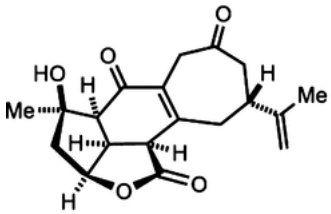
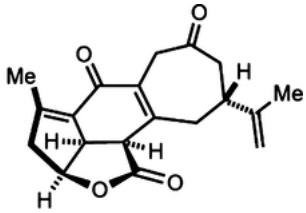


scabrolide A

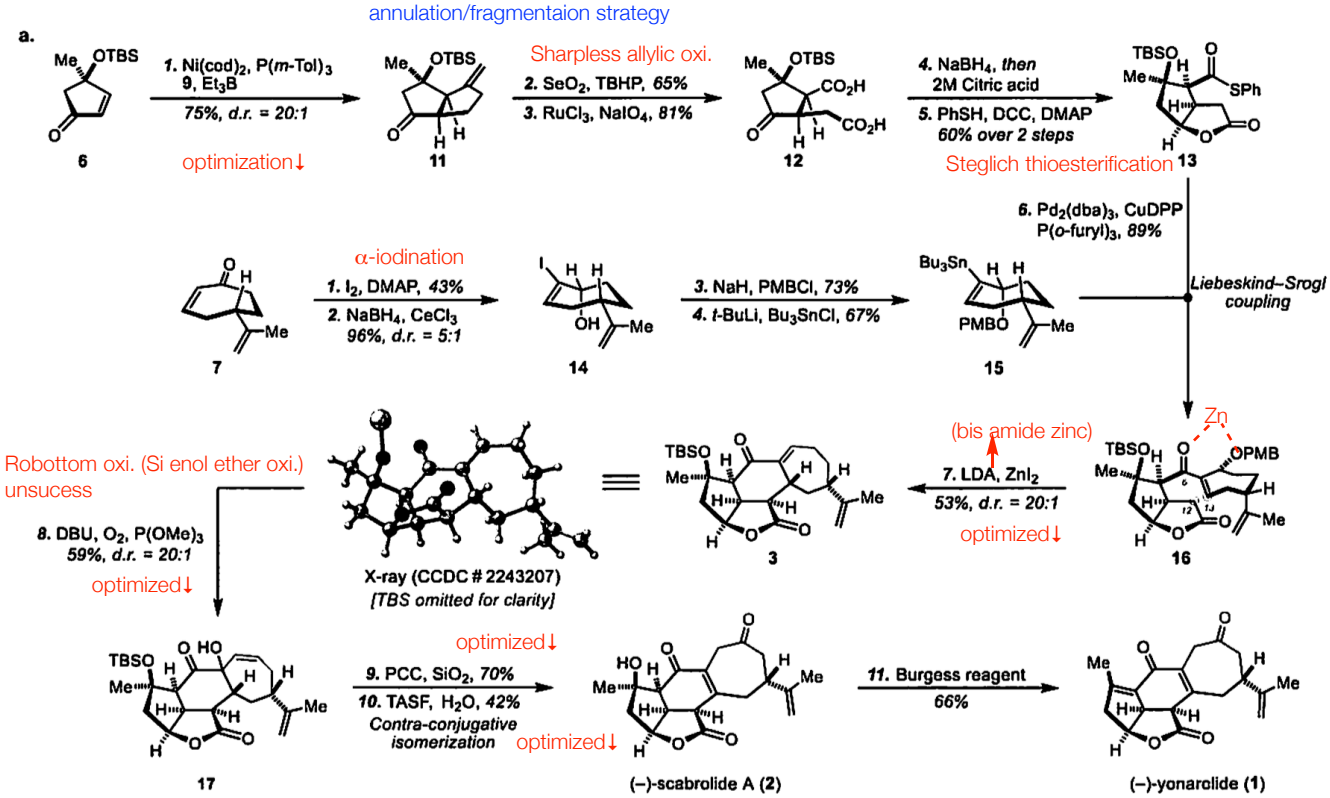


yonarolide

all cis sterochem.

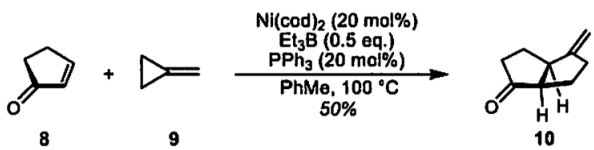
Total Syntheses of Scabrolide A and Yonarolide: Roberto Serrano, Yaroslav D. Boyko, Lucas W. Hernandez, Aleksandras Lotuzas, and David Sarlah* : **Cite this:** J. Am. Chem. Soc. 2023, 145, 16, 8805–8809

annulation/fragmentaion strategy



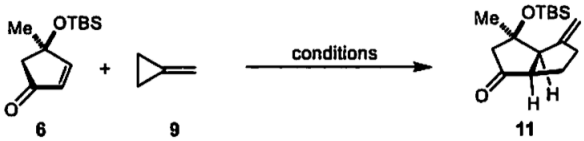
b. 7. Cyclization		c. 8. Oxidation		d. 9. Oxidative transposition		e. 10. Deprotection	
(1) MHDS (M = Na, K)	decomp.	(1) CrO_3, 3,5-DMP	10%	(1) PCC	26–55%	(1) TBAF, THF	elimination
(2) LDA or LHMDS	5–10%	(2) $Mn(OAc)_3$, TBHP	decomp.	(2) PCC, NaOAc	40%	(2) TBAF, AcOH	no reaction
(3) LDA, $ZnCl_2$	30–40%	(3) $Pd(OH)_2$, TBHP	decomp.	(3) PCC, SiO_2	70%	(3) TASF, DMF	elimination
(4) LDA, ZnI_2	53%	(4) $Rh_2(cap)_4$, TBHP	decomp.	(4) PDC	32%	(4) TASF, H_2O (1:2)	17%
(5) LDA, $MgBr_2$	decomp.	(5) DBU, O_2, $P(OMe)_3$	59%	(5) Bobbitt's salt	no reaction	(5) TASF, H_2O (1:10)	42%

a) Original report (Binger, 1988)



analogous to classical TMM cycloaddition

b) Application to enone 6



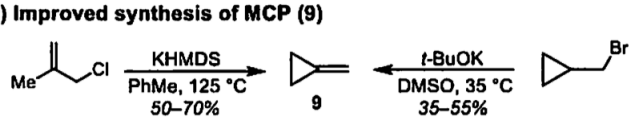
Initial conditions

$Ni(cod)_2$ (20 mol %), Et_3B (0.5 eq.)
PPh_3 (20 mol %), PhMe, 100 °C
Yield: *40–60%, d.r. > 20:1, r.r > 20:1*

Optimized conditions *(see SI for details)*

$Ni(cod)_2$ (10 mol %), Et_3B (0.1 eq.)
$P(m\text{-Tol})_3$ (10 mol %), Et_2O, 75 °C
Yield: *75%, d.r. > 20:1, r.r > 20:1*

c) Improved synthesis of MCP (9)



Previous synthesis

- inconsistent titer of MCP
- irreproducable
- incomplete conversion

New synthesis

- consistent conversion
- scalable and practical (>10 g)