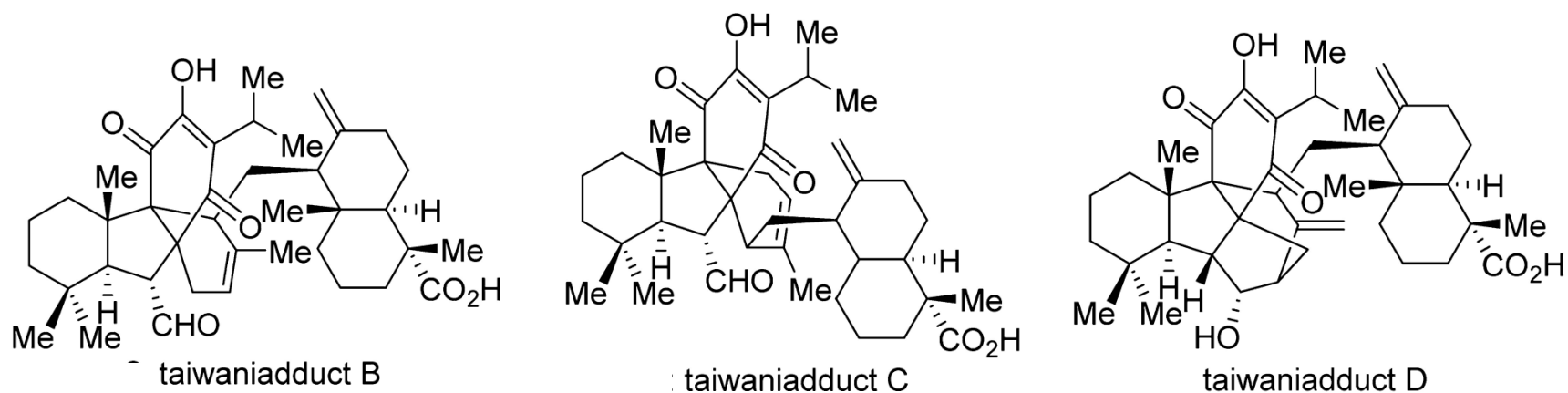


Total Synthesis of Taiwaniadducts B, C, and D

Jun Deng , Shupeng Zhou , Wenhao Zhang , Jian Li , Ruofan Li , and Ang Li

J. Am. Chem. Soc., **2014**, *136* (23), pp 8185–8188



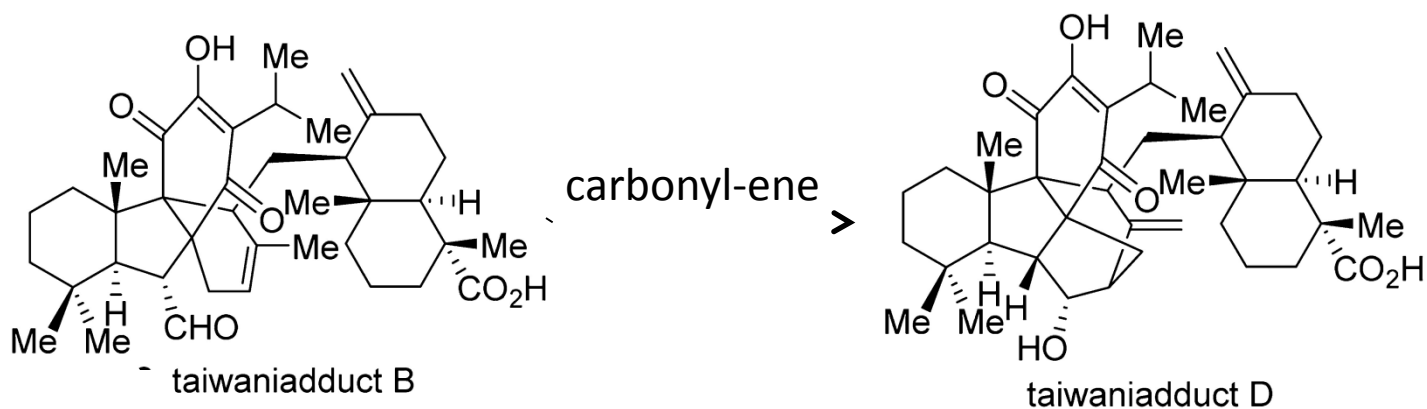
Liming Cao

Wipf Group Current Literature

7/5/2014

Taiwaniadducts

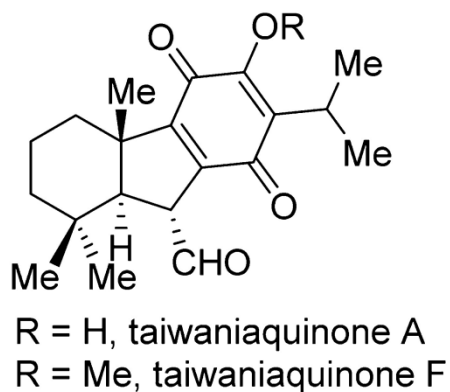
- Taiwaniaquinoids are a class of terpenoids isolated from the endangered species *Taiwania cryptomerioides*.
- Taiwaniadducts possess a characteristic Diels–Alder cycloadduct scaffold.



<http://www.iucnredlist.org/details/31255/0>

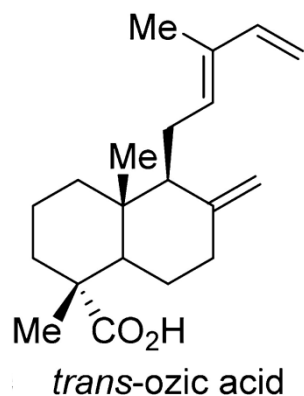
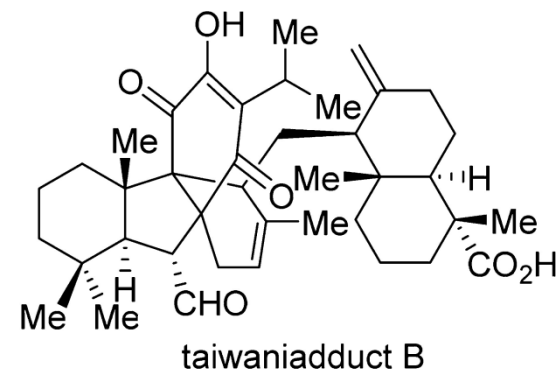
J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

Biosynthetic hypothesis

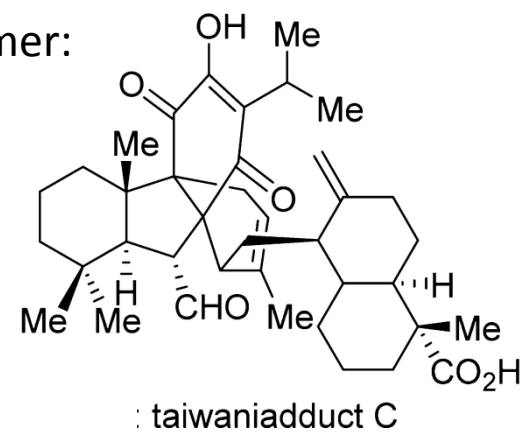


Diels–Alder

>



Regioisomer:

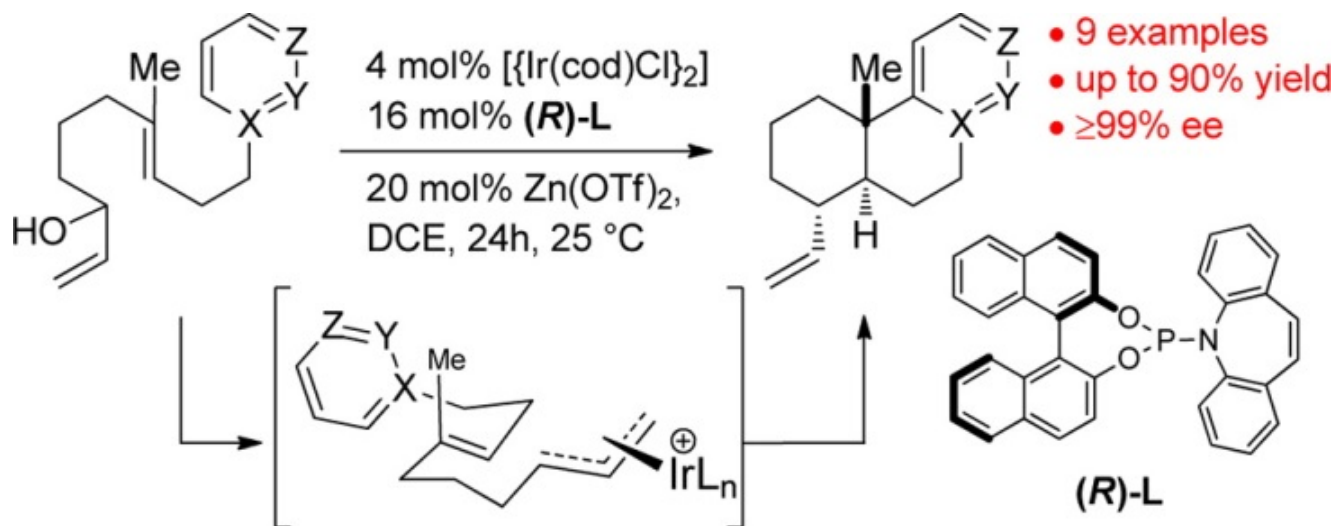


J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

Previous Work

- Iridium-Catalyzed Enantioselective Polyene Cyclization

Carreira:

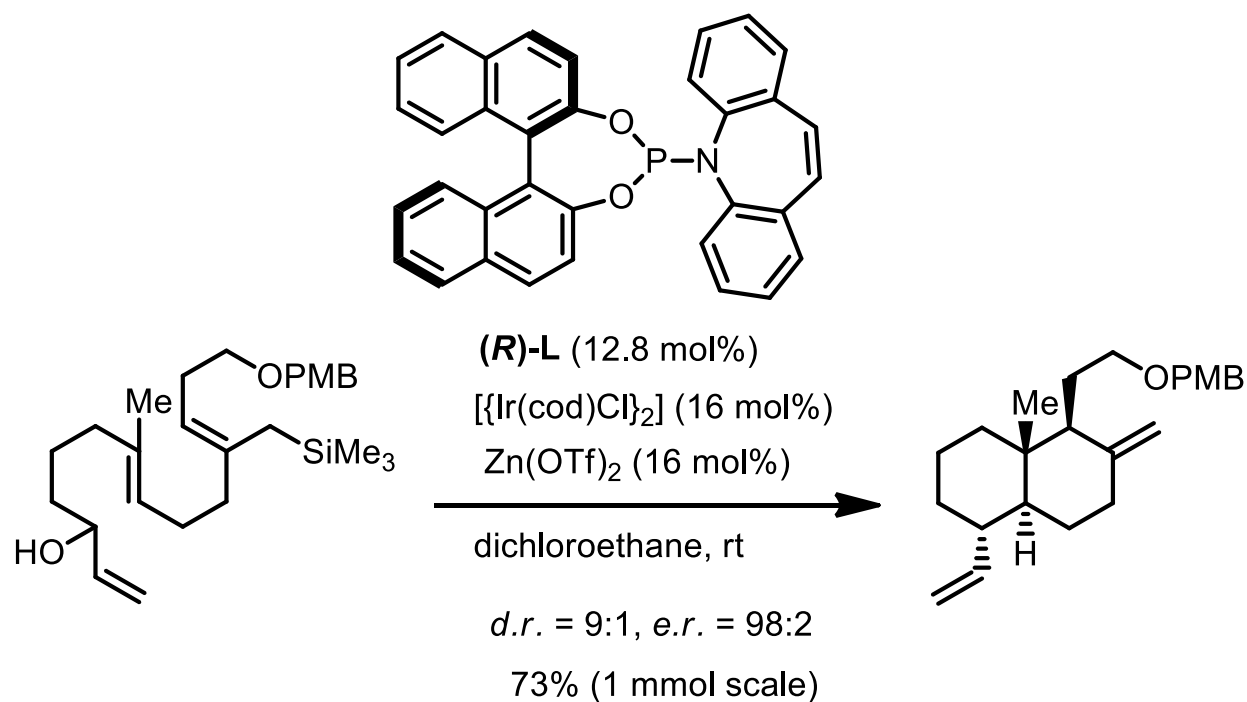


J. Am. Chem. Soc., **2012**, 134 (50), pp 20276–20278

Previous Work

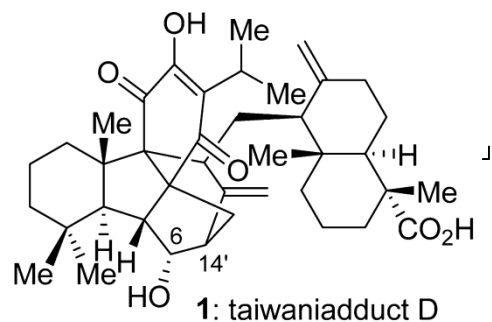
- Total Synthesis of (+)-Asperolide C by Iridium-Catalyzed Enantioselective Polyene Cyclization

Carreira:

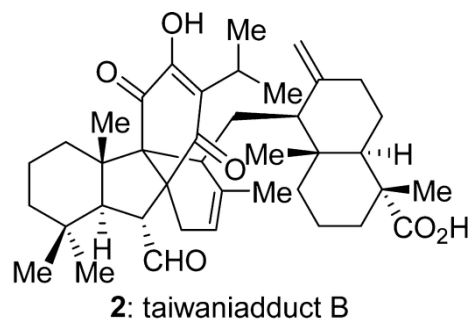


Angew. Chem., Int. Ed. **2013**, 52, 12166

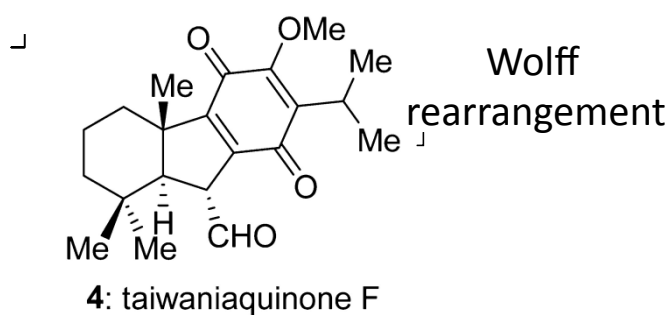
Retrosynthetic Analysis



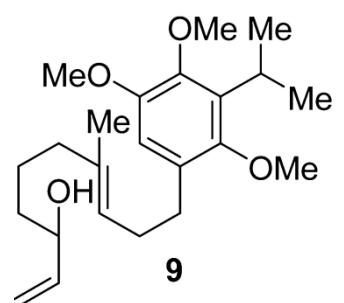
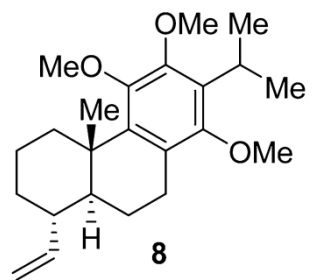
carbonyl-ene



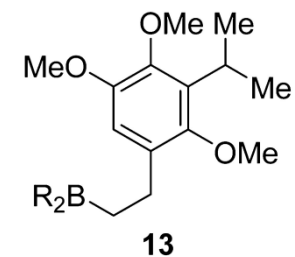
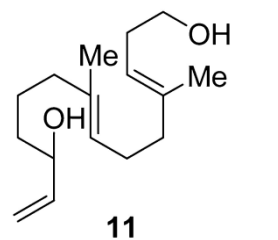
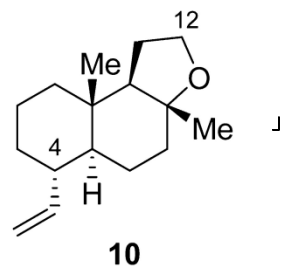
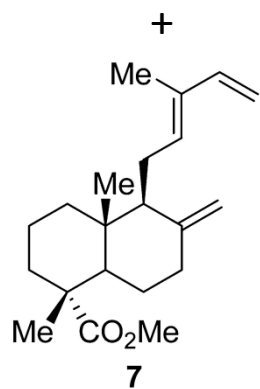
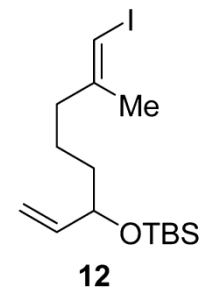
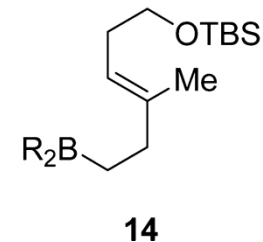
Diels-Alder



Wolff rearrangement

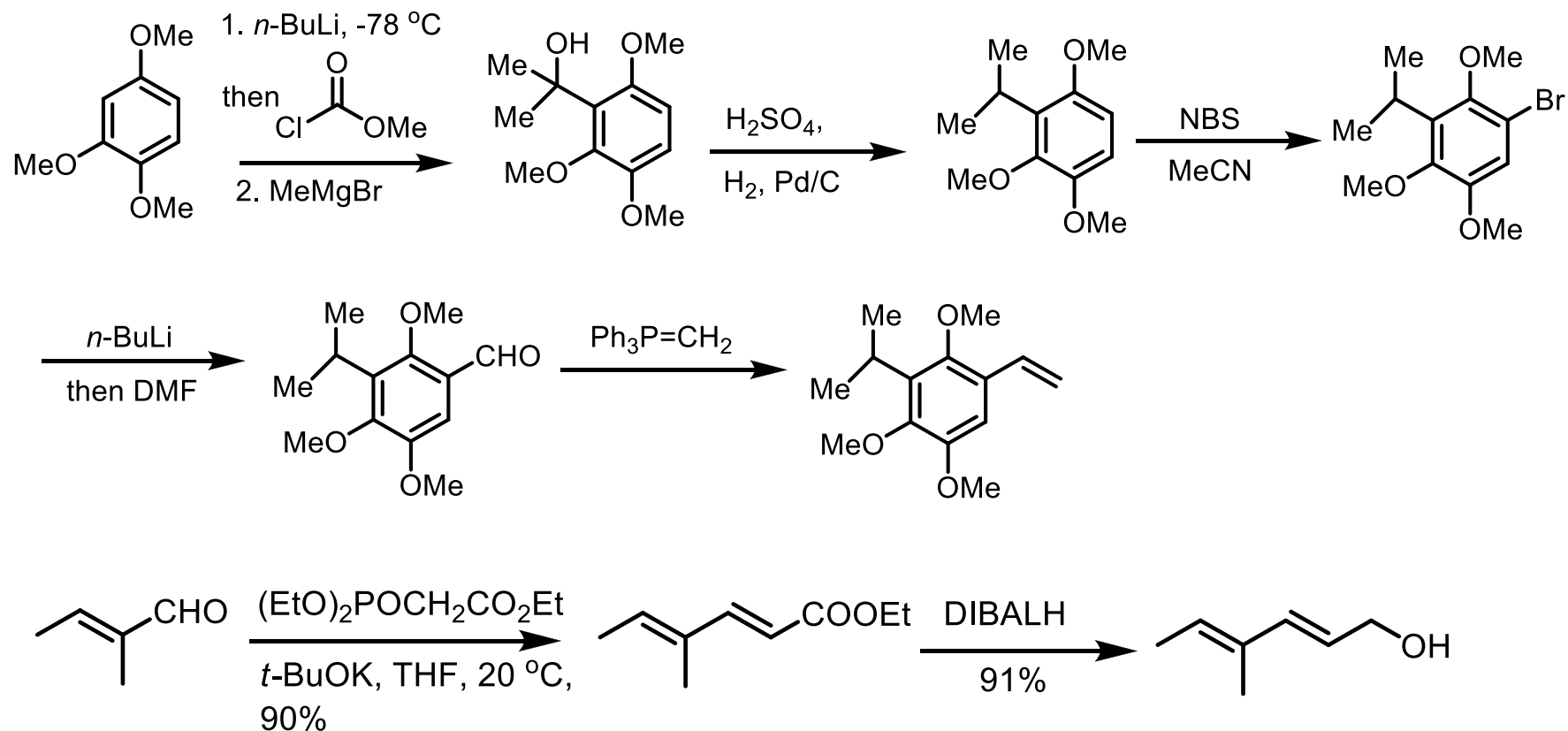


Ir-catalyzed asymmetric polyene cyclization



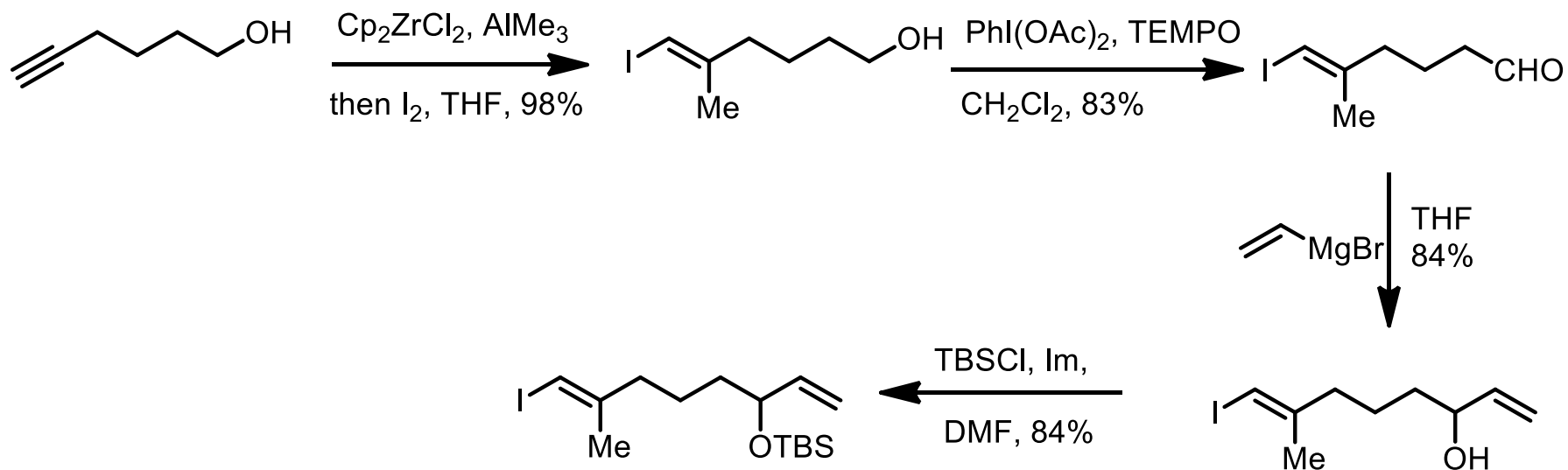
J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

Starting Material



Tetrahedron: Asymmetry, **1997**, *8*, 913-921
Organic Letters, **2013**, *15*, 2022-2025
Tetrahedron **1990**, *46*, 2187-94.
Org. Lett. **2000**, *2*, 1831

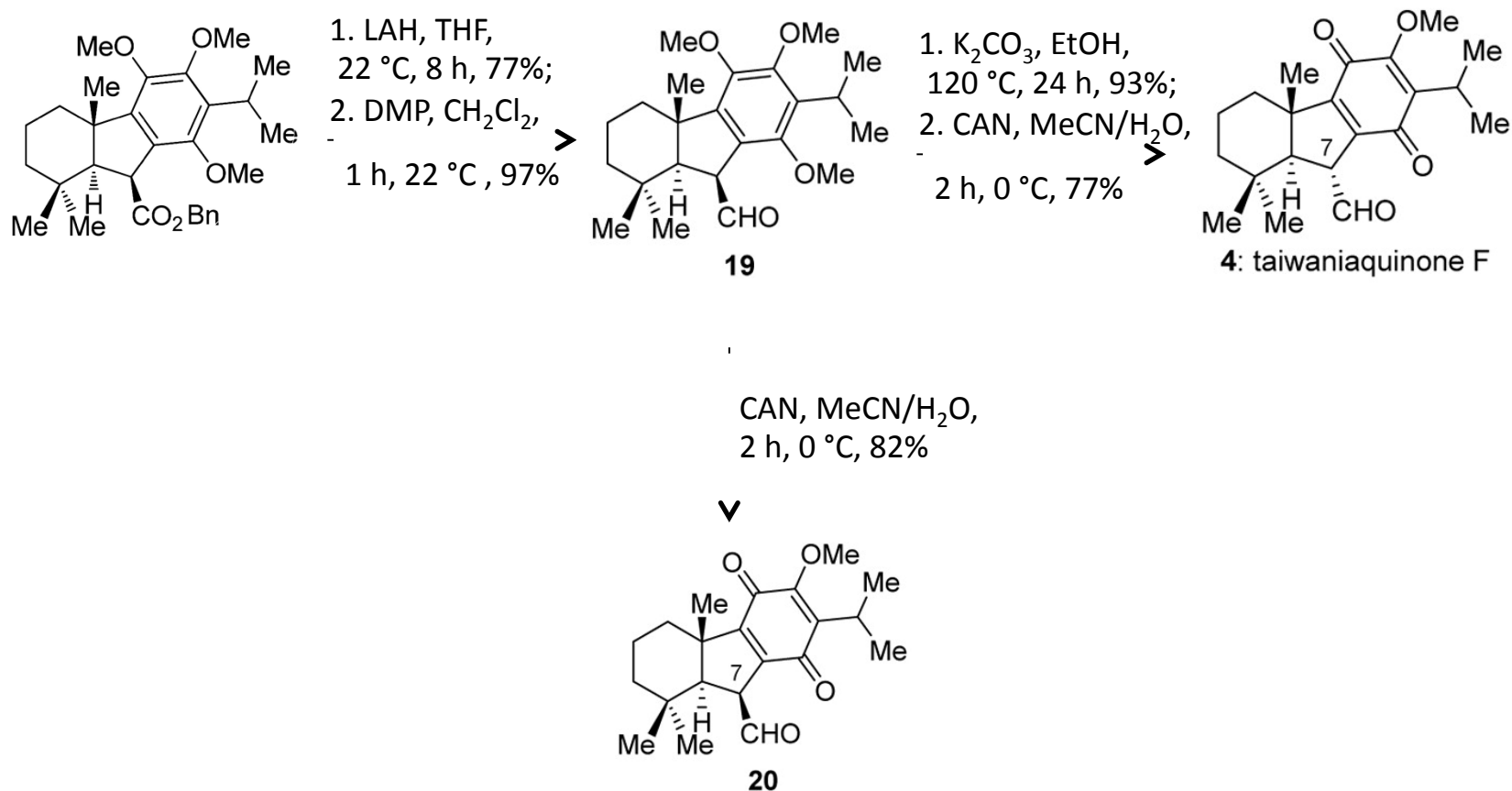
Starting Material



J. Am. Chem. Soc., **2005**, 127 (48), pp 16778–16779

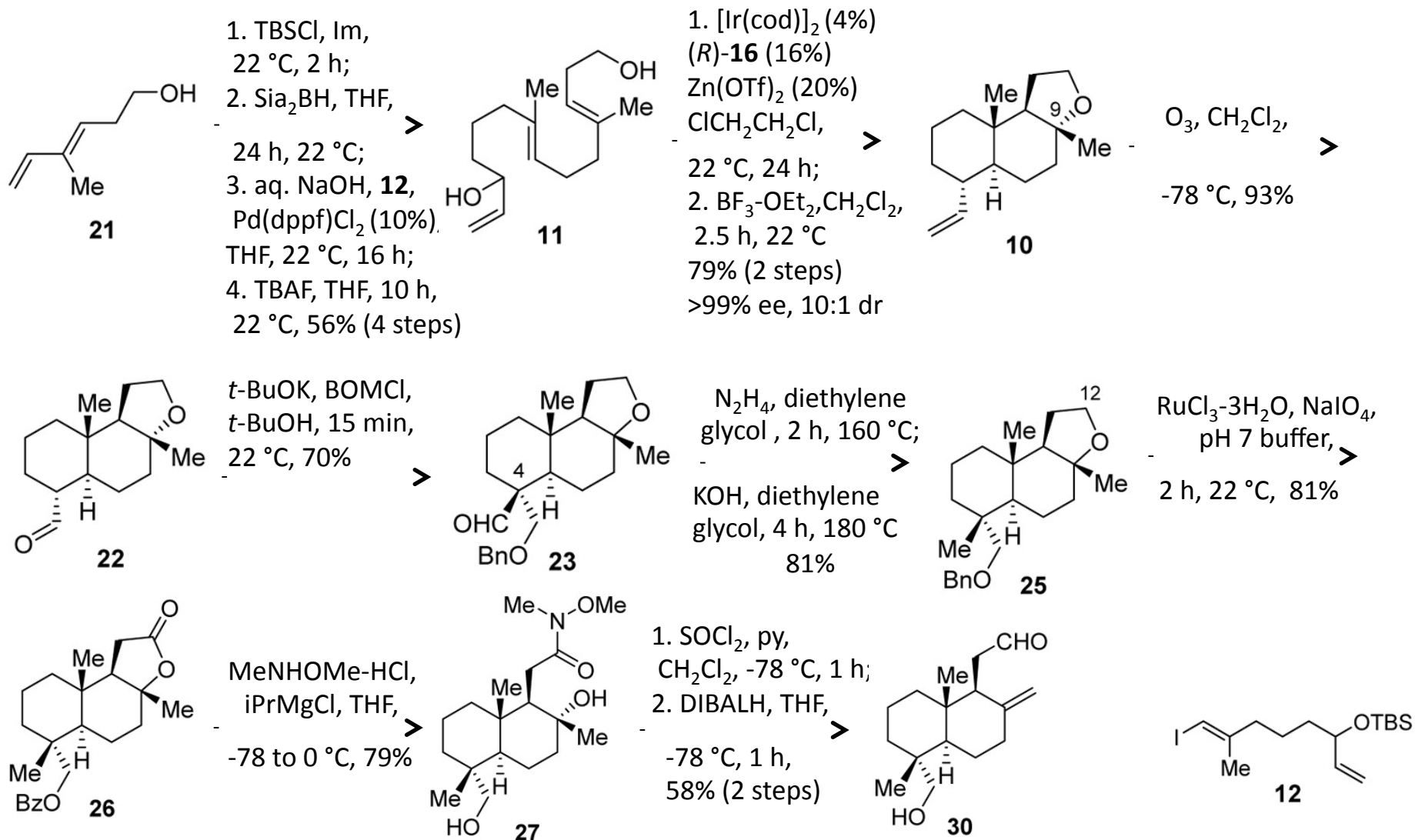
J. Am. Chem. Soc., **2012**, 134 (50), pp 20276–20278

Synthesis of the Dienophile through Ir-Catalyzed Asymmetric Polyene Cyclization



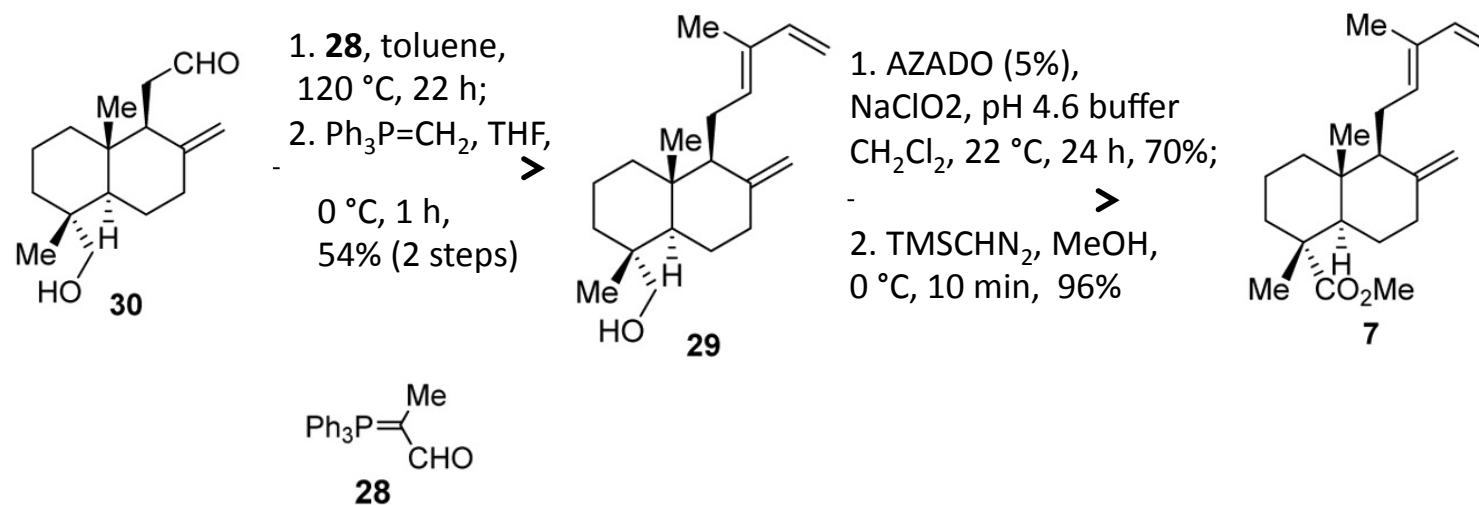
J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188
Org. Lett. **2013**, *15*, 2022

Synthesis of the Diene through Ir-Catalyzed Asymmetric Polyene Cyclization



J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

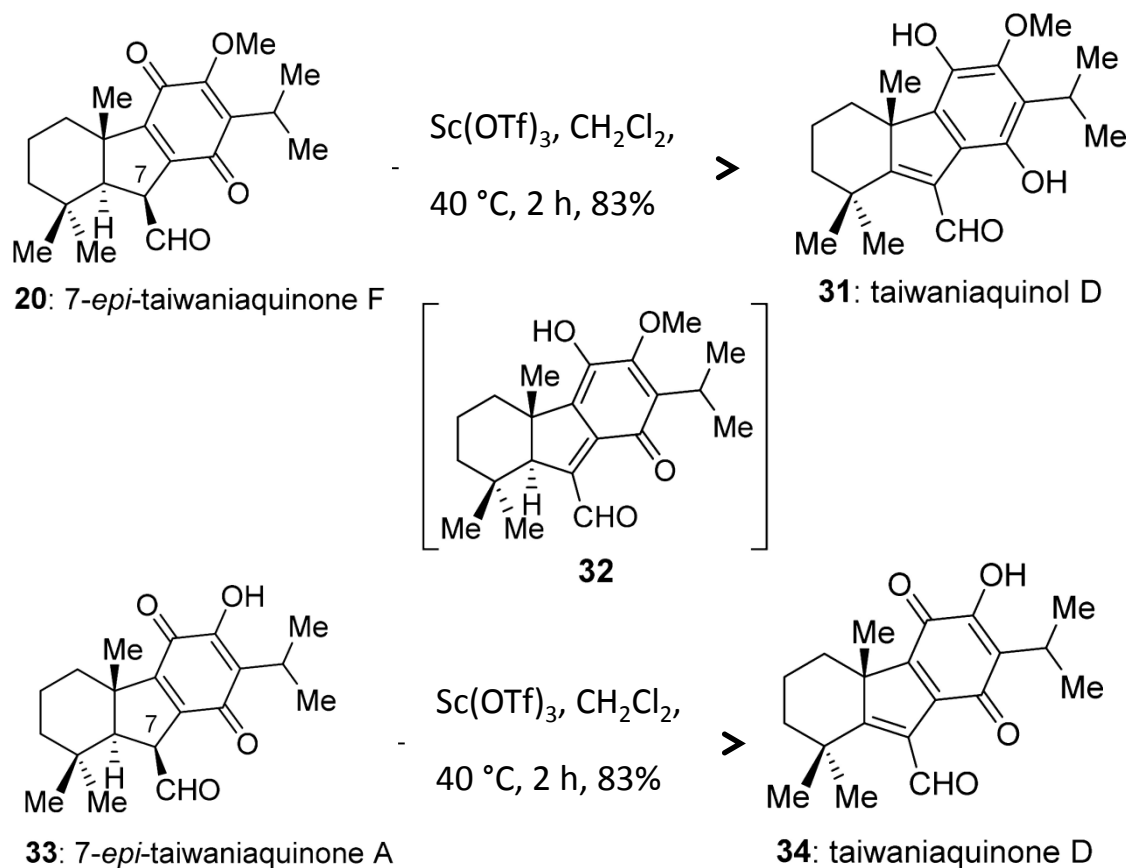
Synthesis of the Diene through Ir-Catalyzed Asymmetric Polyene Cyclization



J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

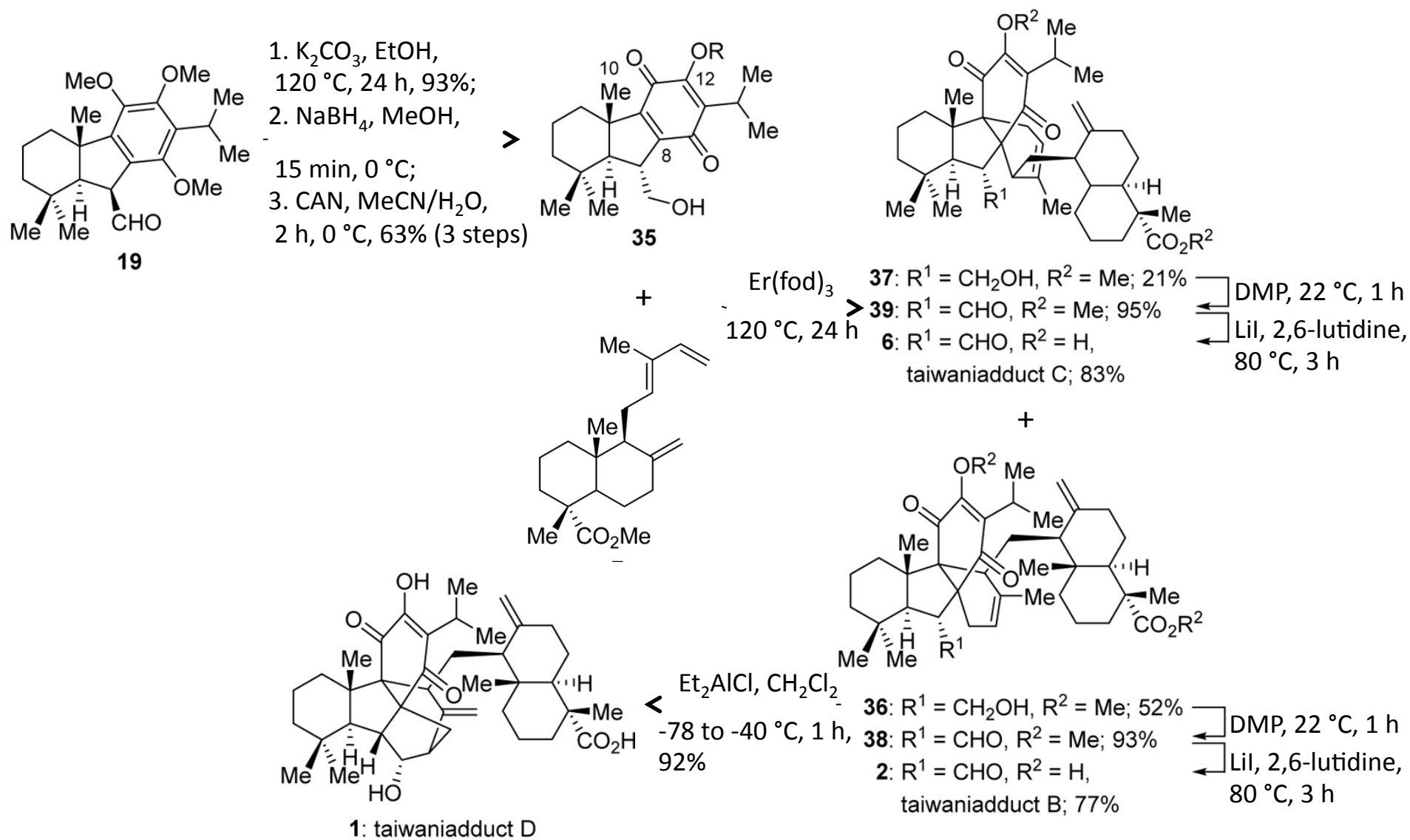
Unexpected Reactions of 7-*epi*-Taiwaniaquinones A and F under Acidic Conditions

- Conventional conditions, such as thermal, acidic, neat, and high-pressure conditions, failed to effect the cycloaddition.



J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

Intermolecular Diels–Alder Reaction and Completion of the Total Synthesis of Taiwaniadducts B, C, and D



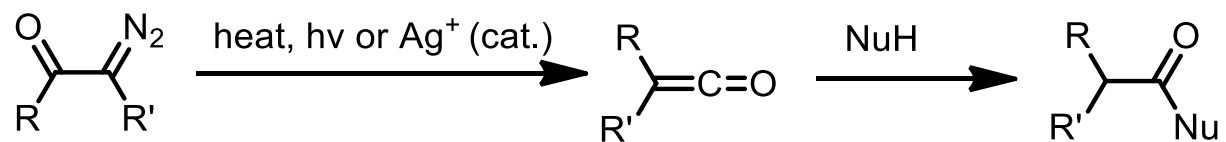
J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

Conclusion

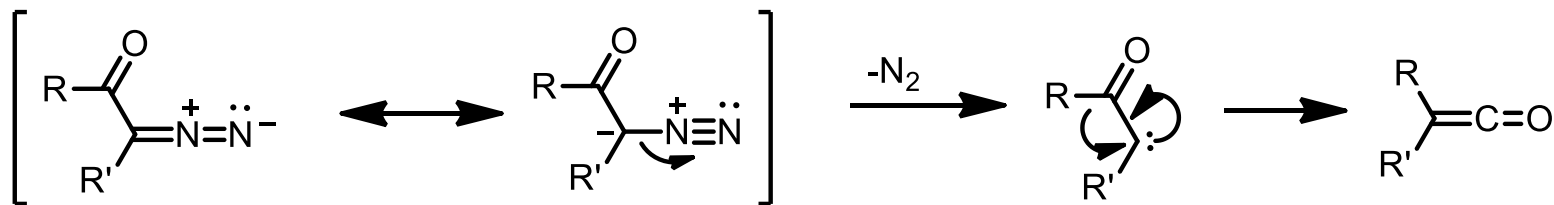
- The first total synthesis of taiwaniadducts B, C, and D have been accomplished.
- Ir-catalyzed asymmetric polyene cyclization was exploited to construct the scaffolds of both the diene and dienenophile.
- Er(fod)₃ promoted intermolecular Diels–Alder and Me₂AlCl mediated carbonyl-ene reactions forged the core of taiwaniadducts D.

J. Am. Chem. Soc., **2014**, *136* (23), 8185–8188

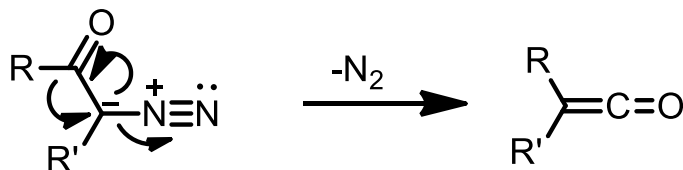
Wolff Rearrangement



Stepwise:



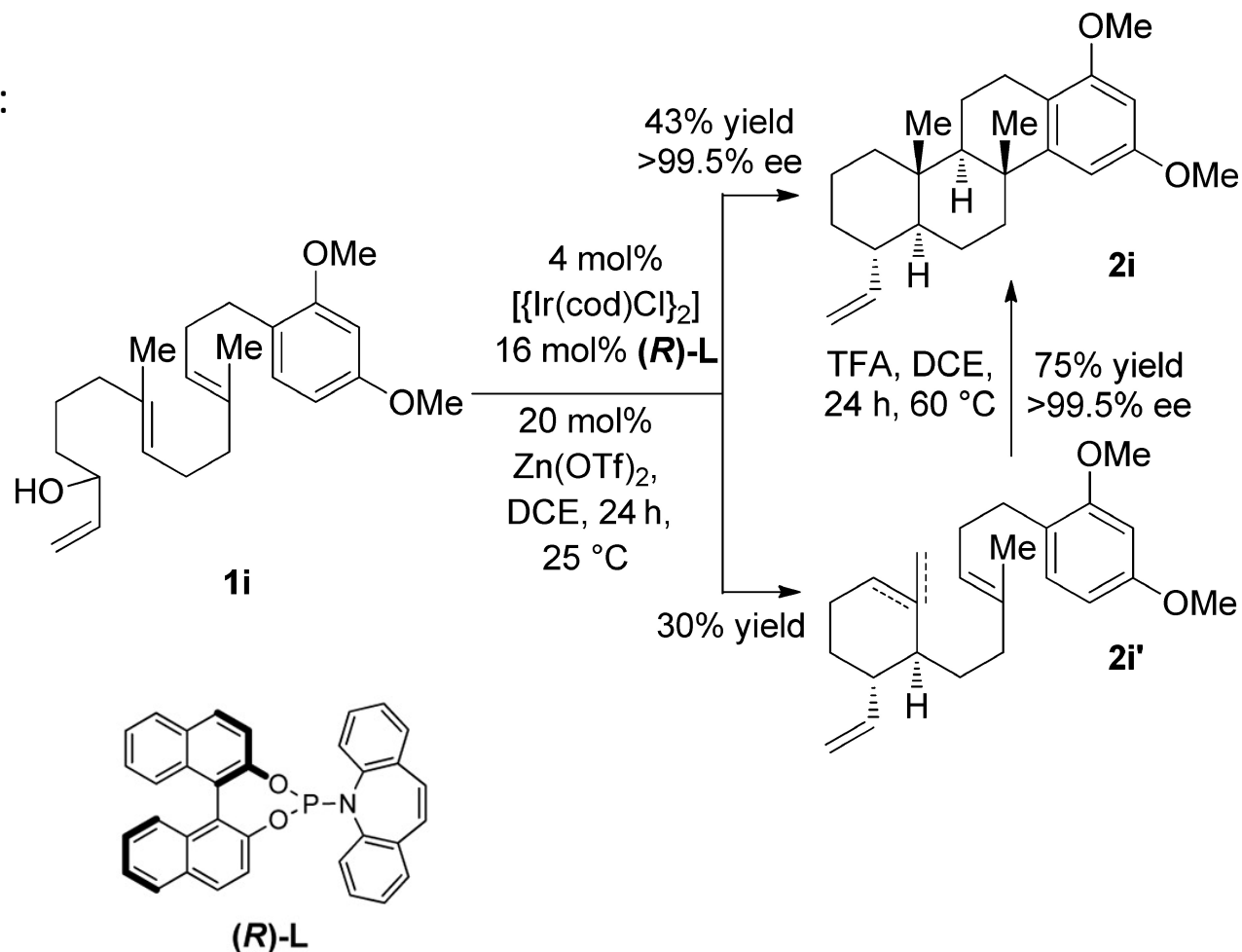
Concerted:



J. Org. Chem. **2002**, *67*, 1574-1579

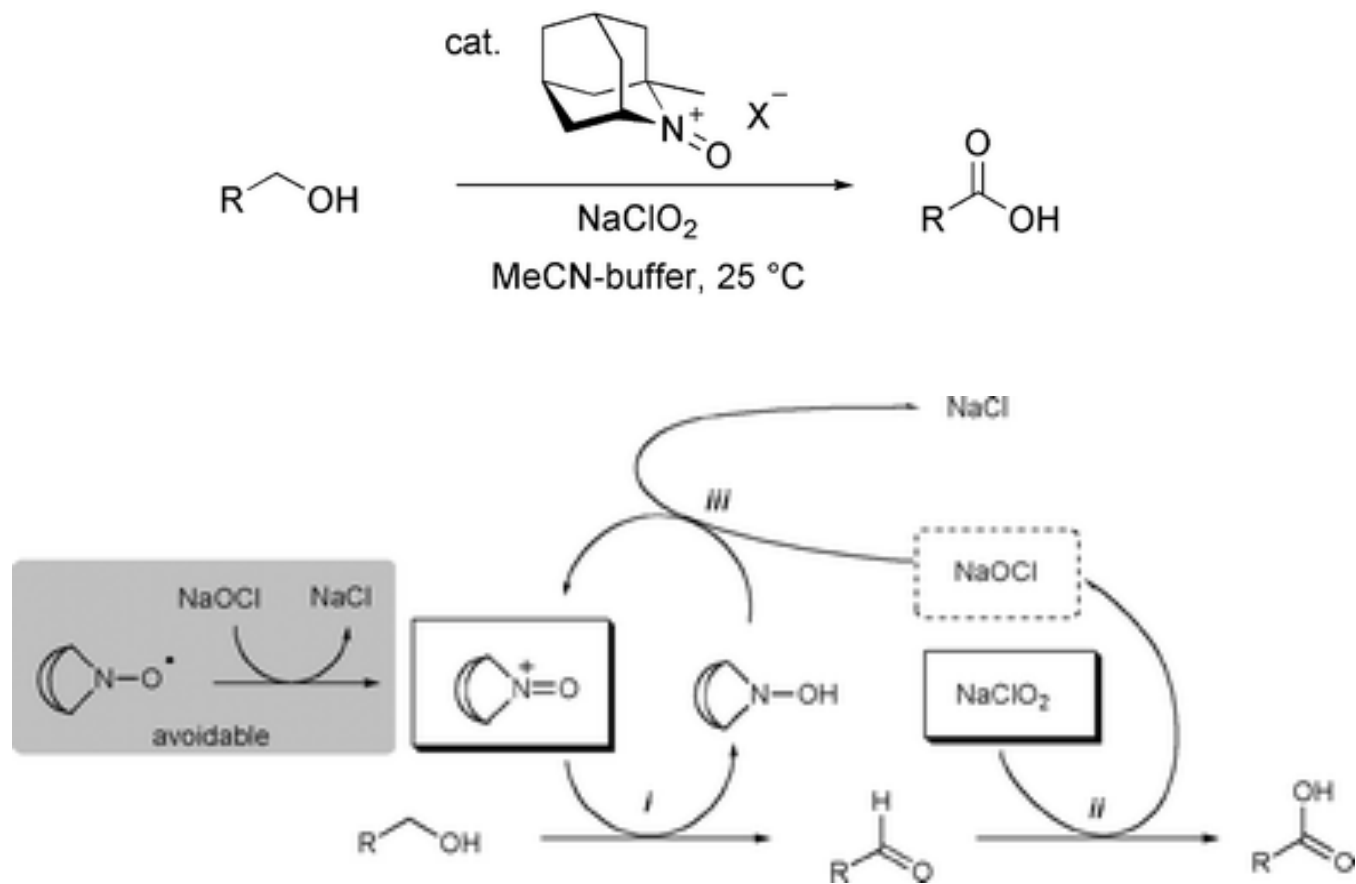
Iridium-Catalyzed Enantioselective Polyene Cyclization

Carreira:



J. Am. Chem. Soc., **2012**, 134 (50), pp 20276–20278

Oxoammonium salt/ NaClO_2 : an expedient, catalytic system for one-pot oxidation of primary alcohols to carboxylic acids



Chem. Commun., 2009, 1739-1741