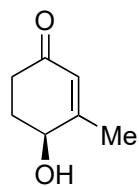


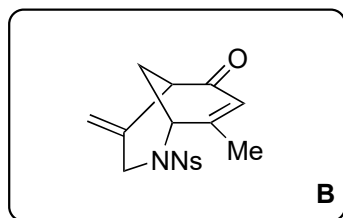
# Total Synthesis of Longeracinyllin A

Li, J.; Zhang, W.; Zhang, F.; Chen, Y.; Li, A. *J. Am. Chem. Soc.* **2017**, *139*, 14893



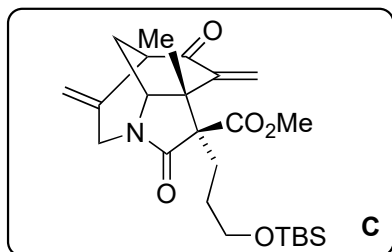
A

1-3



B

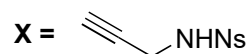
4-6



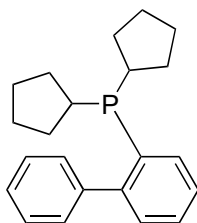
C

7-10

TTBP = 2,4,6-*tert*-butylpyrimidine

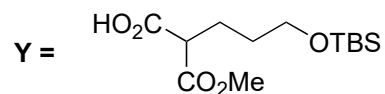


- 1) X, PPh<sub>3</sub>, DIAD
- 2) TBDPSOTf, 2,6-lutidine
- 3) AgNTf<sub>2</sub> cat., TTBP, CyJohnPhos



CyJohnPhos

- 4) *p*-thiocresol, K<sub>2</sub>CO<sub>3</sub>
- 5) Y, EDC·HCl, HOBT, Et<sub>3</sub>N
- 6) DBU, (CH<sub>2</sub>O)<sub>n</sub>



- 7) HF·pyridine
- 8) I<sub>2</sub>, PPh<sub>3</sub>, imidazole
- 9) Zn, CuI, pyridine/water, ultrasound
- 10) [Rh(cod)Cl]<sub>2</sub> cat., PPh<sub>3</sub>, AgBF<sub>4</sub>, H<sub>2</sub>

Name of the Reaction in **Step 1**.

Mitsunobu reaction

Please provide the mechanism of the reaction effected during **Step 3**.

**Hint:** Au(PPh<sub>3</sub>)NTf<sub>2</sub> effects the same reaction. Classify the reaction according to Baldwin rules; favored?

Best try to draw the product natural product like.

6-*exo-dig* cyclization. Yes, favored. Paper named it a Toste-type cyclization.

Please provide the mechanism of **Step 6**.

**Hint:** Several reactions happen in **Step 6**. Ultimately an Aldol condensation takes place.

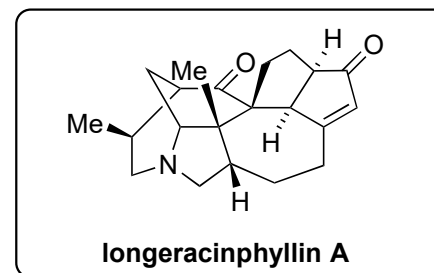
Name of the reaction in **Step 8**.

Garegg-Samuelsson reaction

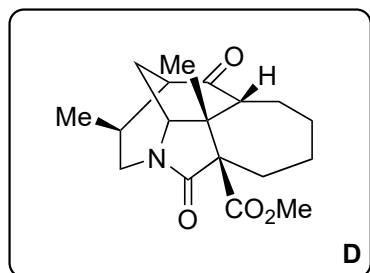
Please provide the mechanism of **Step 9**.

Conditions are named after whom?

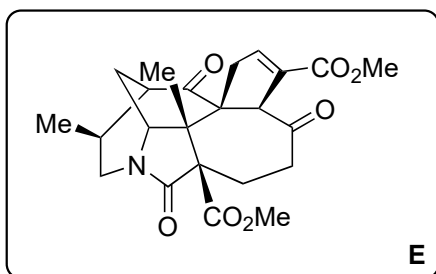
Luche conditions



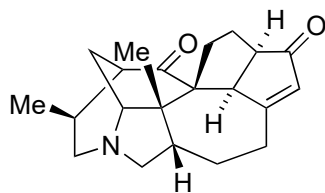
longeracinyllin A



11-14



15-20



**longeracinphyllin A**

- 11) KHMDS, PhSeBr
- 12) mCPBA
- 13) DABCO, air
- 14) dppf, **Z**



TBD = triazabicyclodecene

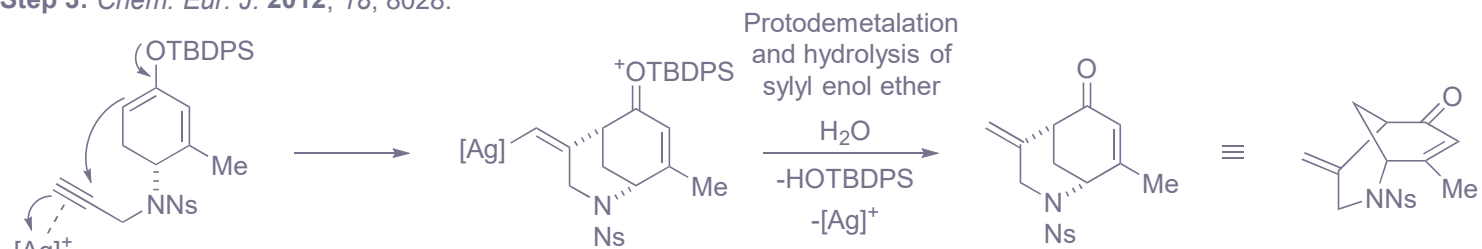
- 15) LiCH<sub>2</sub>PO(OMe)<sub>2</sub>
- 16) Pd/C, H<sub>2</sub>
- 17) TBD
- 18) LiCl, water, MeCN
- 19) Lawesson reagent *then* silica gel, air
- 20) Raney Nickel

Please provide the mechanism of **Step 14**.

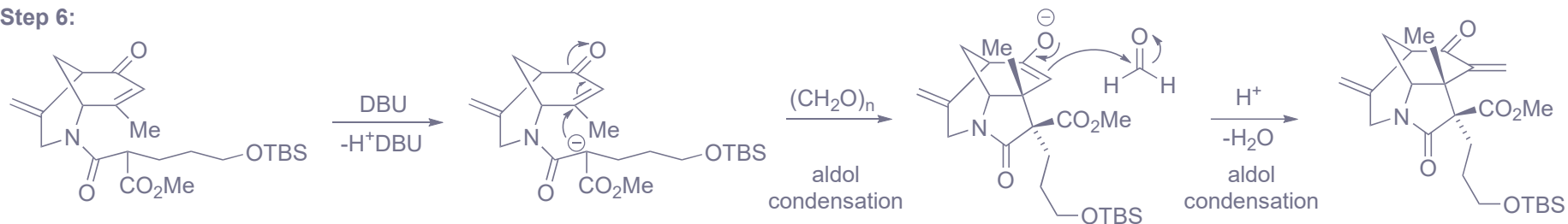
Please provide name of the reaction in **Step 18**.

Krapcho dealkoxycarbonylation

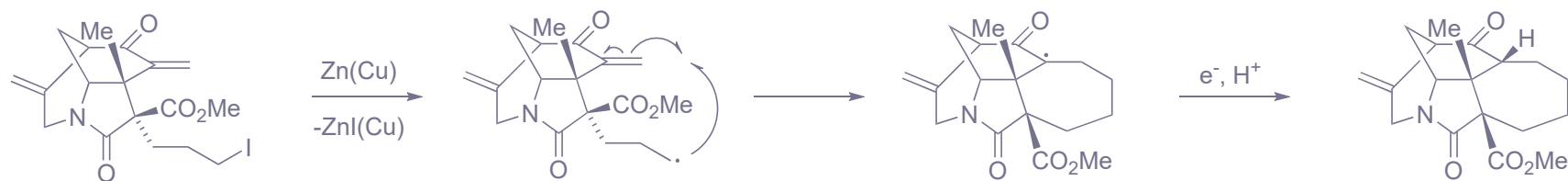
**Step 3:** *Chem. Eur. J.* **2012**, *18*, 8028.



**Step 6:**



**Step 9:**



**Step 14:** *J. Org. Chem.*, **1995**, *60*, 2906. Also possible in a concerted fashion.

