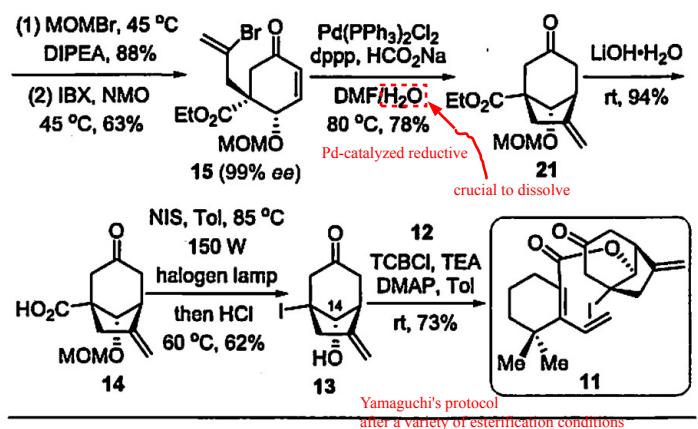
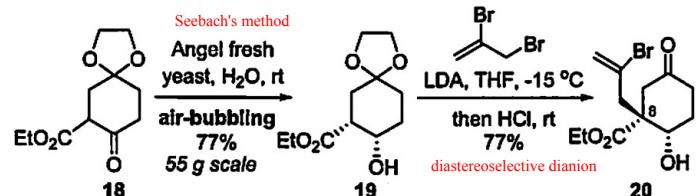
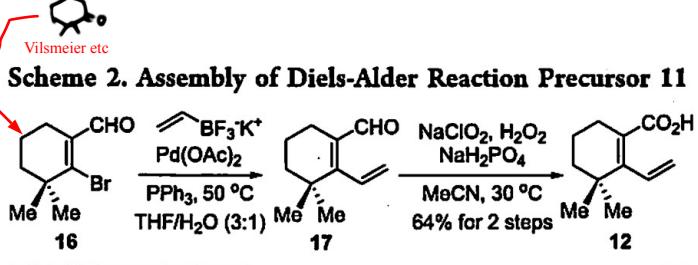
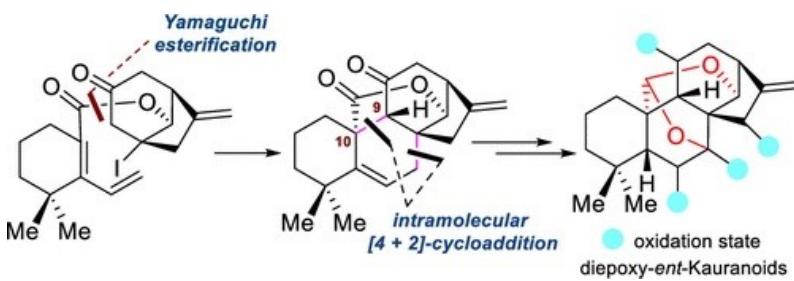


the novel bridgehead-enone-initiated intramolecular cycloaddition

7,20:14,20-diepoxy-*ent*-kauranoids
 a highly reactive [3.2.1]bridgehead enone intermediate

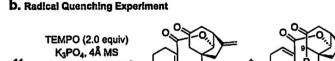


a. Optimization of the Intramolecular Diels-Alder Reaction of 11 via the [3.2.1]-Bridgehead Enone Intermediate 22

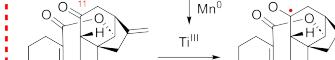
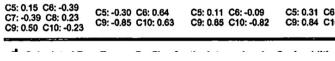
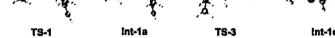
	base, additive, solvent, T	conditions	yield of 9 ^b	yield of 23 ^b	X-ray structure of 9	X-ray structure of 23
entry 1	K ₃ PO ₄ , THF (0.05 M), 60 °C		41%	16%		
2	K ₃ PO ₄ , MeCN (0.05 M), 60 °C		47%	14%		
3	K ₃ PO ₄ (0.05 M), 4 Å MS, 60 °C		62%	17%		
4	Ag ₃ Po ₄ , MeCN (0.05 M), 4 Å MS, 60 °C		0%	0%		
5	Cs ₂ CO ₃ , MeCN (0.05 M), 4 Å MS, 60 °C		31%	9%		
6	K ₃ PO ₄ , MeCN (0.01 M), 4 Å MS, 60 °C		57%	15%		
7	K ₃ PO ₄ , MeCN (0.05 M), 4 Å MS, 80 °C		60%	22%		
8 ^c	K ₃ PO ₄ , MeCN (0.05 M), 4 Å MS, 60 to 80 °C		61%	19%		

^aUnless stated otherwise, the reactions were performed with 11 (0.25 mmol), base (0.75 mmol), solvent (5.0 mL), additive (220 mg) until 11 was completely consumed by the analysis of TLC. ^bIsolated yield. ^cGram scale: 11 (1.00 g, 2.27 mmol), K₃PO₄ (1.45 g, 8.81 mmol), MeCN (45.4 mL), 4 Å MS (20.0 g).

b. Radical Quenching Experiment



c. Spin Density and Mulliken Spin Population



Scheme 3. Completion of the Total Syntheses of Four 7,20:14,20-Diepoxy-*ent*-Kauranoids

