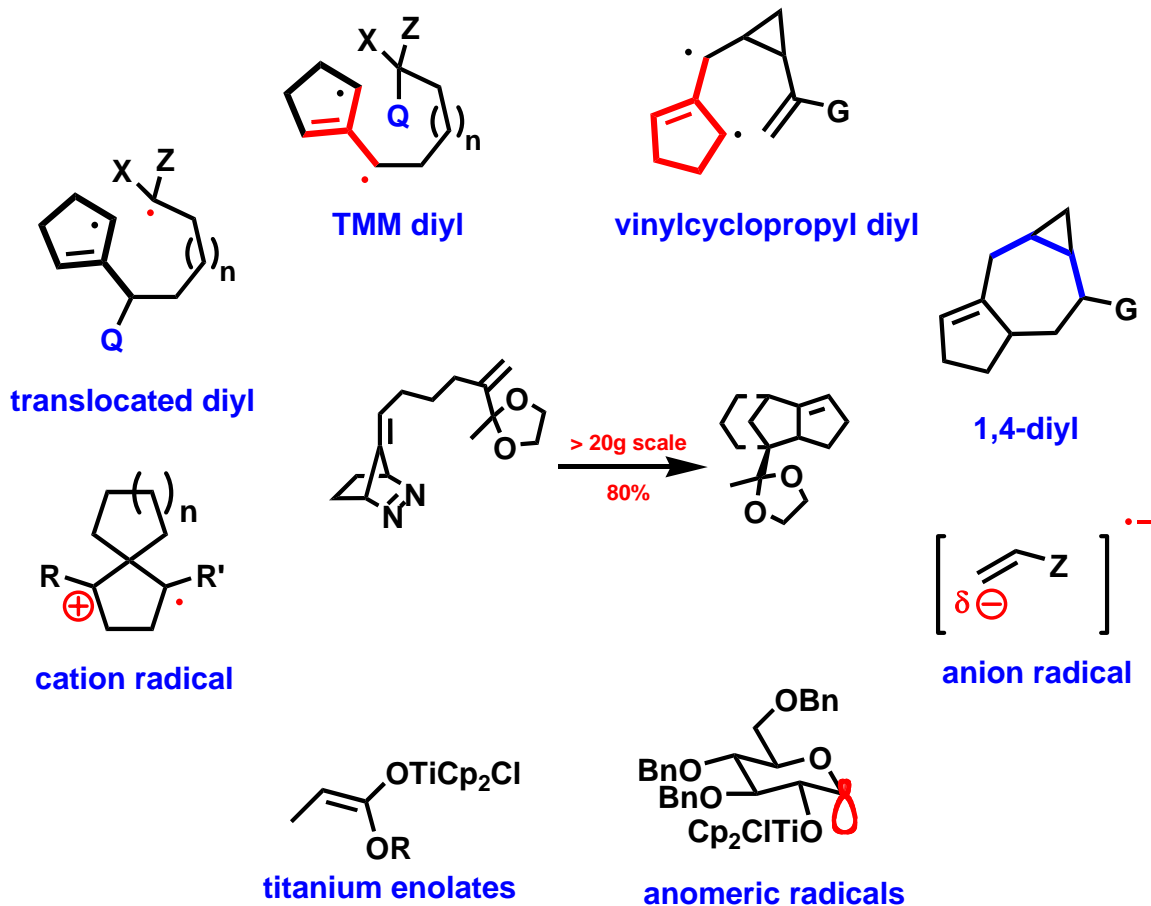
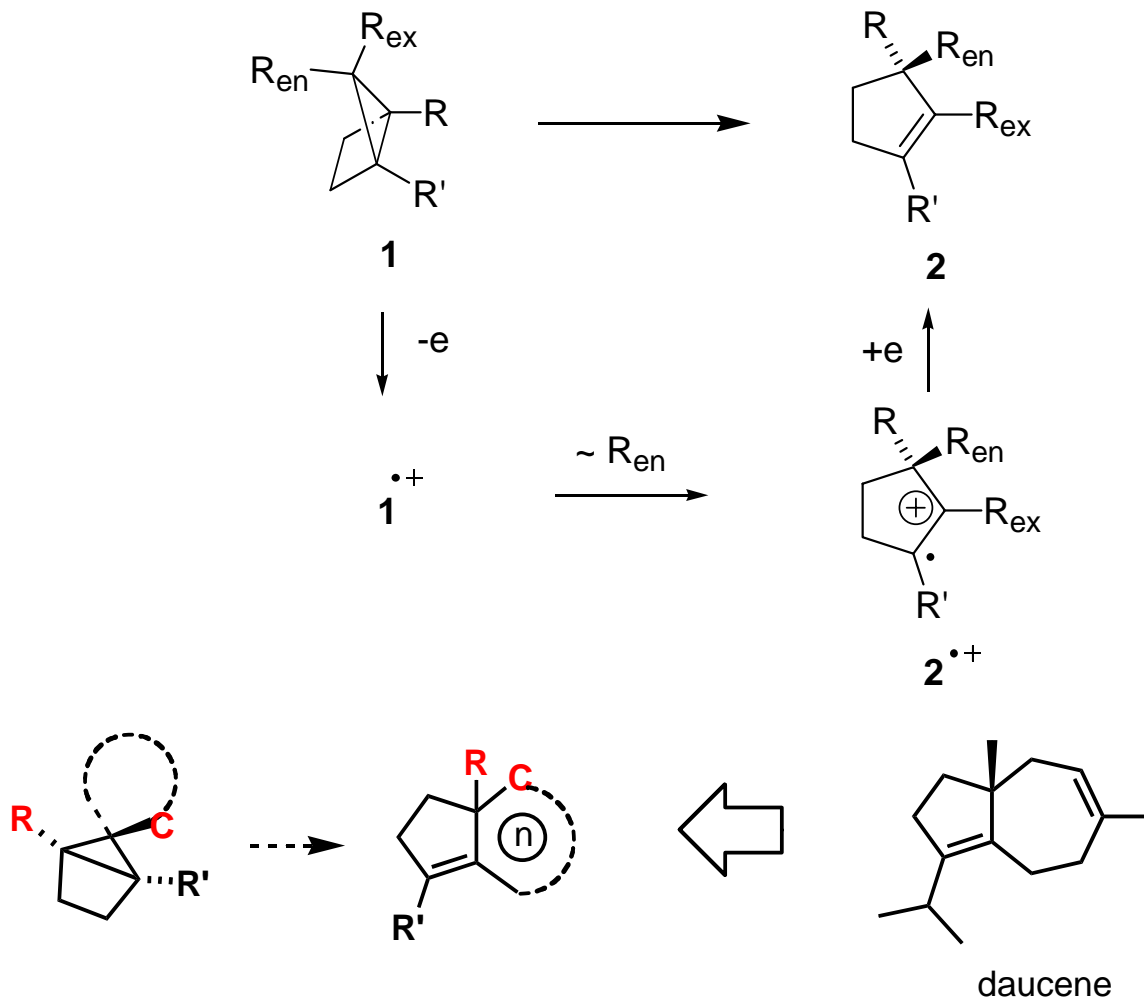


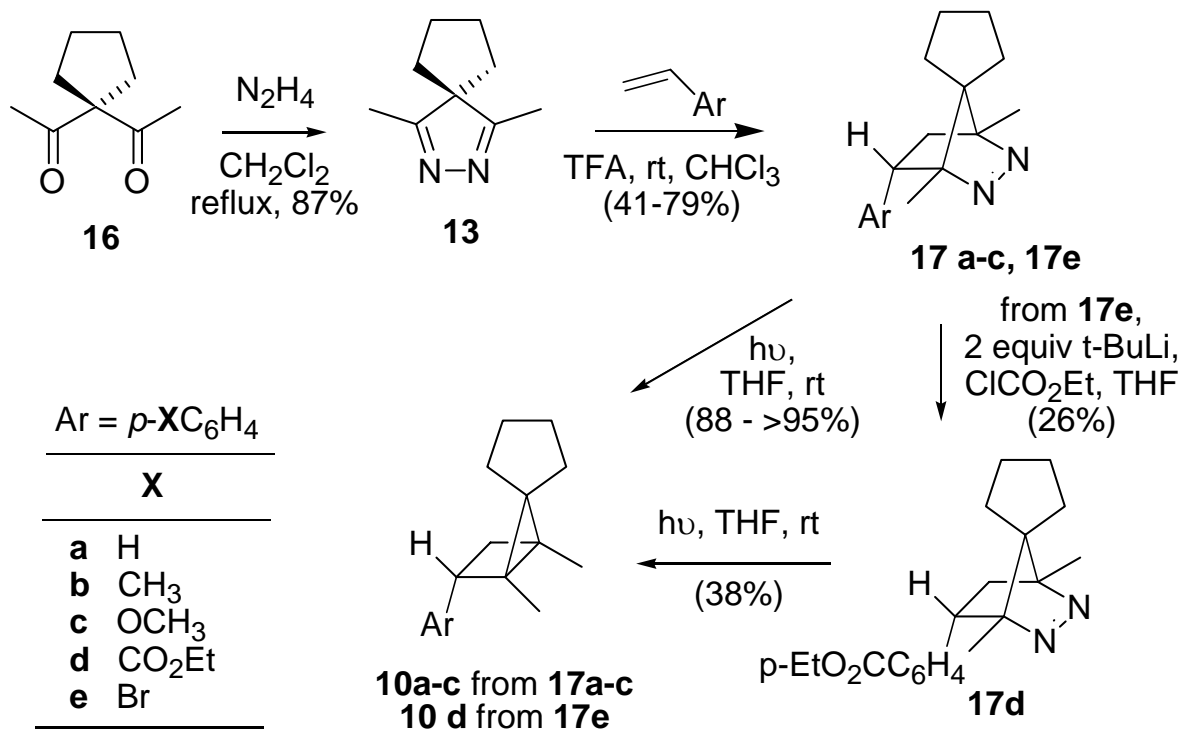
Having fun with reactive intermediates

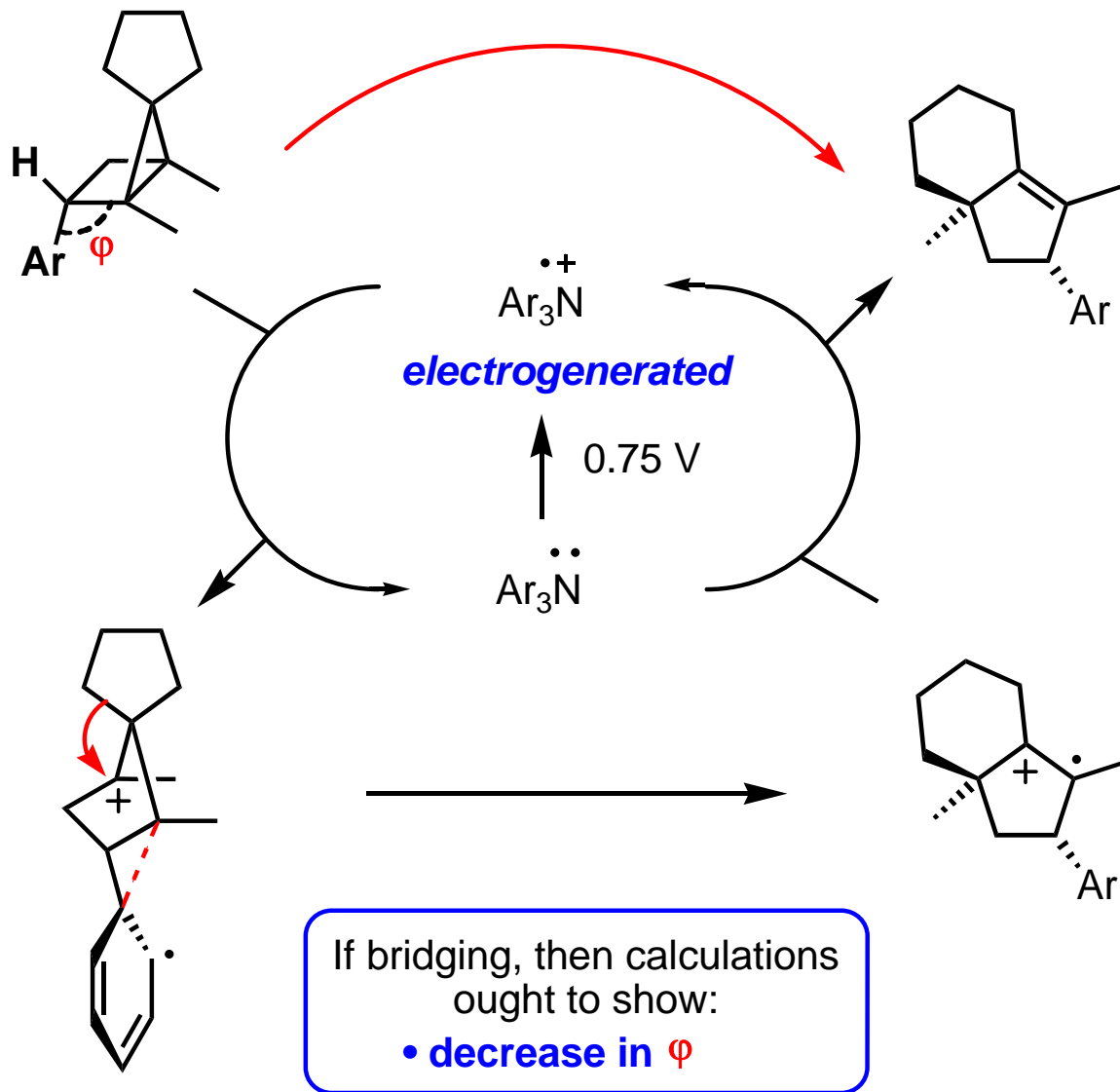


Cation radical rearrangements

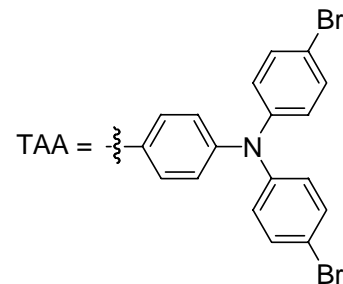
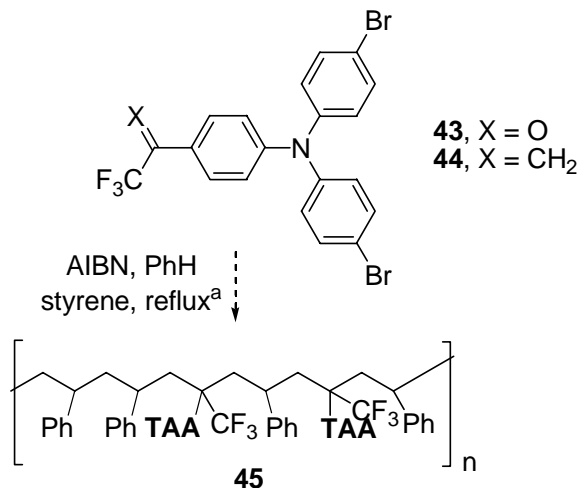
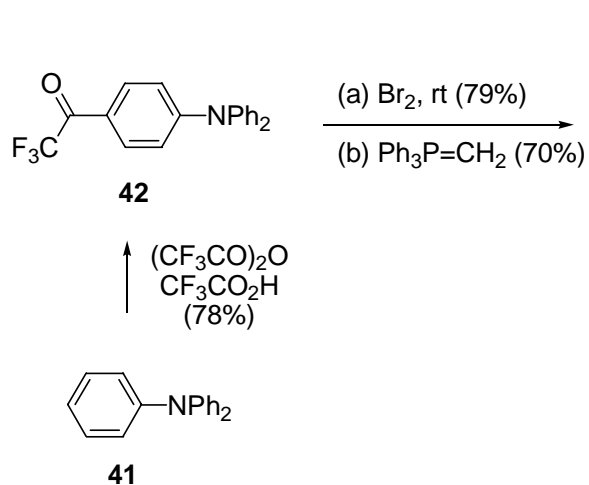
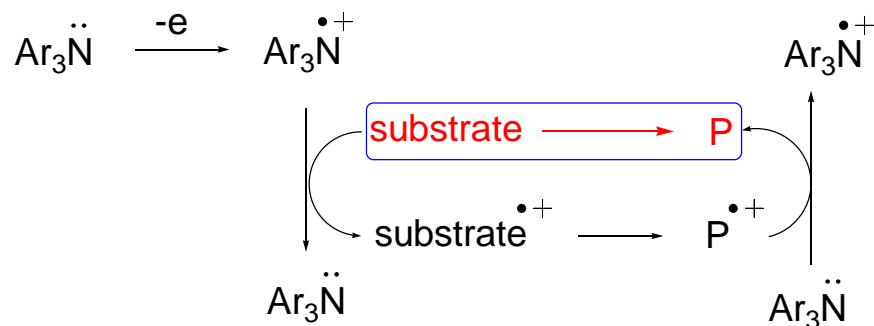


*James Gerken, Dean Tantillo,
Gisele Nishiguchi, Young Sam Park*



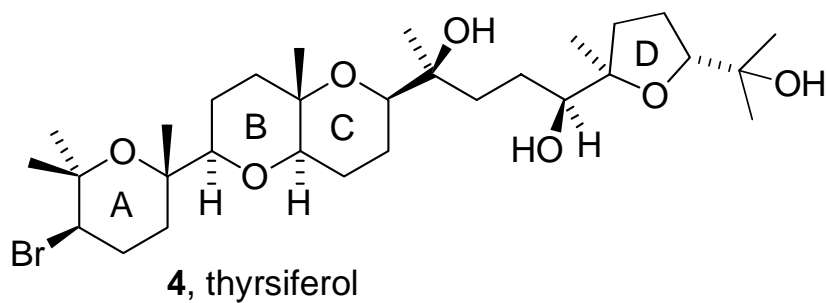


Green it up!

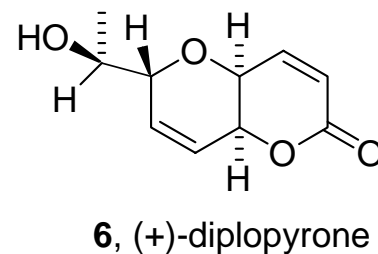
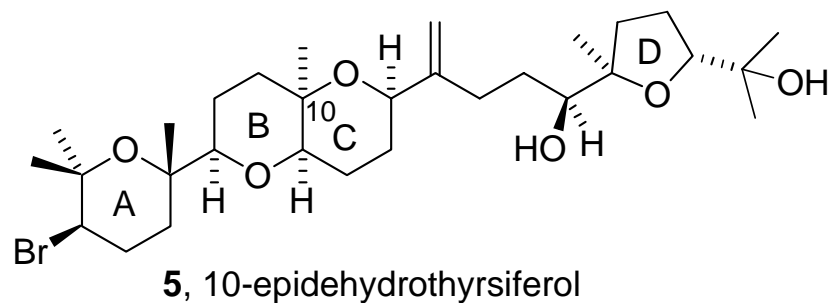


^a 3 mol % of the amine and 97 mol % of styrene affords a copolymer containing 12.1 mol % of the triarylamine.

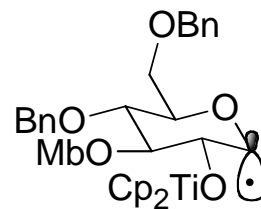
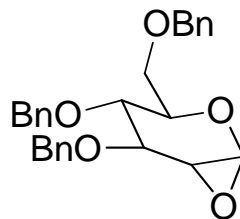
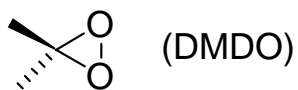
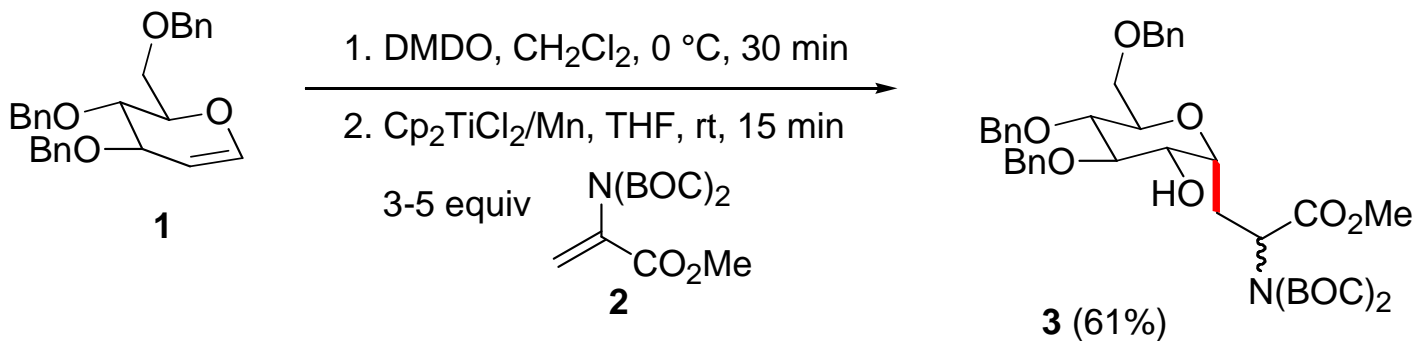
Total synthesis



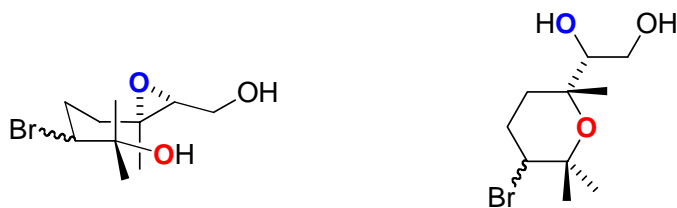
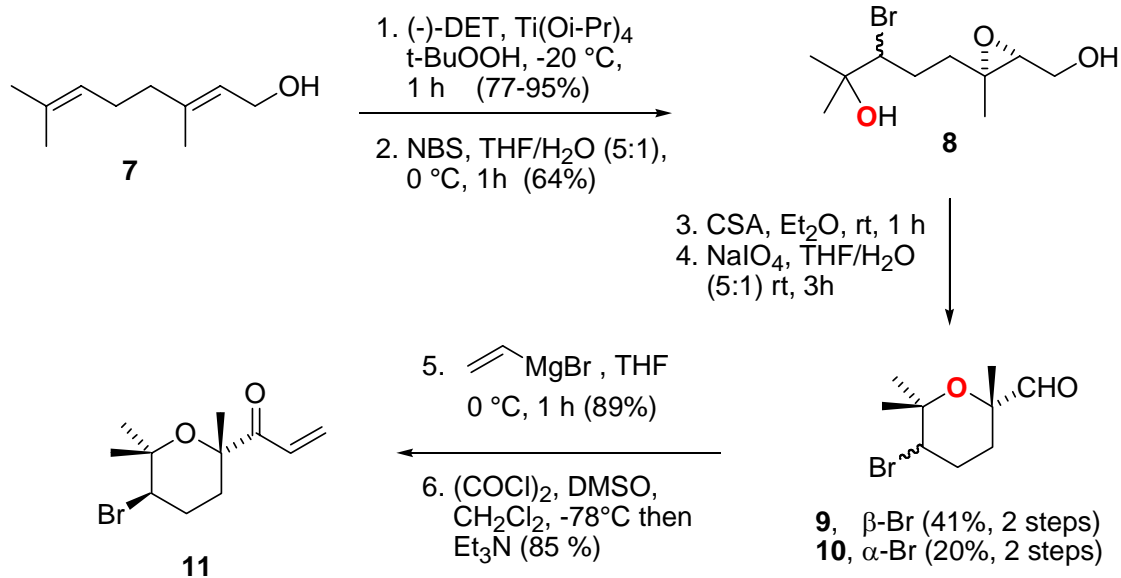
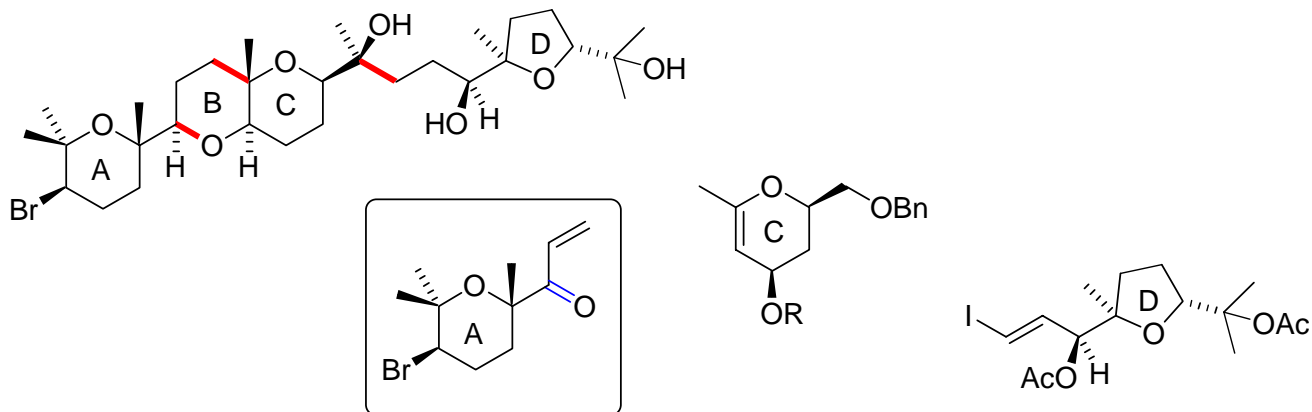
Gisele Nishiguchi
Jack Graham

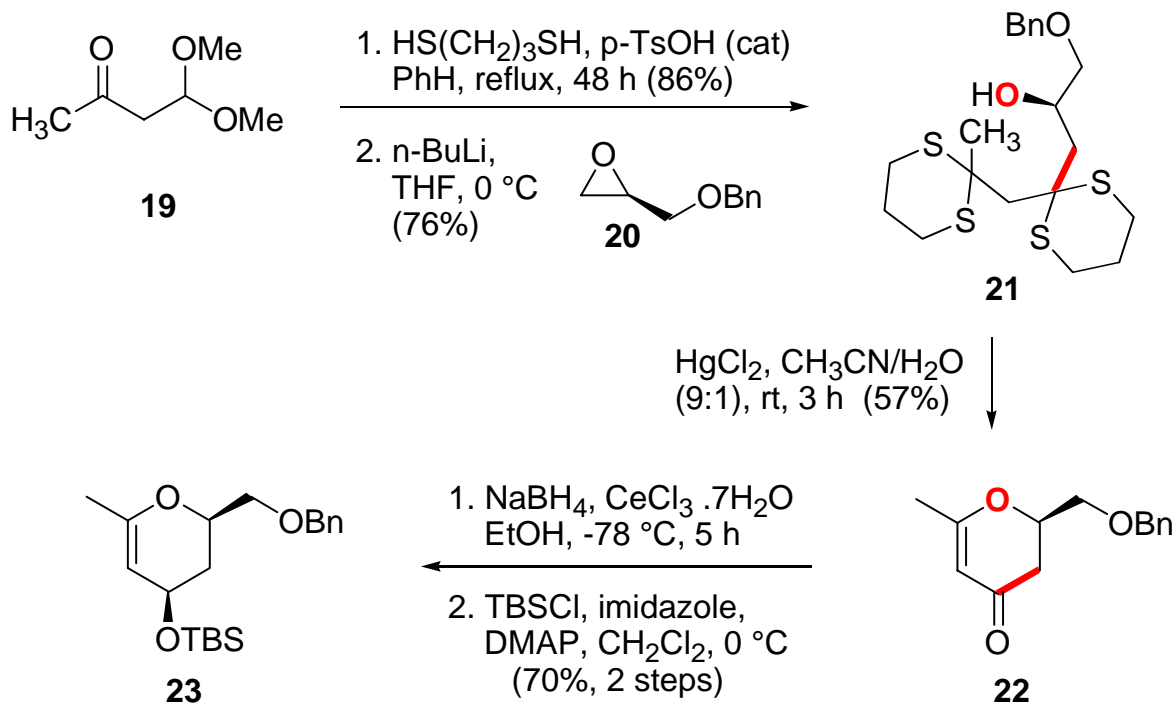
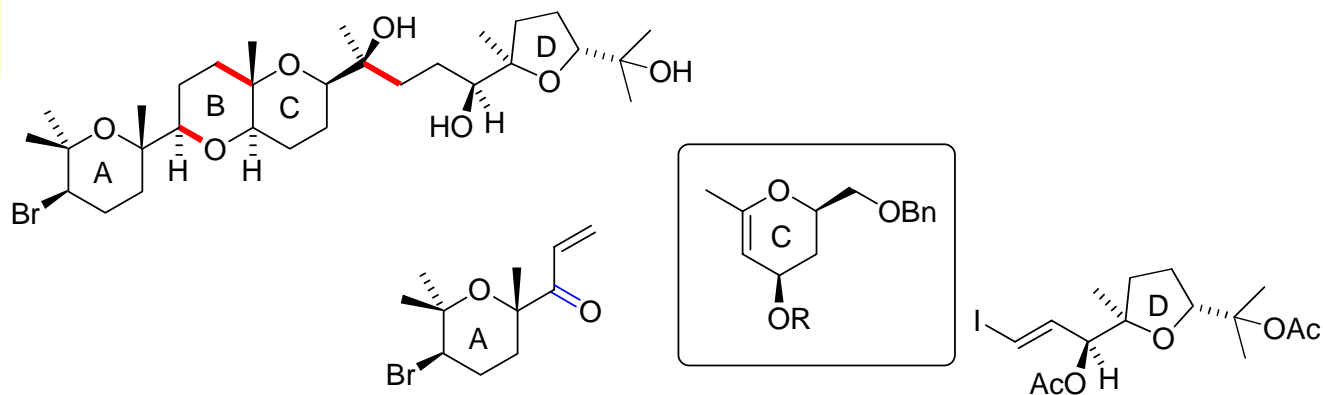


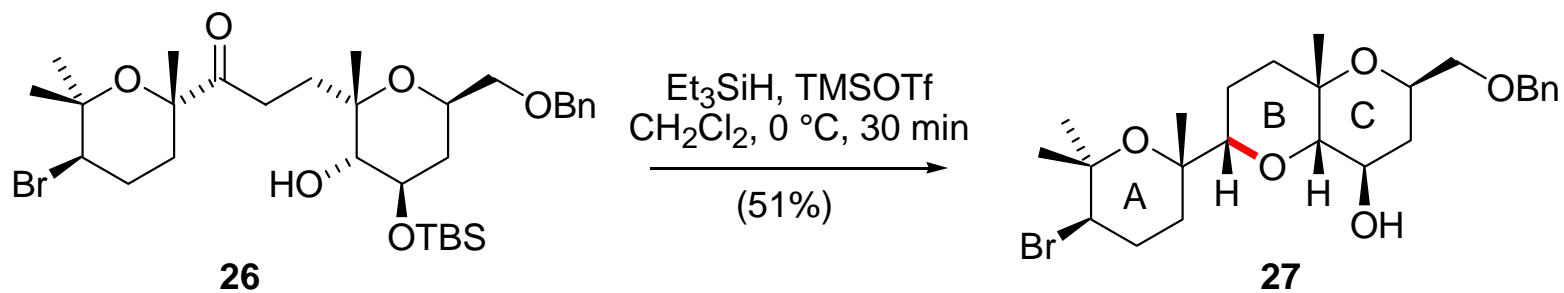
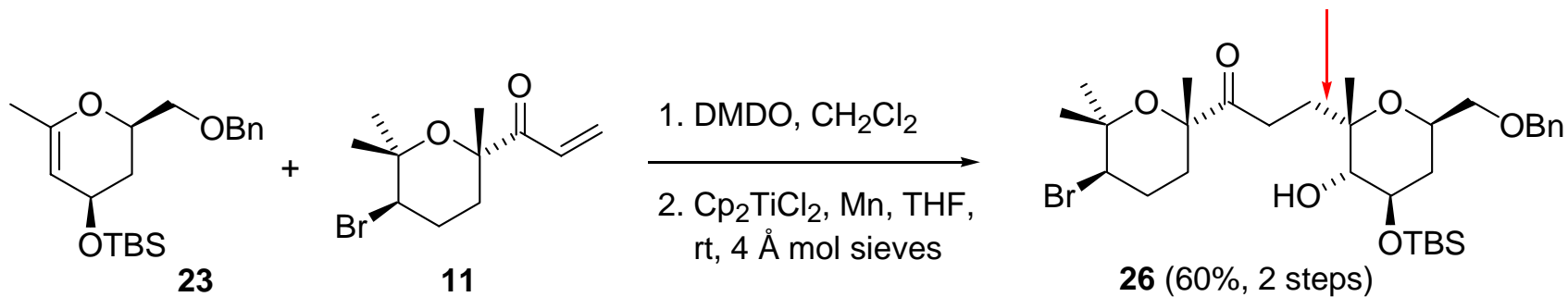
Gisele Nishiguchi
Adam Britto

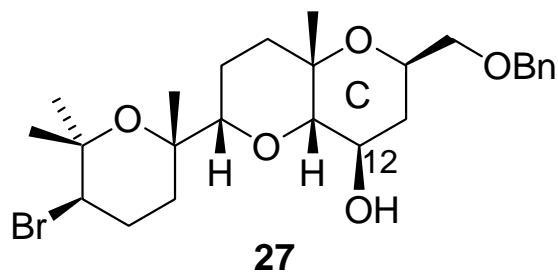
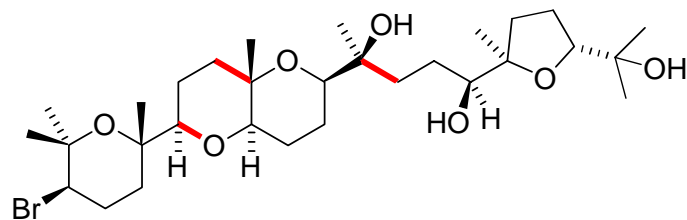


Jon Parrish



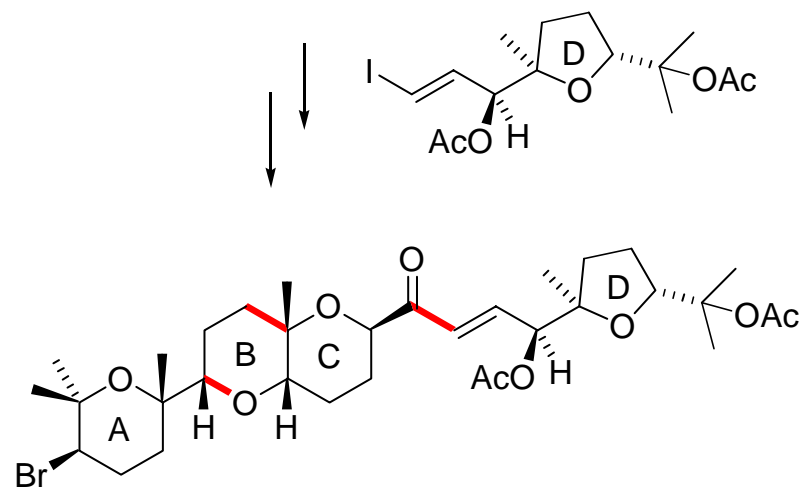
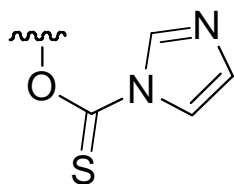
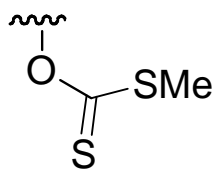
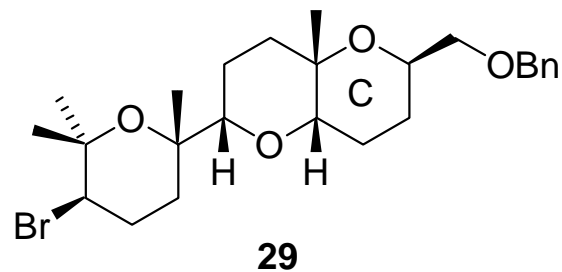




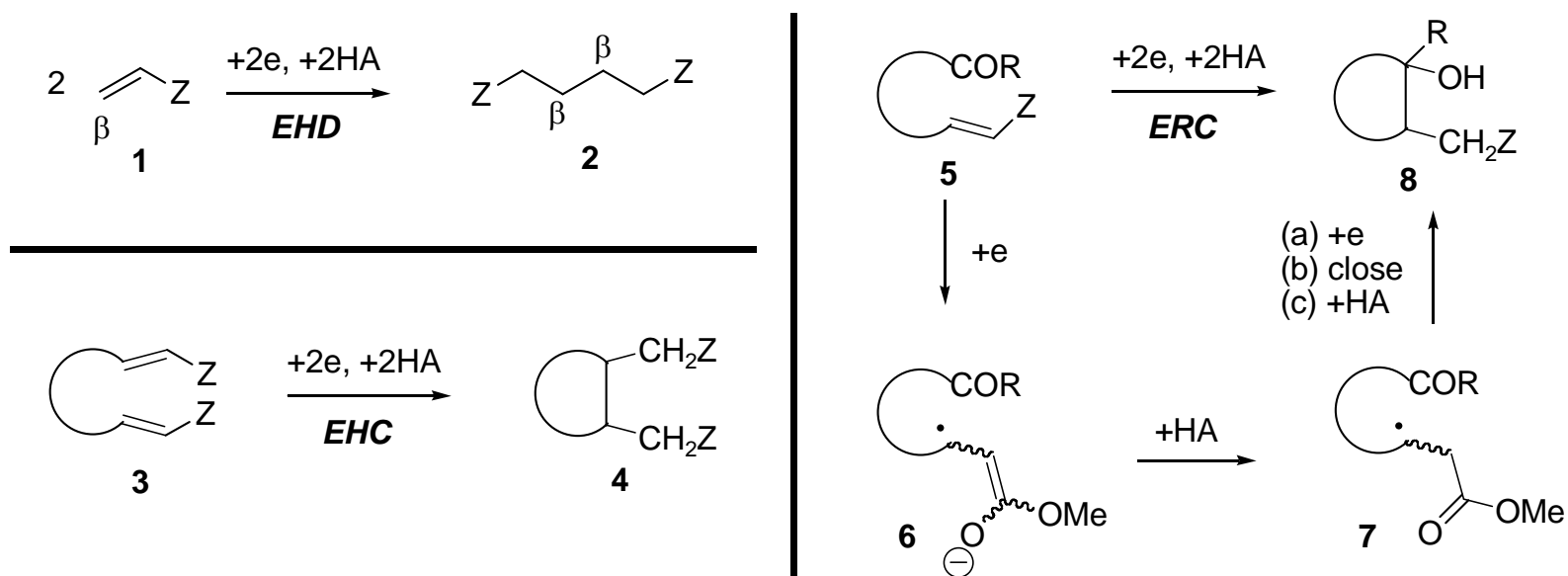


1. NaH, CS₂, MeI,
THF, rt, 2 h (97%)

2. n-Bu₃P.BH₃, AIBN,
dioxane, reflux, 4 h
(69%)



Electrochemistry - catalysis

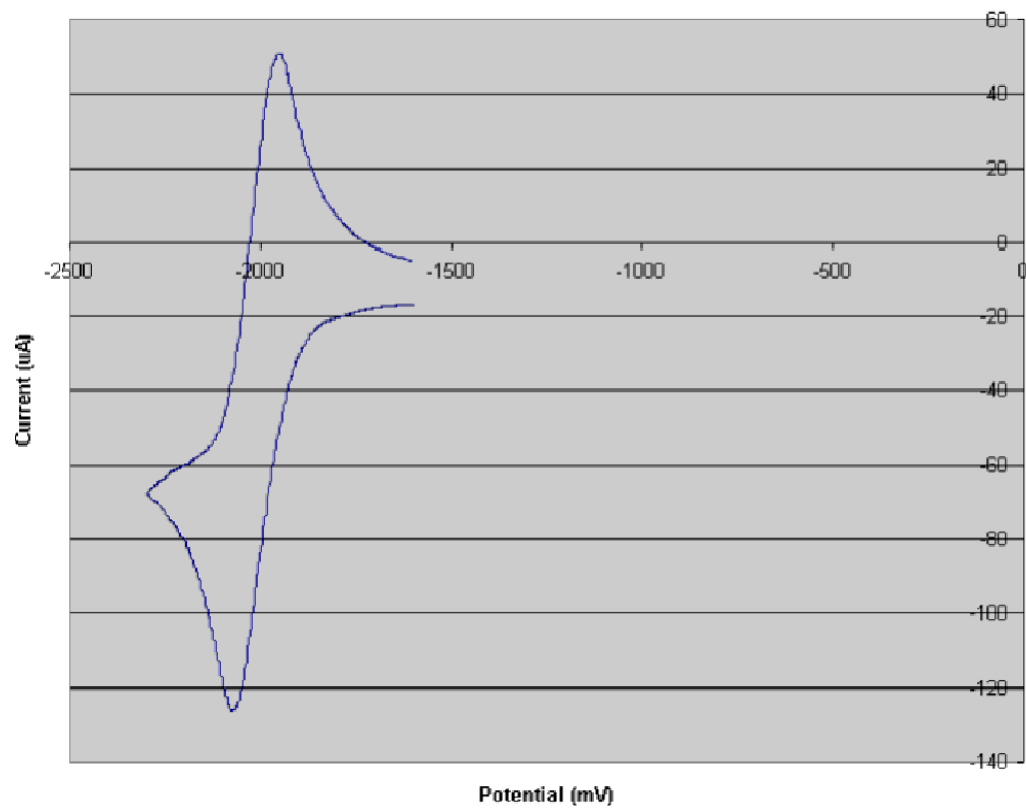


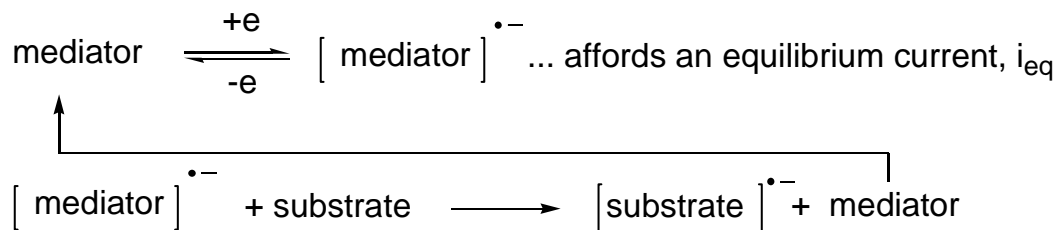
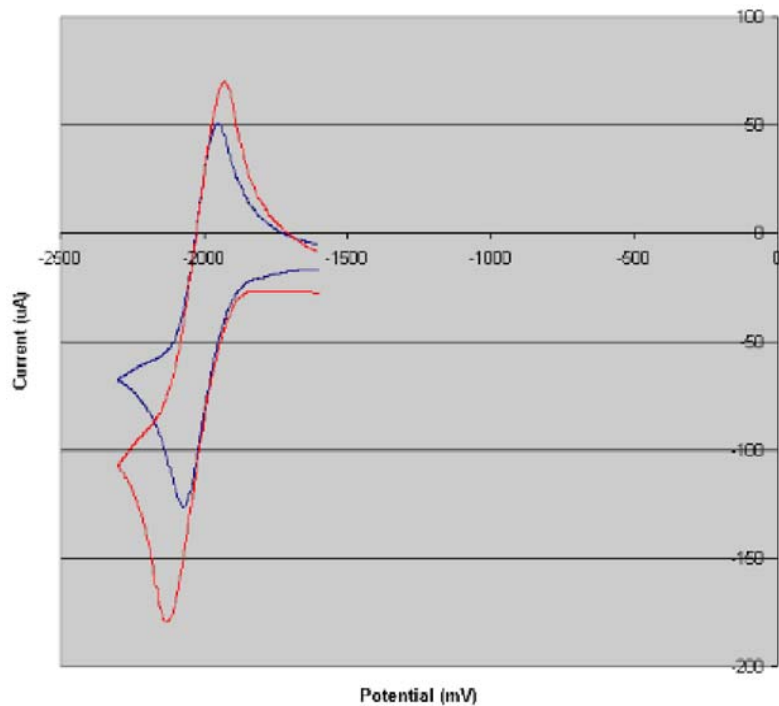
James Miranda & Carolyn Wade



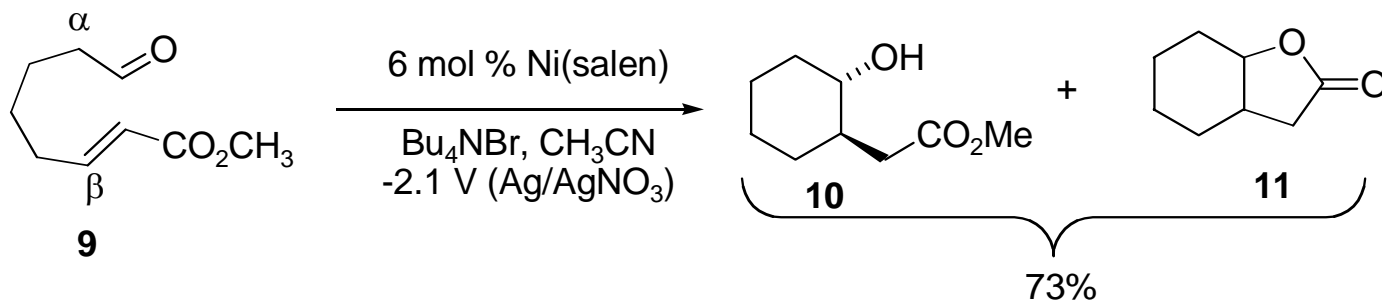
12, R = H

13, R = CH₃

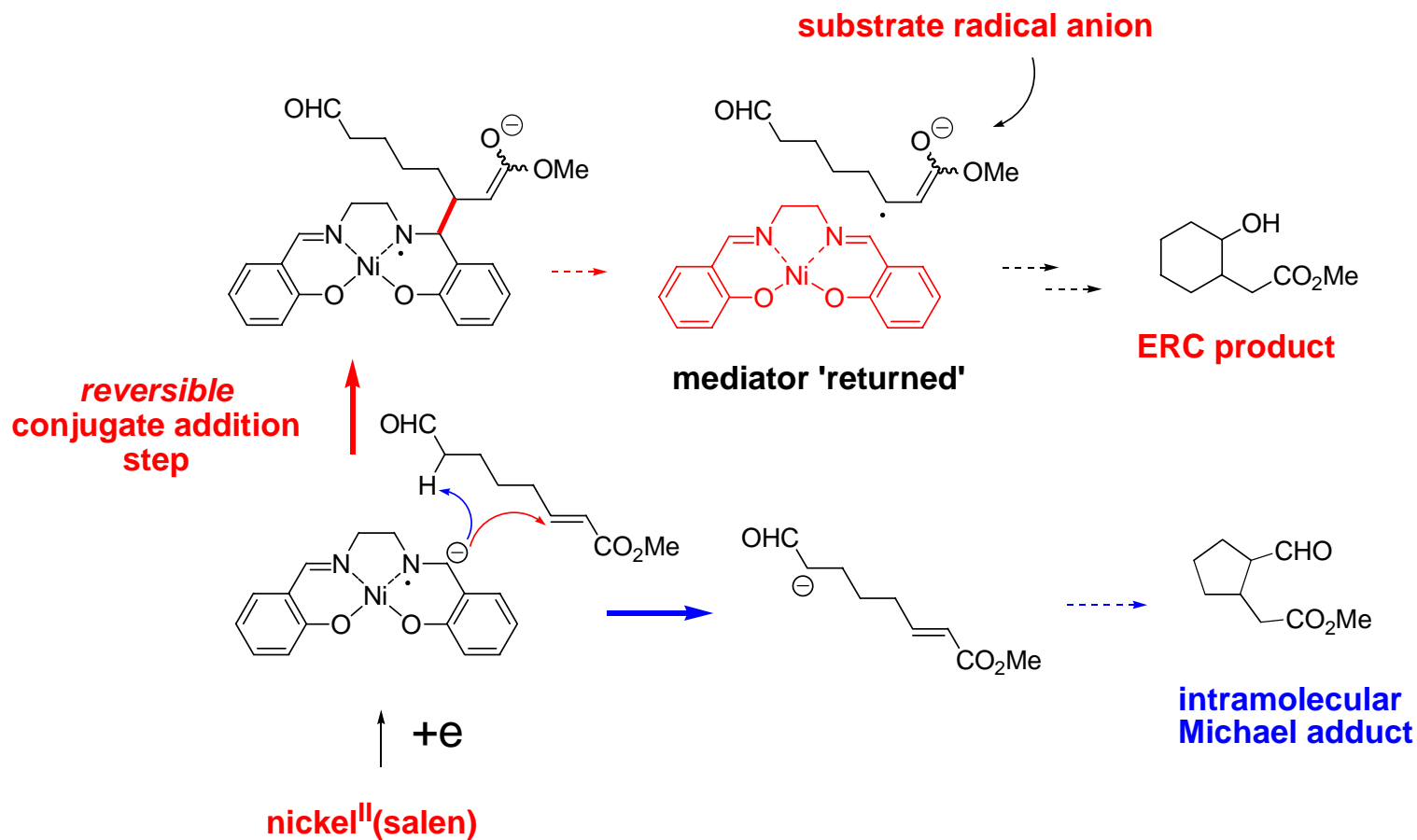




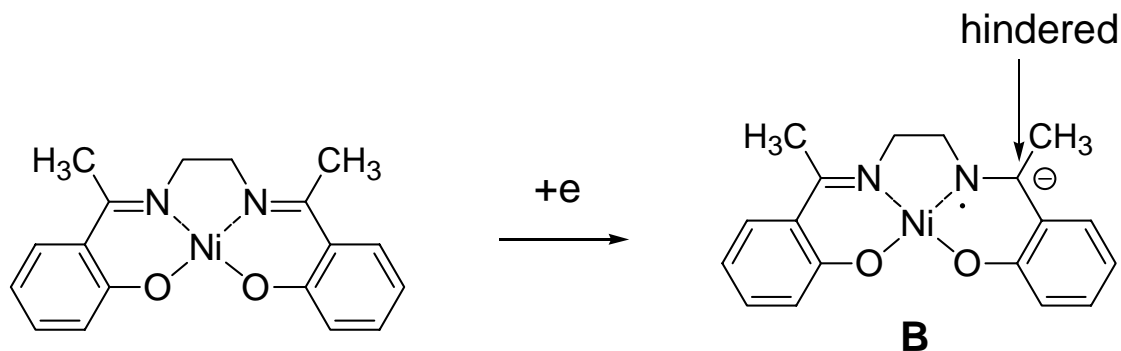
The amount of mediator = equilibrium amount + that generated in the 2nd step. Therefore, current observed = that from the re-generated mediator + that from the initial equilibrium.



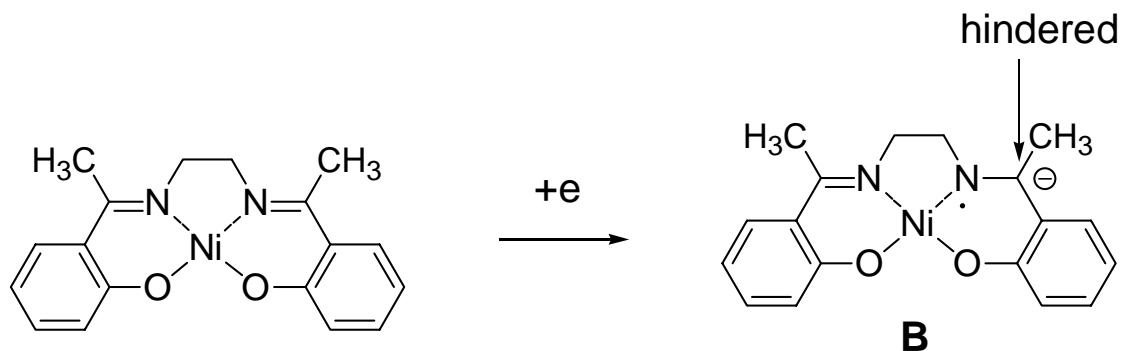
Inner, not outer sphere electron transfer



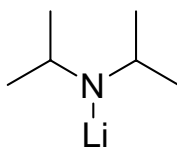
With the modified ligand ...



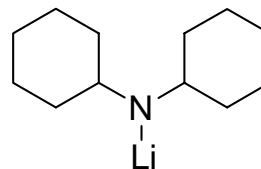
With the modified ligand ...



compare with ...

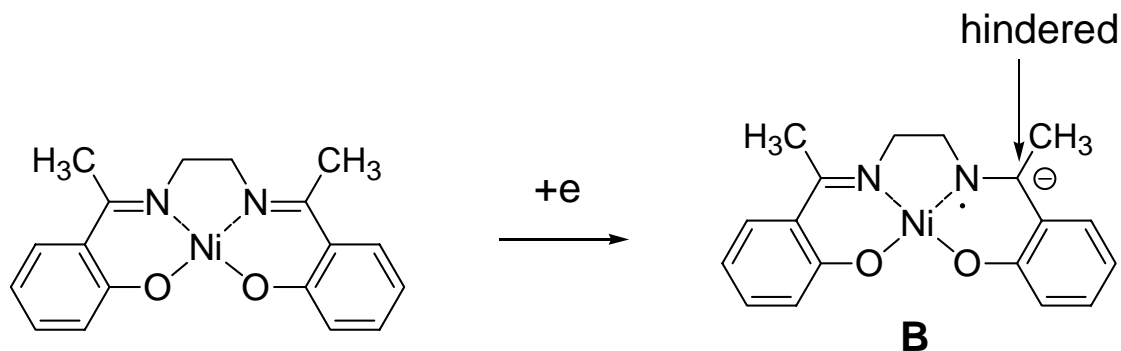


LDA

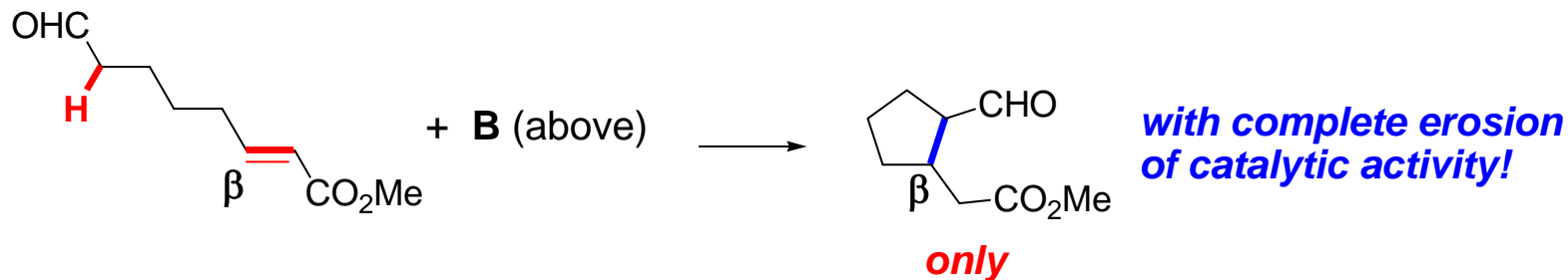


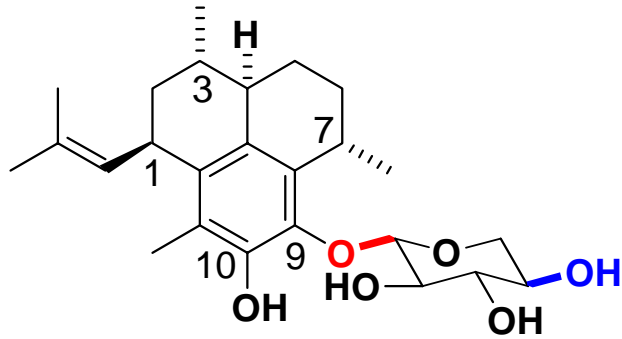
less nucleophilic
than LDA - maintains
base strength

With the modified ligand ...



So too, is **B** less (much less!) nucleophilic - it serves only as a base !

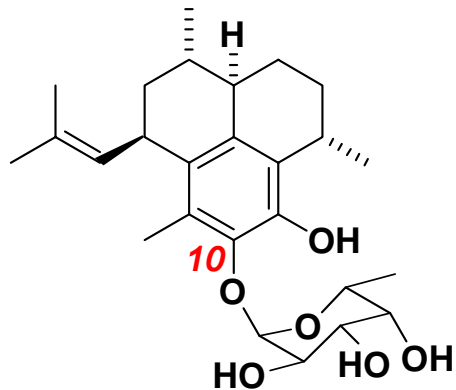




pseudopterosin A
(sugar equatorial)

Anti-inflammatory:
Active topically

Effective in treating
lymphomas, not solid
tumors.



**XV; sugar at C-10
& axial**

Anti-inflammatory &
analgesic properties:
... active **systemically**,
but *1/5 as* active
topically!



Research group members - as of 3/9/05

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Mark Martello
Adam Britto
Jack Graham
Michael Buenostro
Briana Lee

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James Miranda
Jinnie Myung
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UC Cancer Research
Coordinating Committee