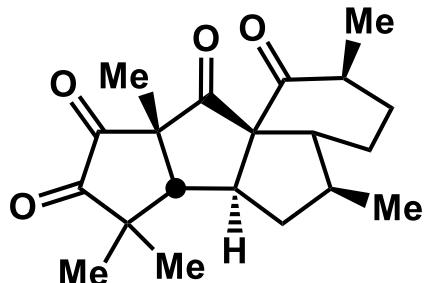


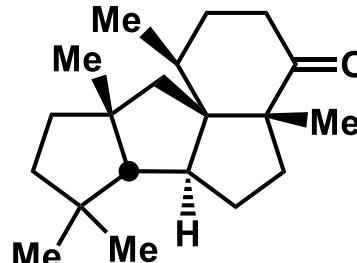
# Enantioselective Total Synthesis of (+)-Aberrarone

Willi M. Amberg and Erick M. Carreira\*

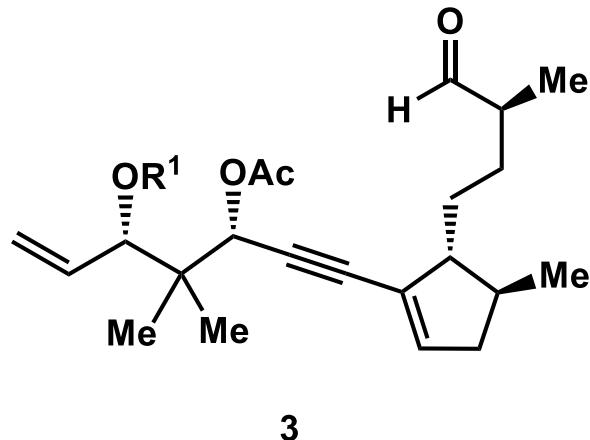


(+)-Aberrarone (1)

- Tetraketone
- 5-5-5-6 Fused rings
- 7 Stereogenic centers



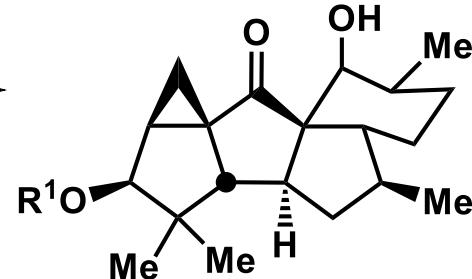
(-)-Conidiogenone (2)



3

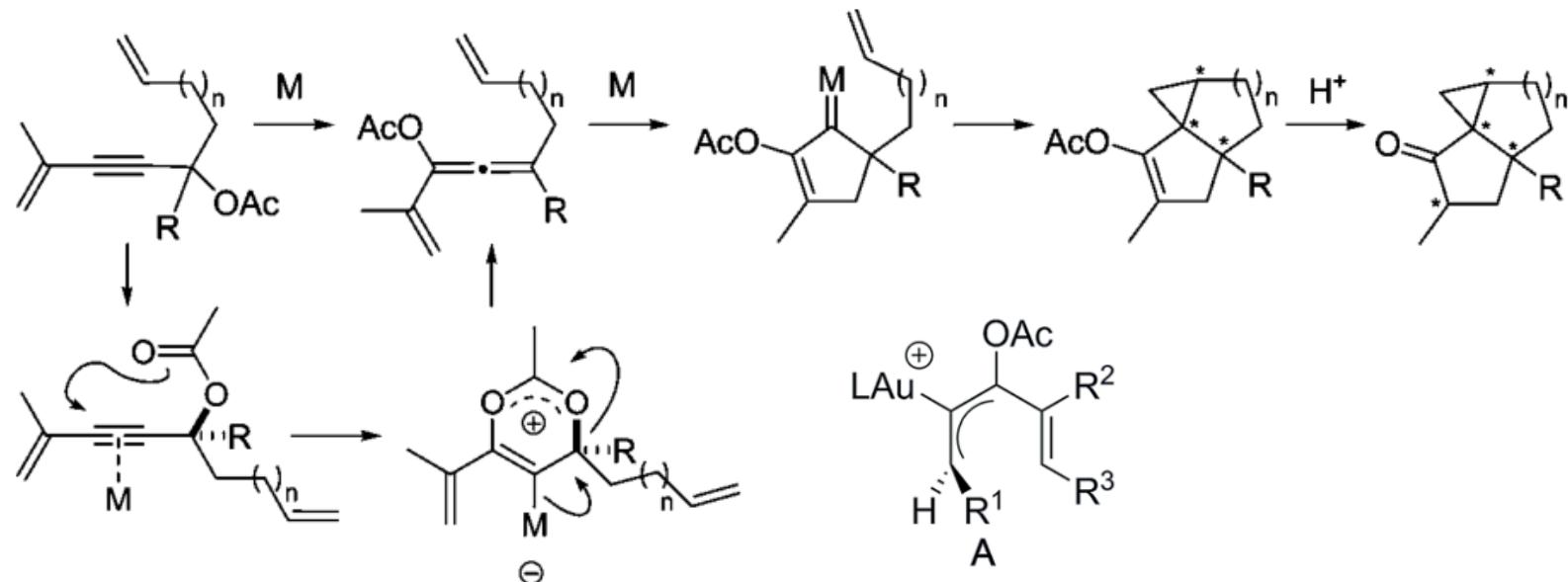
## Key Synthetic Step [M]

- I Meyer-Schuster
- II Nazarov
- III Cyclopropanation
- IV Aldol

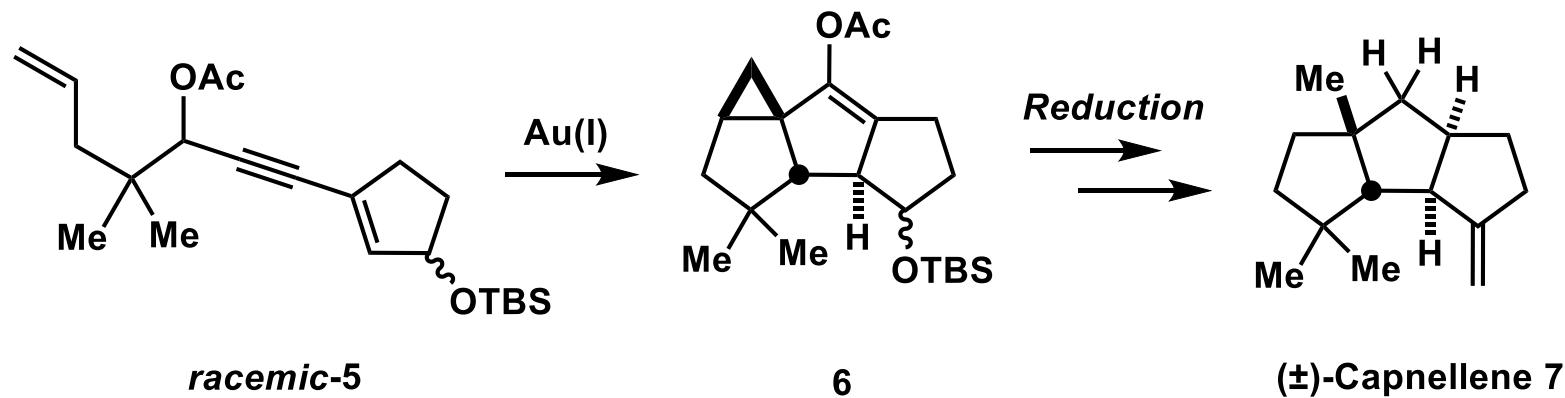


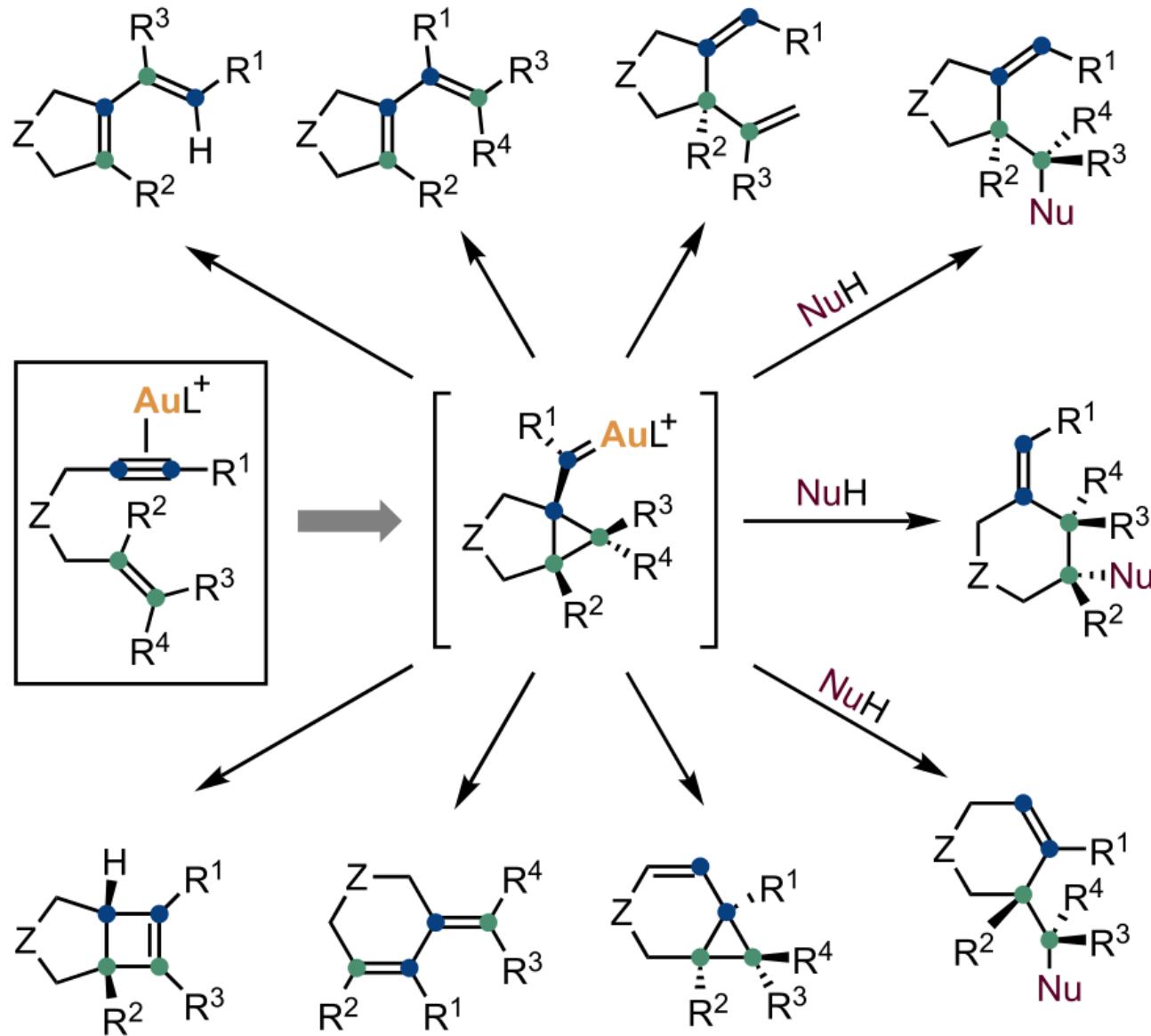
4

Cycloisomerization of Enyl Acetates via 3,3-Rearrangement, Metalla-Nazarov, and Electrophilic Cyclopropanation

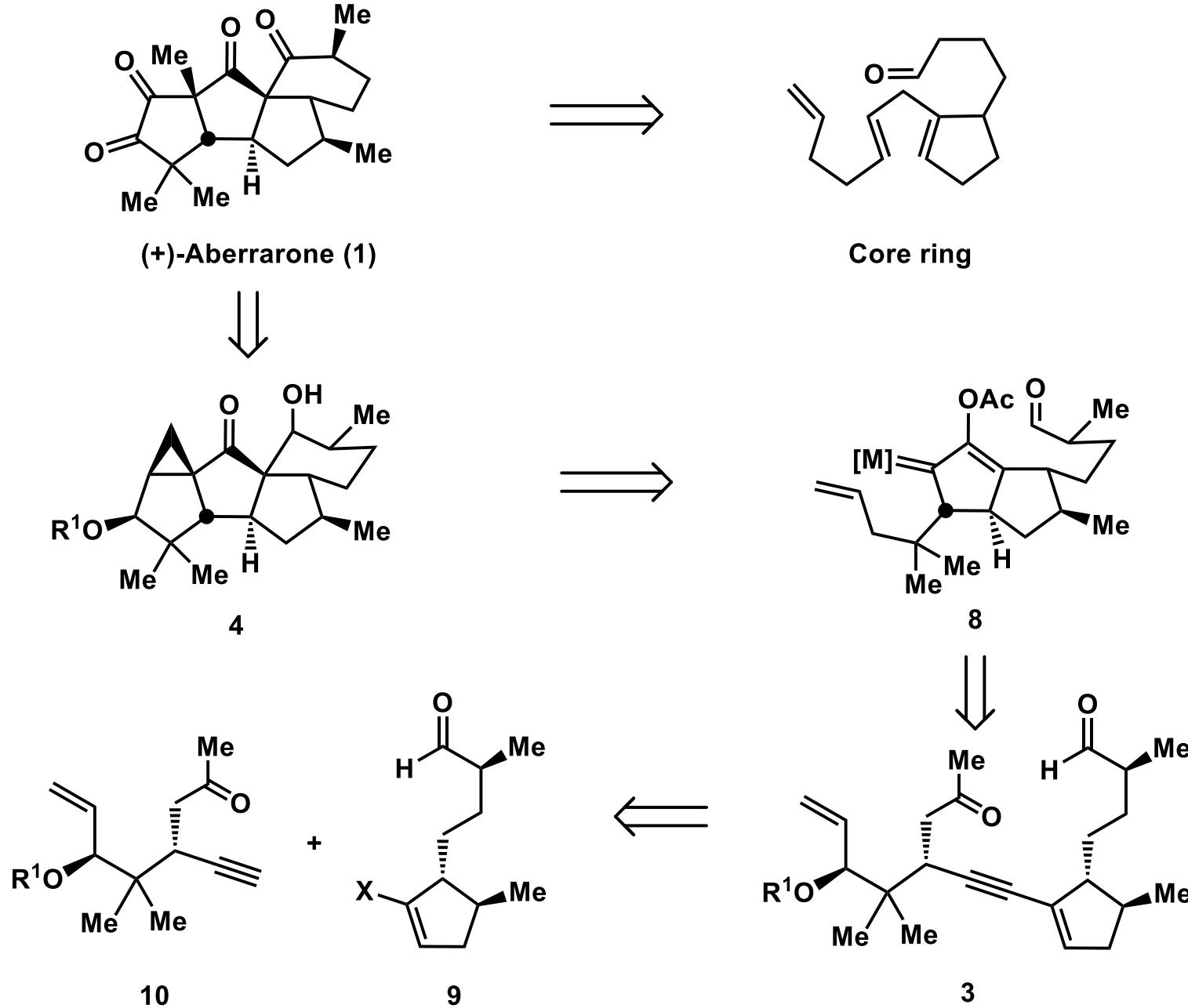


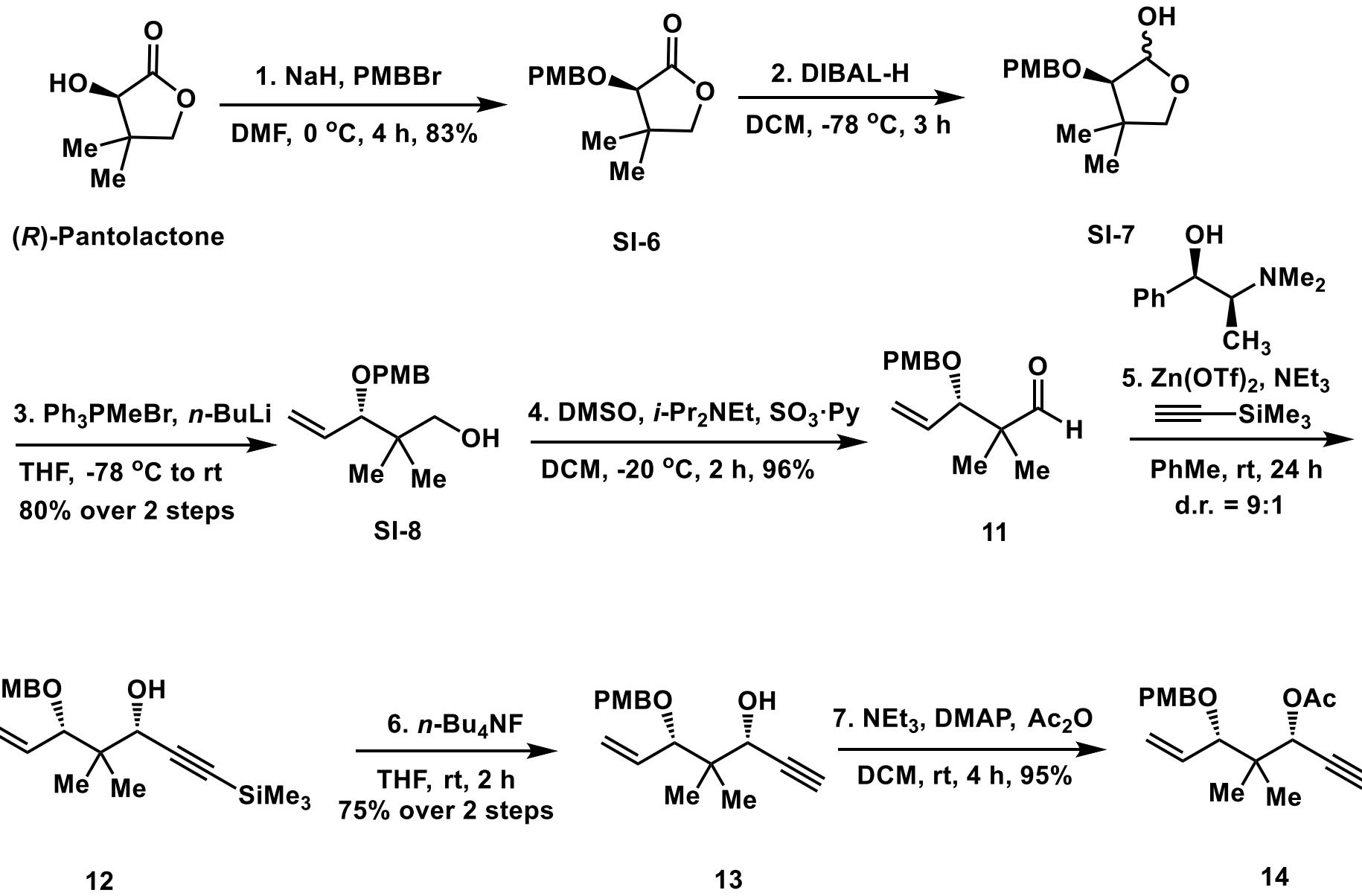
**A. Prior Work:**

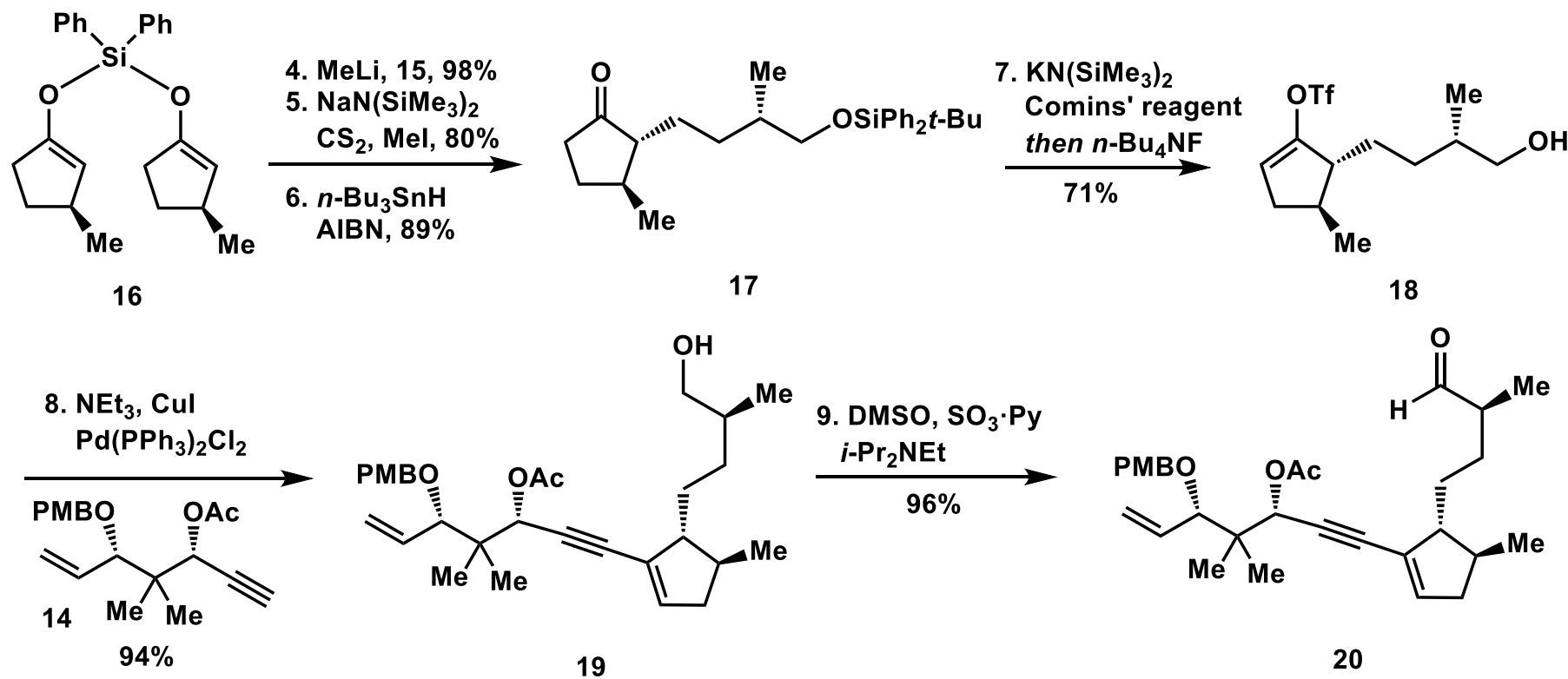
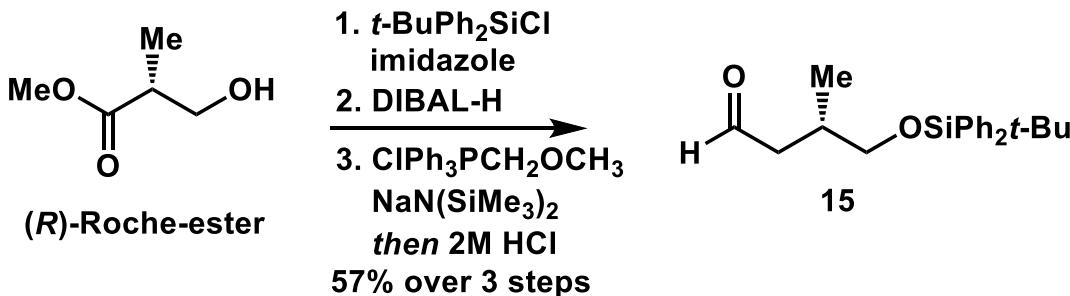




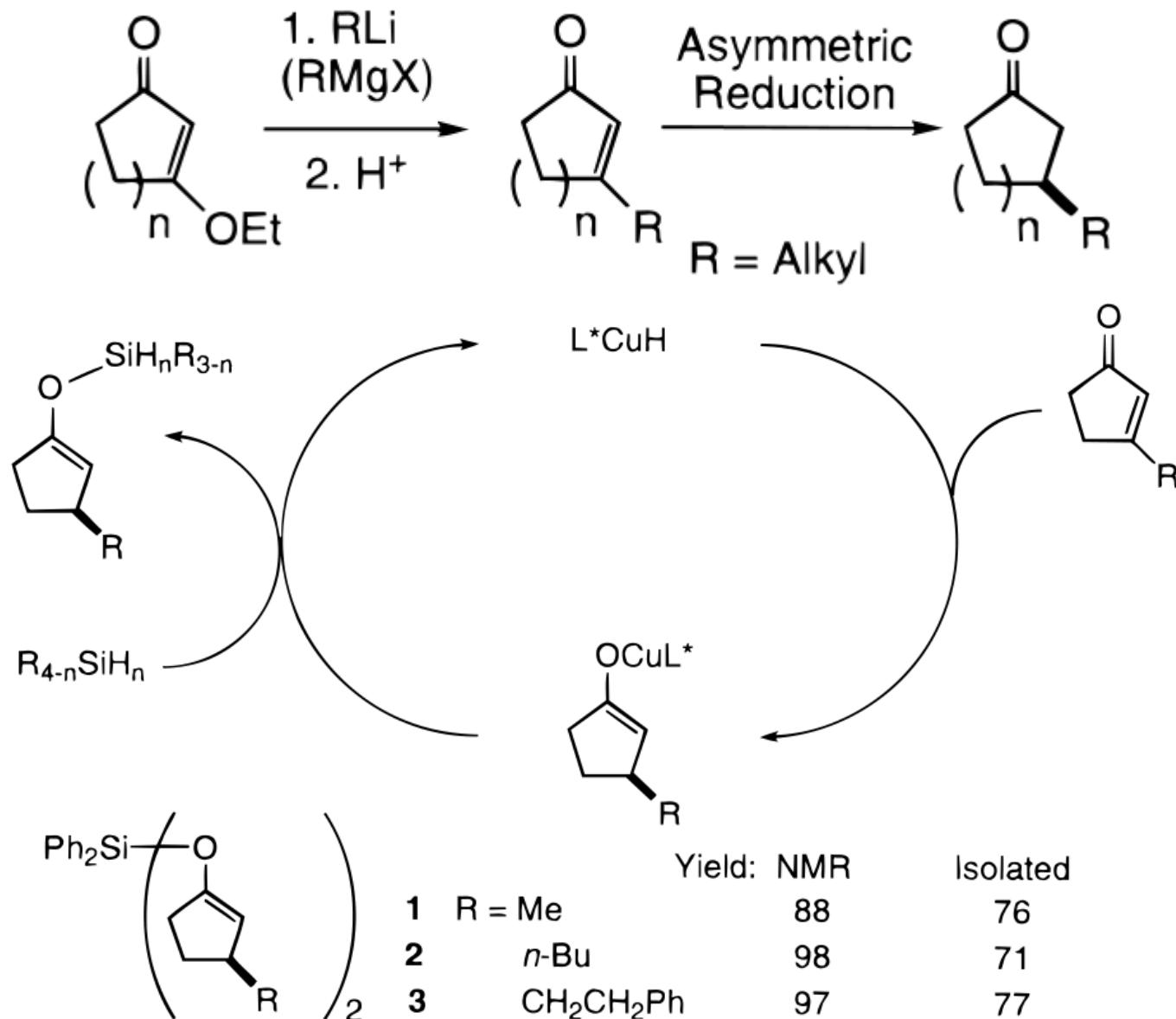
B. This Work:

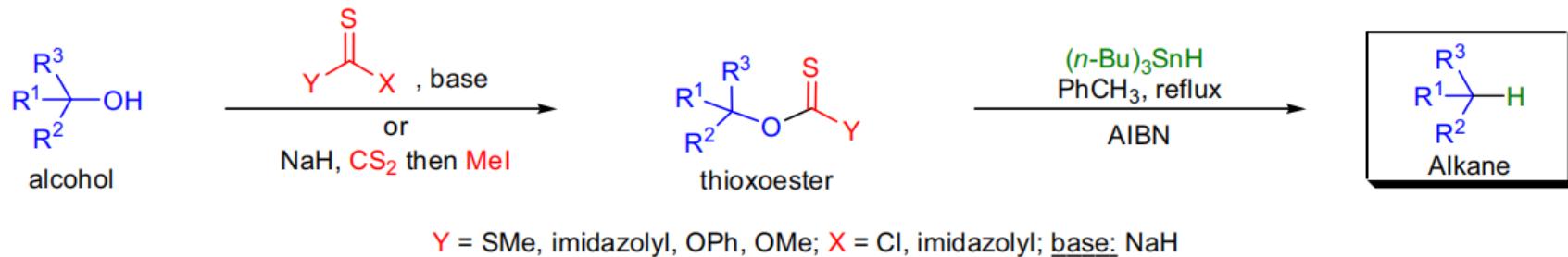






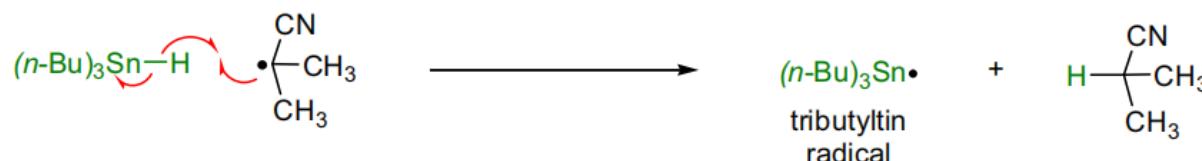
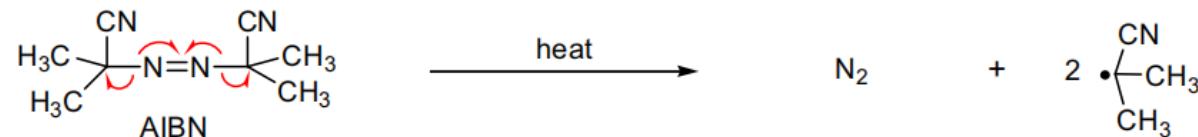
b.



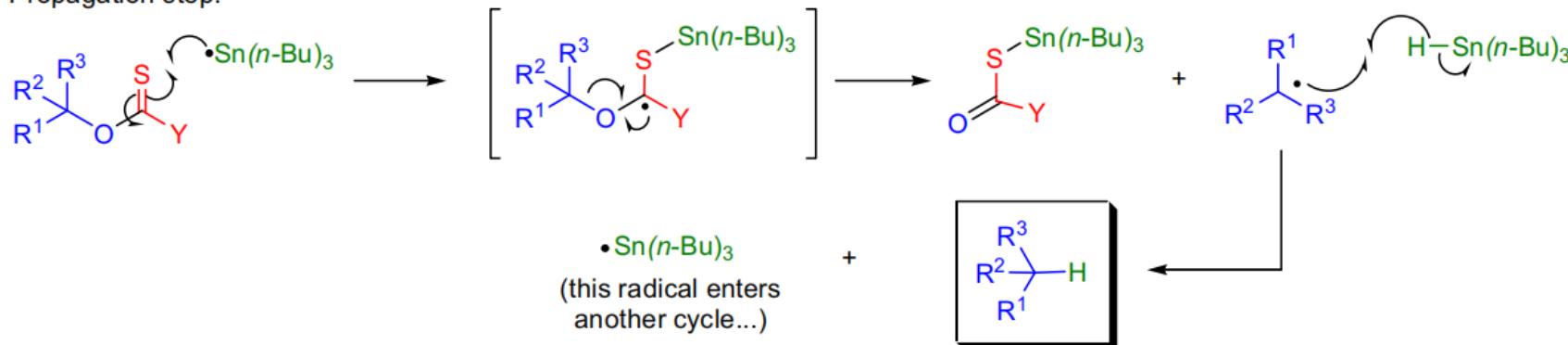


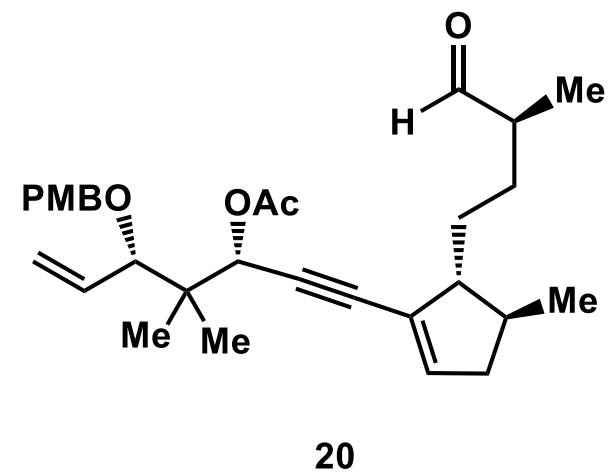
Mechanism: <sup>25,13,26</sup>

Initiation step:

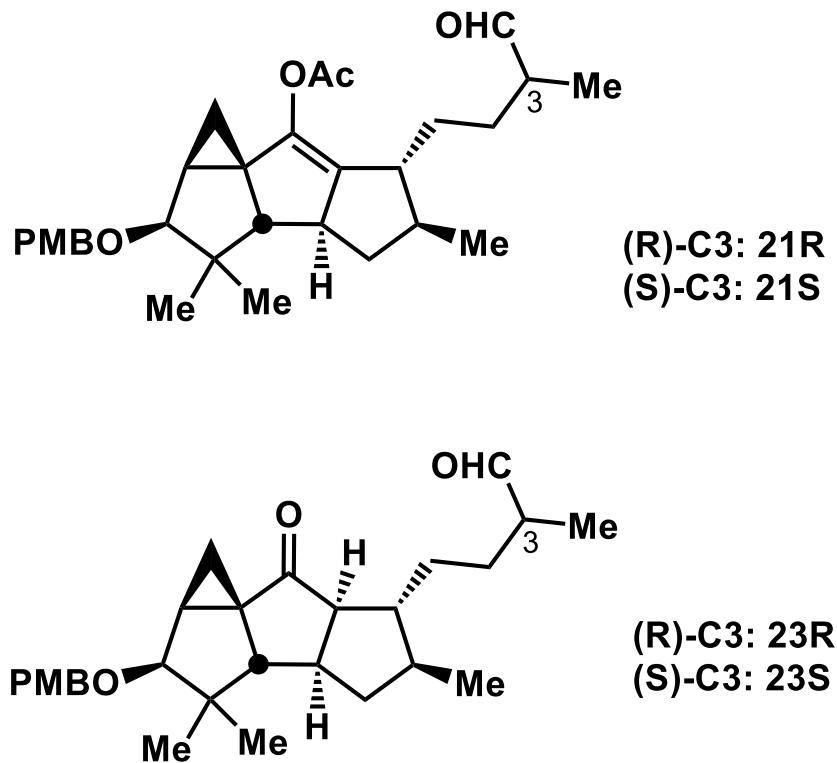


Propagation step:





[Au]  
20 mol %  
*then*  
additive



**Table 1. Study of Conditions and Additives**

Entry	Solvent	Additive	T (°C)/Time	Result
1	THF:H <sub>2</sub> O 500:1	none	0 °C	<b>20</b> (95%)
			12 h	
2	CH <sub>2</sub> Cl <sub>2</sub>	none	0 °C	<b>21R</b> (40%)
			12 h	
3	CH <sub>2</sub> Cl <sub>2</sub>	TiCl <sub>4</sub>	-78 °C	decomp.
			1 min	
4	CH <sub>2</sub> Cl <sub>2</sub>	NaOMe	0–25 °C	<b>21R:21S</b> (1:1) <sup>a</sup>
		MeOH	72 h	<b>23R:23S</b> (1:1) <sup>a</sup>
5	CH <sub>2</sub> Cl <sub>2</sub>	K <sub>2</sub> CO <sub>3</sub>	0–25 °C	<b>23R:23S</b> (1:1) <sup>a</sup>
		MeOH	72 h	
6	CH <sub>2</sub> Cl <sub>2</sub>	Et <sub>2</sub> AlOEt	0 °C	<b>21R:21S</b> (1:1) <sup>a</sup>
			12 h	
7	CH <sub>2</sub> Cl <sub>2</sub>	<i>n</i> -Bu <sub>3</sub> SnOMe	0–25 °C	<b>21R</b> (43%)
			12 h	

<sup>a</sup>The diastereomeric mixture is inseparable.

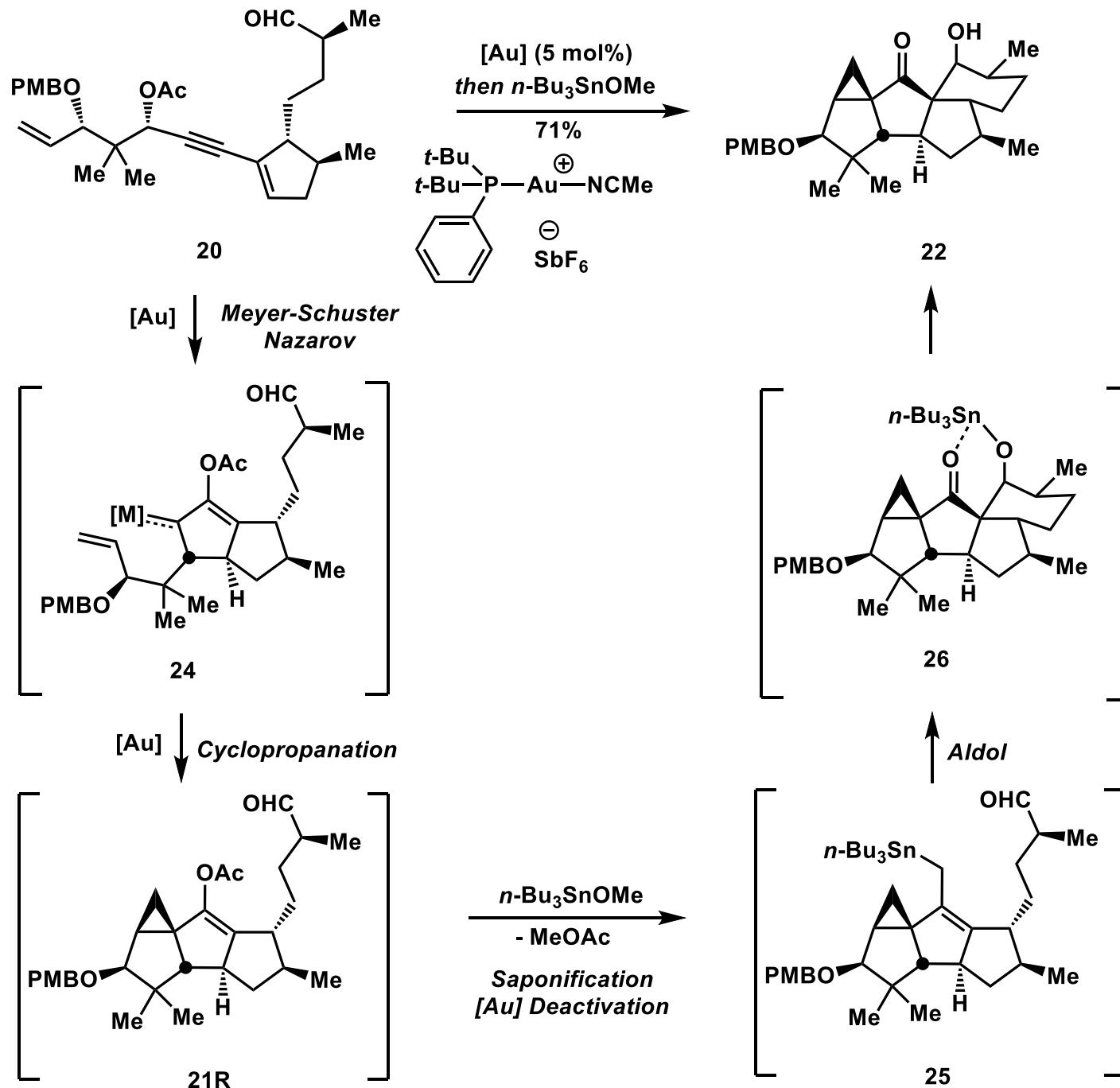
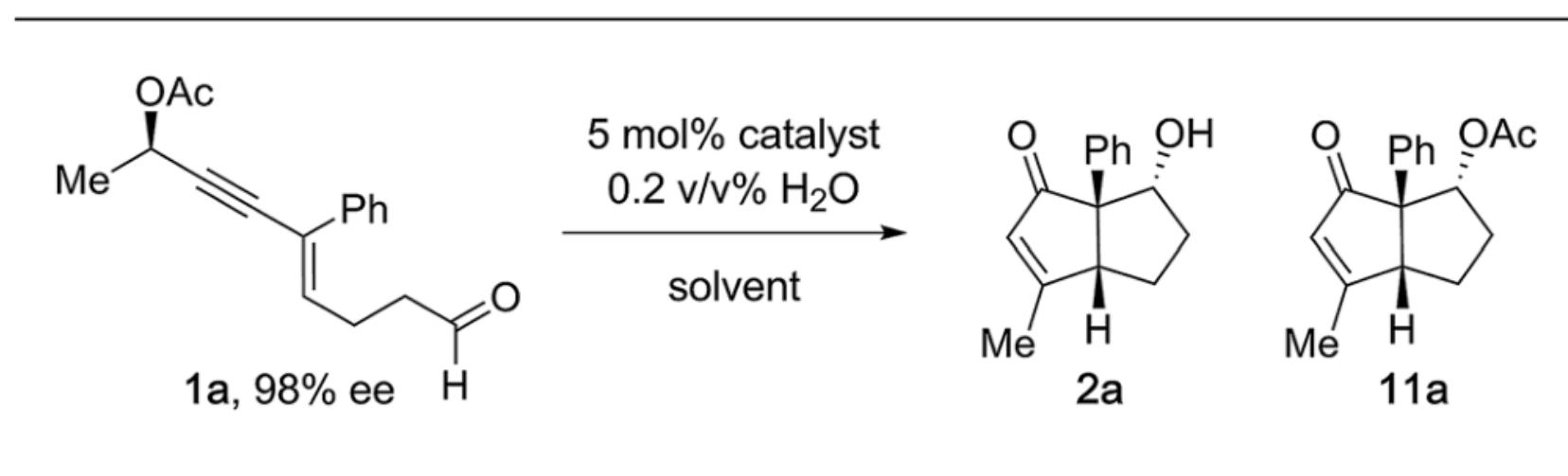
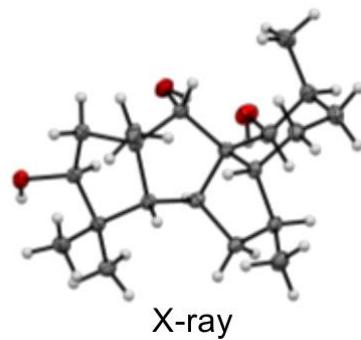
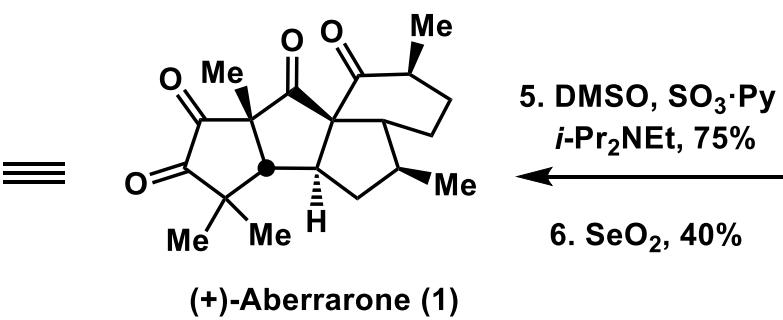
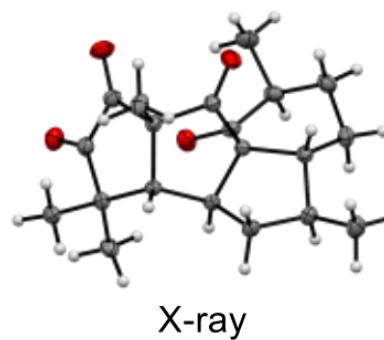
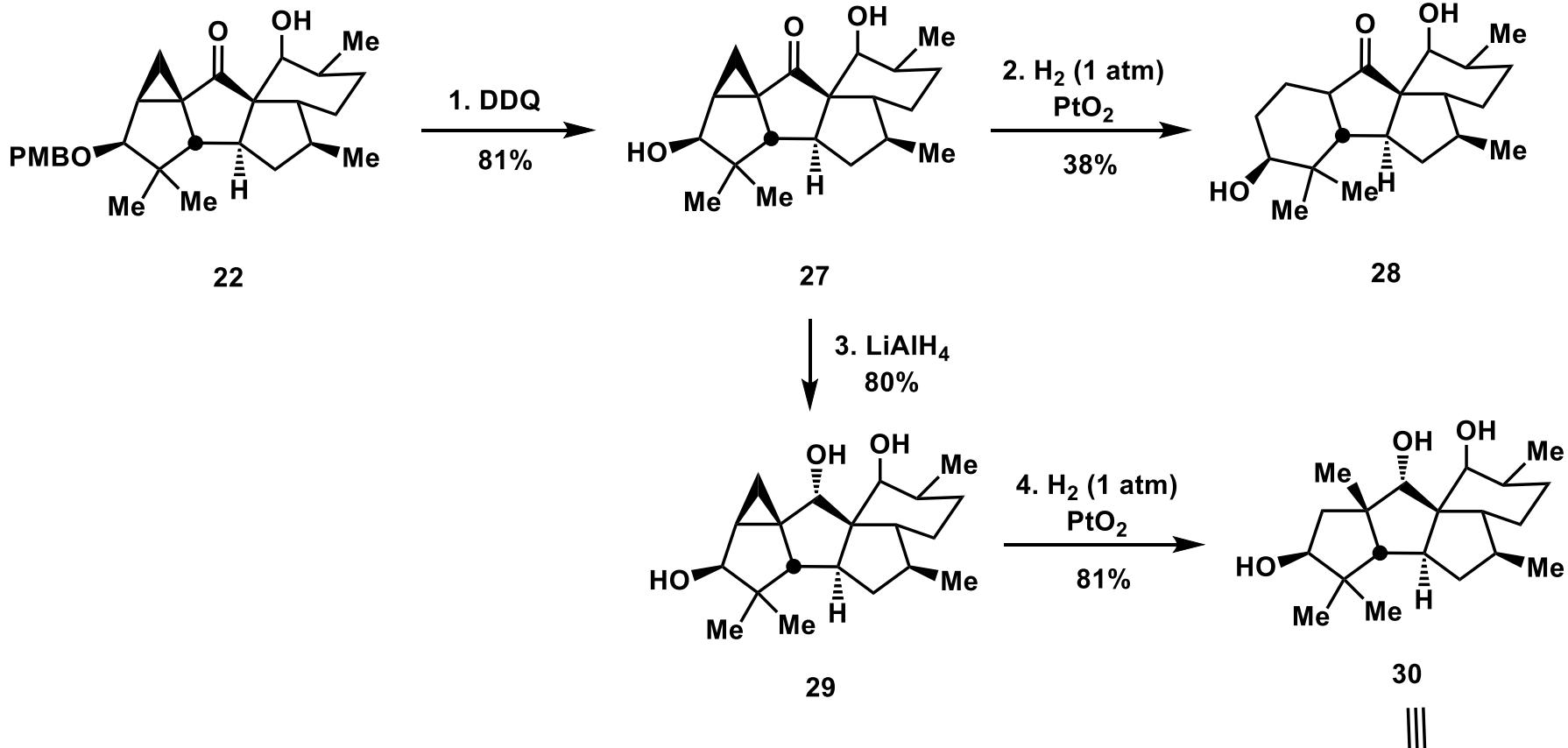


Table 1 Optimization of reaction conditions<sup>a</sup>



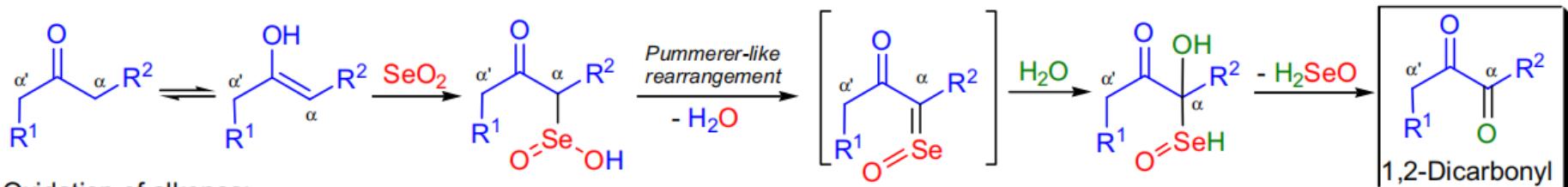
Entry	Catalyst	Solvent	Yield <b>2</b> <sup>b</sup>	Yield <b>11a</b> <sup>b</sup>	ee <sup>c</sup>	d.r.
1	AuCl <sub>3</sub>	THF	42%	—	79%	85 : 15
2 <sup>d</sup>	AuClPPh <sub>3</sub>	THF	67%	—	44%	81 : 19
3 <sup>d</sup>	<b>10</b> <sup>e</sup>	THF	61%	—	67%	81 : 19
4	<b>3</b>	THF	71%	6%	91%	85 : 15
5	<b>3</b>	CH <sub>2</sub> Cl <sub>2</sub>	19%	74%	92%	74 : 26
6	<b>3</b>	Acetone	51%	23%	91%	88 : 12
7	<b>3</b>	Dioxane	50%	18%	91%	60 : 40
8 <sup>f</sup>	<b>3</b>	THF	76%	—	93%	89 : 11



# RILEY SELENIUM DIOXIDE OXIDATION

Mechanism: <sup>24-41</sup>

Oxidation of carbonyl compounds:



Oxidation of alkenes:

