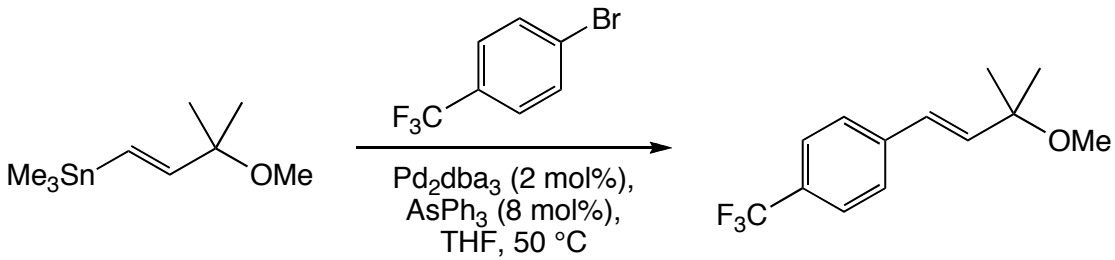
Group Meeting Research

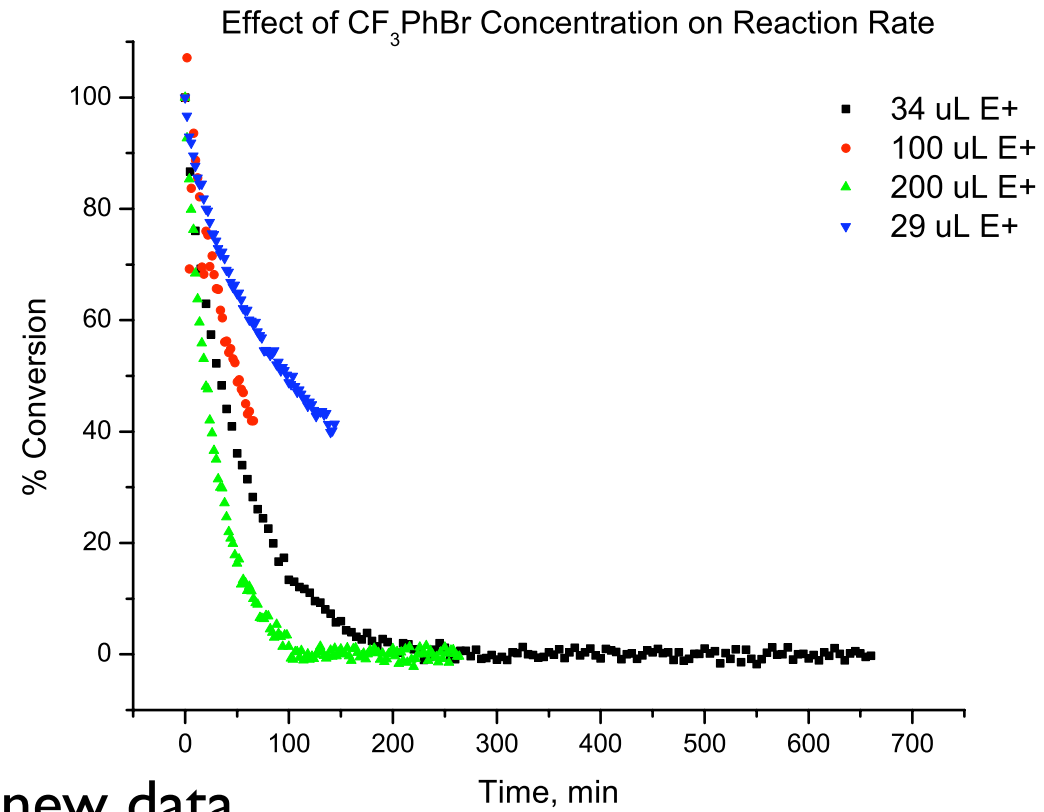
April 6, 2009

Nicki Torres

[Aryl Bromide] Dependence

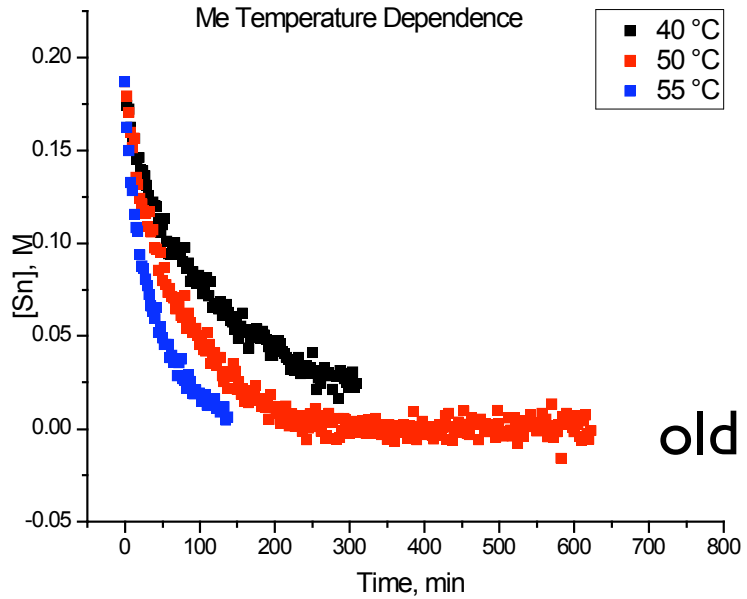


Last time...



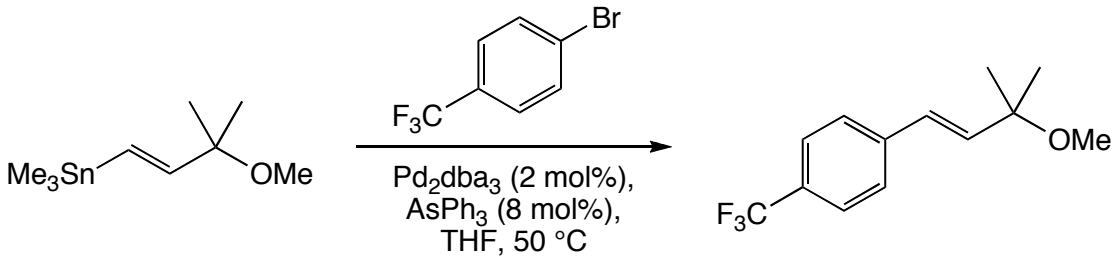
new data

Found that NMR temperature was incorrect. Actually ~46.8 °C

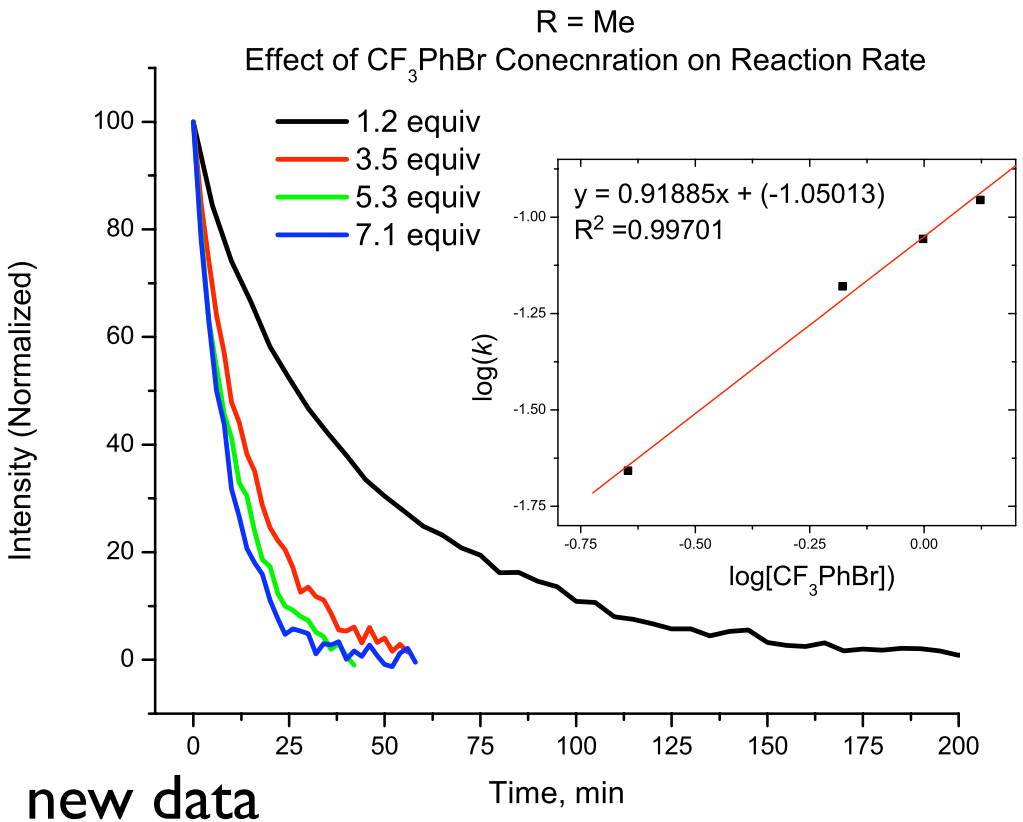


old data

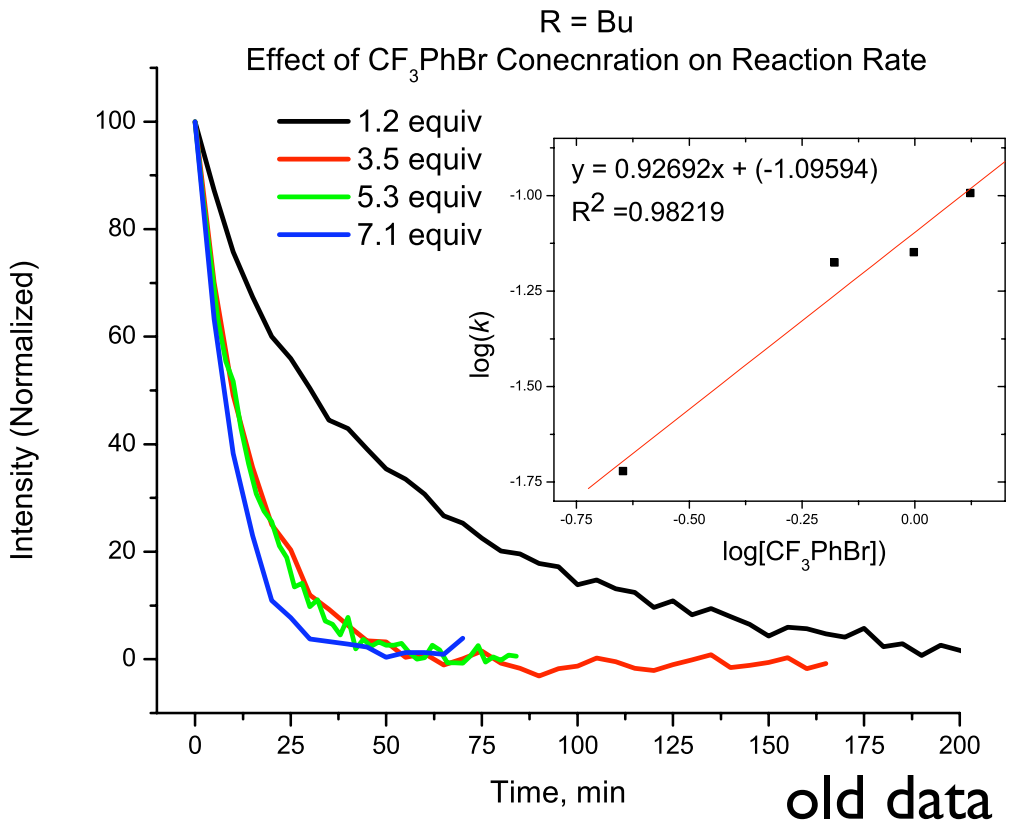
[Aryl Bromide] Dependence at 50 °C



Matches w/ Bu

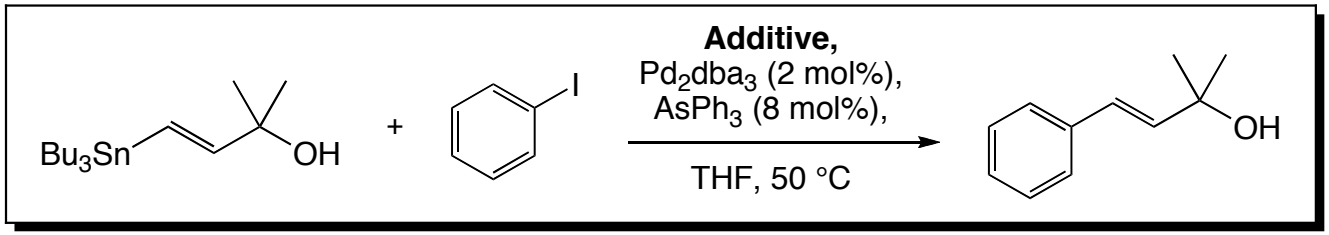


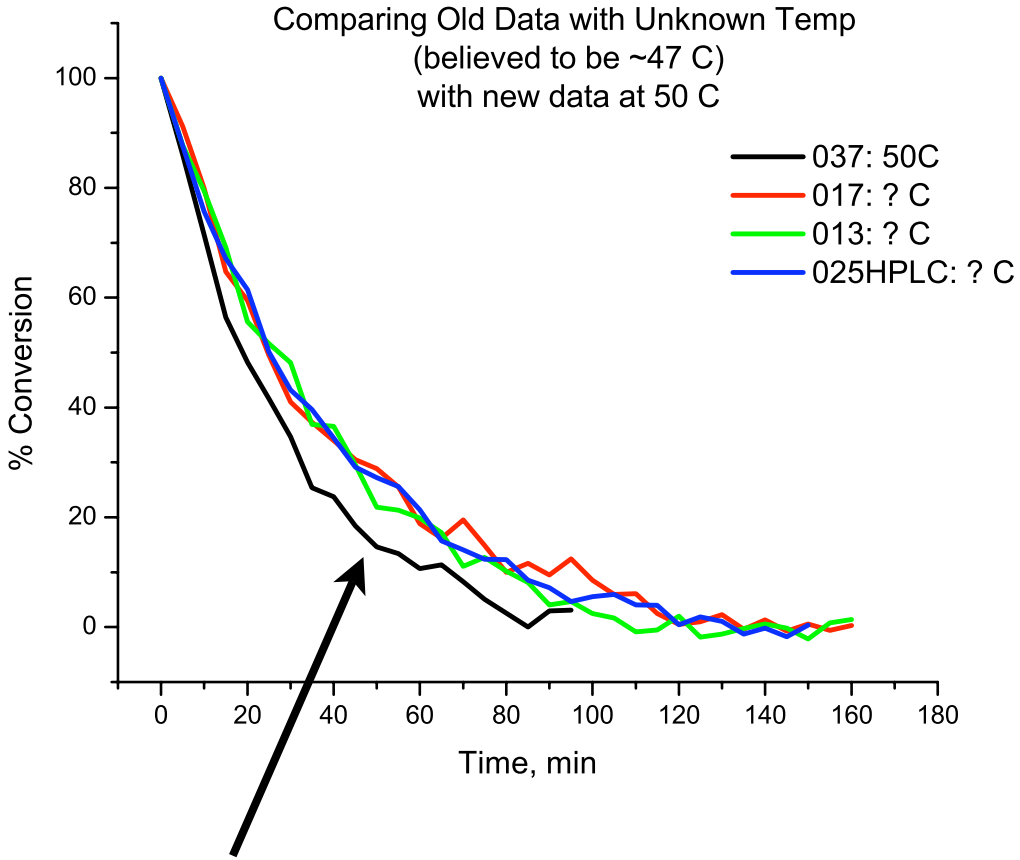
new data



old data

Water as an Additive





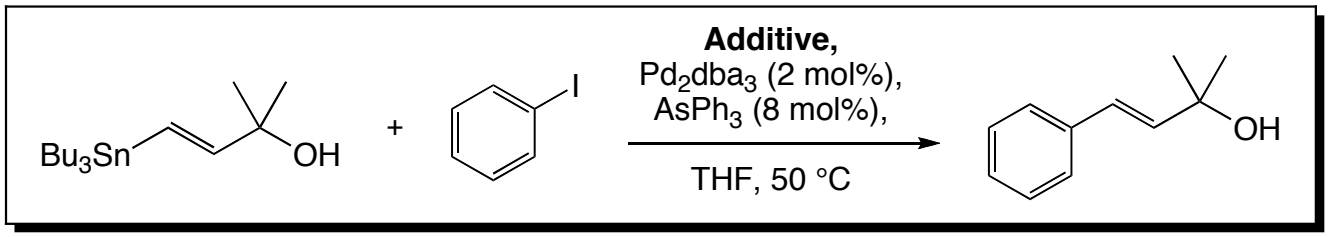
slightly faster than previous expts

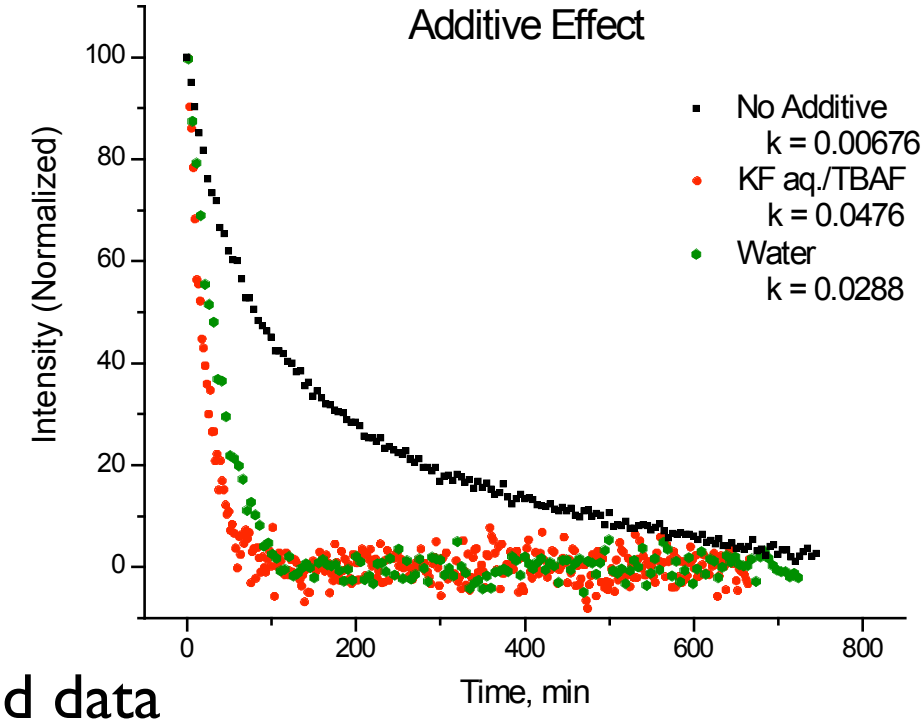
Saw a linear water dependence. Actual rates at 47 °C will be different, but liner relationship should not be temperature dependent

DI vs. HPLC H_2O Experiment done at same temps.... conclusion still valid

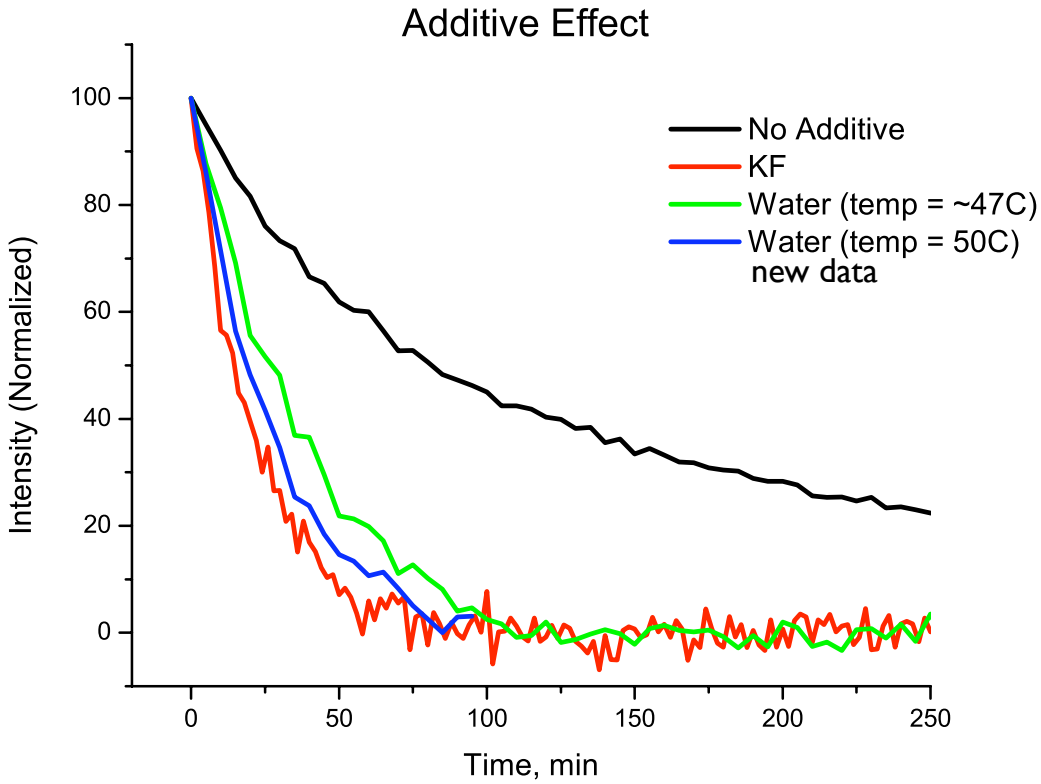
The KF Effect?

How do additives affect the rate of the Stille reaction?



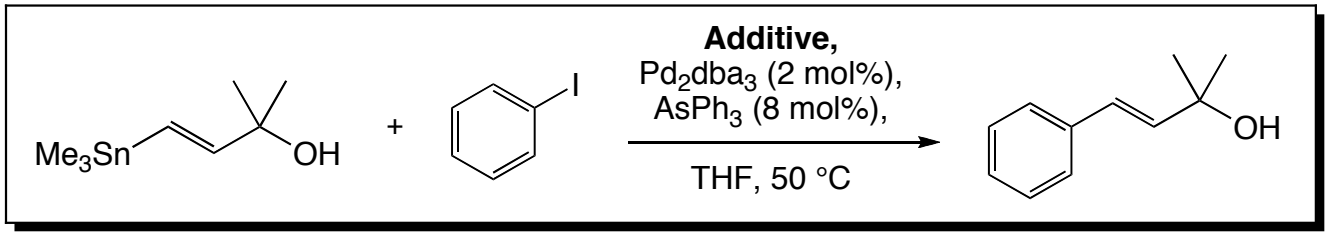


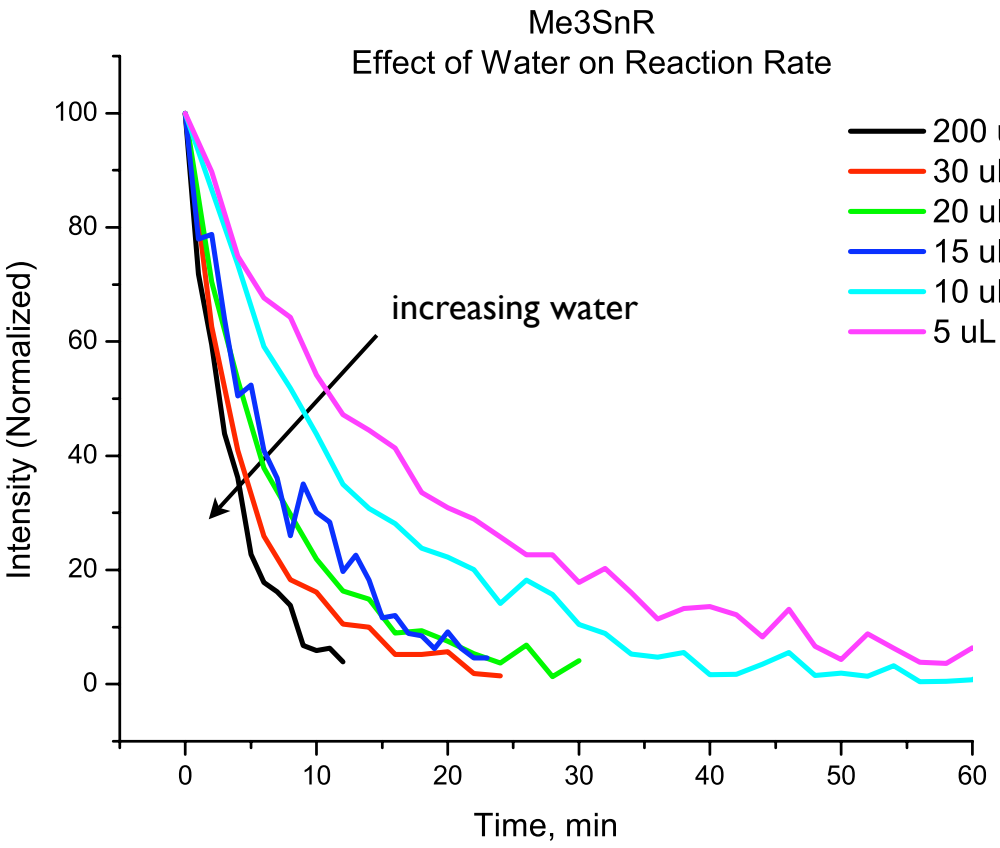
old data

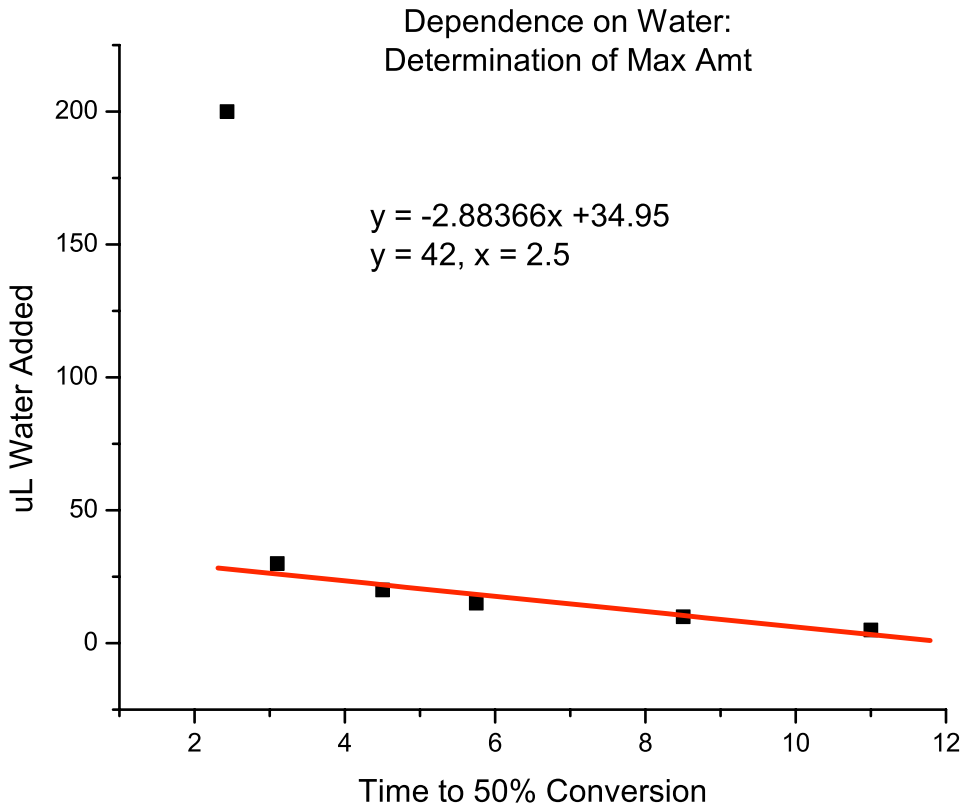


Water activates the Stille Coupling for aryl iodides

Water as an Additive







CuI as an Additive

Shown to increase the rate of reaction for some conditions:

NMP w/ $AsPh_3$ as ligand

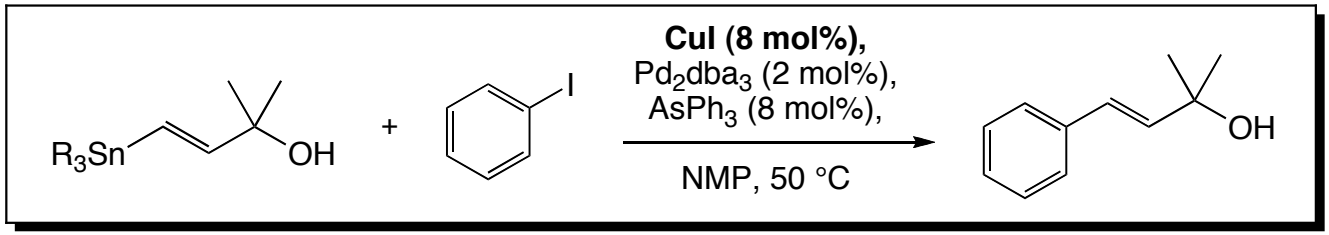
CuI may undergo a transmetallation with stannane to afford more active species for the Pd transmetallation

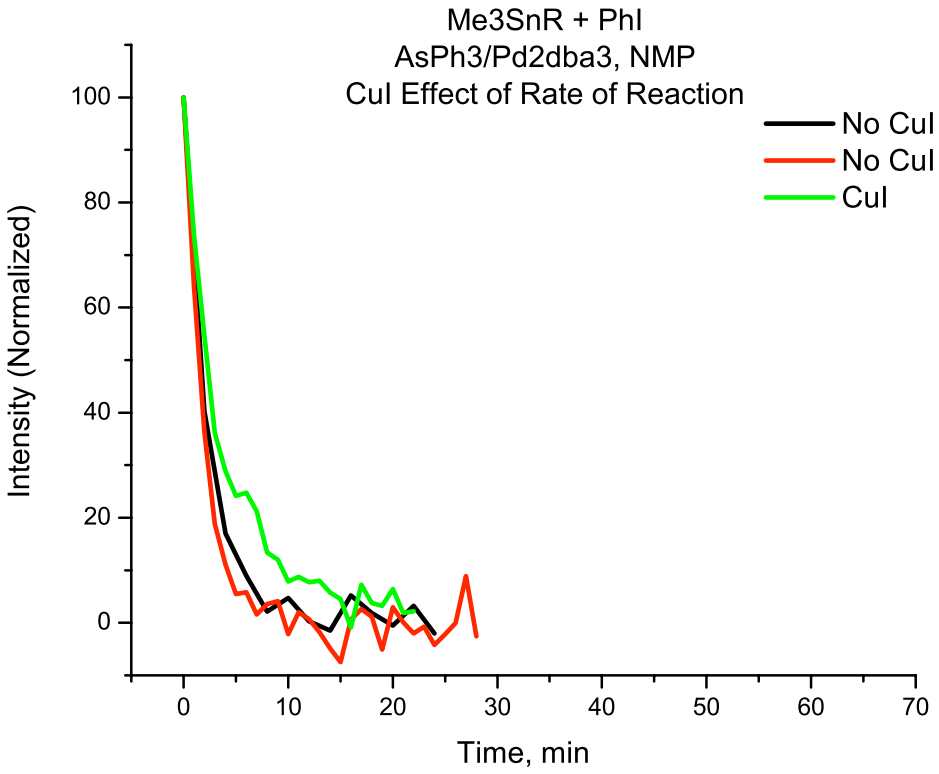
THF w/ PPh_3 as ligand

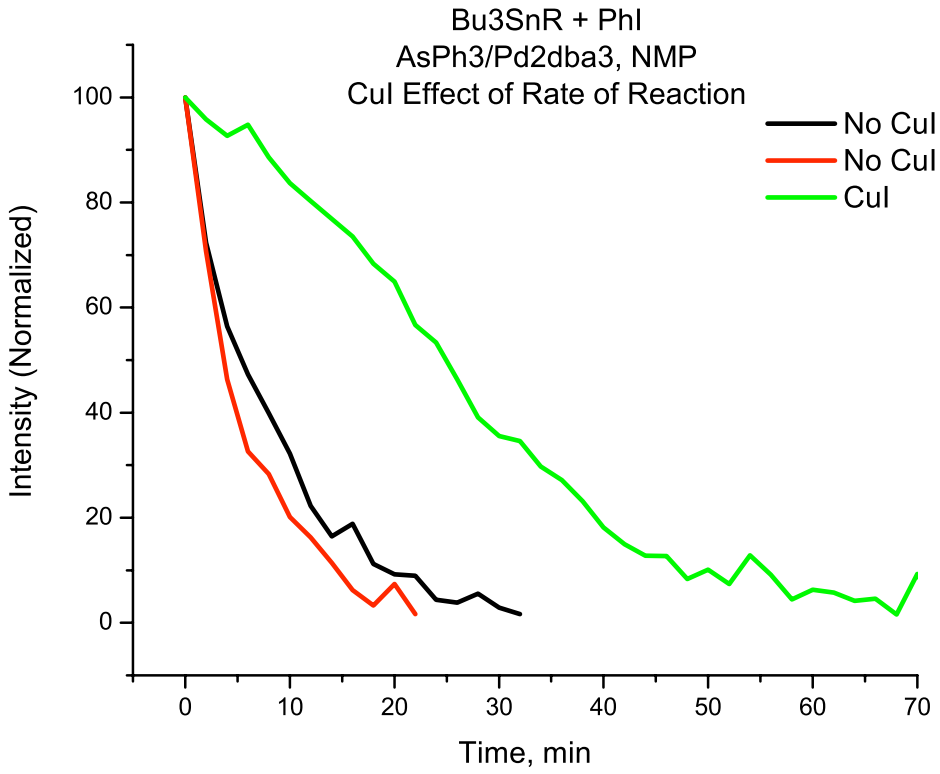
CuI sequesters excess ligand

Farina & Liebeskind et. al. *J. Org. Chem.* **1994**, *59*, 5905–5911.

CuI as an Additive
Aryl Iodides in $AsPh_3$/NMP



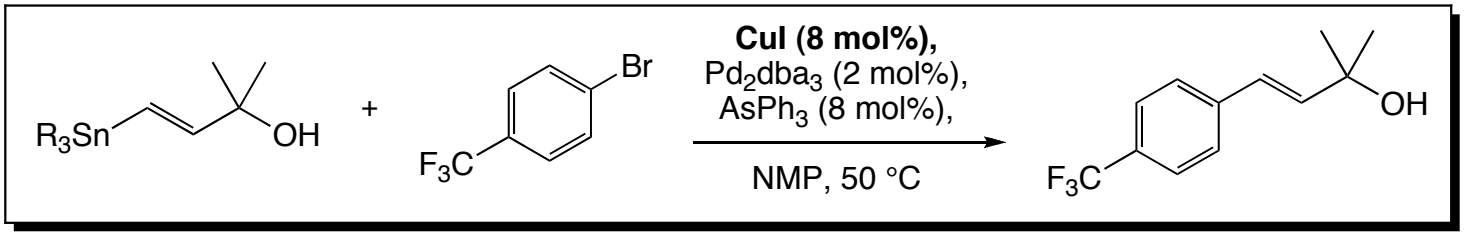


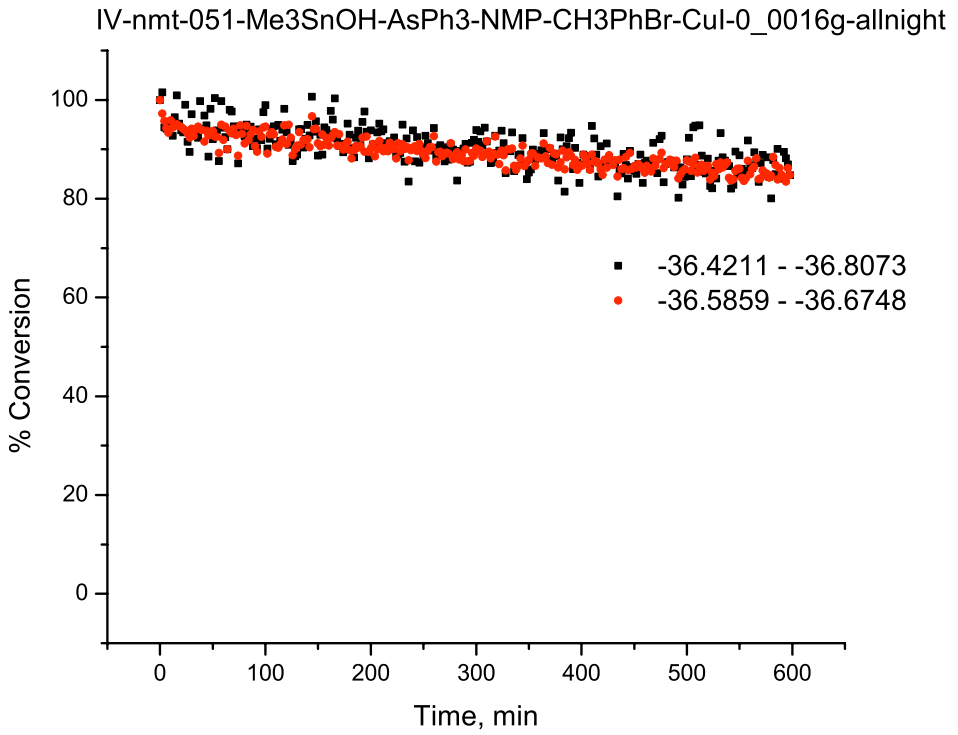


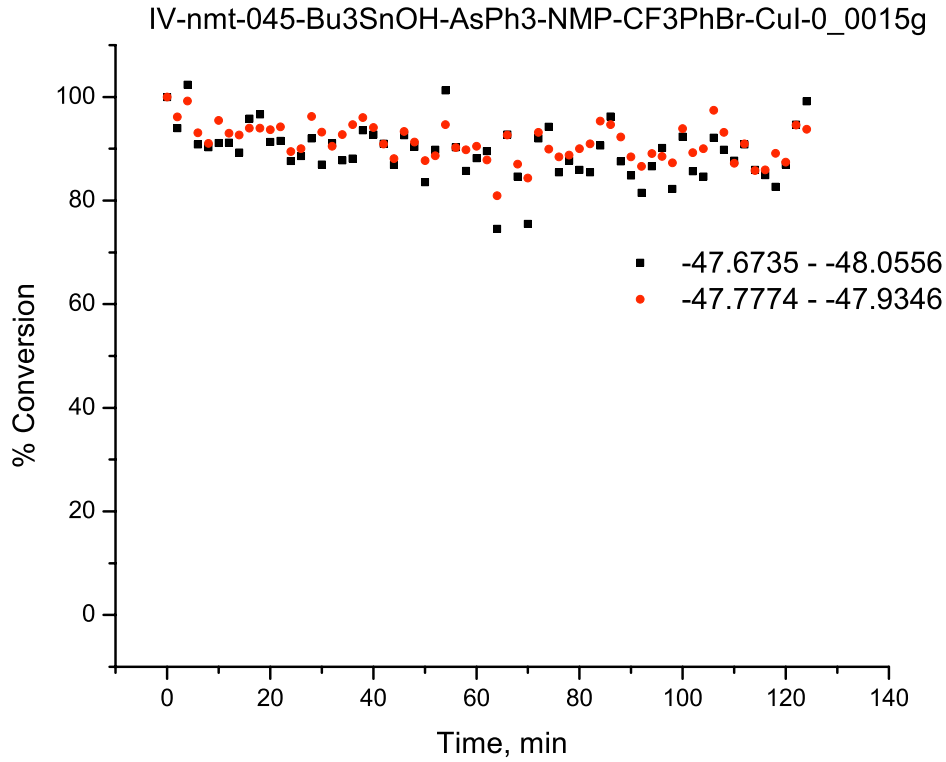
CuI seems to negatively affect the rate and to different extents for Me and Bu

**Note: CuI was not added as a solution and was not soluble.

CuI as an Additive
Aryl Bromides in $AsPh_3$/NMP



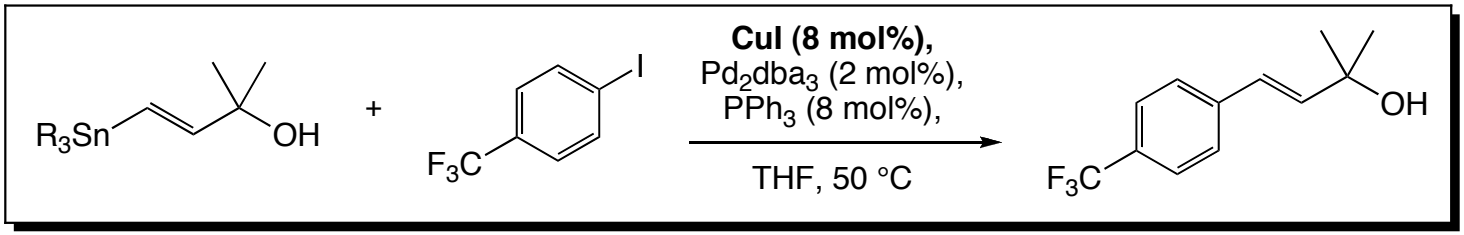


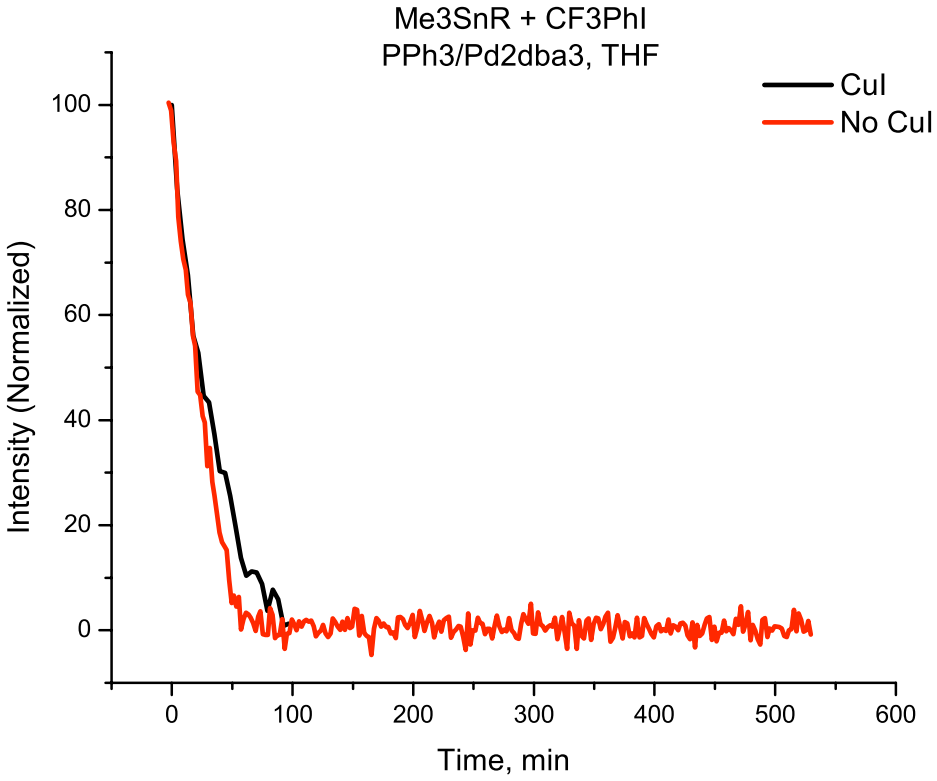


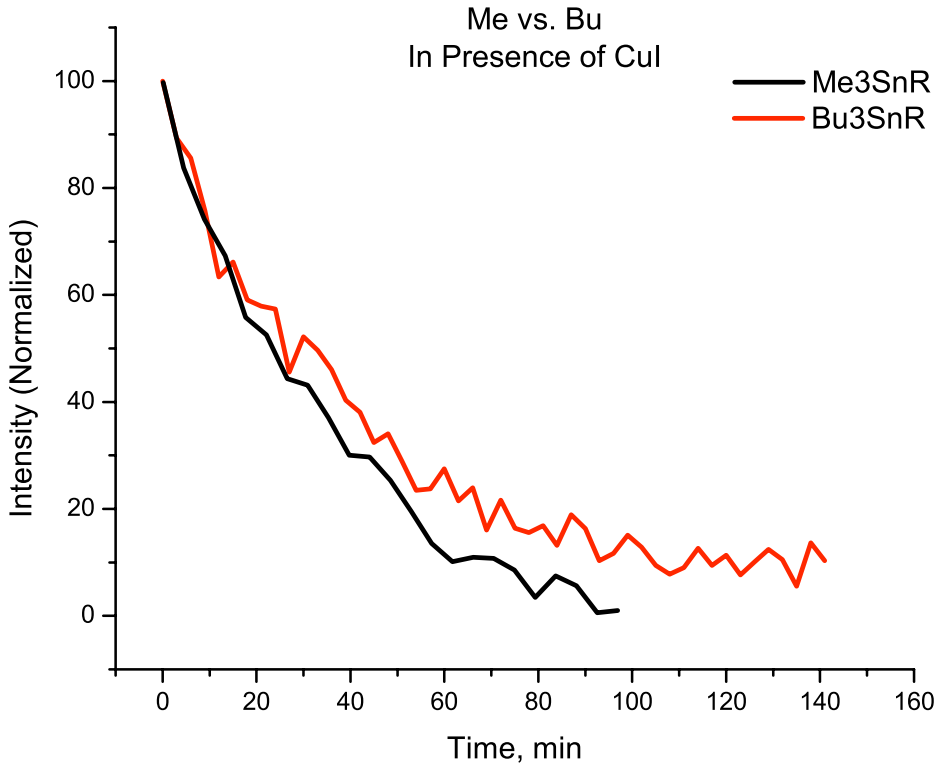
The reactions do not proceed for aryl bromide couplings

Should make faster b/c ox.addn. rds for ArBr, CuI should make more active Pd

CuI as an Additive
Aryl Iodides in PPh_3/THF

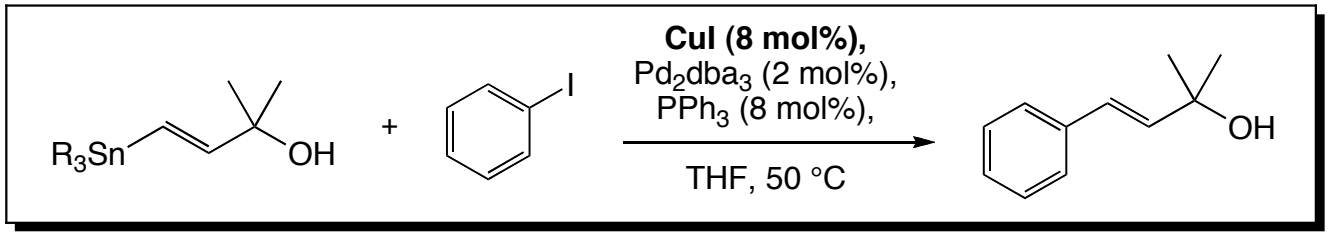


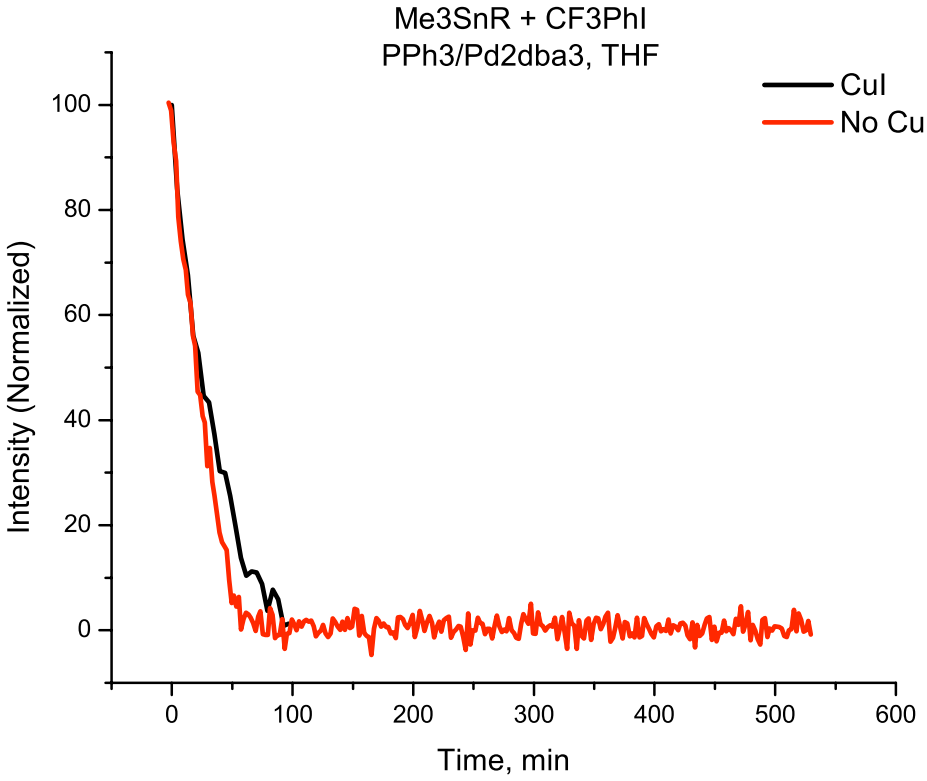


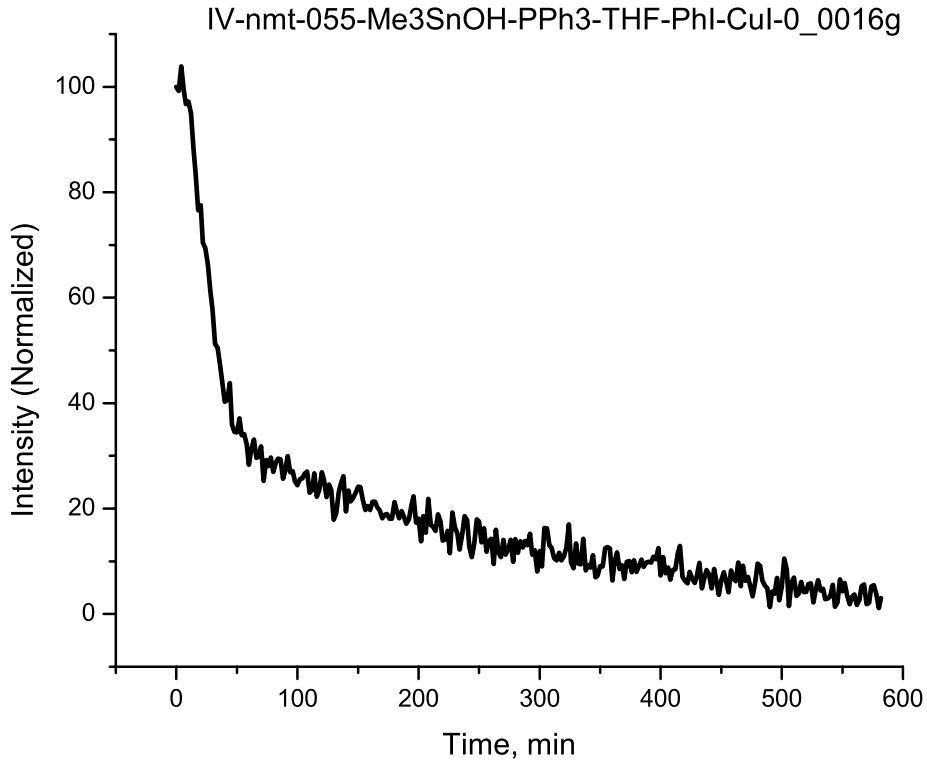


CuI still inhibits the reaction slightly....

CuI as an Additive
Aryl Iodides in PPh_3/THF

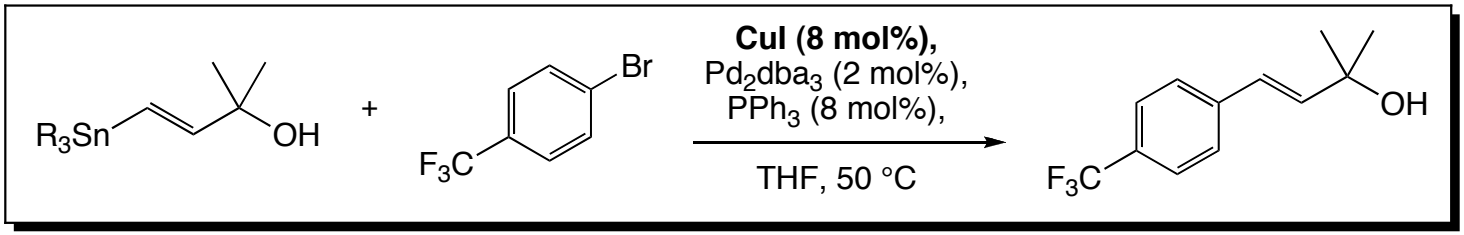


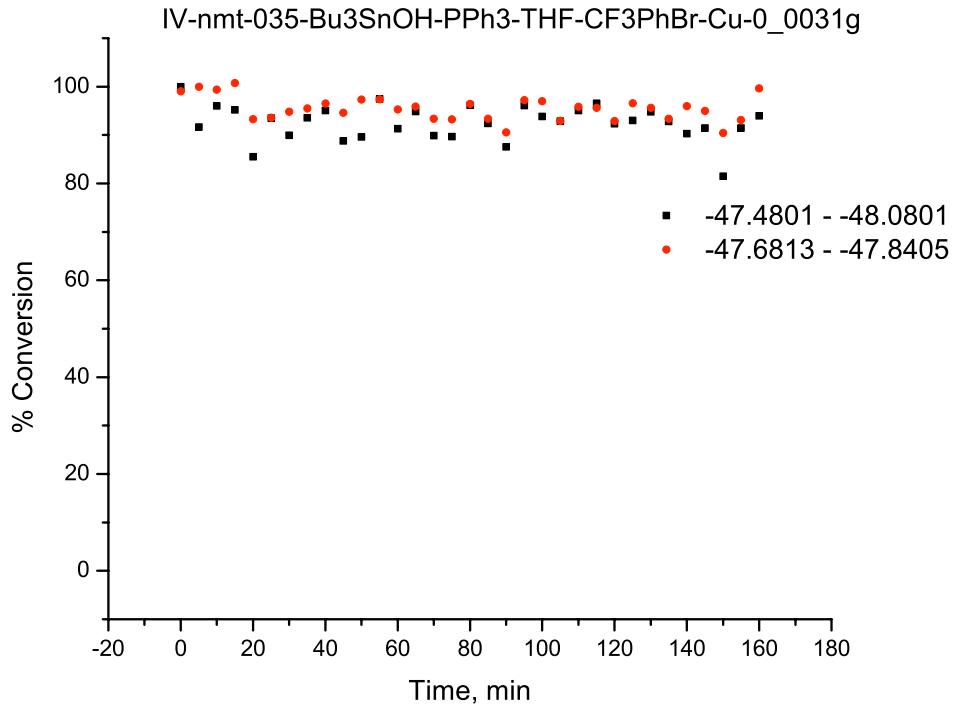




Perhaps some insight into the inhibition when coupled with PhI?

CuI as an Additive
Aryl Bromides in PPh_3/THF





If CuI increases the rate of TM, I wouldn't except rate acceleration compared with reactions w/o CuI, but I wouldn't except reaction suppression.

Next Regarding CuI...

Solubility issues:

- Check benchtop reaction (w/ magnetic stirring) to see if kinetics are similar

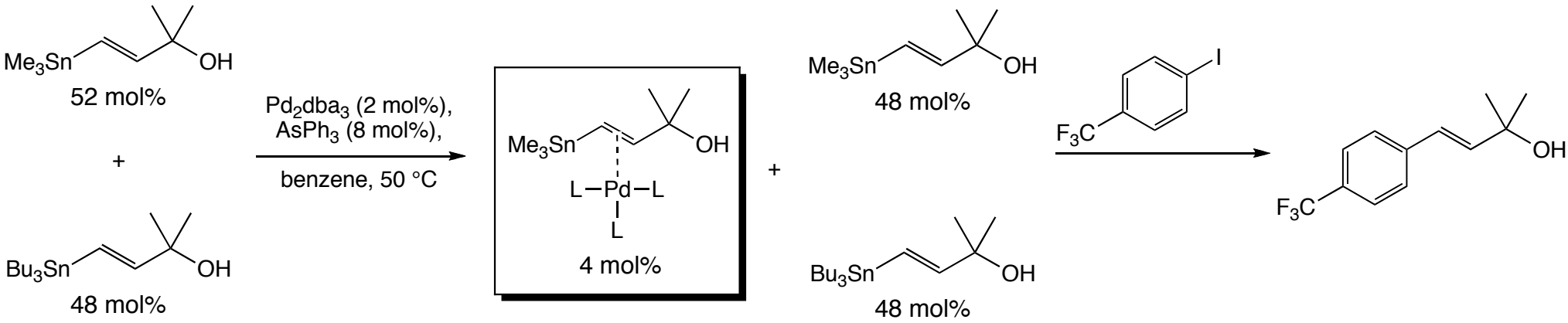
Impurity Issues:

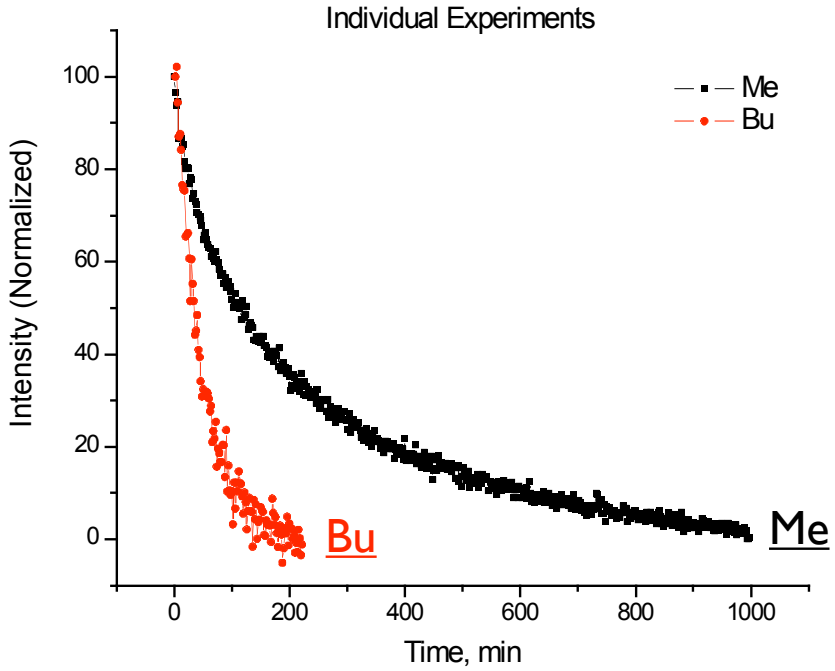
- Purified CuI myself by precipitating from water; perhaps still "wet" (although that should "increase" the rate). Retry with commercial 99.999% CuI

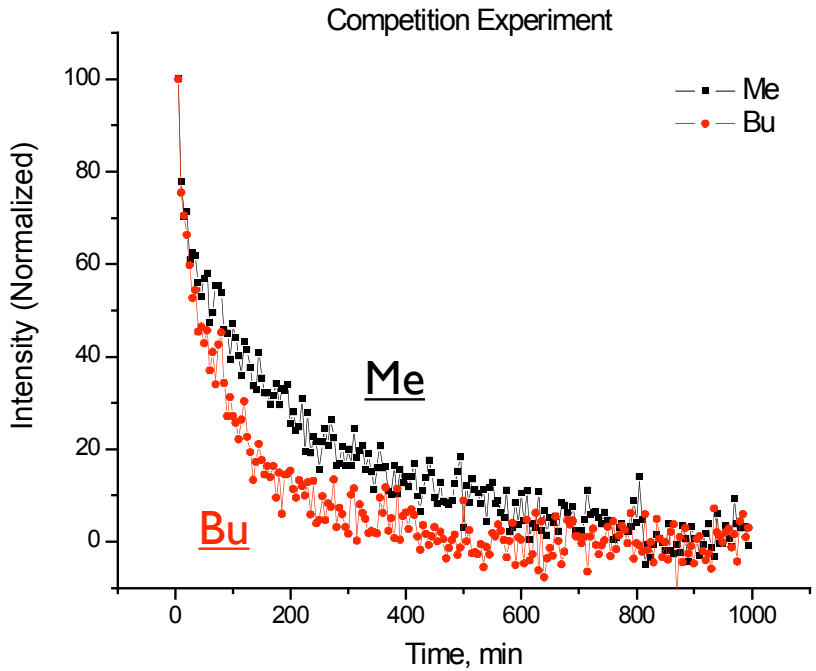
Substrate Issues

- Maybe rate enhancement is substrate dependent.... Run with unsubstituted vinyl tins to compare with Farina's results. If I get the same rates, CuI & mixing probably ok, if not... who knows.

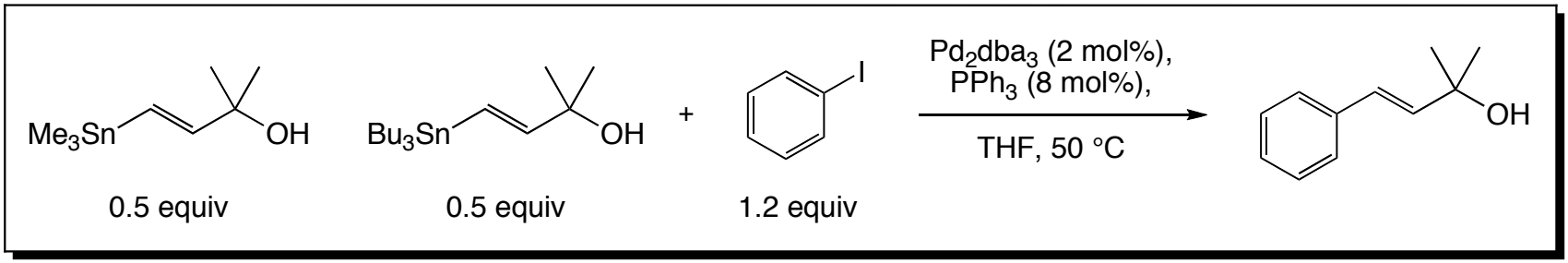
Recall the "Competition" Experiment: Testing Me vs. Bu in Benzene in the Same Catalyst

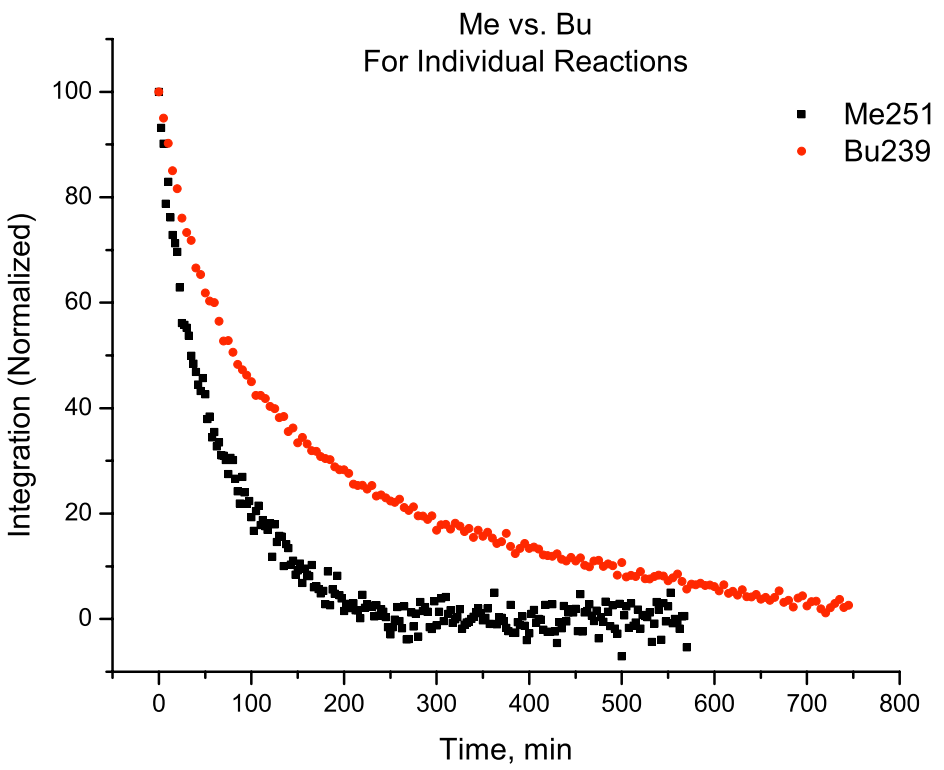


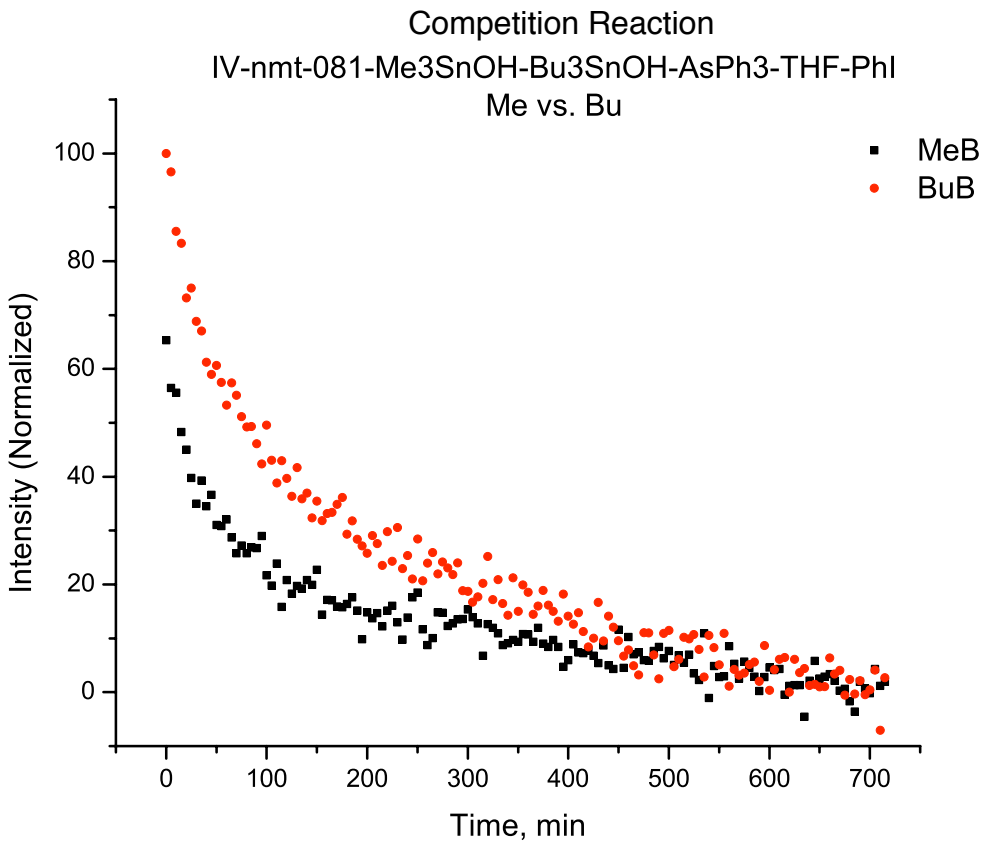




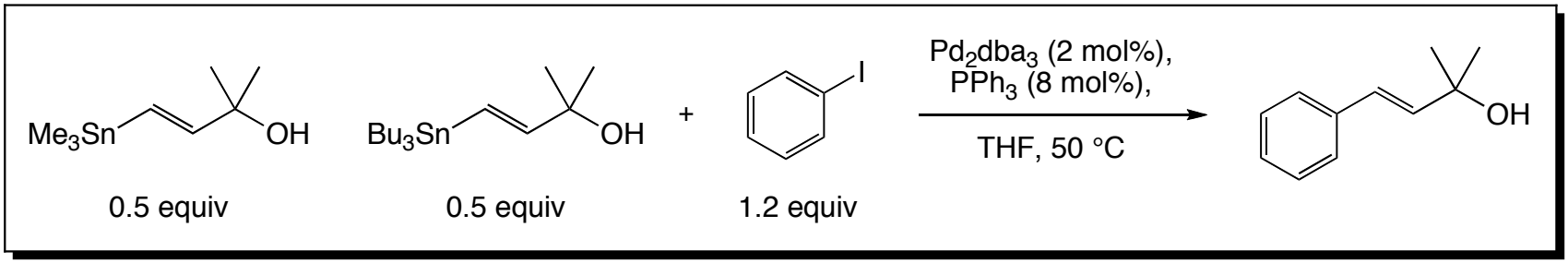
Another Competition Experiment

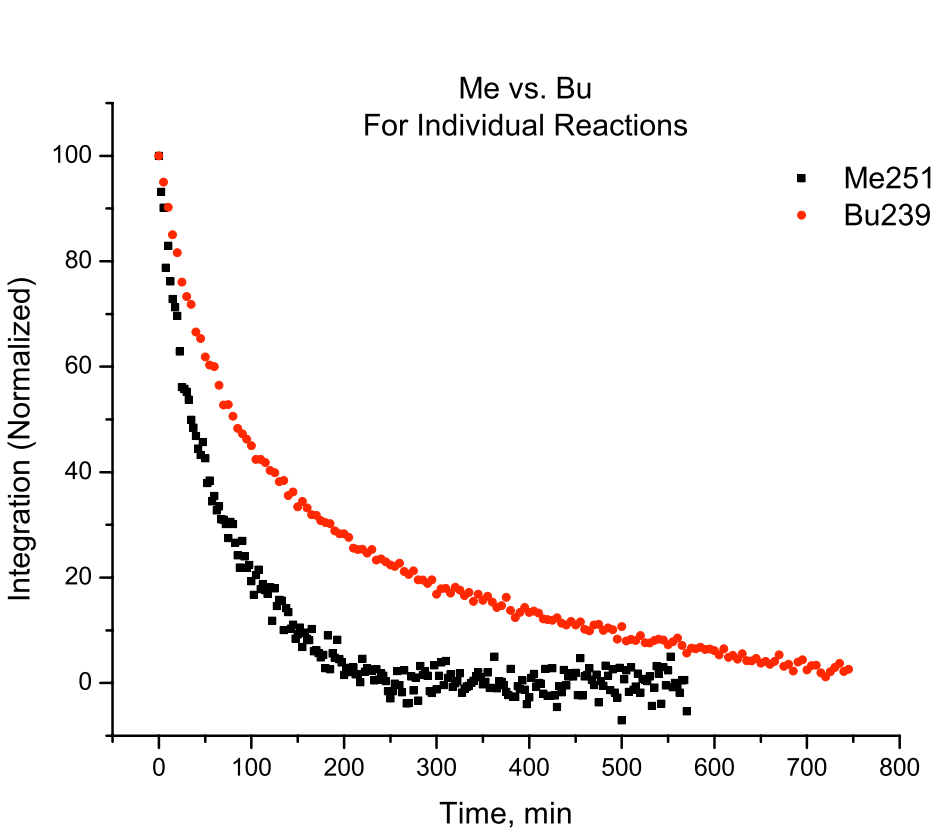


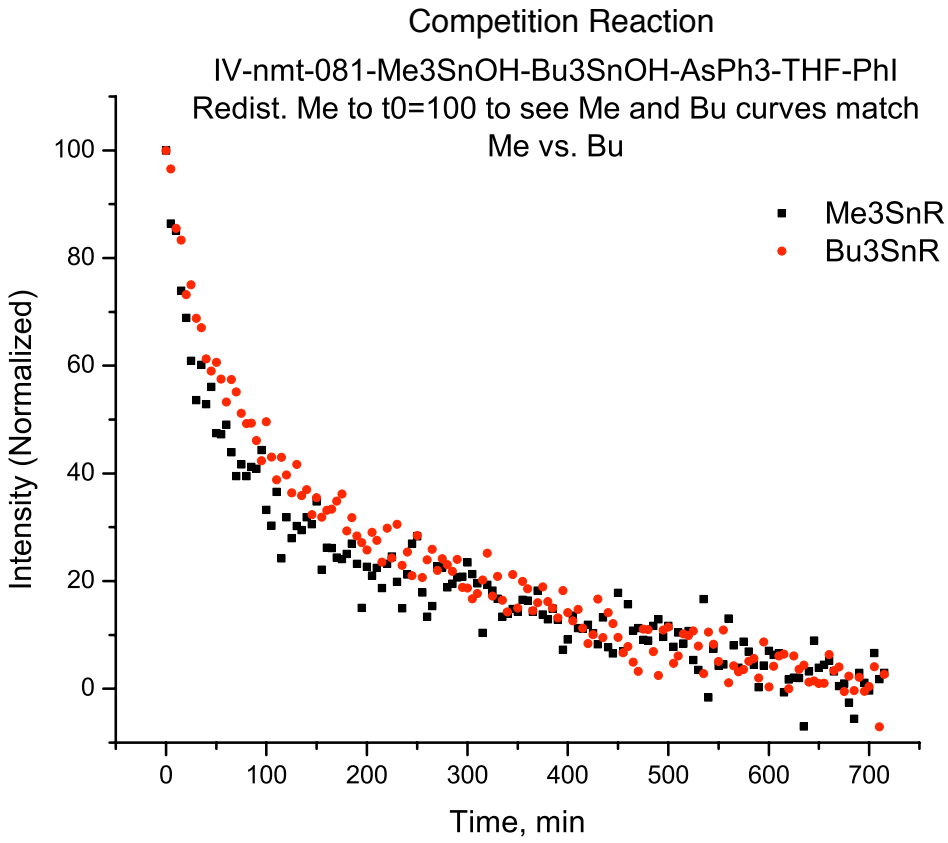




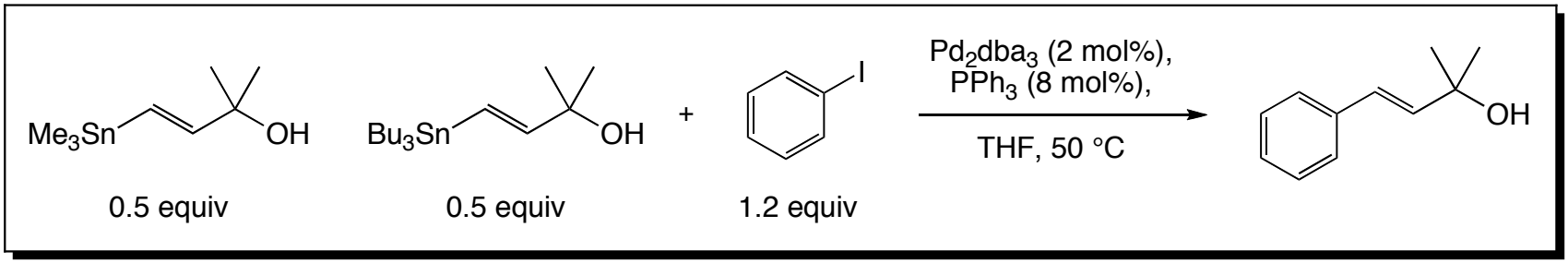
Another Competition Experiment

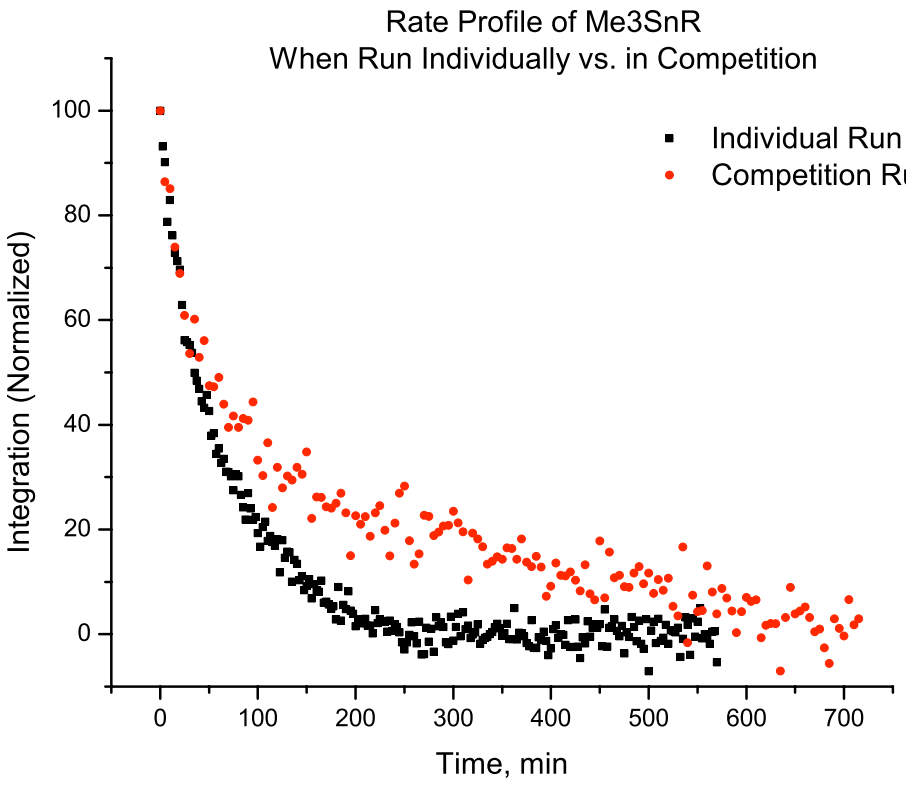


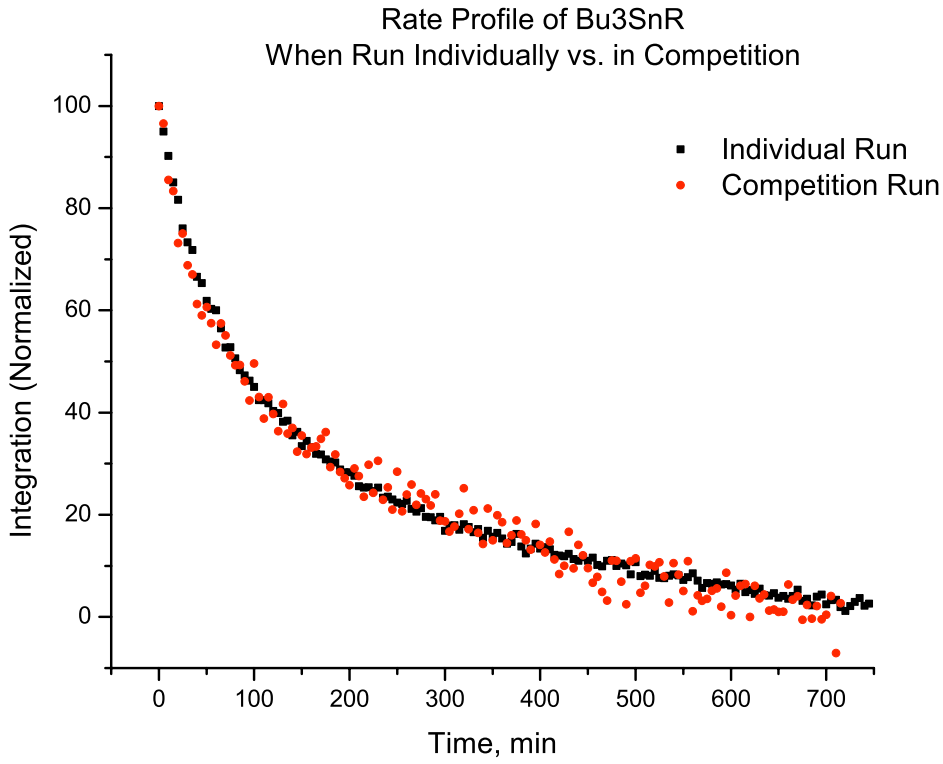




Another Competition Experiment







I don't know what this means yet

2009 NCAA FINAL FOUR DETROIT

THE ROAD ENDS HERE.

PLAY HAS BEGUN!

VS

CAROLINA TAR HEELS

Go Green!!