

Enyne Metathesis and Metallotropic [1,3]-Shift

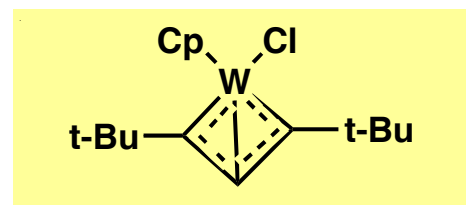
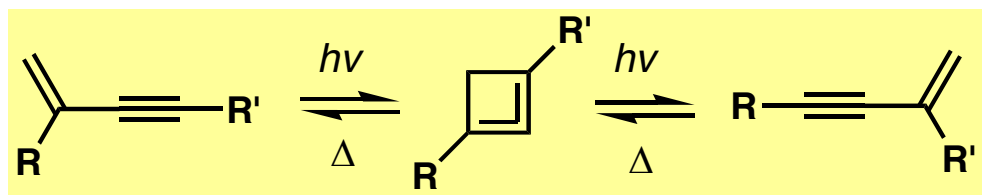
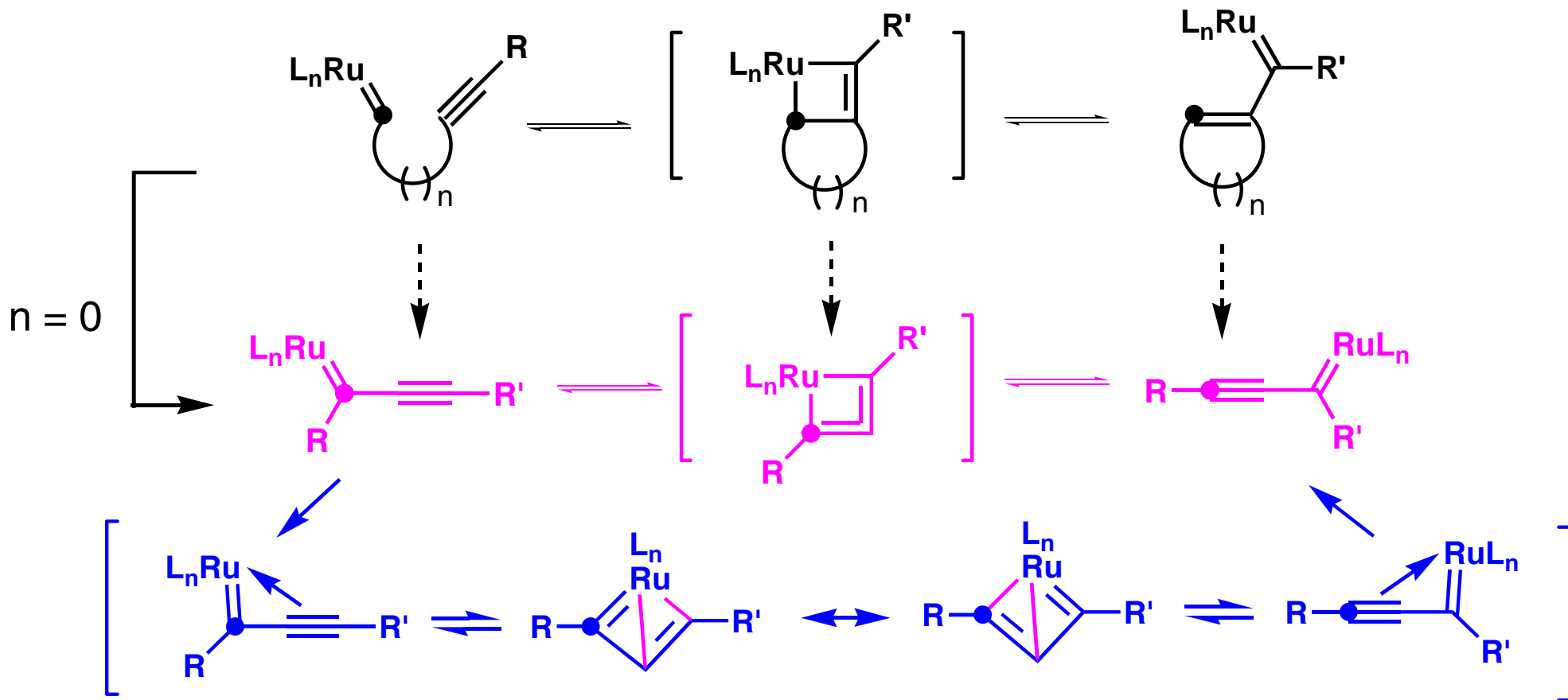
17th ISOM

July 29 – August 3, 2007

Daesung Lee

University of Illinois at Chicago

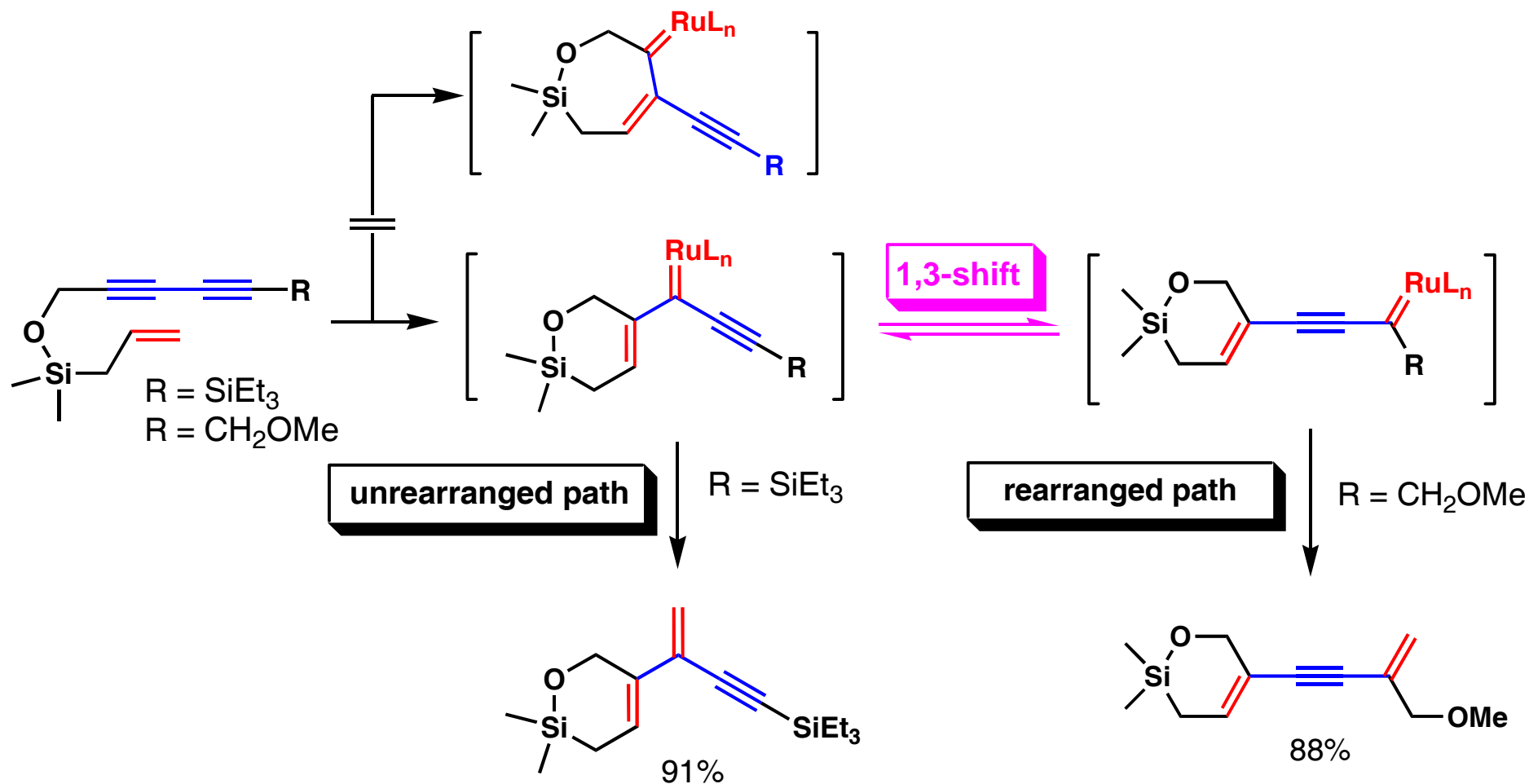
Metallotropic [1,3]-Shift: Special Case of RCM Reaction



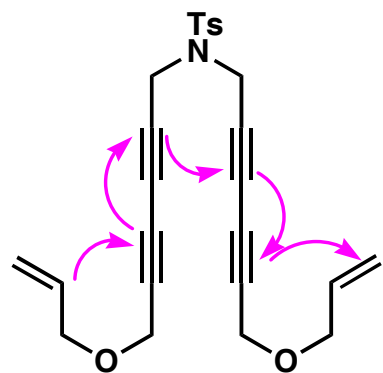
Johnson et al. *J. Am. Chem. Soc.* **1993**, *115*, 12167.

Schrock et al. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

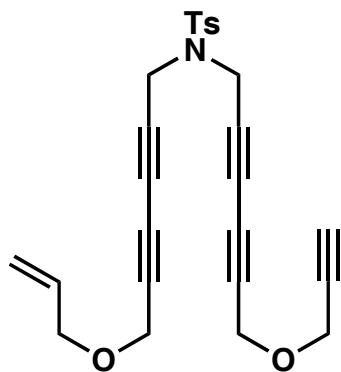
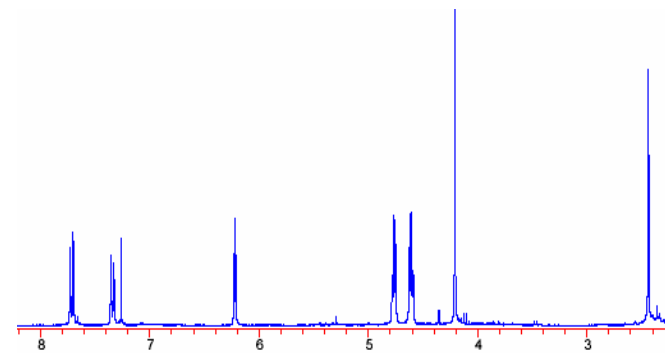
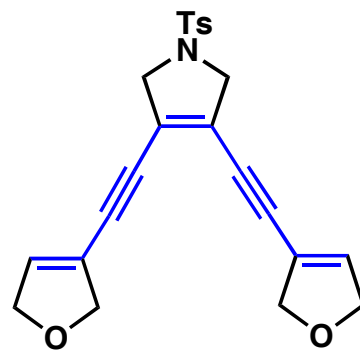
RCM-Induced Metallotropic [1,3]-Shift: Steric Control of Regioisomeric Alkylidene Formation



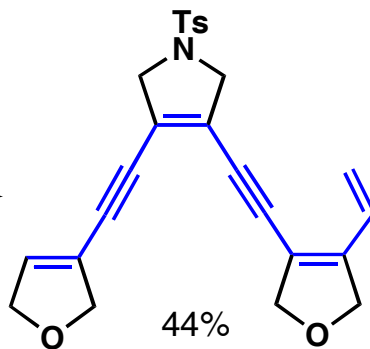
Metallotropy and Metathesis (M&M)



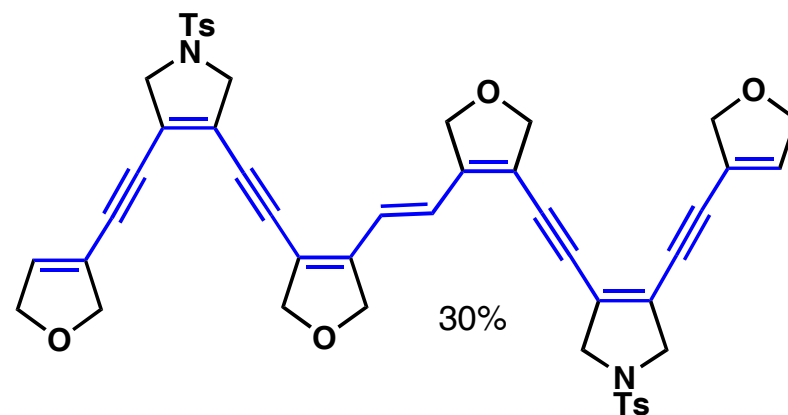
Grubbs II
CH₂Cl₂
5h
86% w/o CH₂CH₂
67% with CH₂CH₂



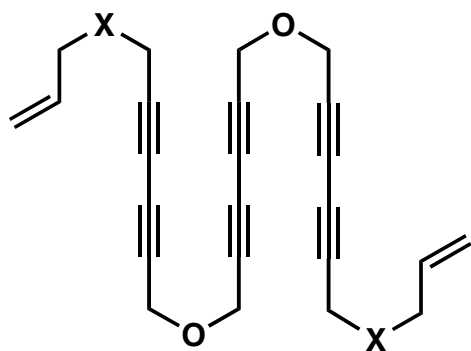
Grubbs II
CH₂CH₂



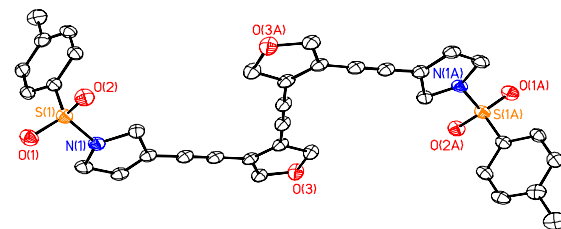
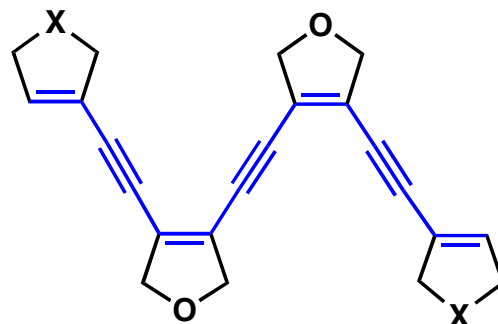
44%



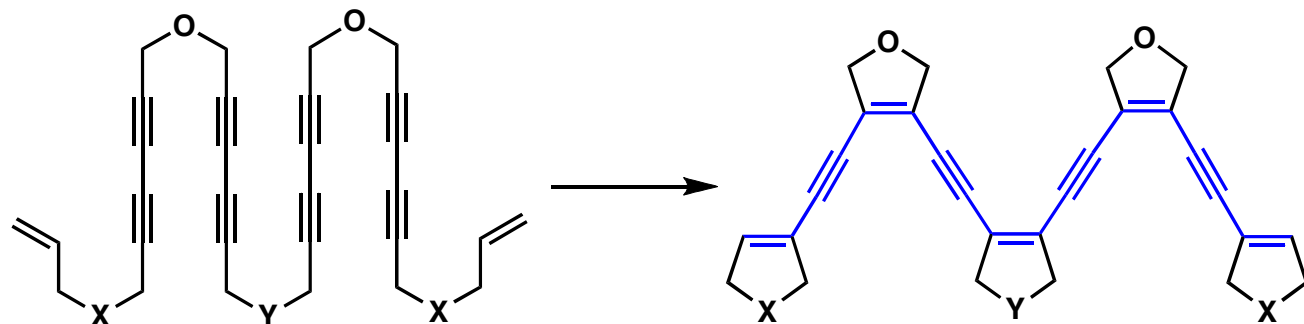
30%



Grubbs II
X = O (63%)
X = NTs (47%)

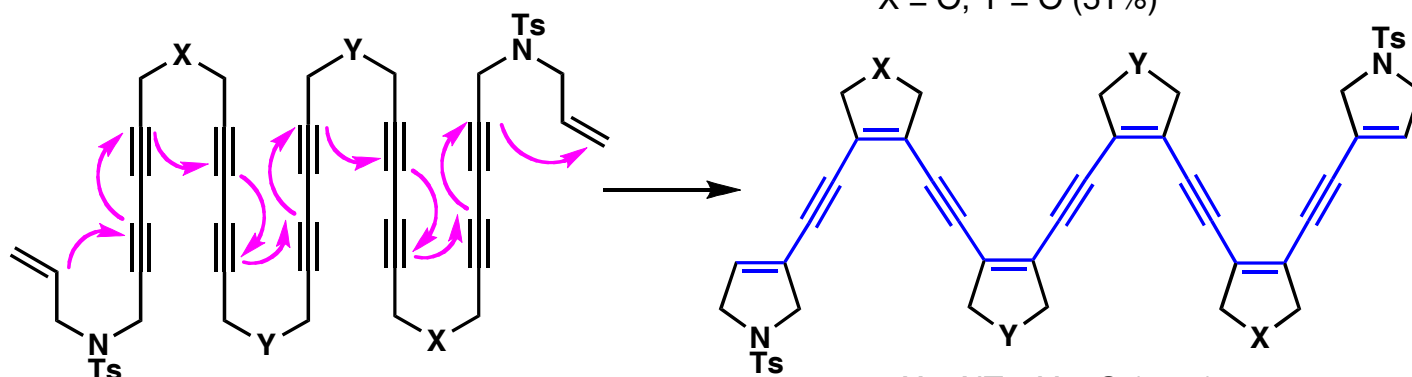
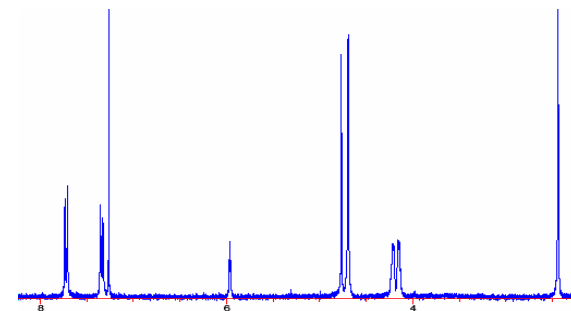


Metallotropy and Metathesis (M&M)



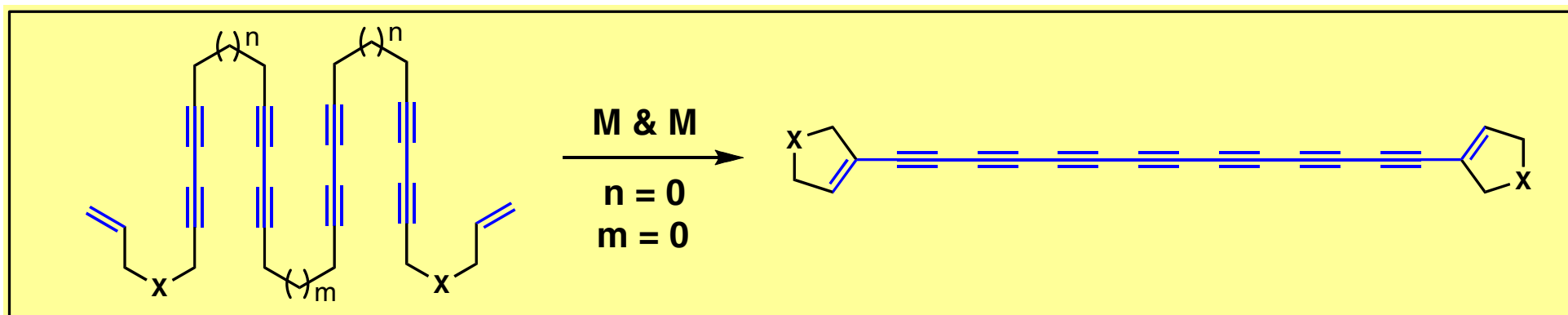
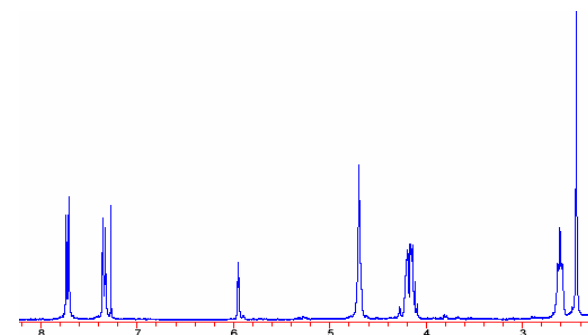
X = NTs, Y = O (45%)

X = O, Y = O (51%)

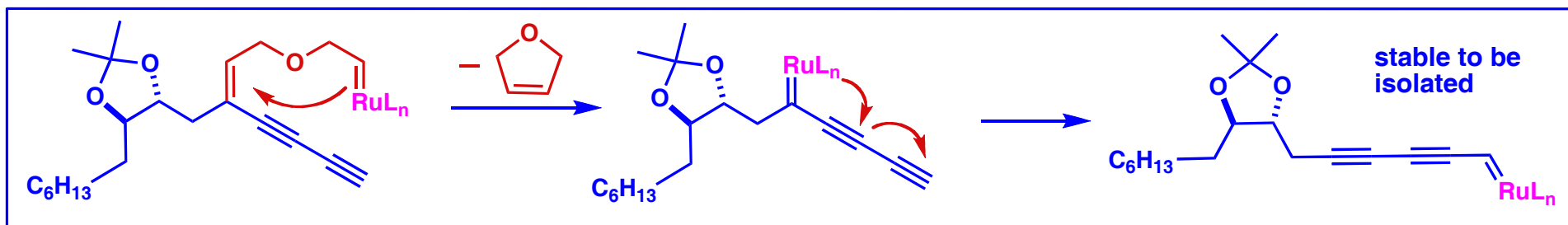
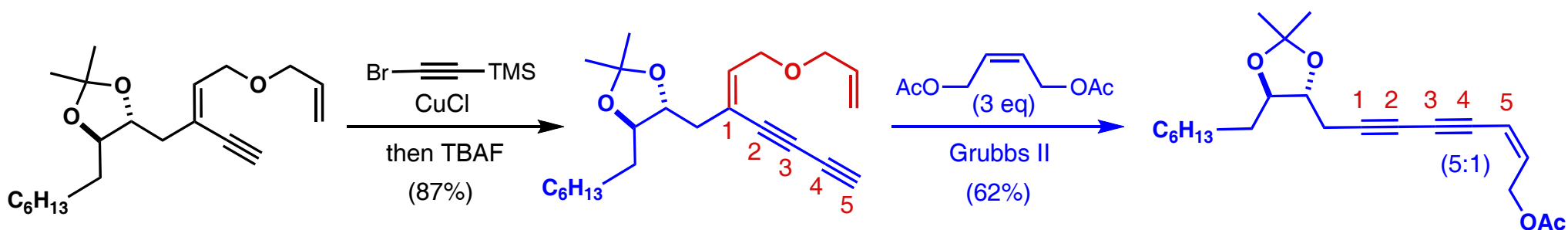
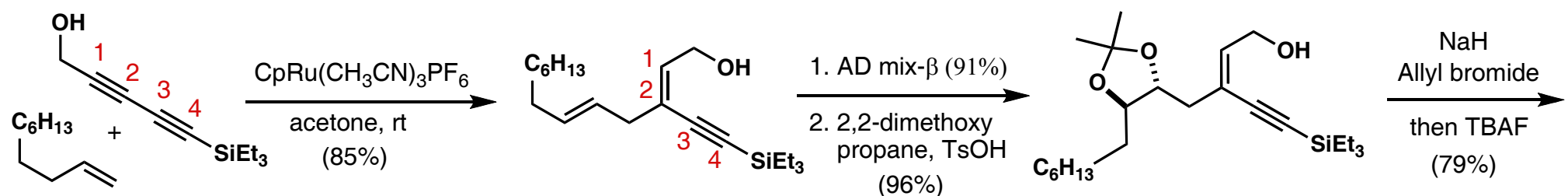


X = NTs, Y = O (36%)

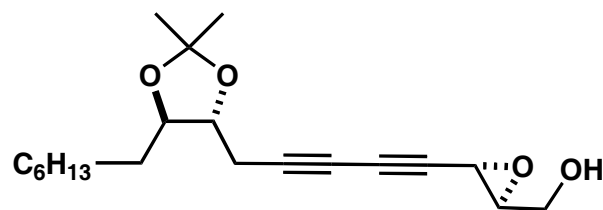
X = O, Y = O (32%)



Relay Metathesis–Metallotropic [1,3]-Shift: Total Synthesis of (3*R*,9*R*,10*R*)-Panaxytriol



1. I₂ (1.7:1, 82%)
2. DIBAL (95%)
3. (+)-DET, TBHP
Ti(OiPr)₄ (89%)



1. PPh₃, I₂ (92%)
2. Zn/AcOH (83%)
3. TsOH, MeOH (94%)

