

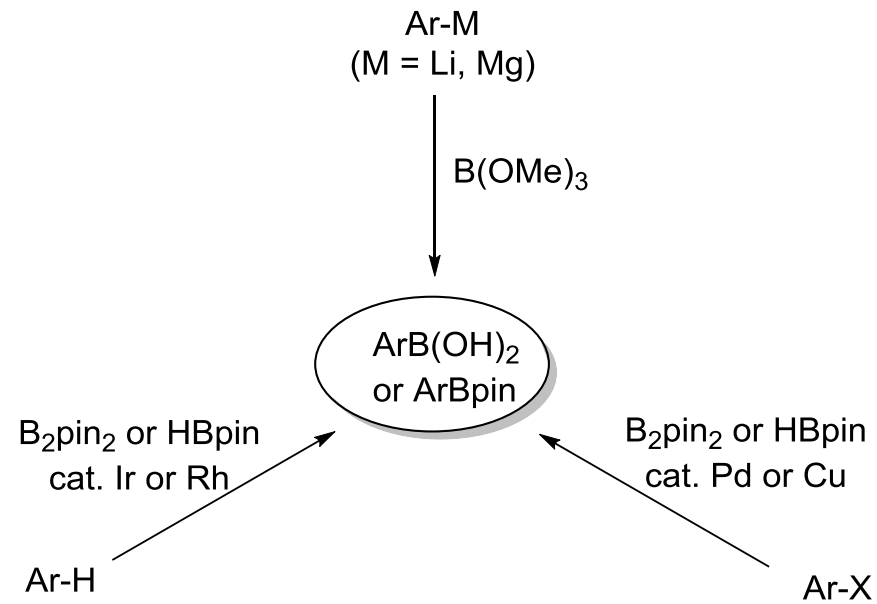
Recent Advances in C-B Bond Formation through a Free Radical Pathway

G. Yan, D. Huang, X. Wu, *Adv. Synth. Catal.* **2017**, 359, 188.

Daniel Meyer
University of Bern

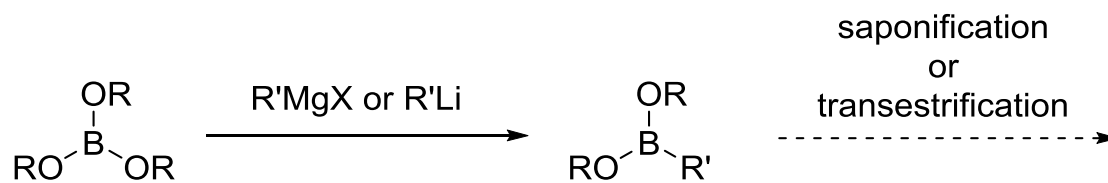
18.01.2018, Topic Review

Classical Methodes



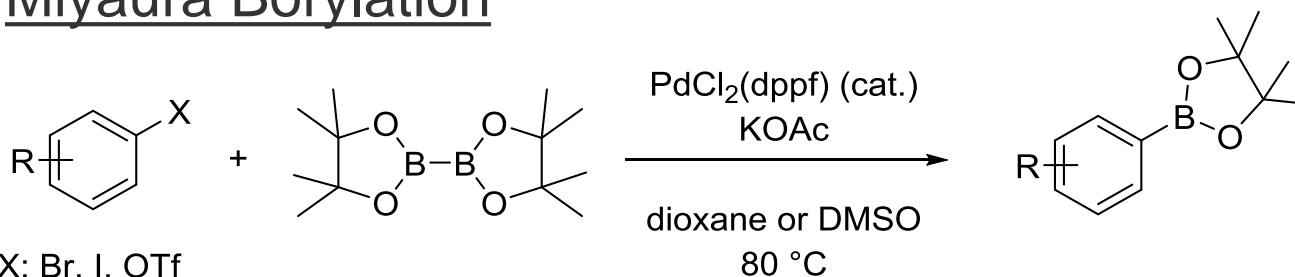
Classical Methodes

Addition of R'MgX or R'Li



E. Khotinsky and M. Melamed, *Ber. Dtsch. Chem. Ges.* **1909**, 42, 3090.

Miyaura Borylation

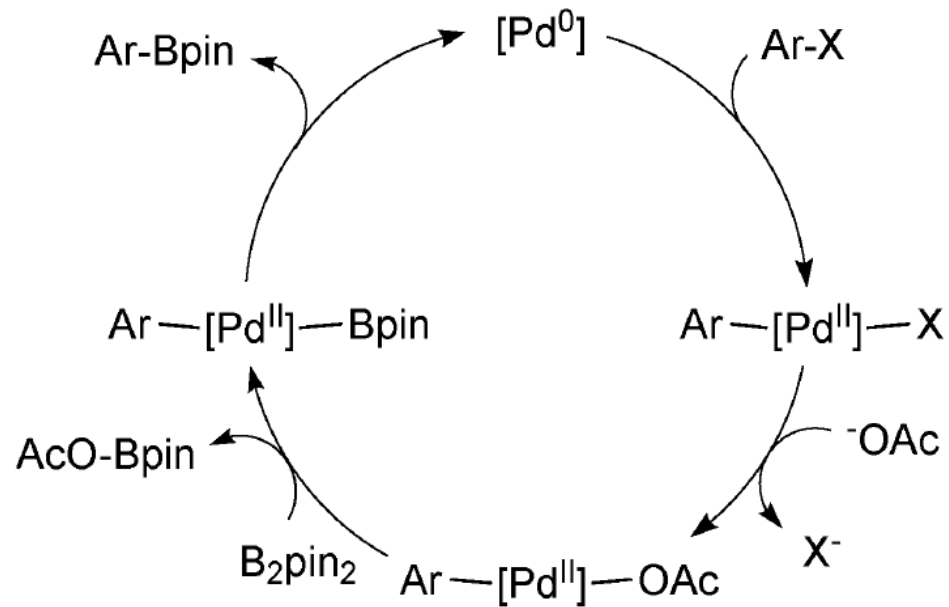


X: Br, I, OTf

T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, 60, 7508.

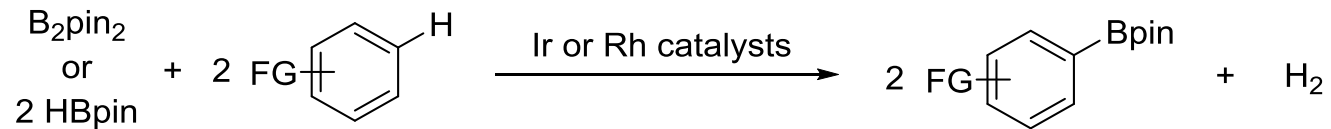
Classical Methodes

Miyaura Borylation



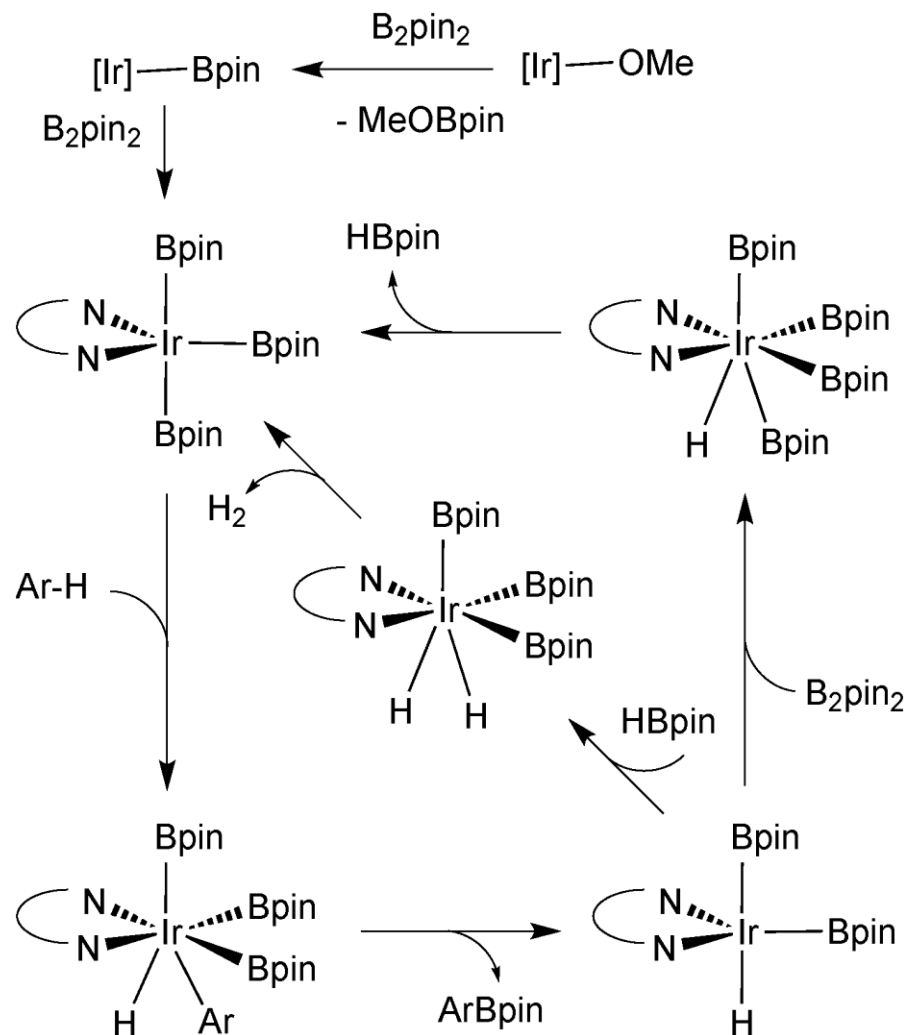
Classical Methodes

Selective Borylation of C-H bonds (Rh or Ir catalysis)

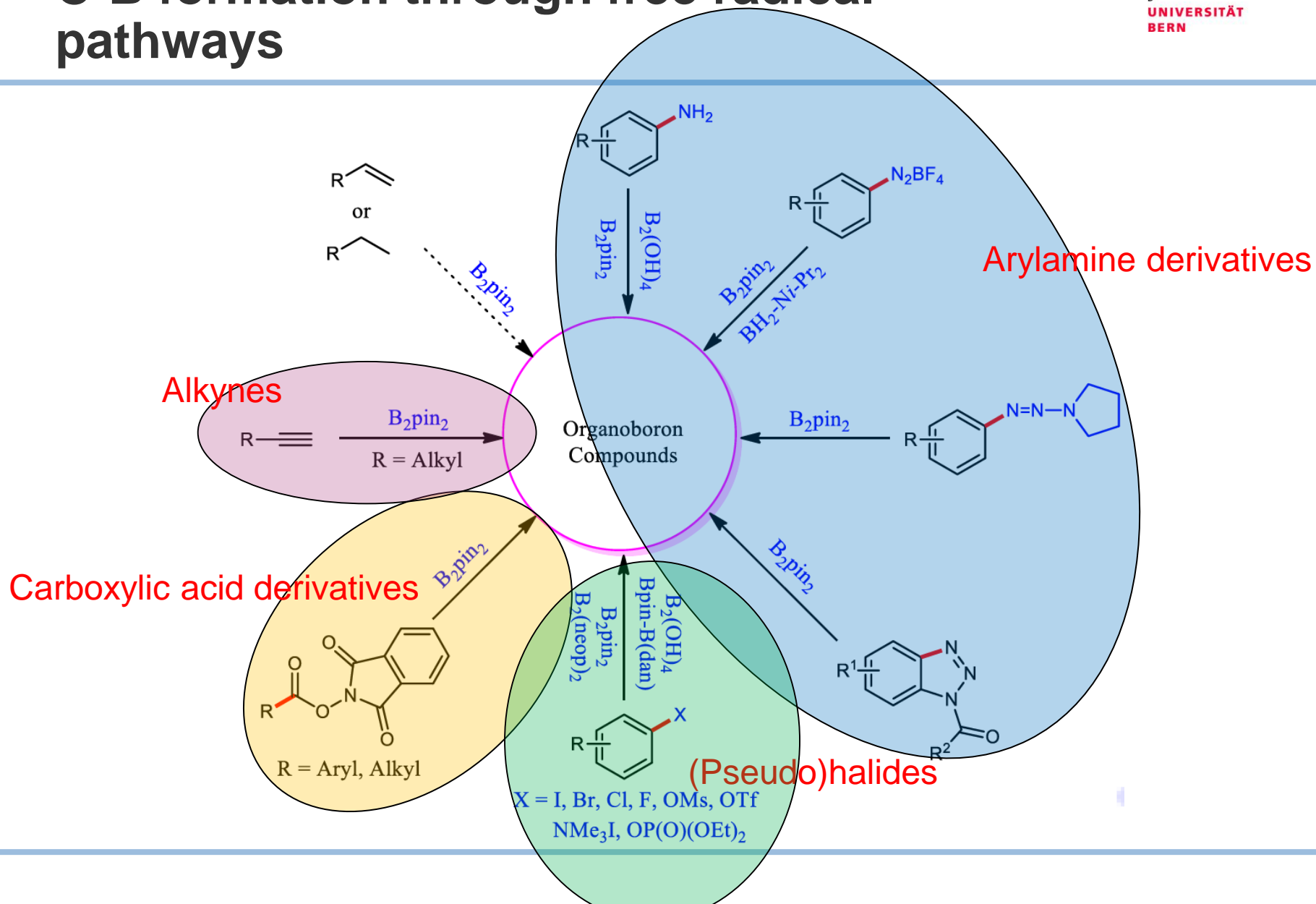


I. A. I. Mkhalid, J. H. Bernard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *100*, 890.

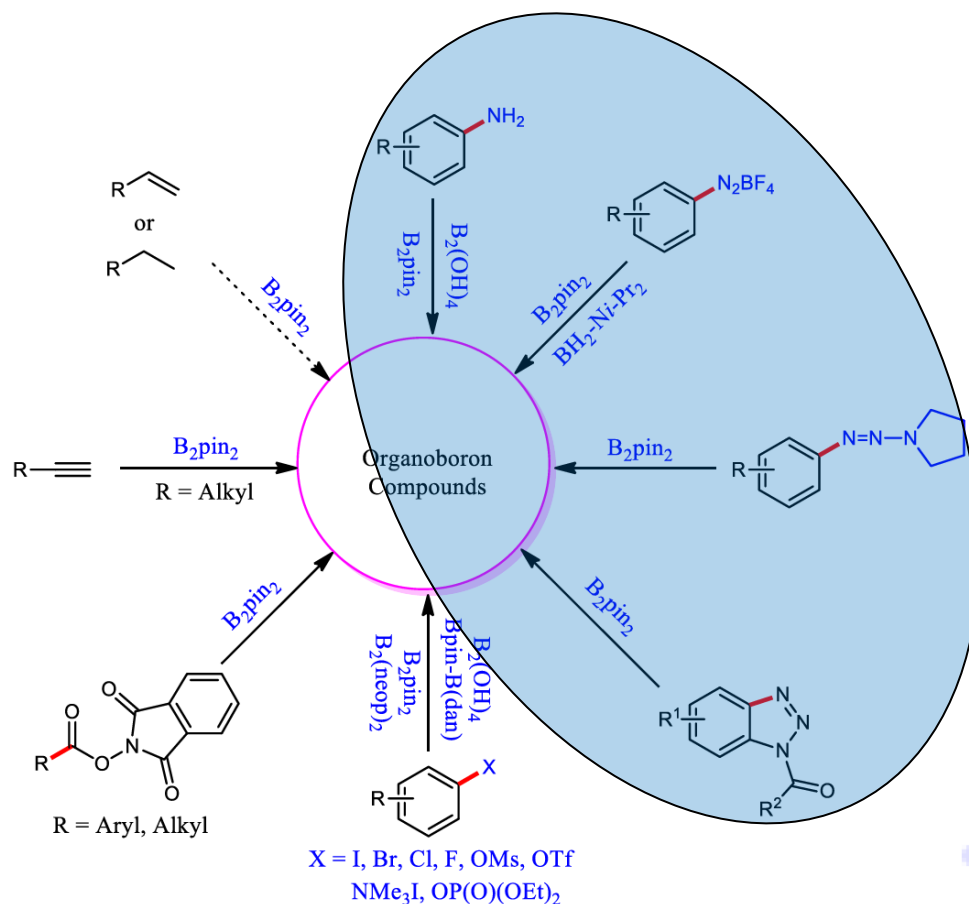
Classical Methodes



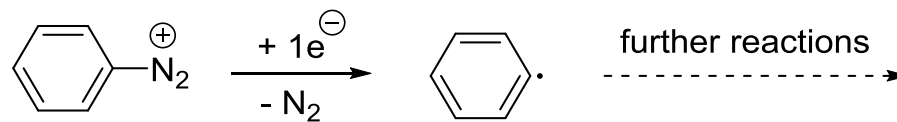
C-B formation through free radical pathways



Borylation of Arylamine Derivatives

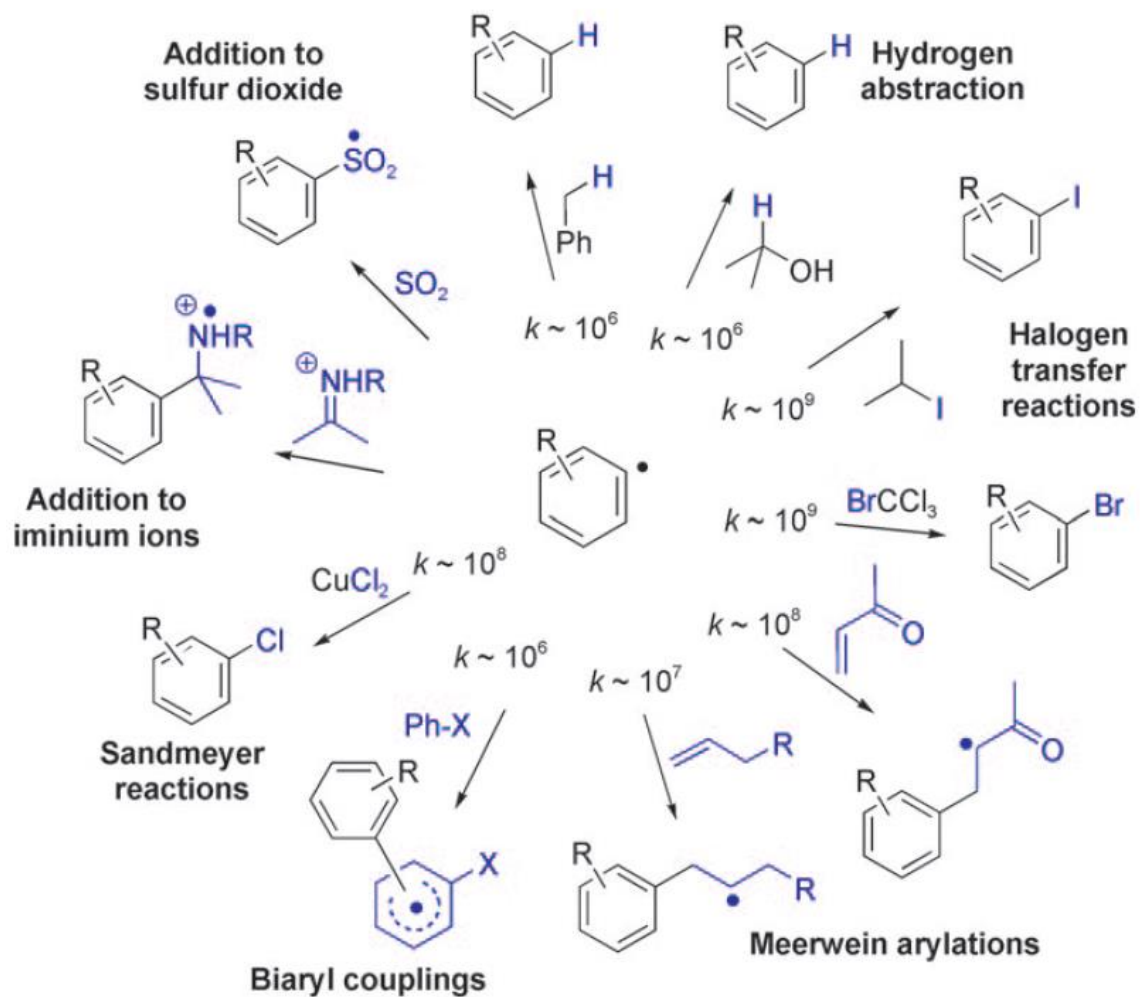


Reactivity Diazonium Salts

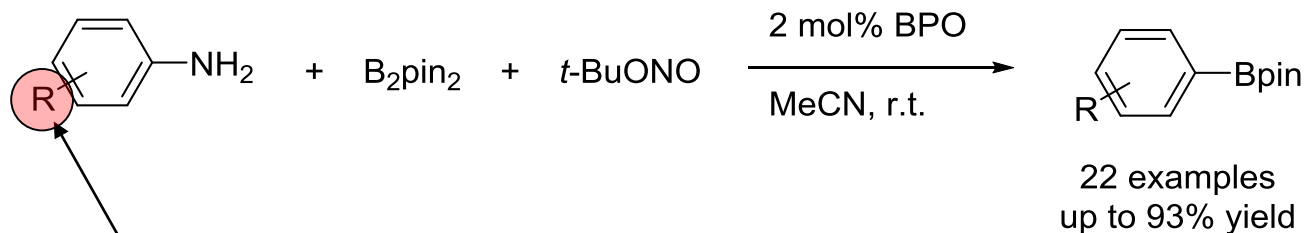


- > Aryldiazonium salts are excellent source of aryl radicals
- > Often used as oxidative quenchers in photoredox chemistry

Borylation Diazonium Salts



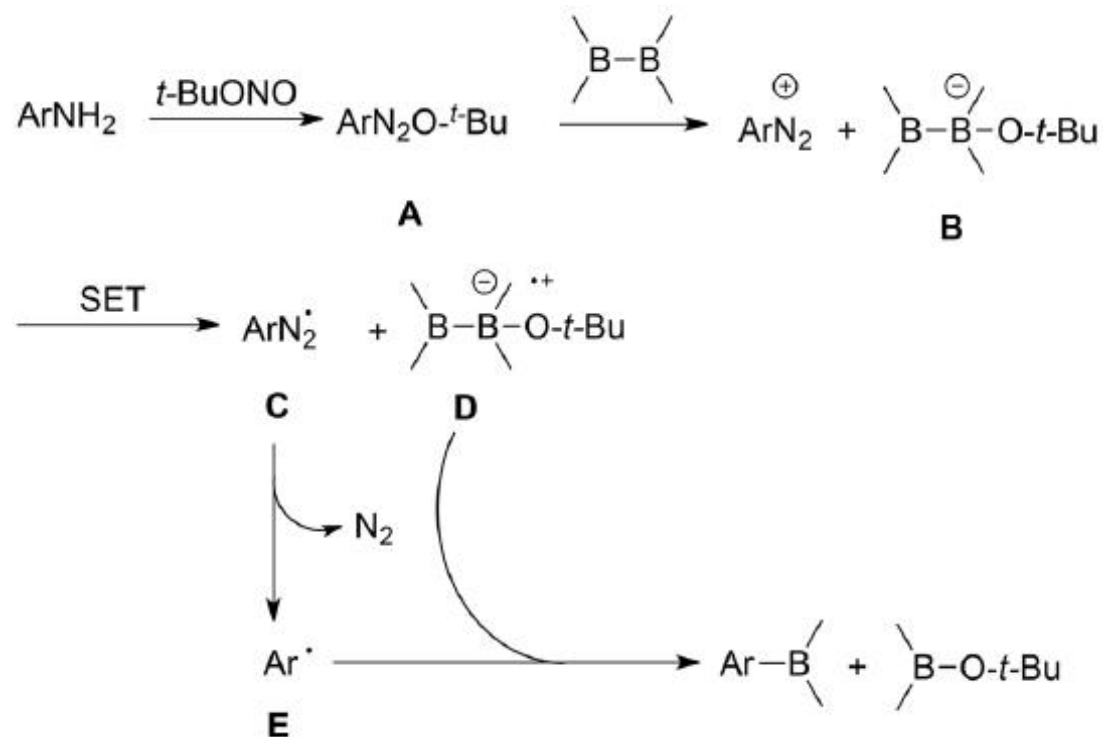
Borylation of Arylamines *via* Diazonium Salts



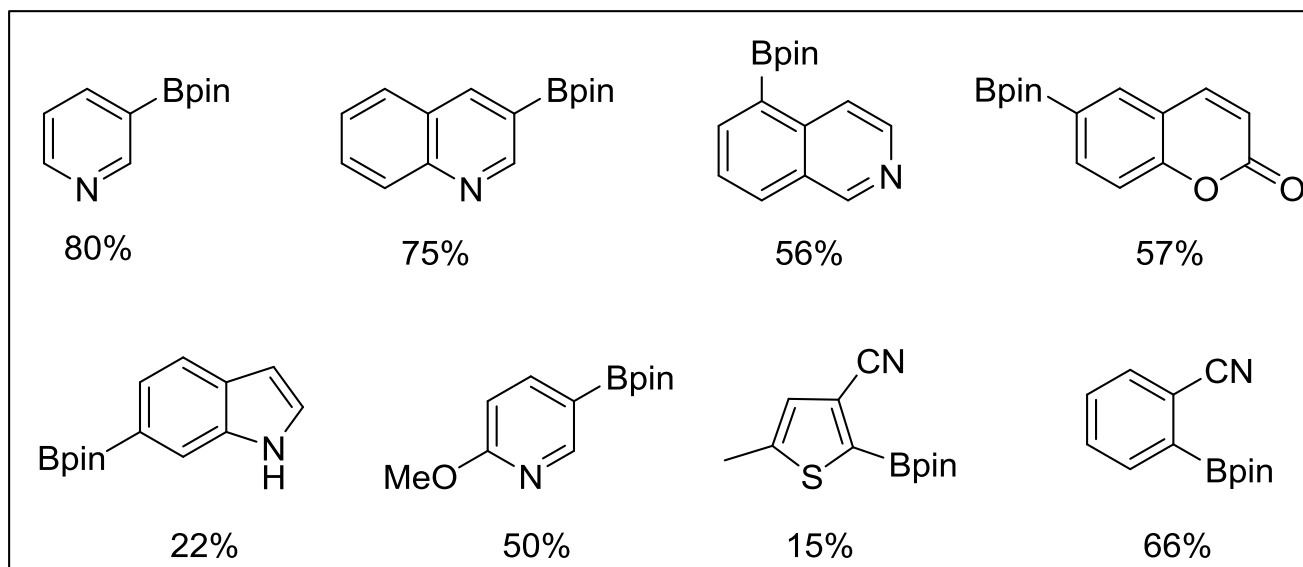
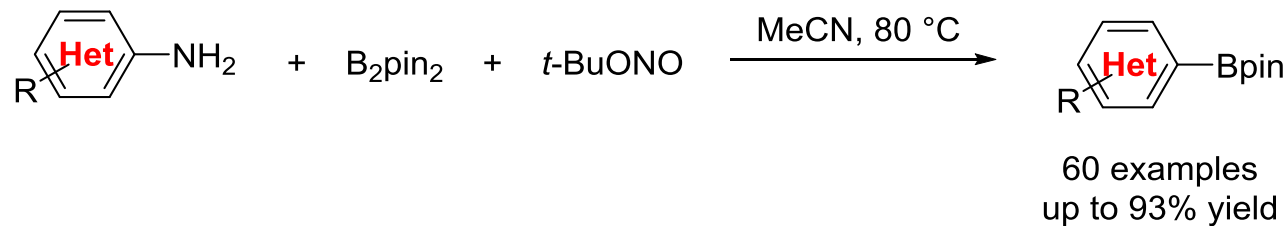
Reaction significantly affected by steric and electronic effects

- > Not working with heteroaromatics
- > Addition of TEMPO dramatically decrease the yield

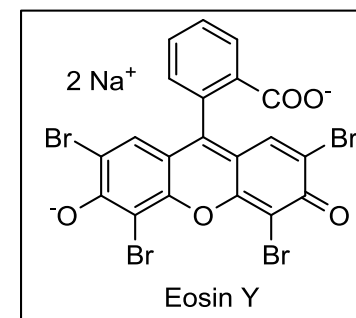
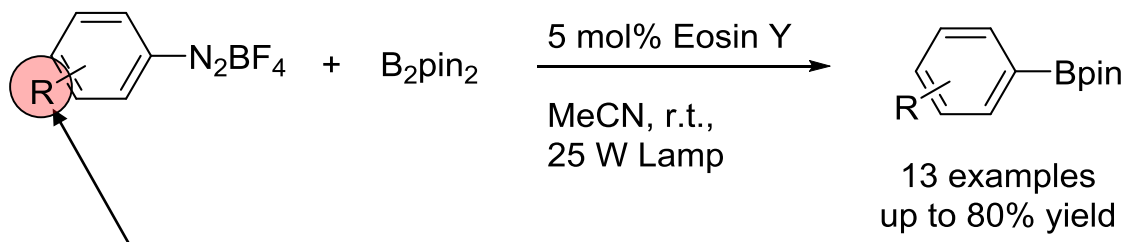
Borylation of Arylamines *via* Diazonium Salts



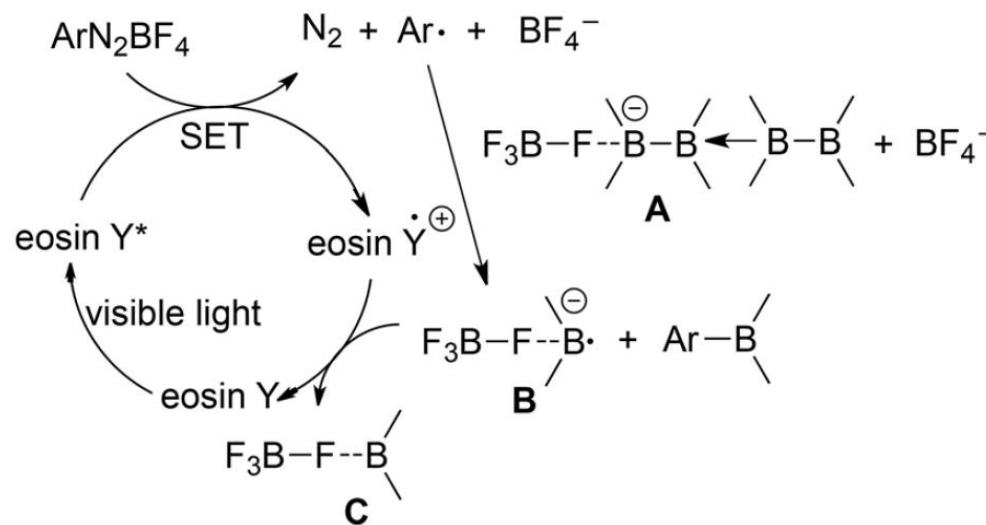
Borylation of Arylamines *via* Diazonium Salts



Borylation of Diazonium Salts using Eosin Y

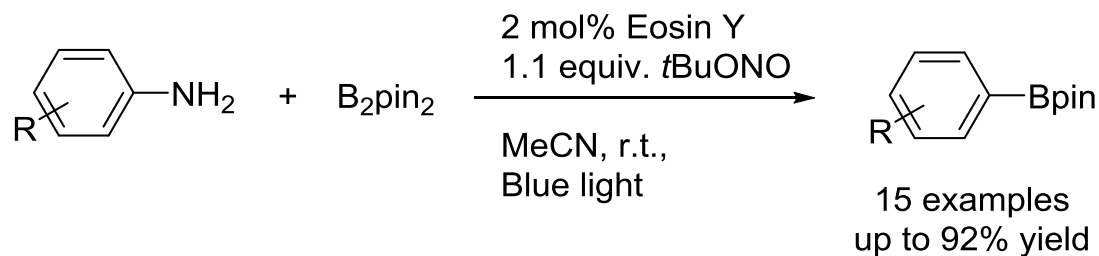


- Reaction significantly affected by steric and electronic effects
- Not working with heteroaromatics

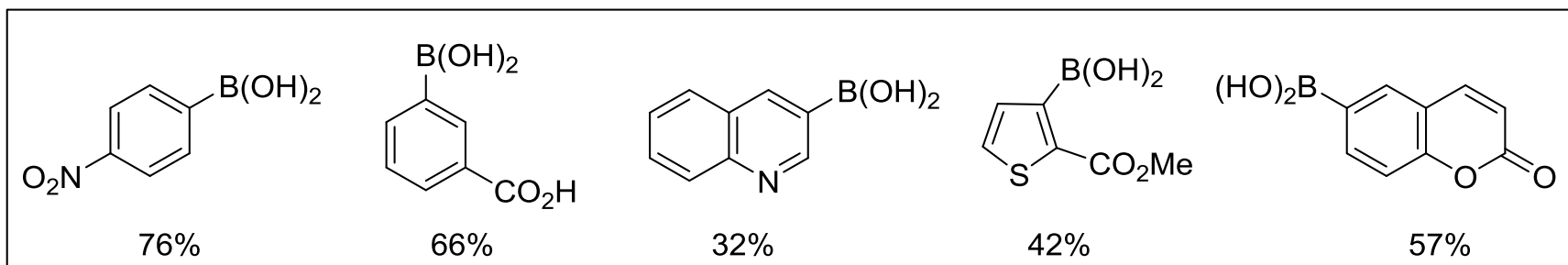
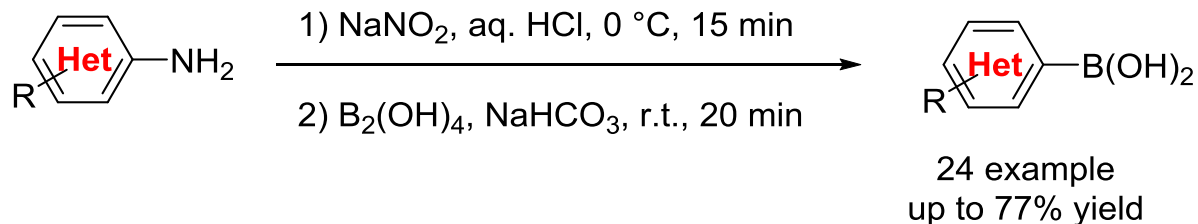


Borylation of Arylamine *via* Diazonium Salts using Eosin Y

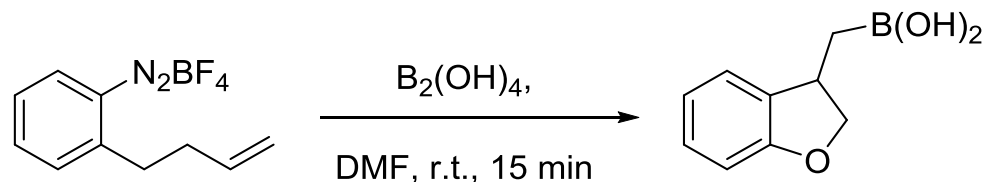
In situ diazotization with *t*BuONO



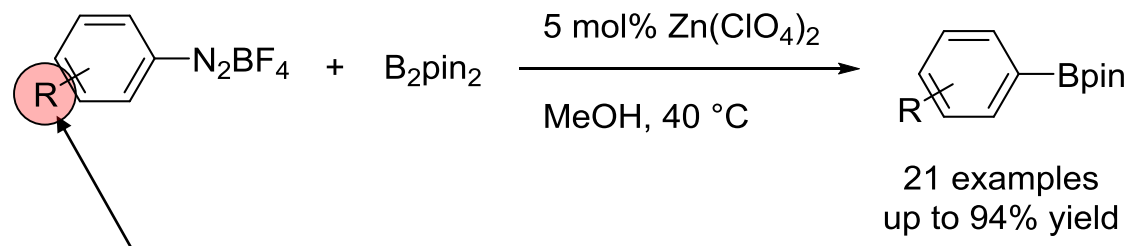
Borylation of Arylamines *via* Diazonium Salts



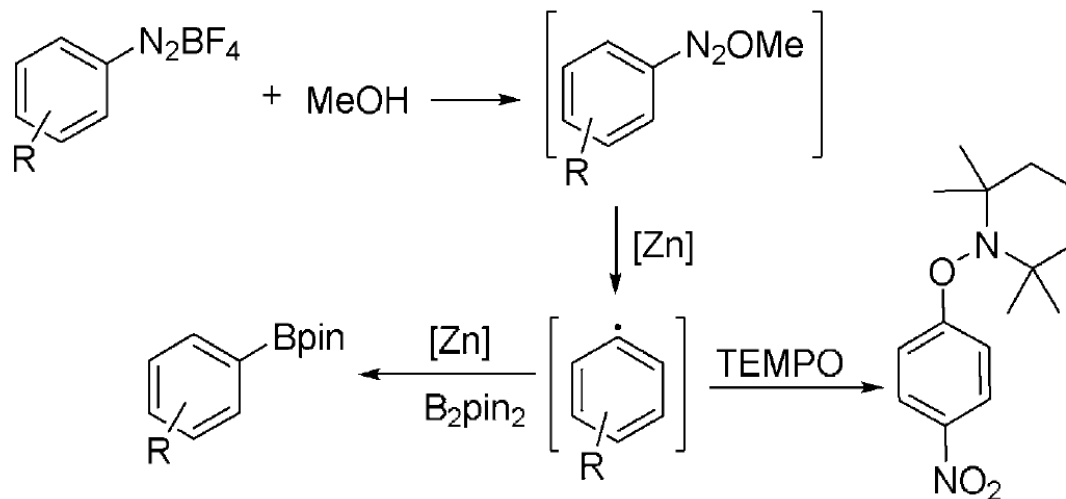
Addition of 1 equiv TEMPO decrease the yield from 62% to 6%
No Phenol-derivatives found



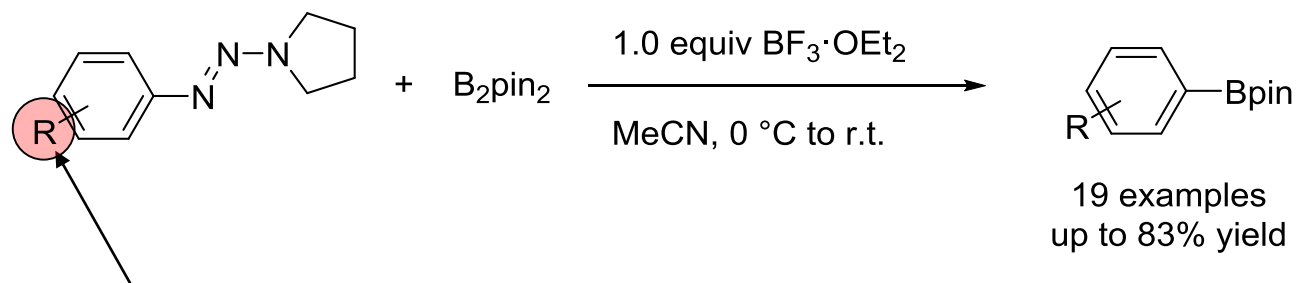
Borylation of Diazonium Salts using Zn



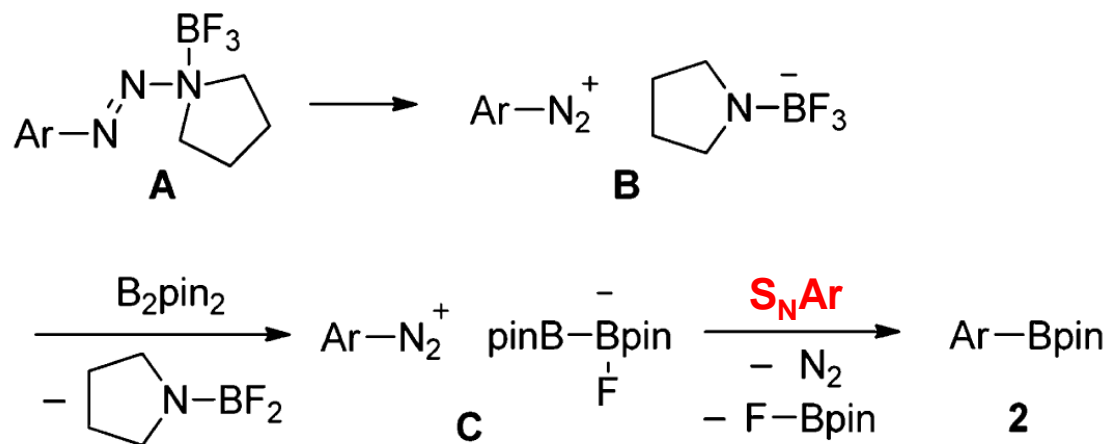
Electron donating- and withdrawing-
groups and halogens (F, Cl, Br, I)



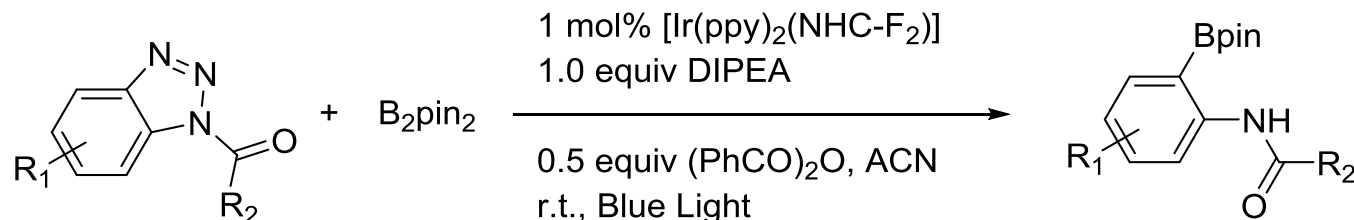
Borylation of Aryltriazenes



Electron donating-group and
halogens (F, Cl, Br, I)



Borylation of Benzotriazoles

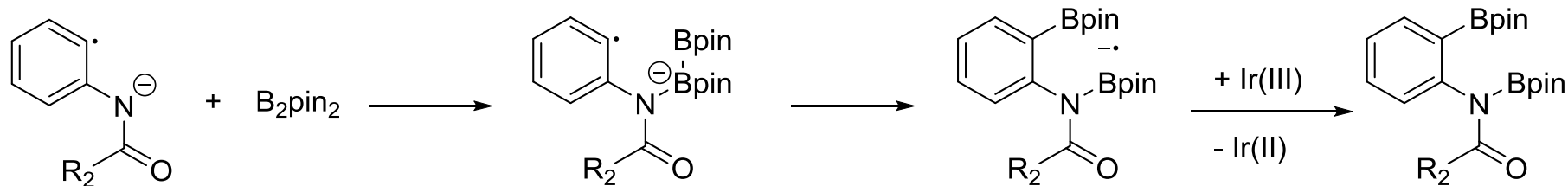
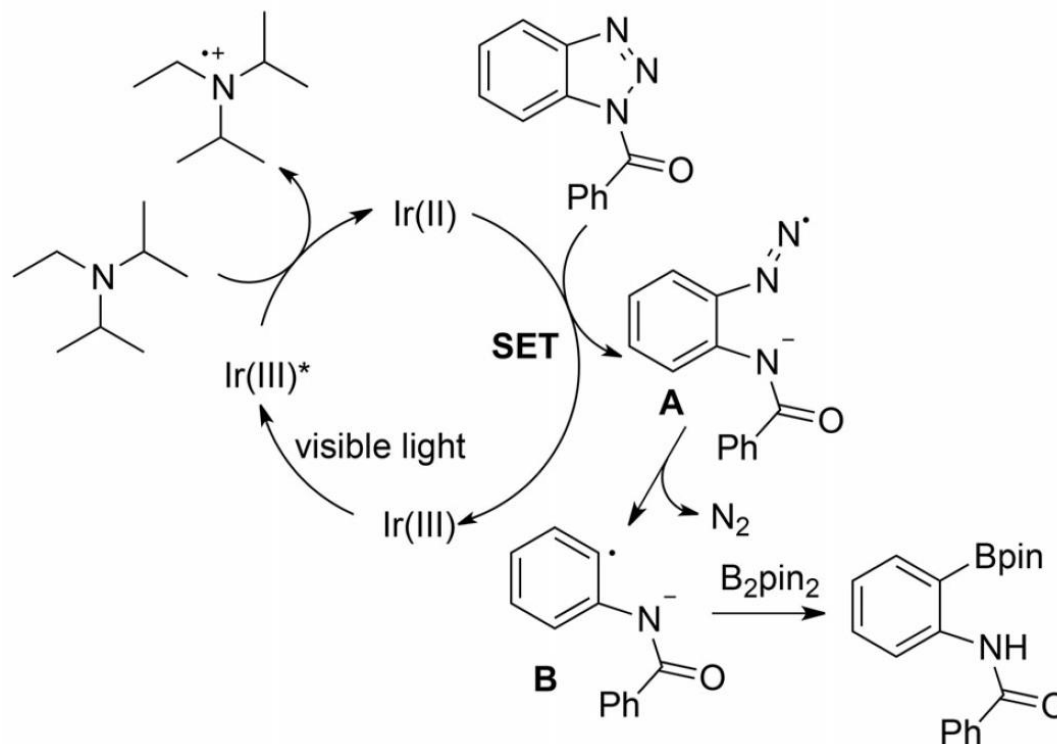


5 examples
up to 85% yield

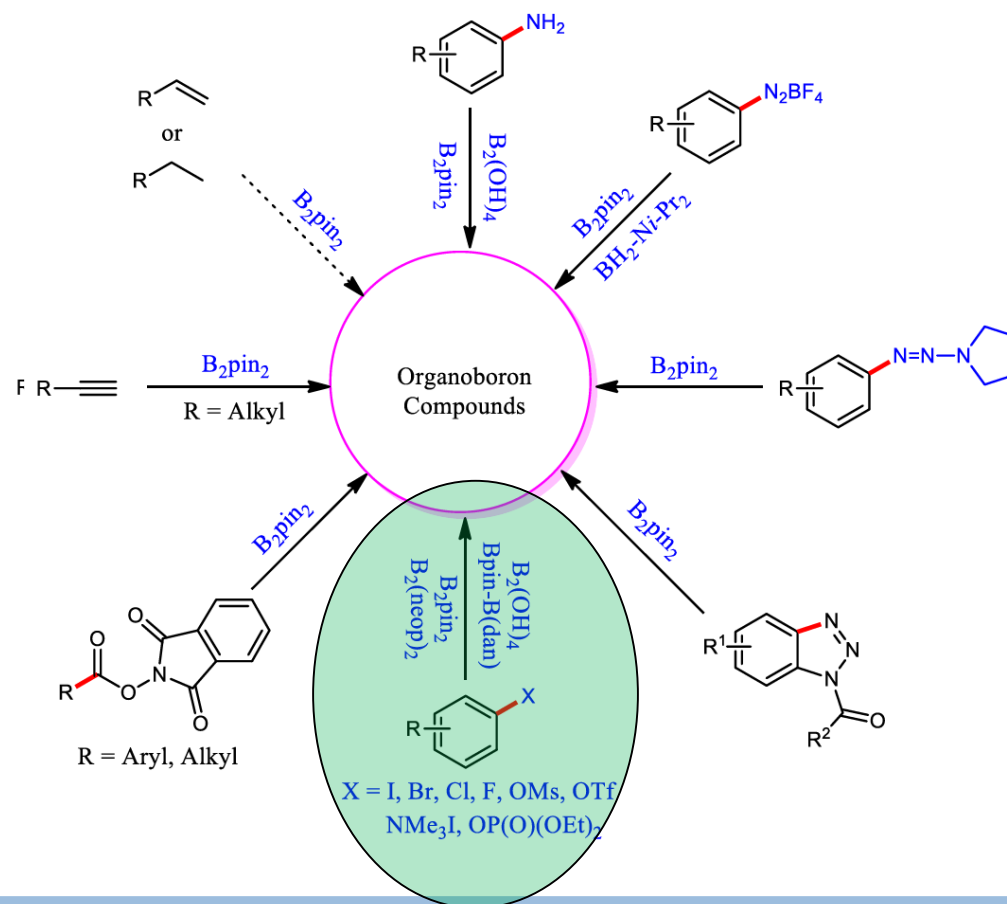
Additive-based robustness screen was performed:
Alkene, alkyne, nitril, ester, indol, etc.

Alkylation and thiolation was also successfully achieved

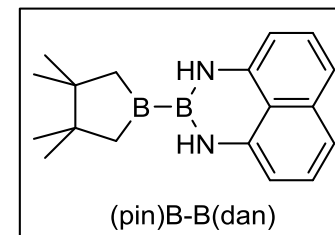
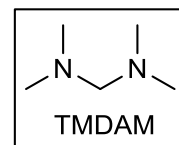
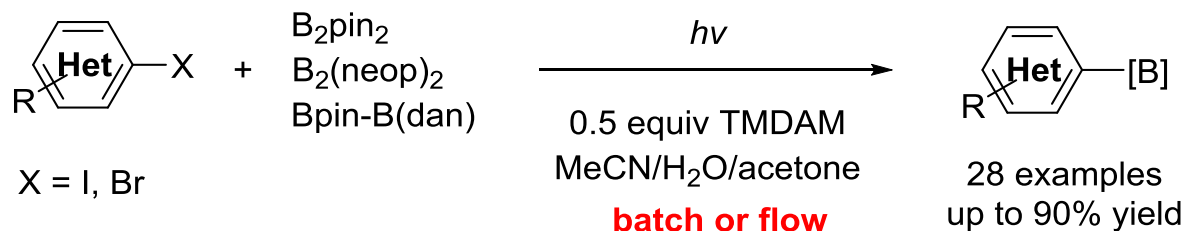
Borylation of Benzotriazoles



Borylation of Aryl (Pseudo)halides



Borylation of Arylhalides under UV



High functional group tolerance (EWG, EDG and pyridine-derivatives)
ortho-, *meta*- or *para*-substitution gave good yields

Addition of Bu₃SnH = more reduced product Addition TEMPO = lower yield

Reaction needs quartz test tube and 300 W high pressure mercury lamp.

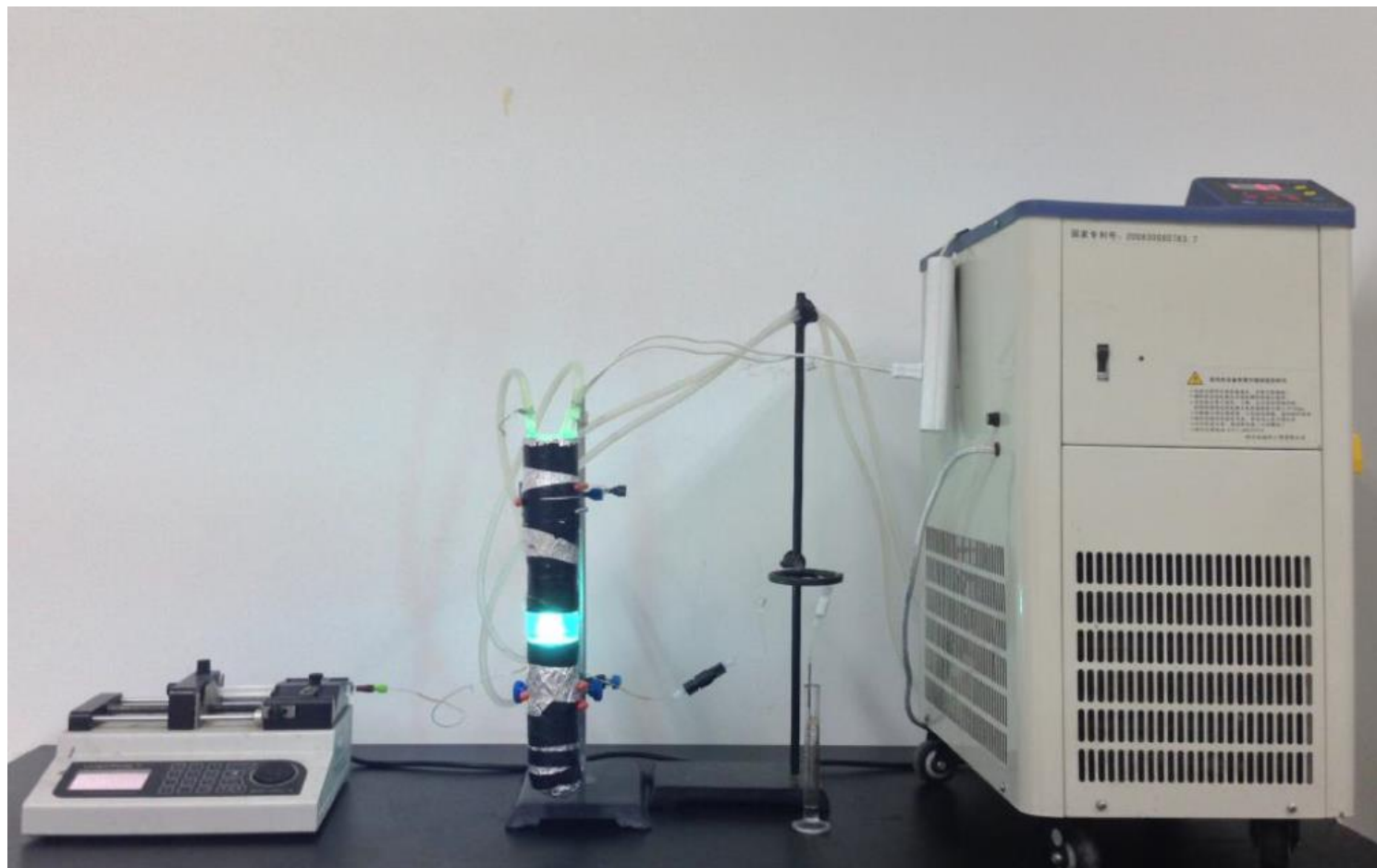
Borylation of Arylhalides under UV

Batch reaction

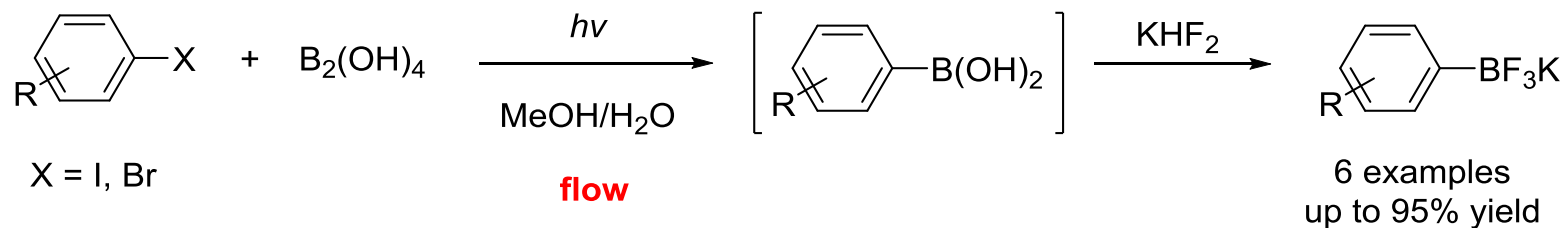
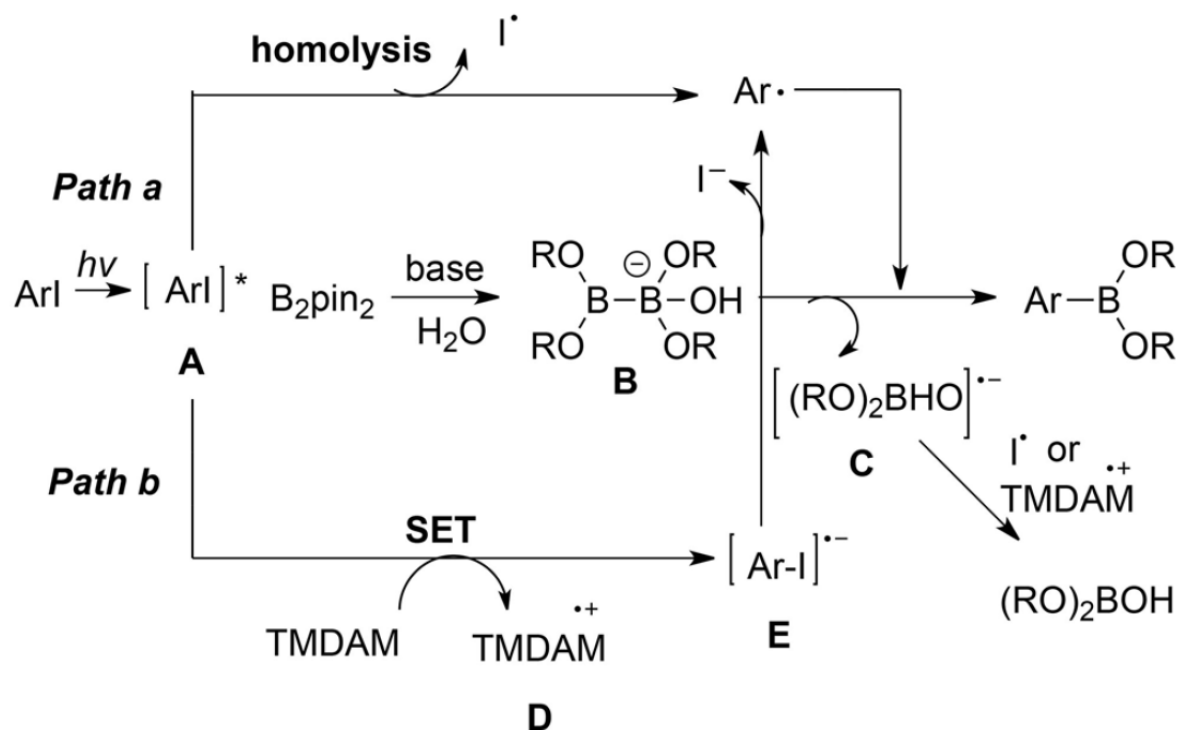


Borylation of Arylhalides under UV

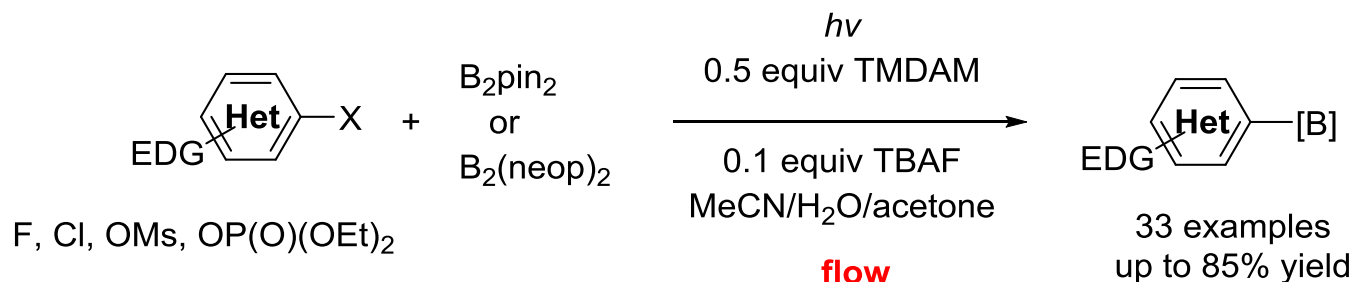
Continuous-flow reaction



Borylation of Arylhalides under UV



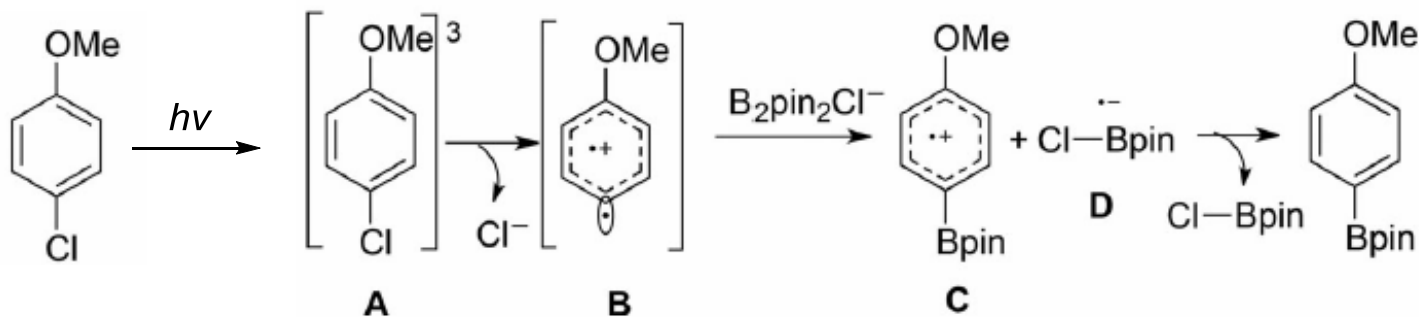
Borylation of Aryl(pseudo)halides under UV



Needs a EDG-group

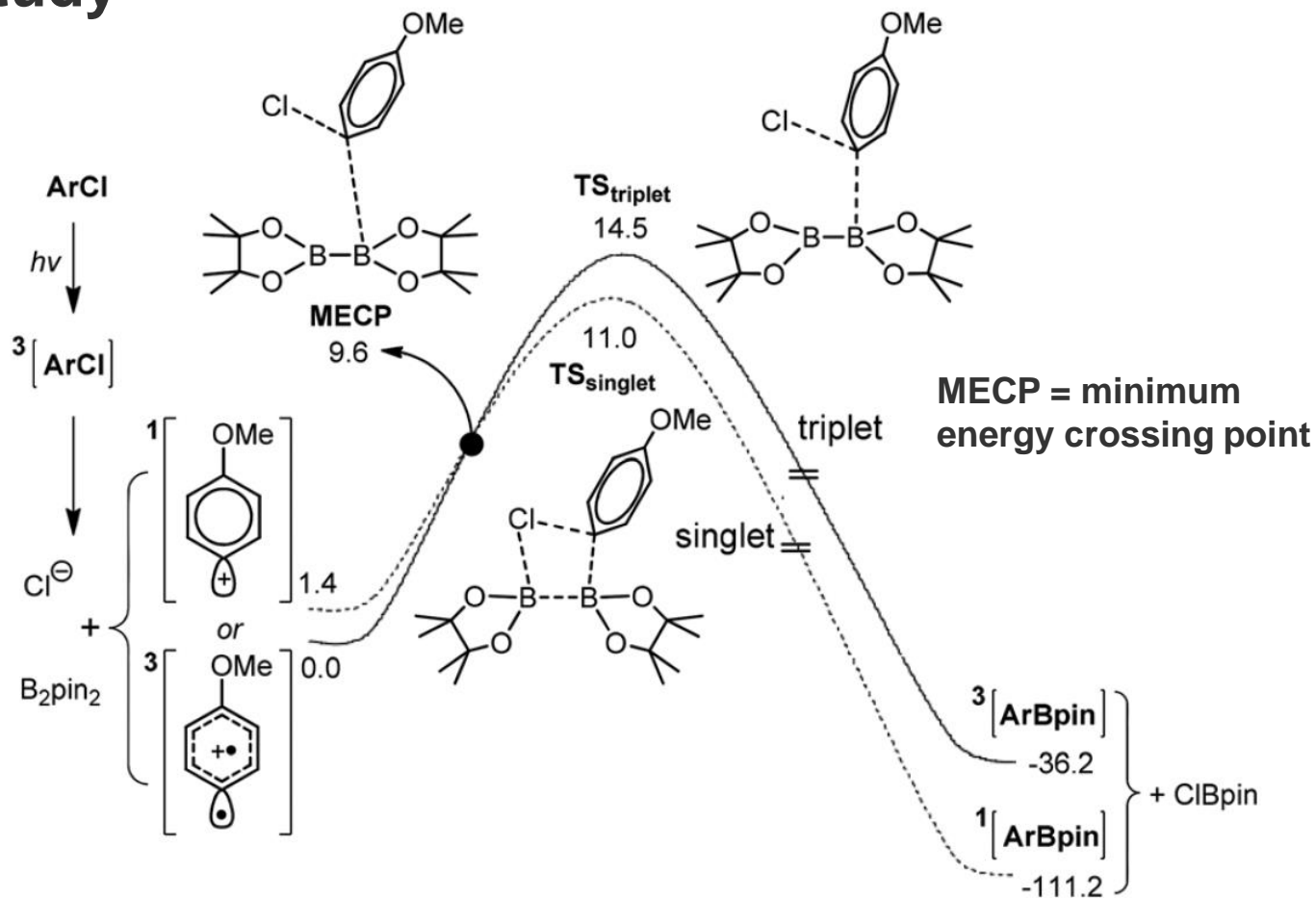
Tolerates free OH- and NH₂ groups

Reaction needs 300 W high pressure mercury lamp.

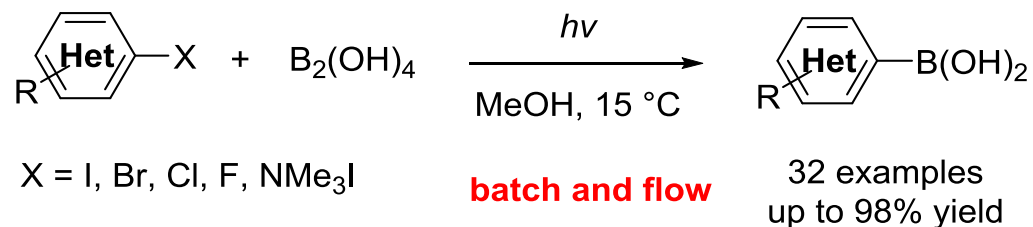


Borylation of Aryl(pseudo)halides under UV

DFT study



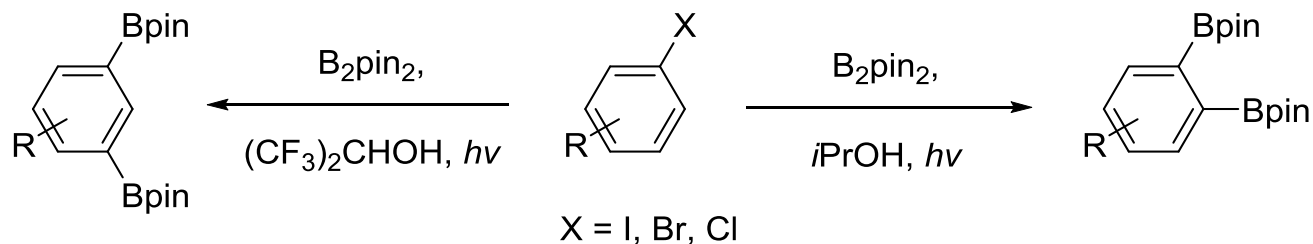
Borylation of Aryl(pseudo)halides under UV



Needs a EDG-group for F and Cl

Boronic esters were also prepared

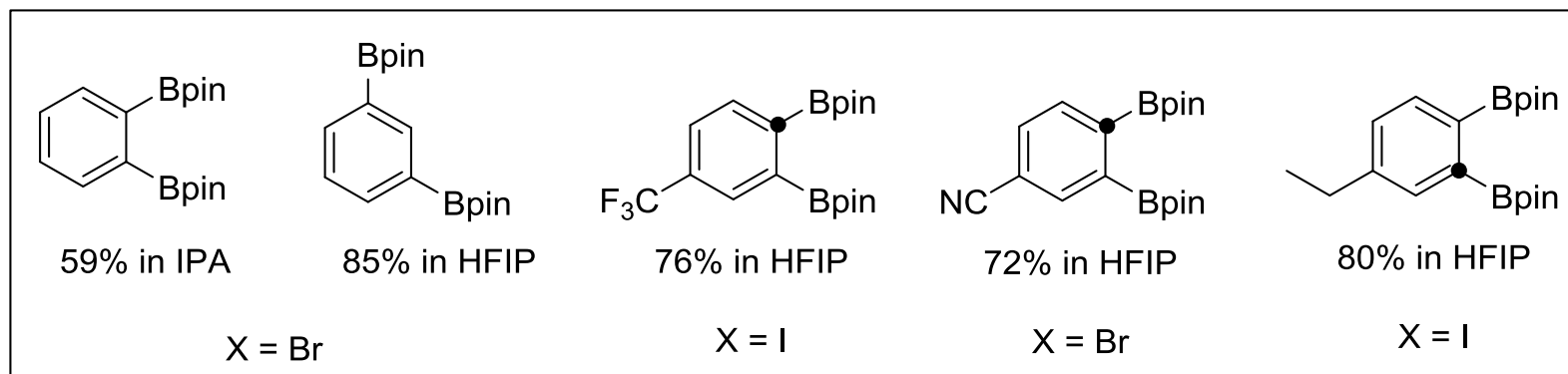
Diborylation of Arylhalides under UV



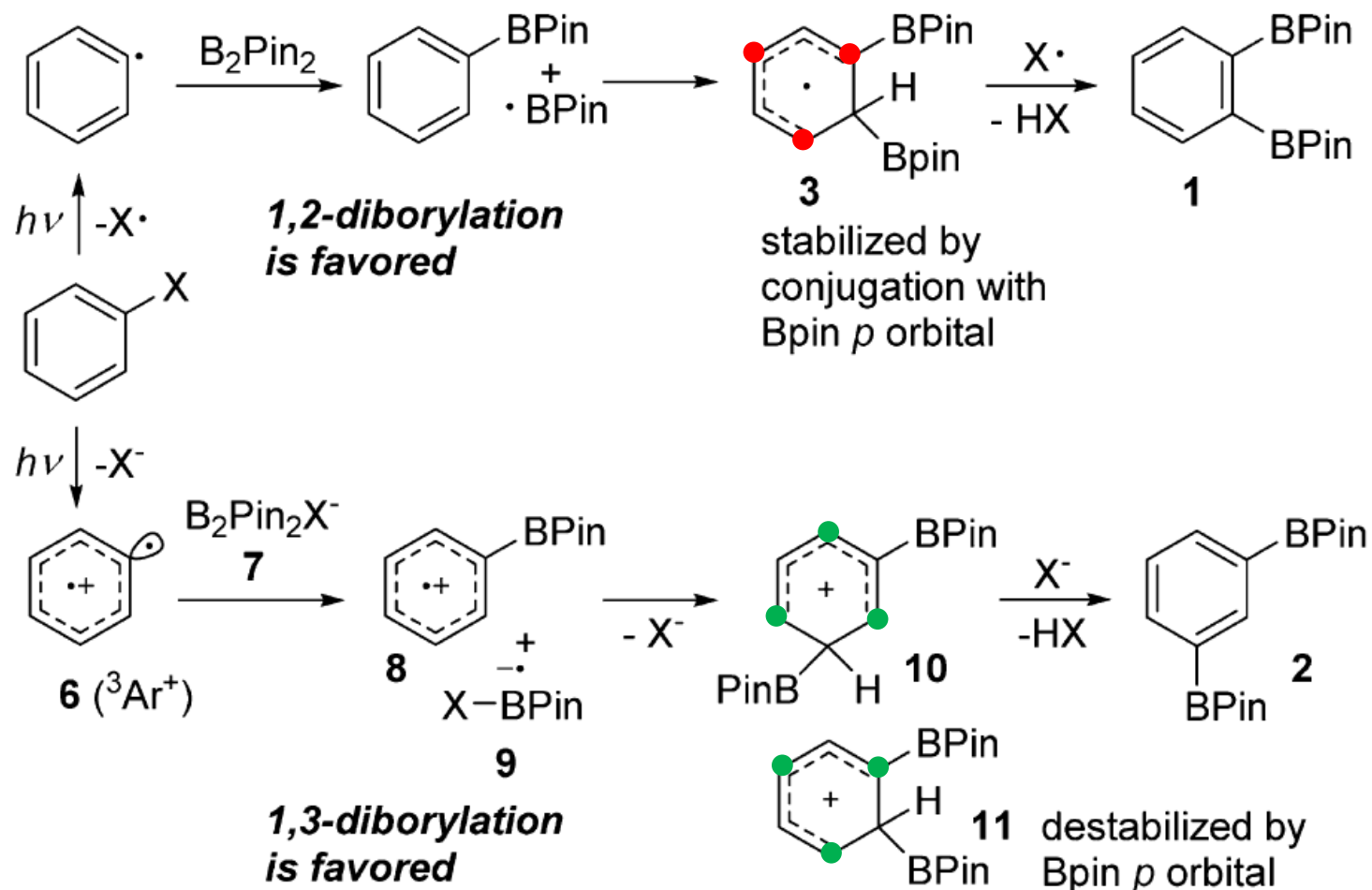
in IPA = 1,2 diborylation

in HFIP = 1,3 diborylation

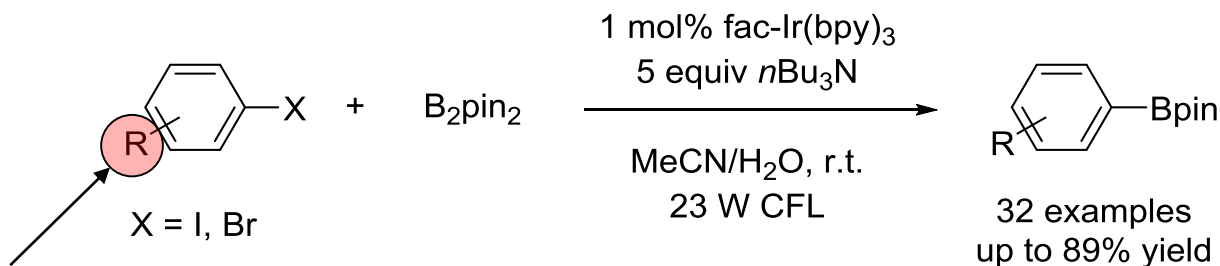
Substituents can change the selectivity



Diborylation of Arylhalides under UV



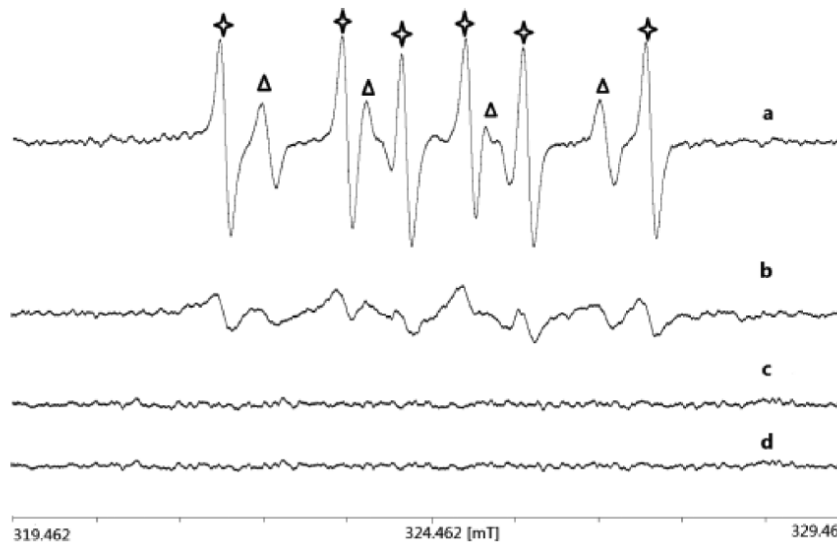
Borylation Arylhalides under VIS



EWG and EDG worked well

Primary and secondary alkylbromides worked as well

ESR showed that a C-centred (sextet) and N-centred radical are formed (quartet)



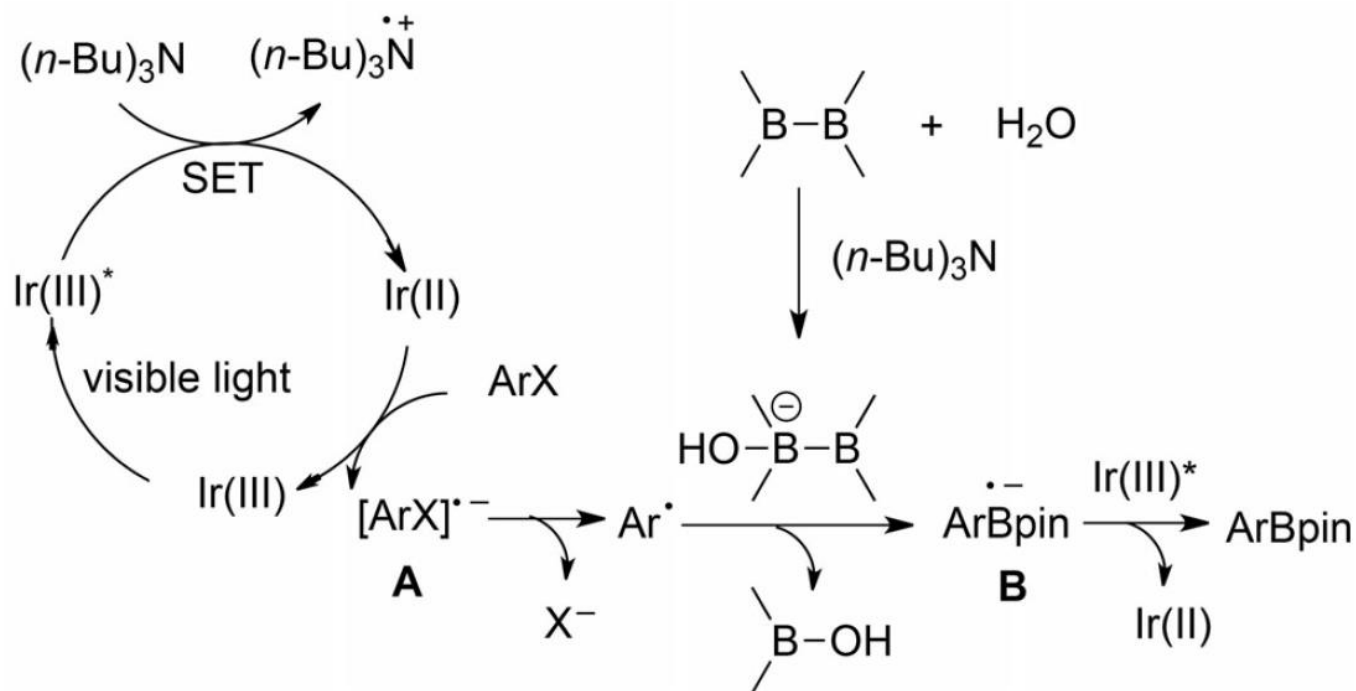
Normal conditions

No Ir-catalyst

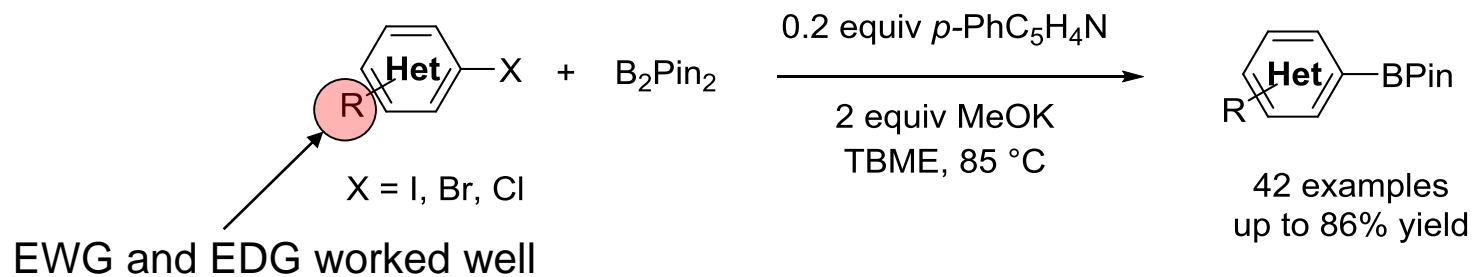
No substrate

No *n*Bu₃N

Borylation Arylhalides under VIS

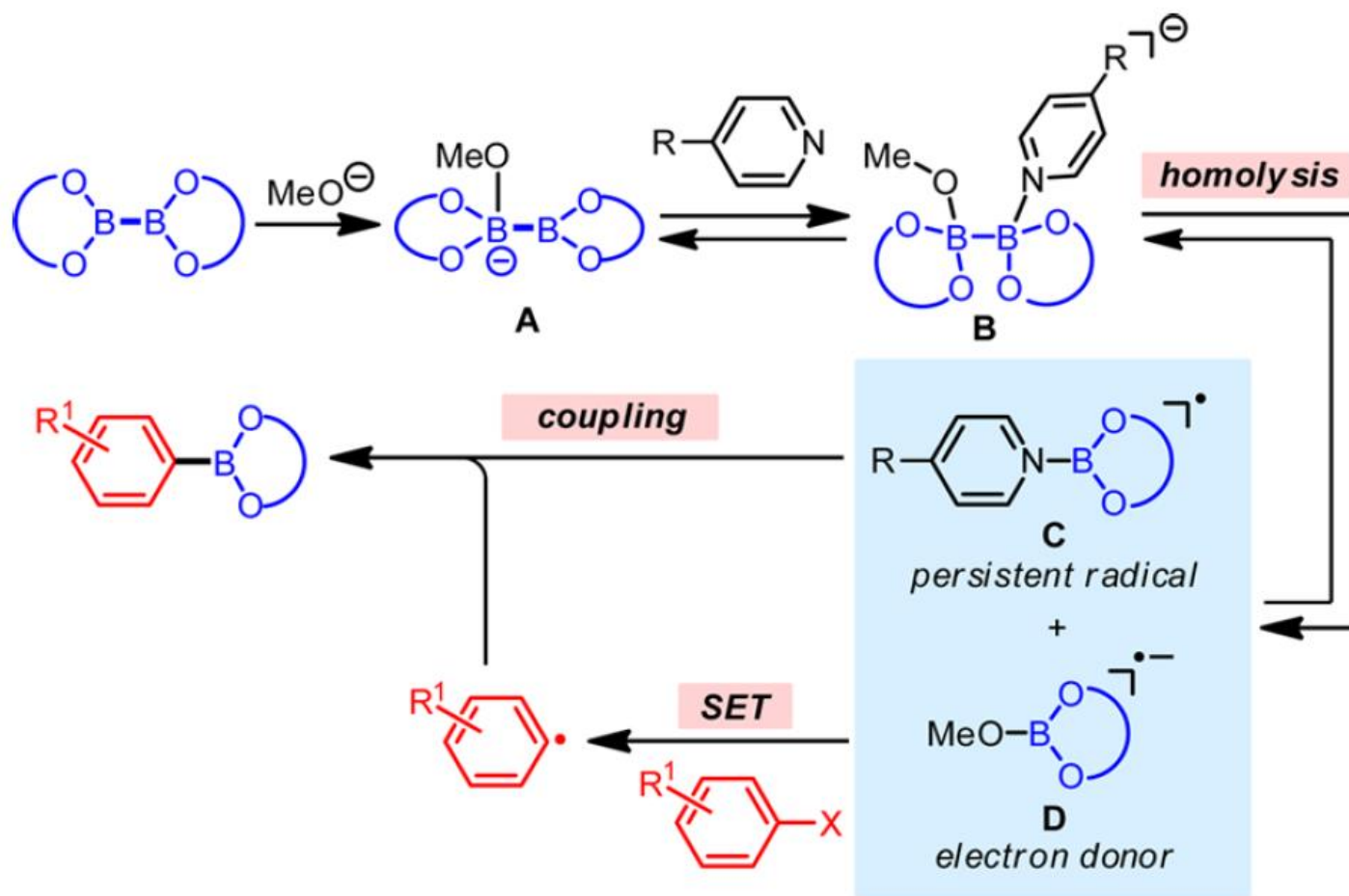


Borylation of Arylhalides

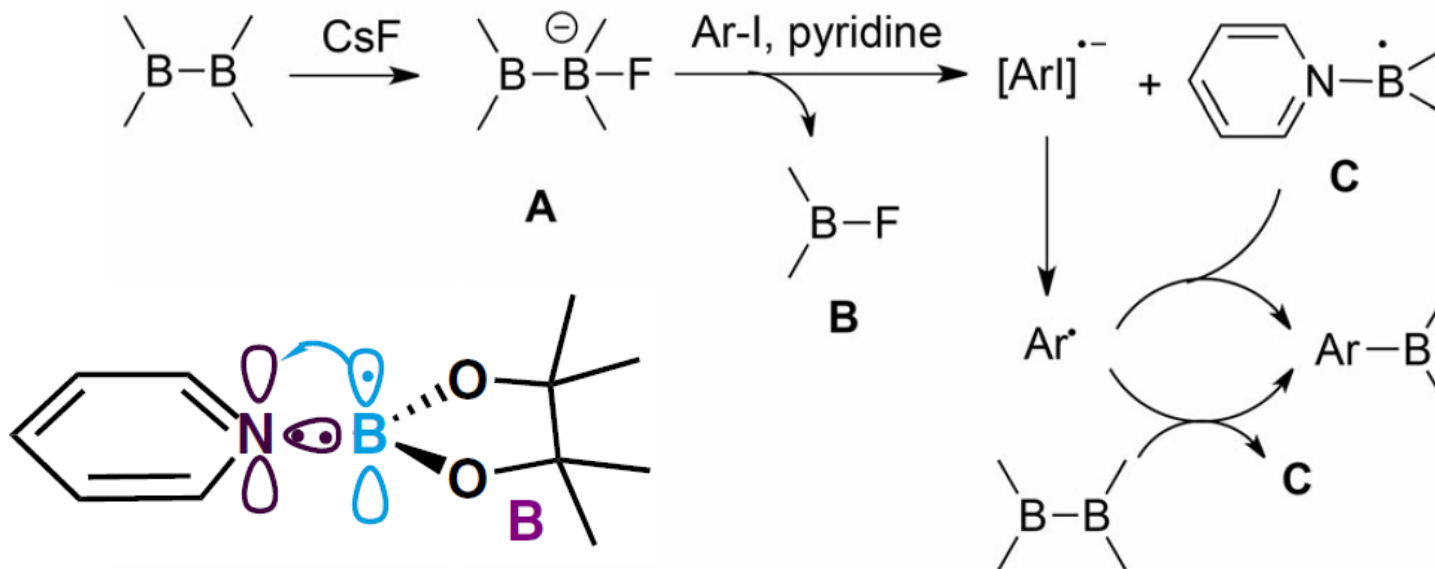
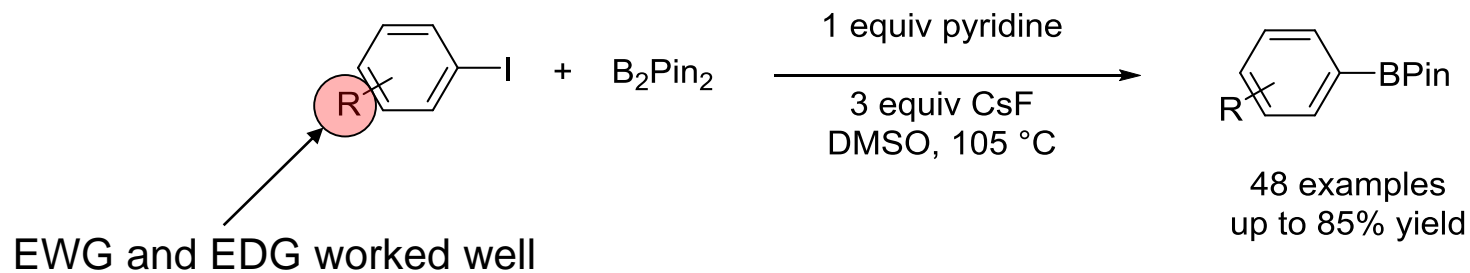


5-exocyclizations and HAT from THF to prove that radical involved

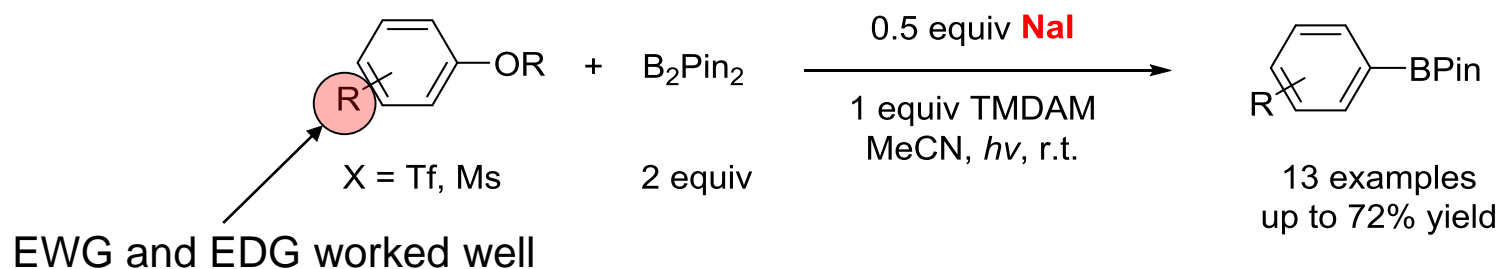
Borylation of Arylhalides



Borylation of Arylhalides

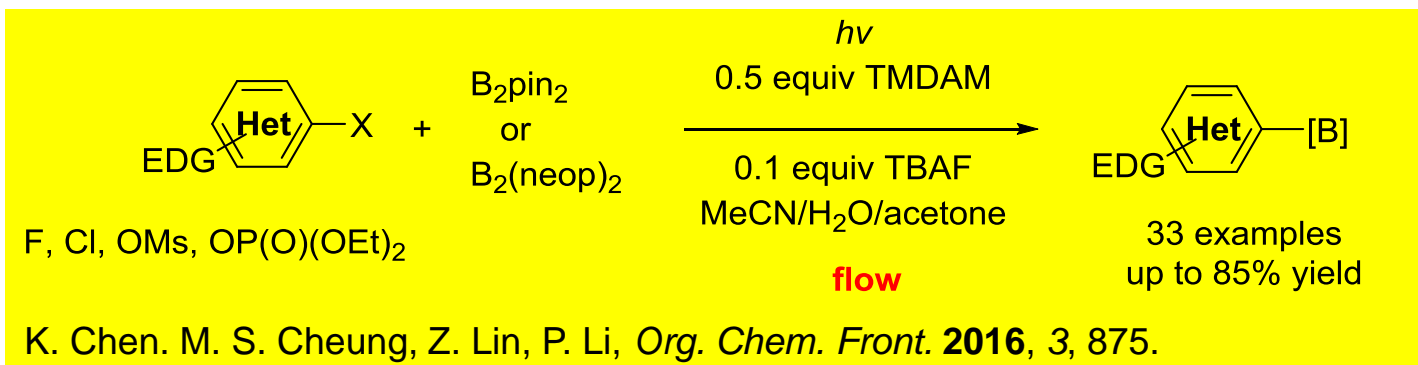


Borylation of Phenol Derivatives

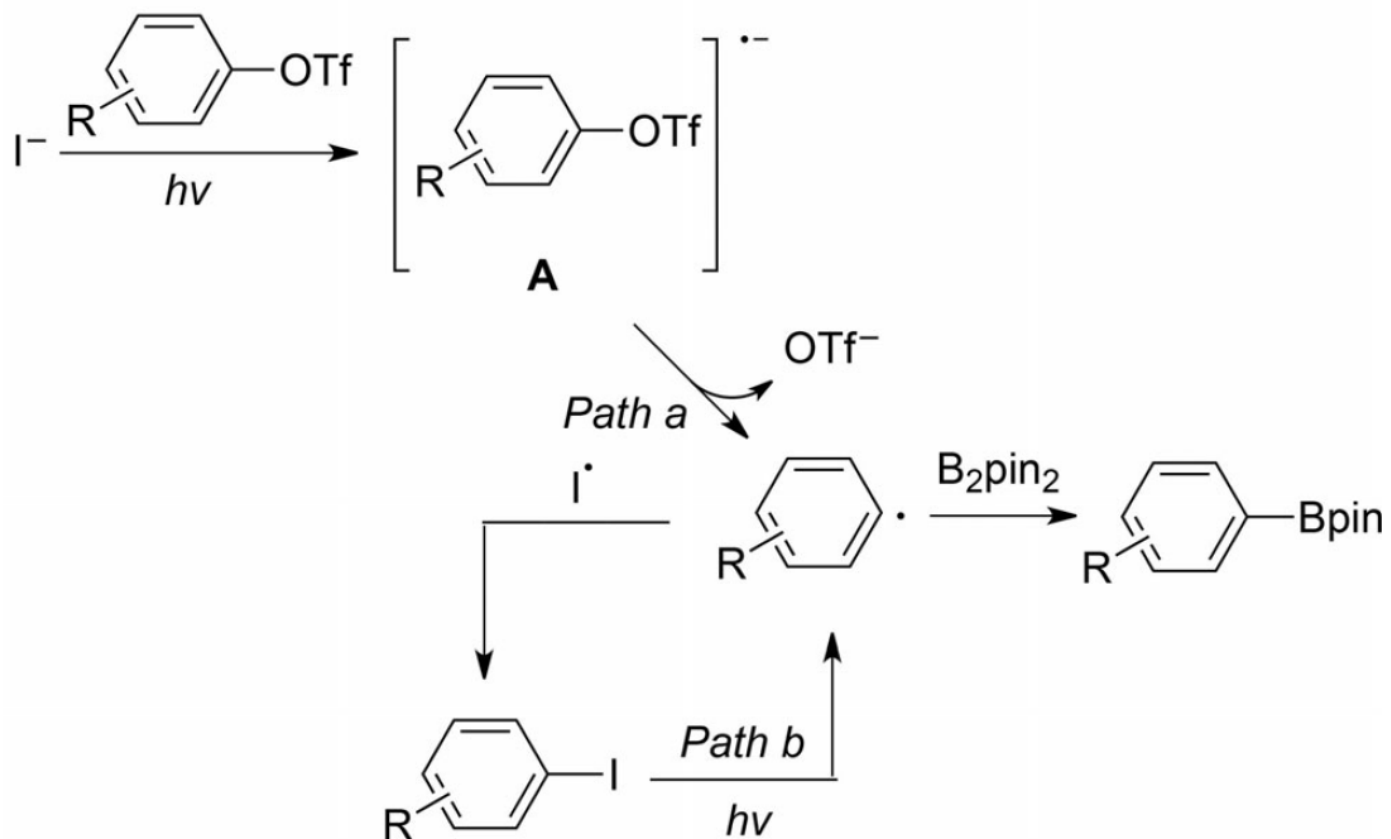


Without NaI only 5% yield

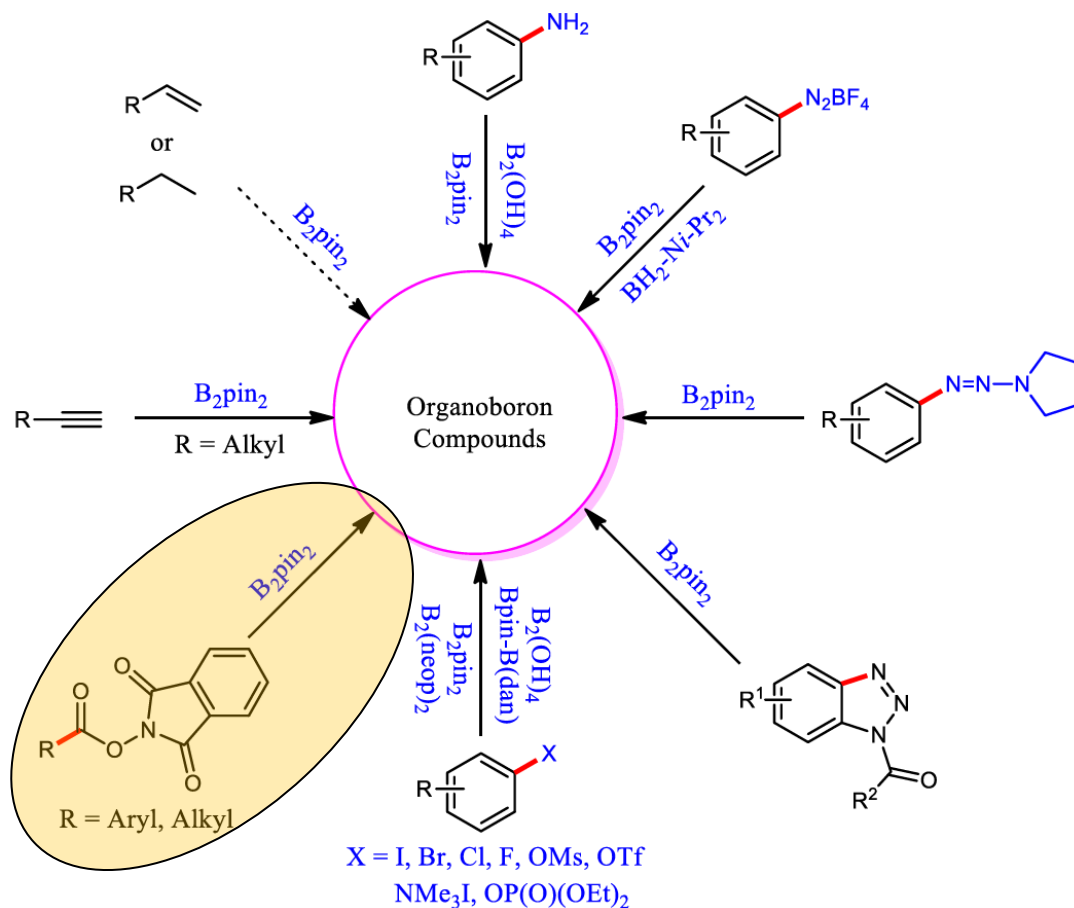
First arylborylation from phenol derivatives without transition metals



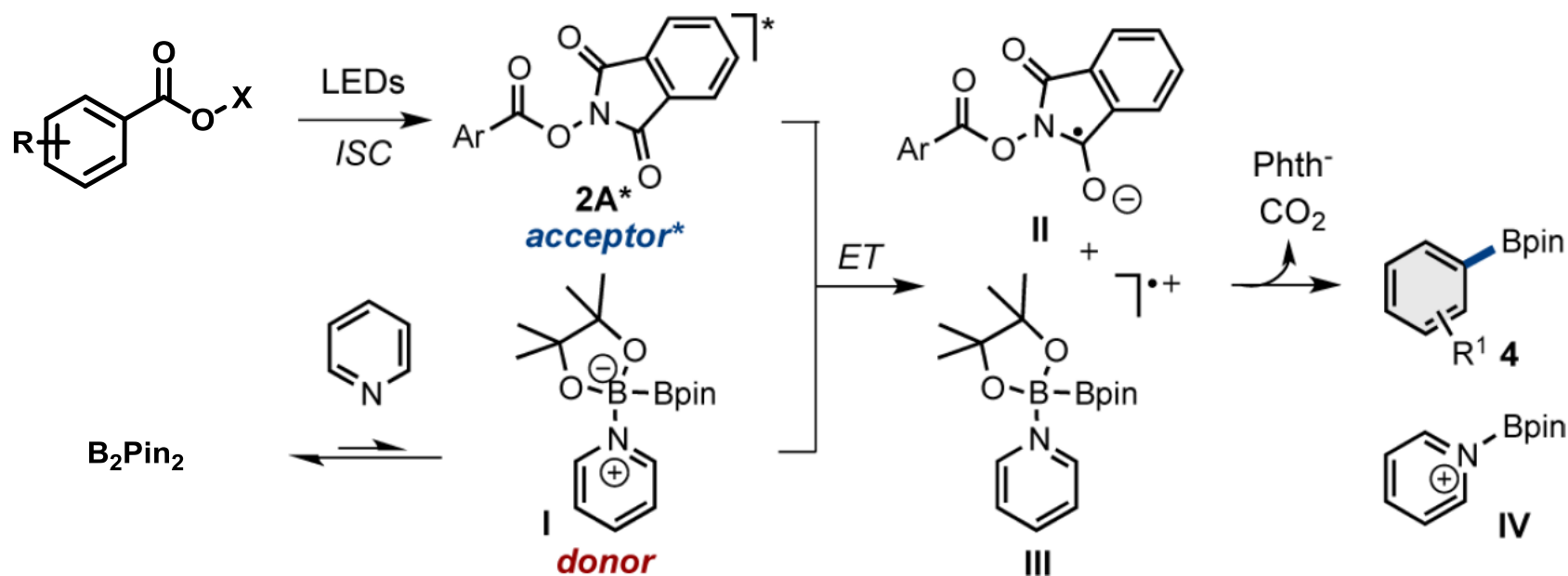
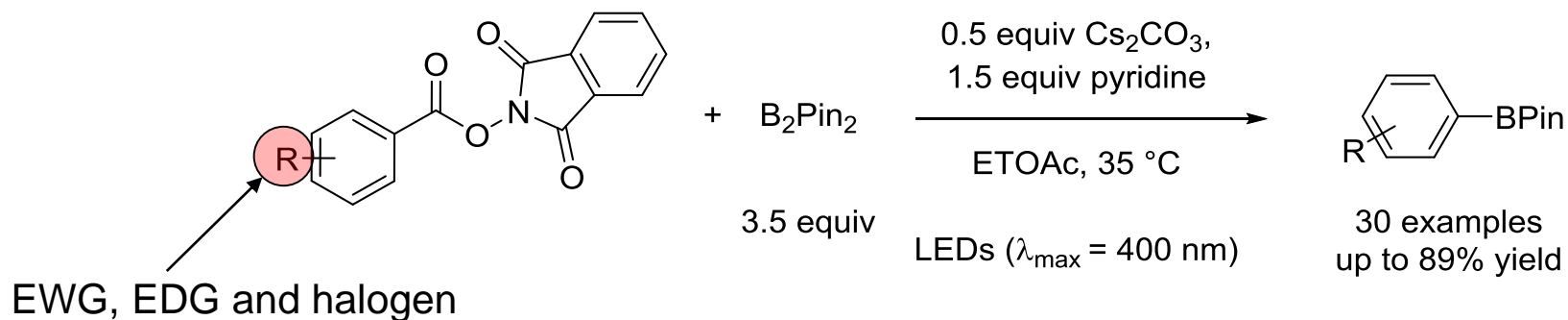
Borylation of Phenol Derivatives



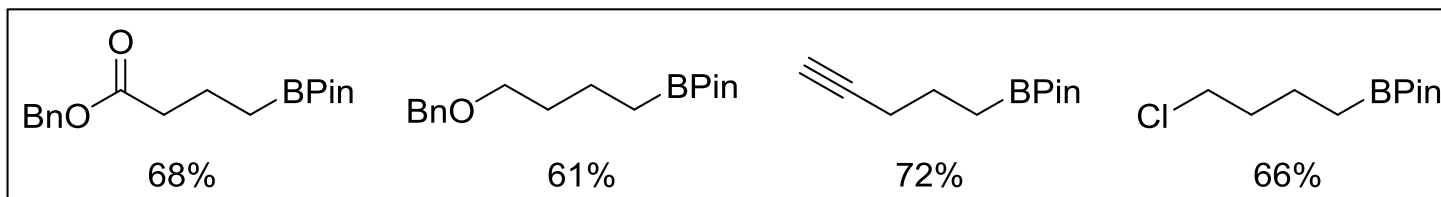
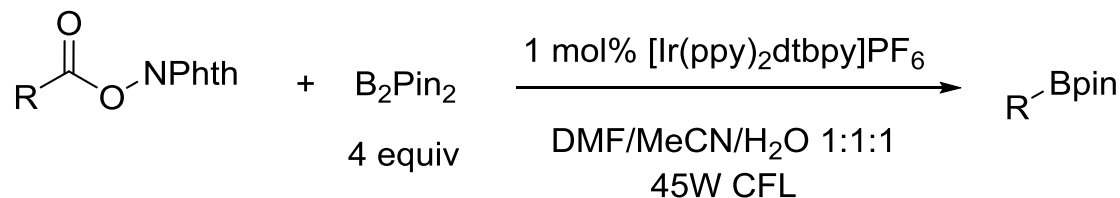
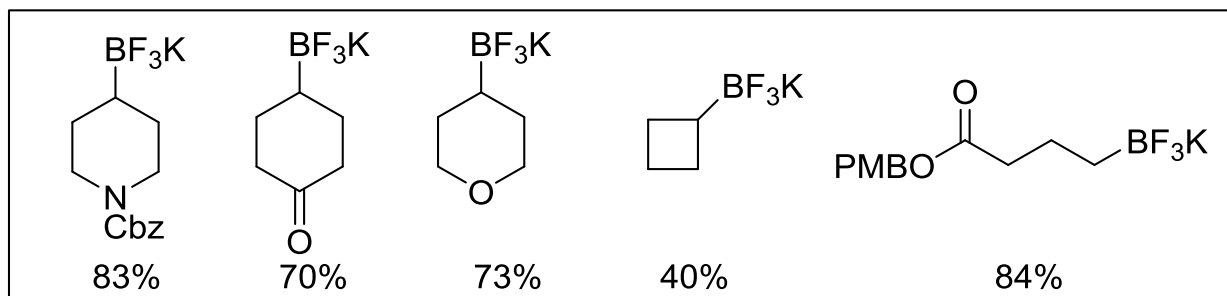
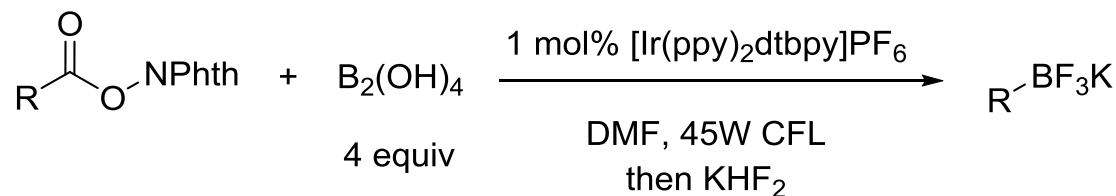
Borylation of Carboxylic Acid Derivatives



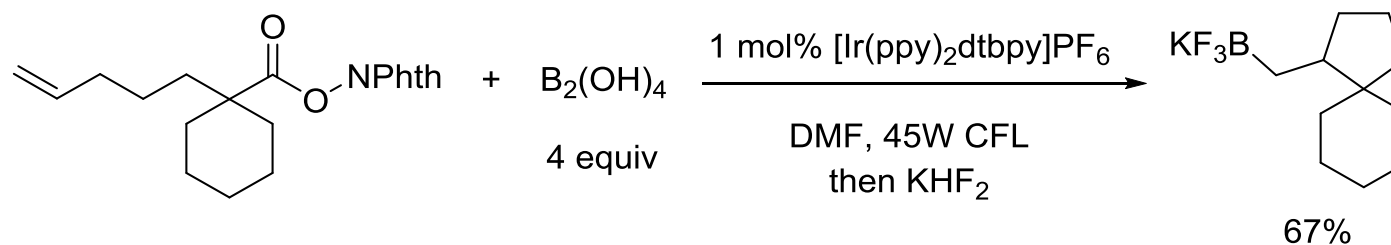
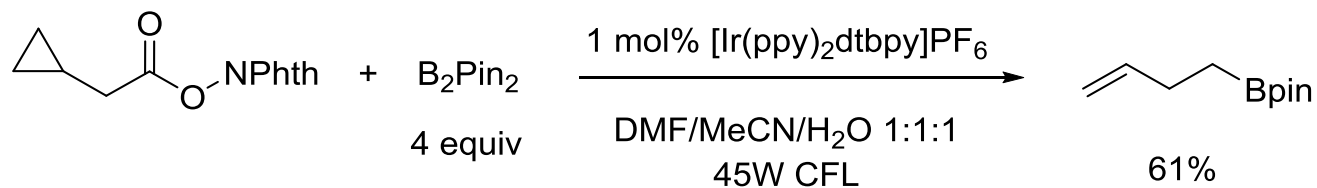
Borylation of Aryl-*N*-Hydroxyphthalimide esters



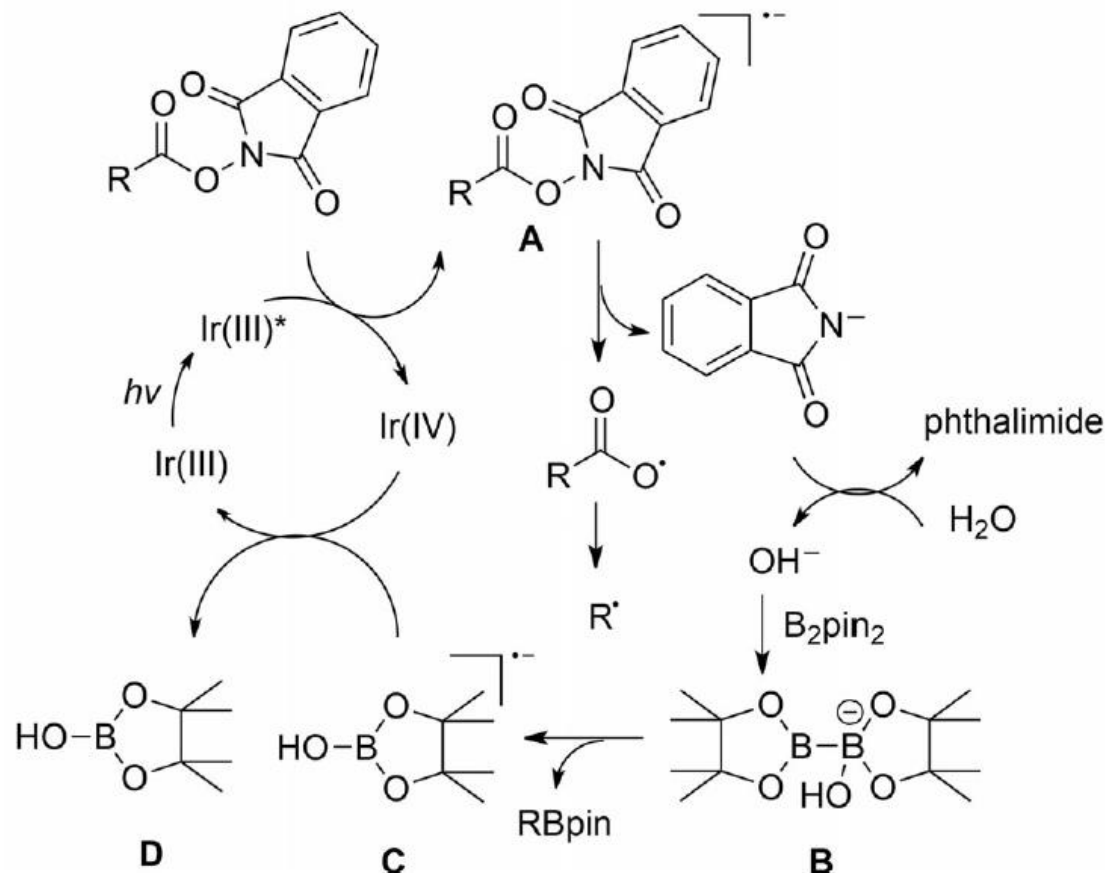
Borylation of Alkyl-*N*-Hydroxyphthalimide esters



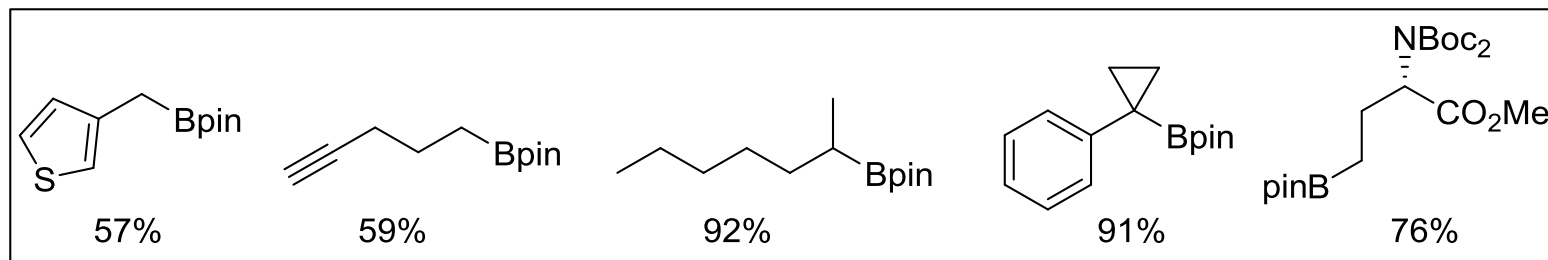
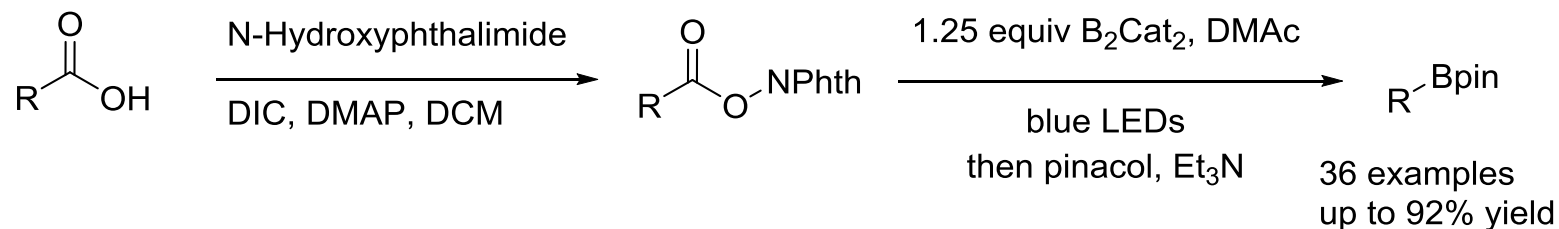
Borylation of Alkyl-*N*-Hydroxyphthalimide esters



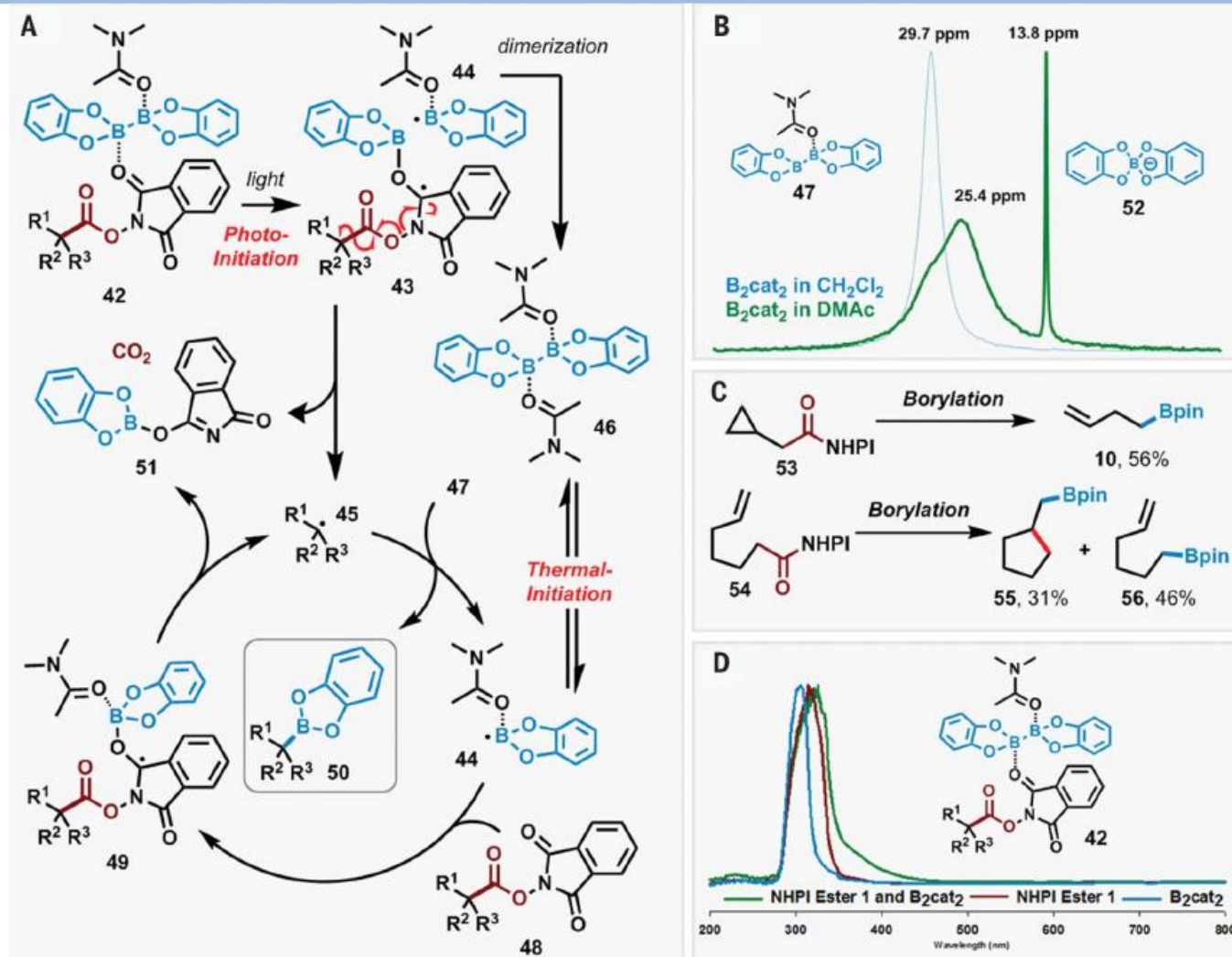
Borylation of Alkyl-*N*-Hydroxyphthalimide esters



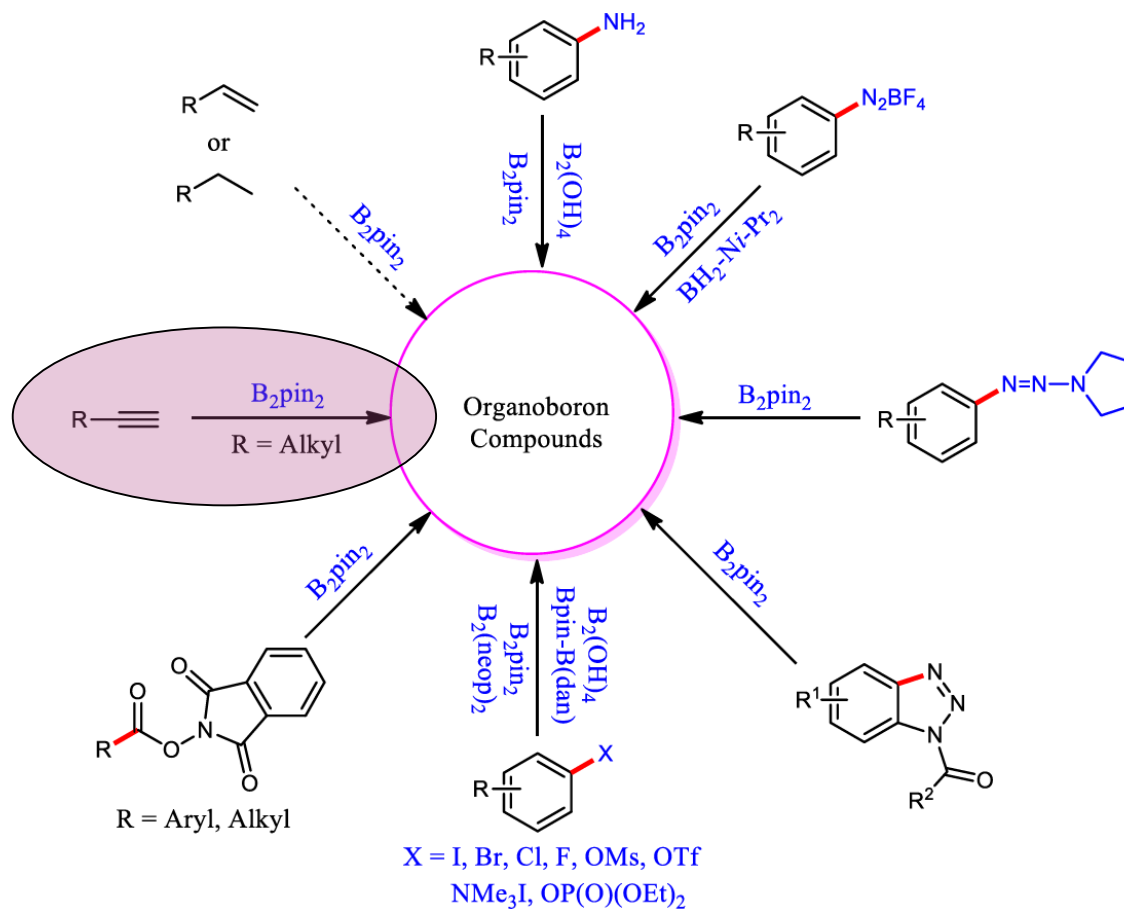
Borylation of Alkyl-*N*-Hydroxyphthalimide esters



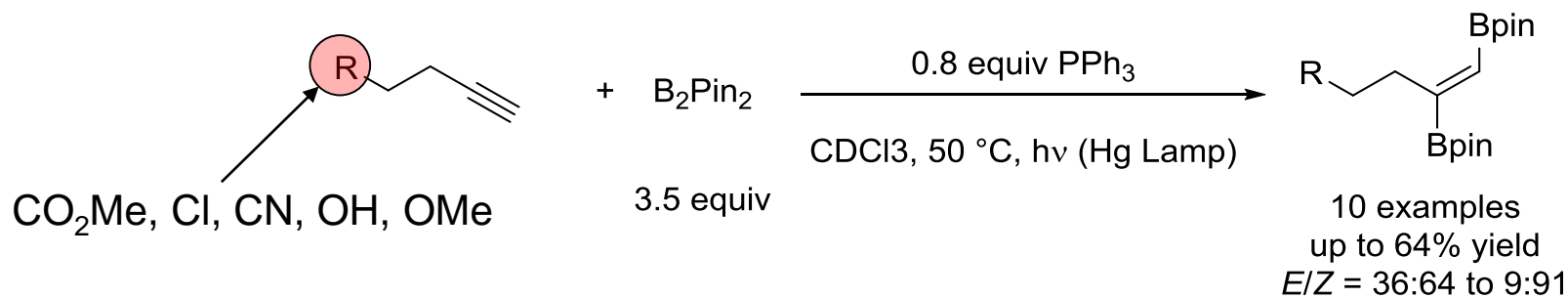
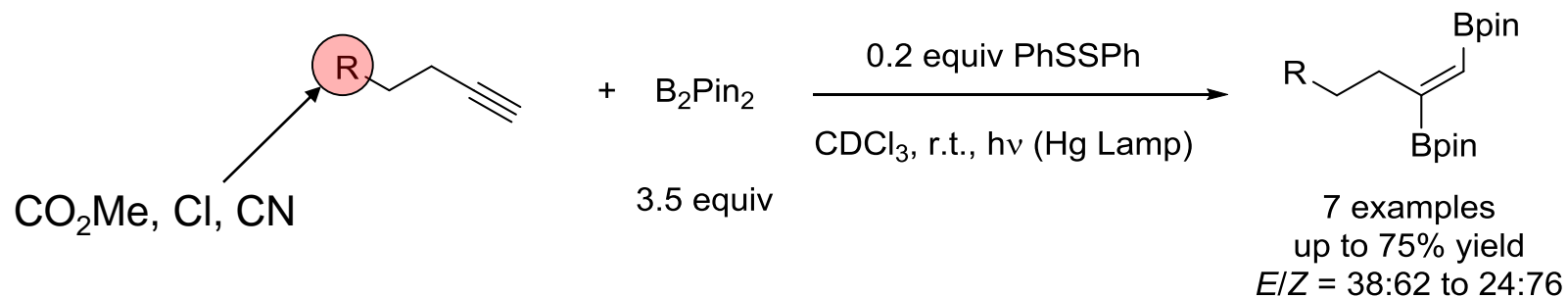
Borylation of Alkyl-N-Hydroxyphthalimide esters



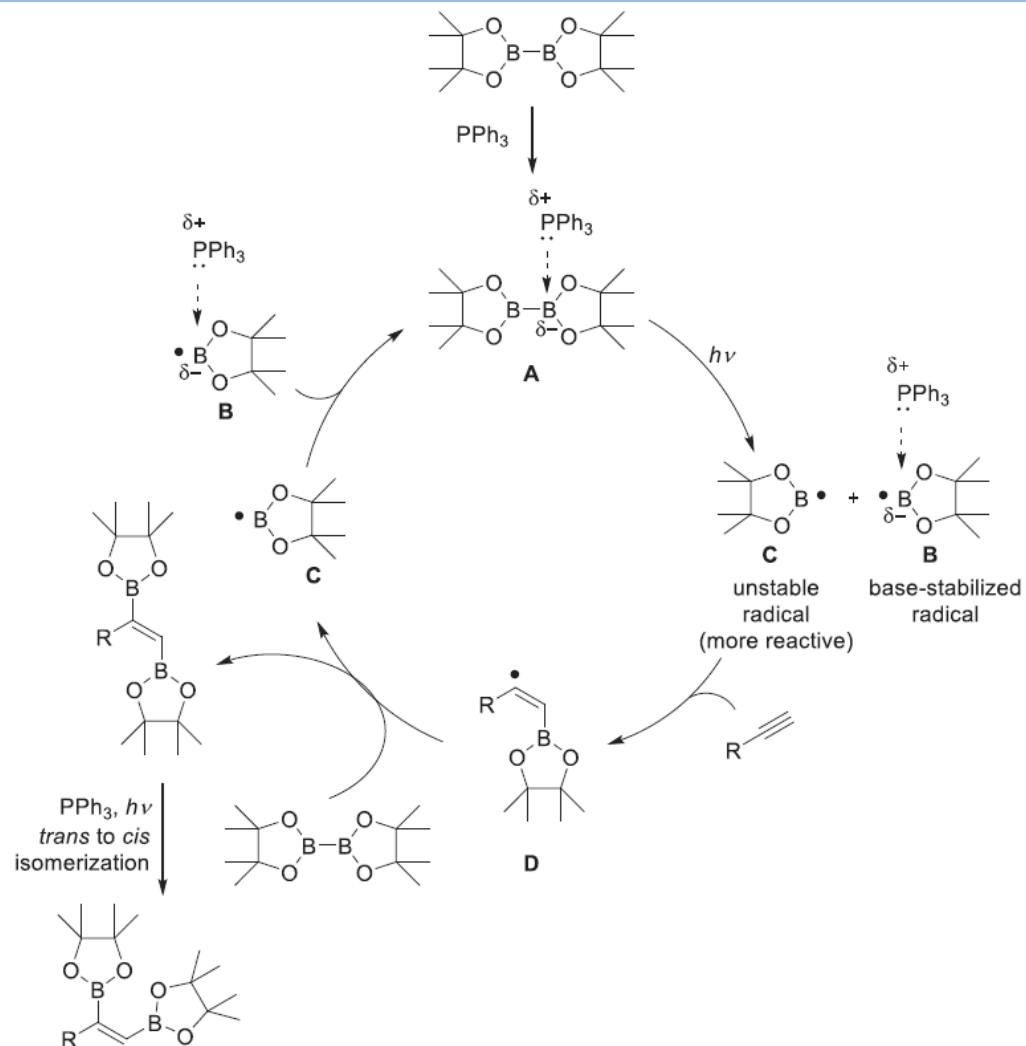
Borylation of Alkynes



Borylation of Alkynes

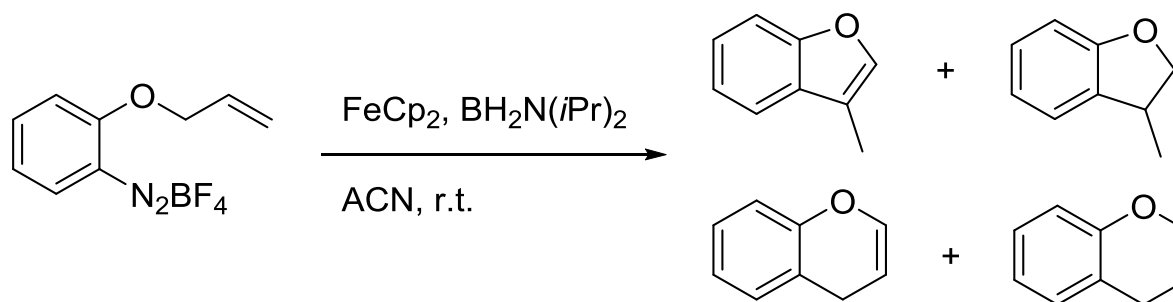
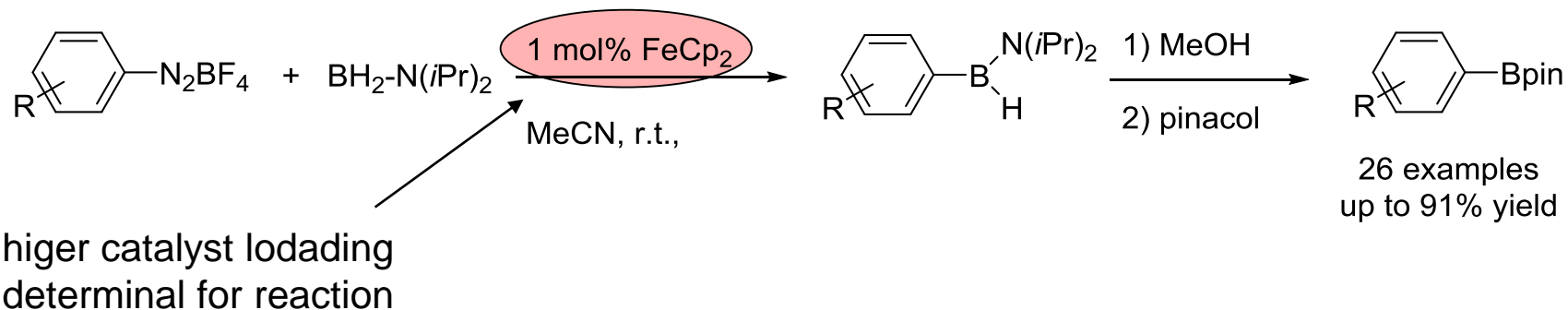


Borylation of Alkynes



Thank you for your attention

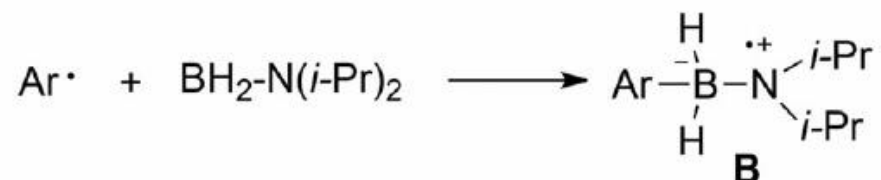
Borylation of arylamine derivatives



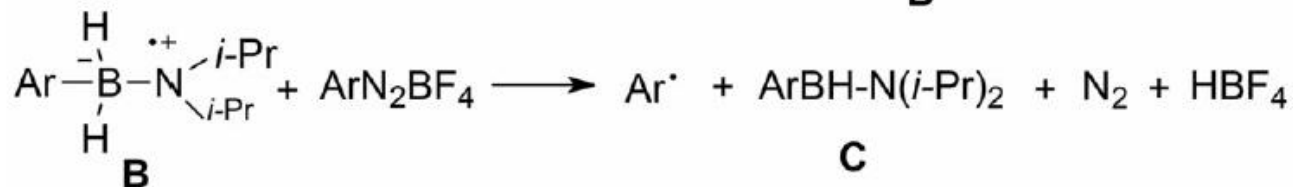
Borylation of arylamine derivatives



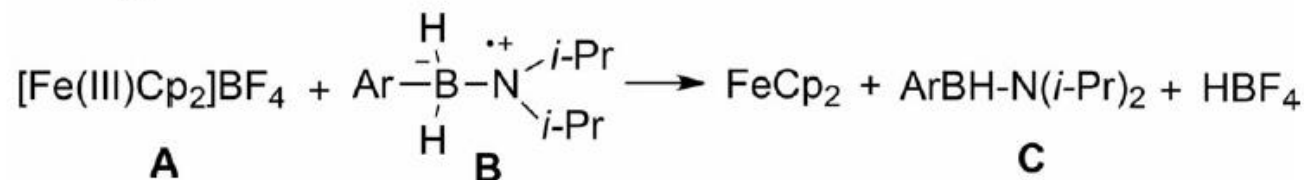
A



B



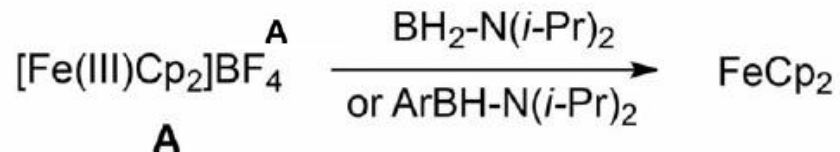
C



A

B

C



A