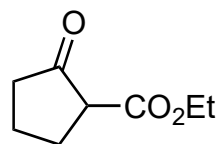


Total Synthesis of (-)-Himalensine A

Shi, H.; Michaelides, I. N.; Darses, B.; Jakubec, P.; Nguyen, Q. N. N.; Paton, R. S.; Dixon, D. J.
J. Am. Chem. Soc. **2017**, *139*, 17755–17758.

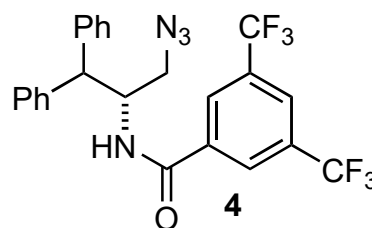
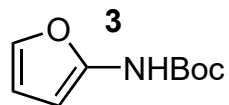
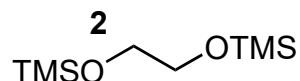
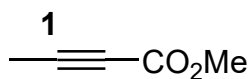


1-8



9-14

- 1) NaH, **1**, 60 °C
- 2) DMSO, HCl, 120 °C
- 3) TMSOTf, **2**
- 4) KOH (aq.)
- 5) cyanuric fluoride, pyr.
- 6) NaHMDS, **3**, then product from 5)
- 7) TsOH, acetone
- 8) **4** (cat.), PPh₃ (cat.) 60 °C



- 9) TFA, then, H₂, Pd(OH)₂, NaHCO₃
- 10) NaHMDS, propargyl bromide
- 11) LiAlH₄ then HCl, MeOH/H₂O
- 12) TIPSOTf, 2,6-lutidine
- 13) AIBN, Bu₃SnH, 90 °C
- 14) CSA, 0 °C

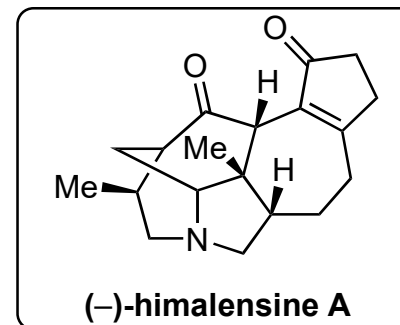
1) "Name" type reaction
Hint: ring expansion, 4-membered ring intermediate

2) Name of the reaction?

8) Name the reaction, provide a mechanism and describe the role of the catalyst.

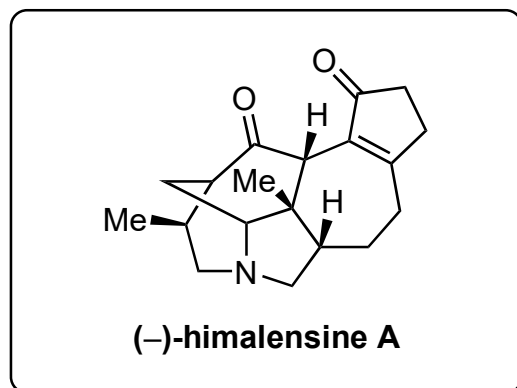
9) *Hint: 2 bonds are cleaved*

11) *Hint: only one carbonyl is affected.*
 One of the intermediate **11'** is not fully converted during the reaction. When subjected to MsCl, Et₃N, it can be converted to **12**. Give the structure of **11'**.

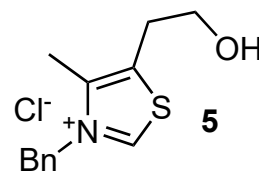
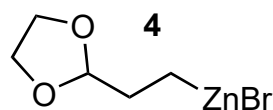




15-22



- 15) Crabtree's catalyst, H₂
- 16) NBS
- 17) pyr., TsOH, oxygen, reflux
- 18) NaHMDS, -78 °C, *then*, PhNTf₂
- 19) Pd₂dba₃, DTBPF, NMP, **4**
- 20) HCl (aq.)
- 21) **5** (cat.), Et₃N, 60 °C
- 22) Vaska's catalyst (cat.), TMDS
then MeOH, formic acid, 60 °C



15) Structure of the Crabtree's catalyst?

17) Name the reaction and provide a mechanism.

19) Name of the reaction?

21) Name the reaction and provide a mechanism.

Hint: cyclization and isomerization occurred.

22) Give the structure of Vaska's catalyst and provide a mechanism.