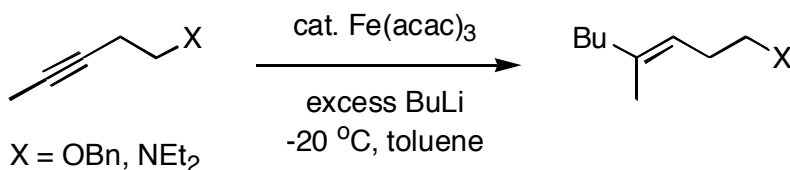


Some Iron-Catalyzed Reactions

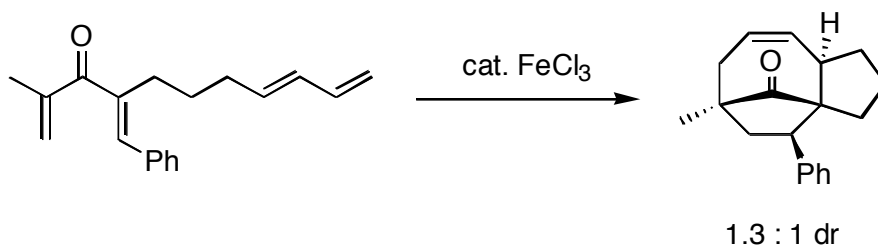
1. In 2001, Hosomi and coworkers demonstrated the effective carbometalation of alkynes with *n*-butyllithium to the corresponding *E*-olefins.



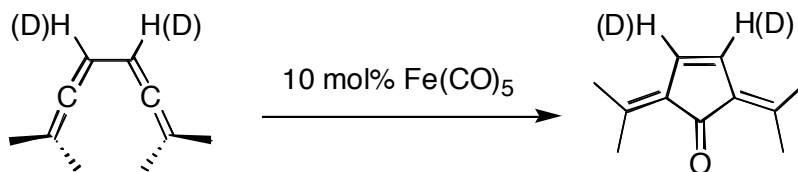
The reaction, however, did not proceed with the simple alkyne, 6-dodecyne. Propose a mechanism that accounts for the observed products. Ignore the oxidation state of the iron species as the active catalyst is unknown and believed to be an iron-ate complex.

2. Iron can be used to catalyze ring-forming reactions.

- a) Push the arrows for the following sweet, sweet transformation.

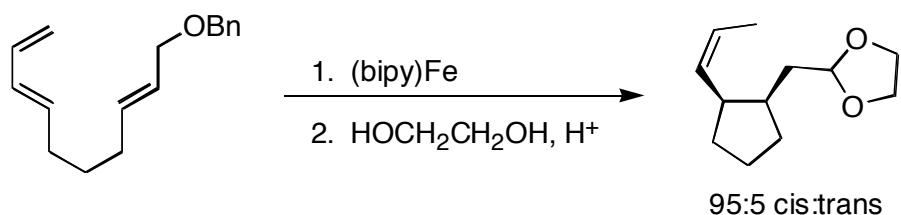
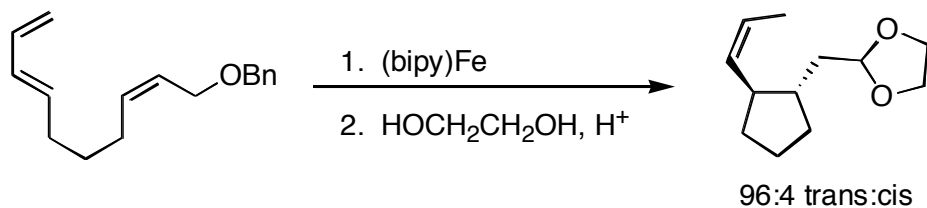


- b) Sigman and Eaton did some nice work elucidating the mechanism of the following reaction:

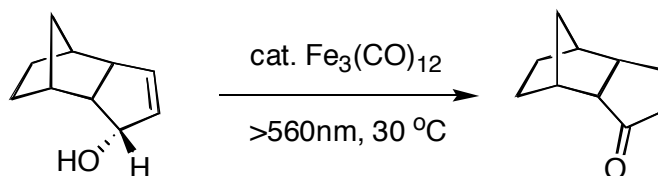
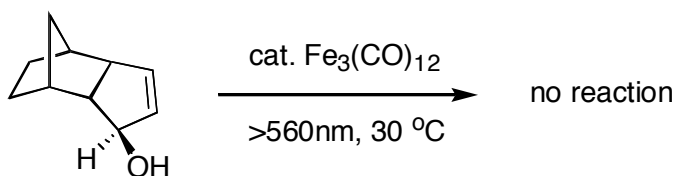


From their kinetic studies, it was found that the reaction has a strong solvent dependence. The rates in various solvents: $\text{CH}_2\text{Cl}_2 > \text{C}_6\text{H}_6 > \text{THF} \gg \text{CH}_3\text{CN}$ (essentially no reaction). Experiments also showed no apparent secondary isotope effect. Account for these observations in the catalytic cycle.

3. Iron can also catalyze ene type carbocyclizations. What is going on here? Account for the observed stereoselection.

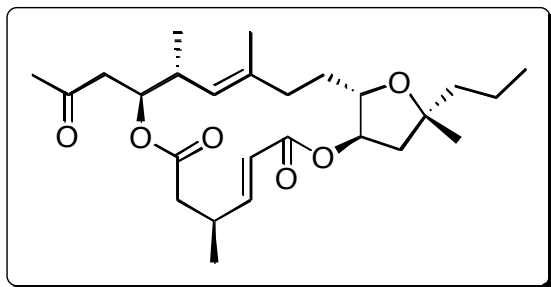


4. Iron carbonyl complexes are able to catalyze double-bond isomerizations. In these reactions, an unsaturated [Fe(CO)₃] species is believed to be the reactive intermediate.

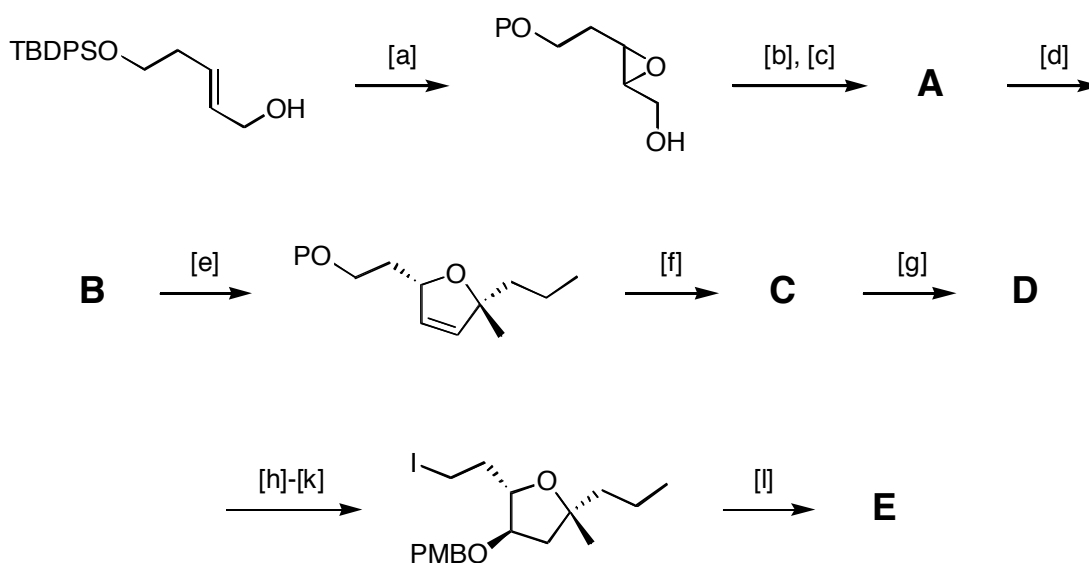


Why is there light? What does the observed reactivity tell us about the role [Fe] is playing in this transformation? What do the Woodward-Hoffman rules say about such a rearrangement?

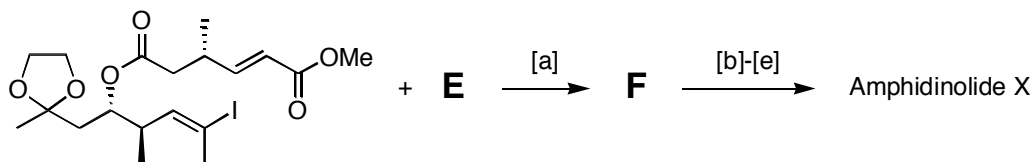
5. Amphidinolide X is made by a marine dinoflagellate, and as of 2004 also the Furstner laboratories. Complete the roadmap for the furanyl half of the convergent synthesis, and then the endgame.



Also, what is the selectivity of the epoxidation in step [a]?



[a] $\text{Ti}(\text{O}i\text{Pr})_4$ cat., L-(+)-DET, $t\text{BuOOH}$, MS 4A, CH_2Cl_2 ; [b] (i) oxalyl chloride, DMSO, TEA, CH_2Cl_2 ; (ii) $(\text{MeO})\text{P}(\text{O})\text{C}(\text{N}_2)\text{COMe}$, K_2CO_3 , MeOH; [c] LiHMDS, MeOTf, THF; [d] PrMgCl , $\text{Fe}(\text{acac})_3$ cat., toluene; [e] AgNO_3 , CaCO_3 , acetone; [f] NBS, DMF/ H_2O ; [g] AIBN, $(\text{TMS})_3\text{SiH}$, toluene; [h] NaHCO_3 , MeOH; [i] $\text{PMBOC}(\text{=NH})\text{CCl}_3$, PPTS, $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{12}$; [j] TBAF, THF; [k] I_2 , PPh_3 , imidazole, $\text{MeCN}/\text{Et}_2\text{O}$; [l] $t\text{BuLi}$, $\text{Et}_2\text{O}/\text{THF}$; then 9-MeO-9-BBN.



[a] $(\text{dppf})\text{PdCl}_2$, Ph_3As , K_3PO_4 , DMF; [b] LiI , pyridine; [c] AcOH; [d] DDQ, CH_2Cl_2 pH 7; [e] 2,4,6-trichlorobenzoyl chloride, TEA, THF; then DMAP, toluene.