be better silylating reagents as they are easy to handle and relatively inexpensive.

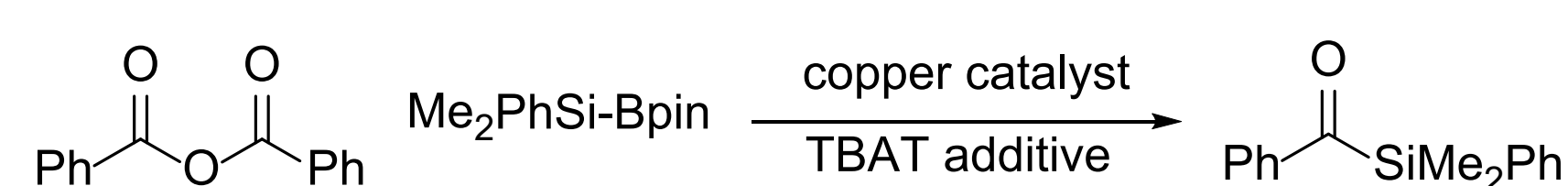


A number of silylations have been developed to form various silanes, but some of the more interesting of these are acylsilanes. These reagents are excellent for performing umolung chemistry, however, no ideal method for synthesizing an acylsilane exists yet in the literature. The traditional synthesis of acylsilanes involves deprotonating a dithiane with tBuLi, trapping it with a chlorosilane and then deprotecting with either mercury or cadmium.³ However, another method exists that relies on copper-catalysis, but uses silylboranes and an expensive fluoride source.⁴

traditional approach:



current copper-catalyzed approach:



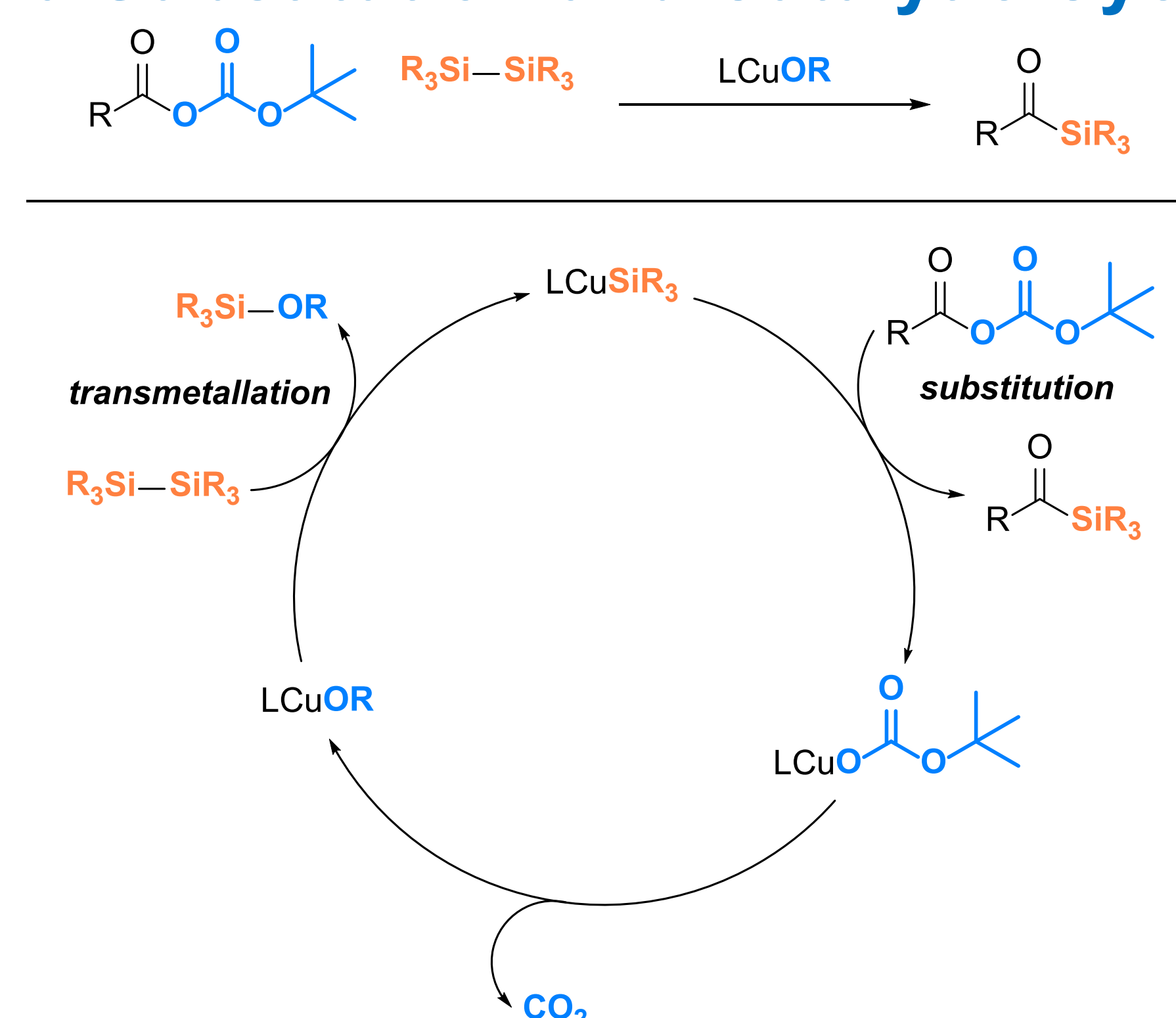
Hypothesis

A sufficiently electrophilic disilane will react in an analogous manner to silylboranes. This produces a copper silyl complex that can then do acyl substitution to make an acylsilane. Alternatively, an α -silyl alcohol can be made in like manner, then oxidized to form an acylsilane.

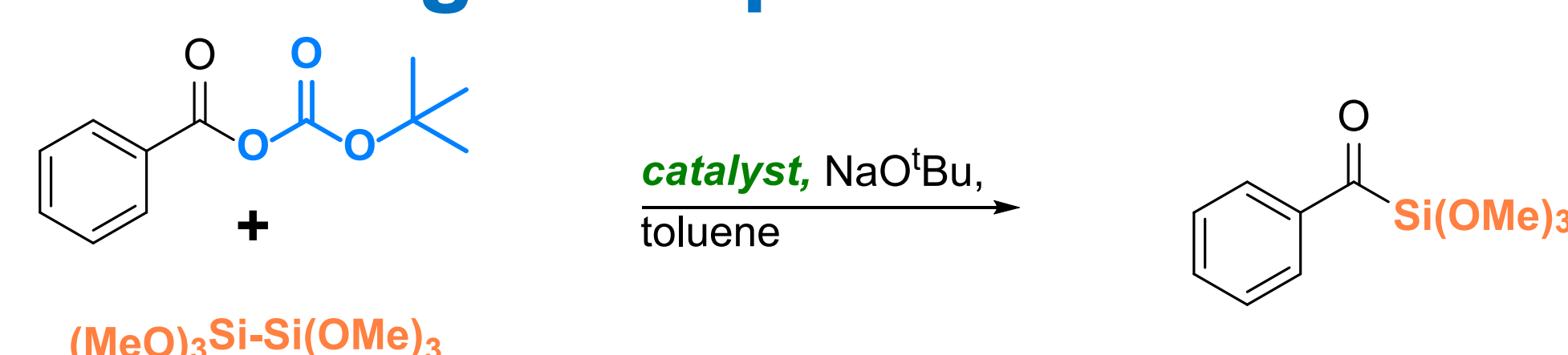
Objectives

1. Develop a catalytic synthesis of acylsilanes using disilanes as the silylating reagent.
2. Synthesize an acylsilane via the oxidation of an α -silyl alcohol.
3. Establish a substrate scope for the synthesis of acylsilanes.

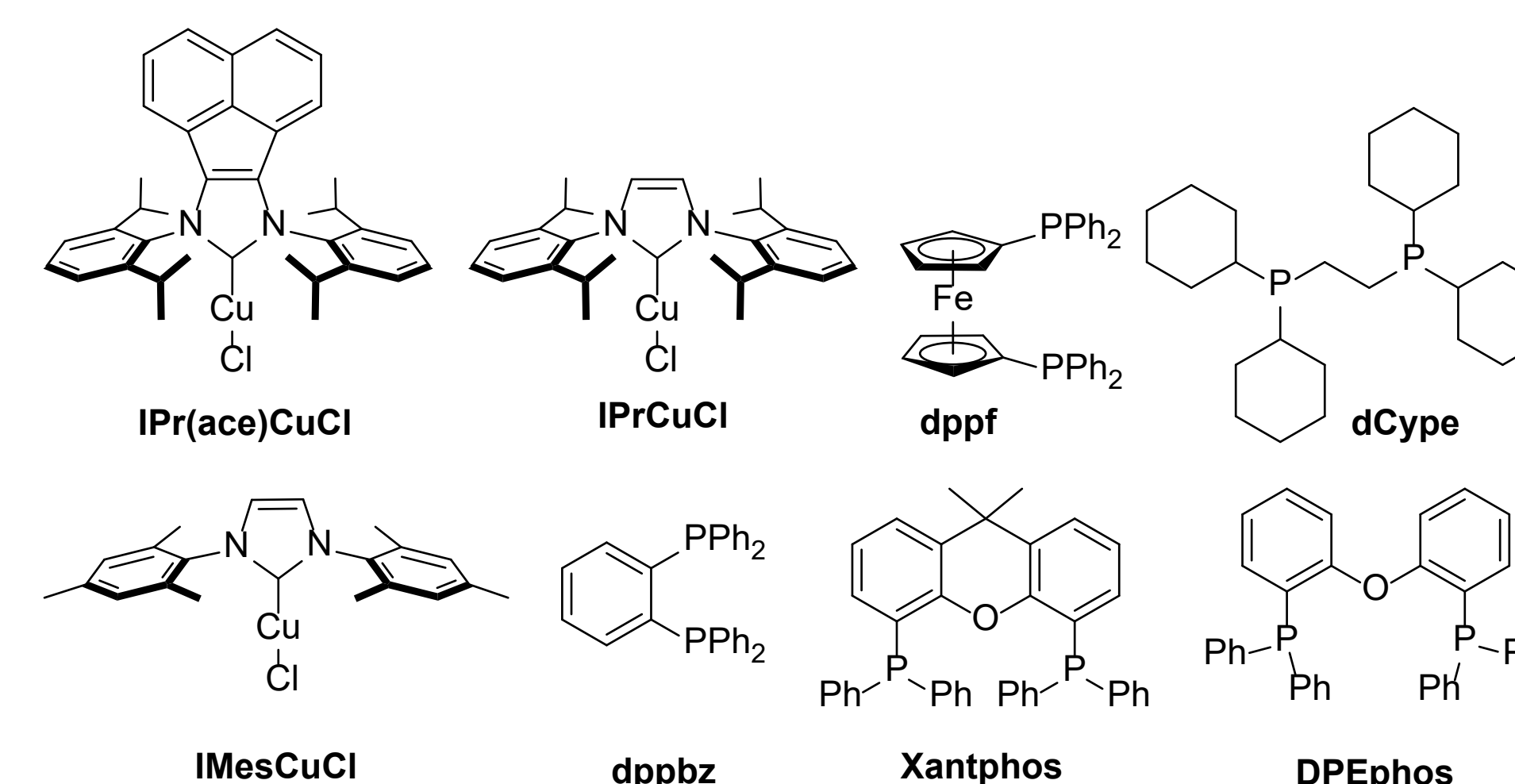
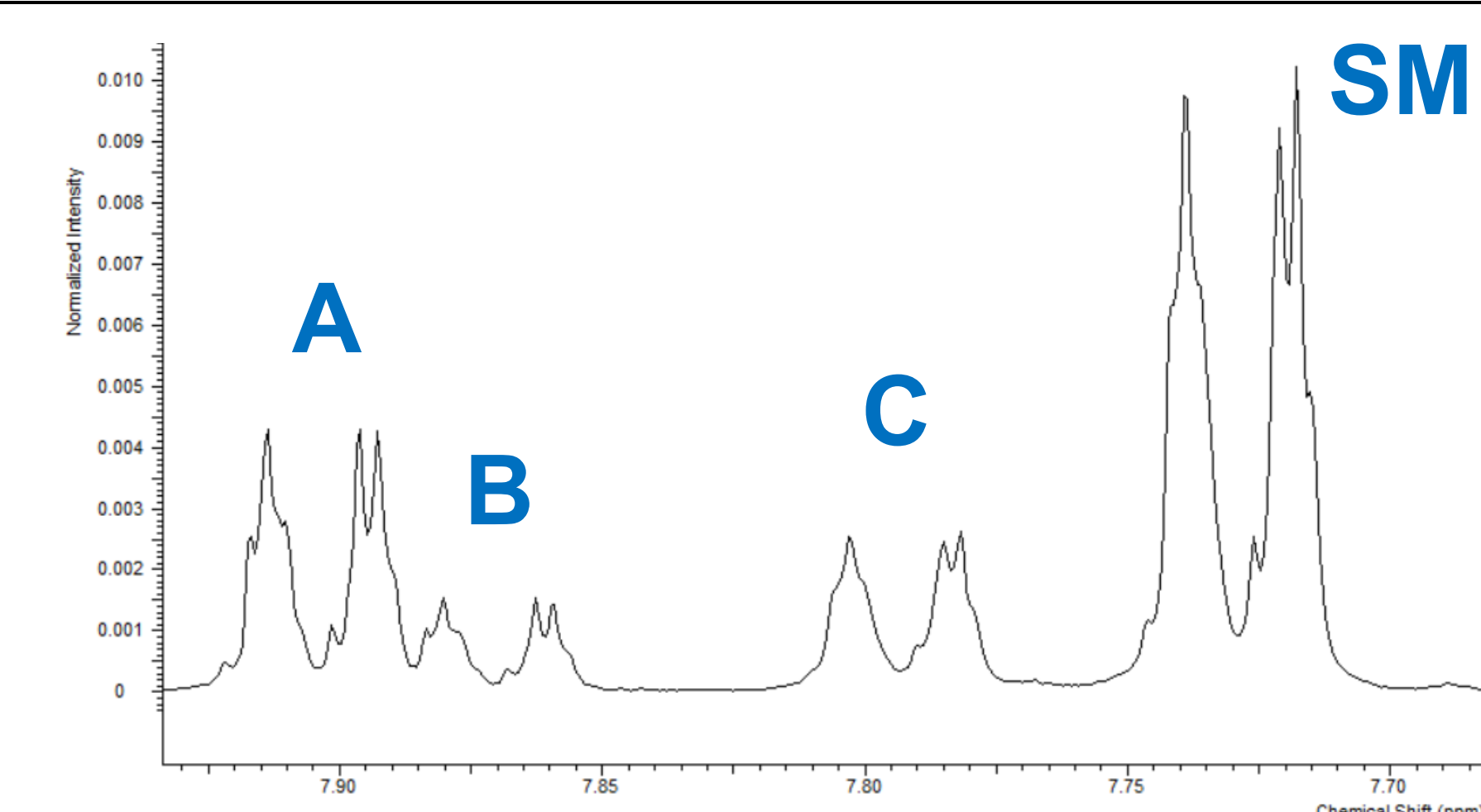
Envisioned Synthesis Acyl Silanes via Substitution and Catalytic Cycle



Ligand Optimization

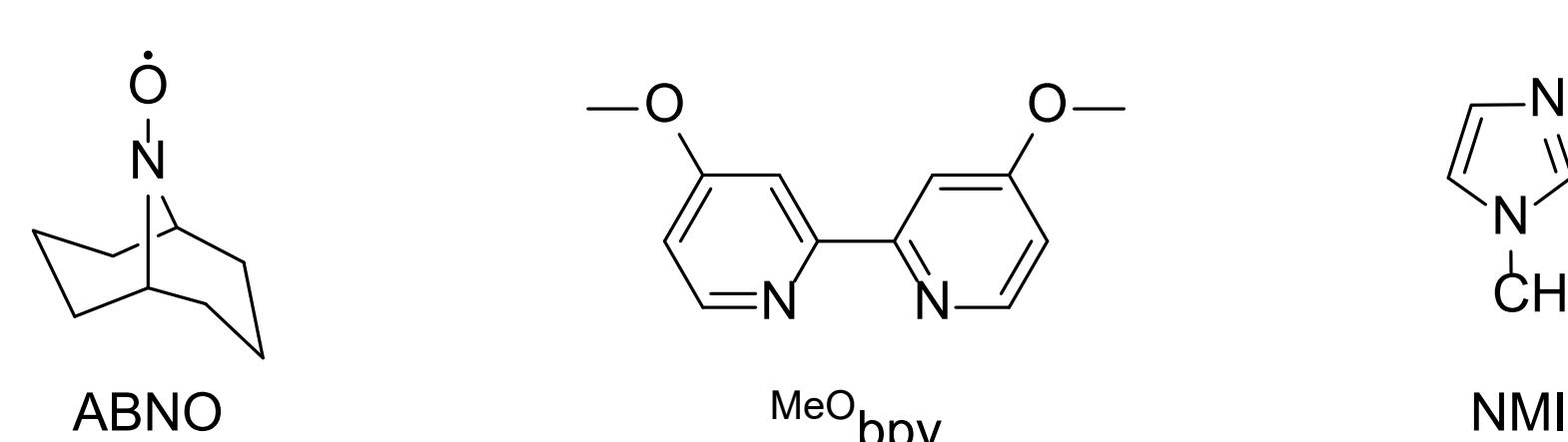
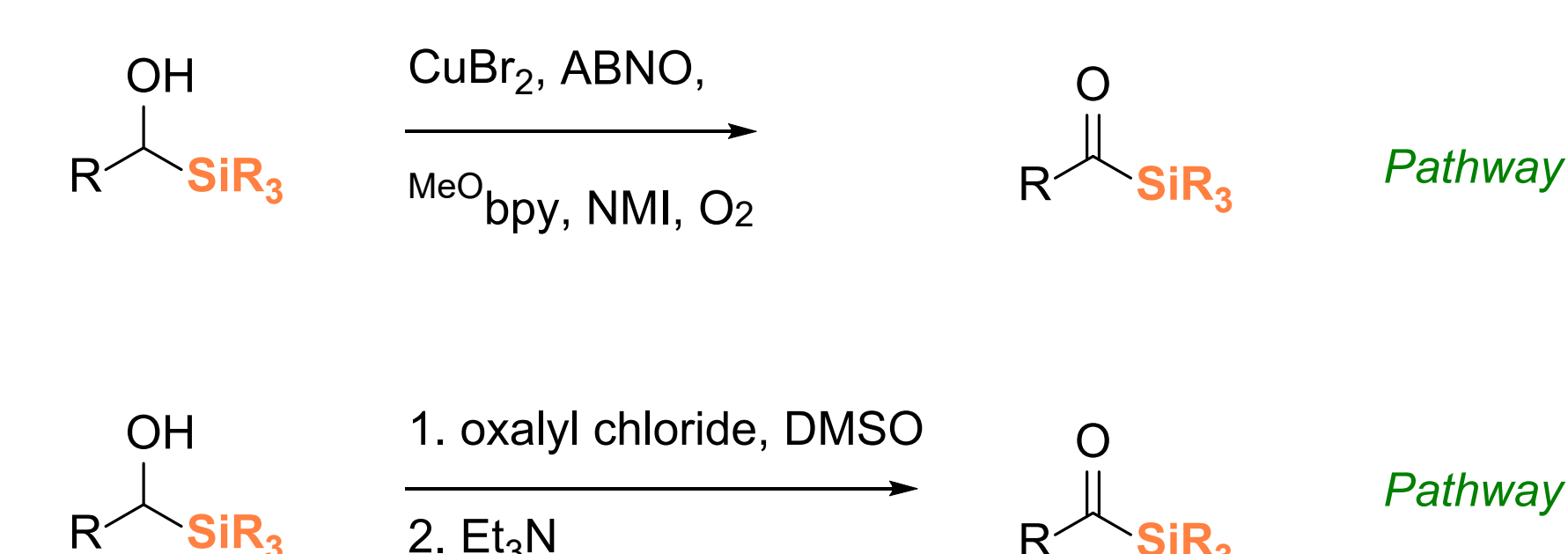


entry	catalyst	starting material	peak A	peak B	peak C
1	IPr(ace)CuCl	29%	24%	6%	12%
2	IPrCuCl	36%	15%	5%	7%
3	dppf/CuCl	32%	24%	6%	11%
4	dCype/CuCl	45%	19%	7%	13%
5	IMes/CuCl	17%	18%	20%	18%
6	dppbz/CuCl	46%	13%	11%	13%
7	xantphos/CuCl	29%	41%	6%	9%
8	DPEphos/CuCl	37%	15%	5%	10%

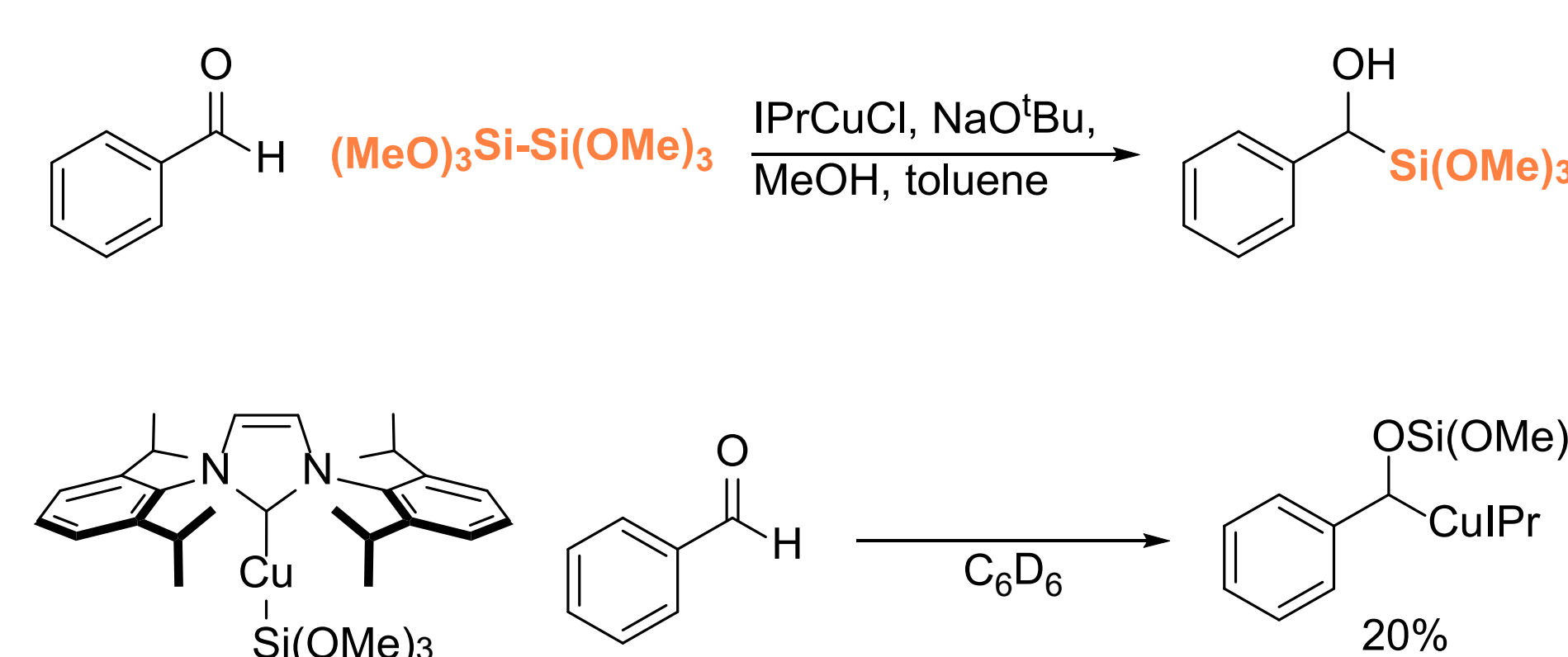


Attempts to perform substitutions of anhydrides using a disilane were inspired by similar transformations developed using silylboranes. Although several products were formed with consistency by a range of copper-ligated catalysts, no detectable amounts of the desired acylsilane were produced.

Envisioned Synthesis of Acyl Silanes via Oxidation



Synthesis of an α -Silyl Alcohol



Even though the above oxidations were carried out using a variety of conditions, they were unsuccessful. It turns out that the method used to synthesize the α -silyl alcohol was undergoing Brook Rearrangement. This was proved by reacting the copper silyl complex stoichiometrically with benzaldehyde.

Future Directions

We plan to attempt to synthesize an acylsilane by oxidizing an α -silyl alcohol that has been made following traditional methods. If this works then further attempts will be made to develop copper-catalyzed syntheses of α -silyl alcohols. Acylsilanes will be reacted with copper alkoxides to form acylcopper species.

Conclusions

Although methods of forming an acylsilane using copper catalysis and a silylborane have been developed, similar reactions using a disilane have so far been unsuccessful. Efforts to synthesize an acylsilane via the oxidation of an α -silyl alcohol have so far been inconclusive as the alcohol has proven difficult to synthesize catalytically. If an acylsilane can be made via oxidation then further work will be done to develop and optimize the catalytic synthesis of α -silyl alcohols. Once optimization is complete, the substrate scope will be explored.

Acknowledgements

We would like to thank Professor Richard 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. (a) Tsuji, Y.; Fujihara, T. *Chem. Rec.* **2016**, *16*, 2294-2313. (b) Fujihara, T.; Tsuji, Y. *Synthesis*, **2018**, *50*, 1737-1749.
2. a) Keelberg, C.; Cheung, M. S.; Lin, Z.; Marder, T. B. *J. Am. Chem. Soc.* **2011**, *133*, 19060. b) Plotzitzka, J.; Kleeberg, C. *Inorg. Chem.* **2016**, *55*, 4813.
3. Page, P. C. B.; Klair, S. S.; Rosenthal, S. *Chem. Soc. Rev.* **1990**, *19*, 147-195.
4. Cirriez, V.; Rasson, C.; Riant, O. *Adv. Synth. Catal.* **2013**, *355*, 3137-3140.