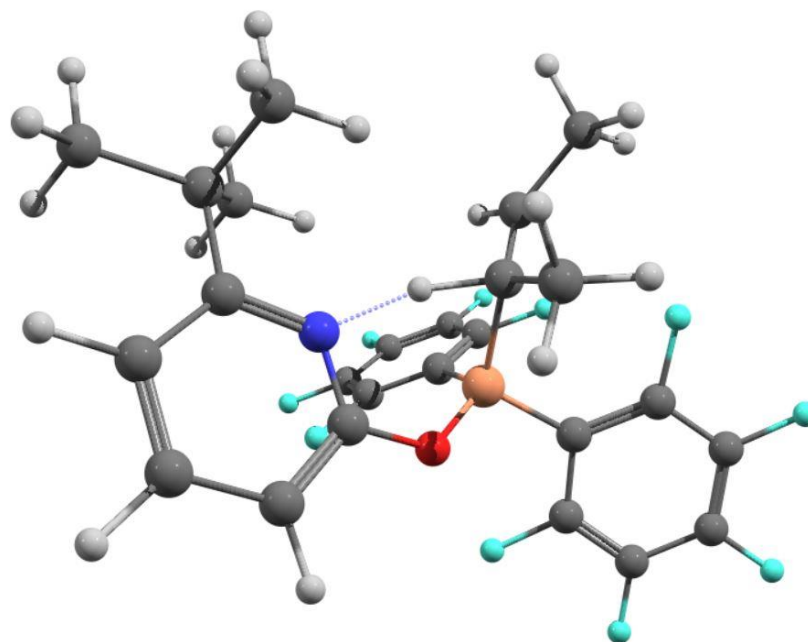


Hydrogenations with Pyridone Borane Complexes: On the Way to Contrathermodynamic Hydrogenations

presented by
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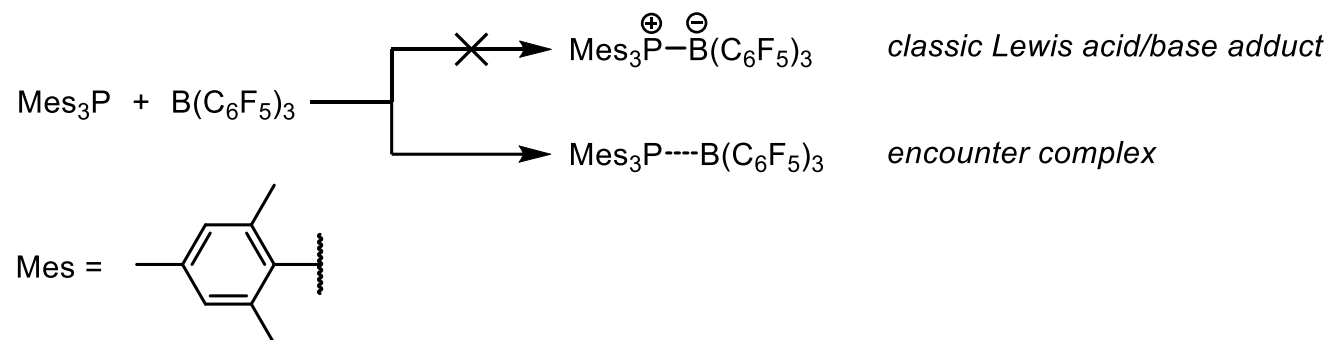




- Discovered by Stephan *et al.* in 2006

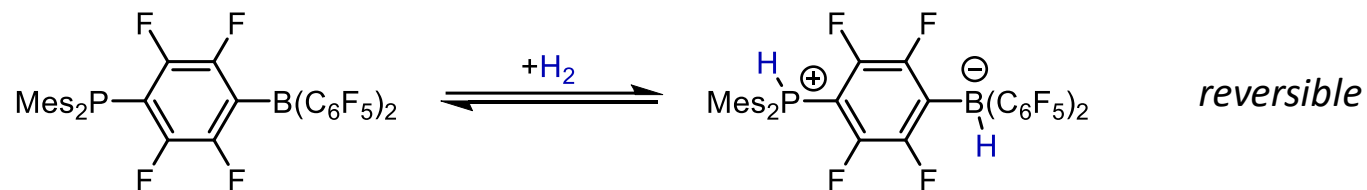
- Formation of ionic adduct prevented

- Encounter complex hold together by dispersion



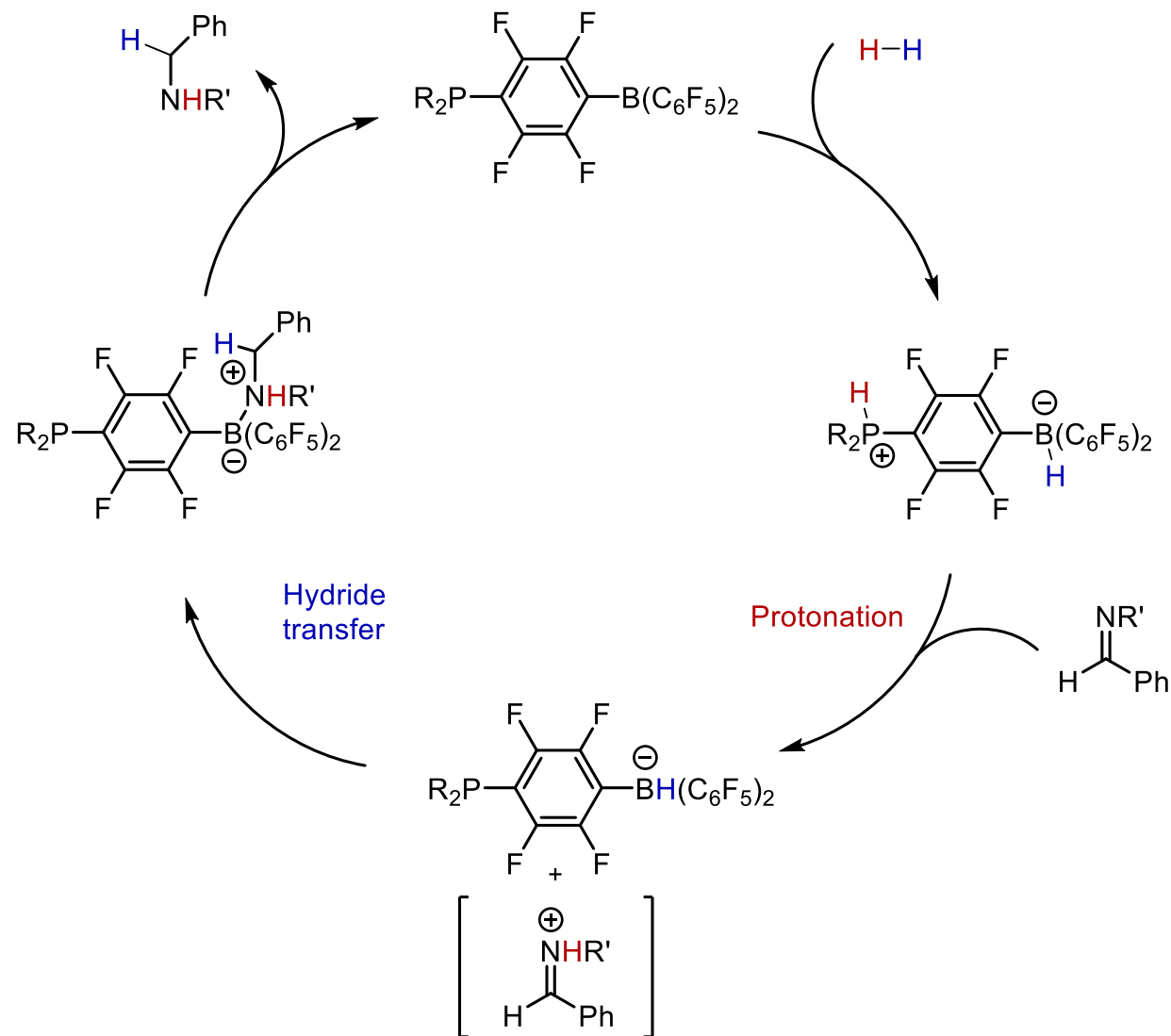


- Hydrogen activation was observed at room temperature
- First reversible, metal-free hydrogen activation



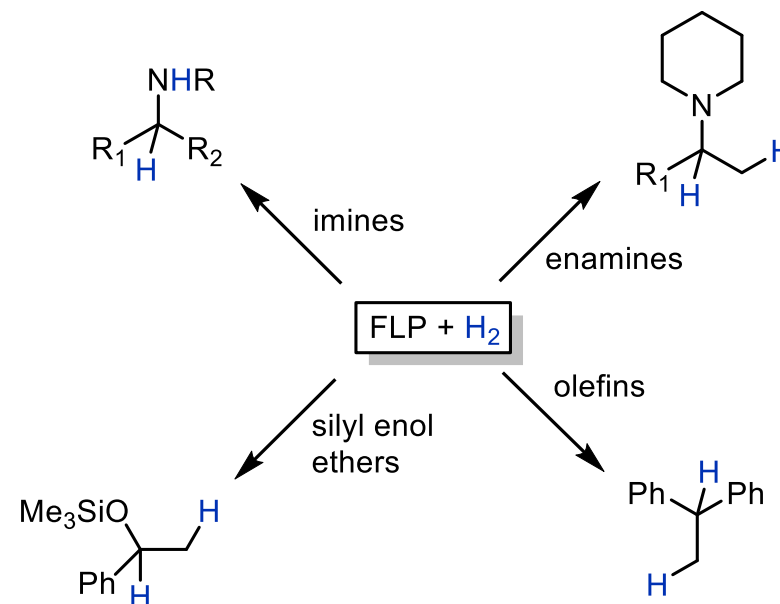


- First metal-free hydrogenation
- Substrate activation through protonation
- Subsequent hydride transfer



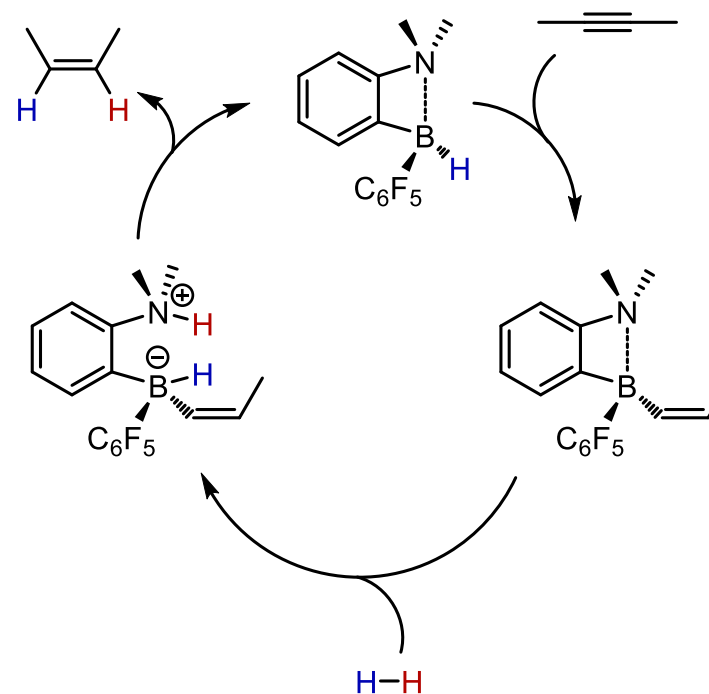
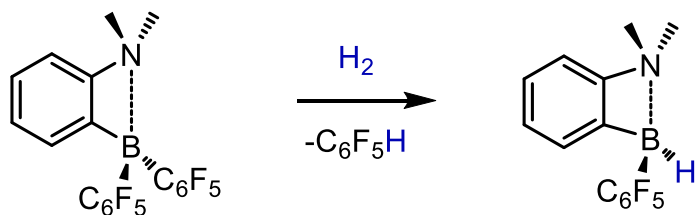


- First metal-free hydrogenation
- Substrate activation through protonation
- Subsequent hydride transfer



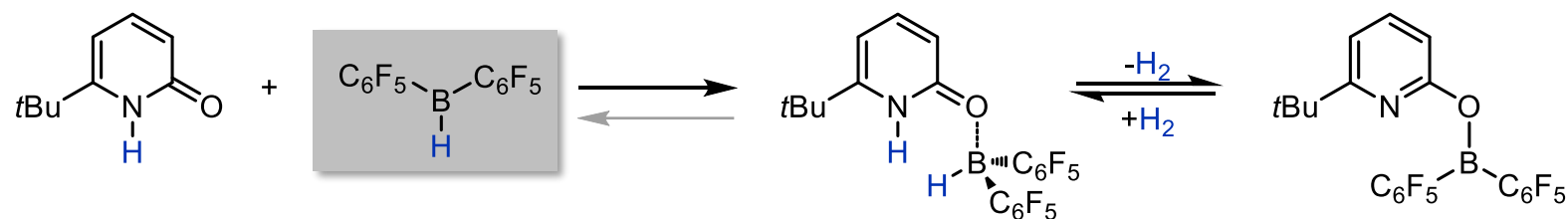


- *In-situ* generation of the catalyst
- Substrate activation through hydroboration
- Highly *cis* selective



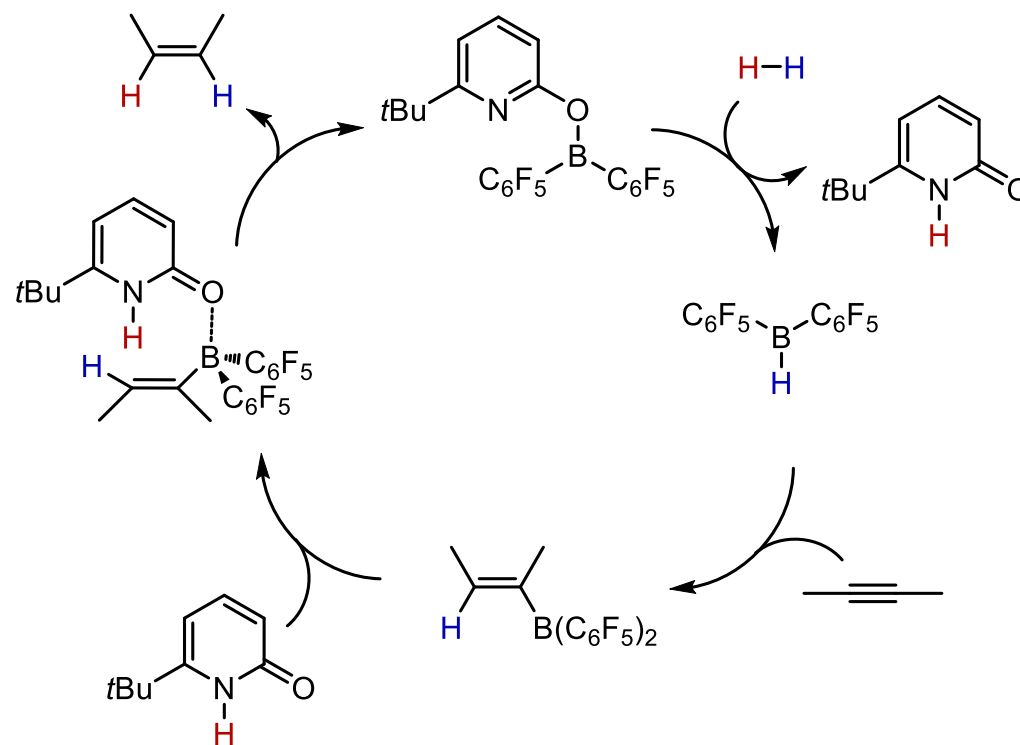


- The pyridone borane system loses hydrogen at room temperature
- Reversible H_2 activation under hydrogen pressure
- Free borane might undergo hydroborations



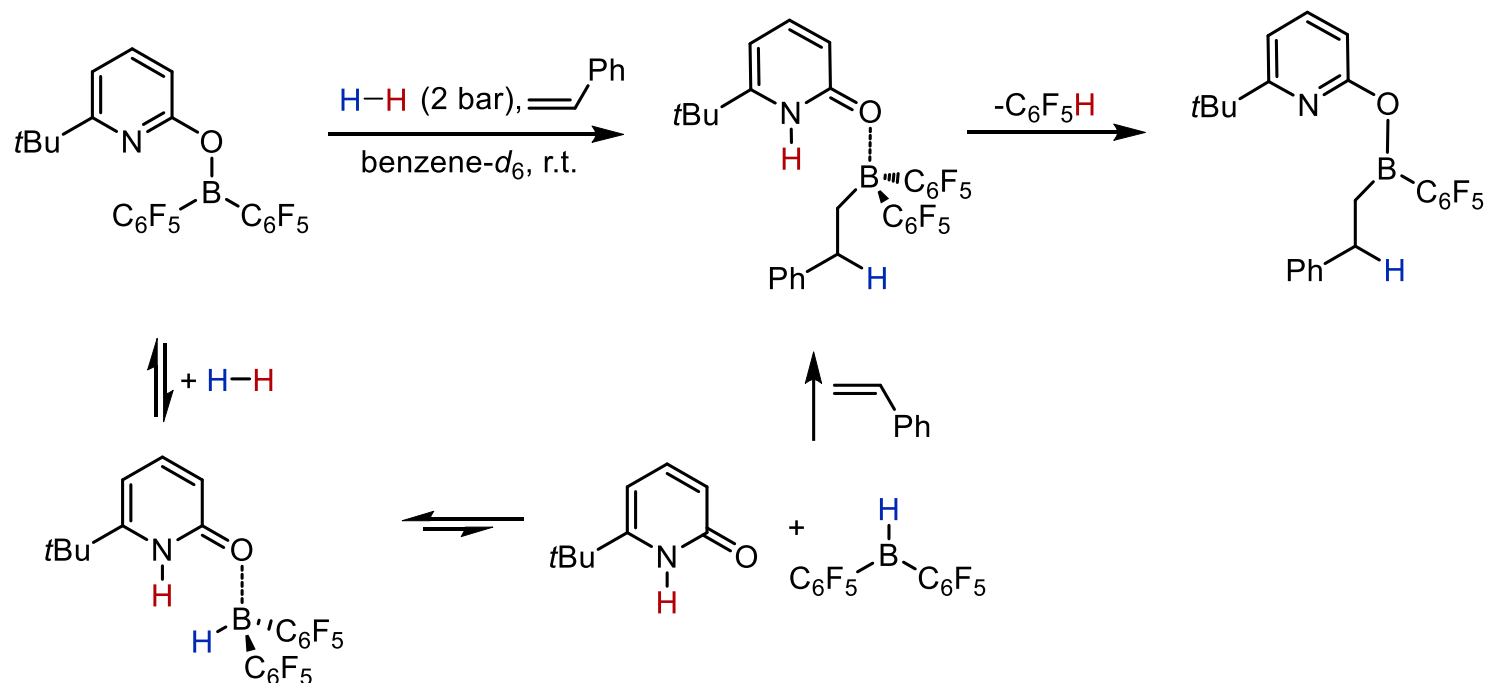


- H_2 activation by the boroxypyridine
- Dissociation of the pyridone borane
- Hydroboration of an alkyne
- Protonative elimination by the pyridone



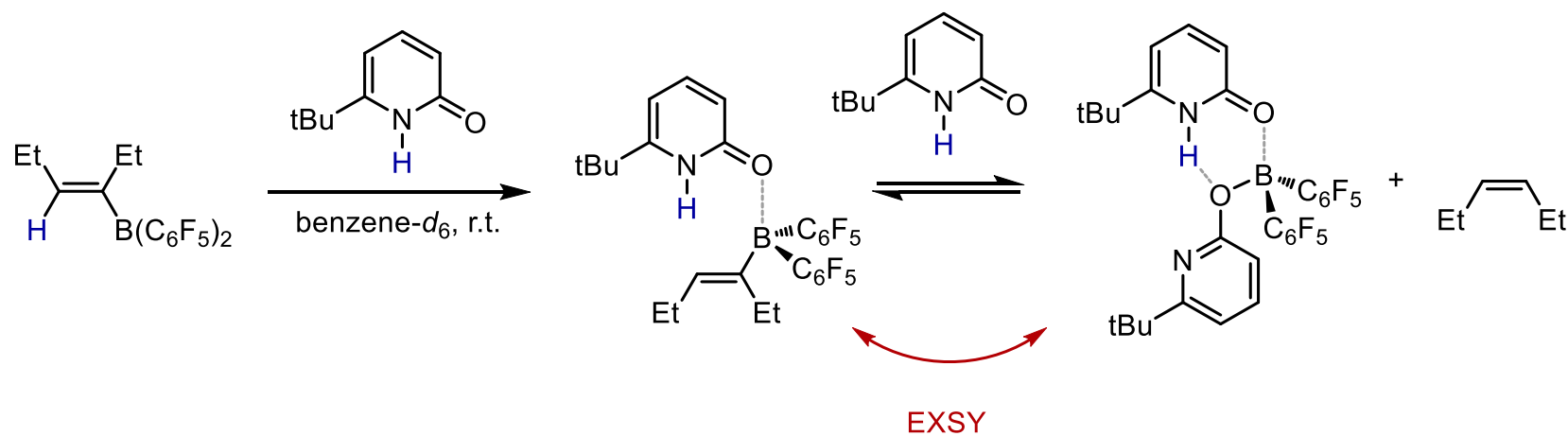


- But: Can protodeborylation take place?
 - Elimination of pentafluorobenzene



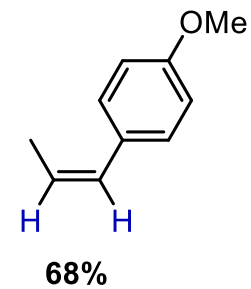
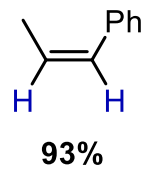
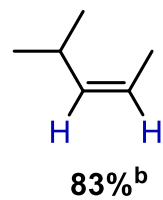
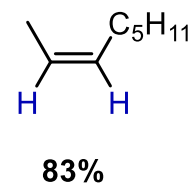
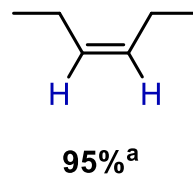
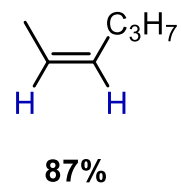
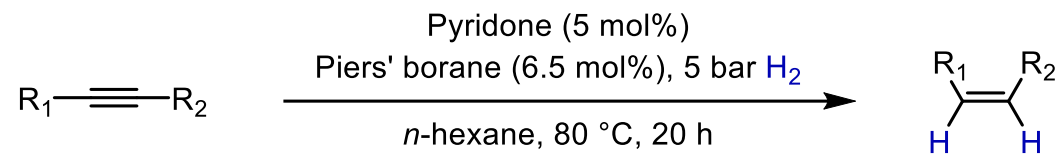


- As the pyridone is added, the *cis* alkene is observed
- Bispyridone complex shows exchange signals



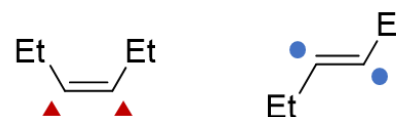


- Borane excess is required for reproducible results

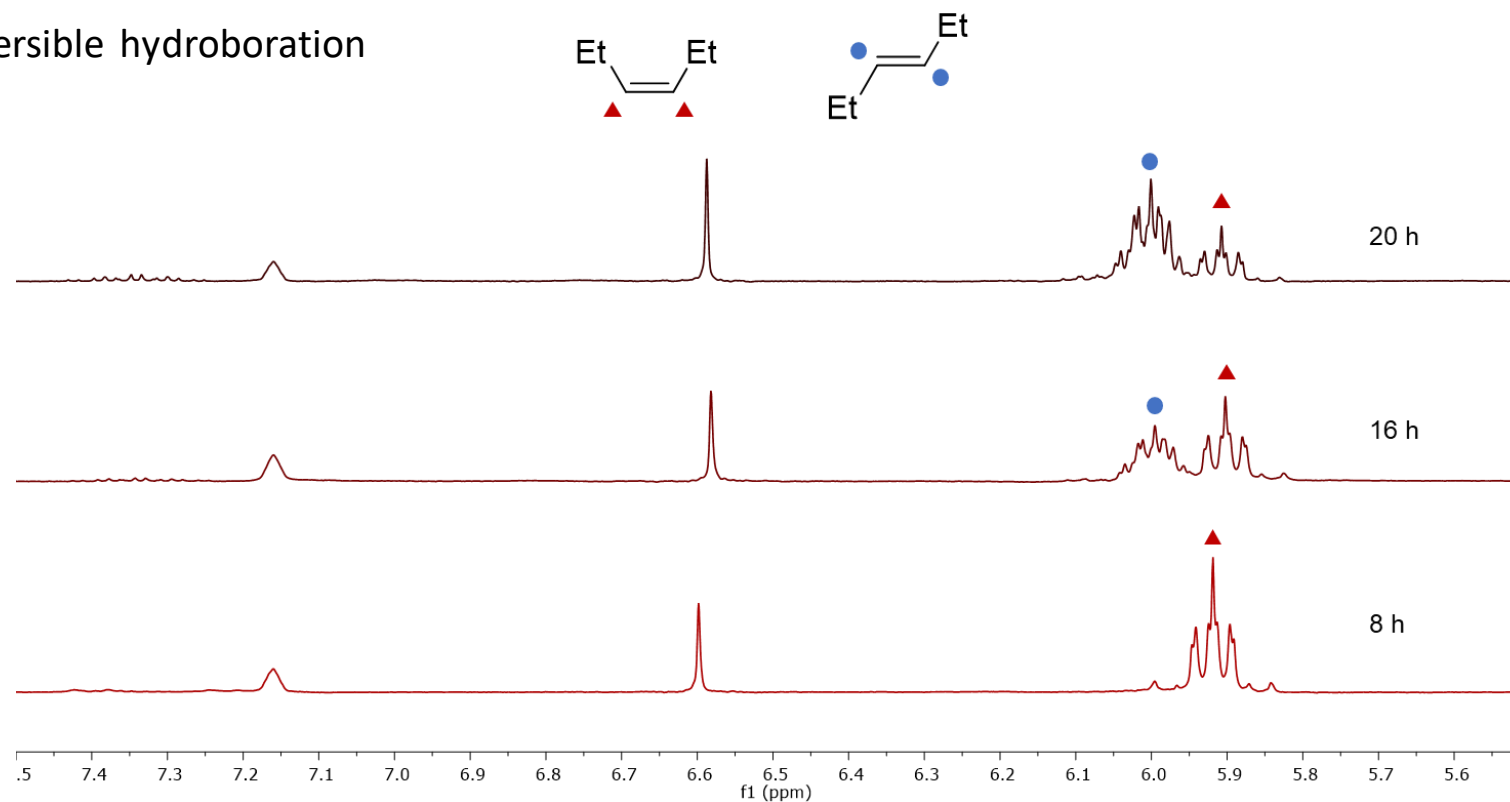




- cis/trans isomerization *via* reversible hydroboration



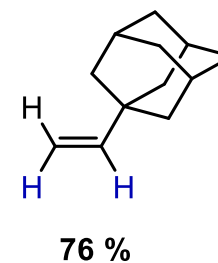
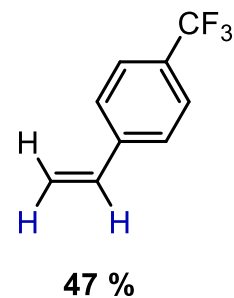
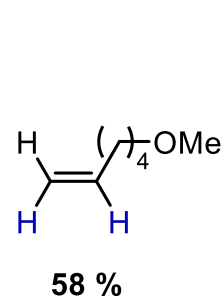
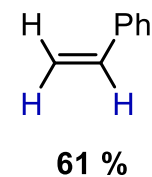
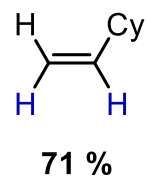
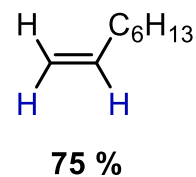
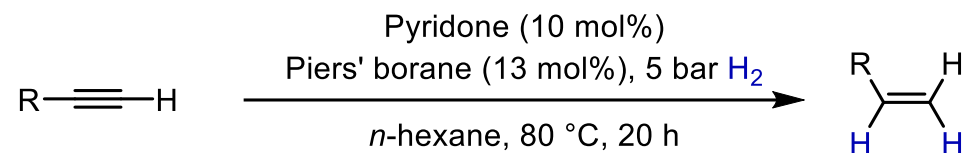
reaction time / h	<i>cis</i> / <i>trans</i>
8	100:0
16	49:51
20	23:77



^1H NMR (400 MHz in *n*-hexane, benzene- d_6 capillary)

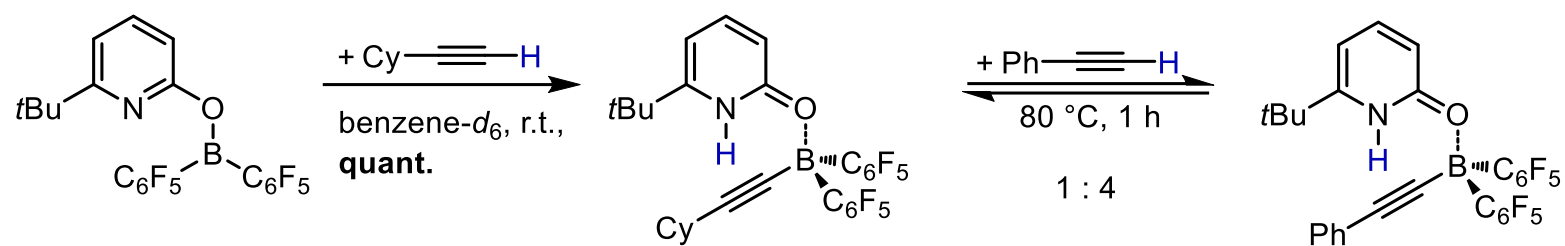


- Irreversible C_{sp}-H activation of terminal alkynes by FLPs
- C_{sp}-H activation with the boroxypyridine reversible?



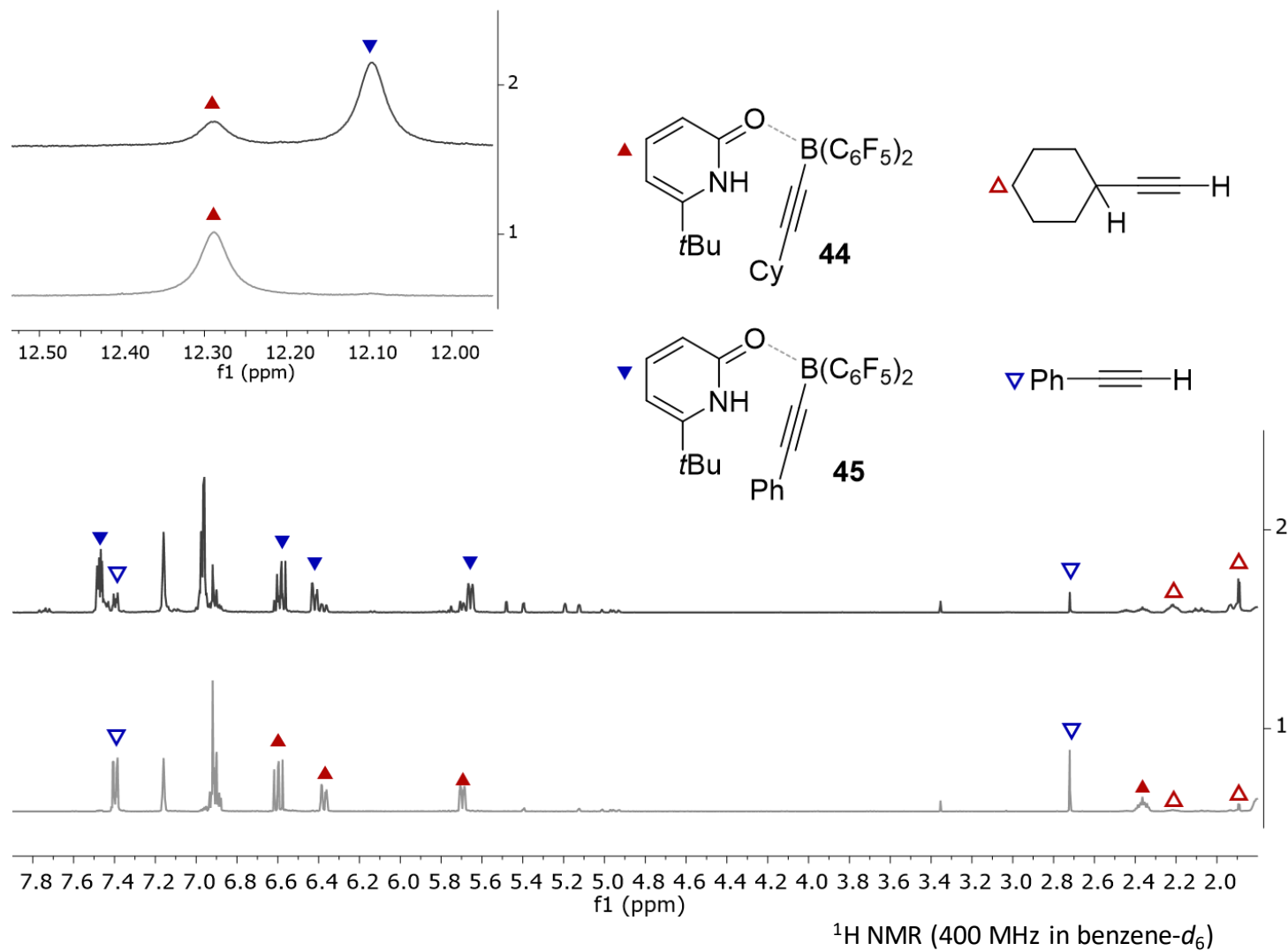


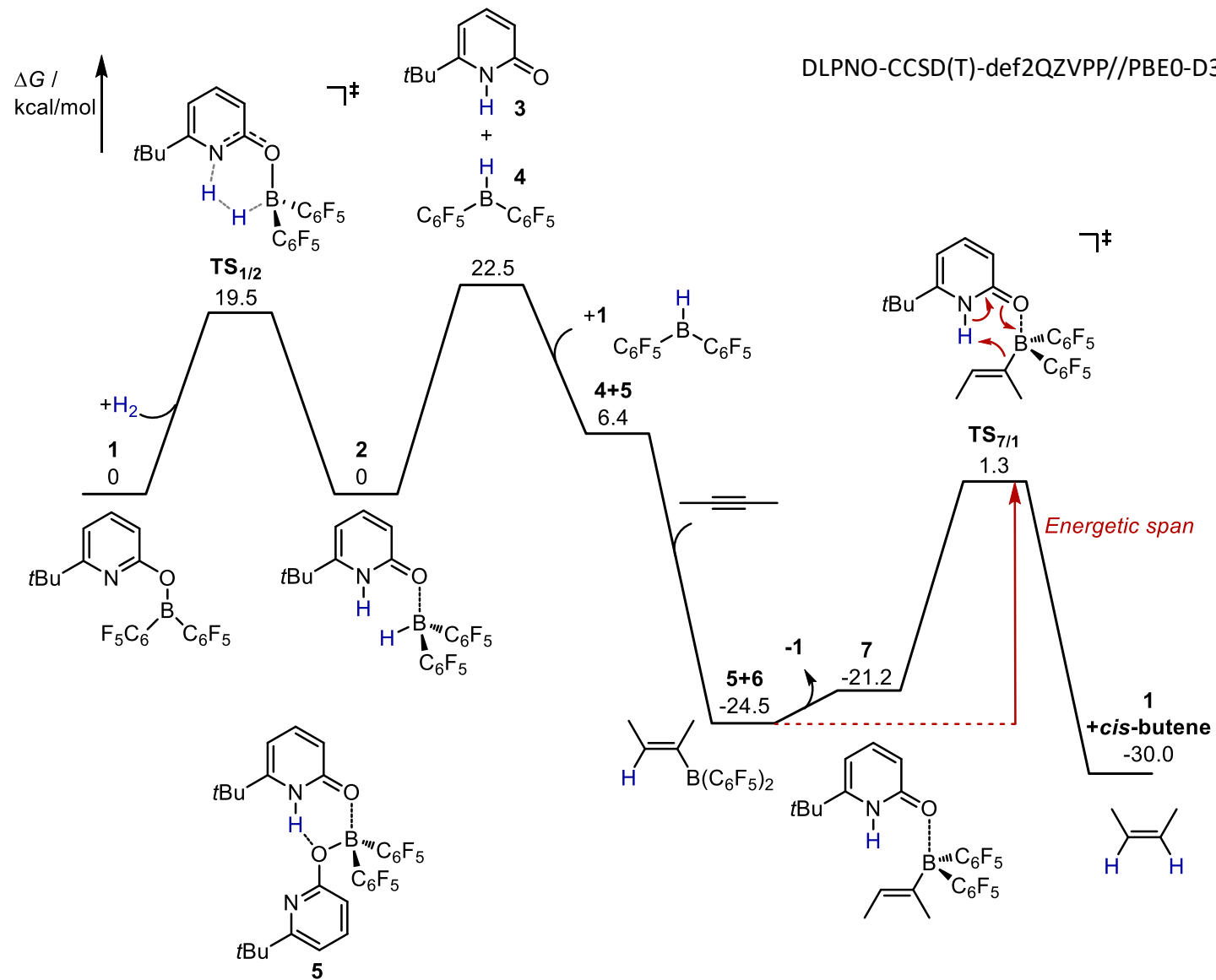
- Exchange of alkynes was observed at reaction conditions





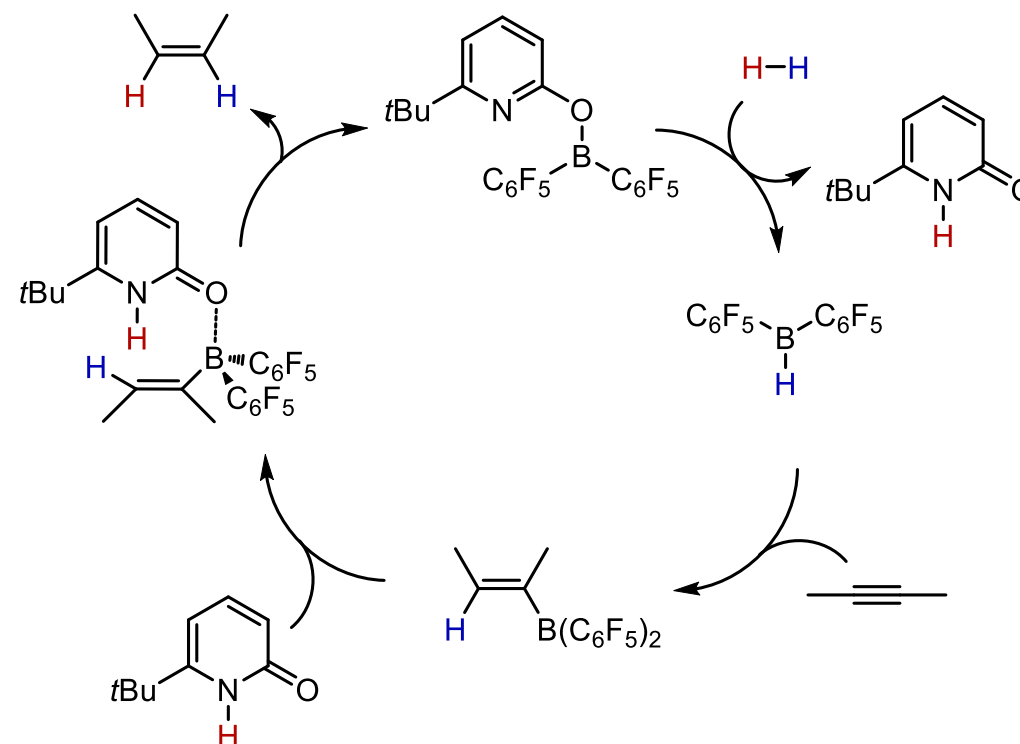
Hydrogenation of terminal alkynes





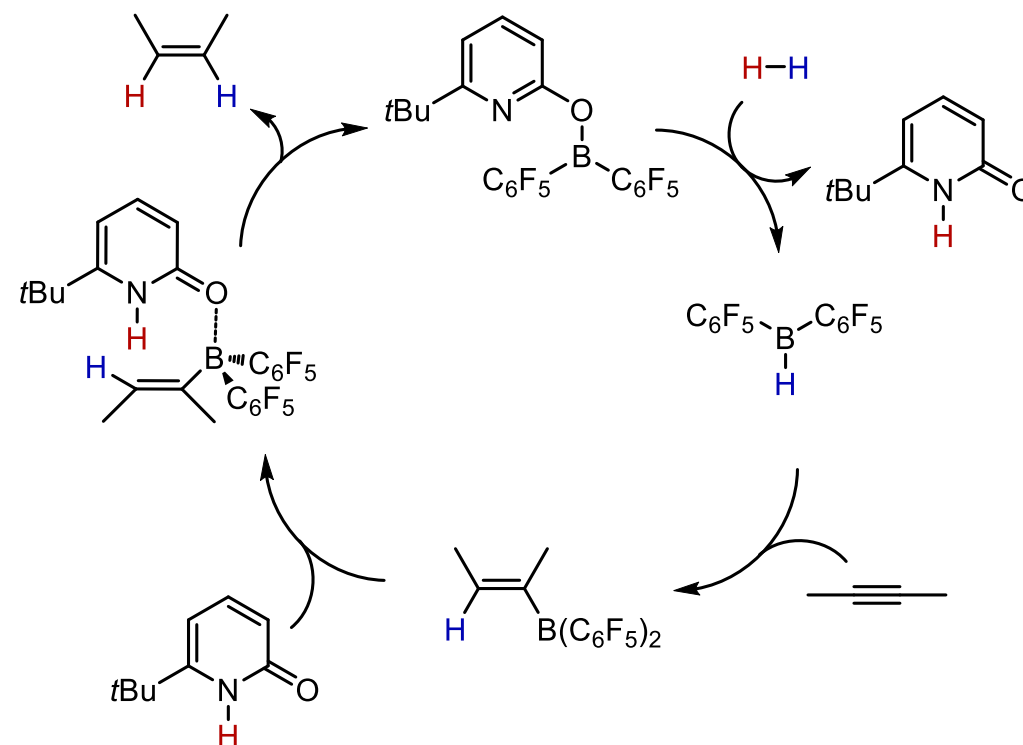


- Catalytically hydrogenate *internal* alkynes *cis* selectively (6 examples, 68% to 95% yield)
- First metal-free semihydrogenation of *terminal* alkynes (6 examples, 47% to 76% yield)
- Mechanistic experiments and computations support the catalytic cycle



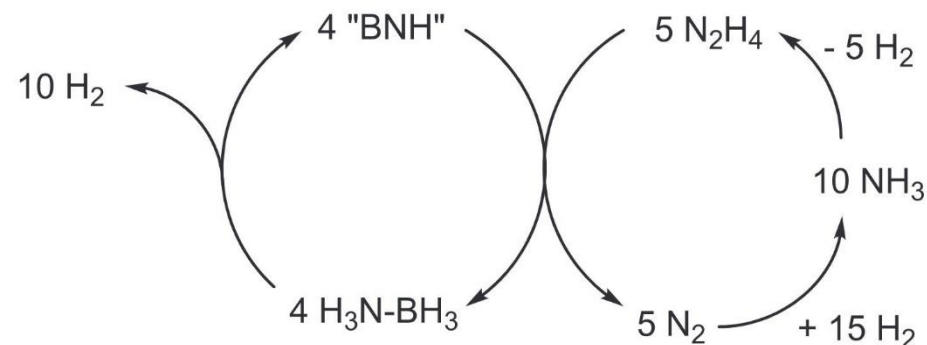
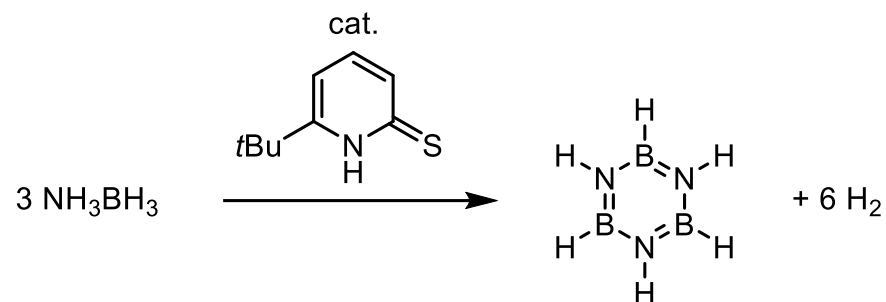


- Why do we need a 1.3:1 ratio of Piers' borane to pyridone?
- Investigate the catalyst at reaction conditions





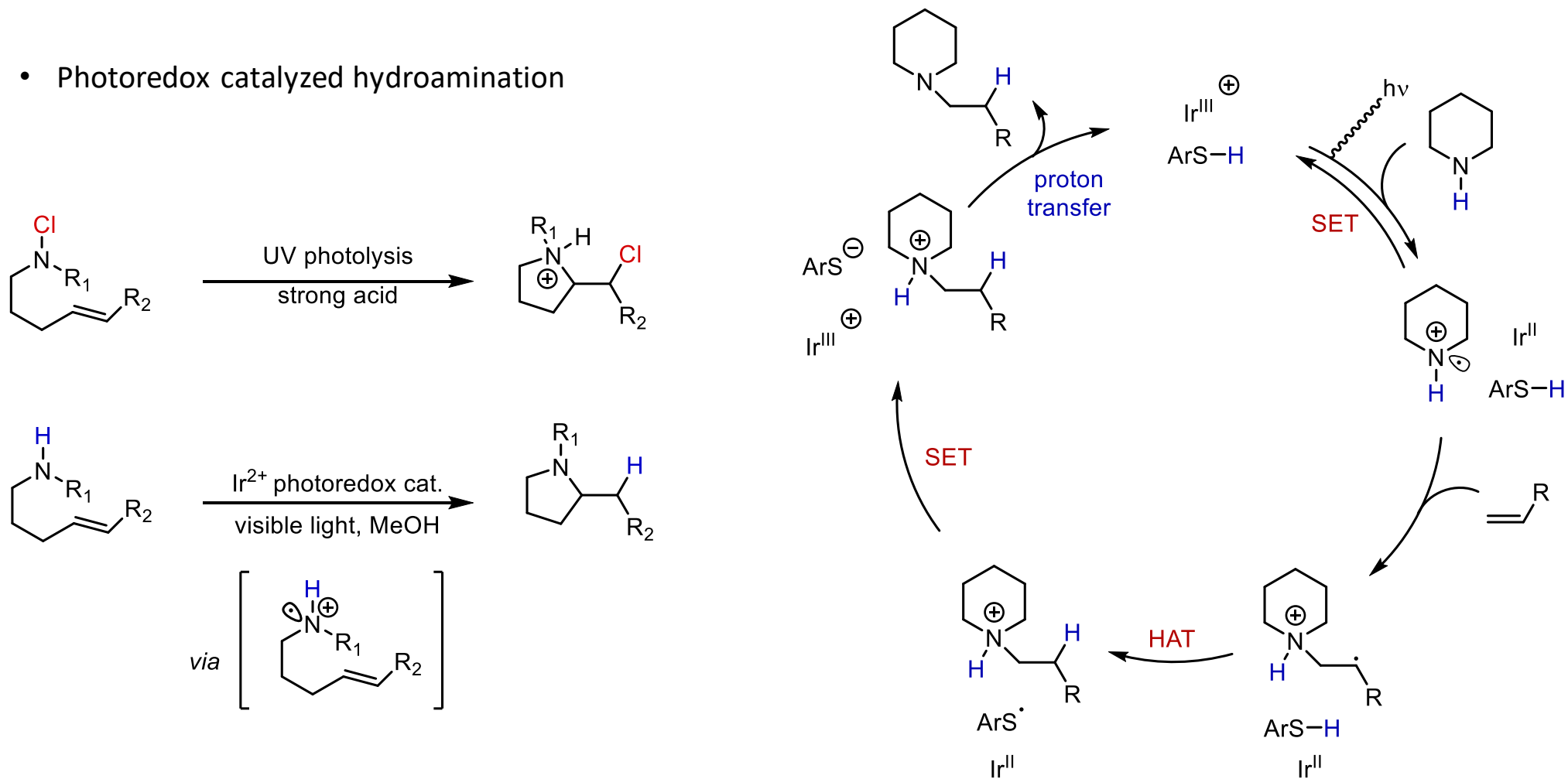
- Efficient way to dehydrogenate ammonia borane
- Reaction with hydrazine in liquid ammonia 60°C
- What about the back reaction?





Part II: On the way to contrathermodynamic hydrogenations

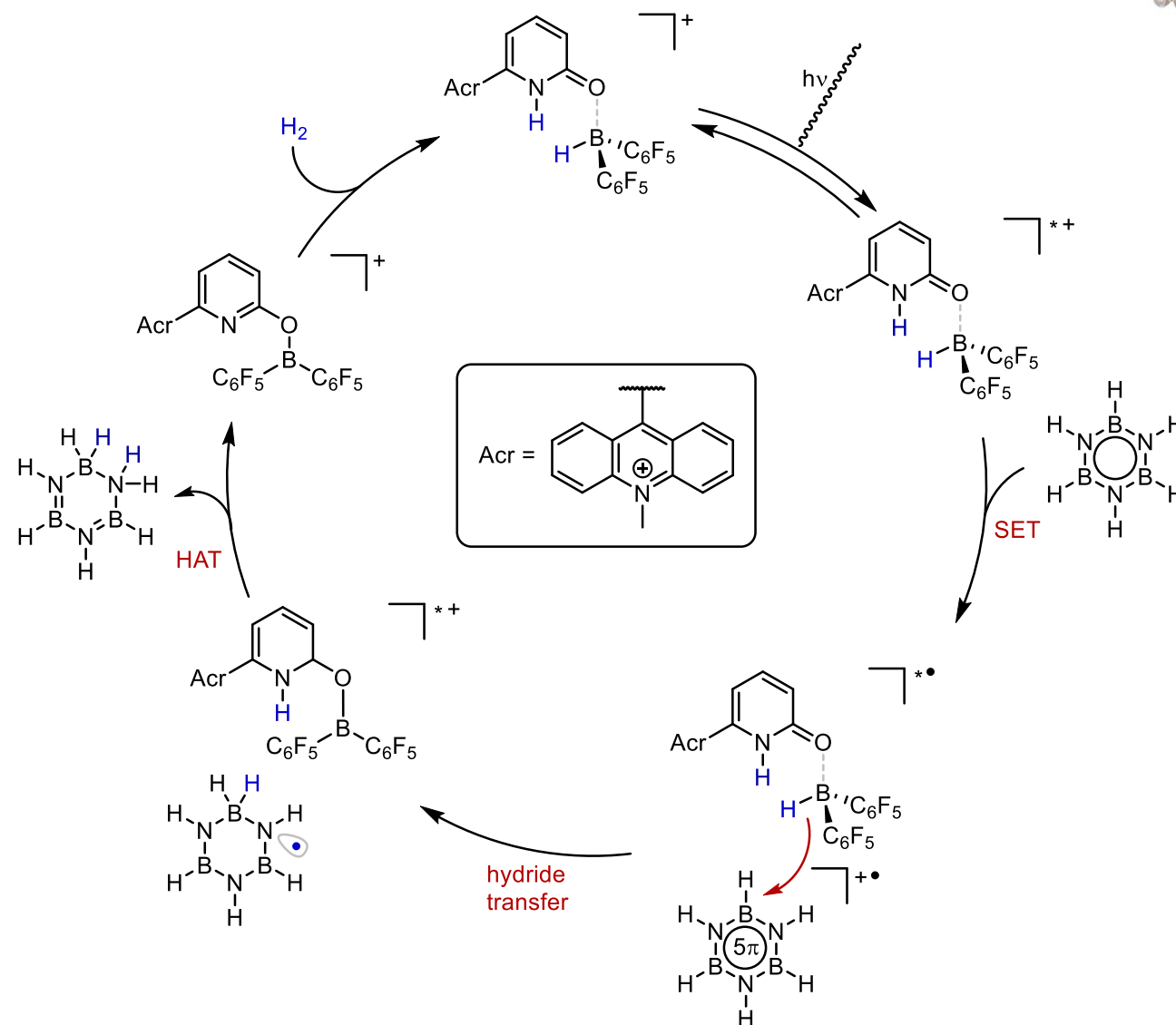
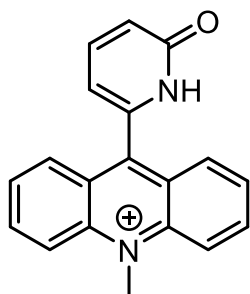
- Photoredox catalyzed hydroamination

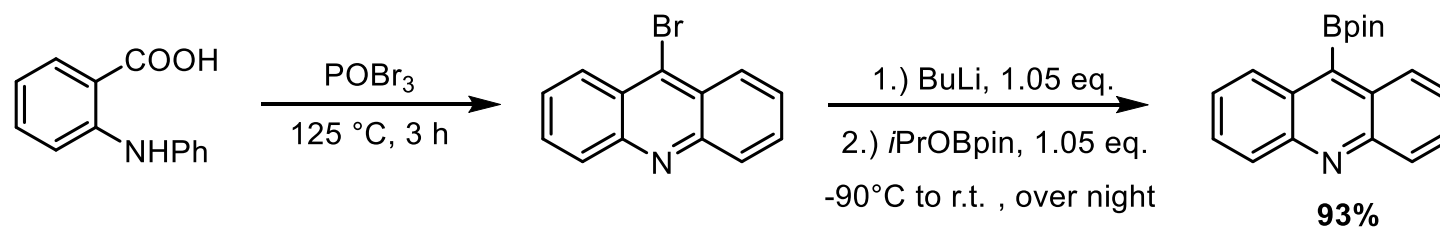
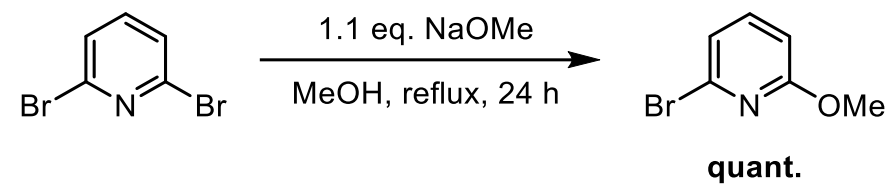
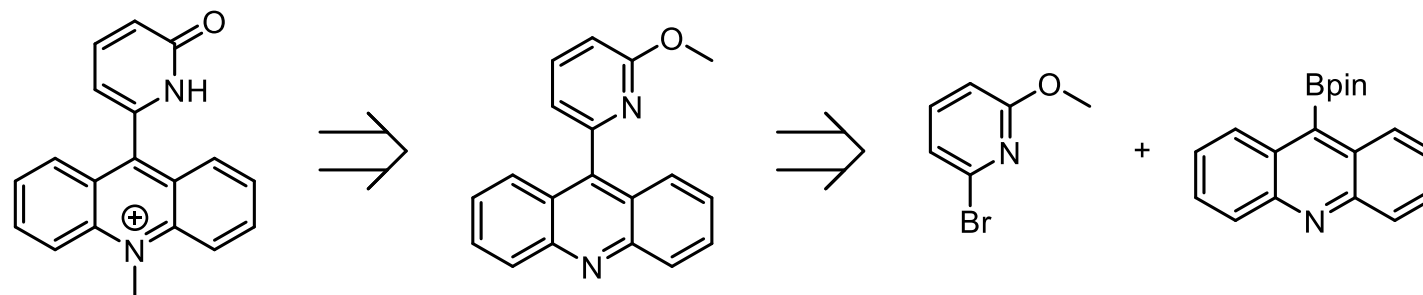


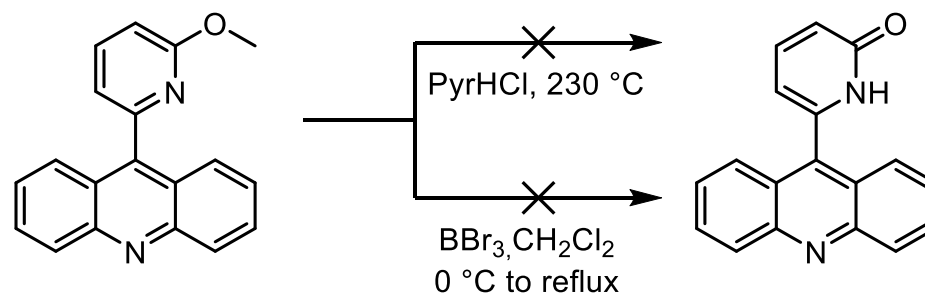
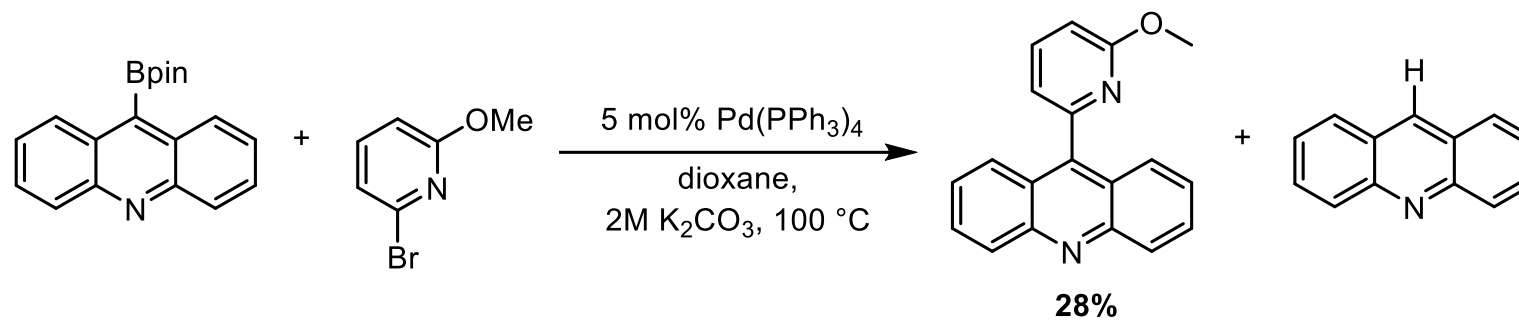


Part II: Hydrogenation of borazine

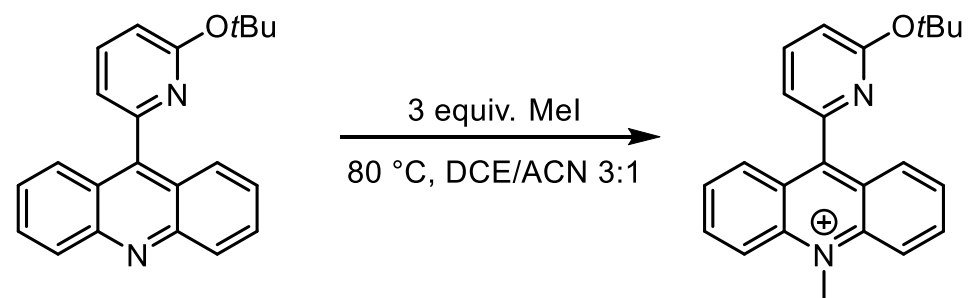
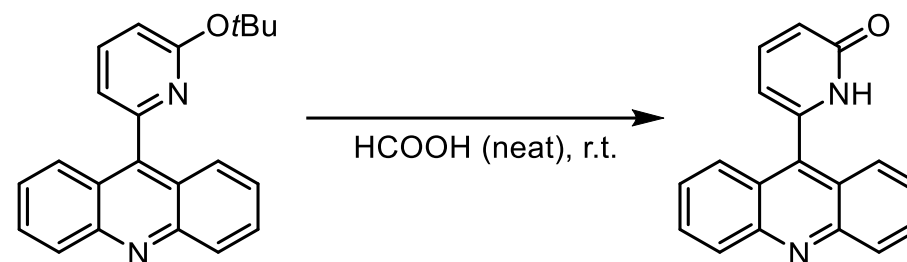
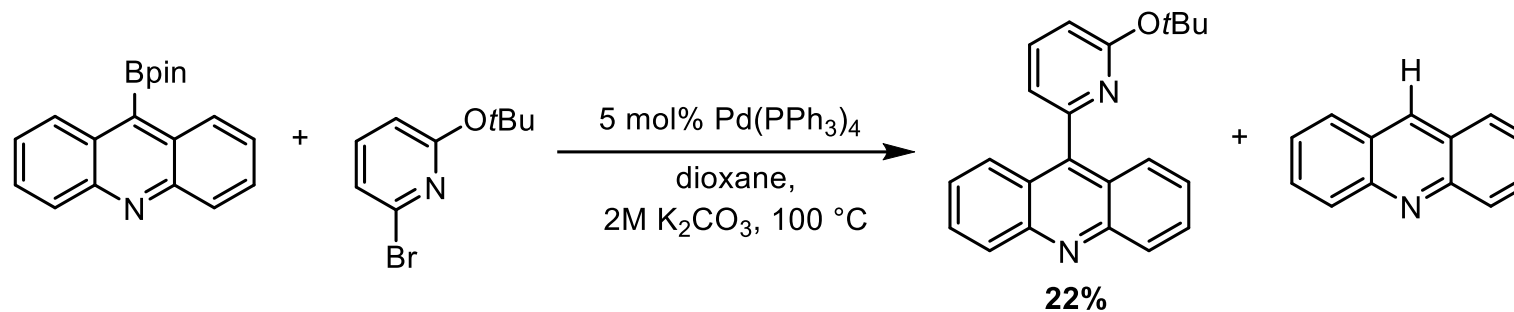
- Synthesis of a photoactive acridinium pyridone
- Excited state might enable hydrogenation of borazine







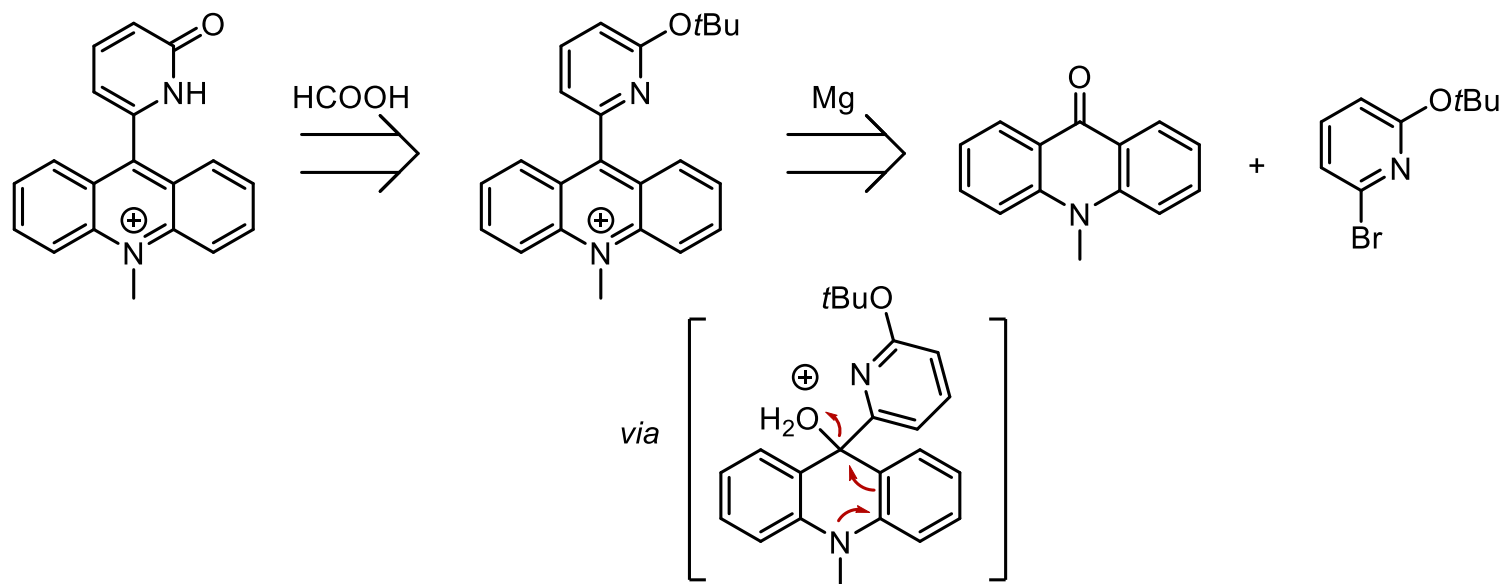
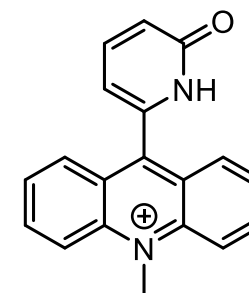
Part II: Synthesis of the acridinium pyridone



detected by ESI-MS

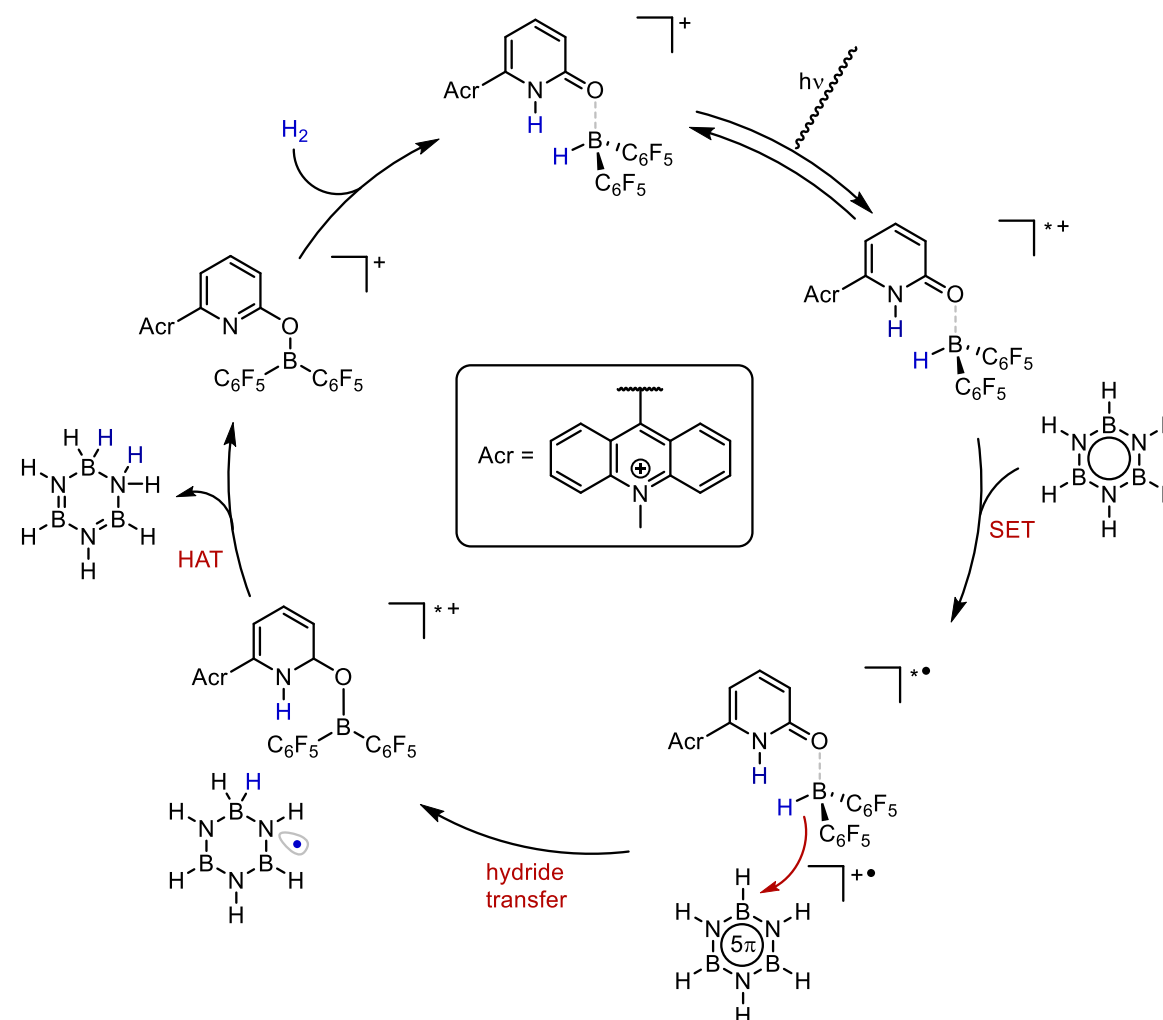


- Synthesis for the acridinium pyridone was developed using a cross-coupling
- Different methylation agents should be used
 - Problem: Pd was used during synthesis





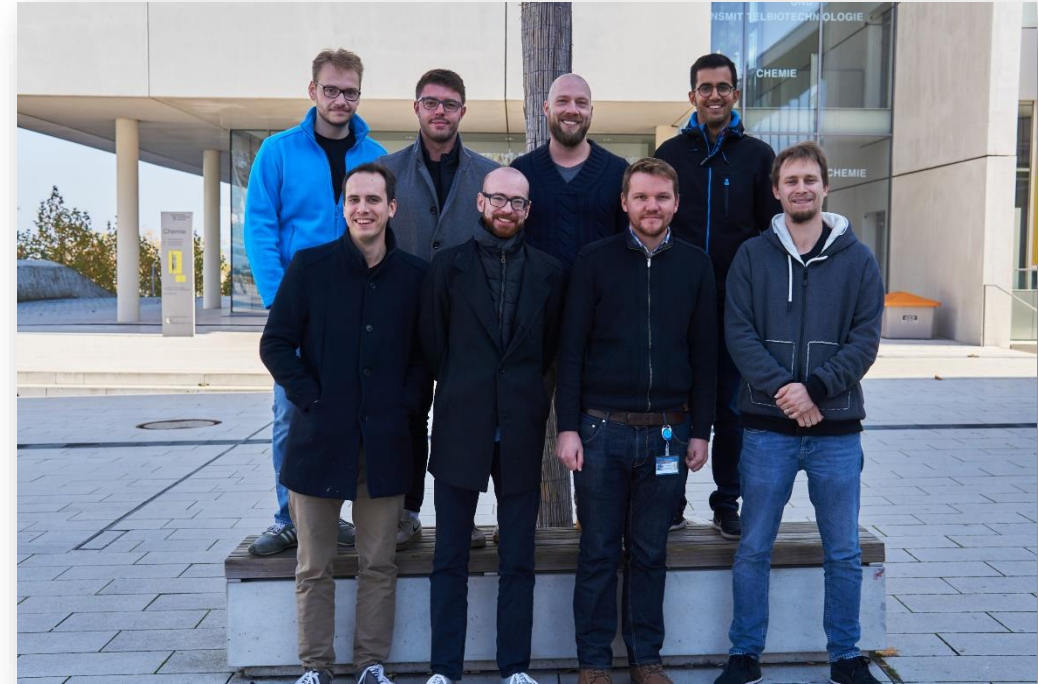
- Elemental analysis of the product
- Measurement of absorption properties
- Measurement of redox potentials





- Urs
- Prof. Schreiner
- Max and Sebastian
- Jama, Tizian, John and Arthur

Thank you!





- Borane excess is required for reproducible results
- Hydroboration product and bispyridone complex observed
- After heating, the product is released and boroxypyridine appears

