

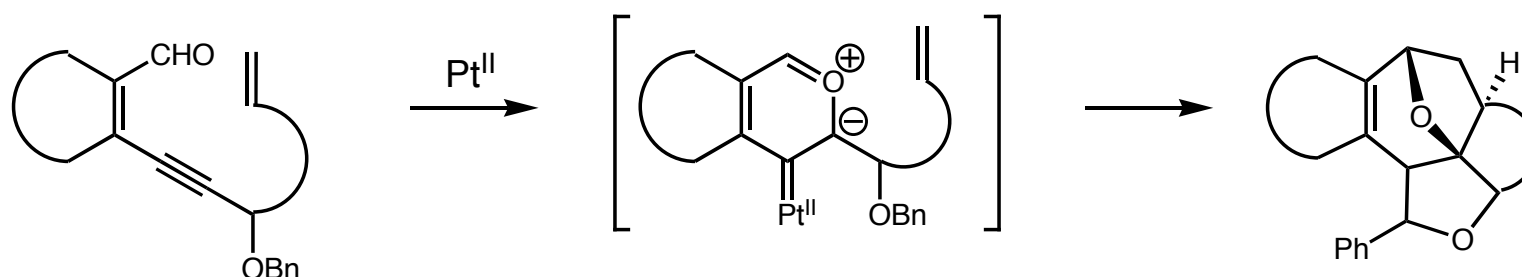
# ***Intramolecular Huisgen-Type Cyclization of Platinum-Bound Pirylium Ions with Alkenes and Subsequent Insertion into a Benzylic C-H Bond***

Chang Ho Oh,\* Ji Ho Lee, Su Jin Lee, Jae Il Kim, and Chang Seop Hong

Department of Chemistry, Hanyang University, Seoul, Korea

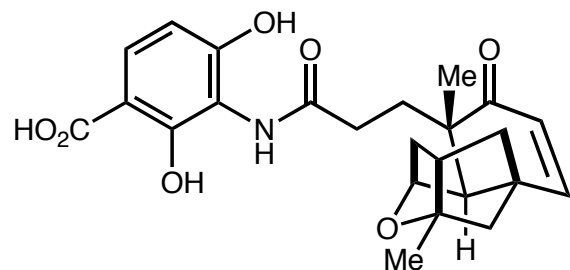
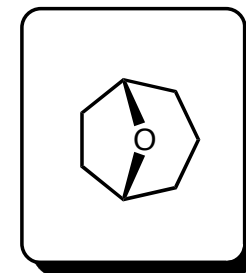
*Angewandte Chemie International Edition*, **2008**, 47, early view.

DOI: 10.1002/anie.200802425



*Wipf Group Saturday Morning Meeting  
Current Literature Abstracts & Reports  
Rob Lettan August 30<sup>th</sup>, 2008*

## Oxabicyclo[3.2.1]octanes in Natural Products

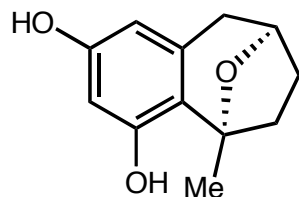


platensimycin

broad spectrum Gram-positive antibiotic

Synthesized by:

Nicolaou (2006, racemic)  
(2007, 2008 asymmetric)  
Snider (2007, formal, racemic)  
E. Lee (2008, formal)

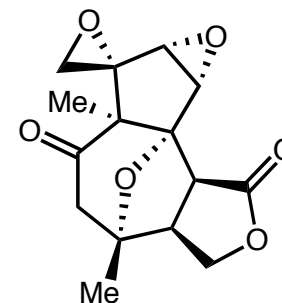


bruguierol C

showed moderate activity against Gram-positive and Gram-negative bacteria

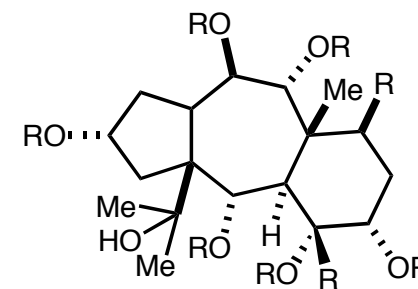
Synthesized by:

Jennings (2007)  
Ramana (2007, bruguierol A)



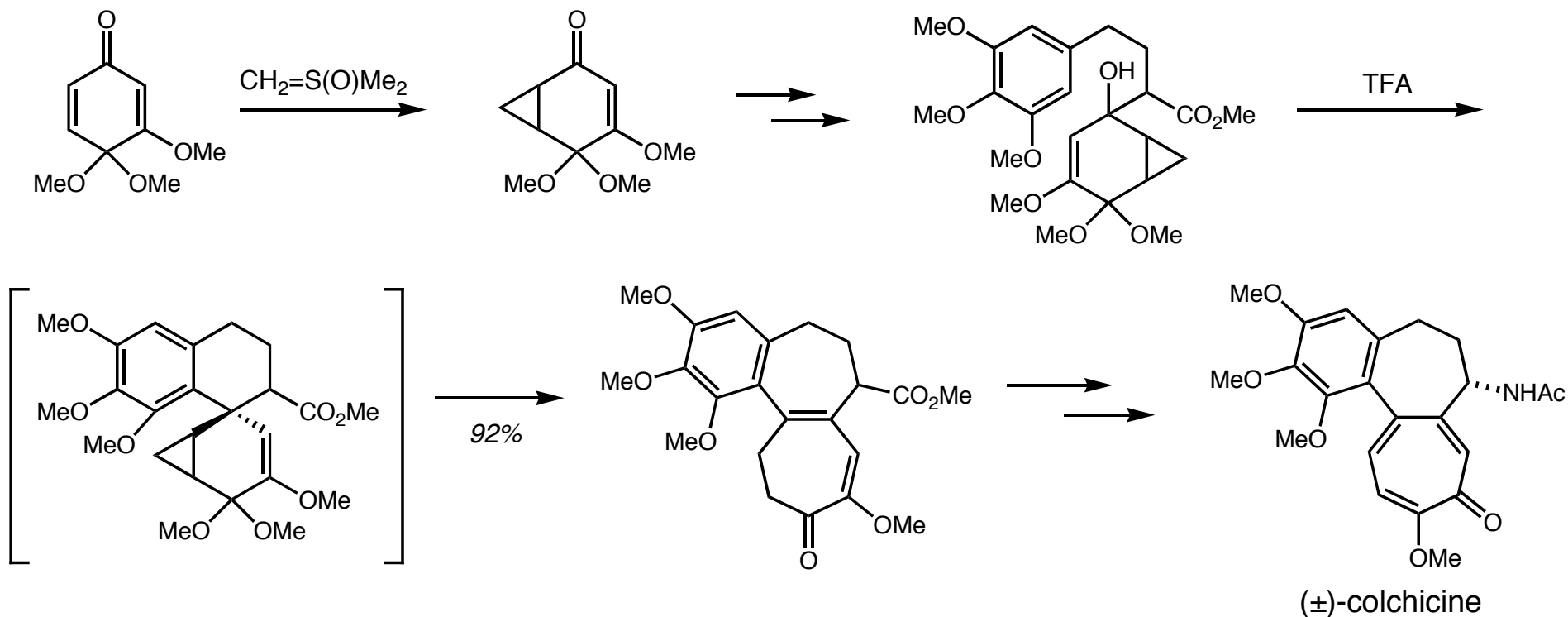
corianlactone

no remarkable inhibition towards  $K_{562}$  cells  
cytotoxic,  $IC_{50} > 50 \mu\text{g/mL}$

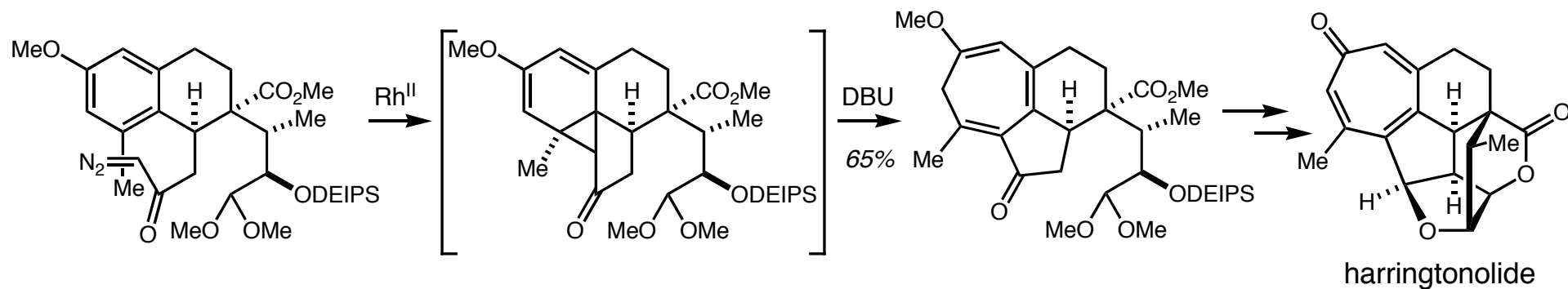


Taxane diterpenoids  
anti-cancer

## Strategies for the Construction of 7-Membered Carbocycles: [6C + 1C] Approach

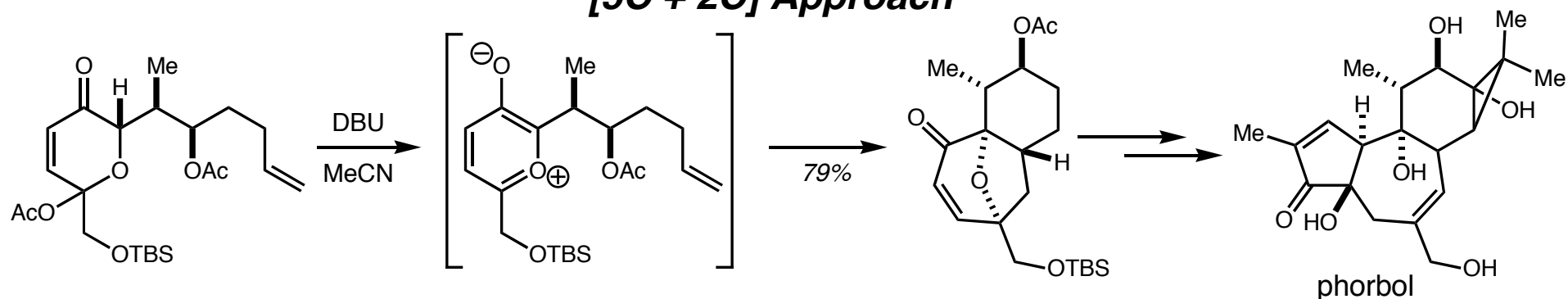


Evans, D. A., et al. *J. Am. Chem. Soc.* **1981**, *103*, 5813-5821.



Mander, L. N., et al. *Aust. J. Chem.* **2000**, *53*, 819-830.

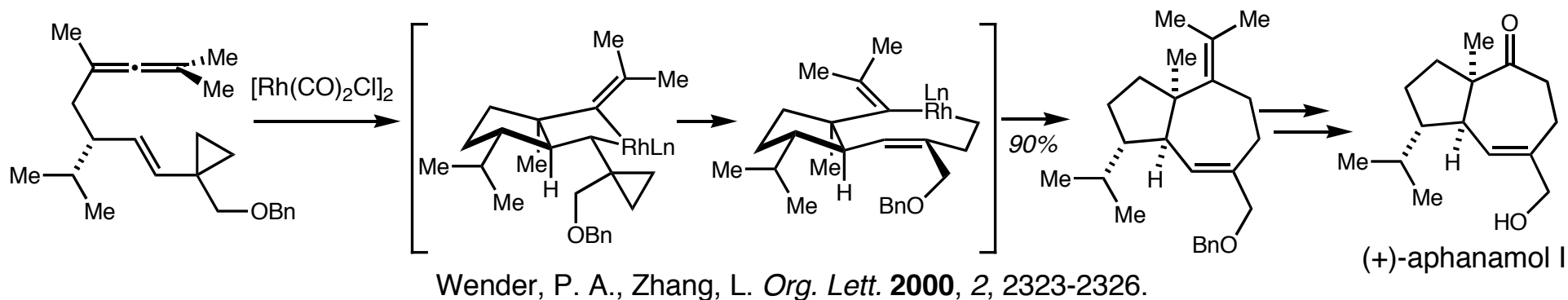
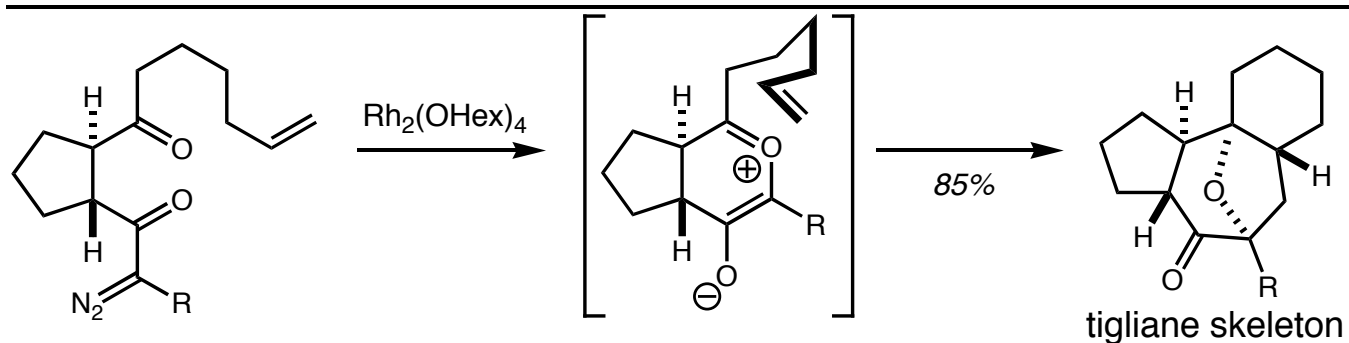
## Strategies for the Construction of 7-Membered Carbocycles: [5C + 2C] Approach



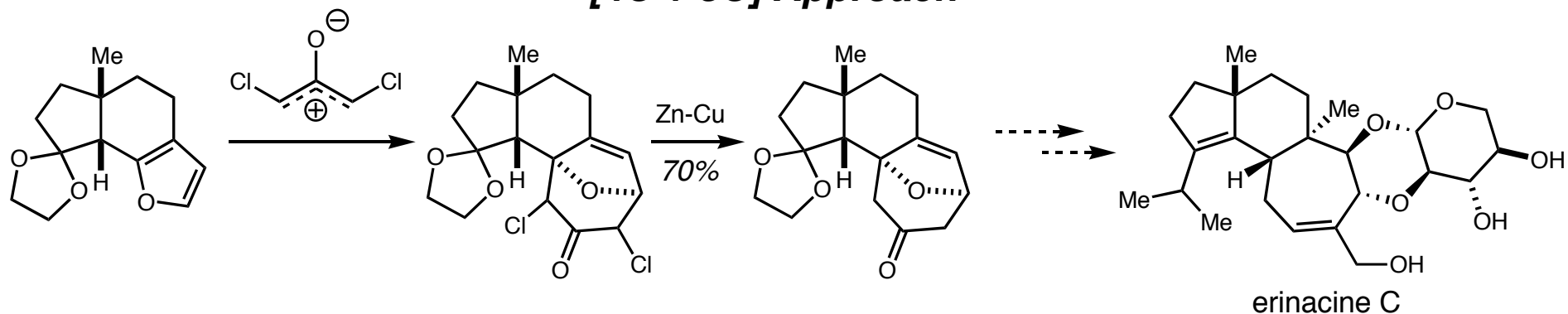
This approach was also used by many others in natural product syntheses:

P. Magnus (guanacastepene, taxanes), J. E. Baldwin (cordytropolone: alkyne trap), and Snider (cartorimine: unsat. ester)

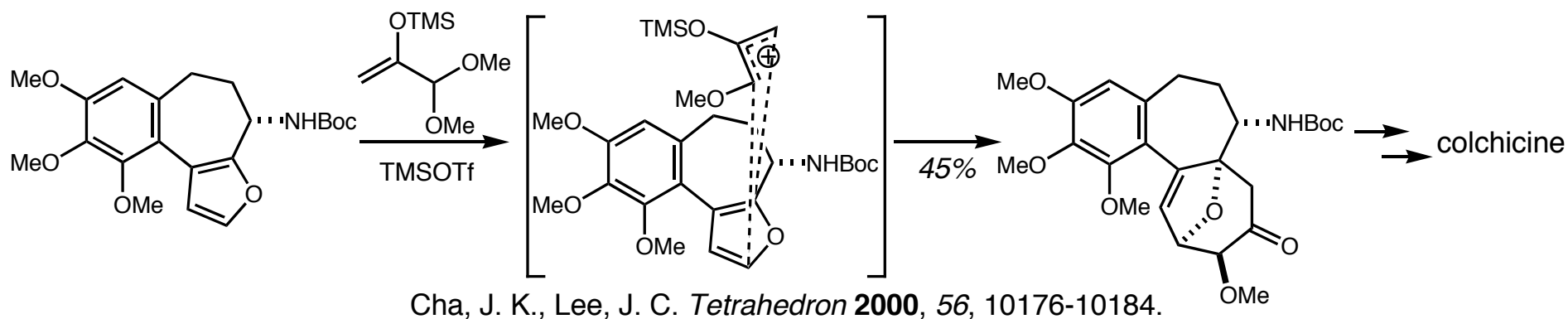
Review: Wright, D. L., et al. *Chem. Eur. J.* **2006**, *12*, 3438-3447.



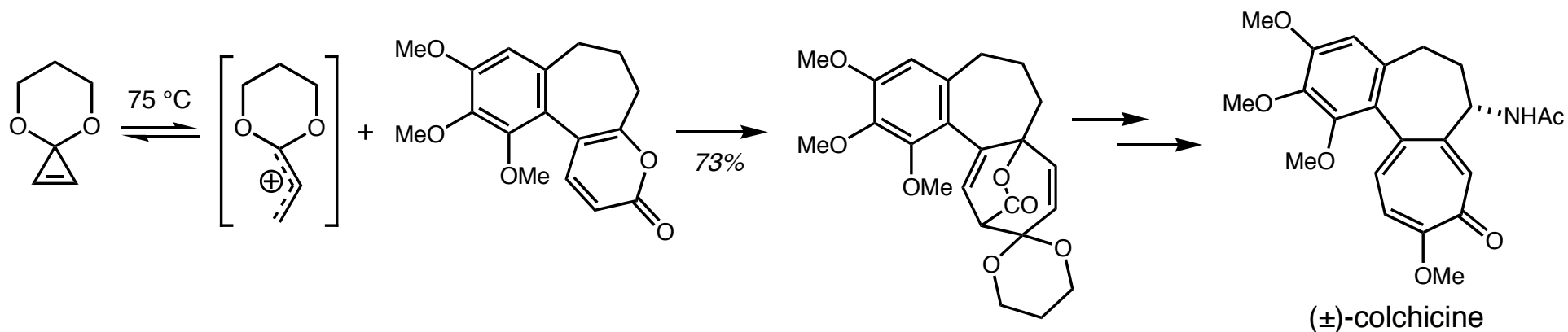
## Strategies for the Construction of 7-Membered Carbocycles: [4C + 3C] Approach



Wright, D. L., et al. *J. Org. Chem.* **1999**, *1*, 1535-1538

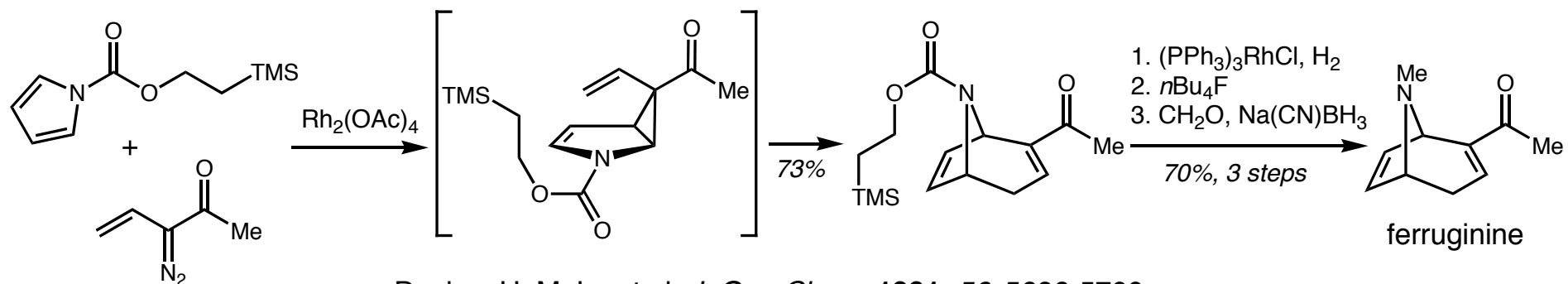


Cha, J. K., Lee, J. C. *Tetrahedron* **2000**, *56*, 10176-10184.

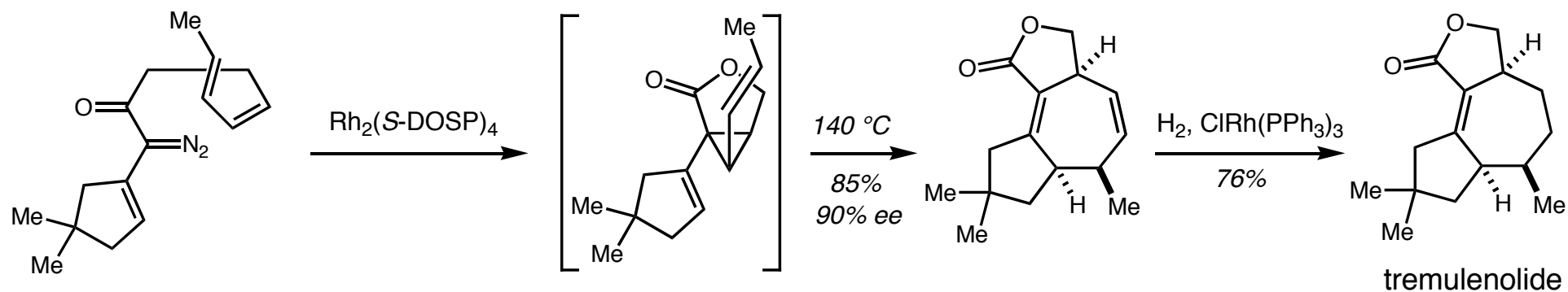


Boger, D. L., Brotherton, C.E. *J. Am. Chem. Soc.* **1986**, *108*, 6713-6719.

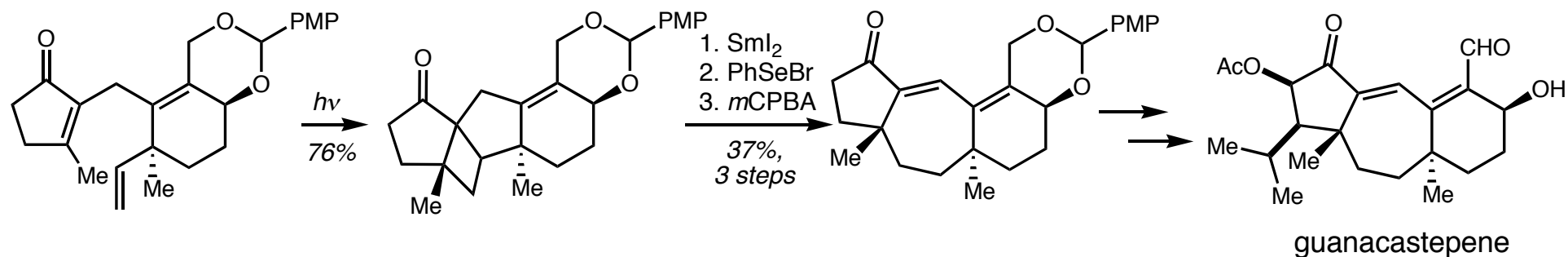
## Strategies for the Construction of 7-Membered Carbocycles: Alternative Approaches



Davies, H. M. L., et al. *J. Org. Chem.* **1991**, *56*, 5696-5700.

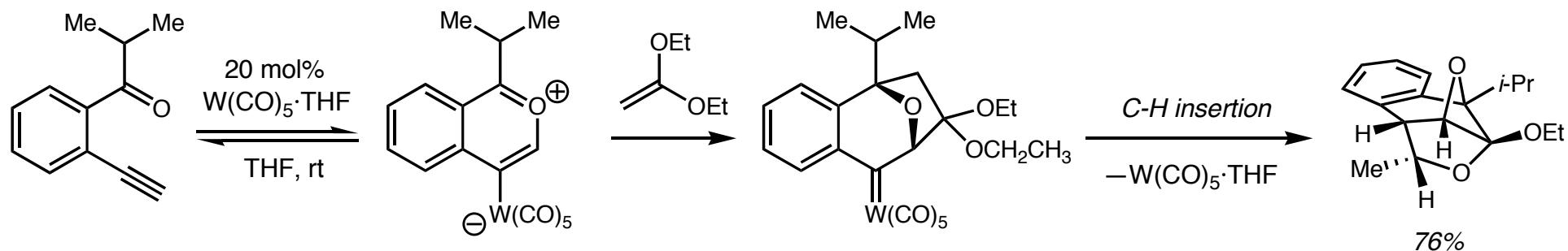


Davies, H. M. L., Doan, B. D. *Tet. Lett.* **1996**, *37*, 3967-3970.

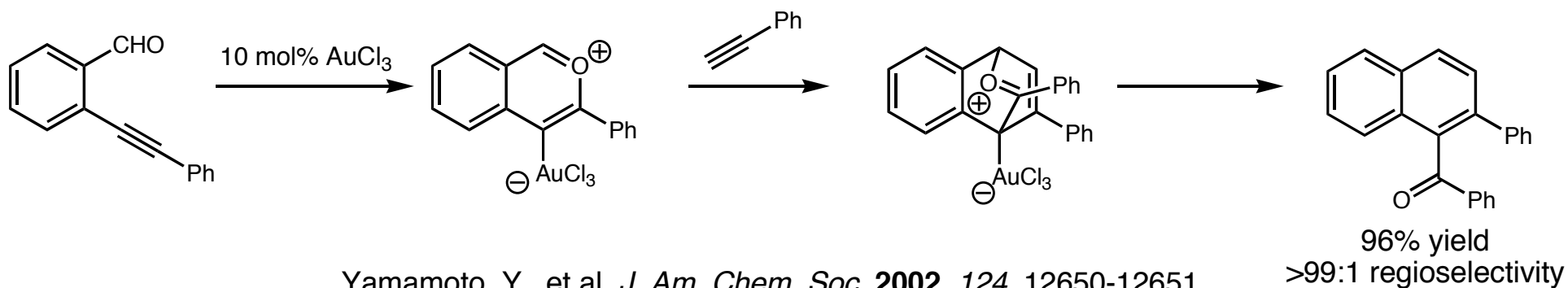


Sorenson, E. J., Shipe, W. D. *Org. Lett.* **2002**, *4*, 2063-2066.

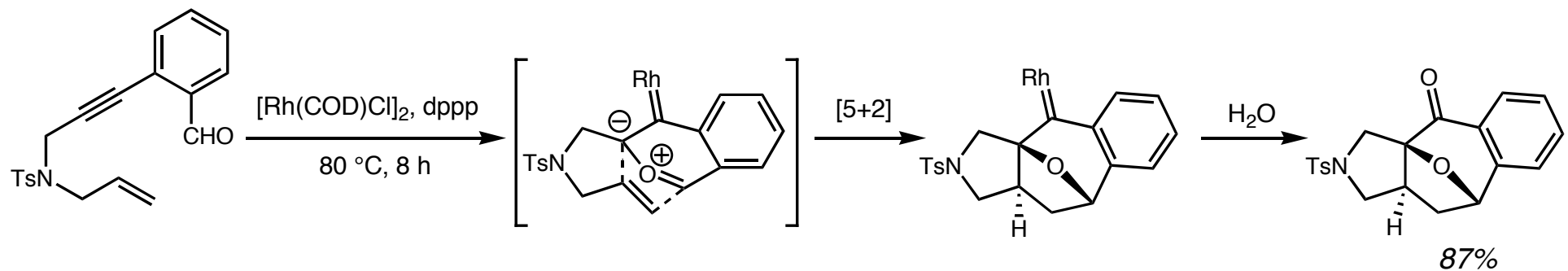
## Transition-Metal Catalyzed Cyclization of Pirylium Ions with Alkenes/Alkynes



Iwasawa, N. et al. *J. Am. Chem. Soc.* **2001**, *123*, 5814-5815.

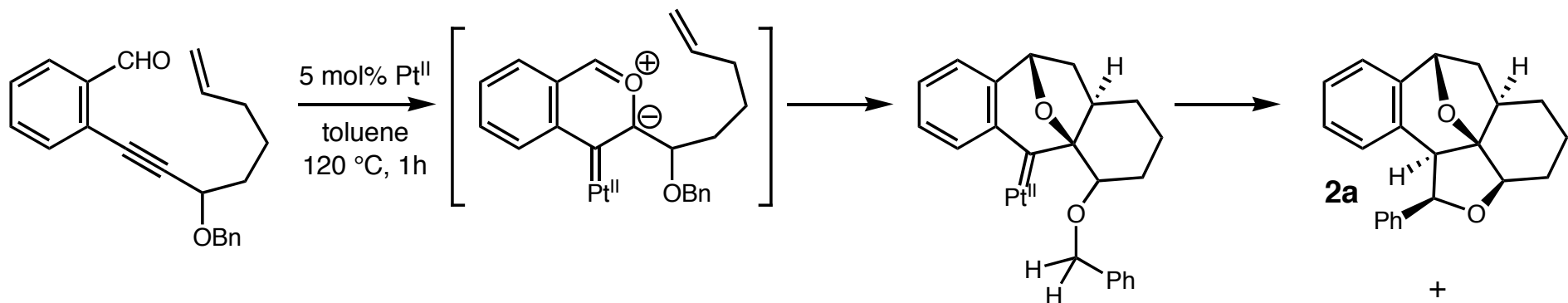


Yamamoto, Y., et al. *J. Am. Chem. Soc.* **2002**, *124*, 12650-12651.

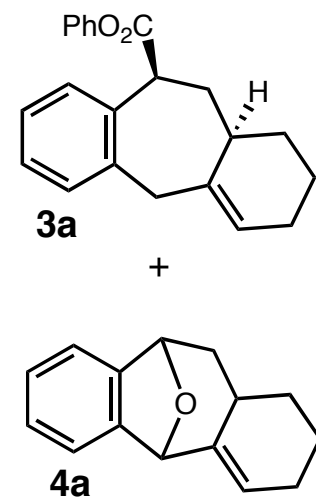


Oh, C. H., et al. *Chem. Commun.* **2005**, 4429-4431.

# Intramolecular Platinum Catalyzed Cyclization of Pirylium Ions with Alkenes and Subsequent C-H Insertion

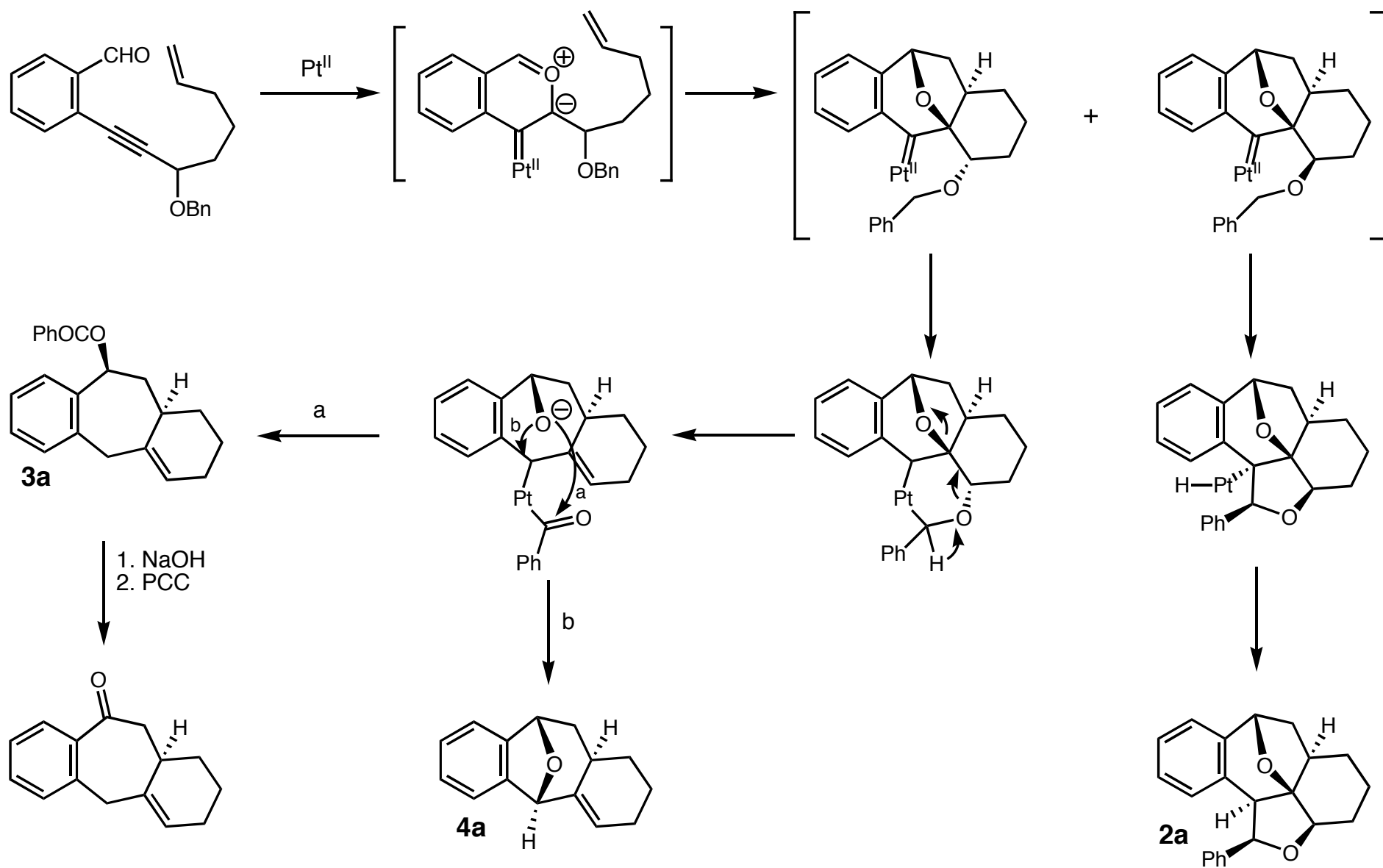


Catalyst	2a	3a	4a
PtCl <sub>2</sub>	25%	—	35%
PtCl <sub>4</sub>	20%	40%	—
Pt(PPh <sub>3</sub> ) <sub>4</sub>	20%	—	—
PtCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	77%	—	—
PtCl <sub>2</sub> (dppe)	61%	10%	—

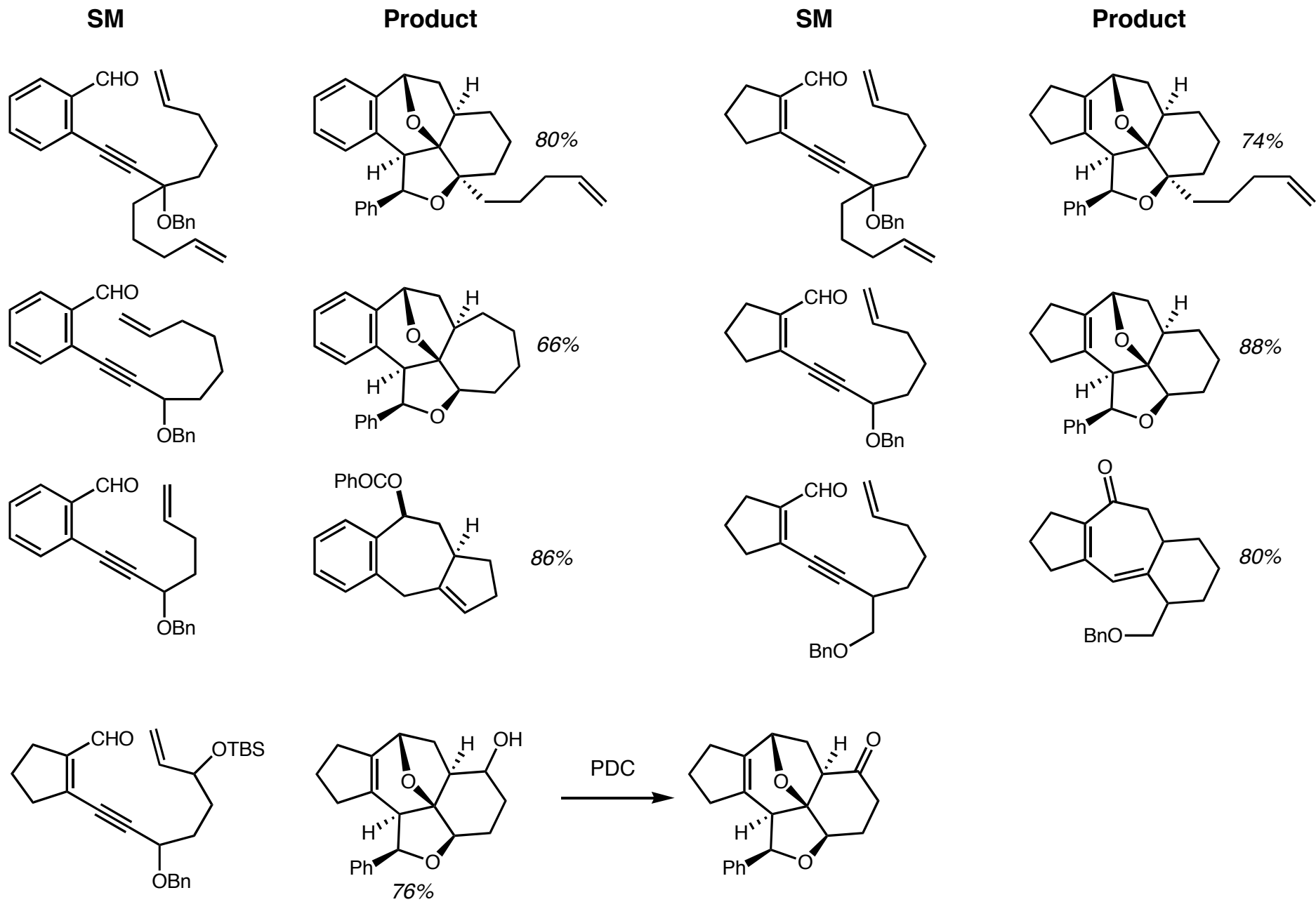




# Mechanistic Proposal



# Reaction Scope



## *Summary*

Methods for the synthesis of 7-membered carbocycles are necessary due to their prevalence in natural products.

Several tactics for the formation of 7-membered carbocycles have been developed, including strategies that employ, [6C + 1C], [5C + 2C], [4C + 3C], and other alternatives.

Oh and coworkers have published a platinum-catalyzed cyclization of pyrlium ions with alkenes to give a tetracyclic platinum-carbene complex, which immediately undergoes insertion into a benzylic C-H bond to give a highly complex ring system.

The power of transition metal-catalyzed pyrlium ion formation and subsequent cyclization has been demonstrated to access various multi-cyclic scaffolds, and lends to possibility of utilization of these methods for the future development of other sophisticated carbon frameworks.