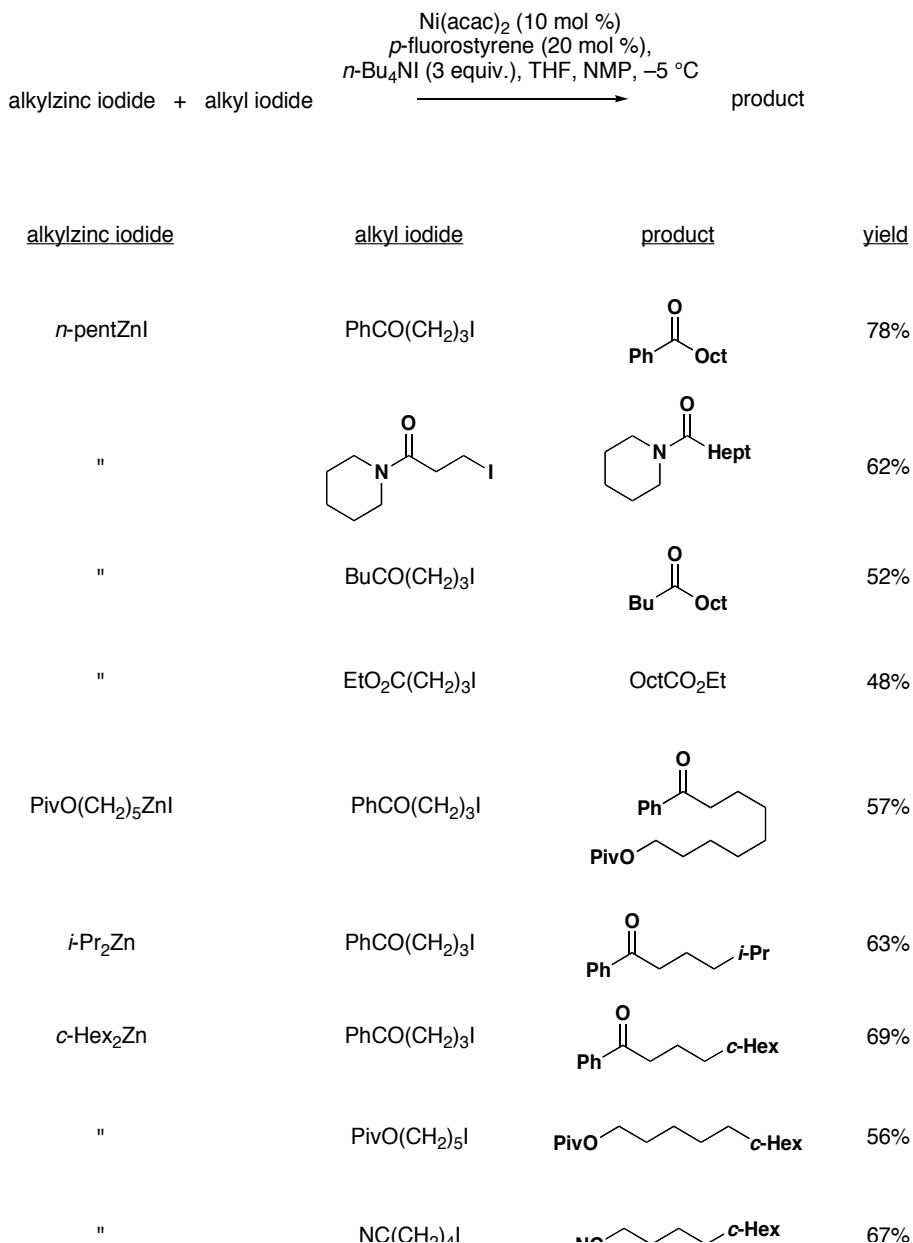
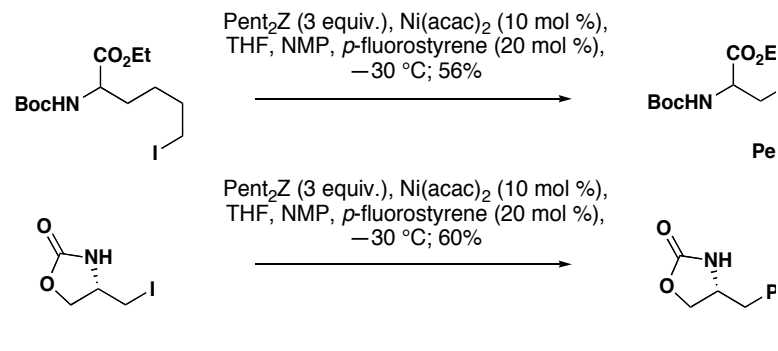


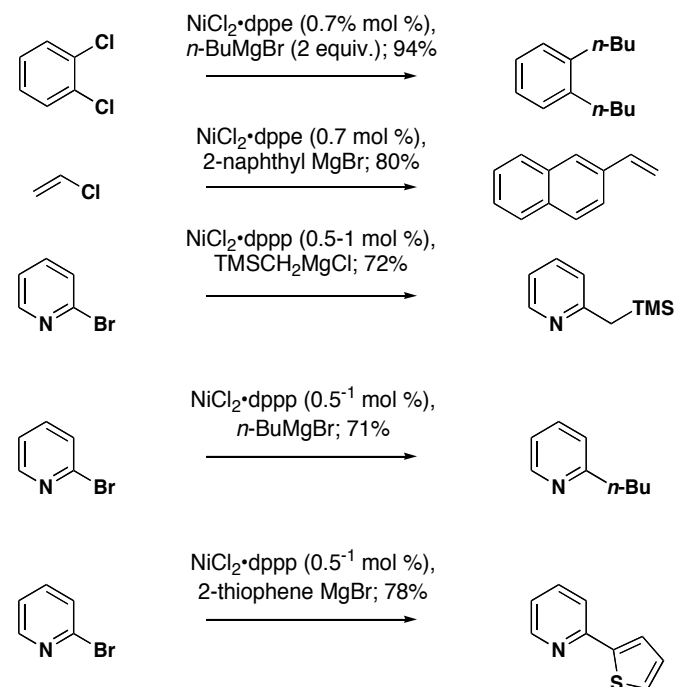
Methodology for the nickel(0)-catalyzed homologation of alkyl halides using organozinc reagents (Knochel, *JOC*, **2002**, 79.):

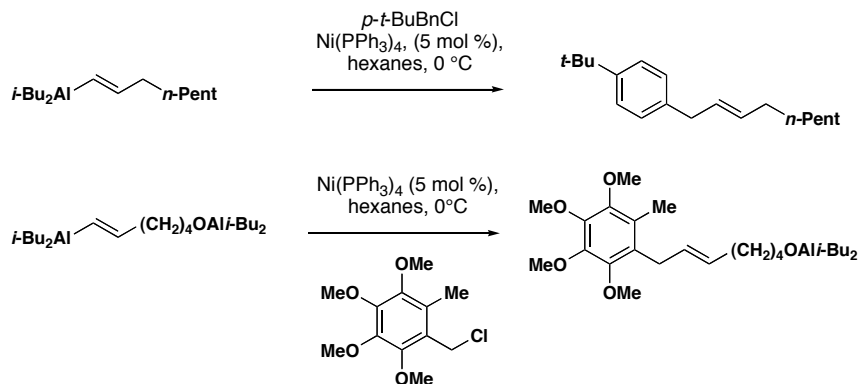
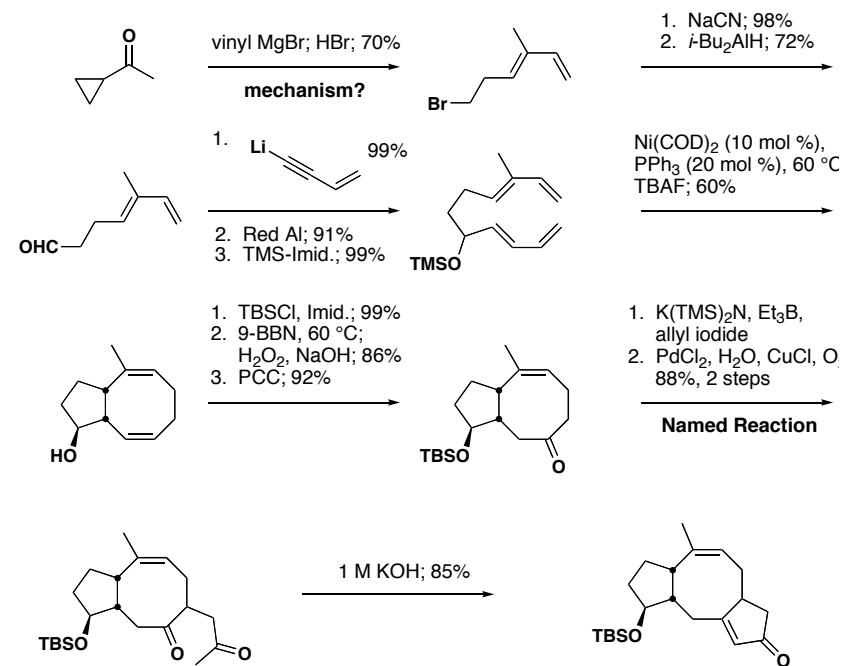
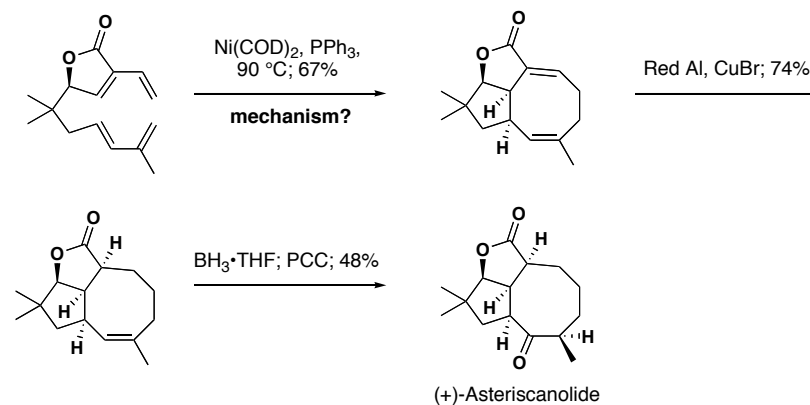
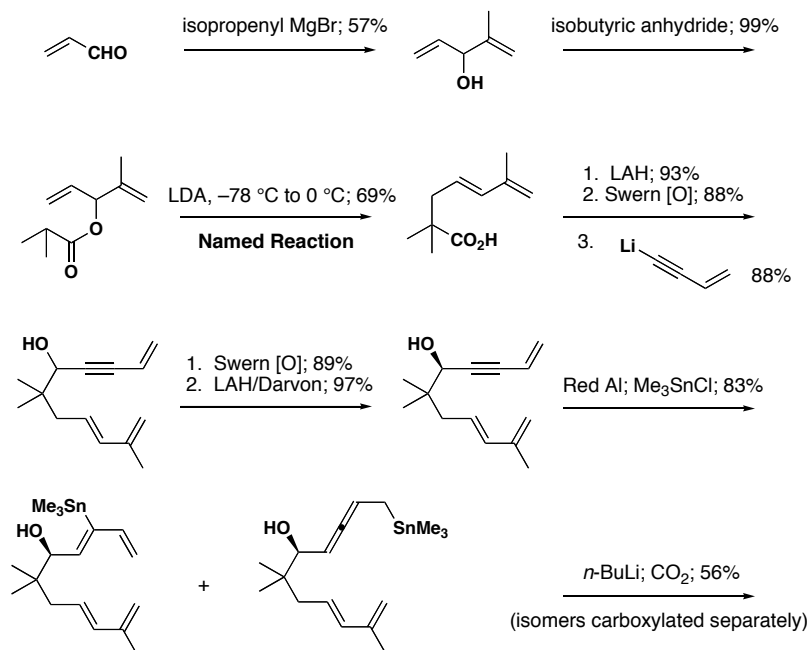


Compatibility with Bronsted acidic functionality:

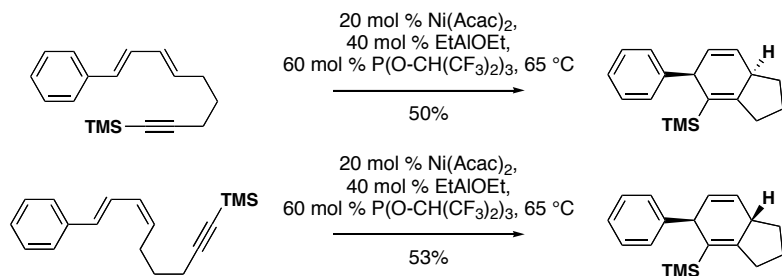


Kumada coupling (Nickel(0)-catalyzed  $\text{Csp}^2$  to  $\text{Csp}^2/\text{Csp}^3$  centers; Kumada, *Bull. Chem. Jpn.*, **1976**, 1958. Kumada, *Tetrahedron*, **1982**, 3347. Kumada, *Tetrahedron Lett.*, **19** Kumada, *Pure & Appl. Chem.*, **1980**, 669. Kumada, *J. Am. Chem. Soc.*, **1972**, 4374.):

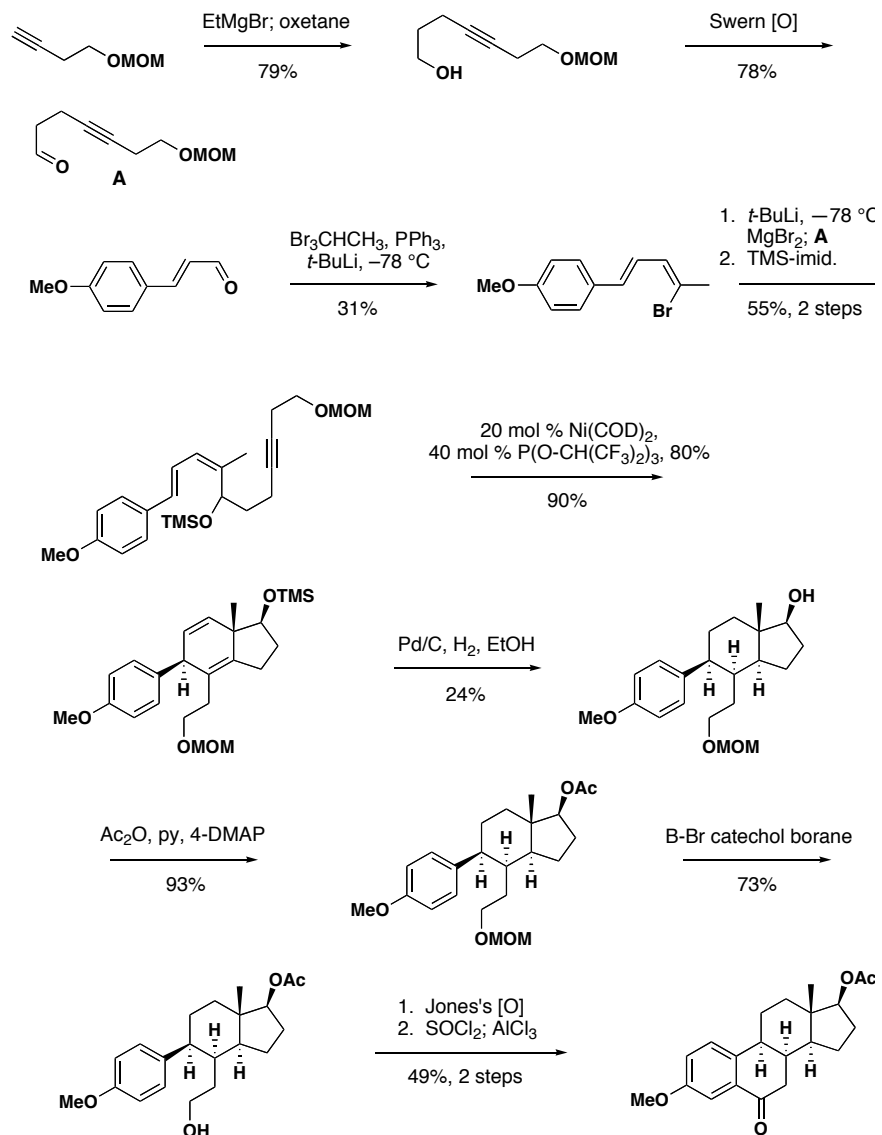


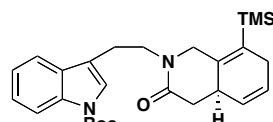
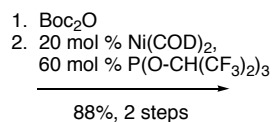
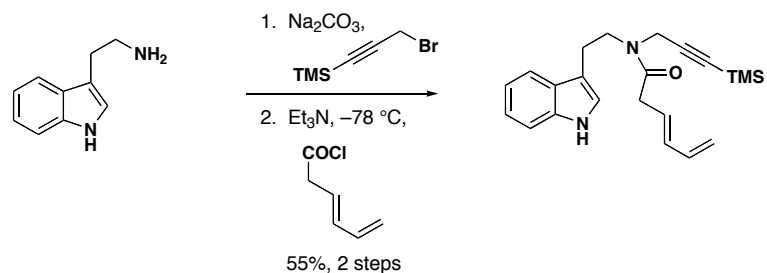
Kumada—Negishi coupling (Lipshutz, *Tetrahedron*, 1996, 7265.):Nickel(0)-catalyzed 4 + 4 cycloadditions and applications to the total syntheses of (+)-Asteriscanolide and Dicyclopenta[a,d]cyclooctene 5–8–5 Ring Systems (Wender, *J. Am. Chem. Soc.*, 1988, 5904. Wender, *J. Am. Chem. Soc.*, 1997, 4908.)

Nickel(0)-catalyzed 4 + 2 cycloadditions: room temperature Diels-Alder reactions that produce 1,4-cyclohexadienes (Wender, *J. Org. Chem.*, **1995**, 2962. Wender, *J. Org. Chem.*, **1996**, 824.)



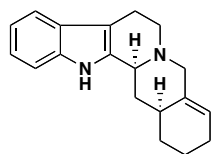
Mechanism:



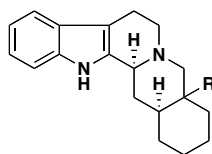


1.  $(\text{PPh}_3)_3\text{RhCl}$ ,  $\text{H}_2$ ; 93%  
2.  $\text{TsOH}$ ; 69%  
3.  $\text{POCl}_3$ , benzene, reflux;  
 $\text{NaBH}_4$ ,  $\text{MeOH}$ ; 86%

Named Reaction

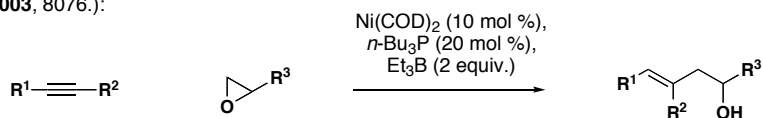


$\text{PtO}_2$ ,  $\text{H}_2$   
Named Catalyst

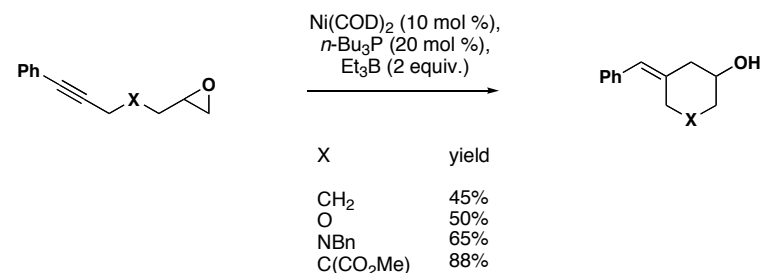


R = □ hydrogen: 33%  
(±)-yohimban  
R = □ hydrogen: 34%  
(±)-alloyhimban

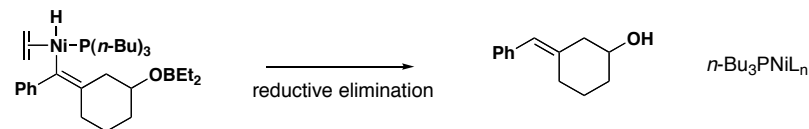
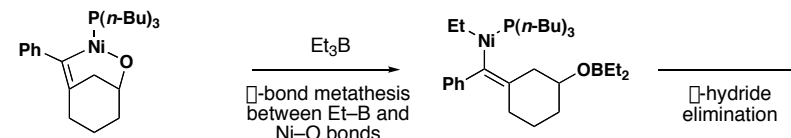
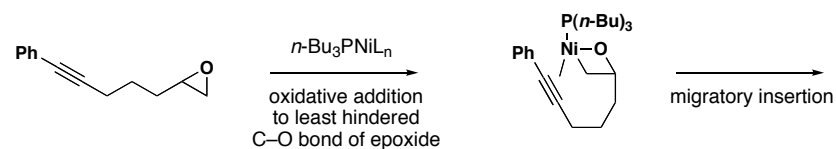
Nickel(0)-catalyzed reductive coupling of Alkynes and Epoxides (Jamison, *J. Am. Chem. Soc.*, 2003, 8076.):

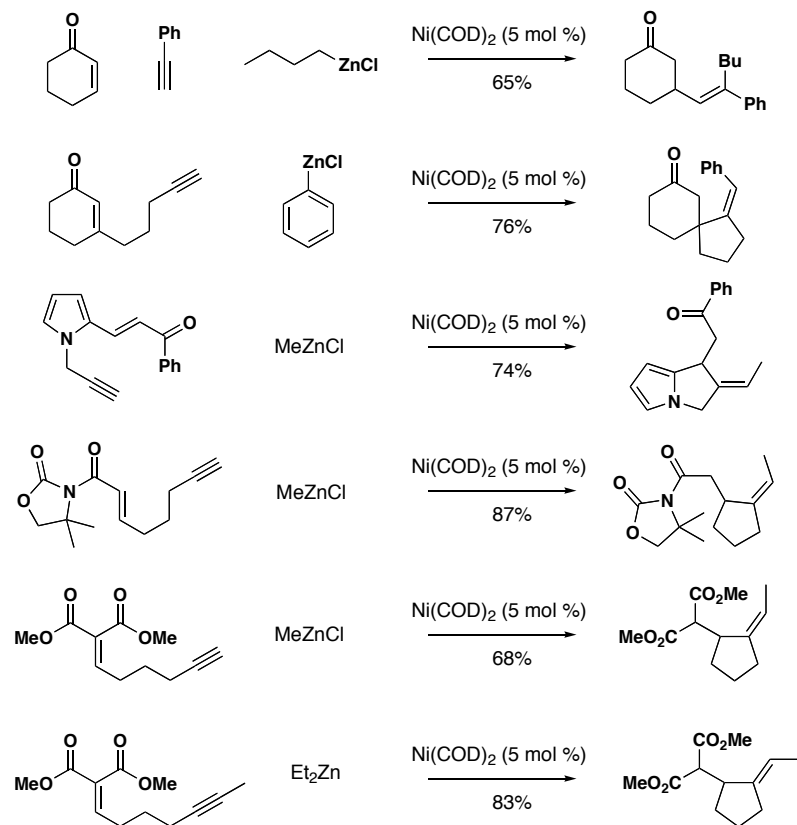


R1	R2	R3	yield
Ph	Me	Me	71%
Ph	Me	<i>n</i> -Hex	68%
Ph	Me	Ph	50%
<i>n</i> -Pr	<i>n</i> -Pr	Et	35%

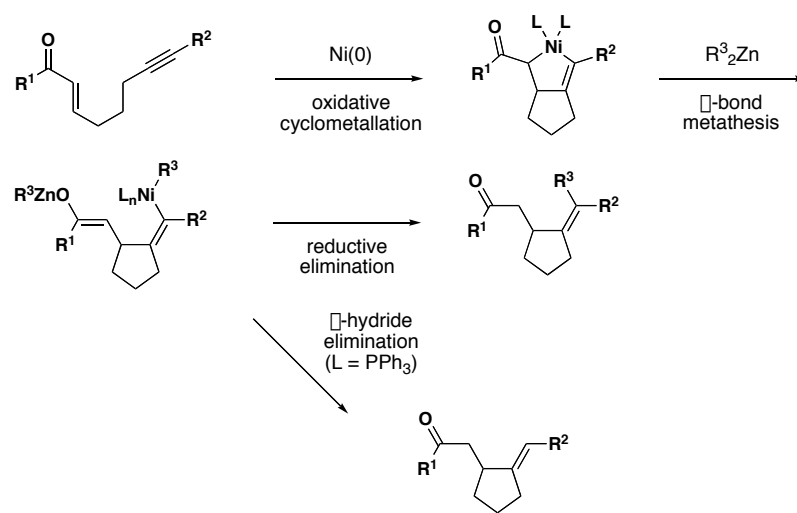
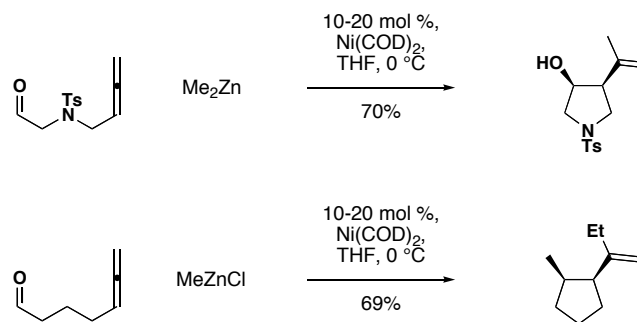


Proposed Mechanism:

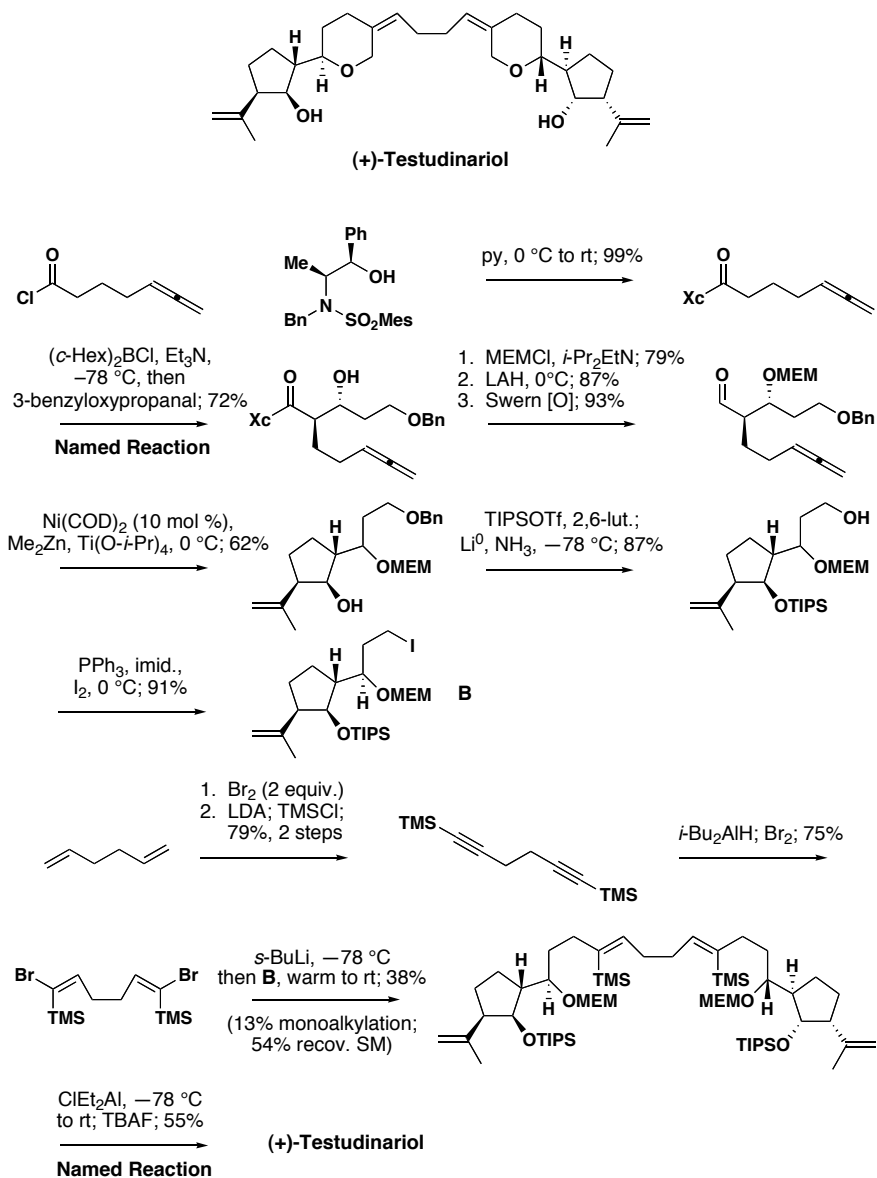


Coupling of an enone, alkyne, and organozinc (Montgomery, *Acc. Chem. Res.*, **2000**, 467.):

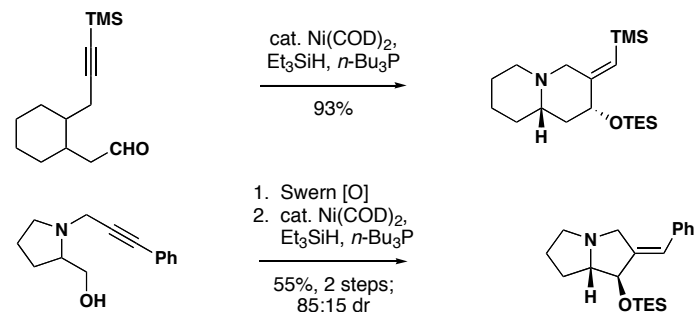
Proposed Mechanism:

Coupling of an aldehyde, allene, and organozinc (Montgomery, *Acc. Chem. Res.*, **2000**, 467. Montgomery, *Org. Lett.*, **2002**, 4009.)

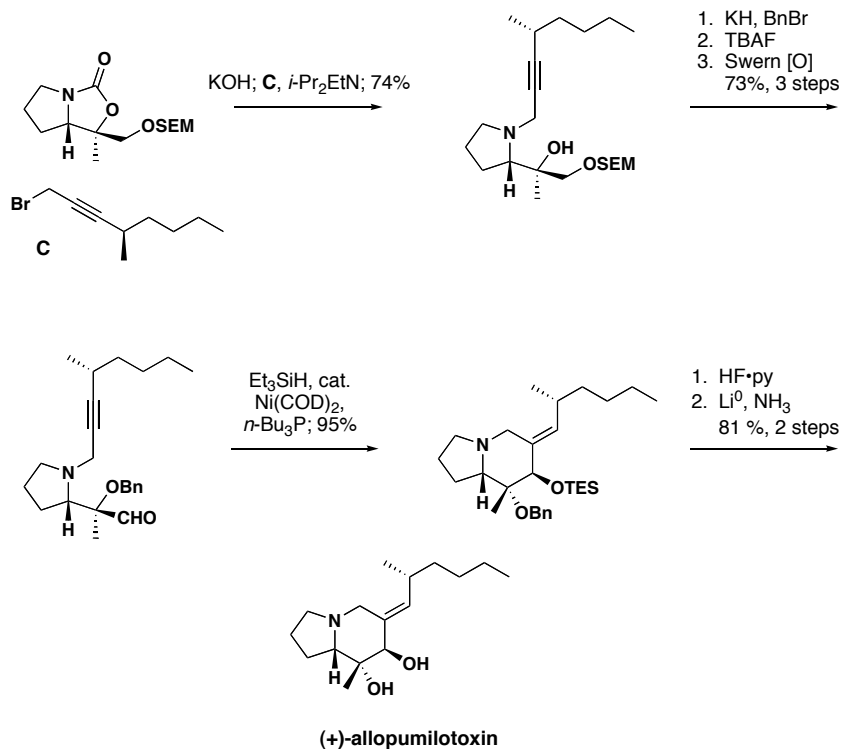
Enantioselective total synthesis of (+)-Testudinariol (Montgomery, *J. Am. Chem. Soc.*, **2002**, 9366.):

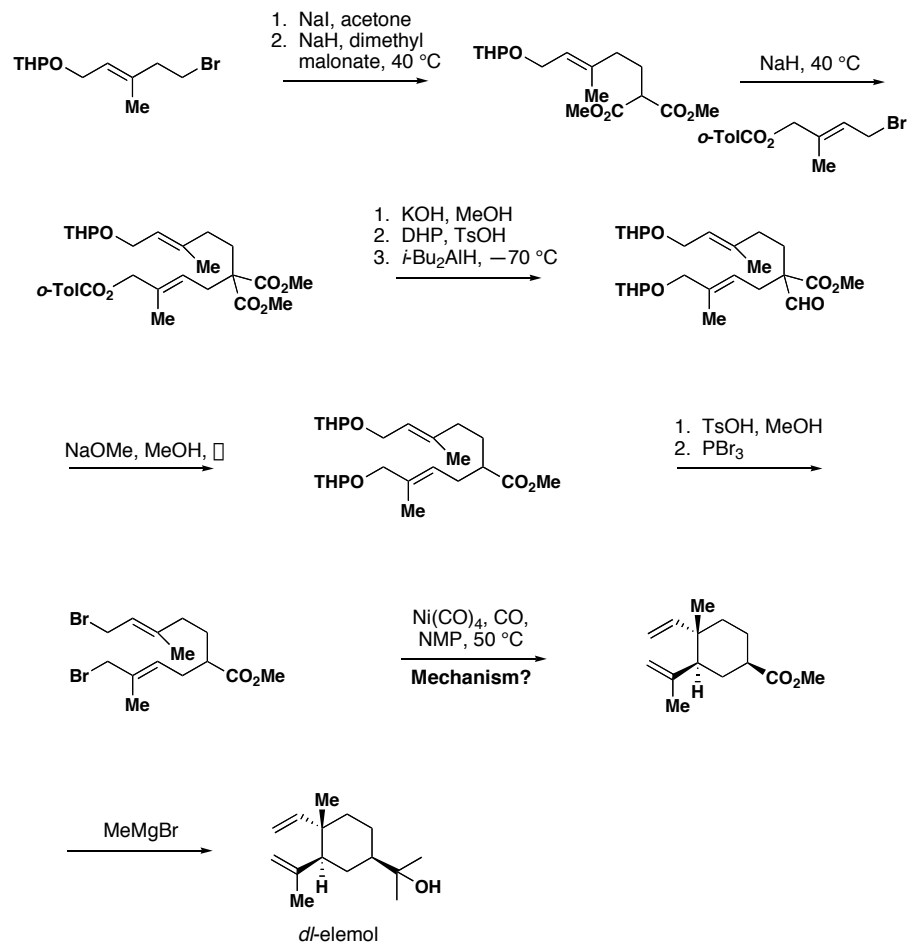


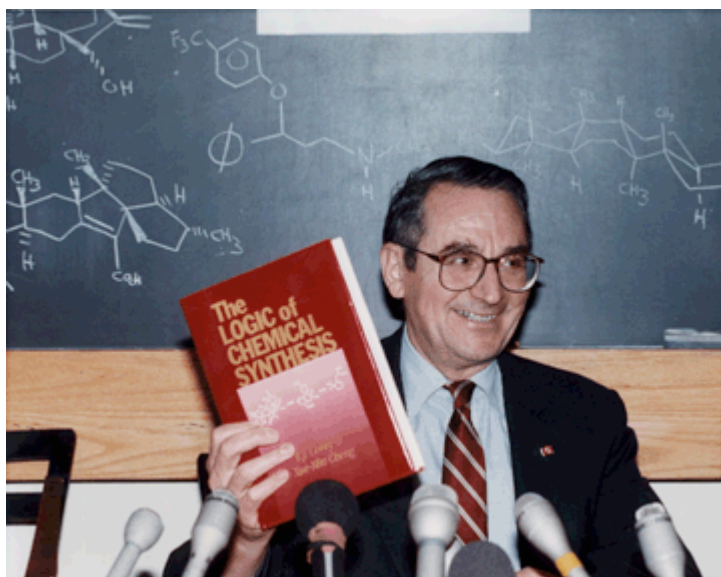
Coupling of an aldehyde, alkyne, and silane (Montgomery, *Acc. Chem. Res.*, **2000**, 467.):



Total synthesis of (+)-allopumilotoxin 267A (Montgomery, *J. Am. Chem. Soc.*, **2000**, 6950.):



Total Synthesis of *d*-Elemol (Corey, *TL*, 1969, 1779; *JACS*, 1967, 2758.):



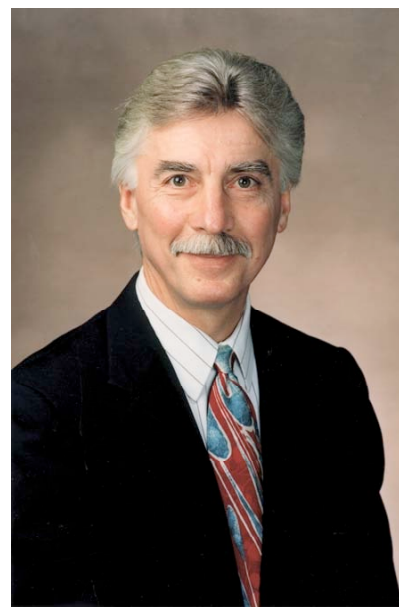
E. J. Corey, Harvard



John A. Montgomery,  
Wayne State University, MI



Timothy F. Jamison, MIT



Paul A. Wender, Stanford