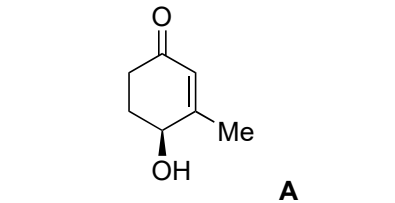
Total Synthesis of Longeracinphyllin A

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



A

1–3

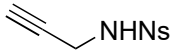
B

4–6

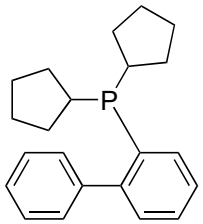
C

7–10

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

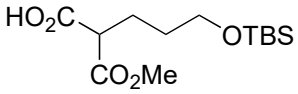
X = 

1) **X**, PPh_3, DIAD
2) TBDPSOTf, 2,6-lutidine
3) $AgNTf_2$ cat., TTBP, CyJohnPhos



CyJohnPhos

4) *p*-thiocresol, K_2CO_3
5) **Y**, EDC•HCl, HOBt, Et_3N
6) DBU, $(CH_2O)_n$

Y = 

7) HF•pyridine
8) I_2, PPh_3, imidazole
9) Zn, CuI, pyridine/water, ultrasound
10) $[Rh(cod)Cl]_2$ cat., PPh_3, $AgBF_4$, H_2

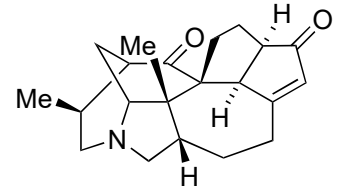
Name of the Reaction in **Step 1.**

Please provide the mechanism of the reaction effected during **Step 3.**
Hint: $Au(PPh_3)NTf_2$ effects the same reaction. Classify the reaction according to Baldwin rules; favored?
Best try to draw the product natural product like.

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.**

Please provide the mechanism of **Step 9.**
Conditions are named after whom?



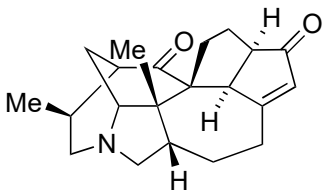
longeracinphyllin A

D

11–14

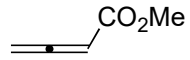
E

15–20



longeracinphyllin A

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

Z = 

TBD = triazabicyclodecene

15) $LiCH_2PO(OMe)_2$
16) Pd/C, H_2
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.**