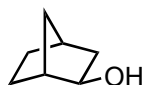
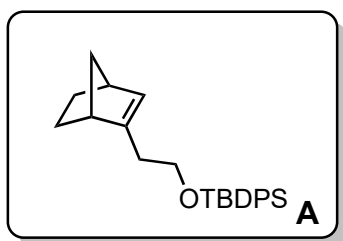


Total Synthesis of (-)-Isoschizogamine

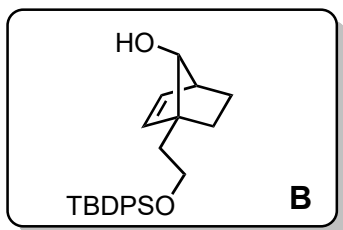
Y. Miura, N. Hayashi, S. Yokoshima, and T. Fukuyama, *J. Am. Chem. Soc.* **2012**, *134*, 11995-11997



1-3



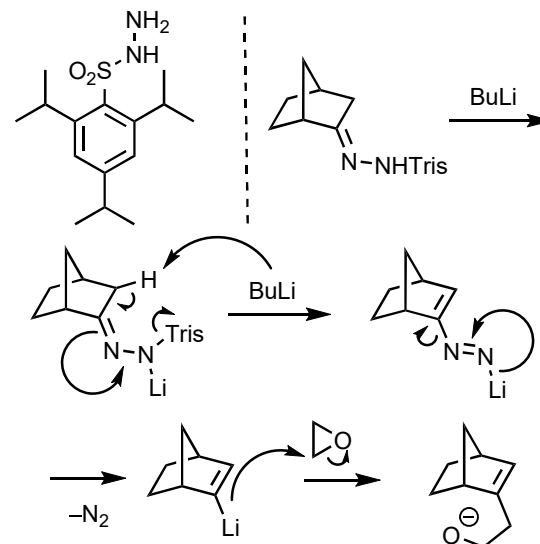
4,5



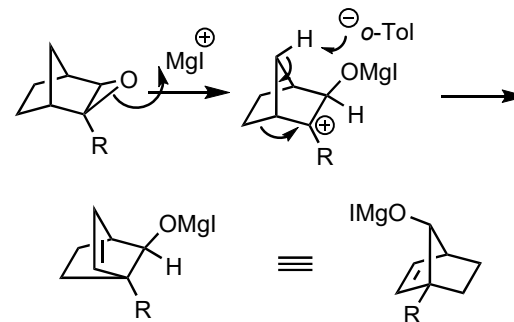
- 1) TPAP, NMO
- 2) TrisNHNH₂, conc. HCl
- 3) *s*-BuLi (2.05 eq.)
then ethylene oxide (2.3 eq.)
then TBDPSCl (1.3 eq.)

- 4) *m*CPBA
- 5) *o*-TolMgI (1.25 eq.)
Et₂O, reflux

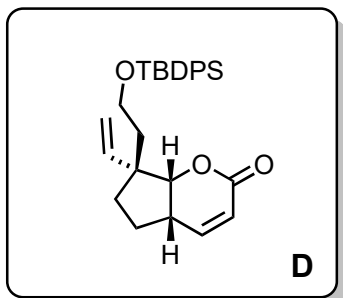
name and mechanism reaction 3?
Shapiro



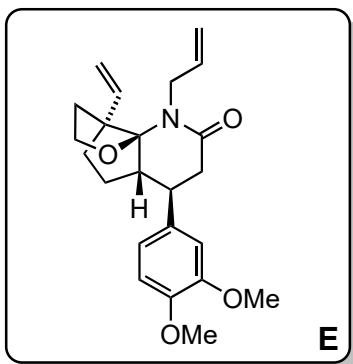
name and mechanism of reaction 5?
Wagner-Meerwein-Rearrangement



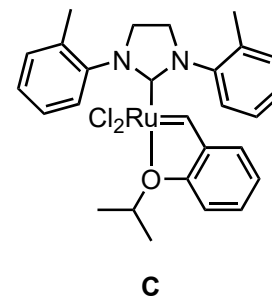
6,7



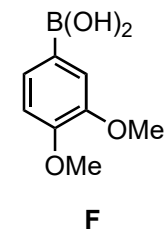
8-12



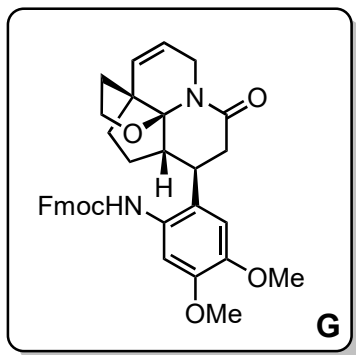
- 6) acryloyl chloride, DIPEA
7) **C** (5 mol-%), 1,6-heptadiene (cat.)



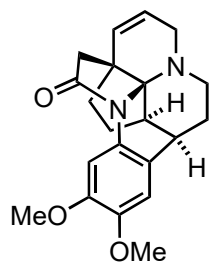
- 8) **F**, $[\text{RhCl}(\text{cod})]_2$ (4 mol-%)
 NEt_3 , dioxane/ H_2O
9) allylamine (20 eq.), 2-hydroxypyridine (5 eq.)
10) DMP
11) conc HCl, MeOH, 0 °C
12) PPTS (0.3 eq.), toluene, reflux



↓
13-16



↓
17-24



(-)-Isoschizoagamine

- 13) Hoveyda-Grubbs II (3 mol-%)
- 14) $\text{Cu}(\text{NO}_3)_2$, $\text{Ac}_2\text{O}/\text{CH}_2\text{Cl}_2$ (3:1)
- 15) NaBH_4 , $\text{Cu}(\text{acac})_2$
- 16) FmocCl, DIPEA

- 17) TMSOTf, 2,6-lutidine
- 18) TBAF, AcOH, THF
- 19) DMP
- 20) $(\text{TMSOCH}_2)_2$, TMSOTf
- 21) piperidine
- 22) LiAlH_4 , THF, reflux
- 23) AcOH/ H_2O (1:1), reflux
- 24) PDC