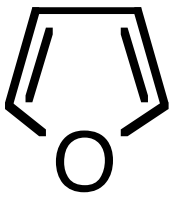
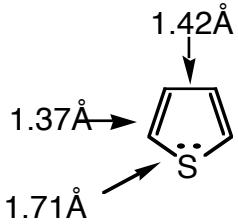
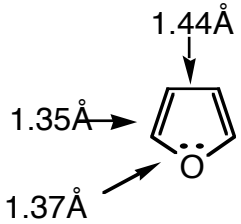
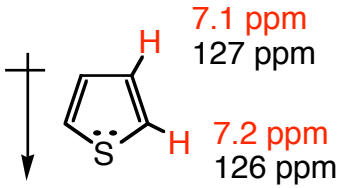


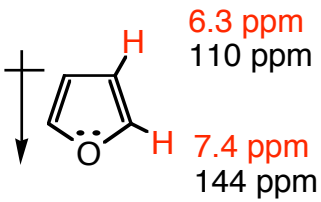
FURAN

The least aromatic 5-membered ring

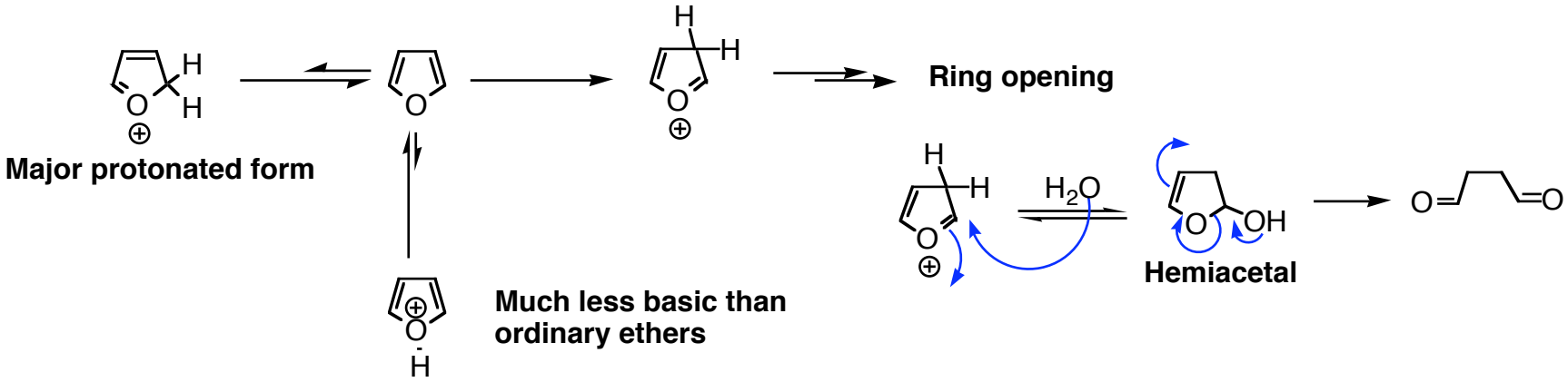








Reaction with electrophiles - Protonation

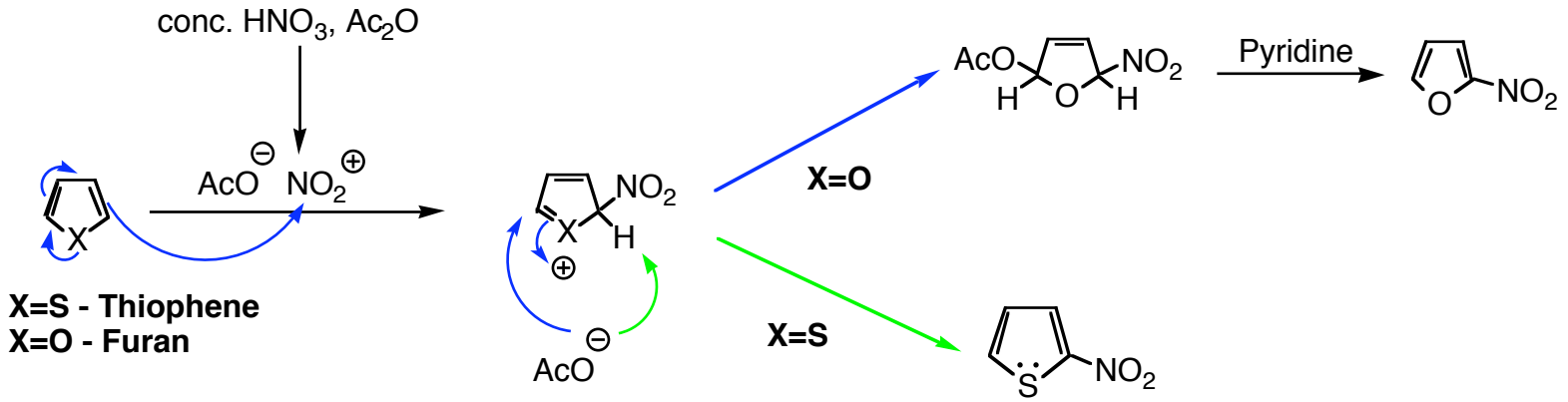


Conc. H_2SO_4 → **Decomp.**

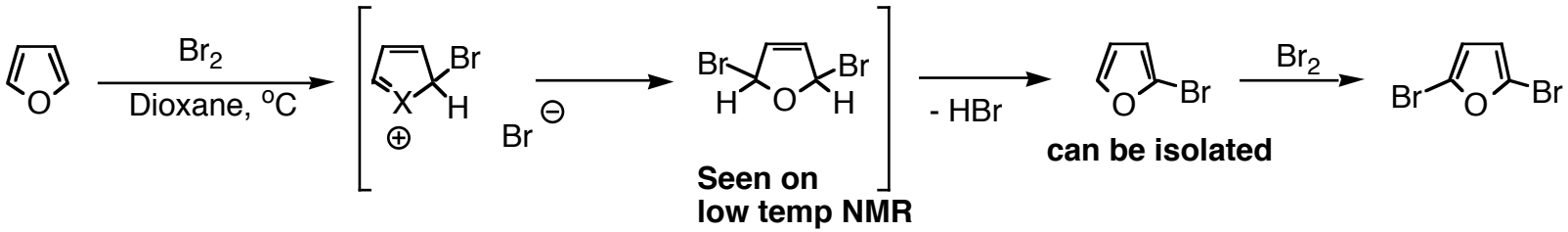
Lewis acids (i.e. $AlCl_3$)

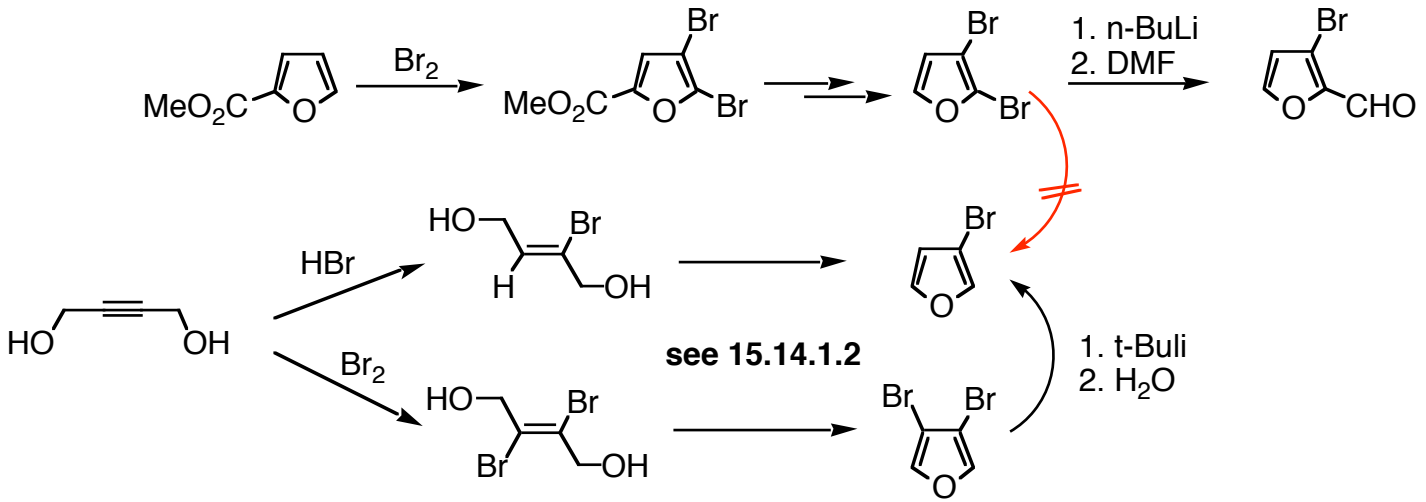
Reaction with electrophiles - Nitration

Cannot use conc. HNO_3 / H_2SO_4

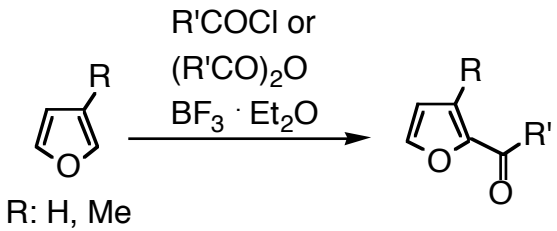


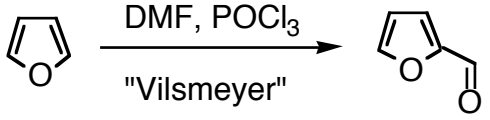
Halogenation





Reaction with electrophiles - Acylation



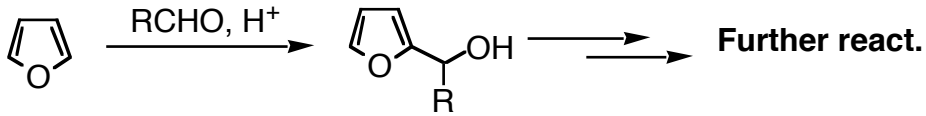


Furfural
Also very readily available by other routes

Alkylation

Generally not practical (polyalkylation, polymerisation)

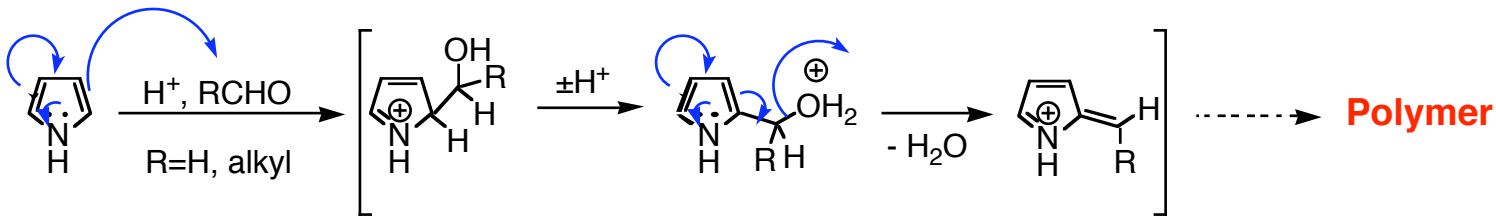
Condensation with Aldehydes and Ketones



Further react.

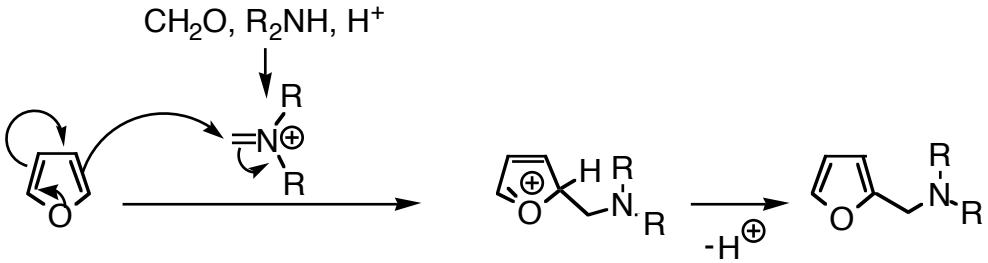
stable
From chloral

C.f.

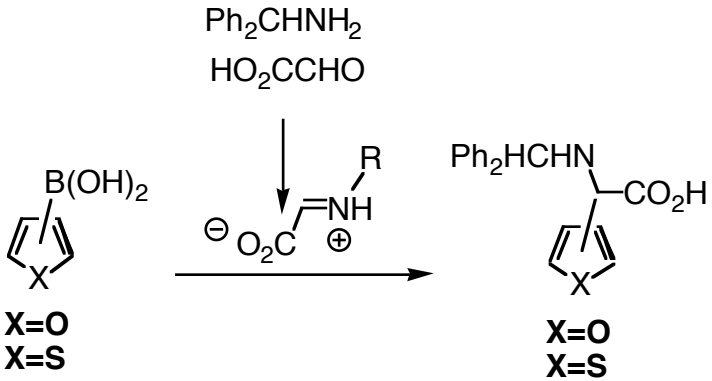


Polymer

Reaction with electrophiles - Condensation with imines / iminium ions

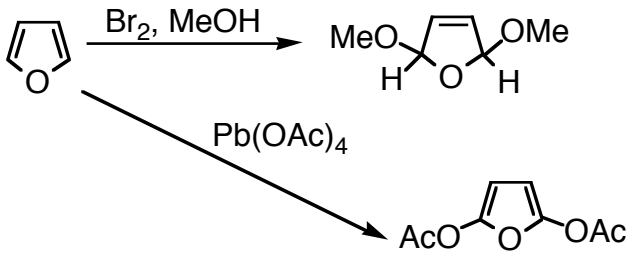


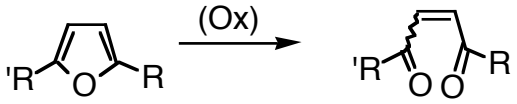
Unsubst furan: iminium ion must be preformed



***ipso* subst.**

Reaction with oxidating agents



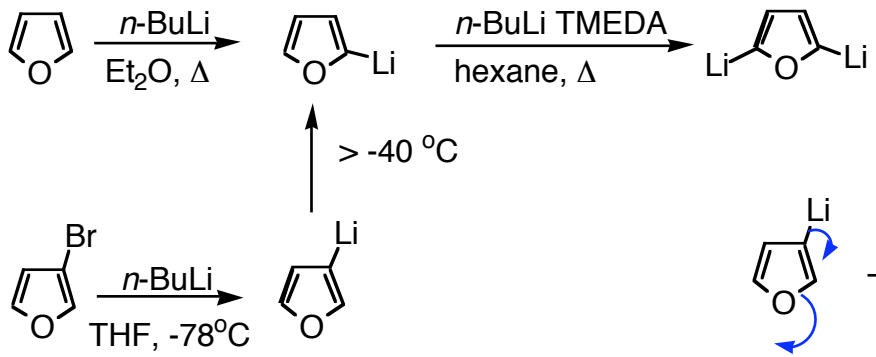


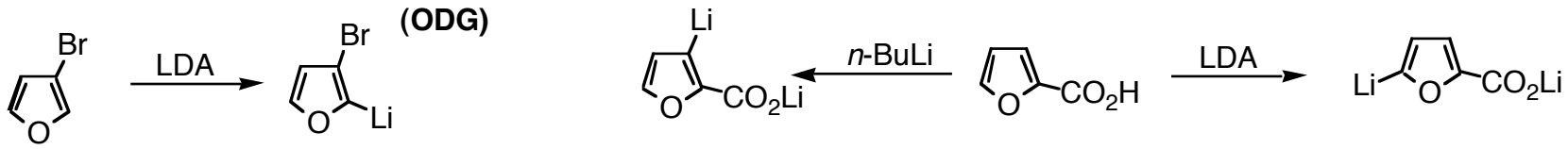
Div. ox. agents p 300
***E*-isomer in most cases**

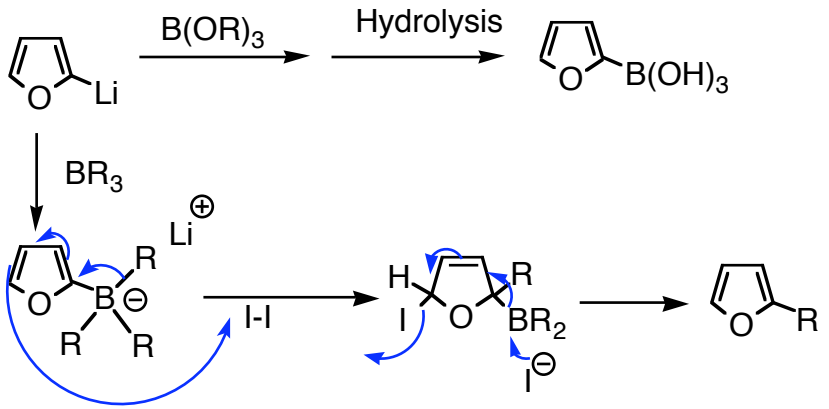
Reaction with nucleophiles

Some ex. on furans activated with -NO_2 group

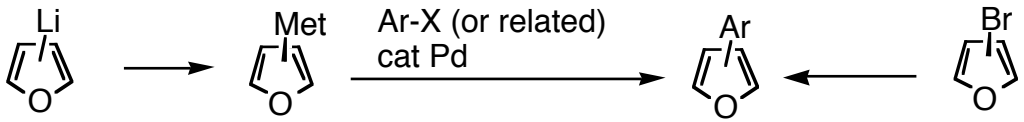
Metallation and further react.

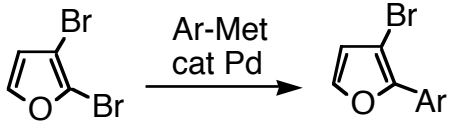


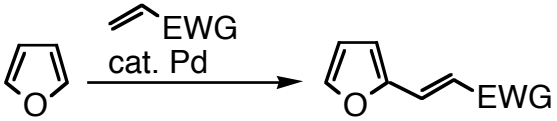




Pd-cat couplings

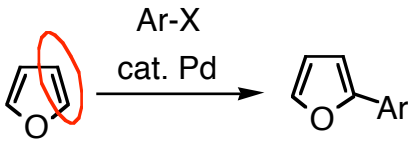




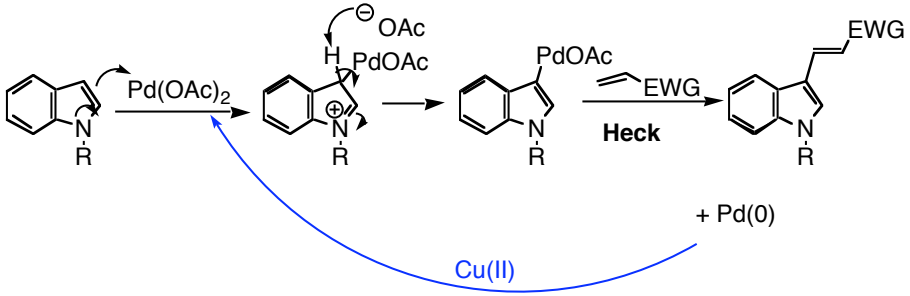


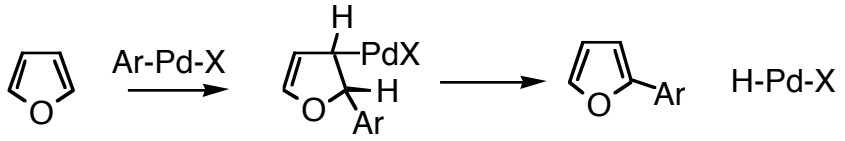
Heteroaryl-Heck

like an alkene in Heck



c.f.

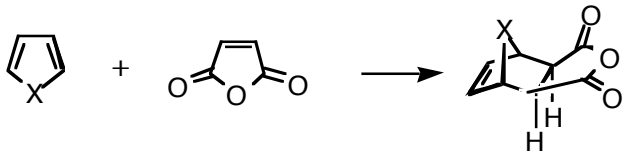




Cycloadditions

Furanes as diene - one of the first DA examples

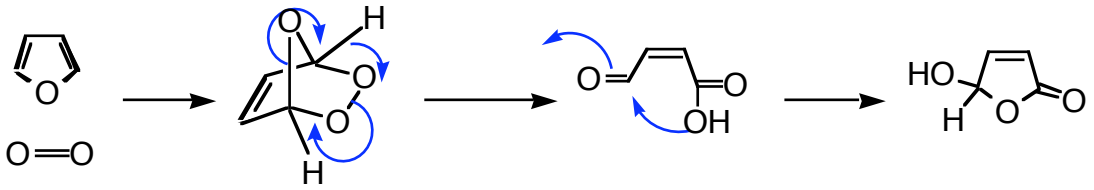
Furan reacts with many dienophiles (alkenes, alkynes, allenes)



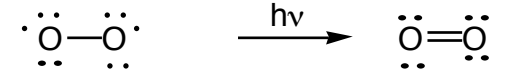
X=O: r.t.; 80%
X=S: 100 oC, 15kbar; 42%

***exo* isolated (termodyn favoured)**
***endo* (kinetic prod.)**

With $^1O_2$



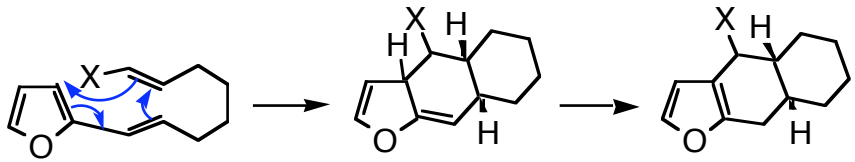
$^3O_2$ (triplet) $\xrightarrow{h\nu}$ **$^1O_2$ (singlet)**



Diradical
3 lines ESR

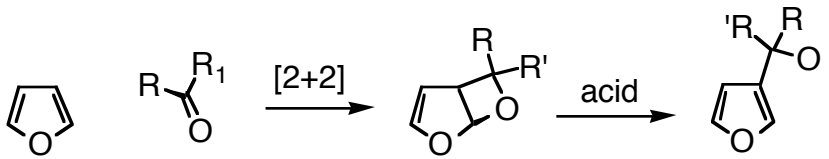
No unpaired el.
1 line ESR

Furan as dienophile (only intramolec. ex)



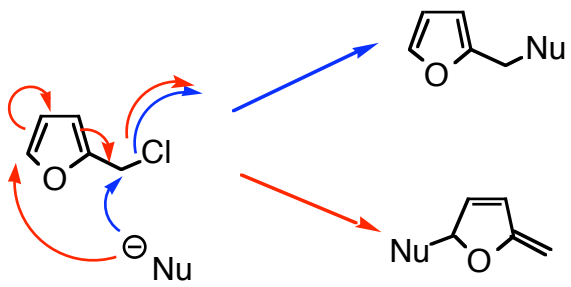
X: EWG

Photochemical cycloaddition



acetal

Furyl-CH_2-X



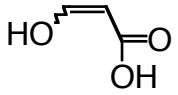
Aminofurans

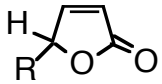
-Aminoform
-Unstable

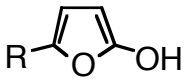
Oxyfurans

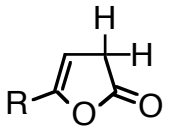
Butenolides (natural prod.)

named as der. of





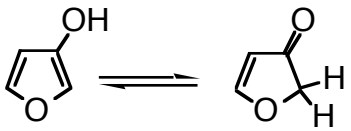




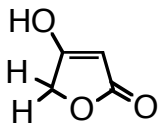
R=Me: β-angelica lactone
Most stable

not detectable

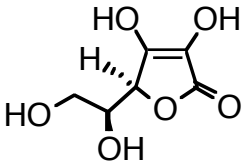
R=Me: α-angelica lactone



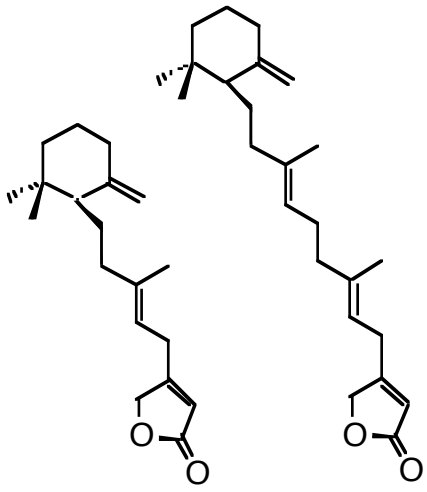
major



tetronic acid



ascorbic acid

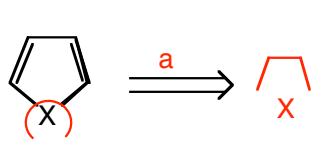


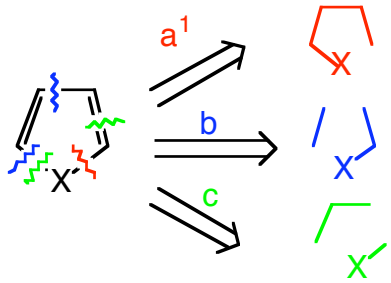
Luffarin W Luffarin B

Isol. marine sponges
cytotoxic

Synthesis of Furans

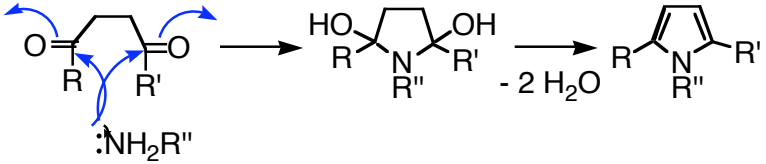
Carbonyl condensations





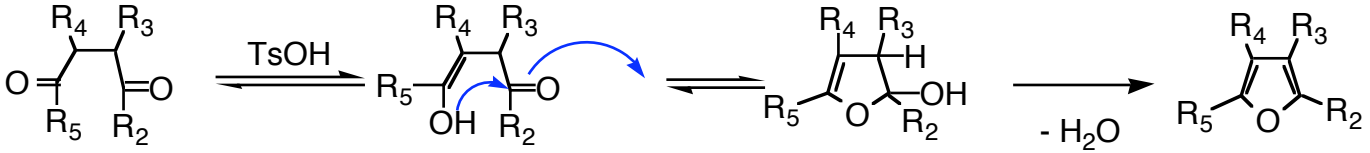
Strategy a - pyrroles

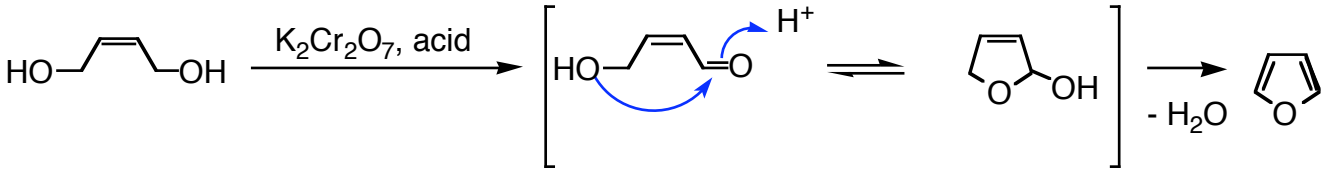
Paal Knorr

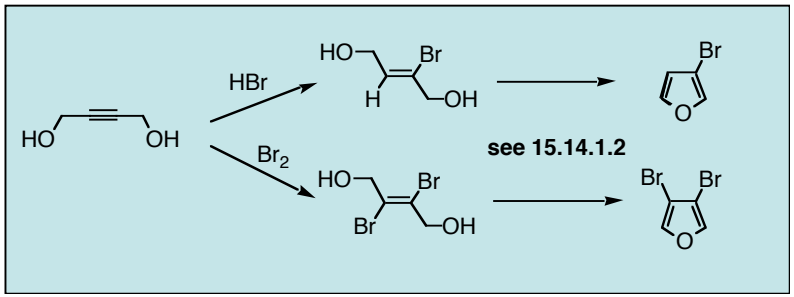


R"=H, alkyl, aryl

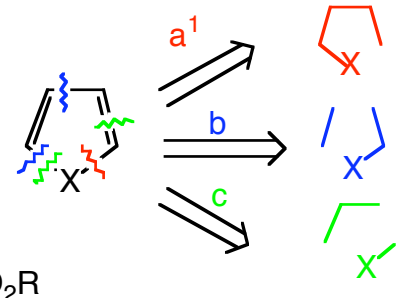
Strategy a[1] Paal Knorr (1,4-dikacarbonyl)



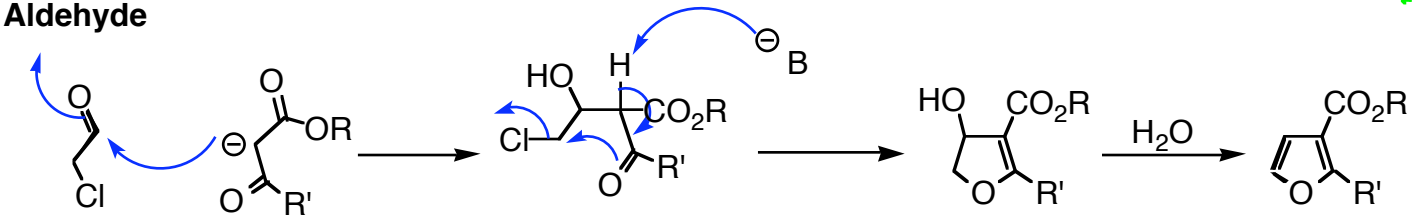




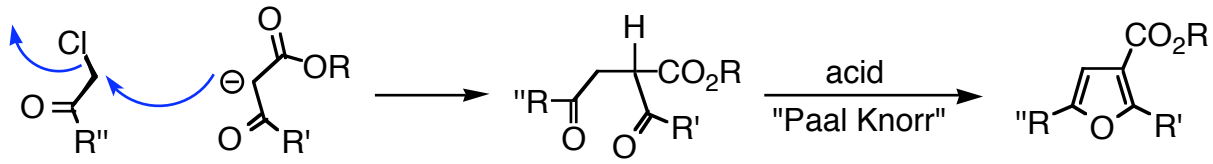
Strategy b

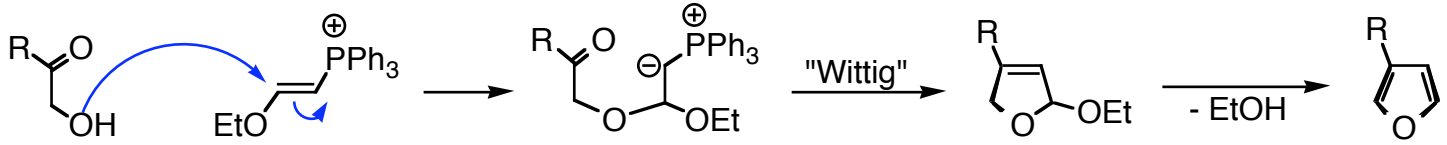


Aldehyde

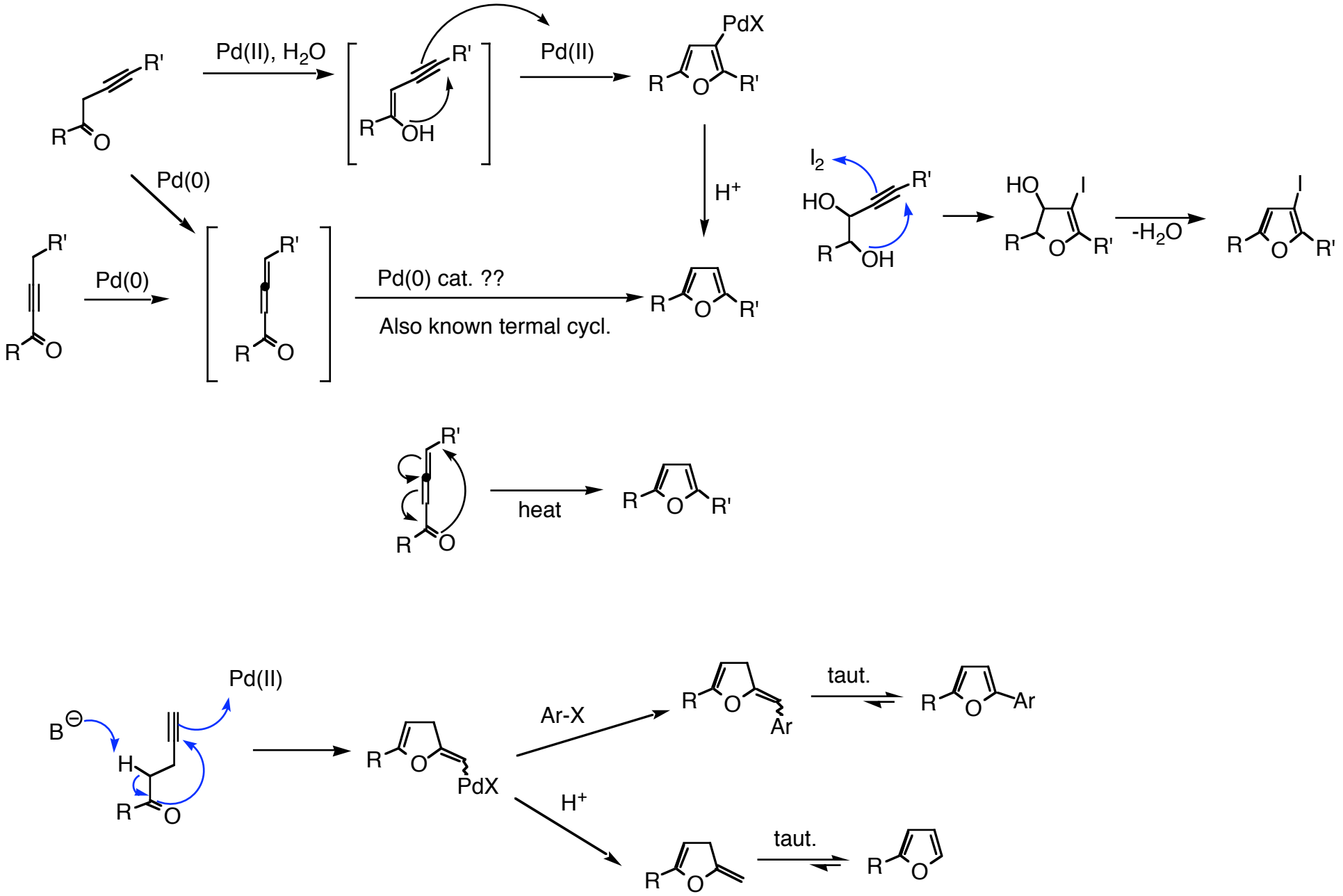


Ketone

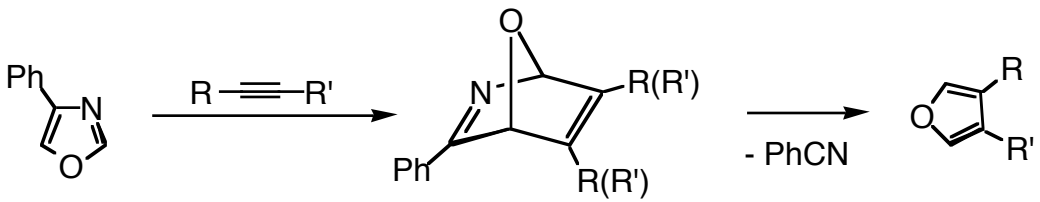




Pd-cat. Cyclisations etc.



Cycloadditions



R / R': i.e. -$SnBu_3$, -$SIMe_3$, alkyls etc.

c.f.