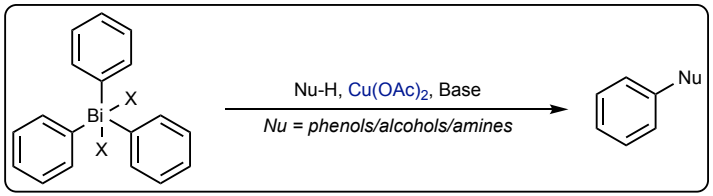
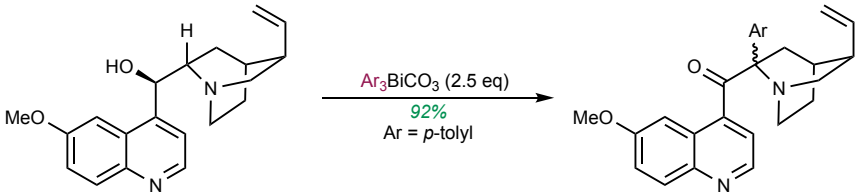
Barton-Mukaiyama Arylation



Not covered:
Phenol C-arylation (See CWD, MOTW)
Pd-catalyzed reactions

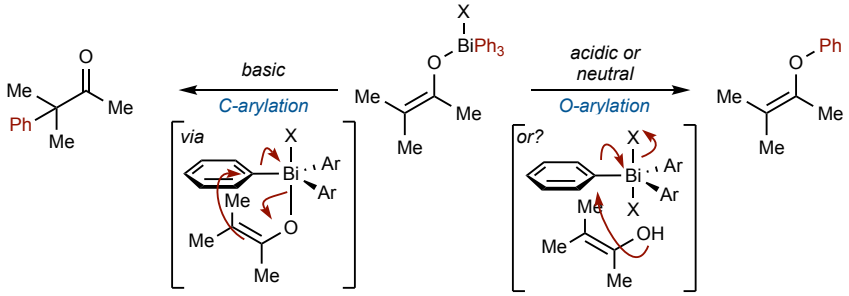
Key References/Reviews:
Chem. Rev. 1989, 89, 7, 1487–1501
Synthesis 2017; 49(08): 1707-1745

Initial use as arylating reagents[1]



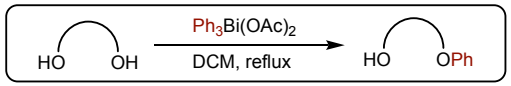
Attempted oxidation of quinine lead to α-arylated ketone

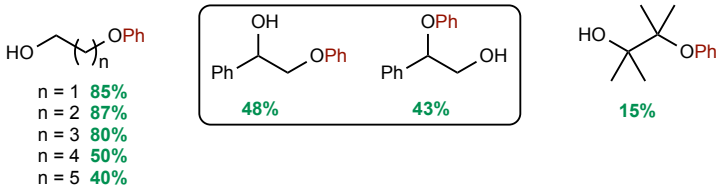
Phenol Arylation with Bi(V) Reagents[2]

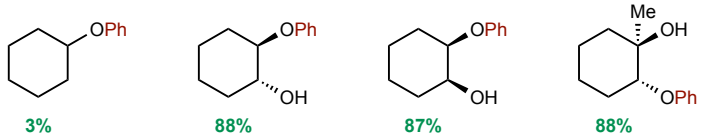


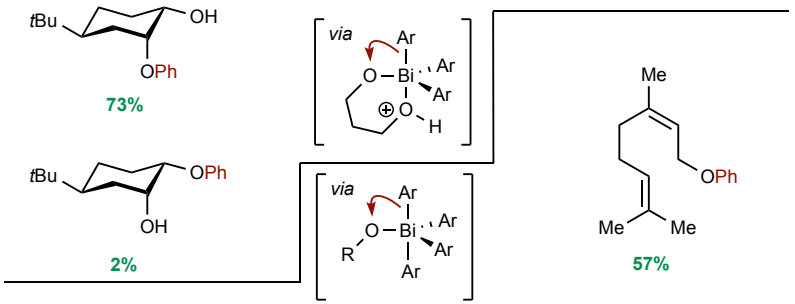
C- vs. O-arylation can be controlled by conditions:
Basic conditions through 5-center TS
Acidic conditions through 3-center TS or direct S_N2

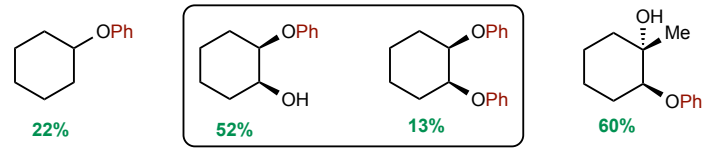
Alcohol Arylation with Bi(V) Reagents[3,4]

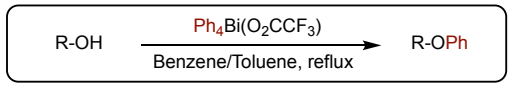


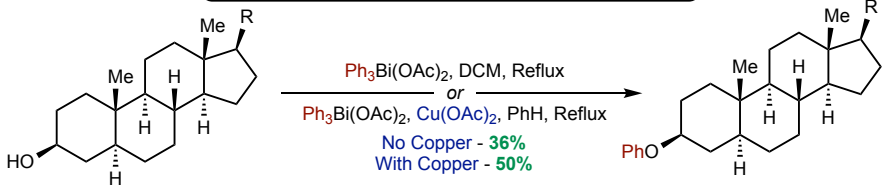




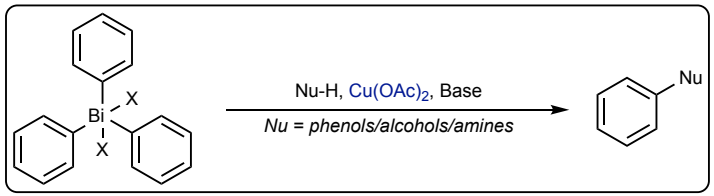


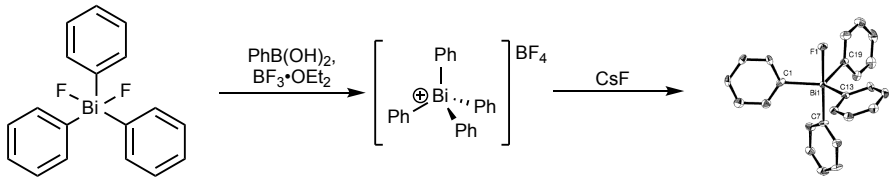






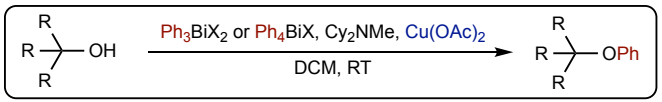
Barton-Mukaiyama Arylation

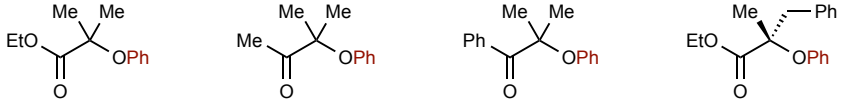


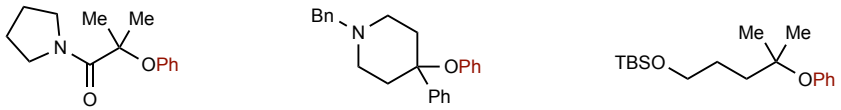


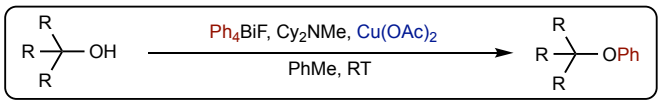
triaryl bismuth(V) dihalides

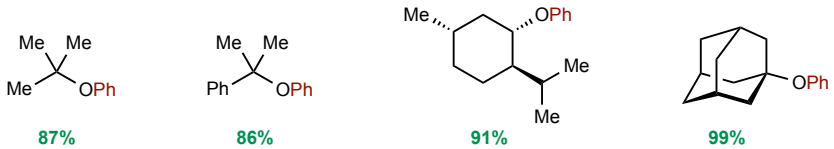
tetraaryl bismuthonium(V) salts[5]



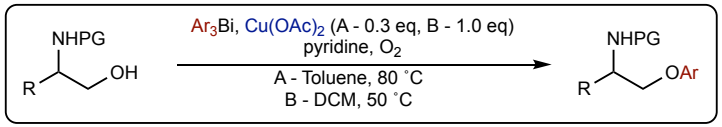


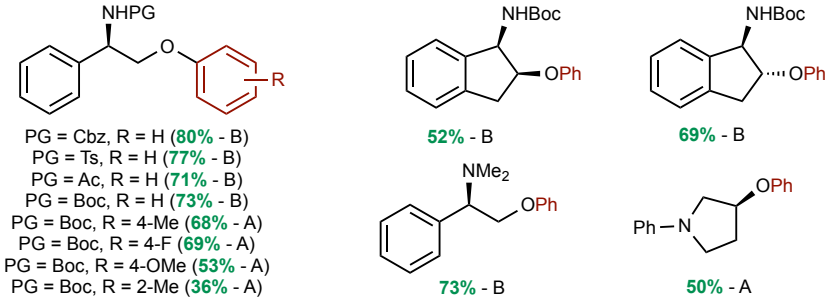


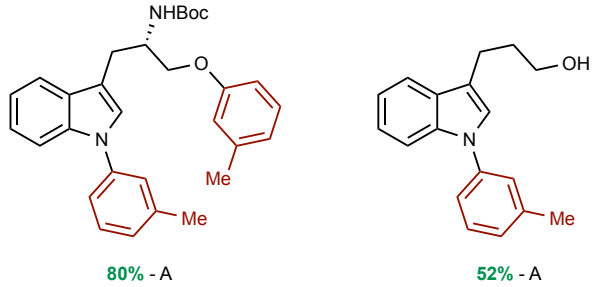




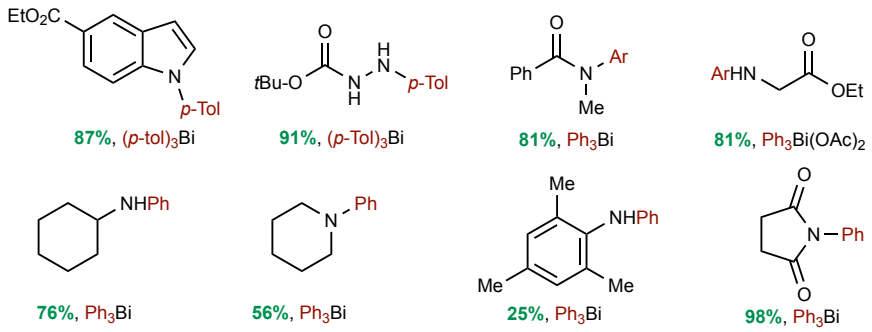
Bi(III) Arylations[6]



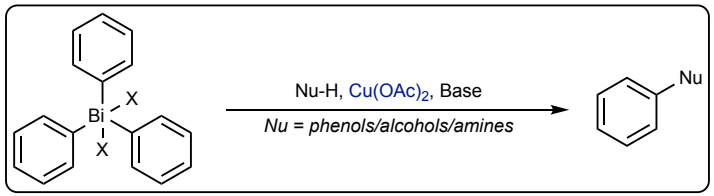




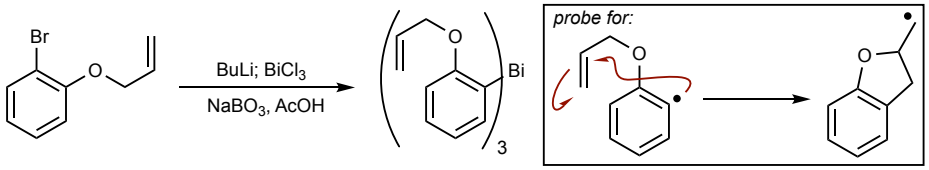
N-Arylation, selected substrates



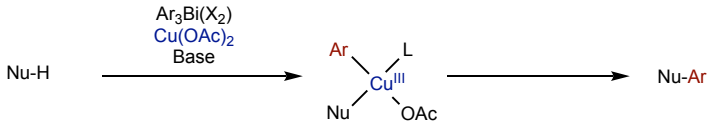
Barton-Mukaiyama Arylation



Mechanistic Investigation[7]



Smoothly arylated alcohols, amines, and phenols under Cu(II) conditions: Radical intermediates are not generated during reactions



Most proposed mechanisms invoke formation of a Cu^{III} species followed by reductive elimination to form the carbon-heteroatom bond

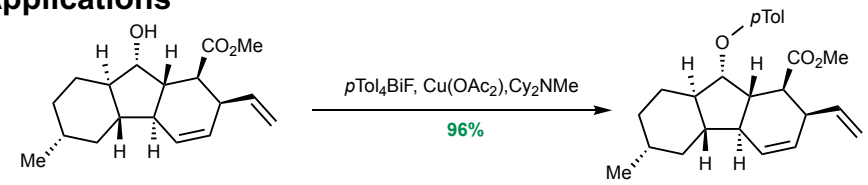
Specifics of Bi^{III} to Bi^{V} oxidation and transmetallation are unknown

Pros and Cons:

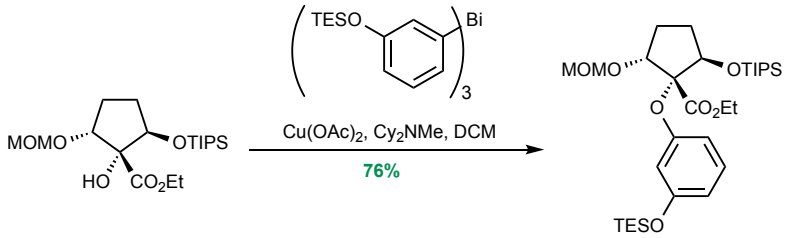
+ High yielding arylations of hindered nucleophiles
+ Mild conditions and high functional group tolerance

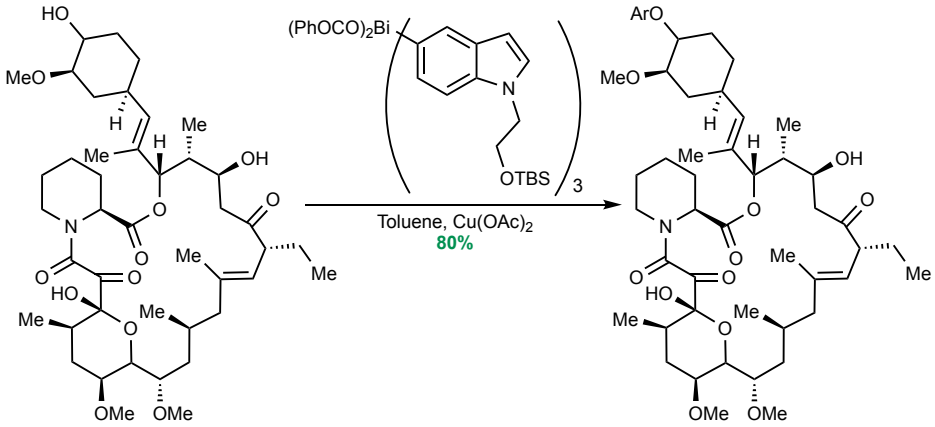
- 3-4 equivalents of arene often required for reactions
- Only simple arenes can be transferred
  - Bi reagents generally made by Grignard addition to BiX_3
- Mechanism not well understood
  - Explained by analogy to Chan-Lam coupling

Applications[8-10]



intermediate in synthesis of Hirsetullone B





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