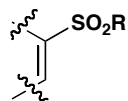
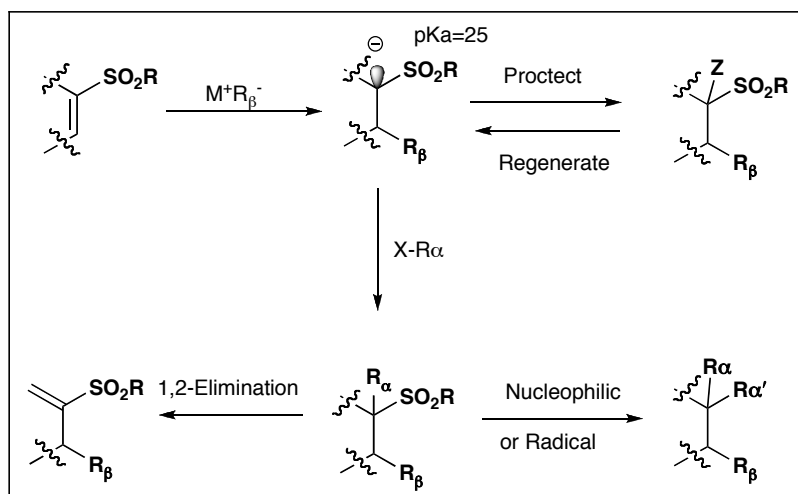


Vinyl Sulfone:

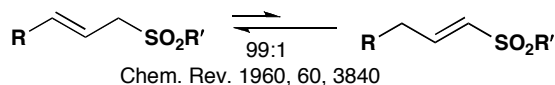


1. Good Micheal acceptor
2. 2π partner in cycloaddition, ethylene, acetylene and ketene equivalent
3. nicely crystalline, ease of handling
4. ready removal (desulfonation)
5. inhibitor of cysteine protease

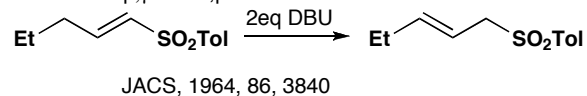


Stability of Vinyl Sulfone:

Equilibrium between β,γ and α,β unsaturated sulfones,



Interconversion between β,γ and α,β unsaturated sulfones

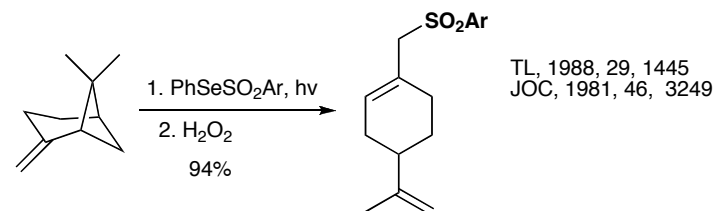
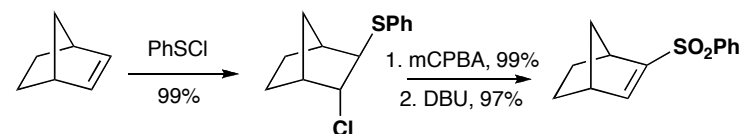
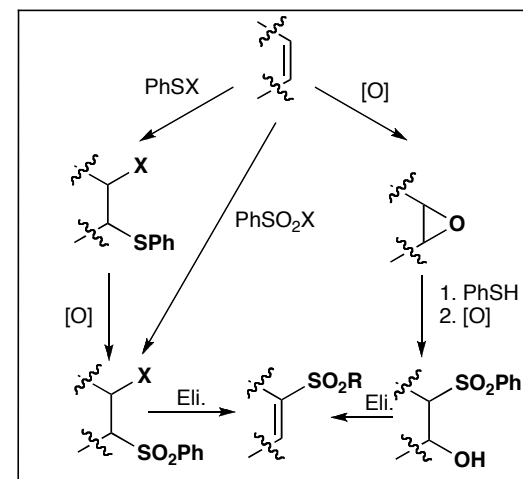


Preparation of Vinyl Sulfone:

A. Addition-Elimination

- ionic
- radical

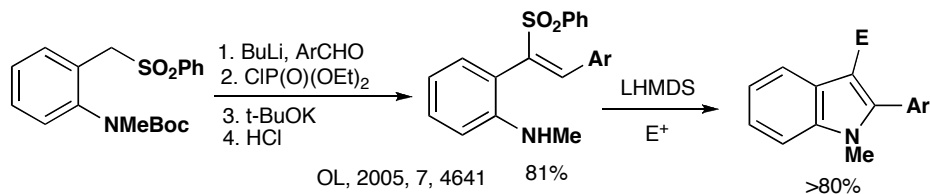
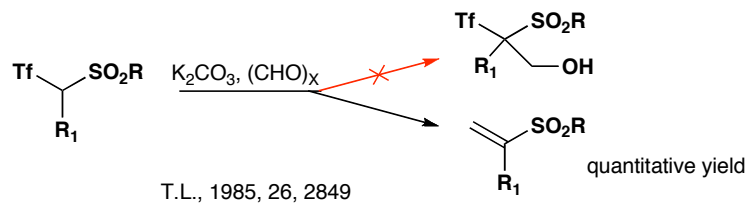
General Process:



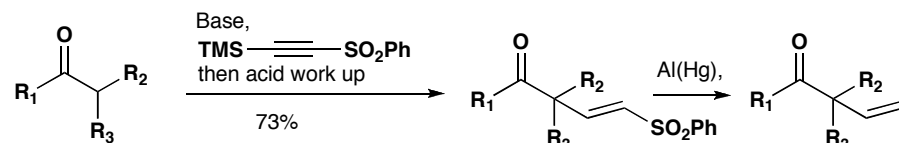
B. Olefination

- Aldol,
- Wittig,
- Peterson,
- HWE

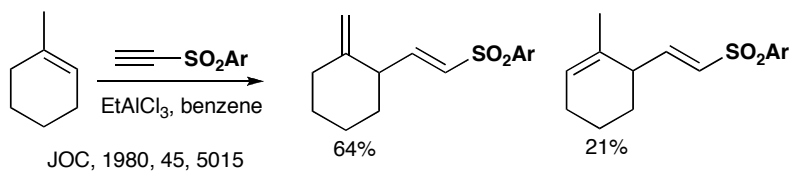
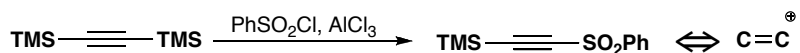
Addition of sulfonyl-stabilized carbanion to carbonyl compound



C. Manipulation of acetylenic sulfone

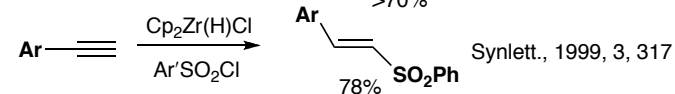
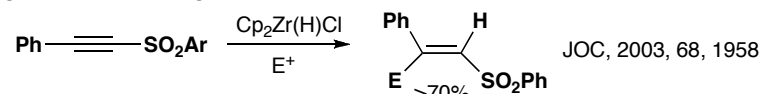


Phenyl trimethylsilyl ethynyl sulfone as vinyl cation sython, JOC, 1982, 47, 4713

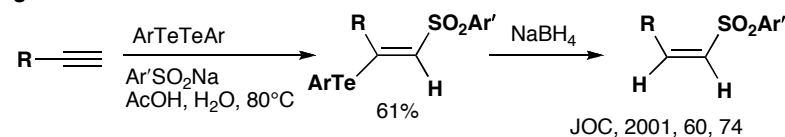


D. Organometallic Reagents

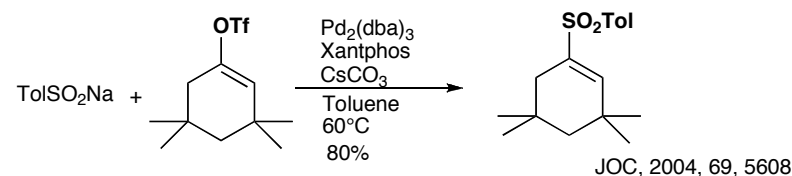
via organozirconium reagents



via organotellurides

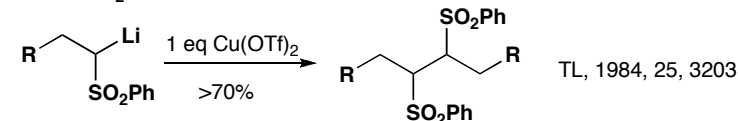
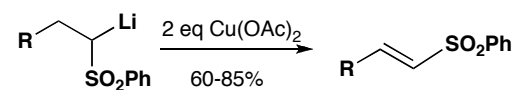


via palladium catalysis

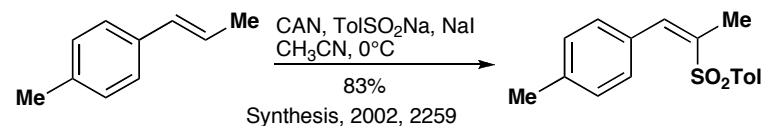


E. Miscellaneous

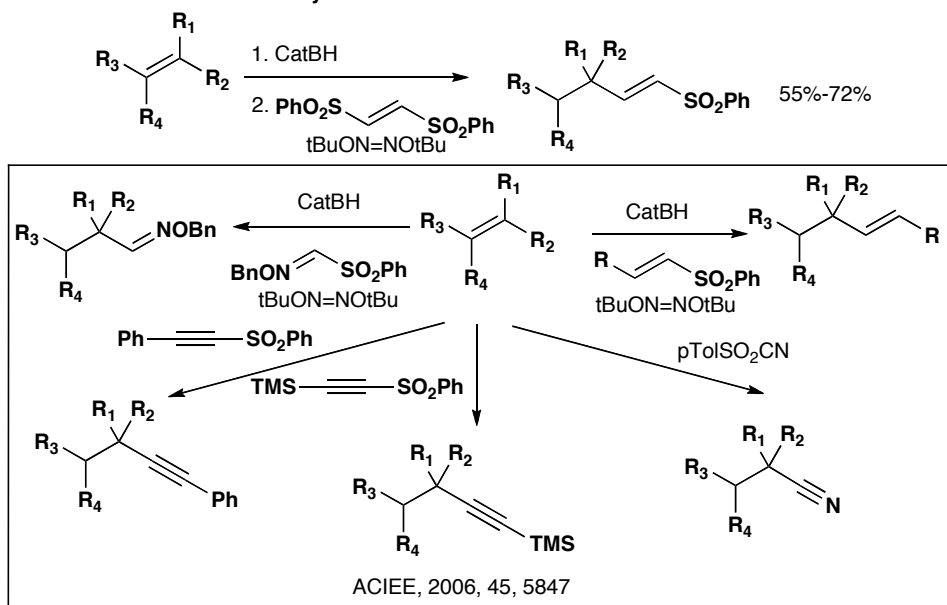
oxidize sulfone carbanion



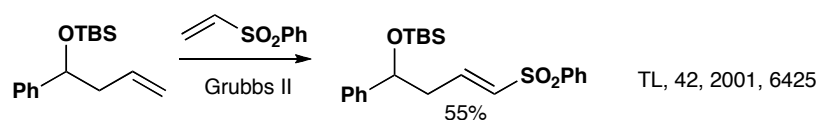
CAN Mediated Reaction



Radical-Mediated Alkenylation



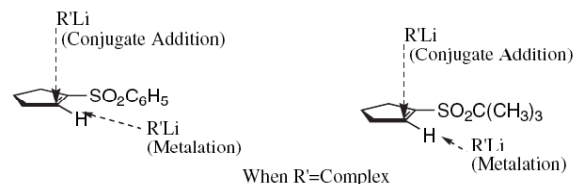
Olefin metathesis



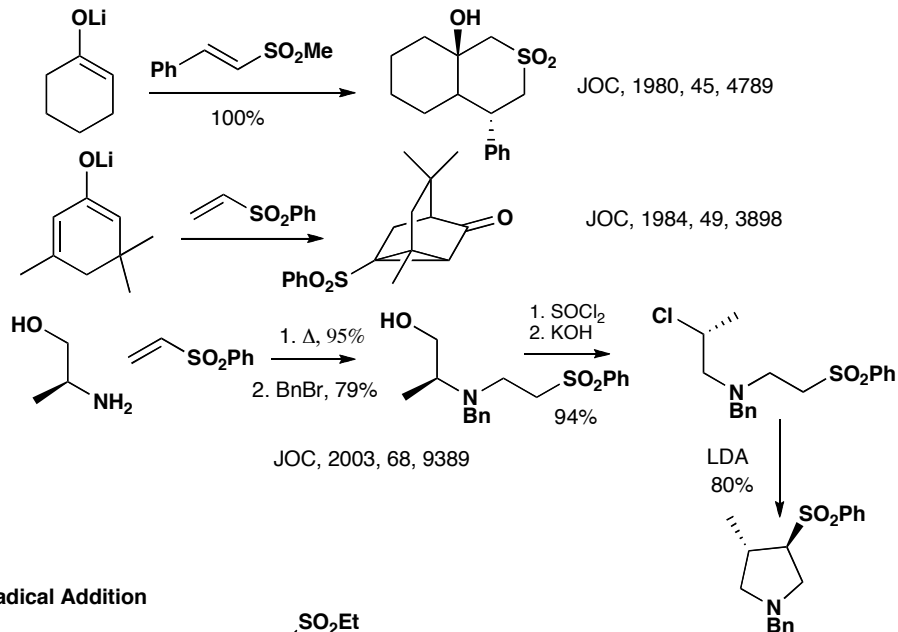
Reactions of Vinyl Sulfones

A. Michael Addition

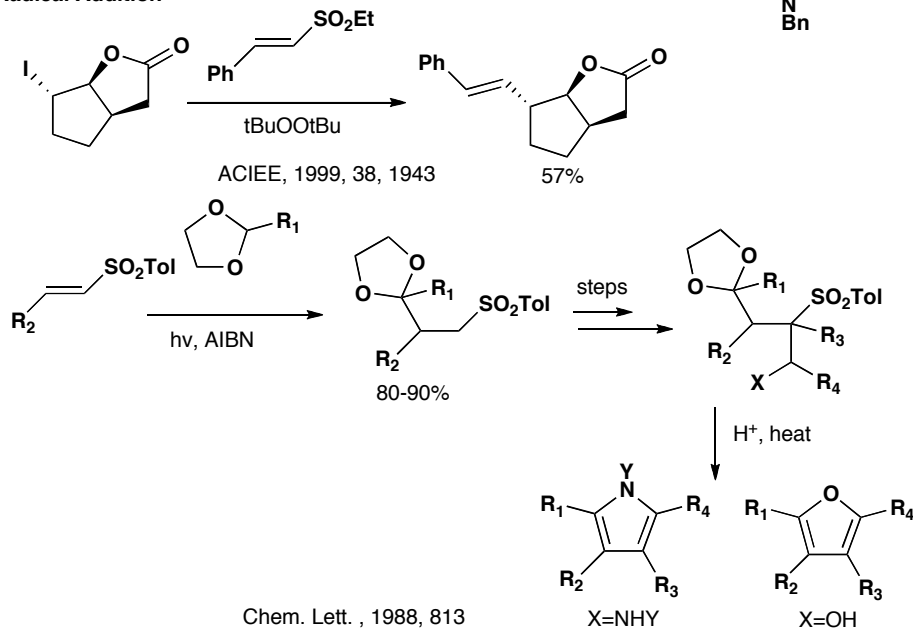
- Hard nucleophiles: competing reaction between metalation and conjugate addition



- Soft nucleophiles: sp^3 functionalized nucleophiles, the trans product in excess sp^2 functionalized anion, the cis product predominated
potassium anions were more reactive



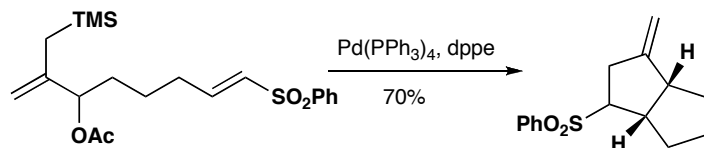
Radical Addition



Vinyl Sulfone in Synthesis

B. Cycloaddition

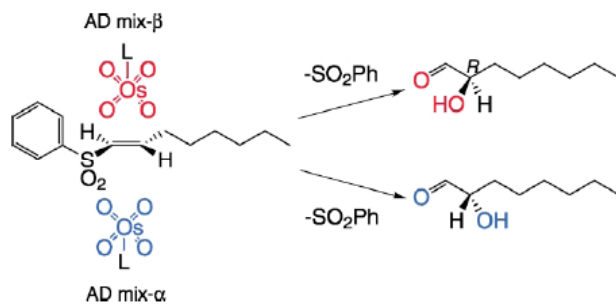
- [2+2]
- [2+3]
- [2+4]



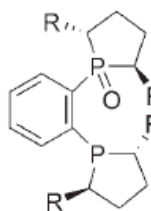
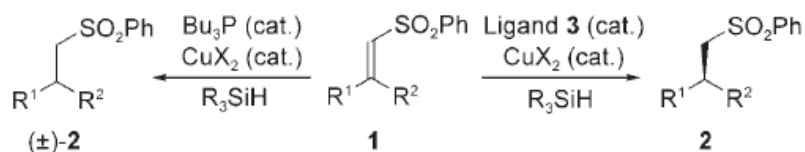
JACS, 1982, 104, 3733

C. Asymmetric Reactions

- Asymmetric Dihydroxylation, T, 2003, 59, 7973



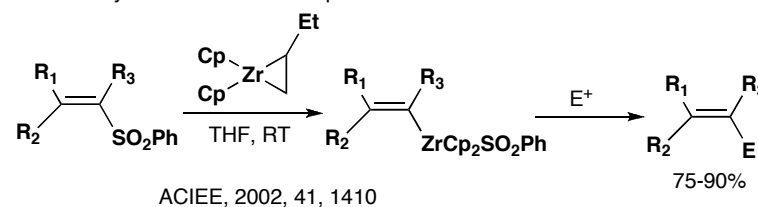
- Catalytic Enantioselective Reduction, ACIEE, 2007, 46, 5955



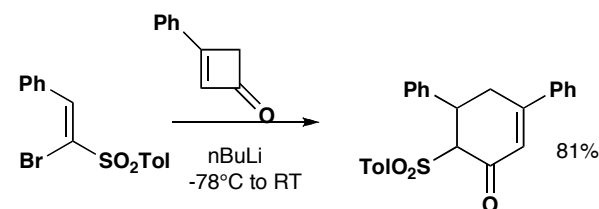
(*R,R*)-**3a**: R = Me (Me-DuPhos (O))
(*R,R*)-**3b**: R = Et (Et-DuPhos (O))

D. Metallation

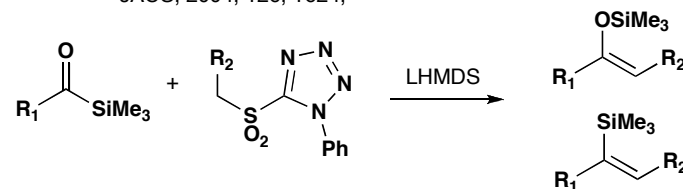
Form the vinyl transition metal complex



E. Miscellaneous



JACS, 2004, 126, 1624,

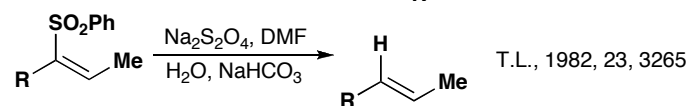
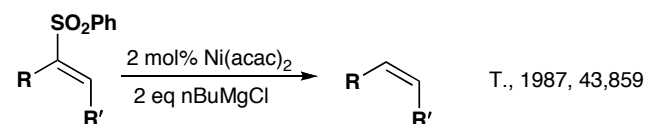


OL, 2003, 5, 2789

Desulfonation of Vinyl sulfone

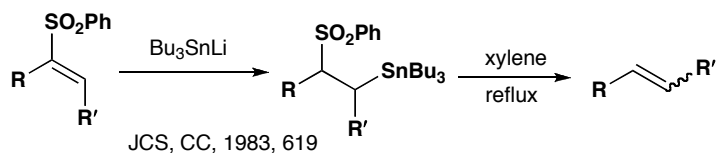
A. Reductive Desulfonation

General process: dissolving metal or metal amalgams, e.g. Al(Hg)

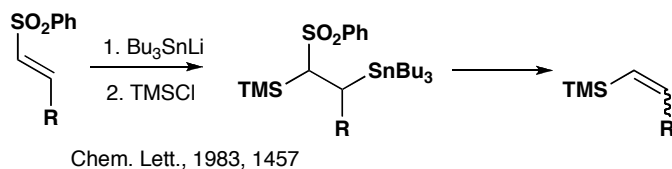


Vinyl Sulfone in Synthesis

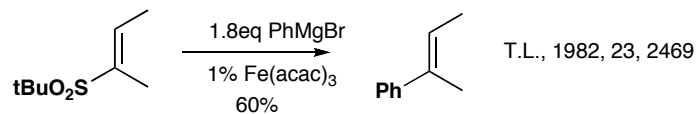
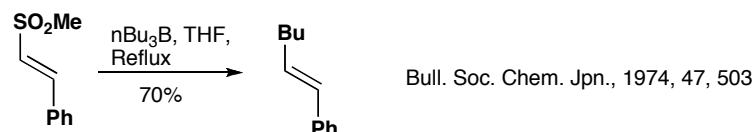
B. Tin-based Methods



Addition functionality into the unsaturated product

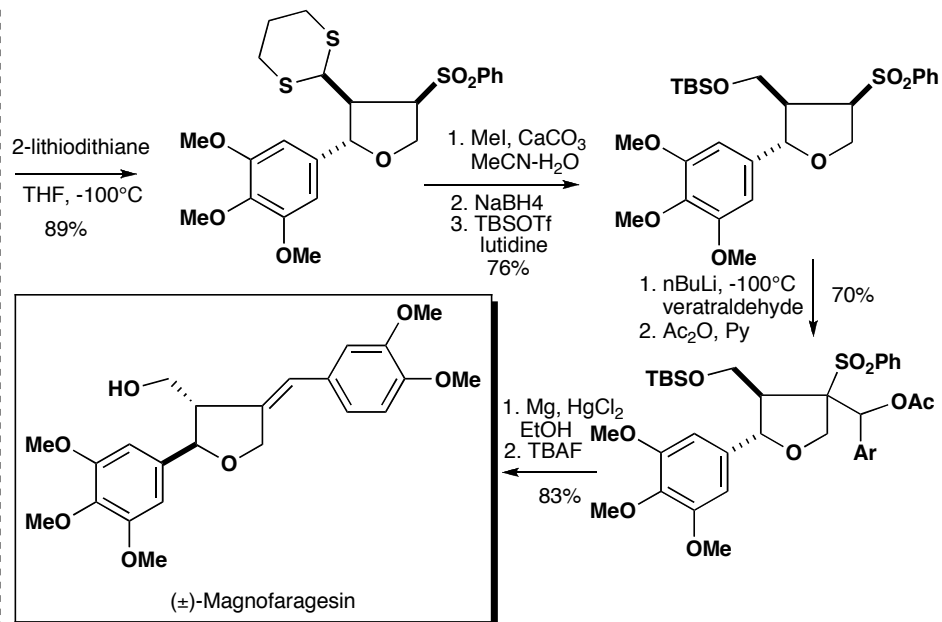
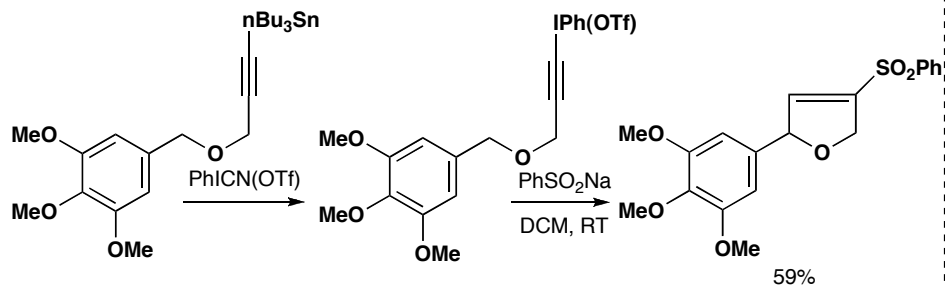


C. Alkylative Desulphonation

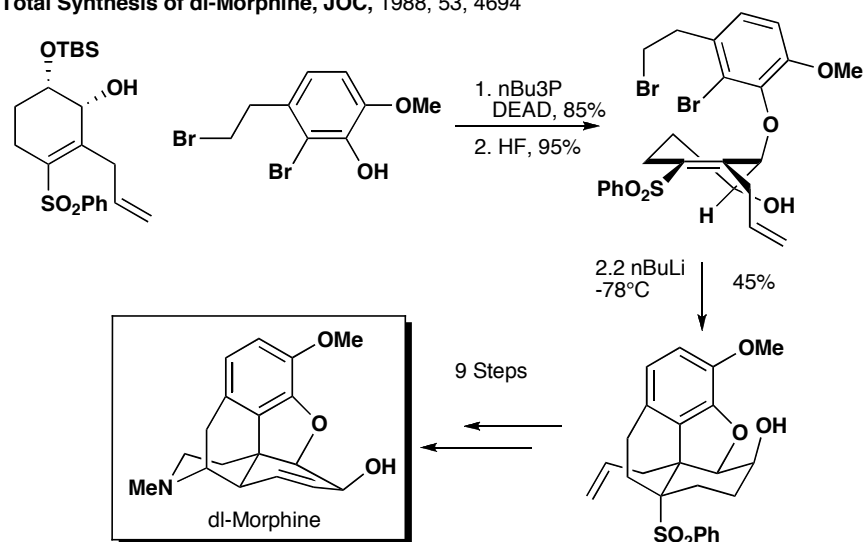


Applications in Total Synthesis

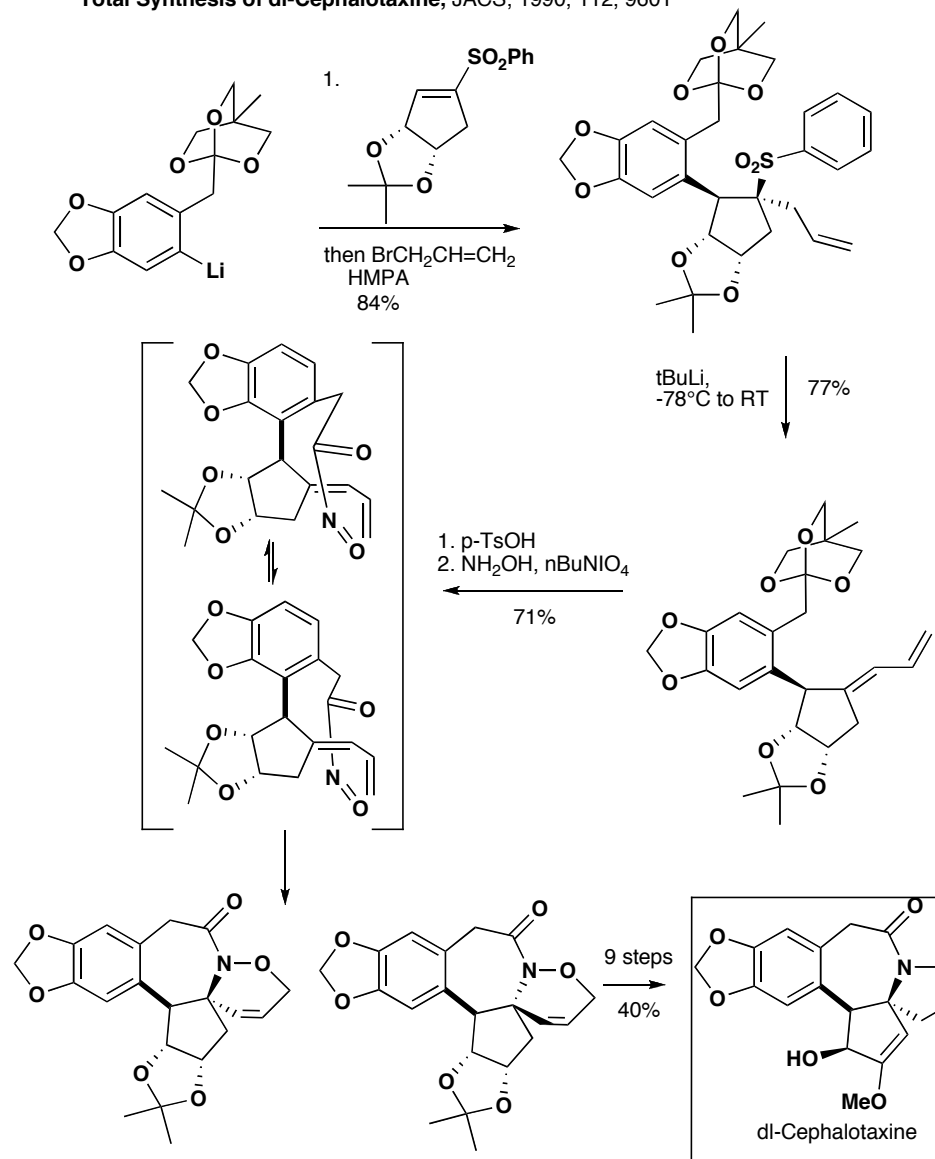
Total Synthesis of (±)-Magnofaragesin, OL, 2006, 8, 3659



Total Synthesis of di-Morphine, JOC, 1988, 53, 4694



Total Synthesis of dl-Cephalotaxine, JACS, 1990, 112, 9601



The synthesis of natural product is analogous to building a pyramid. One needs to forge a strong base before being in a position to complete the structure. The analog extends to further to the merit of the exercise- those pyramids which have been carefully crafted will provide further benefit to all who follow.

Phillips. L. Fuchs